

1991

Comparison of data analysis and experimental techniques for analysis of planetary atmospheres

Kirsten W. Hall
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DOI: <https://doi.org/10.31979/etd.yyh2-zejm>

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**Comparison of data analysis and experimental techniques for
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San Jose State University, 1991

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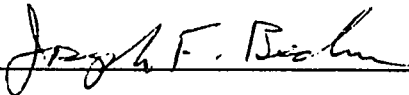
**COMPARISON OF DATA ANALYSIS
AND
EXPERIMENTAL TECHNIQUES
FOR ANALYSIS OF PLANETARY ATMOSPHERES**

A Thesis
Presented to
The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master Of Science

By
Kirsten W. Hall
August 1991

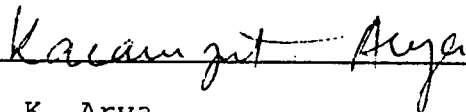
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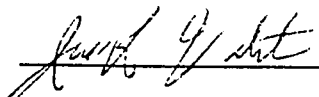
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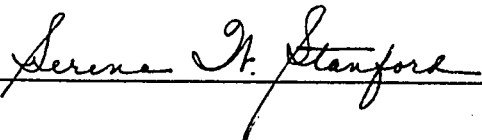


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ACKNOWLEDGEMENTS

The author wishes to express her sincerest appreciation to those individuals whose assistance has been invaluable to the completion of this Thesis. My deepest gratitude goes to Professor Joseph F. Becker whose constant support and encouragement has gone far beyond the role of a thesis advisor. I also especially wish to thank Dr. Jose R. Valentin of the Solar System Exploration Branch, NASA Ames Research Center, not only for his assistance in the writing of this Thesis, but also for his tremendous help in developing the Gas Chromatographic portion of this Thesis research. His help has been invaluable. Also, I am grateful to Professor Karamjeet Arya for his encouragement and many helpful suggestions. I also wish to thank the San Jose State University Foundation and Mr. Glenn Carle of the Solar System Exploration Branch at NASA Ames Research Center who provided the means as well as funded the work described in this Thesis. Finally and above all, I wish to thank Mr. George P. M. West, physics teacher par excellence, who used magic as well as unending though sorely tried patience to exorcise my awe of physics and replace it with sound understanding and the excitement of recognition. Without his initial encouragement this Thesis would not exist.

ABSTRACT

This thesis presents results of four experiments which develop methods of some critical elements for the detection of life, developed for possible use in NASA missions to help scientists gain insight into the origin of Earth.

The first experiment used tunable diode laser spectroscopy, operated at the vapor pressure of water, to detect and identify two water vapor lines in a Martian atmosphere.

The second experiment monitored dynamic changes of hydrocarbon mixtures simulating probe descent through a planetary atmosphere. The limit of accuracy is a dilution of 100.00 to 0.35 ppm in 18.0 minutes.

The third experiment developed a method of hydrocarbon analysis at sub-atmospheric pressures for use on Titan. The detection limit is 9.7 ppm at 3.0 torr.

The fourth experiment detected water vapor in carbon dioxide by selective absorption for possible use on Mars with a detection limit of 56.7 ppm.

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CHAPTER 1.

INTRODUCTION

The search for clues to the development of our solar system is age-old.

Scientists have been puzzled about why life began on earth and not, for example, on the moon. During the Scientific Revolution, scientists began looking to other planets to see if there were any similarities between them and the Earth. They wondered if there were other planets with life, perhaps even other planets with intelligent life. Men such as Tycho Brache, Galileo Galilei, Francisco Fontana, Cassini, and Christian Huyghens all pioneered the scientific study of planets. Tycho Brache, 1580-1600, studied the orbit of planets even before the invention of the telescope, performing all his observations with the naked eye.

Geological developments in the solar system are very closely tied to chemical and biological changes. This is why it is of interest to NASA to study the chemical composition of other planetary bodies (i.e. planets and their satellites).

In a recent report by the Solar System Exploration Committee of the NASA Advisory Council (1) regarding the

major scientific goals and interests of the United States' planetary program the committee stated:

"We expect to gather information crucial to our understanding of the conditions and physical phenomena that produced the solar system. This information is contained in the physical and chemical structure and composition of the solar system bodies - the Sun and planets, satellites, asteroids and comets, as well as meteoroidal debris."

Among the crucial chemicals for life to exist are simple hydrocarbons and water. The first documented recognition of the crucial importance of water appeared in 2000 B.C., in ancient Mesopotamia. These mythological records describe Nammu, the goddess of the oceans, who bore heaven and earth (2). Later Thales conceived of water as the principal element of all matter; a belief which persisted until the experiments of Cavendish who proved that hydrogen and oxygen combined to make water (1766-1798).

The combination of water and hydrocarbons has been shown as a possible method for the formation of life. In 1953, Miller sparked methane, ammonia, and water and synthesized amino acids. Then in the 1970's, Walker and Holland showed that methane oxidizes to carbon dioxide in the presence of U.V. light. In 1980, Pinto (3) showed that

carbon dioxide and water vapor combine to make formaldehyde, but the yield of this reaction is fairly low. Earlier, Pavlovskaya and Pasynskii (4) showed that formaldehyde and nitrates combine to make amino acids (1959).

The reactions of Walker, Holland, Pinto, Pavlovskaya, and Pasynskii make up a plausible scenario. Methane would have been reduced to carbon dioxide by the U.V. light, thus allowing formation of amino acids. However, material from comets was very important to prebiotic chemistry also, because large amounts of organic compounds were transported to Earth and may have been very useful to the formation of life.

Some of the basic instruments used in the detection of hydrocarbons, water, and other important substances include the Gas Chromatograph, the Mass Spectrometer, the Nephelometer, the Ion Mobility Spectrometer, and the Laser Spectrometer.

All these instruments include a detector which measures some fundamental property of a substance with a response which is unique to that substance. The rest of the instrument modifies the sample to assure that the detector's response to it is unique. In the case of gas chromatography, this means separating all the substances which comprise the gas with a column so that the detector senses each one separately.

These basic instruments are constantly being improved and modified to fit the requirements of the application for which they are being used.

Each of the instruments reported in this thesis require a different method of data analysis: Fourier transforms, convolution, signal averaging, and curve fitting. Each method of data analysis may be applied to any instrument, depending on the conditions. For example, if the sample is sensed by the detector quickly enough that you are able to get the information you need, then you may use signal averaging to analyze the data. However, if the detector takes too long to sense a sample, you begin to lose information. To combat this problem you can multiplex your data by triggering the sample many times without waiting for the detector to sense one sample. The multiplexed output is shown in Figure 1-1. Then you can deconvolve your signal to get the impulse response function (Figure 3-6). If the number of overlapped signals is sufficiently high, you can use Fourier Transform techniques to get the impulse response function instead. Curve fitting techniques can also be used if the shape of the signal is known.

In this thesis various mathematical techniques were studied and applied to increase the amount of information obtained from experimental data using several instrumental techniques. The experimental techniques include water vapor

detection for use in a possible Mars mission using 1) Diode Laser Spectrometry and 2) Selective Thermal Modulation; 3) a method of hydrocarbon detection by a probe descending through a planetary atmosphere using Multiplex Gas Chromatography (MGC); and 4) a method of hydrocarbon detection at subatmospheric pressures for possible use in Titan's atmosphere using MGC.

CHAPTER 2.

LASER SPECTROSCOPY

2.1 HISTORY

The word laser is an acronym for Light Amplification by Stimulated Emission of Radiation. The concept of stimulated emission, an essential principle of the laser, was first introduced by Albert Einstein in 1917.

Development of the laser evolved during the late 1950's and early 1960's. Laser research originated out of earlier studies of masers (microwave amplifying devices). Because lasers amplify light in much the same way that masers amplify microwaves, the early lasers were called "optical masers."

The idea of the laser was first proposed by two U.S. physicists, Arthur L. Schawlow and C.H. Townes, in 1958. At the same time, the Russian physicists N.G. Basov and A.M. Prokhorov developed some very similar ideas. The first laser ever constructed was a ruby laser built in the United States, by Theodore H. Maiman, and operated for the first time in 1960. The U.S. physicist Ali Javan operated the first continuous laser in 1961. Semiconductor lasers were first operated in 1962 by three separate teams of U.S. scientists.

2.2 THEORY

2.2.1 SEMICONDUCTOR LASERS

Electrons in semiconductors occupy broad bands of energy levels which are not associated with individual atoms but with the material as a whole. Each original energy level splits into a closely packed bunch of levels which we term an energy band. The width of the band increases as the interatomic distance decreases and the electron-electron interaction increases. Bands can even overlay at small atomic spacings. However, for typical semiconductors the equilibrium atomic spacing results in a sequence of bands with energy "gaps" in between. At low temperatures all the bands will be occupied up to a certain level and all other levels will be empty. The most important features are the highest occupied band (the valence band), the first empty band (the conduction band), and the gap in between (the energy gap). If the temperature of the semiconductor is elevated, it becomes possible for electrons in the valence band to be thermally excited into the conduction band. This process is important since it causes the material to become electrically conducting. None of the electrons in a completely full band can take part in electrical conduction. When a current is flowing, the electrons have to gain an extra velocity component along the direction of the applied field; that is, they must increase their total energy.

Electrons in a full band cannot do this since they would have to move up into otherwise occupied energy state, and this is not allowed by the Pauli exclusion principle. So as soon as one electron is excited from the valence band to the conduction band these de-localized conduction electrons can help in conducting electricity. The motion of all the electrons in a band from which one has been removed is mathematically equivalent to a band containing one single particle, a hole having a positive charge.

A diode, a device which passes current in one direction only, is formed by a junction between p and n materials. Sometimes, as the current flows through the diode junction, it emits radiation. This forms the basis for the light emitting diode or LED.

Since forward biased carriers (n material made negative, and p material made positive) are able to pass the junction barrier so easily, they become minority carriers in excess of the normal concentrations. In other words, electrons in the conduction band fall back down into empty states in the valence band. Recombinations like these in an LED can cause emitted radiation in the same way that electrons emit radiation as they move between atomic energy levels.

Not all semiconductors are efficient emitters, so often doping is used to increase the efficiency of the devices.

The general effect of doping is to introduce new energy levels either just above the top of the valence band or just below the bottom of the conduction band.

Transitions which take place between these levels form the basis of the semiconductor laser as well as the LED. The semiconductor laser puts requirements for population inversion and optical feedback on the diode. Population inversion is defined as the requirement that there must be simultaneous high densities of electrons and holes. These densities can be present for short distances on either side of a forward biased p-n junction. Laser action is only sustained within the narrow active region encompassing the junction. Optical feedback is most often obtained by using the reflections from carefully cleaved end faces of the semiconductor. Although small, the amount of reflection is usually sufficient for lasing to occur. This produces a small, rugged solid state laser device.

The flow of current determines the amount of population inversion and subsequently the gain. Population inversion at low currents is drowned out by the losses and lasing does not occur. Lasing begins and radiative output increases very rapidly with increasing current beyond a critical current (threshold current).

One characteristic which is unique to semiconductor lasers is their very wide beam divergence. This is caused

by the very small dimensions of the active region cross section, which are on the order of the wavelength of light. This causes significant diffraction effects. Lasing usually takes place non-uniformly across the end face of the active region. The beam spread is most often smaller in the plane of the junction that at right angles to it, where the typical angle of divergence is 40 degrees.

The longer lasing wavelengths can be obtained from lead-salt lasers. Although coarse tuning of the laser is carried out by changing the temperature of the surroundings, fine tuning is often performed by varying the current flowing through it. This changes the temperature of the diode, but also has the disadvantage of affecting the power output as well.

One major difference between semiconductor lasers and other types is their exceedingly small size. This severely limits the total power output because at high powers the optical flux can cause mechanical damage to the facets and cause the laser to fail. If high powers are required, arrays of single lasers are used. These may be physically separate or made on the same substrate.

2.2.2 INDIUM ANTIMONIDE DETECTORS

The detectors used in this experiment are 2.0 mm square indium antimonide detectors (Model 1IS-2, Infrared Associates, Cranbury, NJ 08512) which respond to a spectral range, at 77 K , between 1-5 micro meters with a maximum response at approximately 5.4 micro meters. They are mounted in Metal Dewars (Model DMSL-12, Laser Photonics, Bedford, MA) which are filled with liquid nitrogen. The detectors are thin film photovoltaic 2 mm * 2 mm, the basic detecting elements, which have been chemically deposited onto a quartz support and equipped with two electric leads. Gold electrodes connect the film with the leads in order to reduce noise.

The sensors are radiation transducers that operate by converting radiant infrared energy into electrical power. When photons strike the detector, they induce changes in the detector's conductivity which modulates the current flow. The subsequent changes in circuit voltage are amplified with a PPA-15 preamplifier (Infrared Assoc. Inc., New Brunswick, NJ). The data is transferred and displayed to an AT&T Personal Computer through a 100 kHz, 12 bit A/D converter (Model DAS-16F, Metrabyte Corporation, Stroughton, MA).

2.2.3 METHOD FOR IDENTIFYING SPECTRAL LINE

The primary requirement for identifying the spectral line is to have the laser operating in single mode. This can be achieved in our laboratory by operating the laser at the lowest possible current. In this work single mode was achieved by applying a current blanking pulse which caused a 0 % transmission. This way the laser can operate in single mode at higher currents, allowing much greater flexibility and range of the laser. In general, single mode operations can be verified by obtaining 100 % absorption of light by a spectral line at high gas pressures.

The strength of the spectral lines can be calculated if we assume that

$$2.1 \quad I(x) = I_0 e^{-k(\nu) P \cdot L}$$

where $I(x)$ is the final intensity, I_0 is the initial intensity going into the sample cell, and pressure (P) times length (L) is the optical thickness. Then

$$2.2 \quad T = \frac{I(x)}{I_0} = e^{-k(\nu) P \cdot L}$$

where T is the transmission.

Therefore,

$$2.3 \quad \int \ln\left(\frac{1}{T}\right) d\nu = P.L \int \kappa(\nu) d\nu$$

where the left hand side of the equation is equal to the area under the spectral line. Hence, the strength of the spectral line S is defined as (5)

$$2.4 \quad S = \int_0^{\infty} \kappa(\nu) d\nu = \frac{\int \ln\left(\frac{1}{T}\right) d\nu}{P.L}$$

2.3 EXPERIMENTAL SECTION

This experiment uses Laser Spectroscopy to detect water vapor using Voigt curve fitting to analyze the data. A brief description is given of semiconductor lasers as well as other experimental and data analysis details. Finally, the results of these experiments are reported.

2.3.1 APPARATUS

Figure 2-1 shows the experimental apparatus: a modified LS-3 laser spectrometer (Spectra-Physics, Bedford, MA) with a fabricated PbS diode operating at 80 K and emitting in the 2230-2245 cm^{-1} spectral region. The light

beam is passed through a mode selecting grating monochromator, then through a cell of 10 cm path length with calcium fluoride windows, and finally onto the liquid nitrogen cooled detectors. A 2 mW helium neon laser is used for optical alignment of the apparatus.

The optical components of the apparatus are mounted on a half-inch thick aluminum plate. The optical components are sealed with a cover to enable the spectrometer to be purged with nitrogen (a non-absorbing gas).

The Tunable Laser Diode (Model L5621-2130, Laser Analytics, Bedford, MA) is mounted in a Model L5736 Liquid Nitrogen Dewar (Laser Analytics, Bedford, MA). The advantage in this type of cooling system lies in the lack of vibrational noise from the closed cycle helium refrigerator which could distort the signal. The laser diode has a power of 0.15 mW at 245 mA and 80 K and is optimized to tune over 15 cm^{-1} , from 2130 cm^{-1} to 2145 cm^{-1} .

Data acquisition was accomplished using an AT&T model 6300 PC (IBM-XT Clone) with an Intel 8087 math coprocessor and a 16 channel 12-bit high speed 100 kHz A/D board (model DAS-16F, Metrabyte Corporation, Stroughton, MA) with Direct Memory Access (DMA). Data acquisition was controlled by a BASIC program with assembly language subroutines (written by Dr. T. B. Sauke, NASA Ames Research Center). The laser was run at a sampling frequency of 50 Hz (20 msec period).

During each sweep 1500 data points were acquired at 10 microsec/point. During the second half of the sweep the data was co-added to signal average and improve the signal-to-noise ratio. Data was transferred to a Micro-VAX (Digital Equipment Corporation, Santa Clara, CA) and then analyzed using Interactive Data Language, IDL (Research Systems, Inc., Denver, Colorado).

Voigt profiles were used to analyze the data.

2.4 RESULTS

Two lines were identified in the region of 2100-2145 cm^{-1} :

$P(\text{H}_2\text{O}) = 14.7$ torr, $T = 24$ C

LINE 1:

Position (cm^{-1})	Strength (cm/mol)	Doppler Width	Lorentz Width
2136.14	1.94E-22	2.51E-03	2.88E-03
2136.14	1.92E-22	2.51E-03	2.87E-03
2136.14	1.93E-22	2.50E-03	2.87E-03
2136.14	1.96E-22	2.48E-03	2.89E-03
Average:	1.94E-22	2.50E-03	2.88E-03
Theory:	2.08E-22	3.09E-03	
Percent Difference:	6.82 %	19.09 %	

LINE 2:

Position (cm^{-1})	Strength (cm/mol)	Doppler Width	Lorentz Width
2115.02	2.25E-22	7.41E-03	3.70E-03
2115.02	2.22E-22	7.67E-03	3.28E-03
2115.02	1.65E-22	5.80E-04	3.32E-03
2115.02	1.55E-22	1.39E-03	3.26E-03
Average:	1.92E-22	4.86E-03	3.39E-03
Theory:	2.34E-22	3.06E-03	
Percent Difference:	17.95 %	37.04 %	

The detectable water vapor lines were so far from each other that they could not be manipulated to both be in the same mode simultaneously (Figures 2-2, 2-3). Identification

of these lines was not difficult since the region over which the diode operates only has two large water vapor lines, all the rest being an order of magnitude smaller. Looking through a listing of water vapor lines (6), we were able to locate the positions of the two water vapor lines and their theoretical strengths. The line shown in Figure 2-2 is the J9 line at 2136.144 cm^{-1} and the line shown in Figure 2-3 is the J8 line at 2115.018 cm^{-1} (6).

A possible reason for the experimental data not fitting with the theoretical values very well is that the behavior of water vapor is not well understood (7).

The minimum detection level was calculated assuming that the minimum detectable strength was $0.9 \times 10^{-22} \text{ cm/mol}$. This assumption was made because lines below this strength were not detectable. Calculations showed that at typical experimental conditions ($P = 14.7 \text{ torr}$, $T = 24 \text{ C}$, Volume = 25.4 cc , and Diameter of gas cell = 10 cm) the amount of water vapor which was detected was $2.52 \times 10^{-8} \text{ g-mole}$. The minimum detectable limit under these conditions is $1.69 \times 10^{-8} \text{ g-mole}$.

If optimum detection conditions were used such as water lines of wavelength approximately 2 microns, almost 100 times stronger, the minimum detectable limit could be 10^{-10} g-mole . These conditions would of course require a different laser and detector, both of which are commercially

available but not at this time because of funding limitations.

This experimental method may be used for many purposes other than planetary atmospheric analyses, such as pollution detection (8).

CHAPTER 3.

MULTIPLEX GAS CHROMATOGRAPHY

3.1 HISTORY

Chromatography originated in the 1850's with Runge, a German dye chemist (9). He described a separation process known today as paper chromatography. Tswett separated the components of plant pigments by passing solutions of the pigments through columns of solid adsorbents in 1906, thus performing the earliest recorded chromatographic experiments.

Gas chromatography was not used until the early 1940's. Developments from Eucken and Knick in 1936, Turner in 1943, Claesson in the 1940's, and Phillips in the early 1950's helped to develop the modern-day Gas Chromatograph.

In 1952, Janak worked with a chromatograph which utilized carbon dioxide as the carrier gas and a nitrometer as the detector.

By 1955, gas chromatography had been applied to many problems, and commercial gas chromatographs were built.

Gas chromatography has become a very powerful technique for the analysis of gaseous mixtures. Besides being a major analytical technique with a great many applications on Earth, including atmospheric analysis, it also has been

successfully employed on space missions such as the Viking Mars lander (10) and the Pioneer Venus Probe (11).

3.2 THEORY

3.2.1 GAS CHROMATOGRAPHY

Chromatography is a method for the separation and quantitative determination of the various components of a sample mixture. The chromatographic separation is obtained by separating the components of the sample mixture as they are transported through a stationary phase by a mobile phase.

In Gas Chromatography, the stationary phase is either an adsorbent or a liquid spread over a porous inert support structure, the column, and the mobile phase is an inert gas. In most gas chromatographic analyses, a single pulse of sample gas is introduced at the head of the column. As the mobile phase carries the sample along the column, the components of the sample mixture are separated by the stationary phase into bands of components. This process is called differential migration. As the bands, each from a different component of the mixture, emerge at the end of the column they are measured by a detector. Typically, the signal sensed by the detector is converted to a voltage. The change in voltage is then usually displayed graphically with a chart recorder. The size of the peaks which result

are proportional measurements of the concentration of each of the separated components of the sample mixture. The various components have characteristic "retention times" which are just measurements of the amount of time it takes a particular component to migrate through the column.

There are two major drawbacks of conventional gas chromatography. (1) Sometimes the components take a long time to migrate through the column. If the sampled environment is changing during that time, its change cannot be accurately determined. This is the case as a probe descends through an atmosphere. (2) If the concentration of sample is very small, the resulting signal may be engulfed in the electronic noise and as a result the sample will not be detected.

3.2.2 MULTIPLEX GAS CHROMATOGRAPHY

Multiplex Gas Chromatography is a method which eliminates the two major drawbacks of conventional gas chromatography. The sample is repeatedly "injected" into the column by means of a modulator without waiting in between injections for the previous sample to finish migrating through the column (12). The resulting signal is digitized and stored on a computer (Figure 1-1). Then signal processing techniques such as Convolution and Fourier Transforms are utilized to "extract" the chromatogram

(Figures 3-6). The amazing effectiveness of this technique arises in its ability to take an unintelligible raw output signal and end up with a clean impulse response function (chromatogram).

Since many samples are combined into one set of peaks, the signal to noise ratio of the resulting chromatogram is larger than that of just one sample. Thus smaller concentrations of sample may be detected. This is very important when sampling low pressure gases. Also large concentrations of sample gas can cause the column to exhibit non-linear properties. In some cases, the sampled environment can be monitored as a function of time or location.

3.2.3 MODULATORS

A modulator is a device which provides a change in some parameter of a sample such as concentration. There are many types of modulators. In conventional gas chromatography, the modulator is a syringe, a valve, or an absorbent. All three of these modulators introduce the sample into the column in the form of a single pulse.

In Multiplex Gas Chromatography, many more modulators both, physical and chemical, may be used because the sample is injected into the column in a series of rapid pulses. The only criterion for choosing such a modulator is that it

should generate reproducible signals which will be proportional to the chemical concentration. In general a modulator's rate of injection should be high enough to maximize the signal sensed by the detector and yet low enough to maintain the linear behavior of the modulator and column.

A chemical modulator can modulate one or all the components of the gas in which an investigator is interested. All other components must remain unperturbed by the modulation signal. In the case of selective modulation techniques such as the one reported in Chapter 4, this means finding a material which only absorbs the interesting component of the gas. Sometimes the absorbent material need not be completely selective. For instance, if a water vapor experiment is to take place on the martian surface where the composition of the atmosphere is limited to mainly carbon dioxide and a little water vapor, then the modulator should only be selective to the water vapor in carbon dioxide. It will not matter if the modulator absorbs nicotine because there is a high degree of certainty that there will be no nicotine on Mars.

There are some significant advantages to chemical modulation in the determination of gases. A chemical modulation system, such as the one developed for this work, is very simple and consists of only a few components. This

enables the acquisition of many data samples in the same amount of time it would require a conventional gas chromatograph to produce one point. Also, many data points may be averaged together, thereby significantly improving the signal to noise ratio and increasing detection limits. These sorts of considerations are vital when developing a flight instrument.

A very important factor for peak resolution is to have the initial injection closely approximating a delta function. This makes the concentration gradients and signal frequencies large. The delta functions are most easily generated by mechanical modulators. Thermal modulators can also be used with good results, since it is not important to have both the rising and falling concentration gradients to be large. In fact, since heating can be done faster than cooling, a large rising concentration gradient alone can deliver the required power at higher frequencies.

3.2.4 FOURIER TRANSFORMS AND CONVOLUTIONS

The raw data obtained from a multiplex gas chromatographic experiment (for example, see Figure 1-1) is not directly interpretable; therefore, digital signal processing techniques must be used to obtain a final chromatogram. One such technique is the method of convolution.

The convolution of two functions, f and g , is defined by the integral

$$3.1 \quad h(x) = \int_{-\infty}^{\infty} f(u) g(x-u) du$$

A convolution may also be written as

$$3.2 \quad h(x) = f(x) * g(x)$$

From the definition of convolution, it is easy to see that $h(x)$ is a linear function of $f(x)$. The definition also demonstrates that a shift of x in $f(x)$ results in a shift of x in $h(x)$. These two properties allow for the Convolution Theorem;

"If $f(x)$ has the Fourier transform $F(s)$ and $g(x)$ has the Fourier transform $G(s)$, then $f(x)*g(x)$ has the Fourier transform $F(s)G(s)$; that is, Convolution of the two functions means multiplication of their transforms." (13)

If a Fourier transform is numerically computed, its values are only defined at discrete intervals. For example, if the function to be transformed is periodic, its discrete Fourier transform is a series of equally spaced delta functions. In the case of a continuous Fourier transform, the given function is dependent on time and its Fourier transform is a

function of frequency. But in the case of the discrete Fourier transform, the signal is a function of discrete time (τ). If the sampling interval is T , the first sample is taken at $t=t_0$, and $v(t)$ is the signal waveform, then the signal function $f(\tau)$ is defined as

$$3.3 \quad f(\tau) = v(t_0 + \tau T); \tau = 0, 1, 2, 3 \dots N-1$$

The discrete Fourier transform is not defined for cases where there is no starting point for the waveform, such as functions which approach zero asymptotically. Also the sample must end after a finite amount of time, thus the name DISCRETE Fourier transform.

The discrete Fourier transform, $F(v)$, of a function $f(\tau)$ is given by

$$3.4 \quad F(v) = N^{-1} \sum_{\tau=0}^{N-1} f(\tau) e^{-j2\pi v \tau / N}$$

where v/N is the frequency integer measured in cycles per sampling interval, N .

Also the inverse discrete transform, which enables the recovery of the original function, $f(\tau)$, is given by

$$3.5 \quad f(\tau) = \sum_{\nu=0}^{N-1} F(\nu) e^{i2\pi\nu\tau/N}$$

The fast Fourier transform became widely known in 1965. This is more easily illustrated if we write the discrete Fourier transform for $N=8$ in terms of a matrix product,

$$3.6$$

$F(0)$	1	1	1	1	1	1	1	1	1	$f(0)$
$F(1)$	1	X	X^2	X^3	X^4	X^5	X^6	X^7	X^7	$f(1)$
$F(2)$	1	X^2	X^4	X^6	X^8	X^{10}	X^{12}	X^{14}	X^{14}	$f(2)$
$F(3)$	1	X^3	X^6	X^9	X^{12}	X^{15}	X^{18}	X^{21}	X^{21}	$f(3)$
$F(4) =$	1	X^4	X^8	X^{12}	X^{16}	X^{20}	X^{24}	X^{28}	X^{28}	* $f(4)$
$F(5)$	1	X^5	X^{10}	X^{15}	X^{20}	X^{25}	X^{30}	X^{35}	X^{35}	$f(5)$
$F(6)$	1	X^6	X^{12}	X^{18}	X^{24}	X^{30}	X^{36}	X^{42}	X^{42}	$f(6)$
$F(7)$	1	X^7	X^{14}	X^{21}	X^{28}	X^{35}	X^{42}	X^{49}	X^{49}	$f(7)$

where $X = e^{-i2\pi/N}$, $X^N=1$.

This matrix can then be thought of as a complex number whose modulus is one and whose phase is $-(1/N)$. This matrix may be factored in order to reduce the number of necessary multiplications.

The number of multiplications necessary to calculate the transform is $2N \cdot \ln N$, so we gain a factor of $N/\ln(N)$ efficiency in terms of the number of multiplications needed

for the fast Fourier transform as compared with the full blown discrete Fourier transform. This difference becomes critical for very large values of N.

It is important to remember that the discrete Fourier transform remains only an approximation to the Fourier transform. In some cases this approximation is not correct.

All these mathematical techniques may be applied to multiplex gas chromatography in order to calculate the input response function. The input response function is the response of the system to one single input, which turns out to be the chromatogram one would obtain using conventional chromatography. The input response function is defined as

$$3.7 \quad I = \text{FFT}^{-1} \left[\frac{\text{FFT}(\text{Output}) * \text{FFT}(\text{Input})}{\text{FFT}(\text{Input})} \right]$$

For the application of multiplex gas chromatography, the number of points, N, is usually large and thus the fast Fourier transform is used to reduce the number of necessary multiplications. The data analysis method was used in the experiment described in section 3.3. The convolution is most easily performed in these cases by taking the FFT of the two inputs, f and g, to be convoluted, taking their product and inverting the FFT. In the case of gas chromatography, f is the input (injections) and g the output

(multiplexed data). Both f and g have the same number of points, so the convolution will have twice as many points. But if the transform of f is multiplied by the transform of g point by point and then retransformed, the final convolution will be only half the correct length. This type of error can be avoided by inserting the functions g and f with zeros, enough to double their lengths. Power spectra, $|F(v)|^2$, are used quite often in situations where phase is unimportant, such as chemical spectral analysis performed by Fourier transform spectroscopy where only absolute strength measurement is important.

3.3 MONITORING OF VARYING HYDROCARBON MIXTURES

This next experiment uses Multiplex Gas Chromatography to analyze varying hydrocarbon mixtures using Fourier transforms to analyze the data instead of cross-correlation, as used in the next experiment. A brief description is given of the detector used as well as other experimental and data analysis details. Finally, the results of these experiments, at conditions a probe would experience as it descends through a planetary atmosphere, are reported.

3.3.1 EXPONENTIAL DILUTION AS A MODEL OF A CHANGING ATMOSPHERE

In this work, the technique of exponential dilution (ED) (14) was used to change the composition and concentration of a gaseous mixture to emulate the changes in the atmospheric composition that a descending spacecraft will sample (15). The ED technique has previously been used by Koel et al., 1983 (16) to calibrate a GC with a flame ionization detector using a sample containing methane as the only component which was determined.

In the ED technique, a flask of known volume is filled with a gas sample. Then a diluent is introduced into the flask at a constant rate. The diluted sample mixture then flows from the flask into the GC injection valve. The sample inside the flask is diluted exponentially as a function of time. At any time the concentration of the sample inside the flask can be calculated using the following equation (14):

$$C(t) = C_0 e^{-ft/v}$$

where $C(t)$ is the concentration of the sample at time t , C_0 is the initial concentration, f is the diluent flow rate, and v is the volume of the flask. The ED technique can also be used to make changes in sample composition by introducing a new sample in the flask instead of a diluent.

3.3.2 PHOTOIONIZATION DETECTOR

The sensor contains a sealed interchangeable ultraviolet lamp that emits a selected energy line. Lamps with energies of 9.5, 10.0, 10.2, 1.9, and 11.7 eV are available. The absorption of ultraviolet light by a molecule leads to ionization. A chamber adjacent to the ultraviolet source contains a pair of electrodes. A positive potential applied to the accelerating electrode creates a field which drives ions formed by absorption of lamp energy to the collecting electrode where the current, proportional to concentration, is measured. This detector has dynamic range of 7 orders of magnitude.

3.3.3 EXPERIMENTAL SECTION

3.3.3.1 APPARATUS

The chromatographic system developed for this work is shown in Fig 3-1. The system consists of a model PI-52-02 Photoionization detector (HNU Systems, Inc., Newton, MA) with a 11.70 ev lamp. The column was a 1.5 m by 1.1 mm ID stainless steel tube packed with tert-butyl isocyanate bound to poracil C (100-150 mesh). The GC injection assembly was composed of an 8-port Valco valve with 100 microliter sample loops and a Valco electric actuator (Alltech Associates, Deerfield, ILL) for computer control of the valve. A Datametrics Type 1511 Controller and three Model 825

Datametrics Mass Flow Controllers (Santa Clara, CA) with orifices for 10.0, 20.0, and 100.0 scc/min were used to regulate the flow of all the gases used.

Testing of the ED system was conducted with three different gas mixtures. Sample #1 contained methane, ethane, propane, and butane at 100.00 ppm in helium (Matheson). Sample #2 contained those same components but at 1000.00 ppm (Matheson). The final mixture (sample #3), prepared manometrically, contained ten hydrocarbons at the following concentrations: methane and ethane at 71.1 ppm, propane and butane at 142.3 ppm, isobutane and ethylene at 213.4 ppm, acetylene and propene at 227.6 ppm, propyne and propadiene at 355.7 ppm, all in helium. The carrier gas was 99.999% helium (Matheson). The flow rate through the column was 16.0 scc/min.

In order to emulate the variations in sample concentration, the 100.00 ppm gas mixture was used (sample #1). An ED flask of known volume was connected upstream of the sample valve. This flask is a glass vessel of accurately determined volume (239.6 cc) equipped with openings to permit continuous flow. It contains a magnetically driven stirring vane to guarantee complete mixing. This flask was fabricated following the same specifications used for the ED flasks made by Varian, Inc. during the early 1970's. Similar ED flasks were used during

the late 1970's to calibrate the GC that was used on board the Pioneer Venus probe for determining the gaseous components of Venus' atmosphere (11). These flasks are being used to calibrate our newer GC's which are being developed for use in other NASA missions.

Before beginning each experiment, the flask was filled with the sample to be used at a rate of 10.0 scc/min for a period of 2 hours. To ensure that the flask was completely filled with the sample, a few test injections of the sample entering the sample loop were made and no change in intensity of the GC signal was detected. Four dilution experiments were performed using the following diluent flow rates: 1) 12.0 scc/min, 2) 18.2 scc/min, 3) 32.2 scc/min, and 4) 61.6 scc/min. Before starting with the dilution, the multiplex experiment was run for an 18.0 minute period. This initial data was used as a baseline to determine the intensities of the GC peaks for the 100.00 ppm concentration mixture (sample #1). That peak intensity was used as a reference to calculate the concentrations that were used for the exponential dilution plots. The data obtained from the experiments were used to calculate the impulse response functions using equation #3.7 and a program written in IDL. This data was used to generate the exponential dilution curves of concentration with respect to time for both propane and butane. To monitor this concentration as a

function of time, the time corresponding to the average concentration was calculated by integrating over the interval of each data segment and using equation #3.7. The four dilution experiments were run for approximately 40, 75, 40, and 18 minutes, respectively. Four theoretical dilution curves using those same diluent flow rates were also generated. The natural logarithm of the concentrations of each experiment was plotted vs. time followed by calculation of the relative error between those curves and the theoretical ones, as shown in figure 3-2. An additional plot of % relative error with respect to diluent flow rate in scc/min was also generated, and is shown in figure 3-3.

A study was also conducted to test the multiplex ED technique while changing the sample mixture as a function of time. In this experiment, the flask was filled with the ten hydrocarbon mixture described previously. This was followed by the introduction of a mixture containing methane, ethane, propane, and butane, all at 1000.00 ppm in helium (sample #2). The four hydrocarbon mixture was introduced at a constant rate of 9.0 scc/min for a period of 140 min. A total of 1272 injections were generated during that period.

The multiplex ED system was operated using a System 1800-Model B High-speed Microcomputer (Integrated Image Systems, Santa Clara, CA) through an IEEE 488 interface attached to a Nelson Analytical 900 Series A/D Interface

(Cupertino, CA) both providing the modulation signal and acquiring the detector signal. The software used for modulating the frequency of injections and acquiring the output data was supplied by Nelson Analytical but modified by us to perform the multiplex ED experiments. The data acquisition rate was one point per second. After the experimental data was collected, it was transferred to a MicroVAX II (Digital Equipment Corporation, Santa Clara, CA.) to calculate the input response function using equation #3.7. All the data collected in each experiment was divided in segments of 15 minute lengths (900 data points) to monitor the dilution of the sample as a function of time for each second of the experiment. Each 15 minute segment had the same injection sequence. That sequence was chosen from previous MGC experiments done in our laboratory where the S/N of the final chromatogram varied with the frequency of the input signal as well as the probability of injection. The probability of injection determines the frequency and number of injections of the sample gas into the carrier gas stream.

The data acquisition was performed using a SYSTEM 1800-Model B High-speed Microcomputer (Integrated Image Systems) through an IEEE 488 interface attached to a Nelson Analytical 900 Series A/D Interface both providing the modulation signal and acquiring the detector signal. The

program which controlled the Nelson Analytical A/D Interface was written in Basic. It was supplied by Nelson Analytical and modified by us using QuickBasic from Microsoft.

After each experiment was over; the data was transferred to a MicroVAX (Digital Equipment Corporation) via the Procomm software in the PC, the Kermit software resident in both computers, and an RS232 cable. Once the data was resident on the MicroVAX, the input and output signals were separated using Fortran77 and C programs and the data was analyzed and viewed using IDL (Interactive Data Language, Research Systems, Inc.). Each final data point was plotted using a Zeta8 Plotter (Nicolet, computer graphics division) from the MicroVAX computer.

Using an IDL (Interactive Design Language) program, the signal which represents the response of the system to the perturbation of the experimental system was calculated used multiplexed data was separated into a signal by using the fact that cross-correlation has been derived from the convolution property of Fourier transforms (Equation 3.7) which relates the input signal and the impulse response function with the output.

Intensity of the peaks was measured and converted to concentration (for a more detailed expansion, see section 3.3.1). The final data was then plotted, using a Macintosh-Plus Computer and the software program StatWorks. Linear

regression was performed on the data and error bars were calculated using a Hewlett Packard Model 65 computer.

3.3.4 RESULTS

Figures 3-2a and 3-2b illustrate exponential dilution plots of concentration with respect to time calculated using Equation 3.8, and for propane and butane at the starting concentrations of 100.00 ppm (sample #1) for the experiment with a diluent flow rate of 18.2 cc/min. The sample used also contains methane and ethane at 100.00 ppm but these two components are not detectable by the type of PID used. The differences between the experimental values and the theoretical ones calculated using equation 3.8 are higher (Figure 3-2) during the first 16.0 minutes of the dilution due to the faster change in concentration from 100.00 ppm to 30.00 ppm for both propane and butane. After that period of time the experimental values gradually becomes much closer to those calculated by equation 3.8.

Figures 3-3a and 3-3b are the plots of % relative error between the experimental and theoretical curves as a function of diluent flow rate for propane and butane (sample #1) for four different flow rates. For both propane and butane the relative error is directly proportional to the rate of dilution. For propane, the lowest relative error is 5.5% for a diluent flow rate of 12.0 scc/min corresponding

to a dilution time of 64.3 minutes from 100.00 ppm to 0.35 ppm. The highest relative error was 19.8 % for a diluent flow rate of 61.6 scc/min corresponding to a dilution time of 18.0 minutes from 100.00 ppm to 0.35 ppm. For butane the lowest relative error was 6.0% and the highest 26.3%.

The differences between the experimental concentration values and the theoretical ones are due to 1) variations in the gas flow rate when the injection valve is switched to introduce the sample, 2) non-linear chromatographic effects that contribute more to baseline instabilities when the dilution rate is faster, and 3) the fact that Fourier transforms can be used only for stationary systems or slow changing systems. All these effects will result in baseline variations in the calculated chromatogram. These variations, defined as correlation noise, are discussed briefly in the introduction.

Figure 3-4 shows the chromatograms obtained for the study in which sample #3 (containing methane, ethane, propane, and butane, all at 1000.00 ppm) was used to change a mixture of different composition (sample #2: methane, ethane, ethylene, propane, acetylene, isobutane, propene, propadiene, and propyne) by the multiplex ED technique. All the chromatograms were obtained by calculating the impulse response function as defined in Equation 3.7. Figure 3-4a is the chromatogram of the mixture #2 containing 10

components, before the beginning of the dilution. Methane and ethane are not detectable by the PID used. Propyne is strongly retained in the column and appears as a very low, broad peak beyond the end of the chromatogram. Propene and propadiene elute together at the retention time represented by peak 6 in Figure 3-4a. In addition, a negative pressure peak, sporadically present in the data (Figures 3-4b and 3-4c), originated from a change in pressure when the valve turns at the time of injection. Figure 3-4b is a chromatogram obtained by calculating the input response function after 20.5 minutes of the dilution experiment. After that period of time, propane and butane increased in concentration to 602.3 ppm, while all other components decreased, as expected. Finally, 116.5 minutes after the experiment began the only detectable components were propane and butane at concentrations close to 1000.0 ppm (Figure 3-4c).

This study shows that a multiplex ED technique can be used to simulate gaseous environments where a sample is changing with time as long as the composition changes slowly with time. As discussed above, the errors calculated are a combination of uncertainties due to correlation noise. At present, additional data analysis techniques are being developed to monitor an environment where the analyzed sample changes more rapidly than the one reported here.

3.4 HYDROCARBON ANALYSIS AT SUBATMOSPHERIC PRESSURES

This next experiment uses Multiplex Gas Chromatography to analyze hydrocarbon mixtures at subatmospheric pressures (17) using cross-correlation to analyze the data instead of Fourier Transforms, as used in the previous experiment. A brief description is given of the detector used as well as other experimental and data analysis details. Finally, the results of these experiments at low pressures are reported.

3.4.1 METASTABLE IONIZATION DETECTOR (MID)

The MID was first described by Lovelock as an argon ionization detector, although helium and neon can also be used. In current MID operation, the carrier gas molecules, usually helium, are exposed to an electric field and "excited" to a metastable state through collisions with beta particles emitted by a radioactive source. These excited helium molecules will then ionize any molecules that have an ionization potential below 19.8 eV. The resulting electrons and ions are collected by the detector electrodes and measured by an electrometer.

Since its introduction by Lovelock, the MID has been widely studied and used by many researchers with varying degrees of success.

3.4.2 EXPERIMENTAL SECTION

3.4.2.1 APPARATUS

The chromatographic system developed for this work is shown in Figure 3-5. It employed a miniature triaxial metastable ionization detector whose operation is described in section 3.4.1 (18). The detector was mounted on top of the input head of a Keithley 642 electrometer (Keithley Instruments, Cleveland, OH). The detector was operated, in the cross section mode, at 30 V provided by a Keithley 240A High Voltage Supply. The chromatographic column was 1.5 m long by 1.1 mm i.d. packed with 3,4-dichloro-phenyl isocyanate bound to Poracil C (100-200 mesh) (19). The carrier gas was 99.999% He (Matheson) pretreated prior to entering the column by passage through a Matheson 8302 Hydrox Purifier to remove traces of O₂ and H₂O.

The calibration of this system was conducted using mixtures containing various concentrations of methane, ethane, propane, and butane in helium at five different concentrations ranging from 9.7 ppm to 75.1 ppm (prepared manometrically).

In order to simulate sub-atmospheric pressure conditions a low pressure gas sampling system similar to the one reported in Scattergood et al. (20) was adapted to the GC injection assembly. It consisted of an 8-port Valco valve, with a 0.5 second response time, attached to a Valco

electric actuator (Alltech Associates, Deerfield, IL) for computer control of the valve (see Figures 3-5). Two vacuum pumps were used to maintain the pressure in the injection valve at about 3.0 Torr. In order to diminish the amount of air that leaks through the valve when it is turned back and forth to inject the sample, the sample loops were covered with a plastic bag and flushed with helium. Acquisition cycle times were 120 minutes, with 384 injections for each calculation. Each injection was constrained not to occur again for at least 5.0 seconds after the previous one to allow the sample loop to reach the 3.0 Torr pressure after the sample had been injected. Except for this dead time, the average duty cycle was 2.7%.

The difference between this system and the one reported in Scattergood, et al. (20) is that a smaller valve sample loop was used (2 cm³ instead of 20 cm³). Also in that work, the detector was operated in the metastable state at a much higher sensitivity (e.g. higher voltage) than the one needed for this work.

The system was operated as previously reported multiplex chromatographic systems (21) using a Digital Equipment Corporation (DEC) PDP 11/34A computer through an IEEE 488 interface attached to a Nelson Analytical A/D interface providing both the modulation signal and acquiring the detector signal. Analysis of data involved the use of

cross-correlation techniques as described in section 3.2.4.

3.4.3 RESULTS

Although the chromatographic system developed to simulate subatmospheric pressures on board a spacecraft or any other restricted environment consisted of very rugged components, it has been very useful in proving the feasibility of the multiplex GC technique for this application. Work done previously in The Solar System Exploration Branch at NASA Ames Research Center has demonstrated the usefulness of conventional gas chromatography in providing very useful information under very low pressures (approx. 2-3 Torr) of simulated Titan's atmospheric conditions as an exploratory probe descends toward the planet. This was accomplished by using sample loops with a volume of 20 cm³ (20) to enable the collection of enough sample to satisfy the GC detection requirements. However, some degradation in peak resolution and sensitivity was observed due to further dilution of the sample in the sample loop by the carrier gas.

The Helium Ionization Detector was also used in the more sensitive metastable state mode. A more sensitive detector provides the advantage of detection limits as low as a few ppb for the type of sample used in this work. On the other hand, this detector becomes very unstable and too

sensitive to impurities that might be present in the carrier gas resulting in a higher background signal. The carrier gas in this case is prepurified before entering the system but it takes long periods of time before the detector's baseline is low enough to start an analysis. On the other hand, multiplex gas chromatography offers the advantage of not only reducing the size of the sample loop but also using this detector in the cross-section mode at a much lower sensitivity for a lower background noise.

Figure 3-6 shows the chromatogram obtained for the 9.7 +/- 0.2 ppm concentration mixture at 3.0 Torr pressure by cross-correlation of the pseudorandom signal with the detector output signal. The first peak at very low retention times originates from a sudden change in pressure when the sample is injected.

The S/N is influenced by the following sources: 1) Correlation noise caused by an approximation in the cross-correlation calculation. This could be eliminated by more elaborate calculations (12). 2) Unavoidable variations in the pressure in the sample loops when the sample is introduced into the system causing a pressure differential of more than three orders of magnitude. These variations cause small fluctuations in the flow rate resulting in variations in the retention time of the components present in the sample. 3) Detector and electronics noise. Other

important variations which reduce the S/N include the drifting caused by the large change in pressure when the valve is rotated, thermal effects , and electronic effects. The baseline drift was corrected by subtracting a 200 point moving average from each data point during acquisition. This also has the effect of reducing the sample signal when the baseline drifts too fast. These sources of noise kept the improvements in detection limits from being more than just slightly above those obtained by conventional GC.

The calibration curves shown in Figure 3-7 are for ethane, propane, and butane, respectively. Even though a linear response was obtained for these three components at the concentration ranges used, methane did not respond linearly. The cause for this is that when the valve is rotated to inject a new sample, methane present in ambient air that leaks into the valve adds to the amount already present in the sample. Methane has been reported to be present in this laboratory at approximately 3 ppm (22). Even though the valve was covered with a helium bag, the amount of added methane is enough to cause variations in the amount of methane being introduced into the GC.

This study has shown that multiplex gas chromatography can be used effectively for the analysis of gases at very low pressures. At these pressures not enough sample would be collected for conventional GC. Using multiplex GC,

however, enough information can be obtained since more samples can be introduced in a given period of time due to the multiplex advantage and sample throughput gained with this technique. Also, a smaller loop can be used to reduce nonlinear effects. The difficulties encountered during the course of this work can be avoided by using a more sophisticated system. For example, some of the components of this system could include diffusion vacuum pumps that can evacuate the valve sample loops at a much faster rate. Also, miniature mechanical valves are available which provide a much faster response and are less prone to leaks. Smaller columns and detectors will also allow the collection of many more samples in shorter periods of time.

Although the main goal of this work was to test the feasibility of using a MGC system for determining the chemical composition of other planetary atmospheres at low pressures, this system could also be used for analyses of Earth's upper and lower atmosphere on board aircraft by making appropriate changes in columns and detectors.

CHAPTER 4.

SELECTIVE ABSORPTION USING GAS CHROMATOGRAPHIC COMPONENTS

4.1 HISTORY

Selective adsorption of vapors had its origin before World War I. The first apparent application of this method was the gas mask. Later in the 1920's charcoal was used to measure light hydrocarbons in natural gas. In order to perform these experiments, adsorption took place at a low temperature and desorption of the adsorbed hydrocarbons took place at a higher temperature. Using an external oven which slowly travelled along the adsorbent tube, A. Eucken and H. Knick managed to improve the technique in 1936. N. C. Turner combined all the techniques in 1943 and additionally introduced measurements of the effluent's thermal conductivity. All these experiments, in addition to others, culminated in the development of Gas Adsorption Chromatography. The modulation and mathematical data analysis techniques developed in this Thesis have the same origin as Gas Adsorption Chromatography; however, this does not utilize a column, the critical component of chromatography.

4.2 THEORY

4.2.1 SELECTIVE THERMAL MODULATION

Selective Thermal Modulation (STM) is a technique which selectively modulates a sample in a gas stream producing a concentration pulse. Several modulation techniques are discussed in section 3.2.3.

Determination of trace levels of water in gaseous mixtures by Andrawes, 1983 (23) used a gas chromatograph (GC) with a Helium Ionization Detector and a column packed with Poropack N. Also, Hossain et. al., 1976 (24) used a GC system consisting of a Thermal Conductivity Detector (TCD) and two columns in order to separate water from helium, carbon monoxide, carbon dioxide, oxygen, and methane. In the selective modulation work, a selective thermal modulation technique was developed as a method of water vapor determination for use in Mars' atmosphere. The Martian atmosphere consists primarily of carbon dioxide, and may contain trace amounts of water vapor.

The technique reported here uses thermal modulation to selectively modulate the water vapor concentration in helium and carbon dioxide gas streams using a piece of stainless steel tubing coated with sorbitol. A change in the concentration signal of water vapor is generated in the gas stream by changing the temperature of the sorbitol. Due to the selectivity of this technique, the need for a

chromatographic column was eliminated. The technique of signal averaging was used to improve the sensitivity of the water detector.

We feel that the STM instrument is a viable candidate for applied uses especially where size, weight, cost, and simplicity of design rate of second importance only to effectiveness of the instrument.

4.2.2 THERMAL CONDUCTIVITY DETECTOR

The Thermal Conductivity Detector, or TCD, is one of the first successful detectors (25). It consists of a temperature-controlled stainless steel container with two orifices bored in it. Aluminum plates further contain the TCD to provide a high heat conductivity and mass sufficient to obtain a precise control of the temperature. A wire or filament made from metal with a high temperature coefficient of resistance is placed in each orifice. The two filaments are connected into the arms of a Wheatstone bridge. Pure carrier gas flows through one orifice (the reference cell) and the sample gas from the column flows through the other orifice (the analysis cell).

The electronic unit of the TCD incorporates two power supplies and the Wheatstone bridge circuitry. The first power supply, +15 V, regulates the full-wave rectified AC input voltage with some integrated circuits. This power

supply is all solid-state. In order to significantly reduce sensitivity to line voltage fluctuations, the +15 V is channeled back to be used as a reference for the regulator. The purpose of this first power supply is to provide a fixed reference for both the temperature controller and the current supply.

The second power supply provides a selected constant current to the Wheatstone bridge, up to 200 mA and 50 V. A high-gain differential operational amplifier compares the voltage produced from current flowing through the detector bridge with the selected voltage. Any difference between the two voltages produces a differential signal which is amplified and used as a correction voltage for the series current regulator transistor. The stability and regulation of this supply is better than 0.005% of the set current.

The TCD depends on the rate of heat flow from a heated wire placed in a gas stream and the rate of heat loss depends on the thermal conductivity of the gas flowing around the wire. So if the composition of a gas stream changes, its thermal conductivity will also change. Subsequently the wire's heat loss will change, and the wire will settle at a different equilibrium temperature and electrical resistance. Since both the filaments in the Wheatstone bridge are similar, a change in gas composition creates a potential difference that can be measured and

recorded. The potential difference is directly proportional to the concentration of the component in the gas stream which was detected.

The temperature of the wire, that of the surroundings, and the gas flow rate are the three most important conditions which affect the TCD's performance. Therefore, it is most desirable to have the highest possible bridge current, without burning the filament, to raise the temperature of the wire. This creates a bigger difference in the rate of heat loss when there is a small difference in the surrounding gas: thermal conductivity.

The TCD has been successfully used for analysis of trace amounts of water. It is much more stable than the MID for the analysis of water. Sensitivity of the TCD is determined by the thermal conductivity of the gases used.

4.3 EXPERIMENTAL SECTION

This experiment uses Gas Chromatographic components and chemical modulation techniques to analyze water vapor using signal averaging to analyze the data. A brief description is given of the detector used as well as other experimental and data analysis details. Finally, the results of these experiments are reported.

4.3.1 APPARATUS

The Selective Thermal Modulation (STM) system is shown in Figure 4-1. Water vapor samples were prepared by varying the gas flow of the carrier using a Datametrics Type 1511 Controller with two Model 825 Datametrics Mass Flow Controllers (Datametrics, Santa Clara, CA.) and by varying the temperature of a Dynacal Water Permeation Device (VICI Metronics, Santa Clara, CA.). The actual gas flows were measured using a bubble meter, for greater accuracy of the flow rates.

The modulator consisted of a 5 inch length of 1.5875 mm O.D. 1 mm I.D. stainless steel tubing coated with 20 ml of a 10.0 % solution of sorbitol (Applied Science Laboratories Inc., State College, PA), shown to be selectively absorptive to water vapor (26), in methanol (J.T. Baker Chemical Co., Phillipsburg, NJ.). The modulator was coated under a pressure of 5 psig of nitrogen gas which slowly moved the sorbitol-methanol solution through the tubing.

The modulator was encased by a teflon tee through which pulses of cool compressed air were introduced upon command. Continuous heating of the modulator to slightly below the melting point of sorbitol (100 °C) was achieved by applying 50.0 mV (4.00×10^{-6} W) to the stainless steel tubing in order to prevent its saturation with the water vapor present in the sample stream. The sample stream modulation, occurring

every 39.5 seconds, consisted of half-second pulses of cool air blown over the stainless steel tube, cooling the sorbitol coating and momentarily allowing the water vapor absorption. After the pulse of cool air stopped, the modulator heated up again and the sorbitol released the previously absorbed water vapor.

The water vapor which was released represented a change in sample concentration which was detected by the thermal conductivity detector downstream in terms of a change in voltage between the normal amount of water vapor and the pulse of desorbed water vapor in the sample stream versus the reference stream which contained no added water vapor.

The water laden sample gas flowed through the modulator into a Carle Model 100 Micro Detector System (Carle Instruments, Inc., Fullerton, CA.) which includes a thermal conductivity detector that measured the difference between the thermal conductivity of the sample gas and the reference gas. This difference in thermal conductivity was expressed as a change in the output voltage of the thermal conductivity detector. The thermal conductivity detector (TCD) resided in a Model 4300 Valve Oven (Carle Instruments, Inc., Fullerton, CA.) at 105 °C, to ensure that water would not accumulate in the detector. This minimized the nonlinear effects often experienced when working with water. Unfortunately, raising the temperature also reduced the

sensitivity of the TCD.

Initial testing and calibration of the STDM system involved the use of 99.999% helium (Matheson, Newark, CA.). Calibration experiments were conducted at seven different concentrations of water vapor in helium ranging from 41.5 to 184.5 ppm. Subsequently, the system was calibrated using water vapor in 99 % carbon dioxide (Matheson, Newark, CA) to emulate a Martian atmosphere. Due to the low purity of this gas, a cold trap consisting of methanol and dry ice at -40 °C was used to remove water present in the carbon dioxide carrier gas. Calibration experiments were performed at four different concentrations of water vapor ranging from 100.9 to 150.9 ppm (Figure 2). Acquisition times for the calibration experiments were 47 pulses in 32 minutes for water in helium and 95 pulses in 60 minutes for water in carbon dioxide. Subsequent signal averaging of each experiment yielded the final signal. Limiting the upper range of concentrations is that saturation of the modulator occurs at 180-190 ppm. At this concentration, the signal begins to degrade and becomes irregular and non-reproducible.

Data acquisition was controlled using a System 1800-Model B High-speed Microcomputer (Integrated Image Systems, Santa Clara, CA.) through an IEEE 488 bus interface and a Nelson Analytical 900 Series A/D interface (Cupertino, CA.)

both collecting data from the TCD and controlling the operation of the electric switches which activate the modulator. The software used for activating the modulator and acquiring output data was supplied by Nelson Analytical but modified by us to perform the STM experiments. The data acquisition rate was two points per second. Signal averaging techniques were applied to the raw data on a MicroVAX II (Digital Equipment Corporation, Santa Clara, CA.) using a program written in IDL (Interactive Data Language).

4.4 RESULTS

Figure 4-2 represents the signals obtained after performing signal averaging computations for the mixture containing $41.5 \pm .83$ ppm of water vapor in helium (Figure 4-2a) and the mixture containing 100.9 ± 2.02 ppm of water in carbon dioxide (Figure 4-2b). The small peak present in both signals at $t=5$ sec, is caused by a voltage surge caused by turning the electric switch, which controls the flow of cold air, on and off. Figure 4-2a was generated from 32 minutes of data acquisition and the signal-to-noise ratio for water in helium improved by a factor of 13.5 as a result of signal averaging, improving the detection limit from 17.3 ppm for the one pulse signal to 1.3 ppm. Figure 4-2b was generated from 60 minutes of data acquisition and the signal-to-noise

ratio for water in carbon dioxide improved by a factor of 8.1 as a result of signal averaging, lowering the detection limit from 460.8 ppm for one pulse signal to 56.7 ppm. The signal-to-noise is worse than in Figure 4-2a, because of the similarity in thermal conductivity between water vapor ($44.63 \times 10^{-6} \text{ cal-sec}^{-1}\text{-cm}^{-1}\text{-}^{\circ}\text{C}^{-1}$) and carbon dioxide ($41.74 \times 10^{-6} \text{ cal-sec}^{-1}\text{-cm}^{-1}\text{-}^{\circ}\text{C}^{-1}$) at room temperature (27). The position of the water peaks differed depending on the carrier gas used. Water vapor in helium traveled fairly slowly from the modulator to the detector. On the other hand, water vapor in carbon dioxide moved much faster. The significant difference in retention time is due to mass effects. Carbon dioxide is much heavier than helium and is therefore more effective at "pushing" the water vapor along the tubing. Similar experiments were performed using argon to confirm this observation.

Figure 4-3 represents the calibration curves for water in helium (Figure 4-3a) and water in carbon dioxide (Figure 4-3b). A comparison of the slopes of the calibration curves of water vapor in helium, and that in carbon dioxide, reveals only a 8.5% difference between them.

The STM technique can easily be developed for use in any application which requires quantitative analysis of water vapor concentration. The power of this technique lies in its simplicity. It only consists of a few components,

all of which are independent. These advantages may one day allow the STM technique to be widely used in the analysis of gases specifically in analyzing water vapor in the Martian atmosphere from a land rover or a descending spacecraft.

Even though this specific application was the main goal of this study, the technique may be applied to many other areas. The STM can measure water vapor concentrations in gas cylinders, relative humidity in room environments, or any other application associated with the measurement of water vapor concentration.

CHAPTER 5.

CONCLUSION

Four different experimental methods and data analysis techniques have been demonstrated. Each one has its area of applicability. The laser system is ideally suited for use on a planet where the atmospheric composition is known. However, the selective modulation system is best suited to a situation in which you only know the one component of the atmosphere in which you are interested. Both multiplex gas chromatographic techniques described in this thesis are ideally suited for a probe descending through a planetary atmosphere where there is not enough time to perform conventional gas chromatographic analyses.

A comparison of detection limits between both of the experimental methods for detecting water vapor showed that the Selective Thermal Modulation system was 16,000 times more sensitive to water vapor than the Tunable Diode Laser system. However, the laser is a much more stable system. Both these experiments could be useful in the analysis of water vapor in planetary atmospheres as well as many other applications.

The power of the multiplex GC technique has been demonstrated for use under conditions of changing sample

concentrations and also at low pressures. The ability to take uninterpretable multiplexed gas chromatographic data and use Fourier transform and cross-correlation techniques to calculate the impulse response function, or chromatogram, opens the door for gas analysis under conditions which would normally not be possible. Conventional gas chromatography is limited under these conditions.

New techniques will be developed as challenges for future missions are encountered. Some of these missions will include atmospheric probes to Neptune and to a comet. As has always been the case in past NASA projects, interesting applications on Earth will be found in the process of the research.

CHAPTER 6.

FIGURES

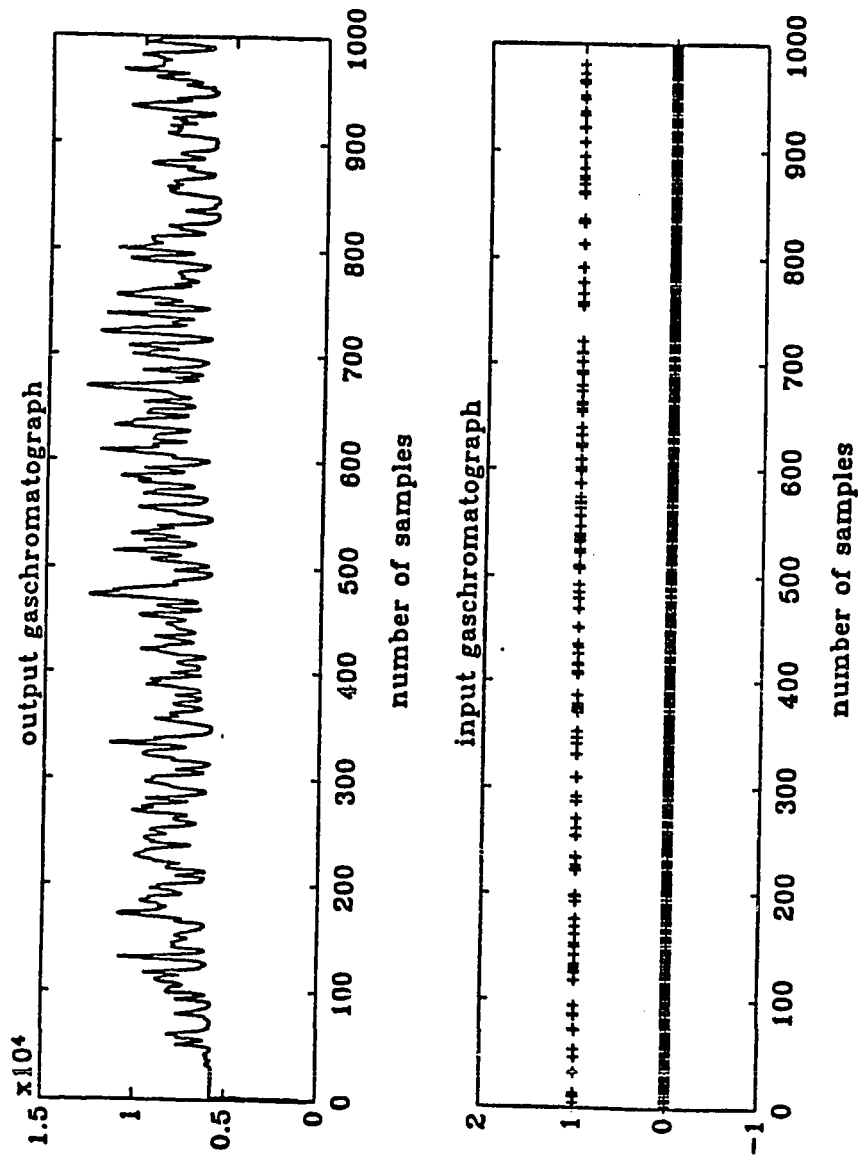


Figure 1-1 Graphs of input and output signals of a typical multiplex gas chromatographic experiment.

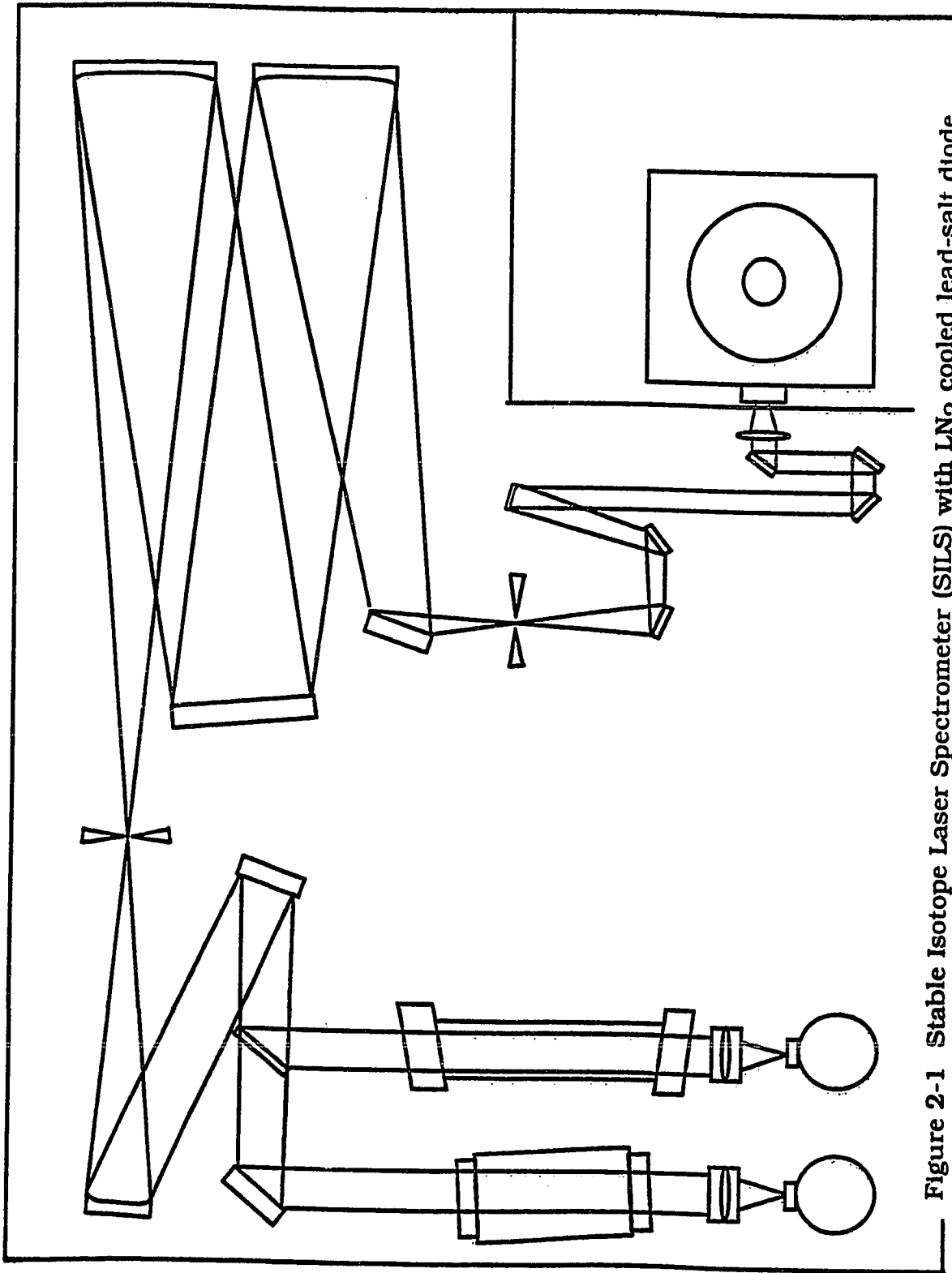


Figure 2-1 Stable Isotope Laser Spectrometer (SILS) with LN₂ cooled lead-salt diode laser, grating monochromator, and LN₂ cooled InSb detectors.

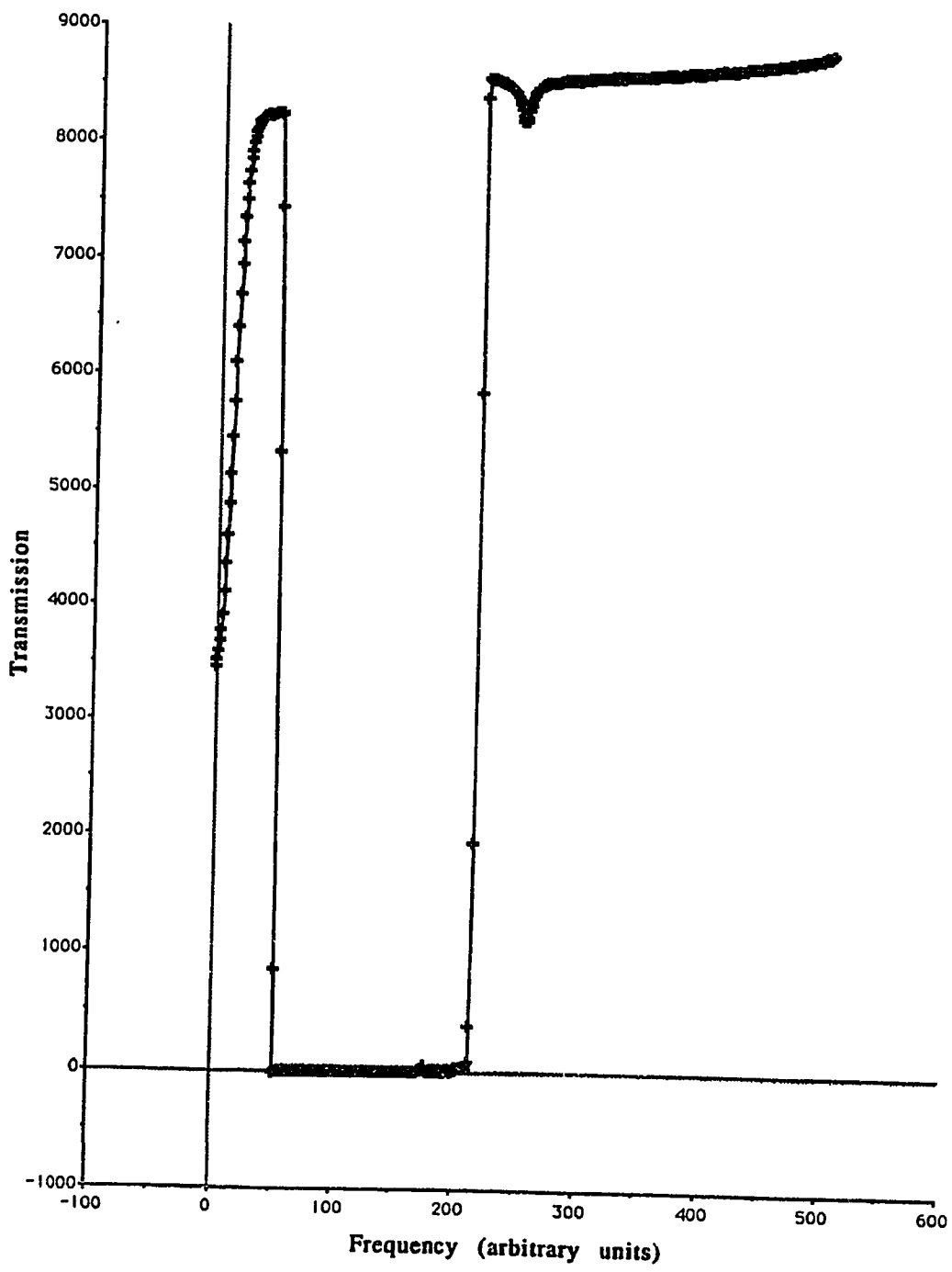


Figure 2-2 Typical spectra of the J=9 water vapor line at 14.7 Torr

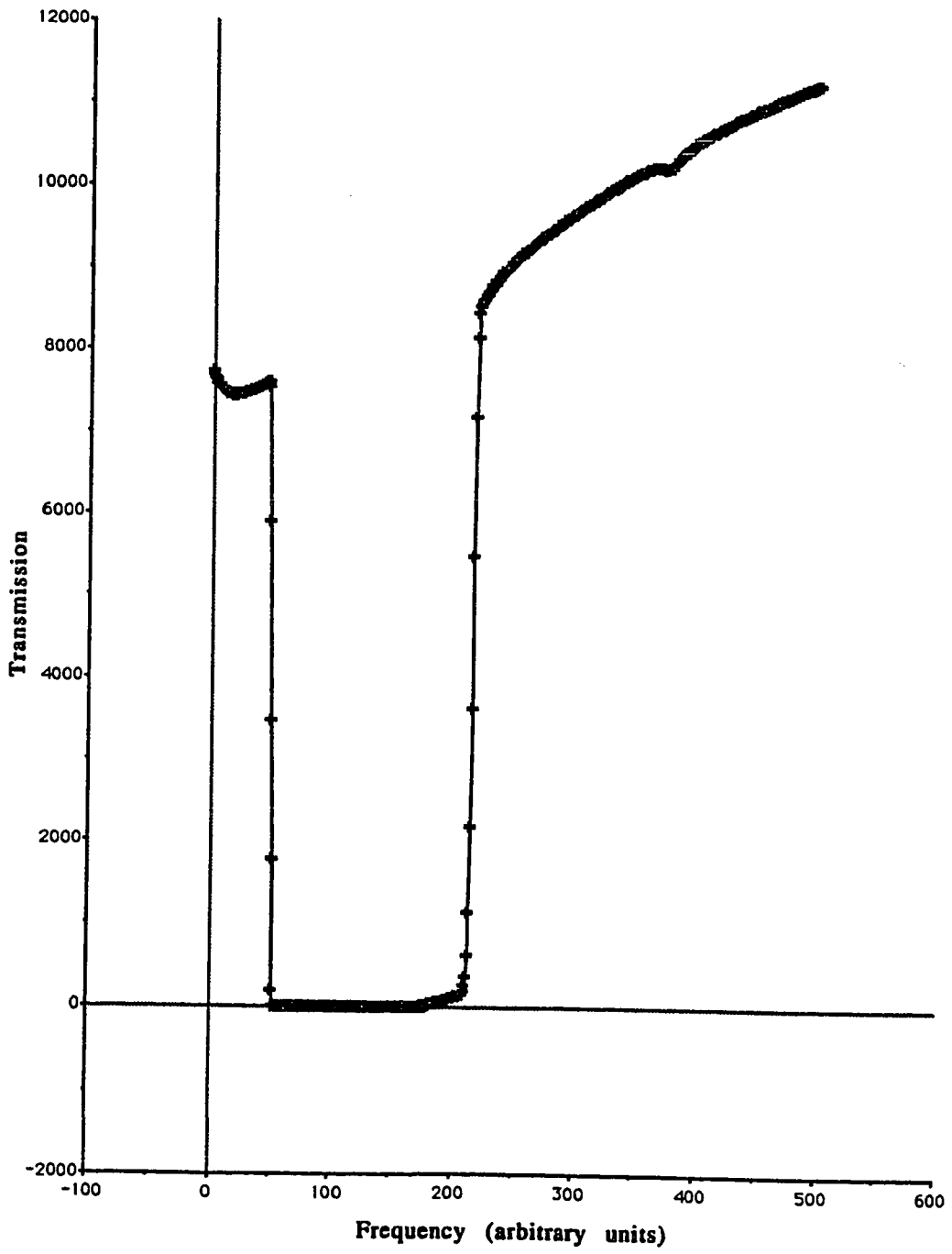


Figure 2-3 Typical spectra of the J=8 water vapor line at 14.7 Torr

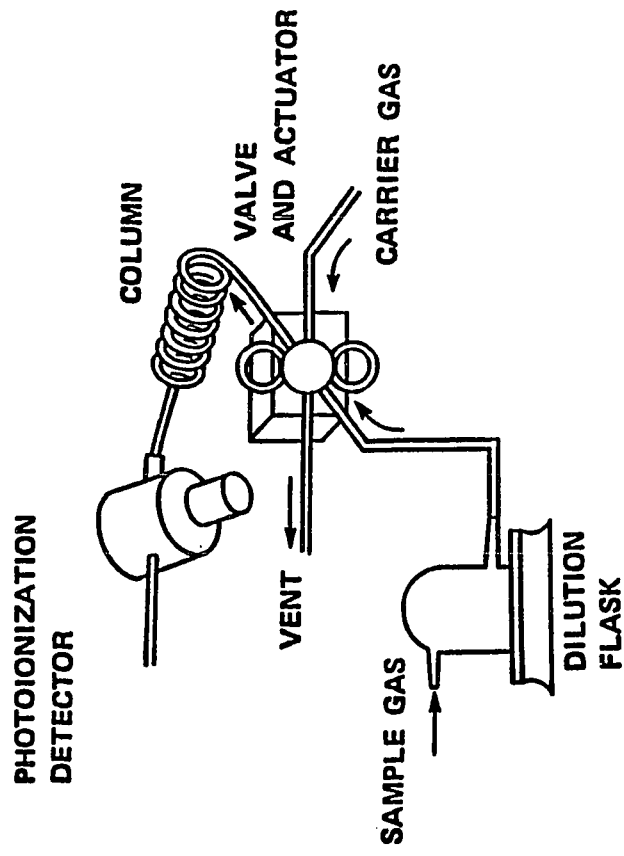


Figure 3-1 Schematic diagram showing the major components of the multiplex exponential dilution flask gas chromatographic system.

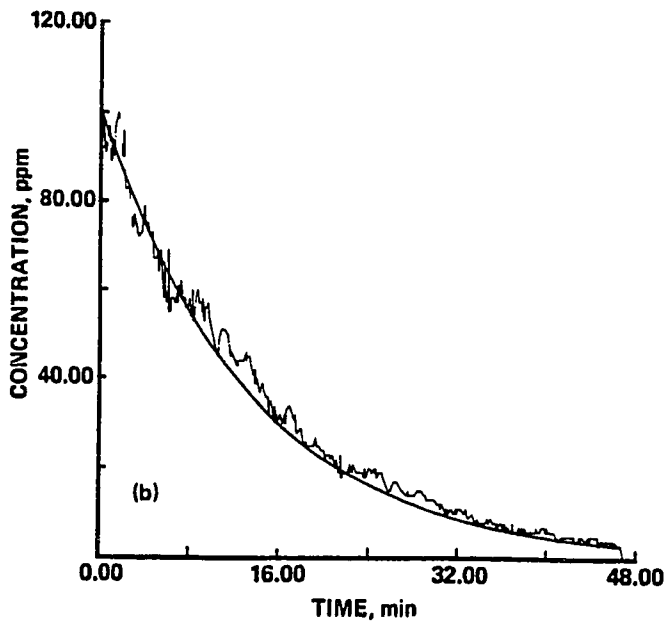
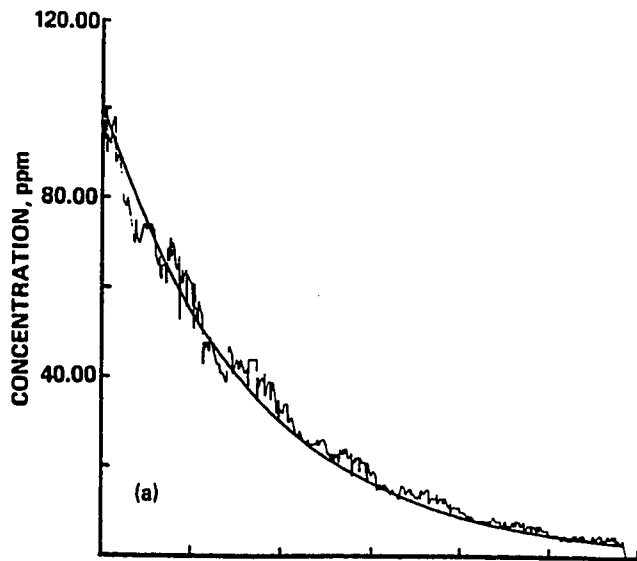


Figure 3-2 Exponential curves showing an exponential decrease in concentration for a) propane and b) butane at an initial concentration of 100.00 ppm, and a theoretical curve calculated using equation #3.7 for comparison with the experimental ones for the ED experiment using a diluent flow rate of 18.2 scc/min.

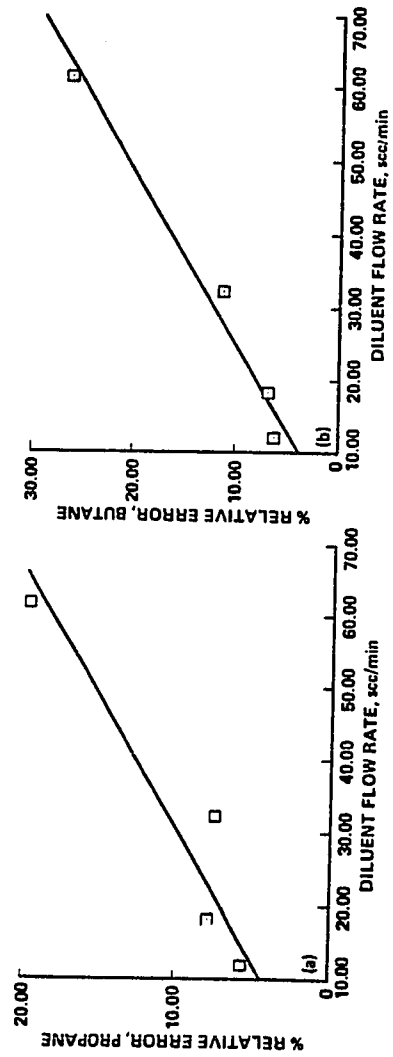


Figure 3-3 Plots of % of relative error between the experimental and theoretical curves as a function of the four diluent flow rates used for a) propane and b) butane. For propane the slope was 0.28 ± 0.07 , intercept = $1.37 \pm 0.2.42$, and coefficient of determination = 0.90 . For butane the slope was 0.42 ± 0.05 , intercept = -0.56 ± 1.69 , and coefficient of determination = 0.98 .

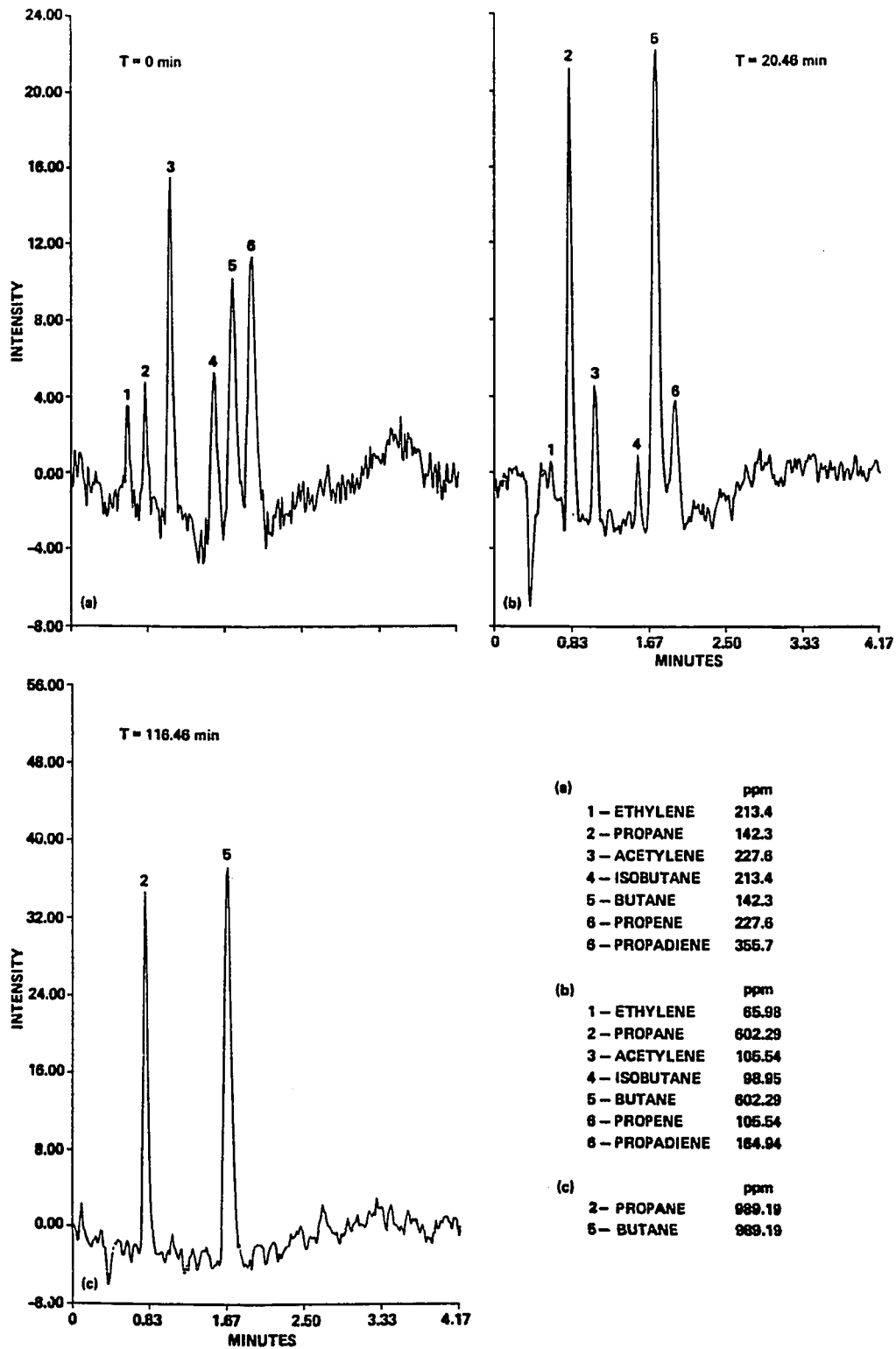


Figure 3-4 Chromatograms obtained from the calculation of the impulse response function at three stages during the change in sample composition. The column temperature was 25 °C and the flow rate was 9.0 cc/min. Intensity is in arbitrary units.

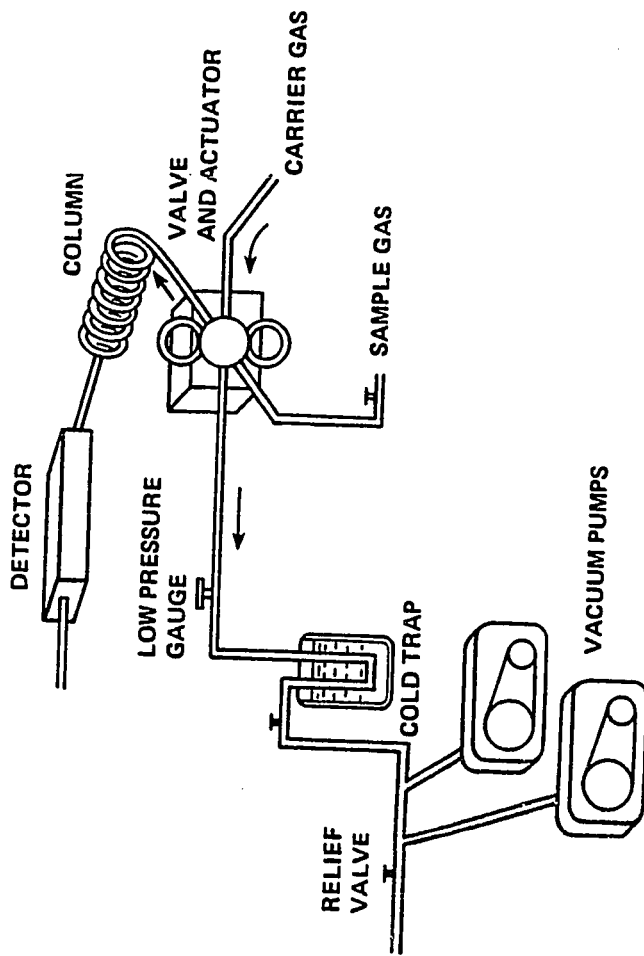


Figure 3-5 Schematic showing the major components of the low-pressure gas chromatographic system.

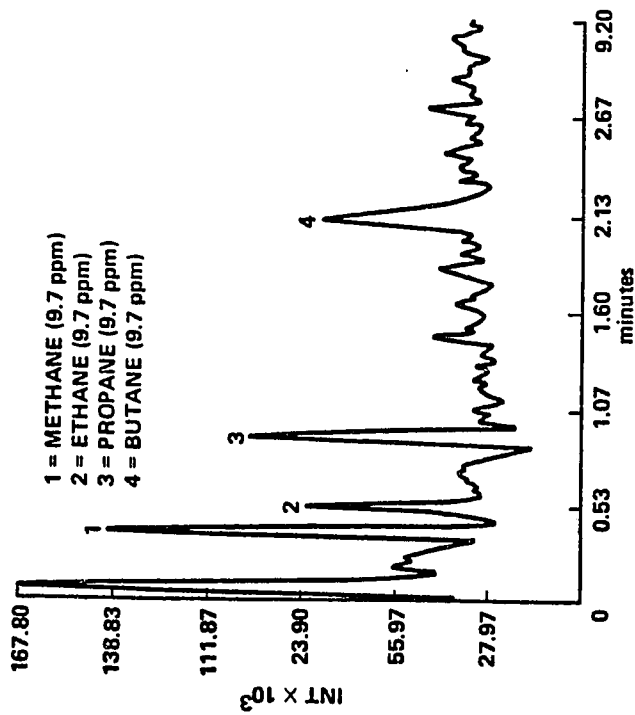


Figure 3-6 Chromatogram obtained at 3.0 torr. The four peaks correspond to 1. Methane, 2. Ethane, 3. Propane, and 4. Butane at 9.7 ppm each. The detector was operated at a voltage of 30 V and a current of 0.0162E-9 A. Column temperature was 25 °C and the flow rate was 12.0 cc/min.

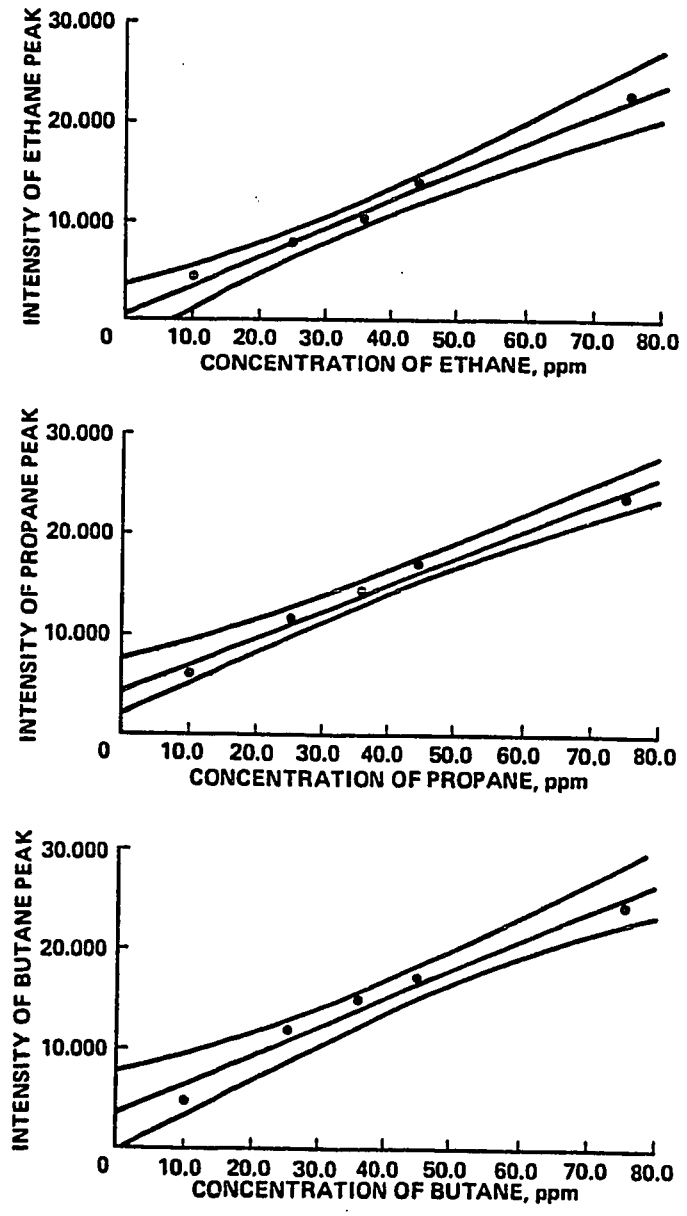


Figure 3-7 Calibration curves showing a linear increase in the intensity of the measured signal with increasing amounts of ethane, propane, and butane, in helium. The coefficient of determination for each curve was 0.982, 0.988, and 0.977 respectively. The confidence band is at a 3 sigma confidence for the line as a whole.

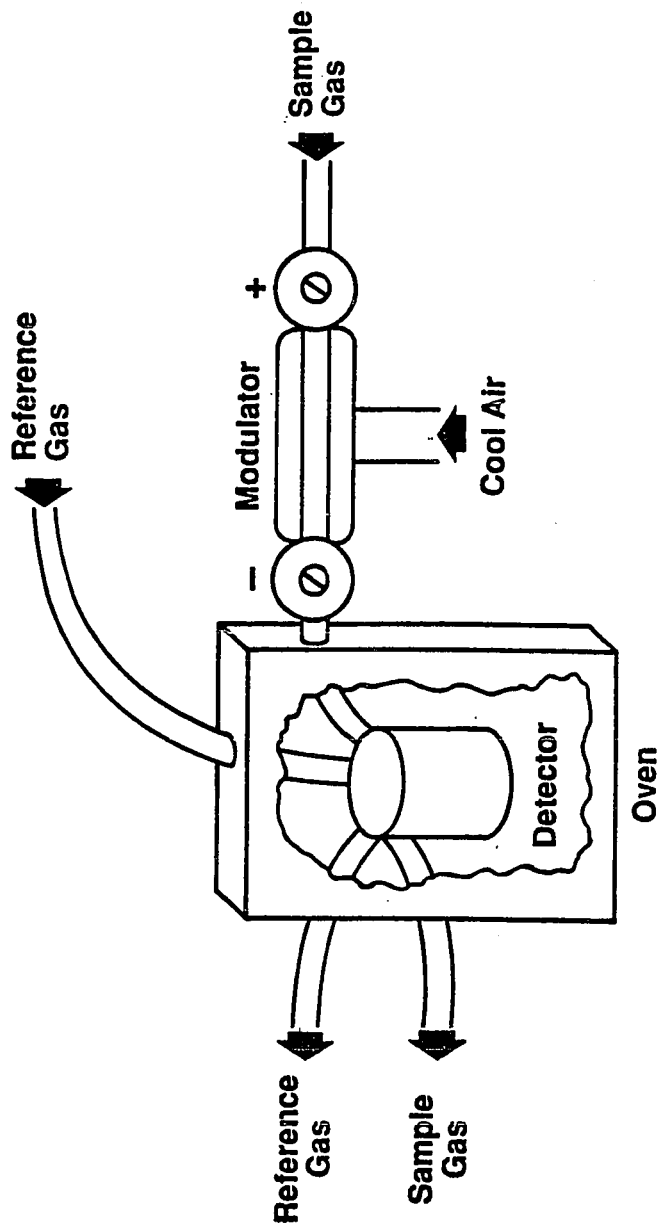


Figure 4-1 Diagram showing the major components of the Selective Thermal Desorption Modulation system.

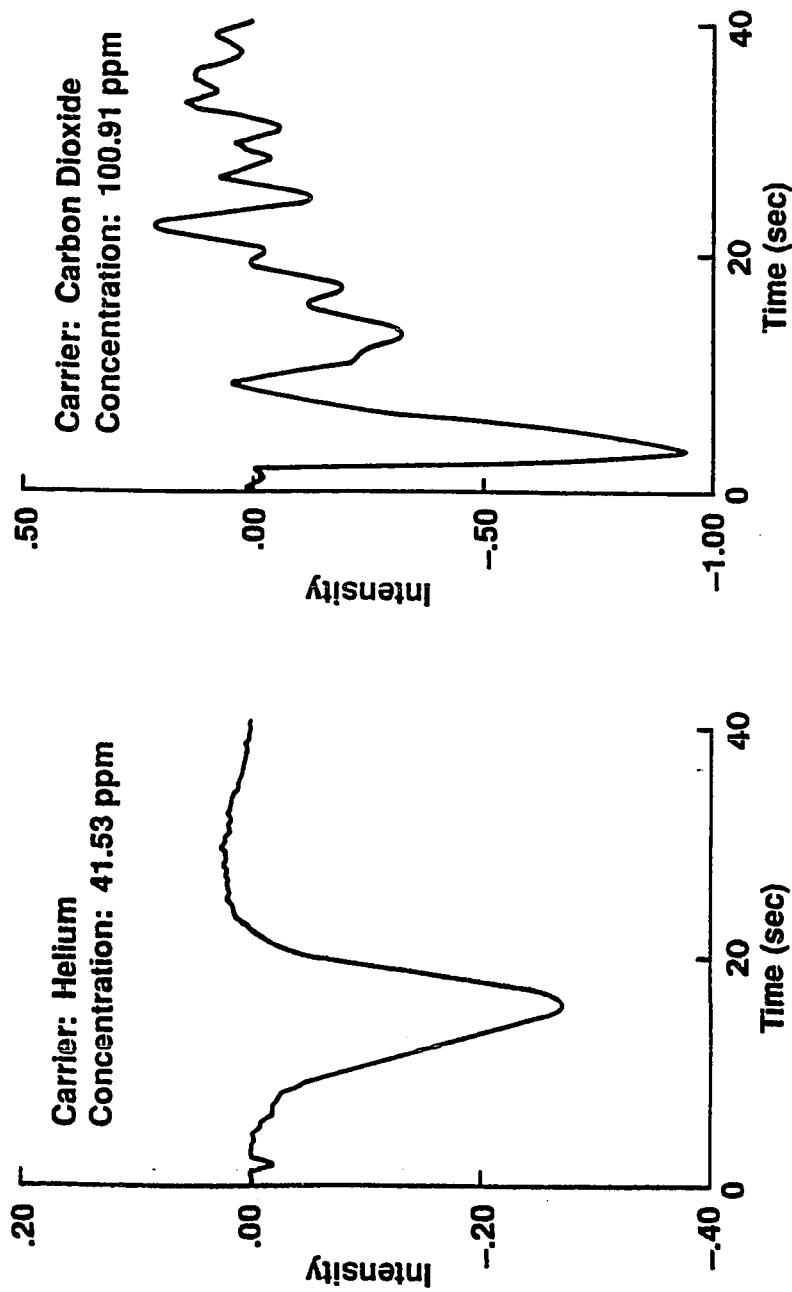


Figure 4-2 Signal obtained from the signal averaging of water vapor in (a) helium, and (b) carbon dioxide. The modulation signal consists of 79 points: heat on, air off, and 1 point: heat on, air on. The data acquisition rate is 2 points/second, and the oven is maintained at 105 °C. The water concentrations are (a) 41.5 ppm (47 modulations), and (a) 100.9 ppm (95 modulations).

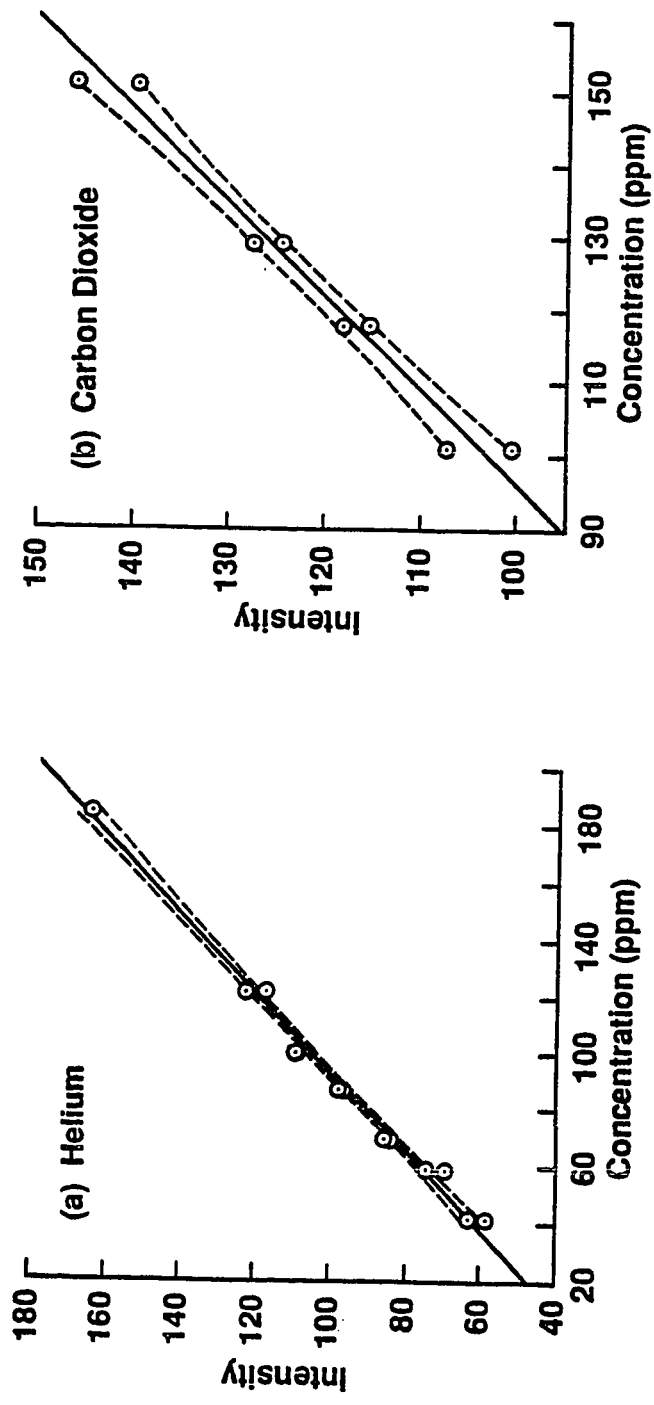


Figure 4-3 Calibration curves showing a linear increase in the signal intensity with increasing concentrations of water vapor in (a) helium, and (b) carbon dioxide. Each point represents (a) 32 minutes and (b) 60 minutes of data averaged together. The slope of the helium-water calibration curve is .72 with a variance of $3.32E-4$ and the intercept is 32.73 with a variance of 3.62 . The slope of the carbon dioxide-water calibration curve is $.78$ with a variance of $3.16E-3$ and the intercept is 24.97 with a variance of 50.11 . The coefficient of determination for the helium-water calibration curve is 0.99 and that for the carbon dioxide-water calibration curve is 0.97 , with the confidence bands at a 90% confidence for the line as a whole (9.M. G. Natrella)

CHAPTER 7.

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