THE INVESTIGATION OF THE USE OF INFRA-
RED SPECTROSCOPY IN THE DETERMINATION OF
THE DEUTERIUM CONTENT IN NATURAL WATER

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ABSTRACT

An infrared spectrophotometric method has been investigated for
the determination of deuterium concentrations in the range of natural
waters. In the final form of equipment used, concentration differences
of 0.0020 mole % D between two samples could be detected. Various
Hawaiian natural water samples were analyzed and the results showed
that the deuterium content of the samples follow the patterns expected
as a result of fractionation in the hydrologic cycle.

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I. INTRODUCTION

A. Properties of Deuterium

The two most abundant isotopes of hydrogen are protium ($_1H^1$) and deuterium ($_1H^2$ or D). The ratio of the natural abundance of these two isotopes is approximately 5000 H : 1 D. Of the two, protium is by far the most important due to its preponderance in nature. Deuterium is useful in research as a tagging atom for the physical and chemical reactions of hydrogen even though it is somewhat different in its properties from protium. The greatest differences exist in the physical properties of the hydrogen isotopes but in general their chemical properties are similar. Like protium, deuterium reacts with oxygen to form water:

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$2D_2 + O_2 \rightleftharpoons 2D_2O.$$
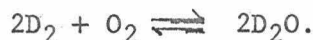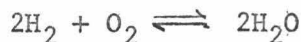
The product formed from the reaction of the deuterium and oxygen is called heavy water, deuterium oxide or deuterated water. Upon mixing the two substances, protium oxide and deuterium oxide, an exchange reaction occurs and equilibrium is established:

$$H_2O + D_2O \rightleftharpoons 2HOD.[1]$$
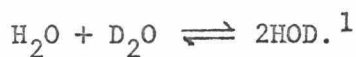
At very low concentrations of deuterium oxide, the only species present are H_2O and HOD. The concentration of deuterium in natural waters varies by about 25%[2] and is in the range of 0.0145 mole % D which is a low enough concentration so that the assumption that deuterium is only in the form of HOD is justified.

B. Geochemical Interest

It is of interest in the field of geochemistry to know the deuterium concentration of natural waters throughout the world. It is known that the concentration of deuterium in these waters follows definite patterns.[3] In the continental surface waters of the United States, the deuterium concentration is determined primarily by prevailing temperature. Because of its higher mass, deuterated water has a higher boiling point than light water. In repeated evaporation and condensation, the lighter water evaporates faster than the heavier water, and the concentration of deuterium in the water sample increases. As the latitude and altitude decrease, the temperature normally increases. Therefore, the deuterium concentration would be expected to increase with a decrease in latitude and altitude. This has proved to be the case.

There are also secondary effects which determine the concentration of deuterium in natural waters. Transport of water by rivers may change the concentration of deuterium in an area by bringing either a higher or lower amount of deuterium from another area. Air passing over cool mountains that reaches intermountain valleys tends to cool these valleys. The result is a lesser concentration of deuterium in the lower altitude valleys than expected. The deuterium concentration of a particular area is also altered by seasonal precipitation and evaporation from the surface of the earth.

The major features of the behavior of deuterium in the hydrologic cycle has been summarized by Friedman, et. al.[3] The

deep water of the oceans is the reservoir for both H_2O and HOD. As evaporation occurs at the surface of the sea, particularly in the subtropics, the deuterium concentration of the surface water is increased up to 1 per cent, and in the water vapor is depleted by some 6 per cent, as compared with the deep ocean source. In the subtropics, further fractionation occurs, due to the reprecipitation of about two-thirds of the water vapor. The remaining water vapor is depleted by about 10 per cent in deuterium, and this moves over land or ocean at high altitudes.

As the vapor moves over land at high altitudes, it is precipitated in the form of rain or snow. As the precipitate falls from the cold high altitudes to the warmer low altitudes, it is re-evaporated and re-equilibrated with the vapor in the lower layers of air. This process tends to increase the deuterium concentration of the precipitate and the liquid water which reaches the surface of the earth contains more deuterium than the vapor derived from the sea. The rain which reaches the earth's surface at low latitudes may contain deuterium in about the same concentration as the surface water of the ocean. In arid regions standing water possesses an even higher concentration of deuterium.

The enrichment of the vapor in deuterium by precipitation is limited at high latitudes because the warmer layers of the atmosphere are absent. The precipitation which reaches the ground is similar to that of high levels at low latitudes or is further reduced by the fractionation that occurs with increasing altitude.

Fractionation of water occurs when a change of state is encountered. This can be between vapor and liquid, liquid and solid, or vapor and solid. There are two types of conditions by which the change of phase occurs. These are fractionation under equilibrium conditions and fractionation under transient conditions.

Under equilibrium conditions, ice formed from liquid, ice formed from vapor, and liquid formed from vapor will have a higher deuterium content than the respective phase from which each was formed. The fractionation under this condition usually is not complete in nature because the two phases are not properly mixed. For instance, in the freezing of a lake, the water below the ice is not replaced by new water and each successive layer of ice formed is depleted in its deuterium content. This is because the surrounding water has been previously depleted in its deuterium content by the formation of ice.

The concentration of deuterium under transient conditions varies according to the distance that the water or water vapor has traveled. An example of this is the forming of an icicle. The base of the icicle has a higher deuterium content than the tip because the deuterium of the liquid is removed as the liquid moves down the icicle.

In Hawaii geochemical research in atmospheric and geologic systems has been limited to rain water.[5,6] As an extension it would be of interest to analyze the natural waters of Hawaii for possible differences in deuterium concentration from island to

island and from sea level to the top of high mountains such as

Mauna Kea (13,796 feet). Another important source of samples

which would be of great interest would be the natural waters and

vapors of the volcanic areas on the island of Hawaii, since both

the atmosphere and the oceans of the earth are believed to have

originated from the gases and vapors of volcanoes.[8]

C. Organic Mechanism Interests

Another area where a sensitive method for determining deu-

terium in water is desirable is in the study of the mechanisms of

organic reactions.[8,9] Through equilibration deuterium frequently

can be exchanged for the hydrogen present in a molecule. Deuteri-

um, therefore, can be used to label organic substances, which con-

tain hydrogen, and the course of a reaction of these labeled mole-

cules can be followed. This can be done by analyzing the products

at various stages during the reaction for their deuterium content.

These products can be burned to form water and the analysis of

this water will show which products contain deuterium, and also

indicate the amount of deuterium.

D. Nuclear Industry Interest

The analysis of deuterated water is also important in the

growing nuclear industry. Some nuclear reactors use heavy water

as a moderator and it is important that the deuterium concentra-

tion remains constant. This requires repeated analysis of the

heavy water. Approximately $2,000,000 of the annual operating

cost for the reactor at Chalk River, Ontario is spent on heavy

water.[10] Therefore it is important to detect small heavy water

leaks quickly. This means that the water around any possible source of leaks must be analyzed frequently for the deuterium content. Tritium, which is also present in the moderator, has harmful biological effects. Leaks from the reactor would contain tritium and great pains must be taken to prevent this from entering the public water supply.

E. Object of This Research

It is the purpose of this research to investigate the use of infrared spectroscopy for determination of the deuterium content in water at concentrations in the natural water range. The standard methods used in the past and at present are described below. Although these methods are sufficiently accurate, they have the disadvantage of being slow and tedious which limits the use of the method. It was hoped that a more convenient method using infrared spectroscopy could be developed which would have an accuracy and sensitivity equal to the best standard methods.

II. HISTORICAL REVIEW

A. Standard Methods

The standard methods used for the analysis of deuterium in water are described in Kirshenbaum.[11] Many methods have been developed and these, with modifications, are applicable over almost the entire deuterium range i.e., from normal water to pure heavy water. The methods of analysis can be divided into two groups. One involved the numerous methods of analysis employing the mass spectrometer, which directly determines the mass of the hydrogen atoms, and second, the direct analysis of the deuterium content of water by determination of one or more of the physical properties of the mixture.

Because of memory effects, water should not be analyzed directly on the mass spectrometer, and therefore it usually is decomposed to hydrogen has. A problem results in analyzing water by this method since fractionation may occur. However, successful decomposition methods have been developed.[12] A more convenient mass spectrometer method involves the equilibration of the water samples with hydrogen or deuterium gas and the subsequent analysis of the gas on the mass spectrometer.[13] This latter method uses a platinum catalyst and a peptizing agent such as fumaric acid to speed equilibration. The method is suitable for almost the entire range of deuterium concentration,[14] and is one of the most reliable mass spectrometer methods.[15]

The second group of methods for the analysis of water for its deuterium content includes density methods, refractometric

methods, and miscellaneous methods based on other property differences of the two isotopes. The difference in density (or specific gravity) of H_2O and D_2O is the basis of densiometric methods. This difference is about 10 per cent. The density of the mixture of very sensitive to the deuterium content. The methods which are based on this difference are among the most precise used. The most important of these are the determination of the density of the samples by the pycnometer methods, the float methods, and the falling drop method. Because the O^{16}/O^{18} ratio varies in water, it is necessary to know the amount of O^{18} present.

The refractometric method uses an interferometer to measure the difference of refractive index of two samples. Once the interferometer is calibrated, the method is both fast and simple. However, the reproducibility is only about 0.01 to 0.02 mole % D.

Other analytical methods include thermal-conductivity, spectroscopic methods, freezing point differences, viscosity differences, vapor pressure ratios, gas chromatography, and differences in potential between hydrogen and deuterium electrodes. Although these methods have their uses, they lack the high sensitivity of the mass spectrometer and density measurements. However, most of these methods have not been fully investigated as to their potential for all aspects of this analysis. In general, methods which involve any physical differences of H_2O and D_2O may be used, but the difference must be sufficiently large to attain the desired analytical accuracy.

The first mentioned methods of analysis have a high degree of accuracy. The sensitivity of the mass spectrometer methods is about 0.0002 mole % D[16] and that of the densiometric methods is about 0.0002 mole % D.[17] These are relatively well established methods and the results are precise. The most serious disadvantage is the extremely refined technique and the time required for an analysis by density methods and the cost of equipment in mass spectrometry. For example, these methods are much too slow for the quick results required in nuclear reactor maintenance. It is desirable then, to develop a method of analysis in which the manipulations are simple and which can be completed in a relatively short period of time.

B. Infrared Methods

The infrared spectra of heavy water shows an absorption peak for the O-D stretching band at 2513 cm^{-1}. As seen below, absorption spectrometry at this wavelength has been used by a number of workers with a degree of success for the determination of the deuterium concentration in water. The sensitivity of infrared spectrophotometers has been improved over the years and consequently there is a hope that the method may achieve the sensitivity and accuracy of the best of the other methods of analysis.

The first use of infrared spectrophotometers for the analysis of deuterated water was carried out by Thornton and Condon[8] in 1950. The concentration of deuterium was in the 0 to 3 mole % D range and the precision obtained was 0.03 mole % D. In 1954, J. Gaunt[18] used infrared absorption to analyze the deuterium con-

centration in water for concentrations of above 99.5 mole % D and below 0.8 mole % D. The higher concentration gave an accuracy of 0.001 mole % D and at 0.8 mole % D the accuracy was 0.008 mole % D. An error of 10 to 15% was found for deuterium concentration of twice the natural abundance. Berglund-Larsson[9] in 1954 found an error of 0.006% for concentrations up to 1.3 mole % D. Gaunt used the matched cell method for his work and the others used a single cell with the instrument operated on double beam.

The greatest contribution to the use of infrared methods has been made in the analysis of heavy water in nuclear reactors. Stevens and Bayly[10] at Chalk River, Ontario in 1958 used the difference-absorption method for the analysis of 99.5 mole % D to 99.99 mole % D with a precision of 0.003 mole % D. A method for low concentrations was also developed. This used a NH_3 "Tri-Non" non-dispersion detector developed by Perkin-Elmer. The detector used in this instrument is based on the sensitivity of ammonia gas to the wavelength absorbed by deuterium. Essentially, the detector is a gas filled condenser-microphone and responds only to those wavelengths that are absorbed by the gas. The precision of the instrument was 0.01 mole % D at 1 mole % D and 0.003 mole % D at 0.03 mole % D. The disadvantages of this method were three-fold. First, the pressure of the ammonia gas decreased over long periods of time eventually making the detector useless. Second, commercial production of the instrument was stopped. Third, the method used two cells, one for the reference water and one for the sample. The sample could be contaminated by dust particles while

this was not possible for the reference thus leading to scattering of light which would interfere with the O-D absorption peak.

Bayly and Stevens in 1959 used a non-dispersion bichromator in an attempt to improve the above method. A photo-conductive cell was used as the detector. Another innovation in this instrument was the use of one cell for both reference water and sample. This eliminated the effects of dust and other contaminations.[19]

In 1960 Andonedis and Wiesemann at the Carolina-Virginia Tube reactor analyzed water of low deuterium content. They were able to detect 0.015 % D by weight. The precision was 0.003 % D by weight at 0.03 % D by weight and 0.01 % D by weight at 1 % D by weight.[1]

Stevens, Bayly, Thurston and Kartha in 1961 analyzed heavy water samples in the range of 1 to 99% D_2O. Two methods were used employing optical densities. The first method used the optical densities at transmission peaks of 2700 cm^{-1} and 1900 cm^{-1}. The standard deviation was 0.01% at 99% D_2O, 0.1% at 40% D_2O and 0.01% at 1% D_2O. The second method was based on the measurement of optical densities at 1645 cm^{-1}, 1460 cm^{-1} and 1220 cm^{-1}. The standard deviation over the entire range was less than 0.15% D_2O.[20]

Abernathy and Morgan in 1962 used the 3390 cm^{-1} D_2O band for the analysis of heavy water in the 99 to 100 mole % D range. They were able to obtain a precision of 0.003 mole % D.[21]

In 1964, Erley and Blake at Dow Chemical Company were able to determine concentrations of 200 ppm using an infrared spectro-

photometer without scale expansion. A wedge cell containing the reference water was placed in the reference beam and the sample was placed in the other beam. The solutions were allowed to equilibrate for ten minutes and the spectra was taken.[22]

The most significant work for the detection of low concentrations of deuterium by infrared method was carried out by Bayly, Stevens and Thurston at Chalk River, Ontario in 1964. The method was developed to test the efficiency of an improved on-stream monitor used to detect leakage of heavy water into natural water in a heavy water reactor.[23] Previous to this research, the precision of this method was limited to about 0.003 mole % D because of the large effect of small temperature change on the extinction coefficient of H_2O. Heating of thin cells by the infrared beam causes a change in absorption and this becomes critical when attempting to measure deuterium by infrared at a concentration of a few parts per million. The technique used was an important modification of previous methods in that thermostated streams of reference water and unknown water were passed through the same cell for an equal amount of time. The instrument was set to record continuously at 2500 cm^{-1} and the sample and reference water were flowed through the cell alternately at one minute intervals. This was repeated several times, and the average of the difference of absorption was used. The second modification was the limiting of the spectral width of the impinging beam. This was accomplished by placing an interference filter in the beam which gave a narrow band at 2500 cm^{-1}. These modifications eliminated the

problem of matching two cells in path length and more important, the drift due to heating effects was kept to a minimum. A Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with an ordinate scale-expander was used. The instrument was run on double beam with two spiral attenuators placed in the reference beam which cut the intensity down to about 4%. A CaF_2 cell with a thickness of 0.25 mm was used for the samples. With the capabilities of the instrument stretched to the limit, it was possible to measure a difference between the reference and standard of 0.0002 mole % D with a precision of 0.0002 mole % D.

III. EXPERIMENTAL

A. Theory

Infrared spectra arise from the different modes of vibration and rotation of a molecule. The rotational spectra occurs at long wavelengths, usually larger than 400 cm^{-1}, whereas the vibrational spectra occurs below 400 cm^{-1} or in the short wavelength region. These energy states, both rotational and vibrational, have discrete energy levels according to the quantum theory. The frequencies at which molecules vibrate are related to the masses of the constituent atoms and the binding energies. From this it can be seen that the O-H and O-D vibration frequencies will be different even when considered on the basis of mass alone. The water molecule absorbs radiant energy strongly from about 3704 cm^{-1} to longer wavelengths except for a region between 2941 cm^{-1} and 1754 cm^{-1}, and deuterium oxide absorbs from about 2777 cm^{-1} except for a region between 2222 cm^{-1} and 1295 cm^{-1}. The transparent region of water (2941 cm^{-1} to 1754 cm^{-1}) is the same region which deuterium oxide begins to absorb. Therefore, this region can be used for quantitative analysis of deuterium oxide with minimum interference from water absorption. The O-D stretching band at 2513 cm^{-1} is strong and as mentioned previously absorption at this wavelength has been used for the analysis of deuterium in water.

The Bouguer-Beer law is applied in infrared theoretically as it is in the visible and ultraviolet regions. The use of the terms absorbance and absorbance index are in accord with the

recommendation of the National Bureau of Standards. The absorbance index can be determined by the path length of the cell and by the spectra of each component at a selected wavelength where the other has weak absorption. This method is difficult to apply in most cases and empirical methods are usually employed. The chief difficulty in applying the Bouguer-Beer law to infrared spectrophotometry is that much of the energy is scattered. This is especially true in the short wavelength region and at high absorbance. This scattered energy invalidates the use of the Bouguer-Beer law. The energy from the source is small for a particular wavelength and the amount of energy changes with a change in wavelength. For instance, the energy at 6666 cm^{-1} may be as much as 100 times as much as that at 1000 cm^{-1}. Because of this small energy, the slit width must be rather wide. For ideal conditions the width at half of the maximum absorbance is comparable to the effective slit width. A slight shift of the wavelength would cause a large change in the absorbance index. Because of this, absorbance indices determined on one instrument cannot be used on another instrument.

Various methods are available for measuring the amount of absorbance. With the cell in the sample beam and the reference beam blocked, the single beam spectra of the reference water and the sample can be compared. This is done by first recording the reference water spectra and then the sample water. An absorption peak at 2513 cm^{-1} in the sample will show the presence of deuterium and the area of this peak will depend on its concentration. A

similar method would be to operate the instrument on double beam with an attenuator placed in the reference beam. Analysis would be carried out as before. The major difficulty in either of these two methods is that the O-D absorption peak is on the side of a water peak which interferes with the O-D peak as can be seen in Figure 1. The advantage of double beam over single beam operation is that a larger portion of the spectrum can be covered and variations in intensity are eliminated. The use of double beam operation is limited, however, because a ratio of intensity between the two beams is used. In effect, a loss of energy in the sample beam is noted. By using single beam operation the intensity is absolute. Because a narrow region of the spectrum is used in the analysis of deuterium in water, and because the absorption is small for low concentrations of deuterium in water the advantage of higher energy attained by single beam operation outweighs the other advantages of double beam operation.

With the instrument operated on double beam and two identical cells placed in their respective beams, a difference in absorbance is noted at 2513 cm^{-1} when the deuterium concentration is the sample cell is different from its concentration in the reference cell. The advantage of this method is that it eliminates the interference from the water peak. A disadvantage is that it is difficult to obtain two cells with identical path lengths.

A good method for quantitative analysis is "cell-in-cell-out" operation. This uses one cell placed in the sample beam
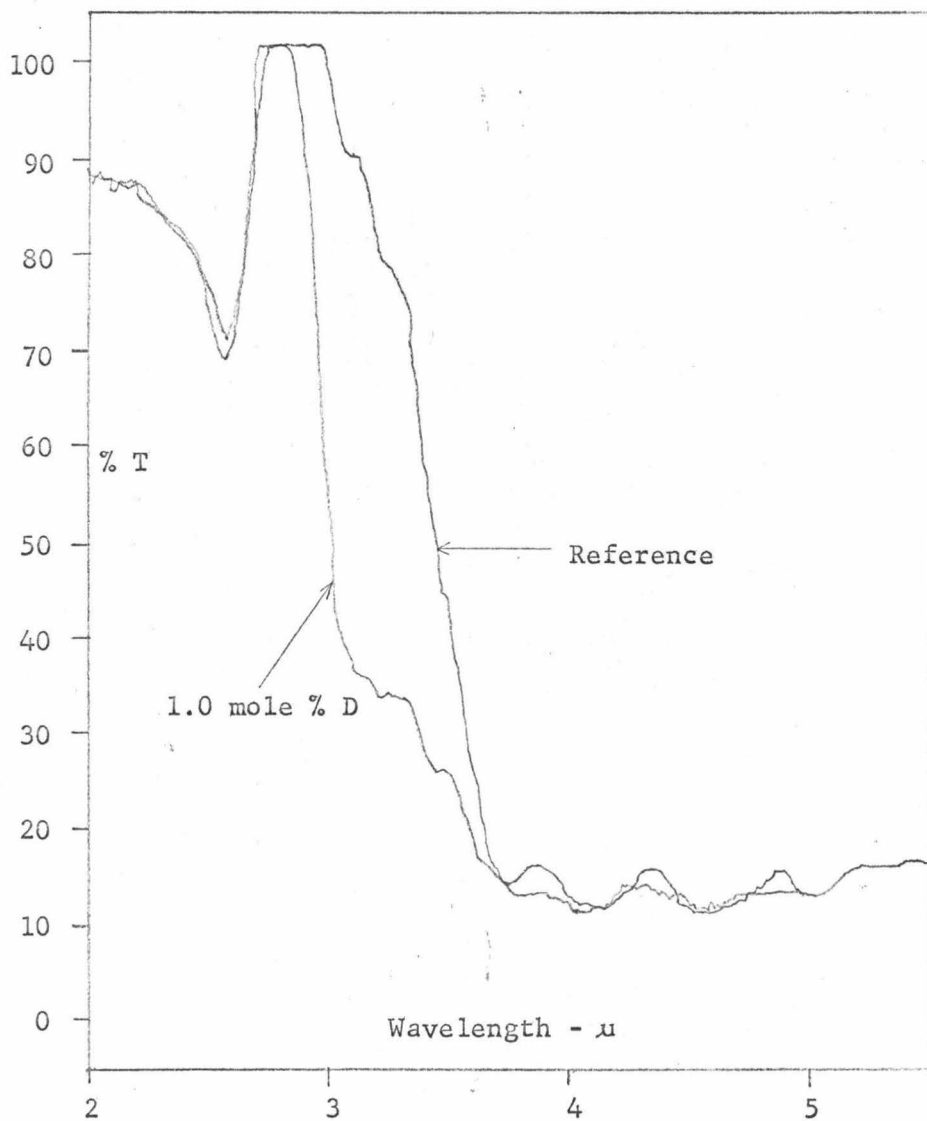
FIGURE 1 - Spectra of 1.0 mole % D Sample Superimposed
on Spectra of Reference Water

with the instrument operated on either single beam or on double beam with an attenuator placed in the reference beam. The slit width and wavelength are set so that maximum response for deuterium absorption by the unknown is achieved. In the case of the O-D stretching band, this wavelength is 2513 cm^{-1}. This method has the advantage of using only one cell and thereby eliminating the problem of matching two cells in path length. By keeping the wavelength constant there is no interference from nearby peaks. The size of the peak is measured in effect only by the difference in absorbance of the reference and sample and not by the area of the peak. Although the instrument can be operated on either single beam or double beam, the single beam is preferred so that maximum energy is attained.

It has been pointed out as a result of the work done by Bayly, Stevens and Thurston that the heating of the cell by the beam affects the amount of absorption.[24] It has been noted by several other workers that the size of the absorption peak of infrared bands in dependent on temperature.[24-29] This is especially true for the O-H absorption bands. As the temperature decreases, the amount of absorption increases. This can be as much as 25% for a difference in temperature of 75° C. Qualitative explanations have been offered and Brown has made some theoretical calculations assuming that the effect is caused by changing band shape due to collisional processes. This effect is not due to instrumentation.

B. Equipment

The infrared instruments used in this research included the Beckman IR-5 and IR-9 Infrared Spectrophotometers. The Beckman IR-5 is an automatic-recording double-beam instrument. The instrument cannot record continuously at a constant wavelength. The scale expansion, slit program and time constant are fixed. This limits the use of this instrument for quantitative analysis. The IR-5 was used primarily for preliminary studies.

The Beckman IR-9 Recording Spectrophotometer is a research model and is far superior to the IR-5. A schematic drawing showing the main parts of this instrument is shown in Figure 2. The instrument is equipped with a slit control which allows the slit width to be varied independently of the wavelength, and both the slit width and wavelength can be reproduced. The wavelength can be kept constant and the recording of the absorbance at this wavelength can be achieved. The instrument is equipped with an ordinate (% Transmission) scale expansion which allows the spectroscopist to expand any portion of the scale by a factor of twenty. The sensitivity of the instrument is especially good and it was hoped that it would be satisfactory for the determination of deuterium concentration differences which are found in natural water.

Four types of cells were used in the investigation of this method. The windows of these cells were CaF_2 except for the NaCl windows of the 10 meter gas cell. Calcium fluoride windows were used because they are transparent in the infrared region to 1111
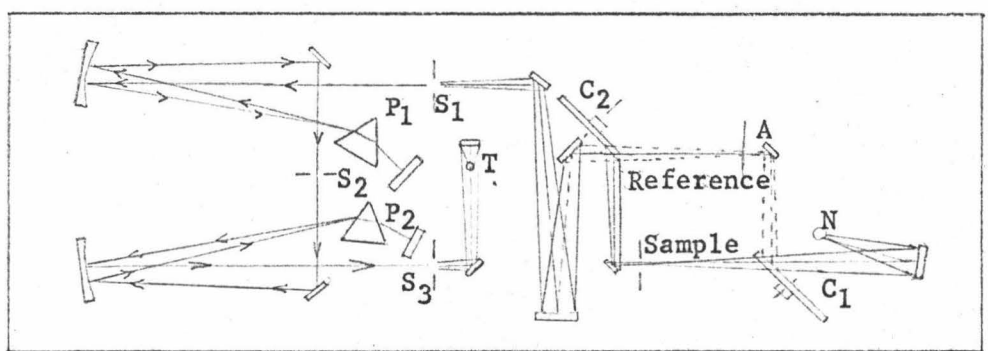
FIGURE 2 - Schematic Diagram of Beckman IR-9 Infrared
           Spectrophotometer

        P = Prism   T = Thermocouple
        S = Slit   N = Nernst Glower
        C = Chopper Motor   A = Attenuator

2.8 meter path - beam makes six traversals
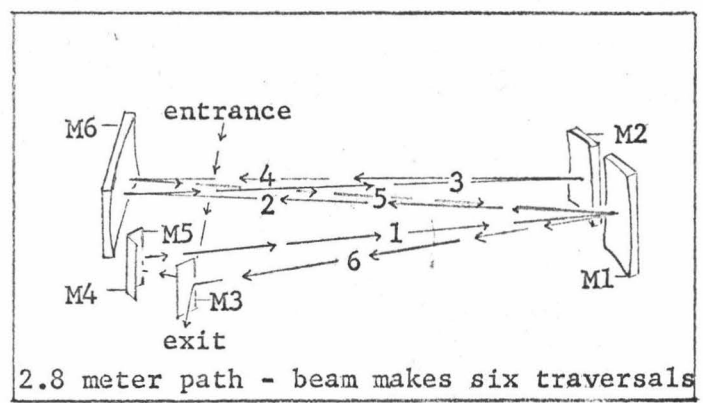
FIGURE 3 - Schematic Diagram of a 10 m Gas Cell

        10 m path - beam makes twenty-two
        traversals

        M = Mirror

cm^{-1}, and they are insoluble in water.

The first type of cell used was manufactured by Connecticut Instrument Corporation. These cells have no fixed thickness nor are they convenient to fill. The path length can be varied by the amount of pressure applied when assembling the cell and also by the expansion of the sample in the cell due to heating by the beam. The cell is shown in Figure 4.

A liquid-type cell of fixed path length was found to be most satisfactory. This was obtained from the Research and Industrial Instruments Company and is of type F-05 CFT. The thickness of the cell can be varied by the use of various spacers. Once a spacer is installed, the path length remains constant and the cell is filled with a syringe. This cell is both convenient to use and has a reproducible path length. It is pictured in Figure 5.

A simple gas cell of 12 cm path length was made from glass tubing and CaF_2 windows. This is shown in Figure 6. A fourth type of cell used was a Beckman 10 meter gas cell. By using a system of mirrors the effective path length can be varied up to 10 meters. The principle of operation of this cell can be seen in the schematic diagram of Figures 3 and 7.

C. Gas Phase Detection

Use of the vapor phase was attempted for the analysis of deuterium in water by two techniques. The first method involved the preparation of a gas cell with a path length of 12 cm (Figure 6). The cell was evacuated and then closed off with a stopcock.
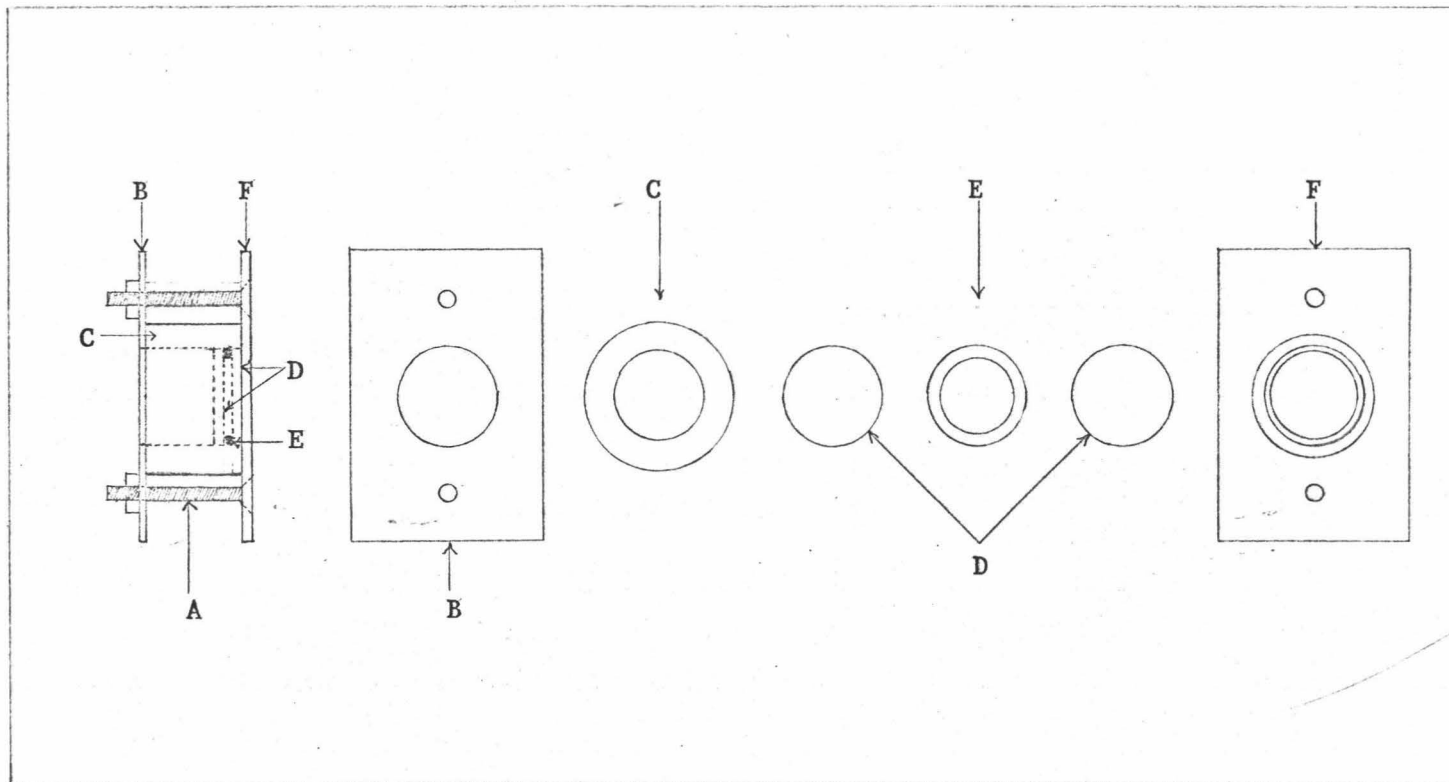
FIGURE 4 - Schematic Diagram of Connecticut Instrument Cell

A = Bolt   D = CaF$_2$ Windows
B = Limiting Plate   E = Spacer
C = Window Holder   F = Cell Mount

The sample was added to the tube above the stopcock and was pulled into the cell when the stopcock was opened. A large amount of vapor was required to attain absorption for the O-D band. A heating tape was used to heat the cell so that with increased vapor pressure a larger amount of sample coule be vaporized.

A ten meter gas cell was also used (Figures 3 and 7). Because NaCl windows were used in the cell, the humidity inside the cell had to be maintained at less than 40%. Therefore, water vapor could not be introduced into the cell directly. Nitrogen gas was used as a carrier gas and also to dilute the water vapor. By keeping the sample and reference water at 10° C the humidity inside the cell was about 35%. The nitrogen gas was first bubbled through the cold reference water and then into the cell. After the cell was filled with the mixture it was closed and the spectra recorded. The spectra of the sample was obtained by using the same procedure.

D. Liquid Phase Detection

The liquid phase measurements were attempted first with Connecticut Instrument Corporation cells (Figure 4). The disadvantages of these have already been pointed out. Both the Beckman IR-5 and IR-9 spectrophotometers were used. The instruments were operated on double beam with an attenuator placed in the reference beam. The spectra was first recorded for the reference water and then the deuterated water, and the two spectra were compared. The same procedure was used for single beam operation.
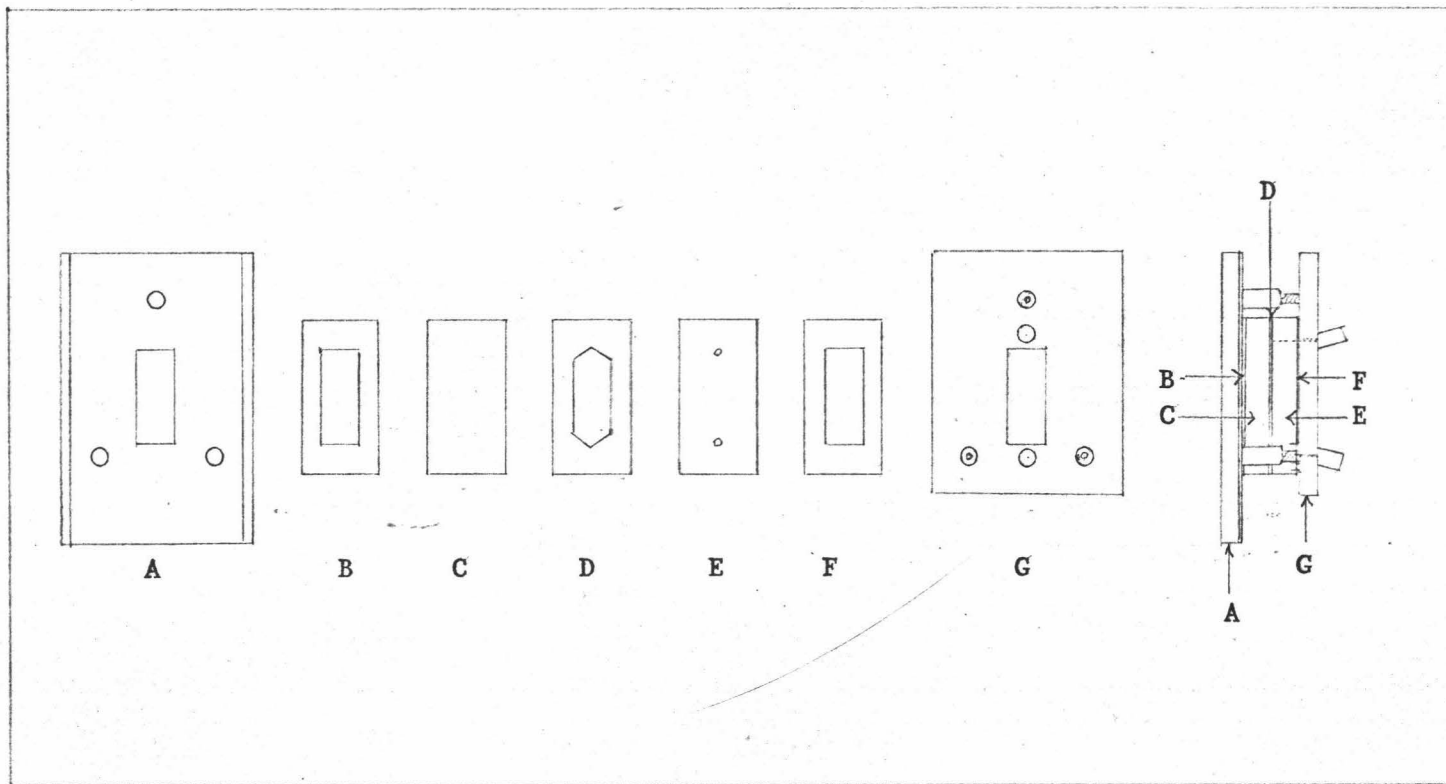
FIGURE 5 - Schematic Diagram of Semi-permanent Cell

A = Cell Mount
B = Gasket
C = CaF$_2$ Window

D = Spacer
E = CaF$_2$ Window
F = Gasket
G = Front Plate

Stopcock

140
mm

CaF$_2$ Window

CaF$_2$ Window

20
mm

← 120 mm →
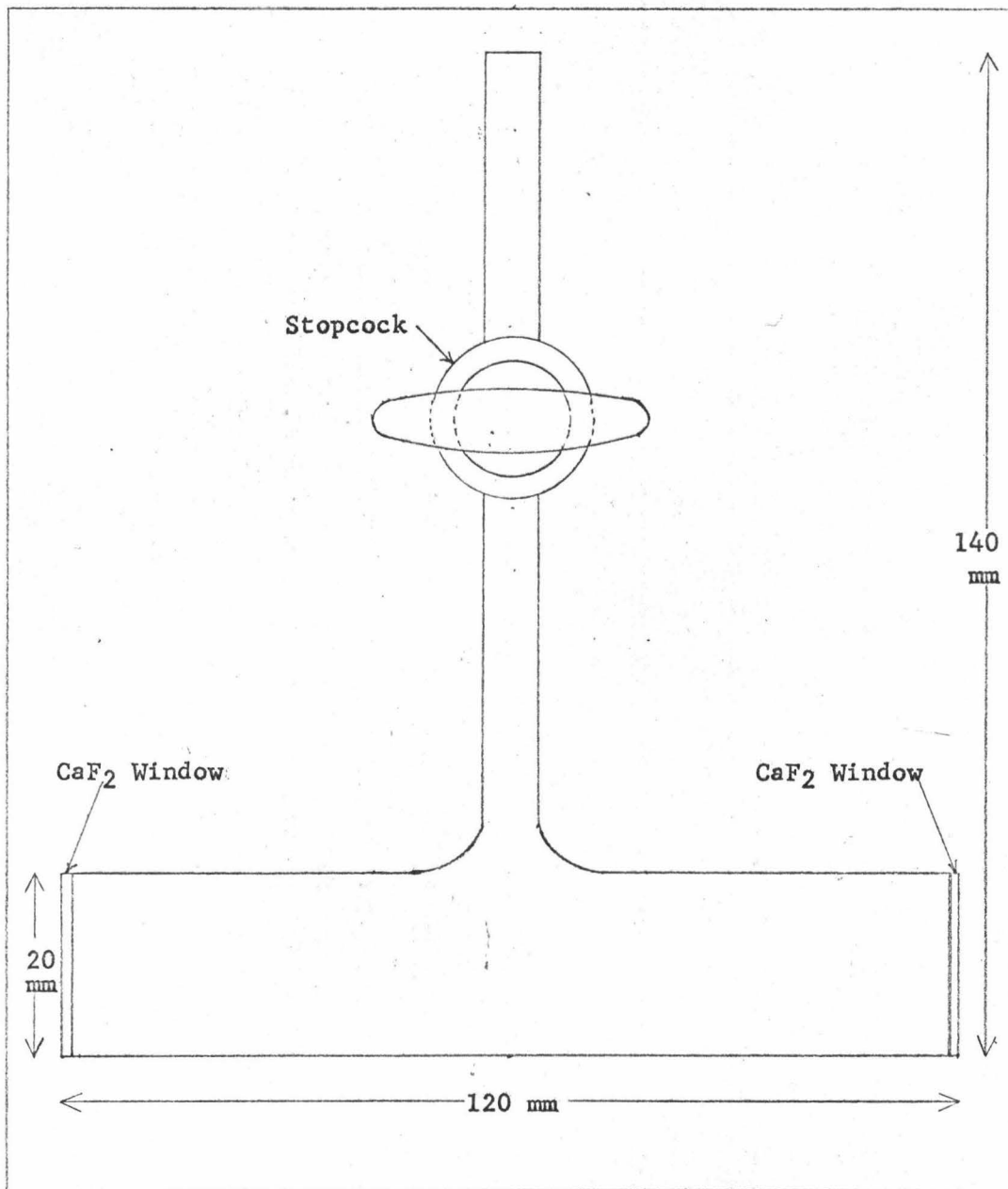
FIGURE 6 - Schematic Diagram of 12 cm Gas Cell
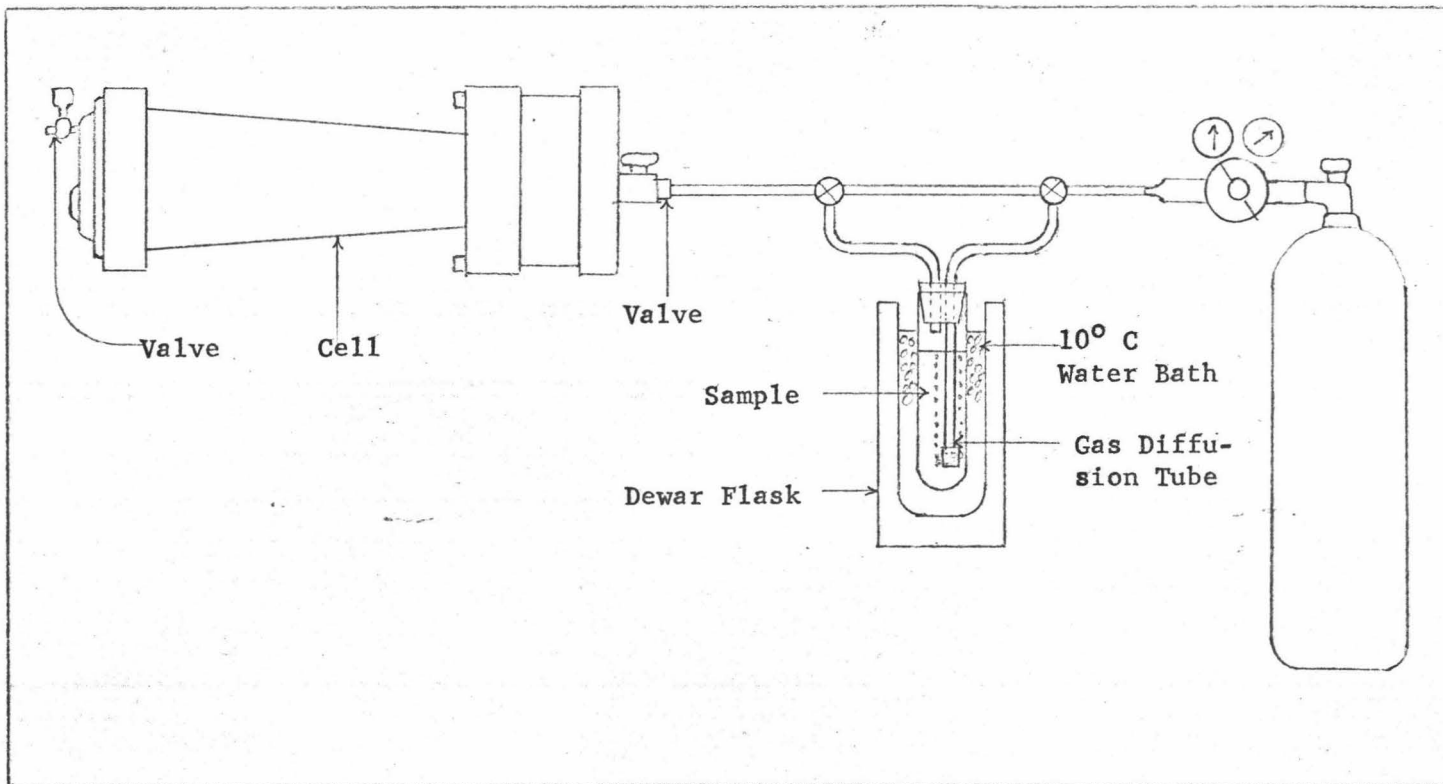
FIGURE 7 - Schematic Diagram of 10 m Gas Cell

Two of these cells were used with one containing reference water and the other containing the sample. The instrument was operated on double beam with the cells placed in their respective beams with the attenuator replaced by the reference cell.

The same procedures as above were used with the fixed path length cell. Because only one of these cells was available, a CIC cell was used as the reference cell for the latter procedure.

E. Preliminary Experiments

In order to obtain the maximum sensitivity of the instrument, the best combination of slit width, path length, wavelength and other variables had to be investigated. The respective procedures for these investigations were the same as those used in the final analysis. A single variable was altered and the absorbance of a standard solution was measured. All other variables remained constant for each investigation. However, either the gain or the trimmer comb was adjusted to bring the pen above 95% T. The results from these experiments were used in the final analysis.

1. Slit Width

Two procedures were used to find the most suitable slit width which would result in the largest absorbance peak with the least amount of noise. The first method kept the energy at maximum value by adjusting the gain. In the second method, the gain remained constant for all slit widths and the reference was adjusted to 97% T with the trimmer comb. The noise was measured by expanding the ordinate scale by a

factor of ten and noise measured over a period of three minutes. The results of these experiments are shown in Tables 2 to 4 and Figures 9 to 14.

2. Wavelength

The wavelength was varied and the absorbance was measured. Two procedures were used for this investigation. First, the gain was varied to adjust the pen to 95% T and in the second procedure the trimmer comb was used to adjust the pen. In the first procedure, a large range of wavelengths was covered and in the second procedure, a short range of wavelengths was covered. The results of the wavelength investigation are shown in Tables 5 and 6 and Figures 15 to 17.

3. Bath Temperature

The ice bath was allowed to warm up and the spectra taken at various temperatures. The first procedure covered a temperature range from 4° C to 45° C. The temperatures above room temperature were obtained by addition of hot water to the bath. This procedure varied the gain to adjust the pen to 99 % T. In the second procedure, the gain remained at a constant value and the trimmer comb was adjusted. The second procedure covered the range between 6° C 24° C. The data for this investigation can be found in Tables 7 and 8 and the spectra and graphs are shown in Figures 18 to 21.

4. Flow Rate

The flow rate was varied under maximum energy conditions and the absorbance was measured. The gain was varied to ad-

just the pen to 98% T. These conditions are similar to the procedure of the final analysis. In the final analysis, the gain remained constant and the flow rate varied at a constant rate. The results of this experiment can be found in Table 9 and Figures 22 and 23.

5. Acetone Filter

The absorbance of the acetone filter and its effectiveness in reducing drift was measured. A spectra of reference water was taken, with and without the filter. The amount of drift over a 5 minute period was measured for each spectra. A spectra of a 0.05 mole % D solution was taken with and without the filter and the absorbance was measured. Also included is the entire spectra without the acetone filter. Figures 24 to 26 and Table 10 show the results of these experiments.

6. Beam

The instrument was operated on single beam and then double beam for a 0.05 mole % D solution, and the amount of absorbance of each was compared to each other. The reference beam was blocked when the instrument was operated on single beam, and an attenuator was used in the reference beam for double beam operation. The gain remained constant, and the attenuator was used to vary the pen. The results of these experiments are shown in Table 11 and Figure 27.

7. Cell Thickness

The length of light path within the cell was varied by

using spacers of different thickness. The gain was adjusted so that maximum energy could be obtained. Various slit widths were also used for each spacer so that the best combination of path length and slit width could be found. The spectra is shown in Figures 28 and 29 and Table 12.

F. Final Analysis

The method finally adopted is similar to that of Bayly, Stevens and Thurston. The apparatus is shown in Figure 8 and the instrument settings are shown in Table 13. The instrument was set to record at a wavelengh of 2513 cm^{-1} and the scale was expanded twenty times. This is essentially the "cell-in-cell-out" method which was described earlier. A continuous flow system was set up with the cell being filled alternately by first flowing the reference water through the cell for two minutes and then the sample for two minutes. This was repeated five times and the spectra was recorded throughout the operation. The flow of water was kept nearly constant at four ml per minute by a needle valve, a long capillary tube and a large waste container. A very small difference in flow rate was observed over the period of time needed for a single analysis. Even though it was not possible to maintain an absolutely constant flow rate, the change in flow rate was constant and this affected only the drift. The temperature of the reference water and sample were kept constant by passing these through an ice bath via an aluminum tube prior to cell entry. The temperature of the bath was kept at 0° C by using a water-ice mixture. To assure constant temperature the

bath was refilled with ice after each analysis even though the bath temperature did not change over a period of one hour.

G. Preparation of Standard Solutions

The standards used for the calibration of the instrument with respect to the deuterium concentration were prepared from 99.77 mole % D obtained from Bio-Rad Laboratories and deionized, distilled water from the Hawaii Institute of Geophysics. The latter was also used for the reference water and was boiled prior to use to eliminate CO_2 contamination. The standard was to be Pacific Ocean water which has a very constant and well established deuterium concentration of 0.0154 mole % D.[3] After plotting absorbance vs. concentration for the standard solutions, the absorbance of the Pacific Ocean water was to be plotted on the graph and the reference water was to be compared to it. However, the Bouguer-Beer Law was not followed in the range of Pacific Ocean water and the curve could not be calibrated with respect to this water. The standards used are listed along with their respective calculations in the Calculations section.

H. Preparation of Samples

The samples analyzed included: Pacific Ocean water (standare) which was collected at Koko Head beach on the island of Oahu which is known to be a satisfactory source for uncontaminated ocean water;[31] Sulfur Bank water from the Kilauea volcano area on the island of Hawaii; ice water from the ice machine in Bilger Hall of the University of Hawaii; and tap water from the Hawaii Institute of Geophysics. All samples were prepared by
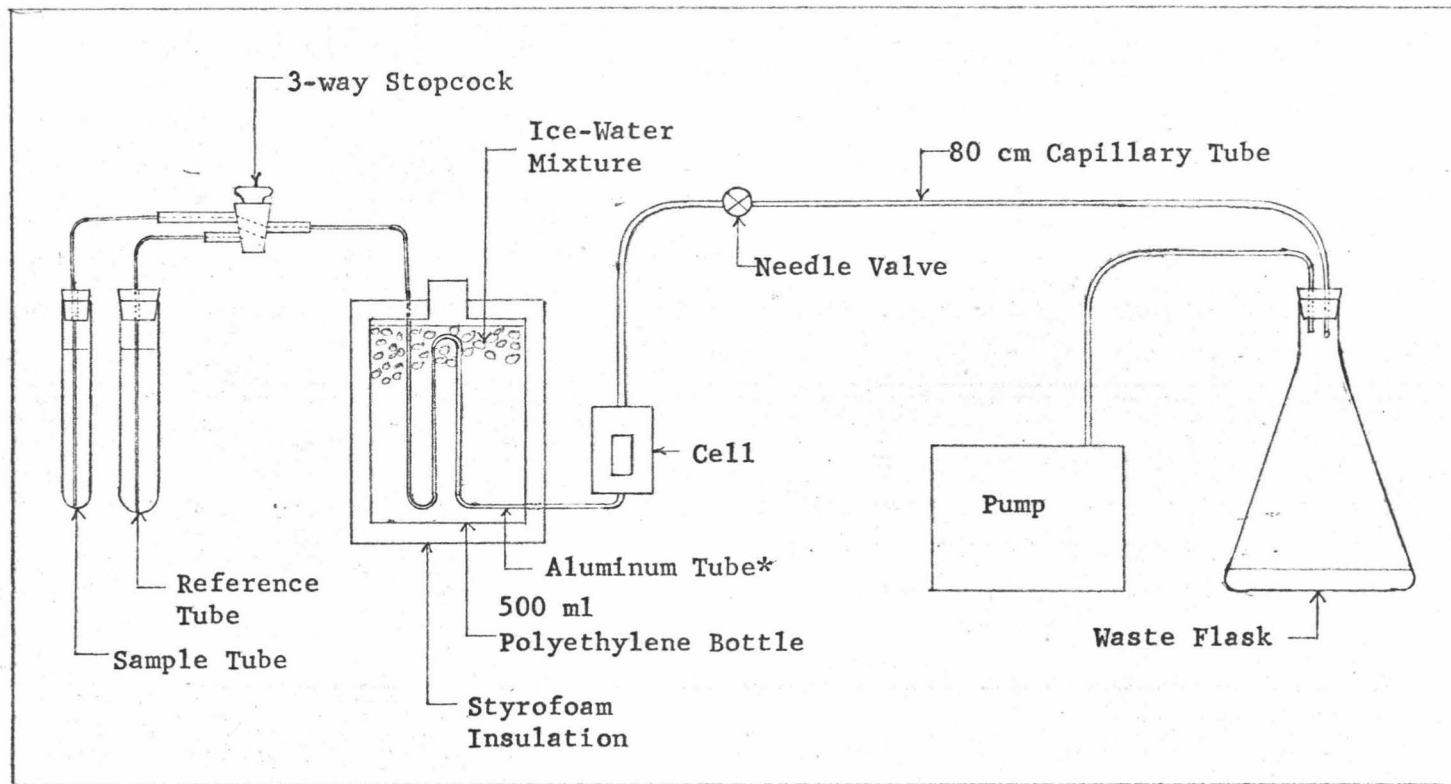
FIGURE 8 - Schematic Diagram of Continuous Flow System

* 35 cm long x 2 mm diameter

standard techniques of complete distillation from a $KMnO_4$ solution made alkaline with Na_2O_2. Measurements on the samples were made by the same procedures as those used for standard solutions.

I. Calculations

1. Calculation for the Preparation of Standard Solutions

The calculation for the dilution of standard solutions are listed in Table 1. These were based on $C_1 \times V_1 = C_2 \times V_2$. A 0.5000 mole % D solution was prepared and from this a 0.0500 mole % D solution was prepared. All other solutions were prepared from these two.

2. Calculation of Sample Temperature for 10 m Gas Cell

Maximum humidity allowed in cell   = 40%

Temperature of cell   = 26° C

Vapor pressure at 26° C   = 25.209 mm Hg

Maximum water vapor pressure in cell

$$(25.209)(0.40) \quad = 10.0836 \text{ mm Hg}$$

Temperature at which vapor pressure

$$\text{is } 10.0836 \text{ mm Hg} = 11.2^O \text{ C}$$

Humidity at 10° C

$$\frac{9.209 \text{ mm Hg}}{25.209 \text{ mm Hg}} \times 100 = 36.5\%$$

3. Calculation of Absorbance

Sample	T	$-\log T = A$
0.0050 mole % D	28	1.447
0.0040 mole % D	21.9	1.340
0.0030 mole % D	17	1.230
0.0020 mole % D	13	1.114

Sample	T	-log T = A
0.0015 mole % D	10	1.000
0.0005 mole % D	7	0.845
Ocean Water Koko Head	-6.0	-0.778
Sulfur Bank Water Volcano Area	-3.5	-0.544
Tap Water Hawaii Inst. Geophys.	0	----
Ice Water Bilger Hall	-17	-1.230

Table 1

Preparation of Standards

C_2 in mole % D	x	V_2 in ml	÷	C_1 in mole % D	=	V_1 in ml
0.5000		200		99.77		1
0.0500		100		0.5000		10
0.0050		500		0.5000		5
0.0040		500		0.5000		4
0.0030		500		0.5000		3
0.0020		500		0.5000		2
0.0015		500		0.0500		15
0.0010		500		0.5000		1
0.0005		500		0.0500		5
0.0004		500		0.0500		4
0.0003		500		0.0500		3
0.0002		500		0.0500		2
0.0001		500		0.0500		1

IV. RESULTS AND DISCUSSION

A. Introduction

As was noted in the previous sections, the approaches to
the problem of deuterium analysis by infrared spectrophotometry
were (1) an investigation of the use of gas phase samples, (2)
an investigation of the use of liquid phase samples, and (3) an
investigation of optimum operating conditions. These are dis-
cussed in detail below.

B. Detection of Deuterium in the Gas Phase

In the first experiments investigating the detection of
deuterium in the vapor phase, the use of a 12 cm gas cell did
show absorption for a 1 mole % D sample, but condensation on the
window was difficult to prevent. It was necessary to heat the
cell above 50° C in order to have a large enough water vapor pres-
sure to attain absorption for the O-D band. Condensation occurred
on the windows because physically they could not be heated uni-
formly. There was no reproducibility with the 12 cm gas cell due
to this condensation. In order for this method to be of any use,
all of the sample must be vaporized, and this was difficult to
accomplish because some areas of the cell could not be heated.
Fractionation rendered condensate richer in HOD than the vapor
and a smaller absorption peak for the O-D band was observed when
condensate was present than when all of the solution was
vaporized.

It was hoped that with the 10 meter gas cell, the amount of
water vapor would be high enough from the vapor pressure at

ambient temperatures, with the long path length that there would
be an easily detectable amount of absorption even at low deuter-
ium concentration. When the spectra was taken for a 1 mole % D
solution, no absorption was found at 2513 cm^{-1}. However, this
method cannot be ruled out completely for deuterium analysis in
higher concentrations, but the investigation was not extended to
cover this range. As mentioned earlier, the windows of the cell
were NaCl and the amount of water vapor that could be used in the
cell was limited to that present at 40% humidity. If CaF$_2$ win-
dows could be used and the concentration of water vapor increased
by temperature or pressure increase, perhaps this method could be
extended, but this was not possible with our equipment. The main
advantage of a gas cell is the high resolution of individual
peaks which can be obtained. This, however, is not of particular
importance in the analysis of water for its deuterium content
because the problem of the overlap of the water peak close to the
O-D peak is not a major one and is dealt with by other methods.
This analysis does not require high resolution; in fact, high
resolution can be sacrificed in favor of maximum energy.

C. Detection of Deuterium in the Liquid Phase

It was possible to measure a difference of 0.05 mole % D
with the Connecticut Instrument Corporation cells, however, the
size of the peak could not be reproduced. This sensitivity was
accomplished only when two cells were employed. Due to the per-
sistance of variation in cell thickness, much patience was
required to achieve this result. This variation made it extremely

difficult to obtain a straight line through the region surrounding 2513 cm^{-1} required when both cells were filled with reference water.

When only one of the CIC cells was used and the instrument operated on either single beam or double beam, the sensitivity was limited to 0.1 mole % D. The reasons for this were two-fold. First, the cell thickness was difficult to reproduce as before, and second, the O-D absorption peak came on the side of a water peak which was not compensated as in the instance when two cells were used.

The results of the fixed path length cell were similar to the above results except that these were reproducible. It was still quite difficult to match the fixed path length cell with one of the CIC cells in path length, therefore a modification of the CIC cell was used. In order to maintain a constant path length an attempt was made to attach a limiting plate to prevent the cell from expanding. This also proved to be ineffective. With the instrument operating on single beam, it was possible to measure a difference of 0.05 mole % D, however, the same problem of interference by the water peak existed. Had two semi-permanent cells of equal path length been available, the results probably could have been improved. Heating of the cell by infrared absorption by water would still limit the usefulness of the method and this method would not be sensitive enough to detect small deuterium concentration variations in the natural water range.

D. Preliminary Experiments

An investigation of various variables was made. The results and discussion of these are listed below. The respective data, graphs and spectra of these variables follow the discussion.

1. Slit Width

Both procedures showed an increase in absorbance with a decrease in slit width. The first procedure also showed that the slit width decreased as the noise increased. It can be seen from the graph (Figure 11) for the first procedure and the graph for noise (Figure 12) that a slit width of 4.0 mm gave the most suitable combination of absorbance peak and noise. A slit width of 4.0 mm was used. The results for this investigation can be found in Tables 2 to 4 and Figures 9 to 14.

2. Frequency

It can be seen from the spectra (Figures 15 and 17), data (Tables 5 and 6) and graph (Figure 16) that the maximum absorbance for deuterium came at a wave number of 2513 cm^{-1}. This is in agreement with the literature. A wave number of 2513 cm^{-1} was used for the final analysis.

3. Bath Temperature

The first procedure showed a slight difference in absorption through the range of temperatures investigated. The maximum came at about 18° C. The gain remained constant throughout the final analysis which was analogous to the second procedure, and therefore more useful information was obtained from this procedure. It shows that the absorbance

does vary with temperature change and therefore, it is important to keep the temperature constant. It can be seen from the second procedure that there is a slight increase in absorbance with a decrease in temperature, giving a cold bath a slight advantage over a warm one. A bath temperature of 0° C was used. The results of these experiments are shown in Tables 7 and 8 and Figures 18 to 21.

4. Flow Rate

It can be seen that the absorbance decreased slightly with an increase in flow rate. By increasing the flow rate it is possible to decrease the drift because of the larger cooling effect of the faster flow rate. This latter advantage outweighs the disadvantage of the small loss of absorbance. The flow rate was adjusted according to the drift and than it was constant at about 4 ml per minute. The spectra and graphs are shown in Figures 22 and 23 and the data in Table 9.

5. Filter

The beam in an infrared spectrophotometer is made up of many wave numbers. The only wave number needed in this analysis was 2513 cm^{-1}. Water absorbs at various other wave numbers and this absorption causes heating of the sample which is harmful. It is desirable to stop all wave numbers except that at 2513 cm^{-1} from striking the sample. An interference filter was not available so an acetone filter was investigated. It was found that the filter does slow down the drift as well as the absorbance. Because of the diffi-

culties caused by the drift, the absorbance loss was accepted in favor of the lesser amount of drift. The entire spectra of acetone shows the amount of energy that is cut out of the beam by the filter. An acetone filter was used. The data for this investigation is shown in Table 10 and the spectra in Figures 24 to 26.

6. Beam

There was no difference in absorption between single beam and double beam. The energy in the sample beam on single beam operation was greater than the energy in the sample beam on double beam operation, therefore, single beam operation was used. The results of this experiment are shown in Table 11 and Figure 27.

7. Cell Thickness

The increase in light path length through the sample achieved by increasing the space thickness required an increase in noise as well as an increase in absorbance. The thickness could not be too small because there was not enough sample present to get the amount of absorbance required. Therefore, a compromise was reached and a 0.25 mm spacer was used. The data for this experiment is shown in Table 12 and the spectra is shown in Figures 28 and 29.

Table 2

Data for the First Procedure (Gain Adjust)
of Slit Width Determination

Wave Number	= 2513 cm^{-1}	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 97% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 20 cm^{-1}/min
Beam	= SB	Concentration	= 0.05 mole % D
Time Interval	= 2 min	Slit Width	= ---
Flow Rate	= 2 ml/min	Bath Temperature	= 25° C
Cell Thickness	= 0.25 mm	Trimmer Comb	= Out

Slit Width	% T	Fine Gain	Coarse Gain
6.0 mm	7.9%	0.80	10
5.0 mm	9.8%	1.52	10
4.0 mm	13.1%	1.85	10
3.0 mm	15.0%	2.64	10
2.0 mm	16.0%	3.21	10

Table 3

Data for the Second Procedure (Trimmer Comb Adjust)

of Slit Width Determination

Wave Number	= 2513 cm^{-1}	Period	= 8 seconds
Fine Gain	= 1.88	Start % T	= 97% T
Coarse Gain	= 10	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 20 cm^{-1}/min
Beam	= SB	Concentration	= 0.0050 mole % D
Time Interval	= 2 minutes	Slit Width	= ---
Flow Rate	= 3 ml/min	Bath Temperature	= 6° C
Cell Thickness	= 0.25 mm	Trimmer	= Varied

Slit Width	% T
6.0 mm	8.6%
5.0 mm	11.5%
4.0 mm	12.2%
3.0 mm	15.0%

Table 4

Data for Slit Width Determination with Respect to Noise

Wave Number	= 2513 cm^{-1}		Period	= 8 seconds
Fine Gain	= ---		Start % T	= 97% T
Coarse Gain	= ---		Scale Expansion	= 10x
Filter	= In		Chart Speed	= 20 cm^{-1}/min
Beam	= SB		Concentration	= 0.00 mole % D
Time Interval	= 3 minutes		Slit Width	= ---
Flow Rate	= 2 ml/min		Bath Temperature	= 25° C
Cell Thickness	= 0.25 mm		Trimmer Comb	= Out

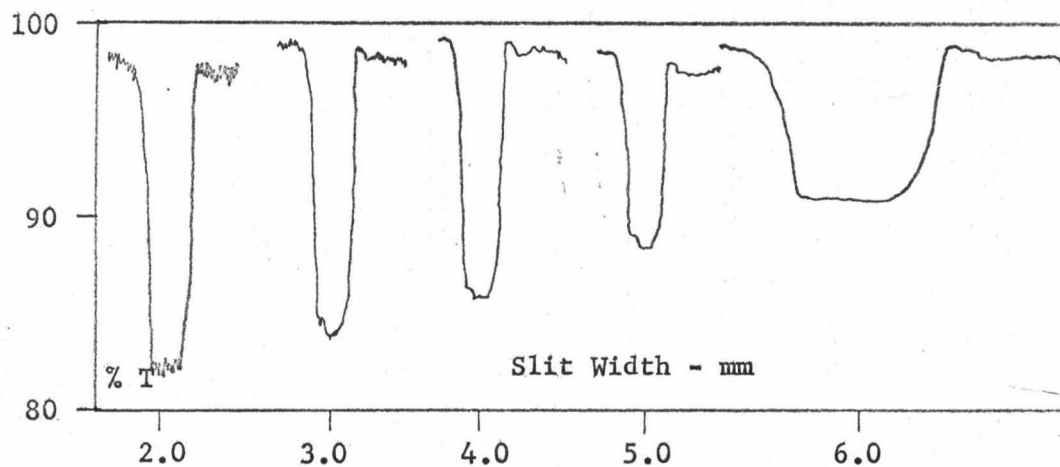| Slit Width	Noise
6.0 mm	1%
5.0 mm	2%
4.0 mm	3%
3.0 mm	5%
2.0 mm	11%

FIGURE 9 - Spectra for the Determination of the Optimum Slit
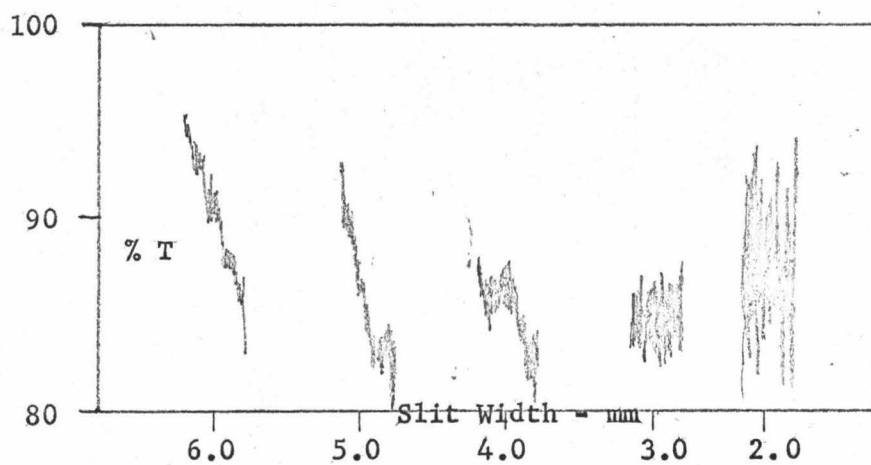Width by the First Procedure (Gain Adjust)

FIGURE 10 - Spectra for the Determination of the
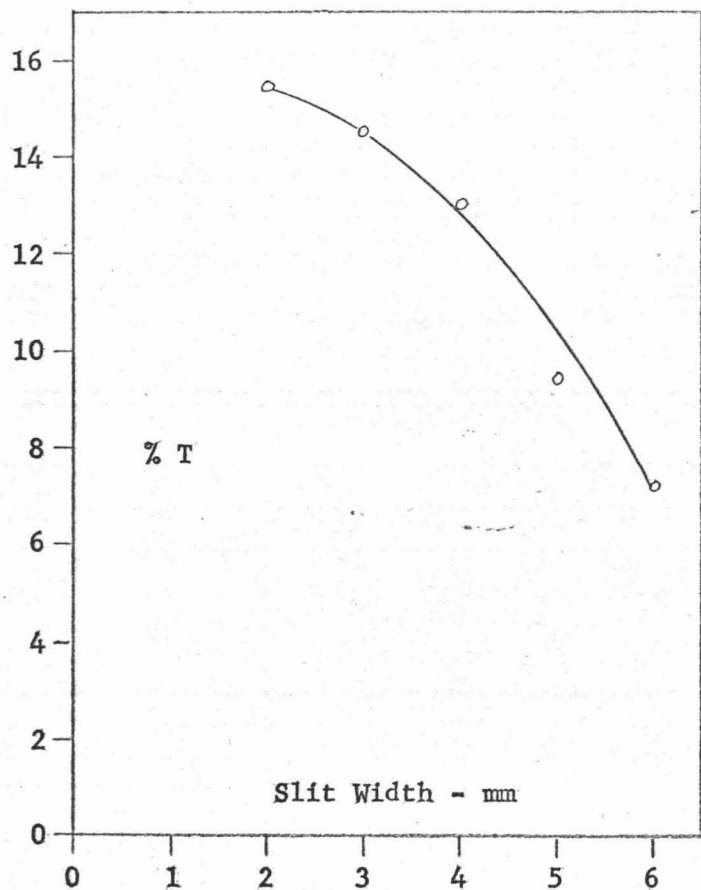Optimum Slit Width with Respect to
Noise

FIGURE 11 - Graph of Slit Width vs Size of Peak for the First Procedure (Gain Adjust) of Slit Width Determination
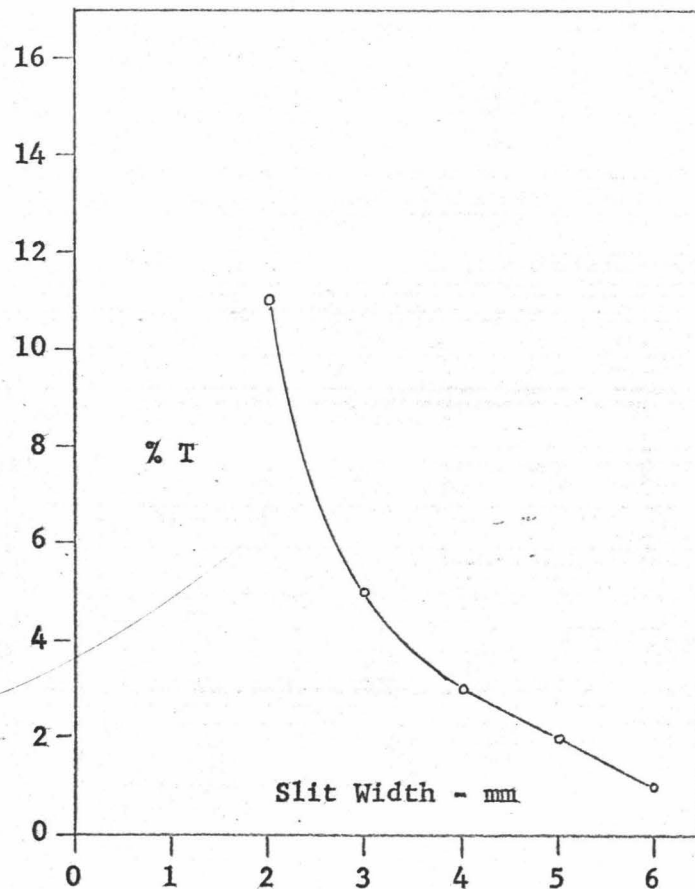
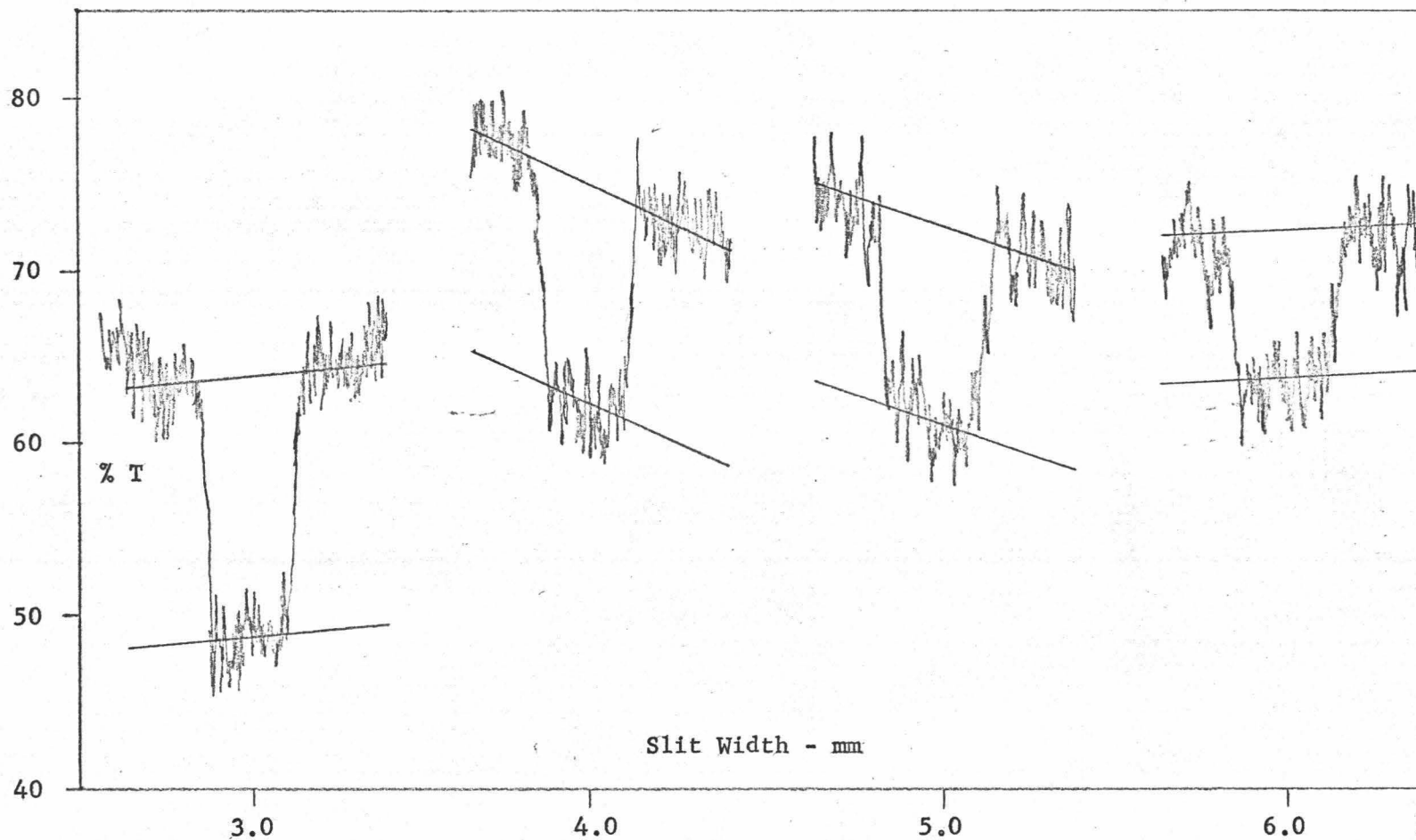FIGURE 12 - Graph of Slit Width vs Noise

FIGURE 13 - Spectra for the Determination of the Optimum Slit Width by the Second Procedure
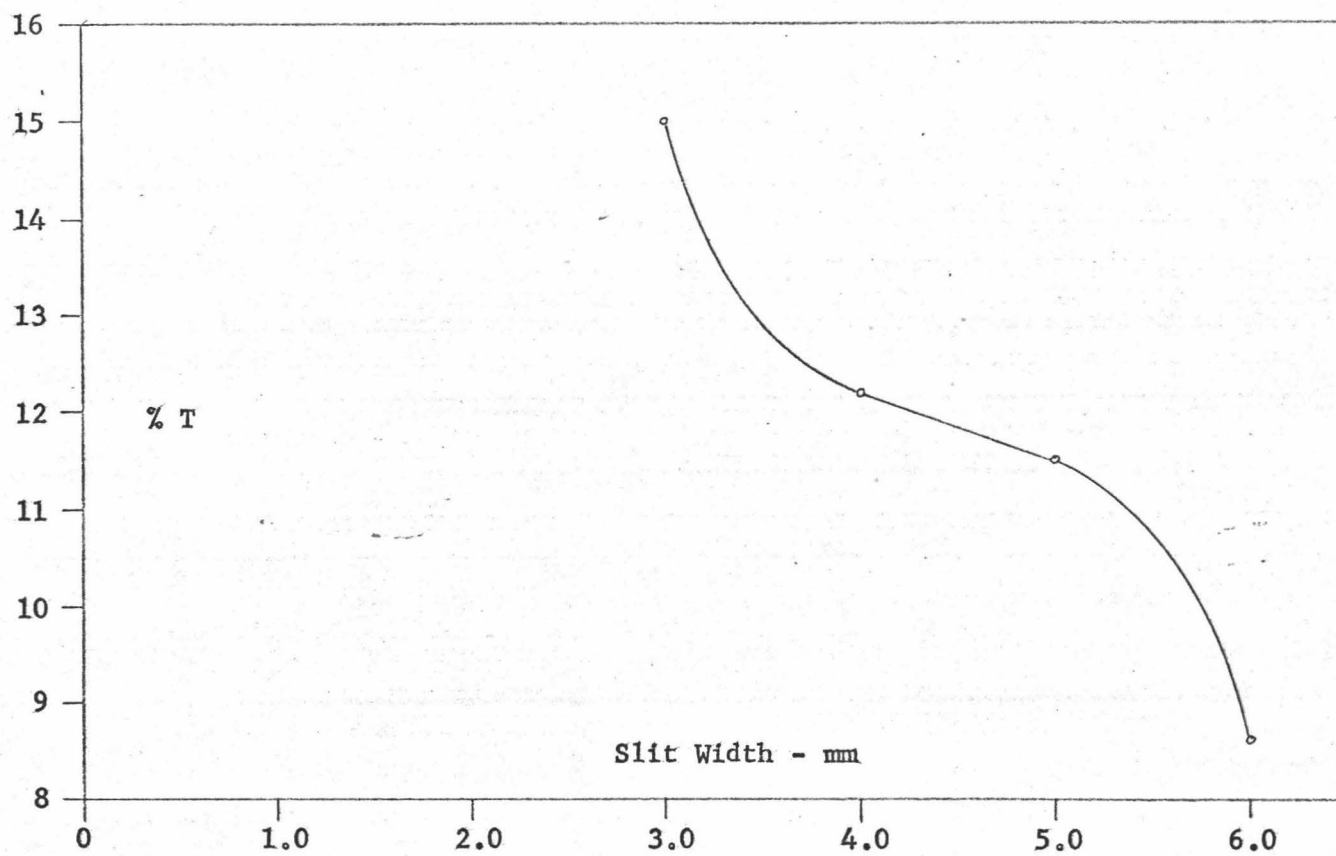(Trimmer Comb Adjust)

FIGURE 14 - Graph of Slit Width vs Size of Peak for the Second Procedure (Trimmer Comb Adjust) of Slit Width Determination

Table 5

Data for the First Procedure (Gain Adjust) of

Wavelength Determination

Wave Number	= ---	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 98% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 20 cm^{-1}/ min
Beam	= SB	Concentration	= 0.5000 mole % D
Time Interval	= 2 minutes	Slit Width	= 4.0 mm
Flow Rate	= 2 ml/min	Bath Temperature	= 25° C
Cell Thickness	= 0.25 mm	Trimmer Comb	= Out

Wave Number in cm^{-1}	% T	Fine Gain	Coarse Gain
2540	62.5%	0.61	10
2530	64.0%	1.09	10
2520	67.5%	1.53	10
2513	68.8%	1.90	10
2500	68.7%	2.11	10
2490	65.5%	2.91	10
2480	60.5%	3.62	10

Table 6

Data for the Second Procedure (Trimmer Comb Adjust)

of Wavelength Determination

Wave Number	= ---		Period	= 8 seconds
Fine Gain	= 1.88		Start % T	= 97% T
Coarse Gain	= 10		Scale Expansion	= 10x
Filter	= In		Chart Speed	= 2 cm^{-1}/ min
Beam	= SB		Concentration	= 0.0050 mole % D
Time Interval	= 2 minutes		Slit Width	= 4.0 mm
Flow Rate	= 3 ml/min		Bath Temperature	= 18° C
Cell Thickness	= 0.25 mm		Trimmer Comb	= Varied

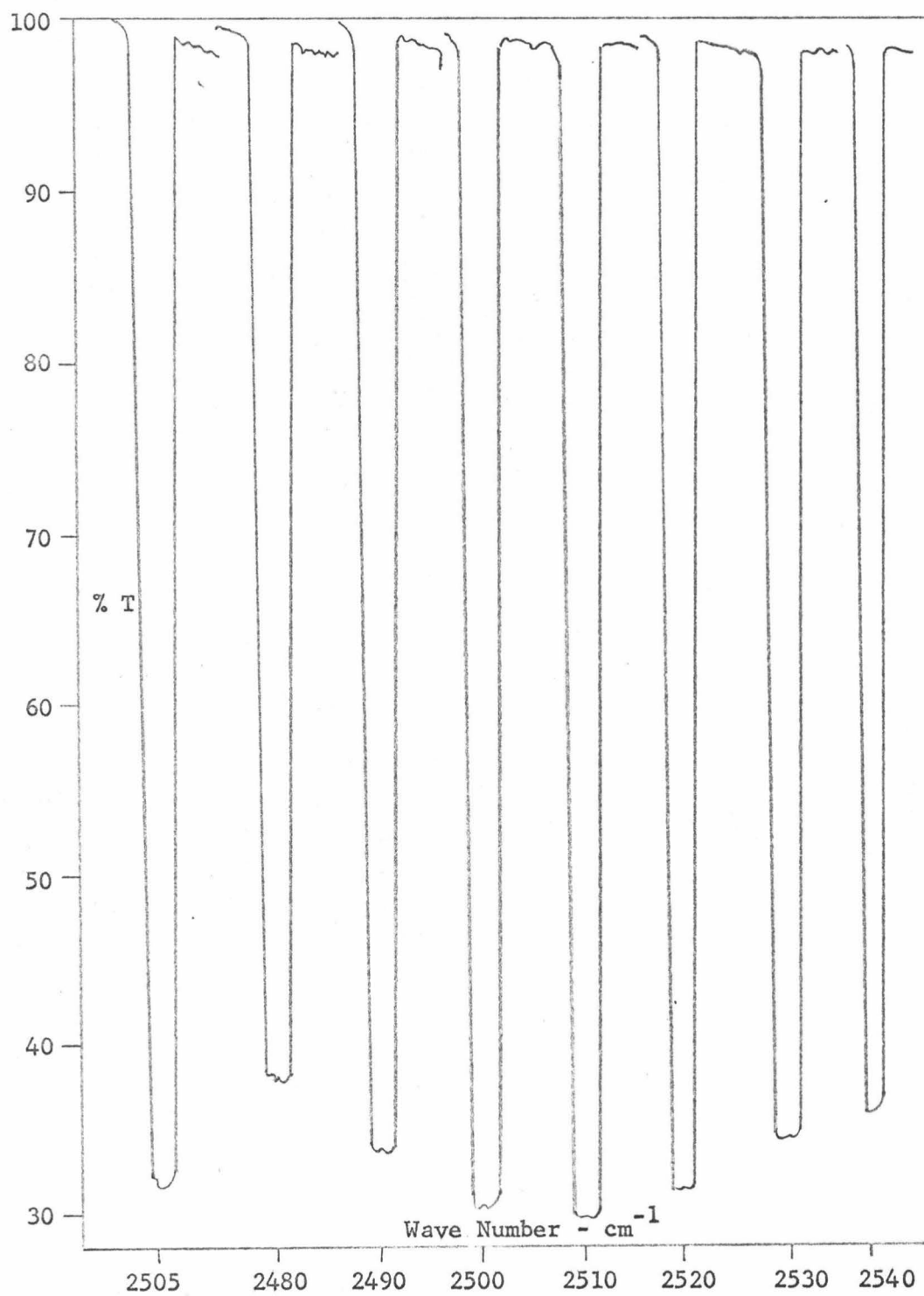| Wave Number in cm^{-1}	% T
2520	13.0%
2513	14.0%
2514	13.0%
2512	12.1%

FIGURE 15 - Spectra for the Determination of the Optimum Wave
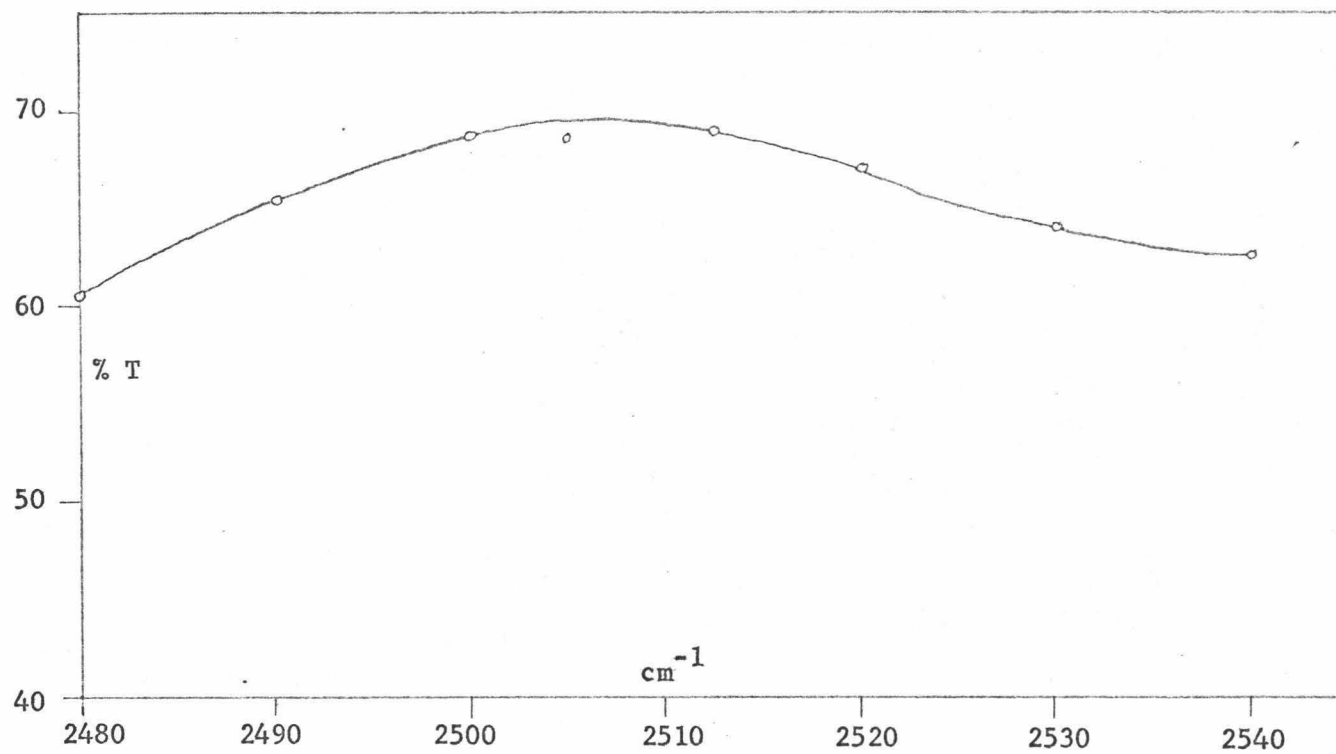Number by the First Procedure (Gain Adjust)

FIGURE 16 - Graph of Wave Number vs Size of Peak for the First Procedure (Gain Adjust) of Wave Number Determination
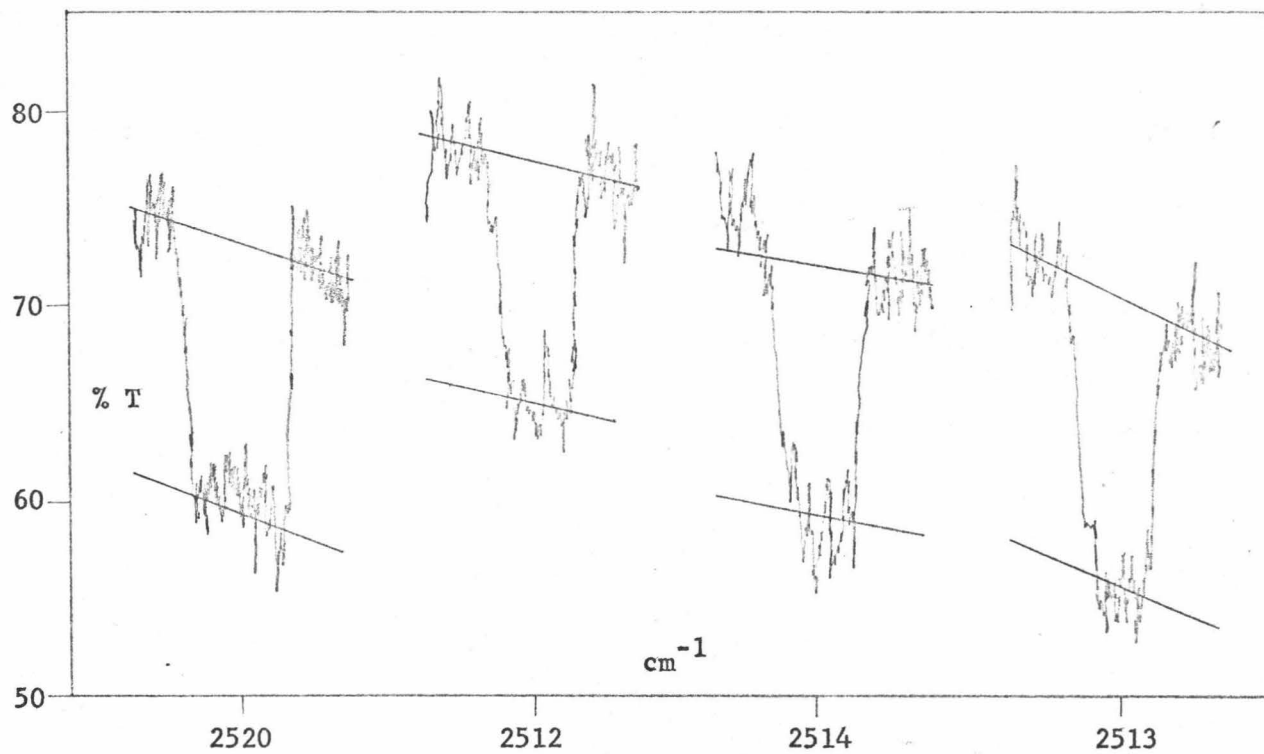
FIGURE 17 - Spectra for the Determination of the Optimum Wave Number by the Second Procedure (Trimmer Comb Adjust)

Table 7

Data for the First Procedure (Gain Adjust)

of Bath Temperature Determination

Wave Number	= 2513 cm^{-1}	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 97% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 20 cm^{-1}/min
Beam	= SB	Concentration	= 0.05 mole % D
Time Interval	= 1 minute	Slit Width	= 4.0 mm
Flow Rate	= 2 ml/min	Bath Temperature	= ---
Cell Thickness	= 0.25 mm	Trimmer Comb	= Out

Bath Temperature in °C	% T	Fine Gain	Coarse Gain
45	11.3%	0.86	10
34.5	12.5%	1.13	10
25.0	12.7%	1.55	10
18.0	13.1%	1.82	10
11.5	13.0%	2.01	10
4.0	12.7%	2.61	10

Table 8

Data for the Second Procedure (Trimmer Comb Adjust)

of Bath Temperature Determination

Wave Number $= 2513 \text{ cm}^{-1}$ Period   = 8 seconds

Fine Gain   = 1.88   Start % T   = 97% T

Coarse Gain   = 10   Scale Expansion   = 10x

Filter   = In   Chart Speed $= 20 \text{ cm}^{-1}/\text{min}$

Beam   = SB   Concentration   = 0.005 mole % D

Time Interval = 2 minutes   Slit Width   = 4.0 mm

Flow Rate   = 3 ml/min   Bath Temperature = ---

Cell Thickness = 0.25 mm   Trimmer Comb   = Varied

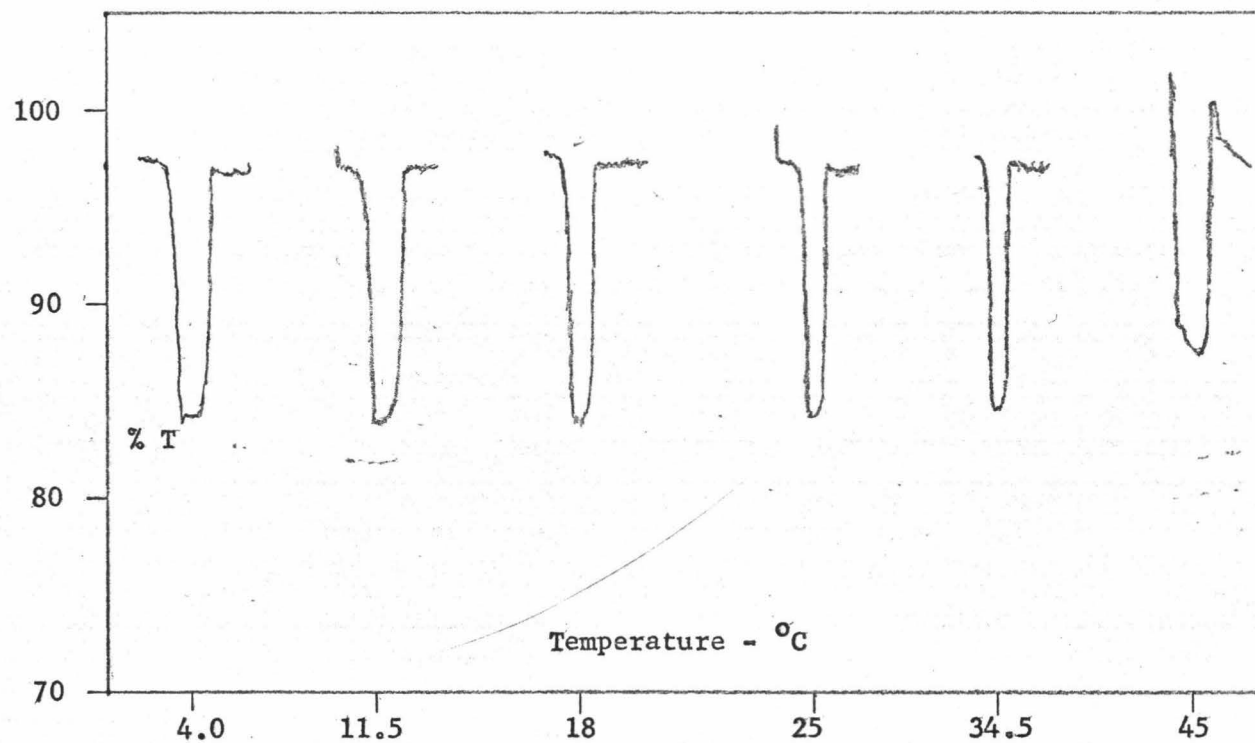| Bath Temperature in $^{\circ}$C	% T
6	15.0%
11	14.8%
18	14.0%
23	11.0%

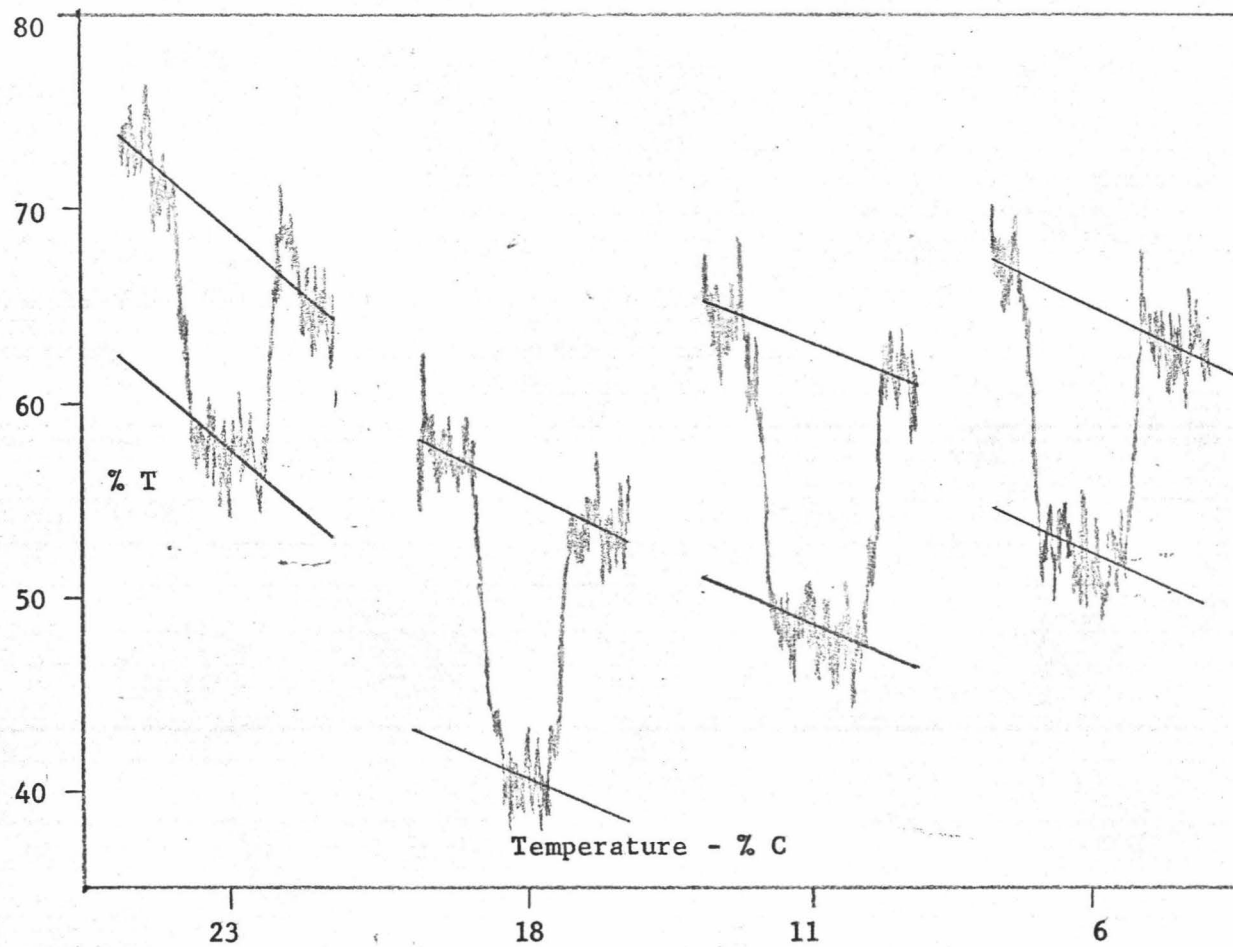FIGURE 18 – Spectra for the Determination of the Optimum Bath Temperature by the First Procedure (Gain Adjust)

FIGURE 19 - Spectra for the Determination of the Optimum Bath Temperature
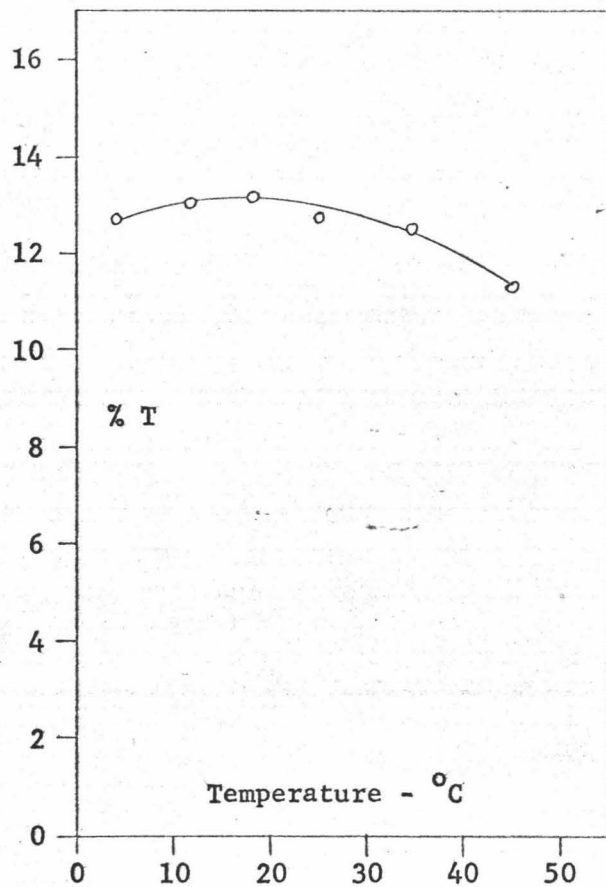by the Second Procedure (Trimmer Control)

FIGURE 20 - Graph of Bath Tempera-
ture vs Size of Peak
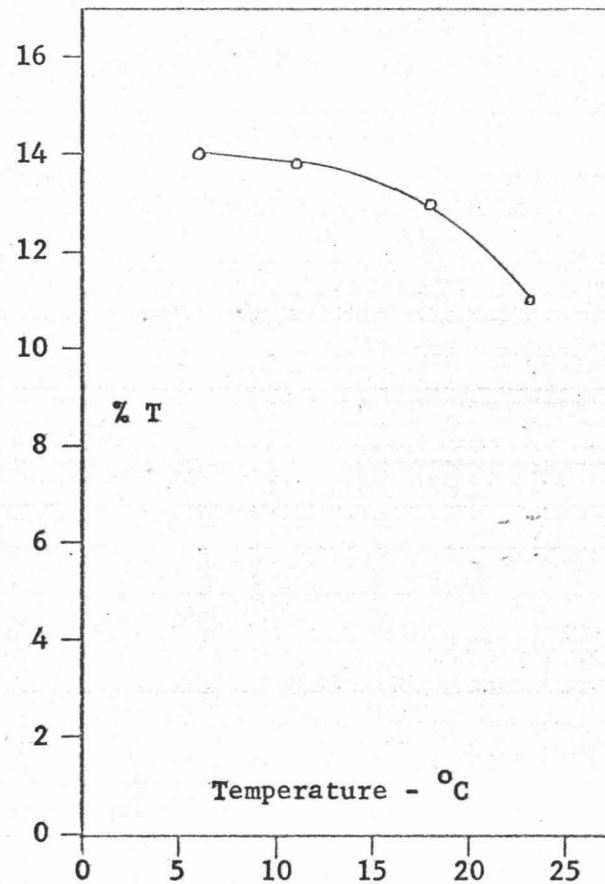for the First Procedure
(Gain Adjust) of Bath
Temperature Determina-
tion

FIGURE 21 - Graph of Bath Tempera-
ture vs Size of Peak
for the Second Proce-
dure (Trimmer Comb Ad-
just) of Bath Tempera-
ture Determination

Table 9

Data for Flow Rate Determination

Wave Number	= 2513 cm^{-1}	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 97% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 20 cm^{-1}/ min
Beam	= SB	Concentration	= 0.05 mole % D
Time Interval	= 1 minute	Slit Width	= 4.0 mm
Flow Rate	= ---	Bath Temperature	= 25° C
Cell Thickness	= 0.25 mm	Trimmer Comb	= Constant

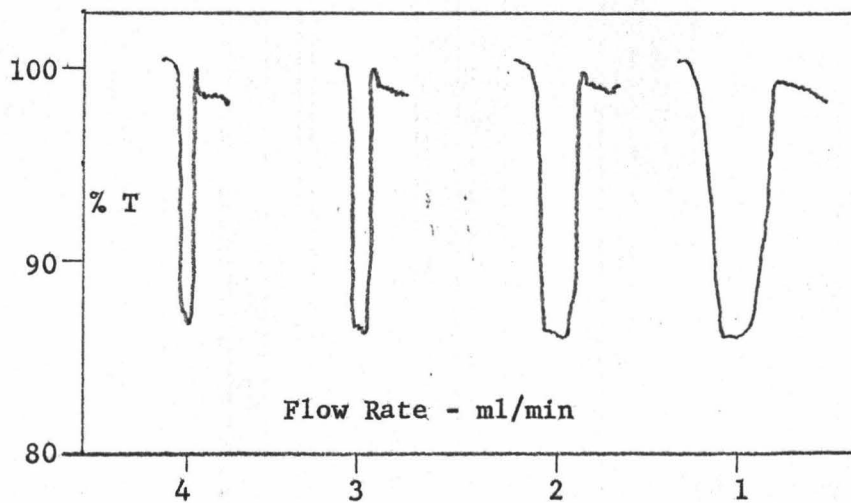| Flow Rate in ml/min	% T	Fine Gain	Coarse Gain
1	13.8%	1.43	10
2	13.6%	1.59	10
3	13.1%	1.72	10
4	12.6%	1.95	10

FIGURE 22 - Spectra for the Determination of the
Optimum Flow Rate
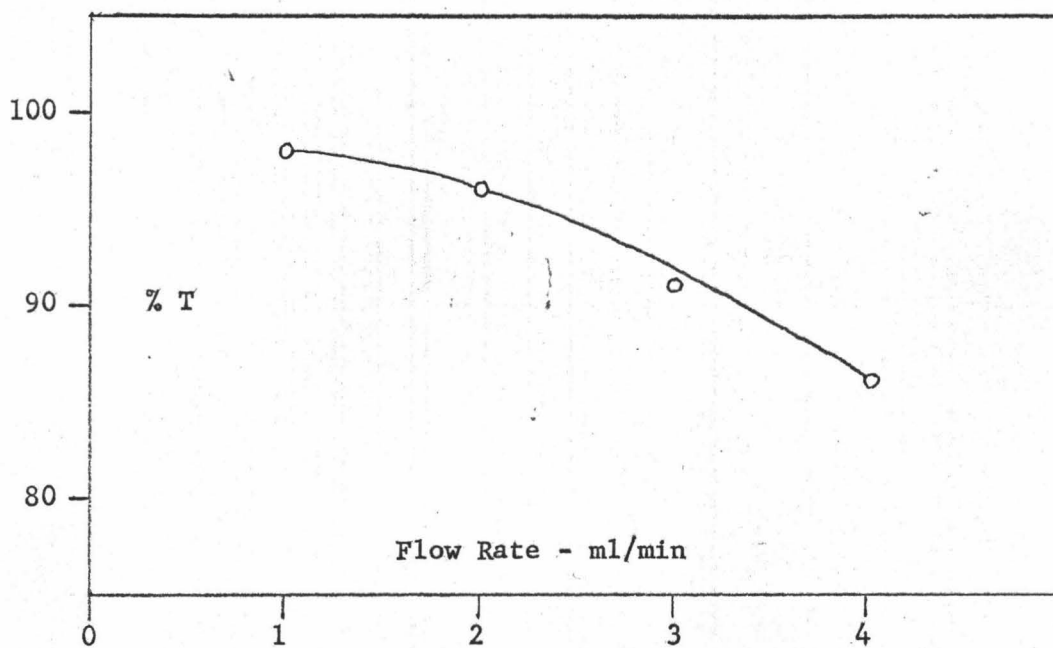
FIGURE 23 - Graph of Flow Rate vs Size of Peak

Table 10

Data for Filter Determination

Wave Number	= 2513 cm^{-1}	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 97% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	= 200 cm^{-1}/min
Beam	= SB	Concentration	= 0.05 mole % D
Time Interval	= 5 minutes	Slit Width	= 4.0 mm
Flow Rate	= 2 ml/min	Bath Temperature	= 25° C
Cell Thickness	= 0.25 mm	Trimmer Comb	= Out

Drift per 5 Minutes	Filter	% T
1.8%	In	9%
2.2%	Out	10%
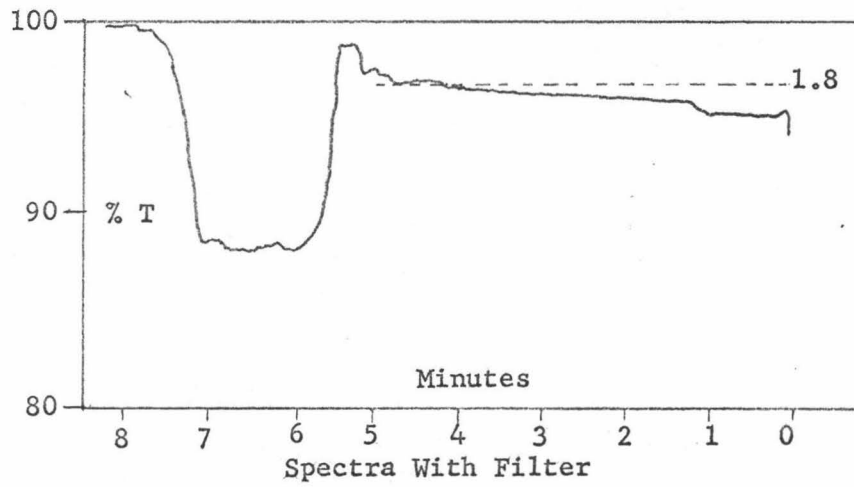
FIGURE 24 - Spectra to Determine the Effectiveness of an Acetone Filter to Drift and Size of Peak
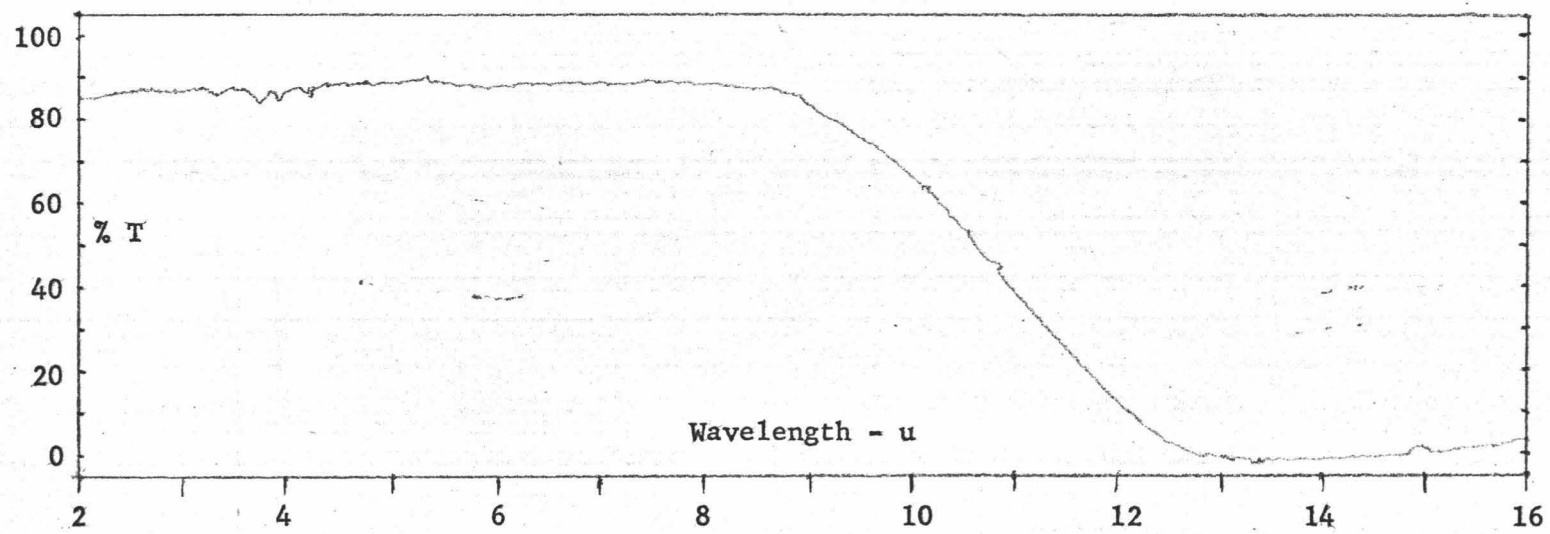
FIGURE 25 - Spectra of Empty Cell
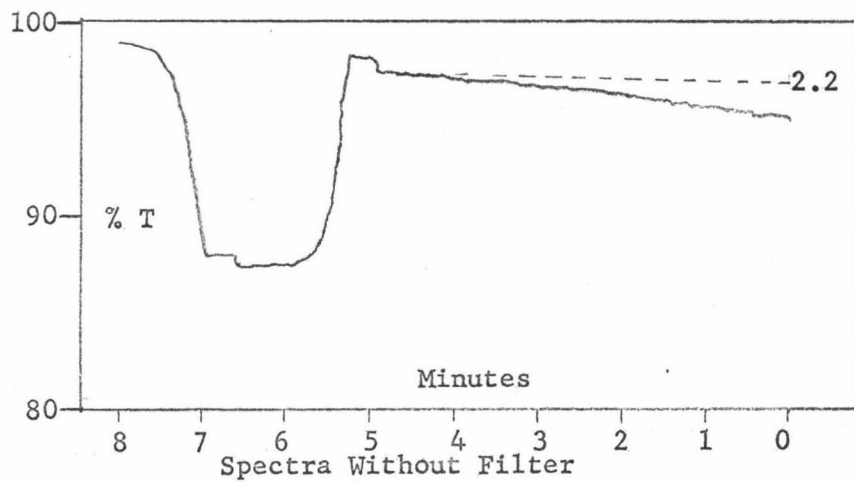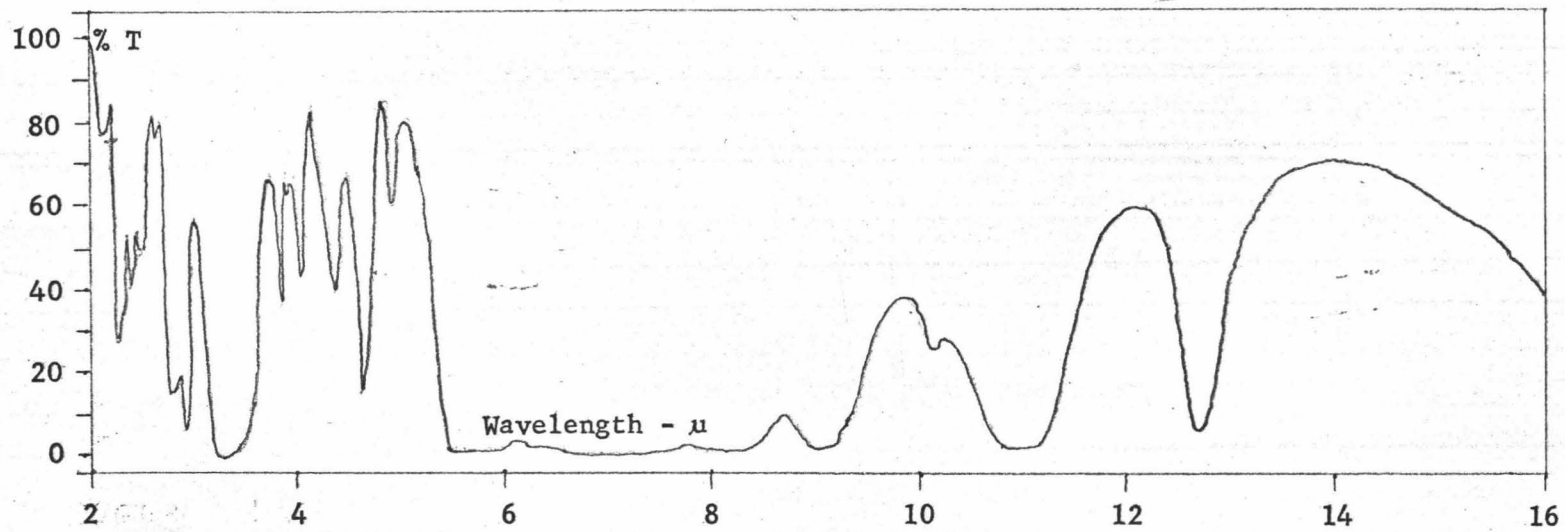
FIGURE 26 - Spectra of Acetone Filter

Table 11

Data for Beam Determination

Wave Number = 2513 cm^{-1} Period = 8 seconds

Fine Gain = 1.88   Start % T = 95% T

Coarse Gain = 10   Scale Expansion = 1x

Filter = In   Chart Speed = 20 cm^{-1}/min

Beam = ---   Concentration = 0.5 mole % D

Time Interval = 2 minutes   Slit Width = 4.0 mm

Flow Rate = 3 ml/min   Bath Temperature = 18° C

Cell Thickness = 0.25 mm   Trimmer Comb = In

Beam	% T
SB	71%
DB	71%
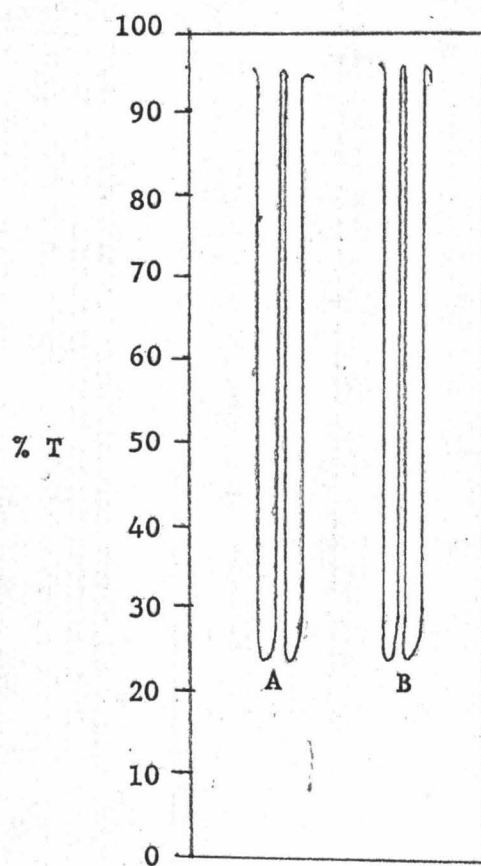
FIGURE 27 - Spectra to Compare Single
Beam Operation with Double
Beam Operation

A = Double Beam
B = Single Beam

Table 12

Data for Cell Thickness Determination

Wave Number	$= 2513 \text{ cm}^{-1}$	Period	= 8 seconds
Fine Gain	= ---	Start % T	= 95% T
Coarse Gain	= ---	Scale Expansion	= 1x
Filter	= In	Chart Speed	$= 20 \text{ cm}^{-1}/\text{min}$
Beam	= SB	Concentration	= 0.05 mole % D
Time Interval	= 2 minutes	Slit Width	= ---
Flow Rate	= 2 ml/min	Bath Temperature	$= 25^\circ$ C
Cell Thickness	= ---	Trimmer Comb	= Out

Cell Thickness in mm	Slit Width in mm	% T
0.25	4.0	13%
0.25	3.0	15%
0.25	2.0	16%
0.25	5.0	9.8%
0.25	6.0	7.9%
0.10	6.0	3%
0.10	2.0	6.5%
0.53	4.0	11%
0.53	6.0	5%
0.53	3.0	18%
0.36	4.0	10%
0.36	3.0	13%
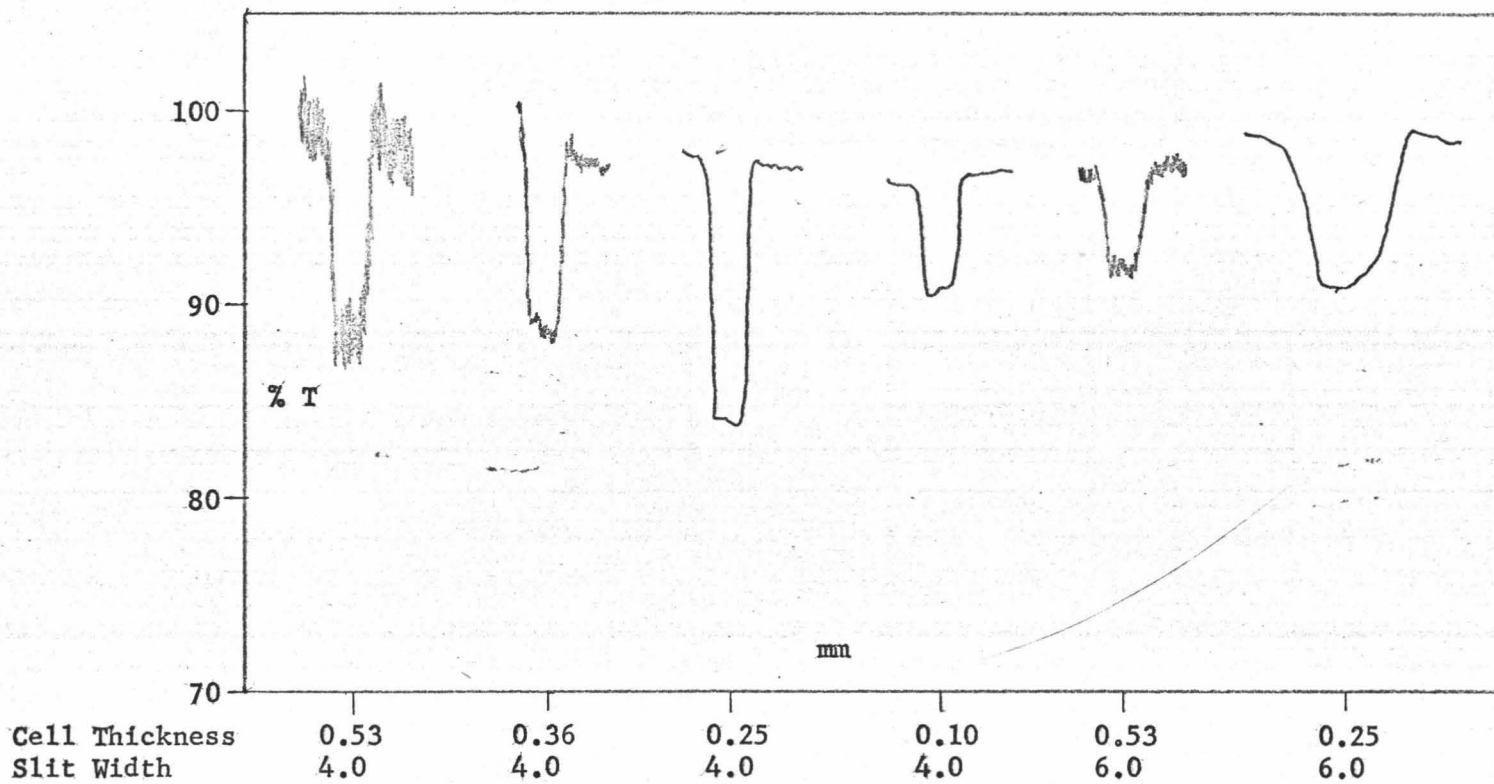
FIGURE 28 - Spectra for the Determination of the Optimum Cell Thickness
(Part 1)

Cell Thickness	0.53	0.36	0.25	0.10	0.53	0.25
Slit Width	4.0	4.0	4.0	4.0	6.0	6.0

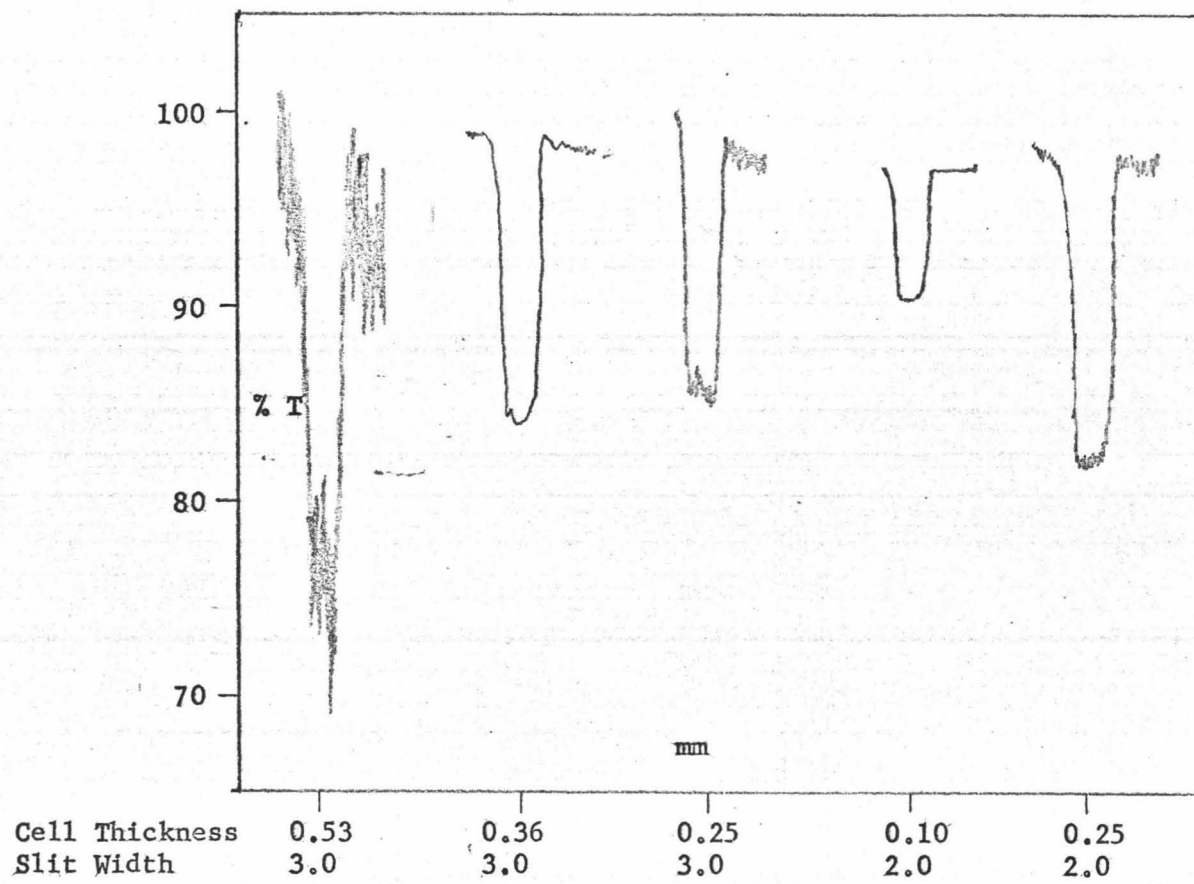| Cell Thickness | 0.53 | 0.36 | 0.25 | 0.10 | 0.25 |
| Slit Width | 3.0 | 3.0 | 3.0 | 2.0 | 2.0 |

FIGURE 29 — Spectra for the Determination of the Optimum Cell
Thickness (Part 2)

E. Final Analysis

The method finally used was essentially a "cell-in-cell-out" method with the sample and reference alternately flowed through the cell at a constant flow rate and a constant temperature. The results using this method were short of the goal. It was possible, however, to measure a difference of 0.0020 mole % D, which is in the range of natural water. Information on the Bayly, Stevens and Thurston method became available during this research, and the final form was a modification of their technique.

The advantage of the method developed in this research over that used by them is that a number of samples can be analyzed without waiting periods. In the previous work, the samples and reference waters were required to equilibrate in temperature with the bath water before an analysis could be made. In this research, one sample could be replaced by another sample in the two minute interval during which the reference water in being analyzed. The sample was temperature equilibrated while it flowed to the cell through the constant temperature bath. This is a definite advantage in speeding up the whole operation. Another advantage in the modified system is the use of an ice bath which as a two phase ice-water system is easily maintained at 0° C constant temperature. A slight increase in absorbance for deuterium was found when the bath temperature was lowered to 0° C as compared to 25° C giving an additional advantage in using an ice bath.

The main disadvantage of the method was that a straight line was not obtained when absorbance was plotted against concentration, for concentrations lower than 0.0020 mole % D. The reason for this was probably the lack of temperature control within the sample. As mentioned earlier, an interference filter was not available. Although some of the energy was absorbed by an acetone filter and the CaF_2 windows, a large percent of the total radiation passed through the sample. This resulted, then, in the heating of the thin layer sample, due to absorption of infrared radiation by water. In order to maintain a constant drift rate, as is shown in the spectra (Figure 30), it was necessary to keep all conditions constant. A slight change in flow rate, for example, would cause a temperature change in the sample because the rate of cooling of the sample would be altered.

Another limitation of this method is the amount of noise encountered. When the scale was expanded twenty times, the noise as well as the absorption peak was expanded. The noise was in the order of about 5% transmittance. At very low concentrations, the noise was larger than the absorption and this became one of the limiting factors in attaining the ultimate sensitivity. The average of the noise was used as the base line for both the reference and the sample. Although the noise was kept at a minimum by galvanometer period suppression, a sufficient amount was still present to interfere with the O-D absorption peak at low concentrations. The method requires much patience and time to reproduce the variables. This disadvantage becomes important when there is a time limit or a large number of samples to be analyzed. In its

present state, this method would not be suitable for the analysis of slight variations of deuterium in natural water because the sensitivity is low and the method would detect only the major deuterium content variations in natural systems.

F. Standard Solutions

A series of standard solutions were prepared and the spectra taken (Figures 30 to 35). The graph of absorbance vs. concentration (Figure 40) shows that the Bouguer-Beer law is followed between 0.0020 mole % D and 0.0050 mole % D. Below 0.0020 mole % D, the Bouguer-Beer law is not followed and cannot be used for analysis of the deuterium concentration in water at this low concentration.

G. Samples

Samples were collected from (1) the Pacific Ocean at Koko Head, (2) ice from the ice machine in Bilger Hall, (3) tap water from the Hawaii Institute of Geophysics, and (4) water vapor from the Sulfur Bank in the volcano area of the island of Hawaii. With the exception of the ice, the results of the deuterium determinations in the available samples were as expected from theoretical considerations.

The hydrologic cycle patterns can be applied to these samples and the results can be explained by these patterns. There is a difference in vapor pressure between H_2O and HOD and fractionation occurs. The most important factor in this fractionation is temperature and the deuterium concentration is determined primarily by the prevailing temperature. As a general rule, the deuterium

concentration decreases with an increase in latitude and an increase in altitude. This is because the temperature usually decreases with an increase in latitude and altitude. Other factors which alter the deuterium concentration are transport of water by rivers; air passing over cool mountains to lower intermountain valleys; and seasonal precipitation and evaporation from the surface of the earth.

The deep waters of the oceans act as a reservoir for both light water and heavy water. The surface of the oceans has a fairly constant deuterium concentration (0.0154 mole % D for Pacific Ocean water). A series of evaporation and re-precipitation of the ocean water fractionates the water so that the water vapor that reaches the continents is deficient in deuterium.

Precipitation of the vapor causes further fractionation. As the small droplets fall from the cooler high altitudes through the warmer lower layers of the atmosphere to the surface of the earth, fractionation occurs. The droplets are enriched in deuterium and the precipitation that reaches the surface of the earth has a higher deuterium concentration than the vapor from which it was derived. The warm regions of low latitudes and low altitudes, i.e., subtropic areas would have a deuterium concentration slightly lower than that of the surface of the ocean.

Fractionation also occurs on the surface of the earth. In arid regions the concentration of deuterium can be increased to a higher concentration than the surface of the ocean.

Any change in phase will result in fractionation. In the

formation of ice, the ice will have a higher deuterium concentration than the water from which it was formed. Two types of equilibrium occur which cause fractionation. First, the liquid-ice equilibrium causes an increase in the deuterium content of ice and second, the vapor-ice equilibrium also increases the concentration of dueterium of ice.

The samples, which were analyzed, had a lower deuterium content than the reference water and it was not possible to measure their respective deuterium contents. This could be done if a series of standard solutions could be prepared having less deuterium concentration than the reference water. However, light water of a known value was not available. The Bouguer-Beer law is not followed below 0.0020 mole % D and cannot be used below this concentration.

The Pacific Ocean water sample was slightly less concentrated than the reference water as is shown in Figure 36. The average altitude of the island of Oahu is near sea level and any precipitation that reaches the surface of the island would have nearly the same concentration as the precipitation that reaches the surface of the ocean. There are no large land masses or high mountains to appreciably alter the conditions for precipitation from the conditions which occur over the sea. The precipitate would have a fairly high deuterium content. It has been found that the water vapor from the subtropic ocean is depleted in its deuterium content by some 6% as compared to deep ocean water. Upon precipitation of this vapor, the remaining vapor is depleted

by about 10%. Fractionation occurs as the precipitate falls to the earth which increases the deuterium content above that of the original vapor. Evaporation from the surface of the land increases the deuterium content further. This is especially true of warm climates such as that of the Hawaiian Islands which are subtropical. After several cycles of precipitation and evaporation, the surface waters of the islands would be expected to have deuterium concentrations similar to that of the oceans and possibly of higher concentration. Another possible source for the high deuterium content of the reference water is that the reference water was brought to a boil to eliminate CO_2 contamination. Any evaporation occurring would also increase the deuterium concentration of the reference water.

The sample of ice from the ice machine in Bilger Hall gave results that were opposite to the theoretical prediction. The liquid water from which the ice was formed had approximately the same deuterium concentration as the reference water and the ice formed from this water should have a higher deuterium concentration. This would be fractionation under equilibrium conditions and two equilibriums would exist. First, an equilibrium would exist between liquid and solid and the second would be between ice and vapor. Both of these equilibria would contribute to an increase in the solid phase of the deuterium concentration over that of the liquid phase. The results of this analysis cannot be explained satisfactorily. Three possible explanations exist, but it is doubtful that the combination of these would alter the

results by such a large amount. First, the source of water for the ice could have had a deuterium concentration which was appreciably lower than that of the reference water. Second, the reference water was boiled previous to its use. This would tend to increase its deuterium content and it could possibly have a higher deuterium content than the source water for the ice. The third explanation would be the incomplete equilibrium between the phases due to incomplete mixing of the three phases. However, the ice should still have a higher deuterium concentration than the liquid phase, but the fractionation would be limited. The spectra for this analysis is shown in Figure 37.

The spectra (Figure 38) for the tap water sample shows that there is no difference in deuterium concentration between the tap water and the reference sample. The tap water is the source of water for the distilled water which was used for the reference. A single distillation should deplete the concentration of deuterium by a small amount. Therefore, the tap water would be expected to have a deuterium concentration that is higher than the reference water. Two explanations are possible to explain this discrepancy between the experimental results and the theoretical results. First, the boiling of the reference water would increase its deuterium concentration and thus counter the single distillation when it was distilled. The second explanation is that the sample was collected on a different day than the reference and could possibly have a different deuterium concentration.

The sample of Sulfur Bank water from the volcano area had less deuterium content than the reference water. There are several possible explanations for this. The sample was taken from an area of slightly lower latitude than the reference water and this lower latitude would tend to give it a slightly higher deuterium concentration. On the other hand, the altitude of the sample area was about 4000 feet as compared to sea level for the reference water. This would tend to make the sample deficient in deuterium content. Whereas the other samples were collected as a liquid on the surface of the earth, this one came from beneath the surface in vapor phase. One would expect the vapor phase to be depleted in deuterium as compared to the liquid phase. The vent from which this sample came has the possibility of acting like a fractionating column with a number of theoretical plates which would tend to deplete the concentration of deuterium. It was assumed that the reservoir of the water vapor was supplied by the seepage of rain water into the ground. The area from which the samples were collected is on the edge of Kilauea Crater. The precipitation at this altitude would be low in deuterium content and this precipitated water would be a likely source of water for the reservoir.

Table 13

Instrument Settings for Final Analysis

Wave Number	2513 cm^{-1}
Slit Width	4.0 mm
Beam	SB
Period	8 seconds
Slit Control	Manual
Scale Selector	0 to 100
Fine Gain	1.648
Coarse Gain	10
Balance Control	OK
Glower Current	0.6 amperes
Scale Contract	Off
Rep Scan	Off
Scan Limits	Off
Chart Speed	20 cm^{-1}/min
Scale Expansion	95-100:100
0% Adjust	7.294
100% Adjust	7.749
Pen Gain	1
Trimmer Comb	In
Flow Rate	3 ml/min
Cell Thickness	0.25 mm
Bath Temperature	0° C
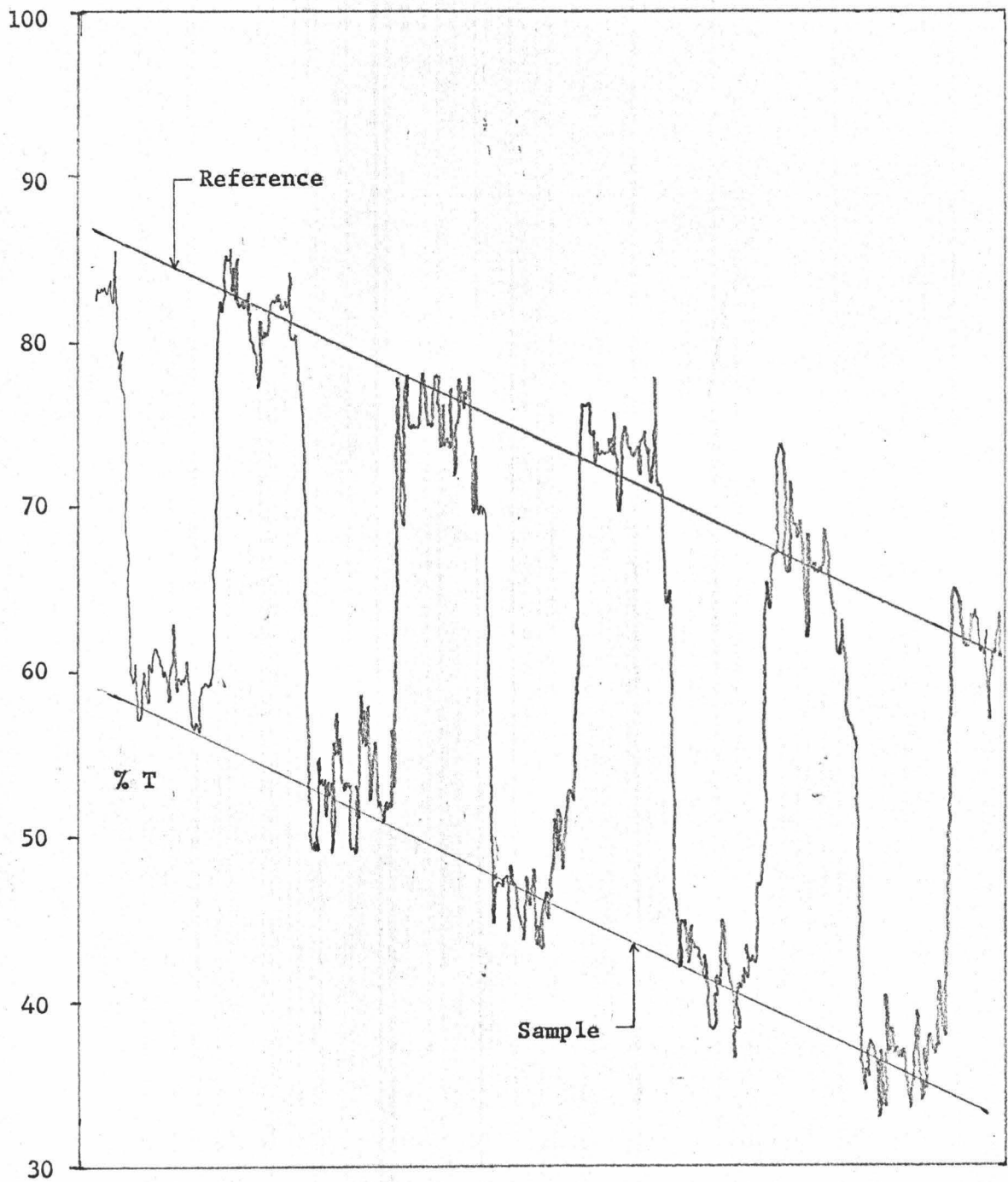
FIGURE 30 - Spectra of 0.0050 mole % D Standard
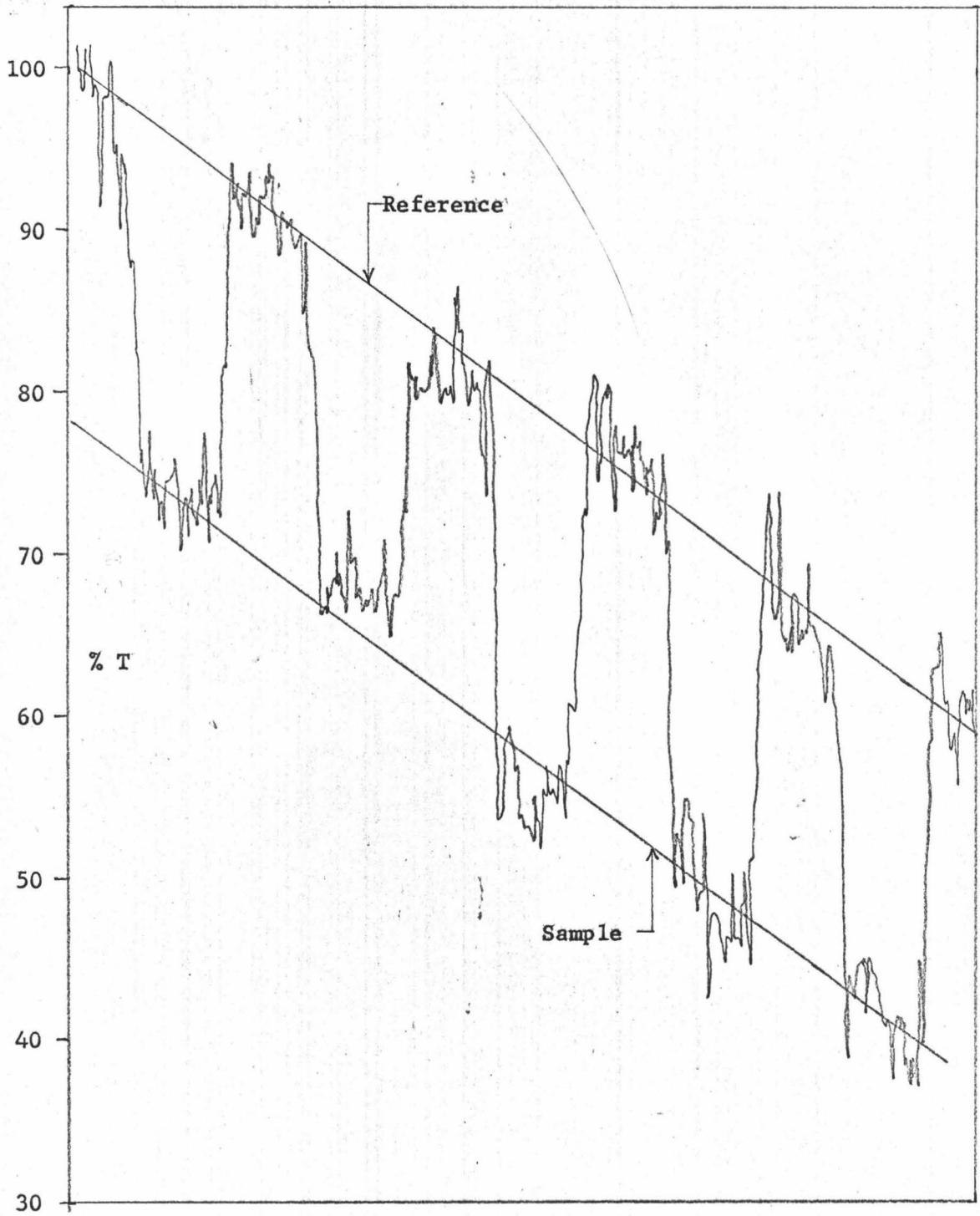
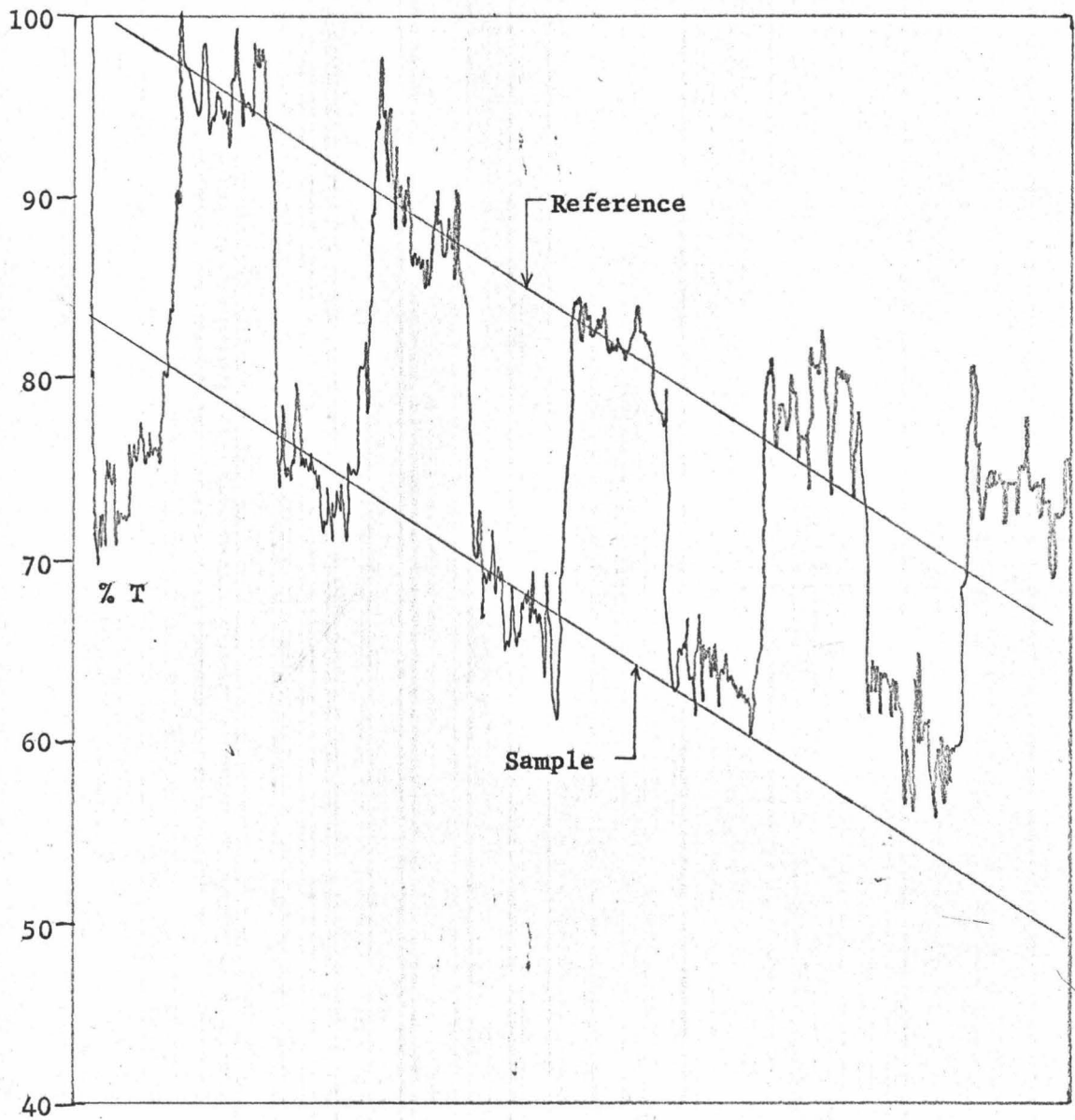FIGURE 31 - Spectra of 0.0040 mole % D Standard

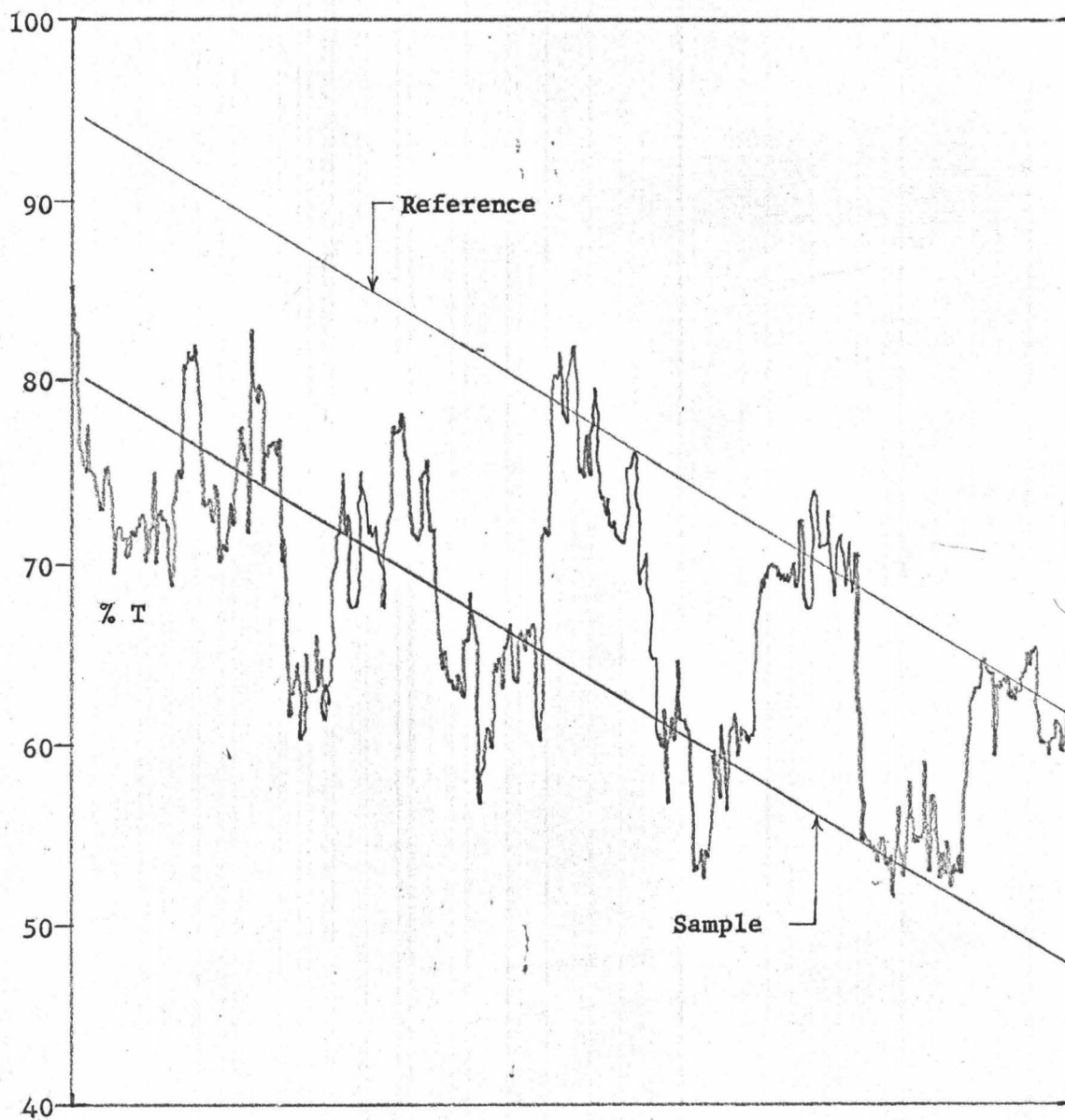FIGURE 32 - Spectra of 0.0030 mole % D Standard

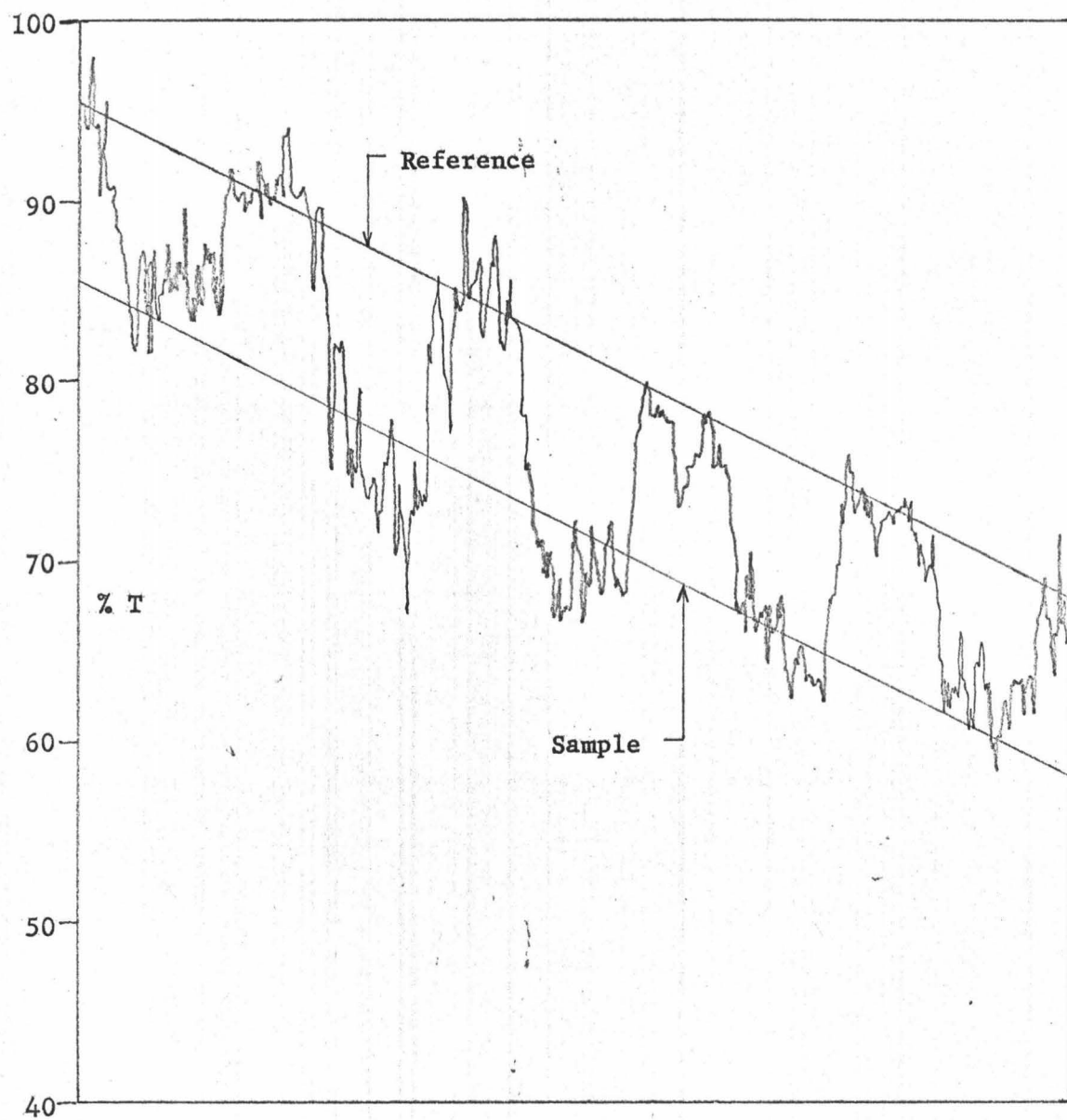FIGURE 33 - Spectra of 0.0020 mole % D Standard

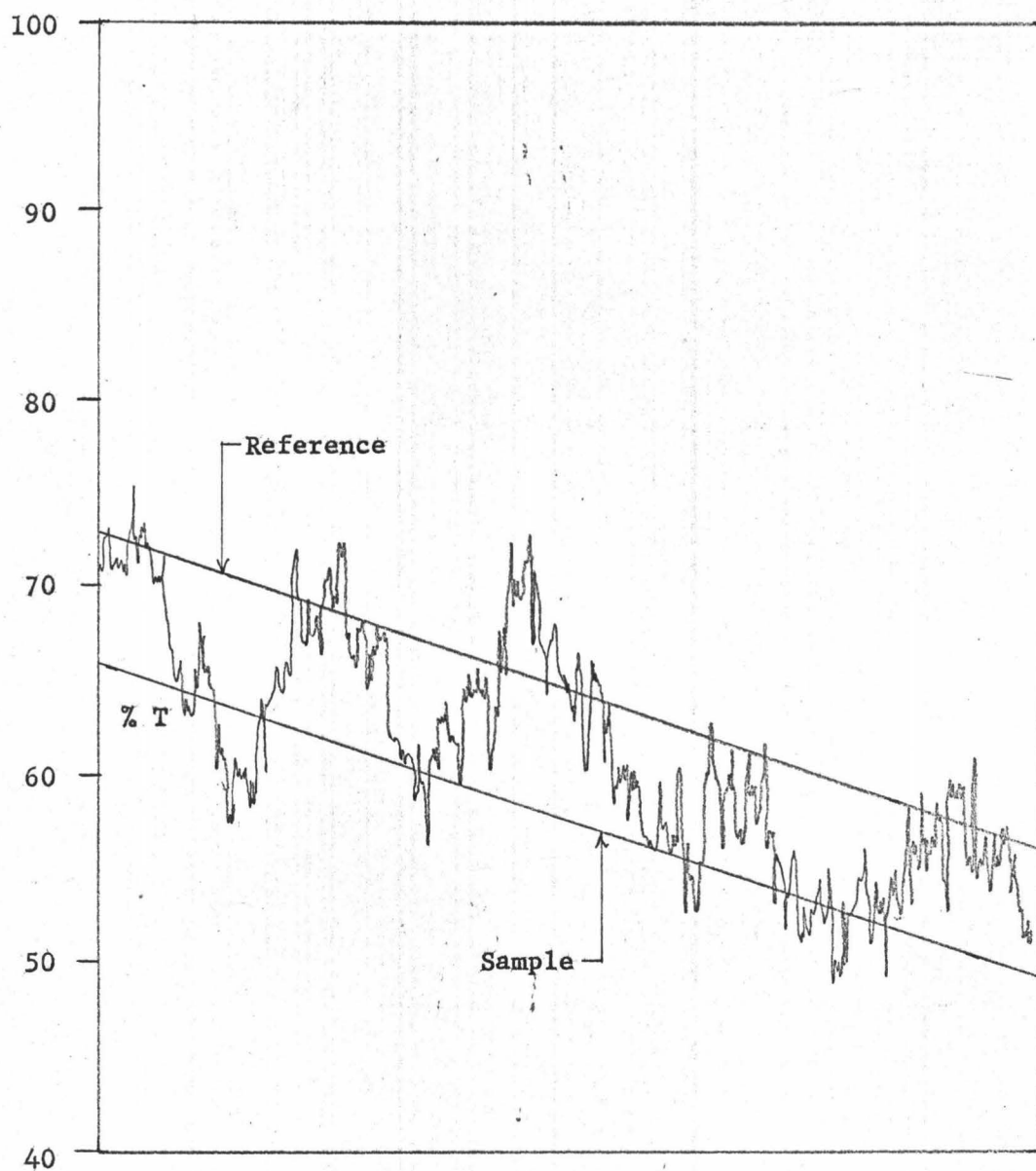FIGURE 34 - Spectra of 0.0015 mole % D Standard

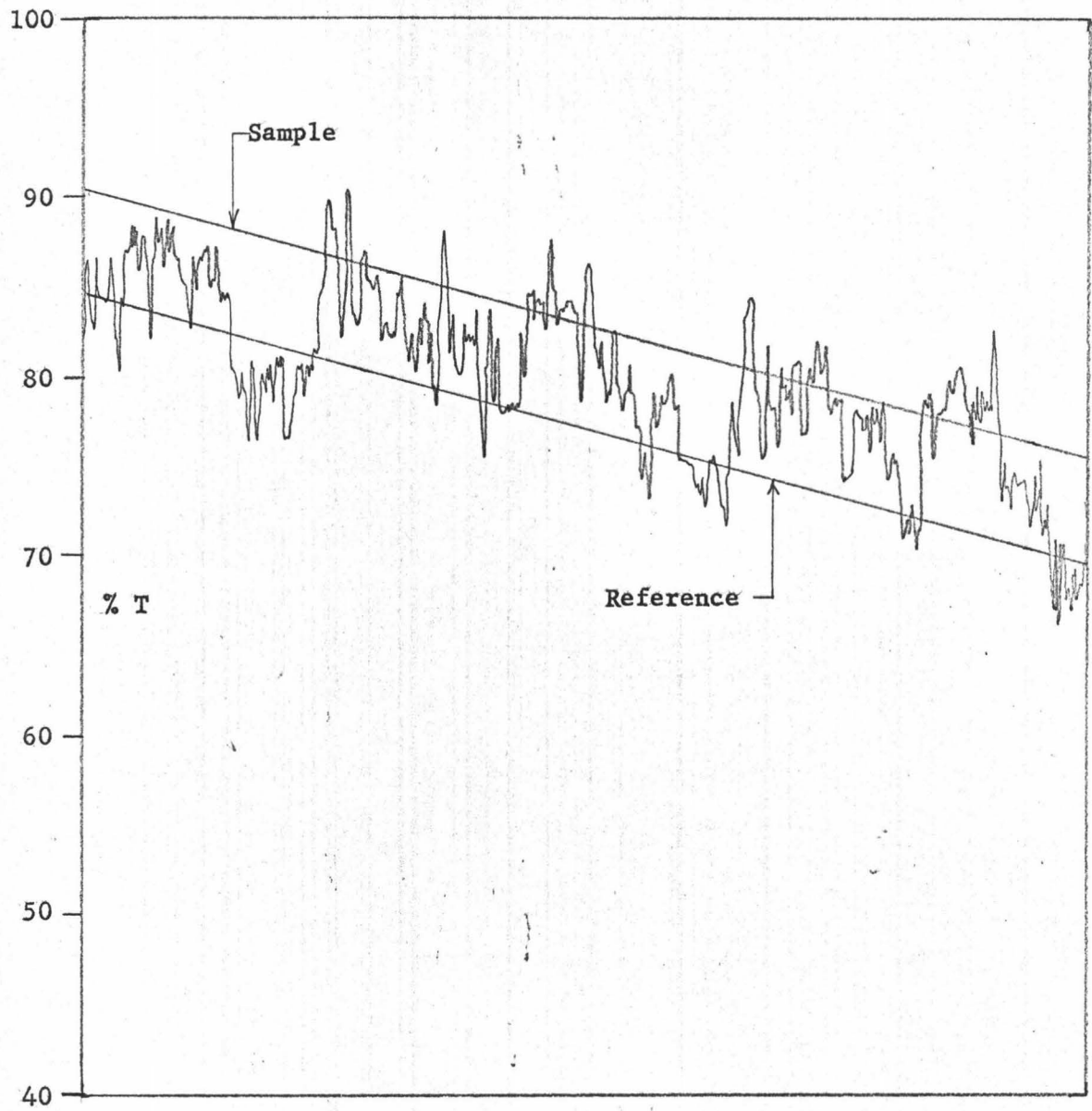FIGURE 35 - Spectra of 0.0010 mole % D Standard

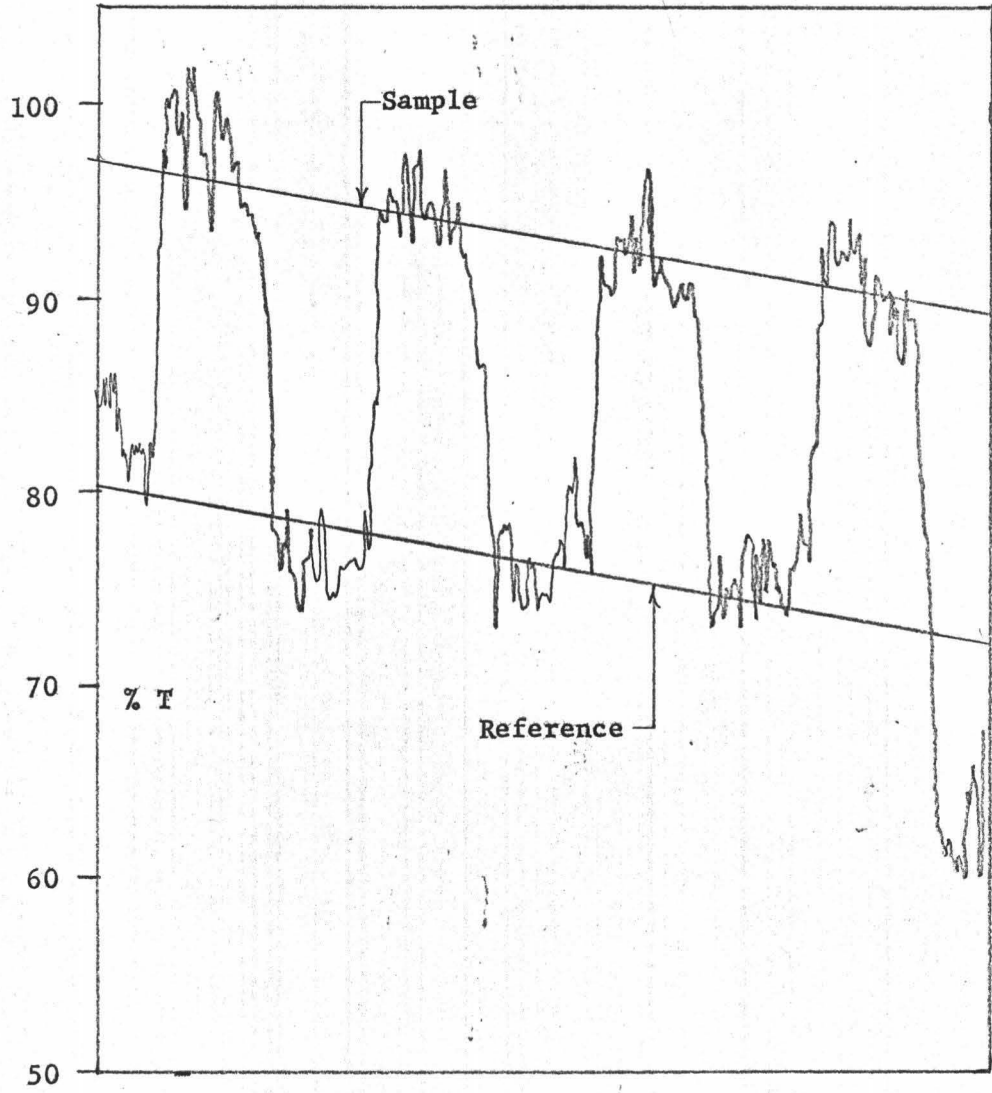FIGURE 36 - Spectra of Ocean Water Sample

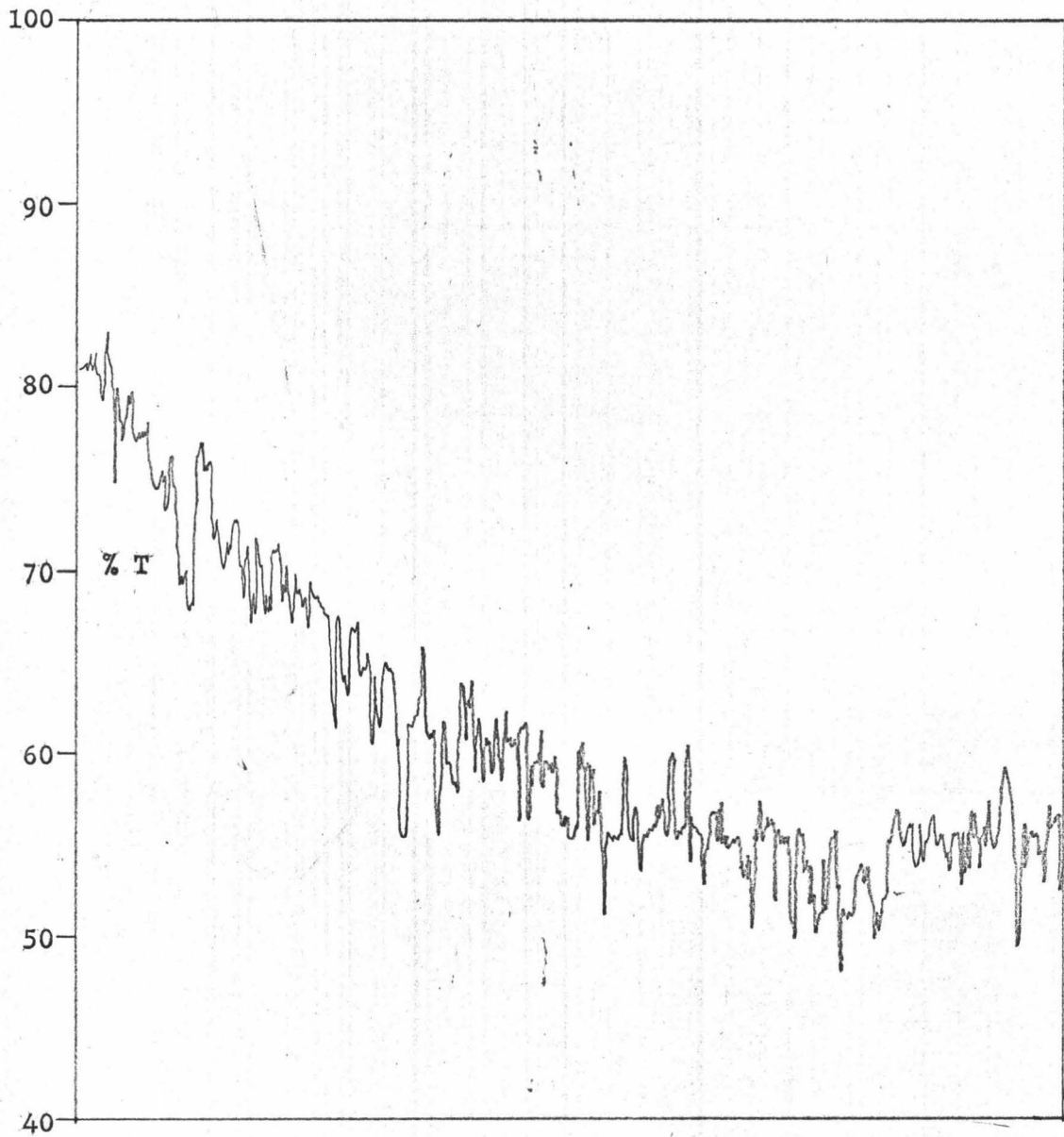FIGURE 37 - Spectra of Ice Water Sample
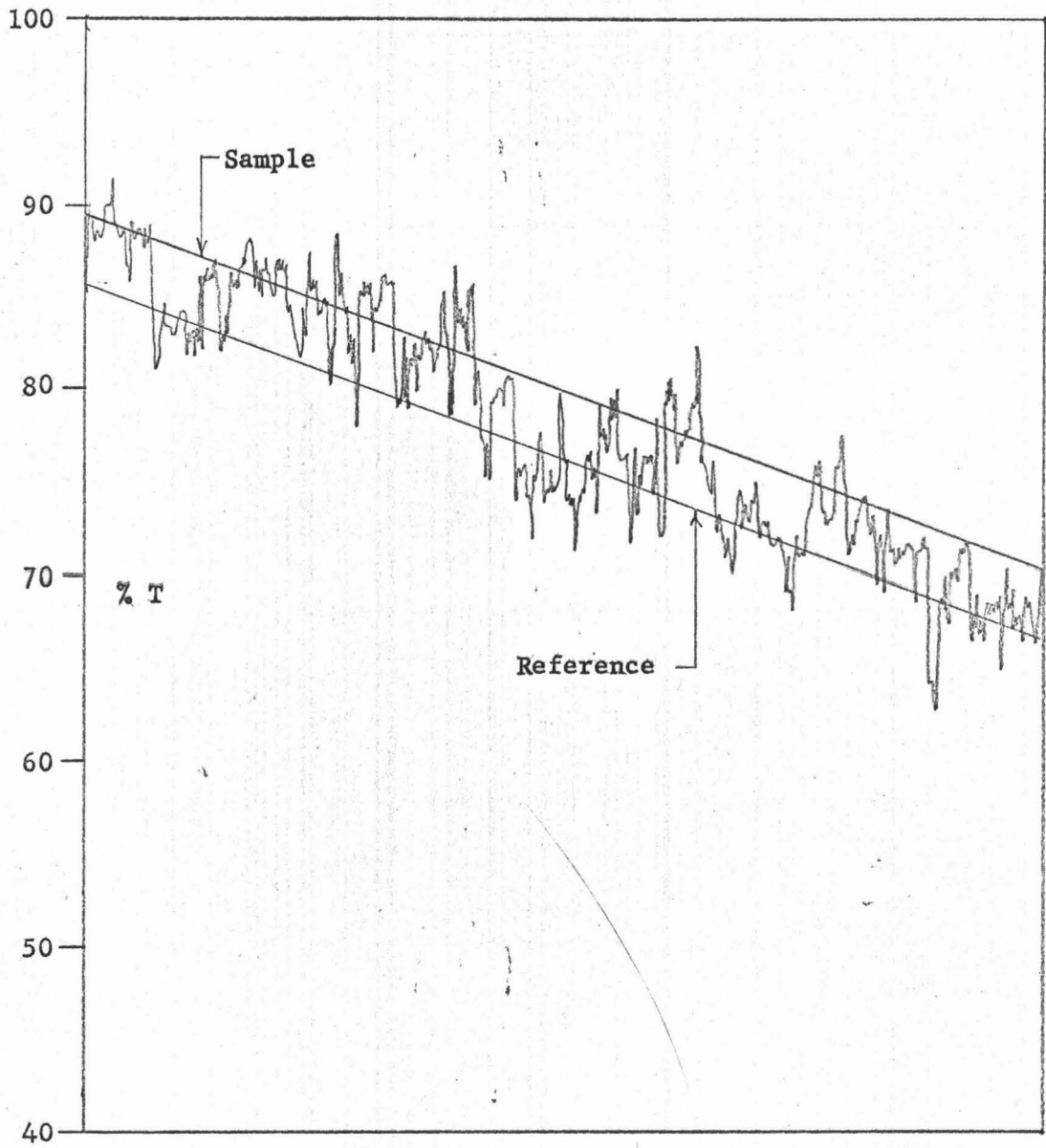
FIGURE 38 - Spectra of Tap Water Sample

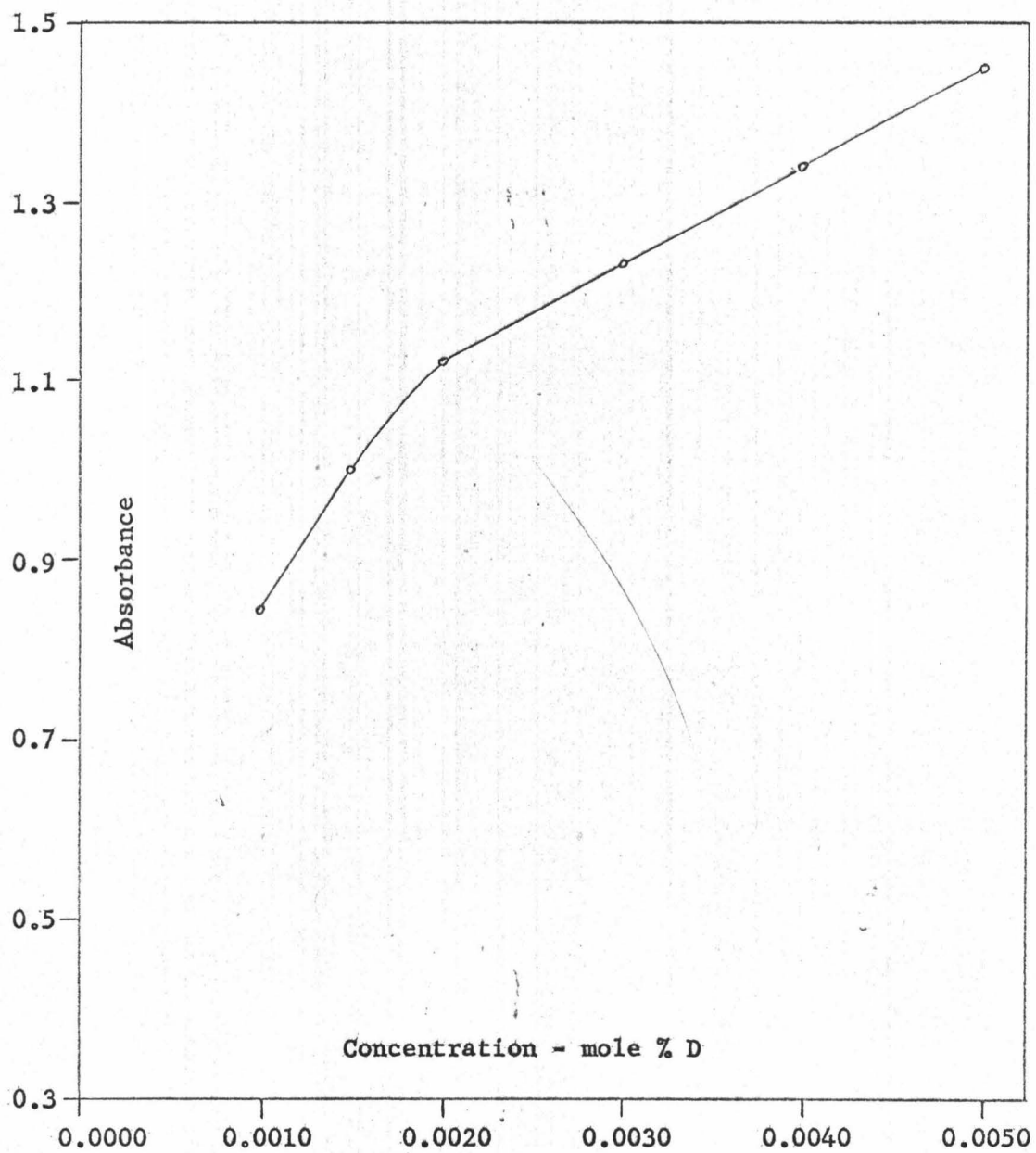FIGURE 39 - Spectra of Sulfur Bank Water Sample

FIGURE 40 - Graph of Concentration vs Absorbance for Standards

Table 14

Concentrations of Standard Solutions

and Samples in Terms of δ * Values

Sample	True Concentration**	R	δ
0.0050 mole % D	0.0213 mole % D	1.38	38%
0.0040 mole % D	0.0203 mole % D	1.32	32%
0.0030 mole % D	0.0193 mole % D	1.25	25%
0.0020 mole % D	0.0183 mole % D	1.19	19%
0.0015 mole % D	0.0178 mole % D	1.16	16%
0.0010 mole % D	0.0173 mole % D	1.12	12%
Reference Water	0.0163 mole % D	1.06	6%
Ocean Water	0.0154 mole % D	1.00	0%
Sulfur Bank Water	0.0149 mole % D	0.968	-32%
Tap Water	0.0163 mole % D	1.06	6%
Ice Water	0.0124 mole % D	0.806	-19%

* = (R - 1) x 100

** As compared to Standard Ocean Water (0.0154 mole % D)

V. SUMMARY

An infrared method for the analysis of the deuterium content in the natural water range was investigated. Several methods of analysis were attempted in both the gas phase and the liquid phase. The method that was finally adopted was similar to that used by Bayly, Stevens and Thurston.[24] The method used was essentially a "cell-in-cell-out" technique. This means that only one cell is used for both the reference and the sample at a constant wavelength and the difference in absorbance between sample and reference is measured. The method used in this research utilized a flow-through system in which the reference water flowed through the cell at a constant rate for a period of two minutes and then the sample flowed through the cell for the same period of time. This was repeated five times and the average of the transmittance of each was used. From these averages the difference in absorbance between the reference and sample was measured and then plotted against concentration as is shown in Figures 30 to 40. It has been pointed out by several workers that the absorbance increases with a decrease in temperature[25-30] and that a small variation of temperature in the sample will have a large effect on the absorbance.[24] The main source of sample heating is absorbance by water of the infrared beam. Three modifications were employed in an attempt to keep the effect of heating to a minimum. First, a continuous flow of reference water and sample water through the cell tended to cool the cell. Second, the sample and reference waters were passed through an ice bath before entering the cell. The cold water entering the

cell had a larger cooling effect on the sample than it would have if the bath temperature was warmer. It also gave a larger absorbance peak than a warmer temperature because the absorbance increases with a decrease in temperature. The third modification was the use of an acetone filter which absorbed some of the energy before the beam entered the cell. This, however, was not as effective as the interference filter used by Bayly, Stevens and Thurston.[24] An interference filter was not available and thus could not be used.

A straight line was formed between 0.0050 mole % D and 0.0020 mole % D when concentration was plotted against absorbance (Figure 40). Below 0.0020 mole % D the line bends downward. This is probably due to the large amount of scattering encountered in infrared spectroscopy. This is especially true for the large slit width used and small absorbance peak. Another possible cause would be a variation in the temperature of the cell. This would limit the usefulness of this method for the determination of deuterium concentration in natural water. The method is much more convenient than mass spectrometric methods and densiometric methods.

Samples were collected from the ocean at Koko Head which is not contaminated by runoff from the land, ice from the ice machine in Bilger Hall, tap water from the Hawaiian Institute of Geophysics, and Sulfur Bank water from the Kilauea Crater on the island of Hawaii. With the exception of the tap water, the samples were less concentrated than the reference water and
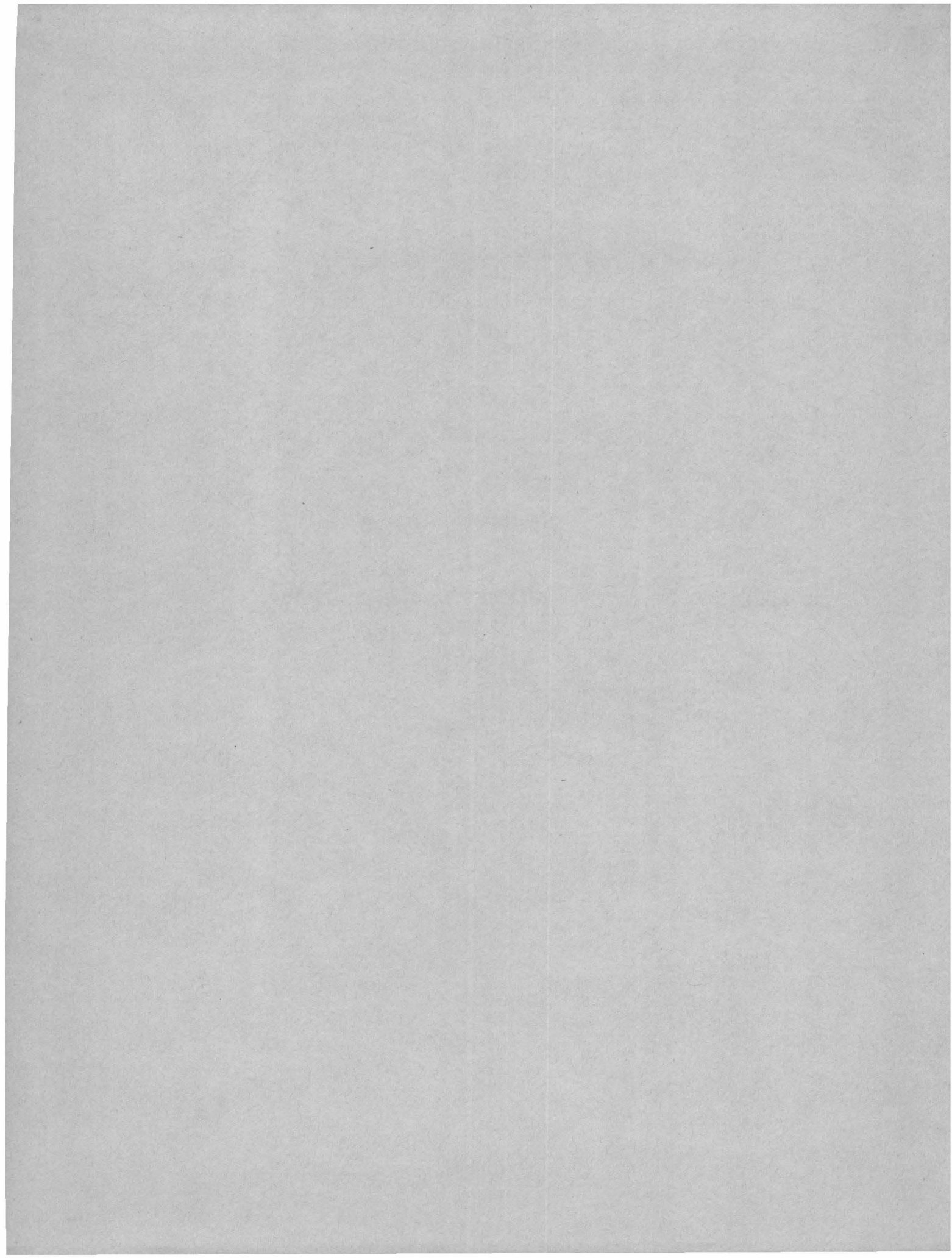
because the Bouguer-Beer law was not followed the samples could not be analyzed with confidence. The hydrologic cycle patterns are summarized and the results of the samples can be justified by these patterns.

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