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REACTION GAS CHROMATOGRAPHY: A STUDY OF CARBON-HYDROGEN ANALYSIS OF CHROMATOGRAPHIC PEAKS

by

GEORGE WILLIAM SCHEIL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"REACTION GAS CHROMATOGRAPHY: A STUDY OF CARBON-HYDROGEN ANALYSIS OF CHROMATOGRAPHIC PEAKS"

submitted by GEORGE WILLIAM SCHEIL in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date... June 21, 1973.

ABSTRACT

The basic requirements for carbon-hydrogen analysis of chromatographic peaks by reaction gas chromatography are discussed. Major objectives of the project were the determination of the hydrogen/carbon ratio of hydrocarbons with an accuracy better than 0.5% relative error, and a simplified instrument design which allows a high degree of automation. An instrument capable of meeting the basic requirements is described. A gas sampling valve samples the chromatographic peaks. The samples are oxidized at 700°C to carbon dioxide and water in a reactor packed with cupric oxide. The carbon dioxide and water are separated on a Porapak N column and measured by a thermal conductivity detector. A digital voltmeter records the peak heights.

Corrections for systematic linearity and sample adsorption errors are necessary to obtain the necessary accuracy in the H/C ratio. The analysis of 5-10 µg samples of 31 hydrocarbons shows a precision of 0.23% relative standard deviation and a median error of 0.2% (relative) when each sample is analysed in triplicate. The formulas of all the hydrocarbons, as calculated from the results are correct. Analysis of oxygen-containing compounds shows a median error of 0.9% (relative). The increase in the error for these compounds is partially

due to impure samples. Compounds containing sulfur, nitrogen, or halogens interfere with the determinations. Suitable modifications are suggested to reduce or eliminate the interferences.

DEDICATION

This thesis is dedicated to my parents without whose help and encouragement it would never have been written.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. W. E. Harris for his guidance and encouragement during the course of this project and in the writing of this thesis.

I would also like to thank the many technical staff members of the University of Alberta for their assistance in constructing and maintaining the equipment used in this project.

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Table of Contents

Table of Contents

List of Tables

List of Figures

List of Figures

I

INTRODUCTION

1-1 GENERAL BACKGROUND

Until 1960 the analytical chemist depended on the classical Pregl method for determination of carbon and hydrogen in organic compounds. single analysis required from one to three hours to complete. The sample was weighed, placed in the furnace and heated for some time to complete the oxidation of the sample over cupric oxide. Then the carbon dioxide and water produced were absorbed in weighed absorbent flasks and these flasks were then reweighed to determine the weight difference.

In 1960 Sundberg and Maresh[1] and Duswalt and Brandt[2] simultaneously published papers which detailed a gas chromatographic finish to the determination. In the first paper the weighed sample was oxidized over cupric oxide with helium carrier gas, he water converted to acetylene in a separate reactor nd the products trapped in a liquid nitrogen trap. The trap was then heated and the carbon dioxide and acetylene separated on a silica gel column and determined with a thermal conductivity detector. Duswalt and Brandt used the same method except that the oxidation was carried out in an oxygen stream.

By taking advantage of the rapid analysis

of the combustion products possible using gas chromatography (GC), the work of Duswalt and Brandt reduced the analysis time to 20 minutes.

Vogel and Quattrone[3] proposed a third variation for the determination by completing the combustion in an oxygen-filled bomb. The analysis time was 17 minutes.

Other workers extended the method to include the analysis of nitrogen[4-6]. In the mid-sixties a number of commercial analysers based on a gas chromatographic finish to the determination began appearing. Only the Perkin-Elmer model 240 and the F & M model 185 analysers have been widely accepted[7]. A comparison of these two analysers and the classical methods has shown that the slightly less reliable results of the analysers are outweighed by the significant decrease in analysis time and the smaller samples required[7].

A few workers have successfully eliminated the GC column by relying instead on sorption-desorption reagents to measure the different products[8-9]. Dugan and Aluise[10] used an open tube, uncatalysed oxidation with a helium/oxygen mixture for the analysis of carbon-hydrogen-nitrogen-sulfur-oxygen in 16 minutes. Rezl[11] diluted the sample with helium in a piston

and then used frontal analysis with a thermal conductivity detector for the determination.

Belcher and Fleet[12] and Kirsten[13] analysed samples as small as 50 µg for carbon and hydrogen. Kennedy[14] used a sealed sample tube for analysis of volatile samples.

All of the above methods depend on an initial weighing of the sample. While an electronic balance is generally used for this weighing, the step still limits the speed and usefulness of the methods. If the sample is a gas, different methods must be used.

Perhaps the most important area of analysis in which the samples are gases is in the identification of the peaks on a chromatogram. While the retention time is sometimes enough to identify an unknown peak in a simple mixture, most peaks require additional information. For the analysis of hydrocarbons the ratio of carbon to hydrogen can provide the additional information necessary. For analysis of petroleum samples, the carbon/hydrogen ratio can determine the degree of unsaturation and the retention time can provide an estimate of the carbon number. For a large percentage of samples the isomeric form of the unknown is not important and more complex methods of analysis, such as mass spectrometry, are unnecessary.

Cacace[15] was the first to attempt the direct analysis of peaks from a GC column. The sample peaks were introduced into the reactor directly from the column. The oxidation was carried out with a reactor packed with cupric oxide and reduced iron. The carbon dioxide and hydrogen produced were then separated on a column of acetonylacetone on Celite and measured by a thermal conductivity detector. The areas of the peaks were found to be proportional to the carbon/hydrogen ratio. Due to the problems of introducing the entire peak into the reactor and the difficulty of maintaining sufficient resolution of the peaks, the standard deviation exceeded 3%. In a series of papers[16-18] Revel'skii, et al., modified this method by introducing the samples from a sampling valve. In these papers the peak heights of the carbon dioxide and hydrogen produced by the reactor were correlated with the carbon and hydrogen numbers of the sample with an error of approximately 5%. Unfortunately the method was not completely explained, and little data was provided. The accuracy reported is not sufficient to differentiate decane and decene from one another.

Berezkin and Tatarinski[19] also used a sample valve for sampling the unknown peaks and deter-

mined carbon, hydrogen, nitrogen and oxygen simultaneously. The sample was split; part going to a reactor containing carbon black, which produced a mixture of carbon monoxide and nitrogen; the remainder of the sample was oxidized over cupric oxide and copper, which produced carbon dioxide, water and nitrogen peaks. The products from the two reactors were separated on two separate columns connected to opposing sides of a thermal conductivity detector to give a composite chromatogram with both positive and negative peaks. The heights of these peaks gave the ratio of the various atoms in the original sample to an accuracy of 1%. No sample size or analysis time were reported and data was provided for only a few easily determined compounds.

Franc and Pour[20] also attempted the determination of the C/H ratio for gas chromatography samples by measuring the sum of both carbon dioxide and hydrogen, absorbing the carbon dioxide and remeasuring. The results were not equal to the classical methods, which have an accuracy of about 0.3% absolute or 2-5% relative error.

In 1972 Liebman, et al.,[21] reported a method for determining C/H ratios using a sampling valve, oxidation over copper oxide, separation of the carbon

dioxide and water produced, and measurement by thermal conductivity. Several determinations had to be averaged to achieve an error of 0.5% absolute.

The work of Berezkin and Tatarinski and Liebman, et al., above came to the authors' attention after our own work was nearly completed.

While the works cited above are in basic agreement concerning the method of analysis, they still leave several gaps in the analysis of GC samples. A more exhaustive analysis of a wide variety of samples is necessary and the accuracy and precision of the analysis must be further increased to positively differentiate between compounds of similar carbon/hydrogen ratios.

The present study is an attempt to meet these requirements and also to examine the instrumentation for the analysis. The system used must be capable of high precision and speed, and should not impose excessive limits on the type or size of the samples analysed.

1-2 SYSTEM CHARACTERISTICS

Several desirable characteristics for the

system described above are: (1) fast analysis time, (2) minimal data handling, (3) direct sampling, (4) high sensitivity, (5) high accuracy and precision, (6) freedom from interferences, (7) wide range of sample sizes, (8) simplicity of design.

Analysis time

The 20 to 30 minute analysis time of the commercial analysers must be greatly reduced to obtain a reasonable number of samples during a single gas chromatographic run. The analysis of a typical gas chromatographic run requiring 30 minutes and containing ten components requires that the diagnostic system must be capable of completing each analysis within one or two minutes. At such an analysis rate, one or two runs of the original mixture should provide reasonably complete data on the carbon/hydrogen ratios of each unknown peak.

Data handling

Due to the short analysis time, the system should be semi-automated with a master control unit capable of issuing all necessary commands to the system after the operator initiates the sampling operation.

Consideration must also be given to the choice of peak area or peak height for the determination of the carbon dioxide and water peaks as they pass through the detector.

Area integration is the usual choice for gas chromatography, since numerous integrators are commercially available. However, these instruments are generally not capable of better than 1% precision under excellent conditions and performance is further degraded when the peaks have significant overlap. The use of moderately sophisticated computer facilities to handle the curve fitting procedures then becomes necessary to maintain accurate results.

The use of peak height has several advantages. As noted, several previous systems have used peak height with success. With the system now required to produce only base line and peak maxima readings, the necessary calculations can easily be handled by a small computer or carried out manually. Peak height also works better in cases where resolution is less than optimal. The only restriction is that peak tailing should approach a value of base line plus normal system noise by the time the succeeding peak reaches its maximum reading as shown in Figure 1.1. The second peak height will not be in error in this example. If area measurements are used, this degree of overlap requires corrections

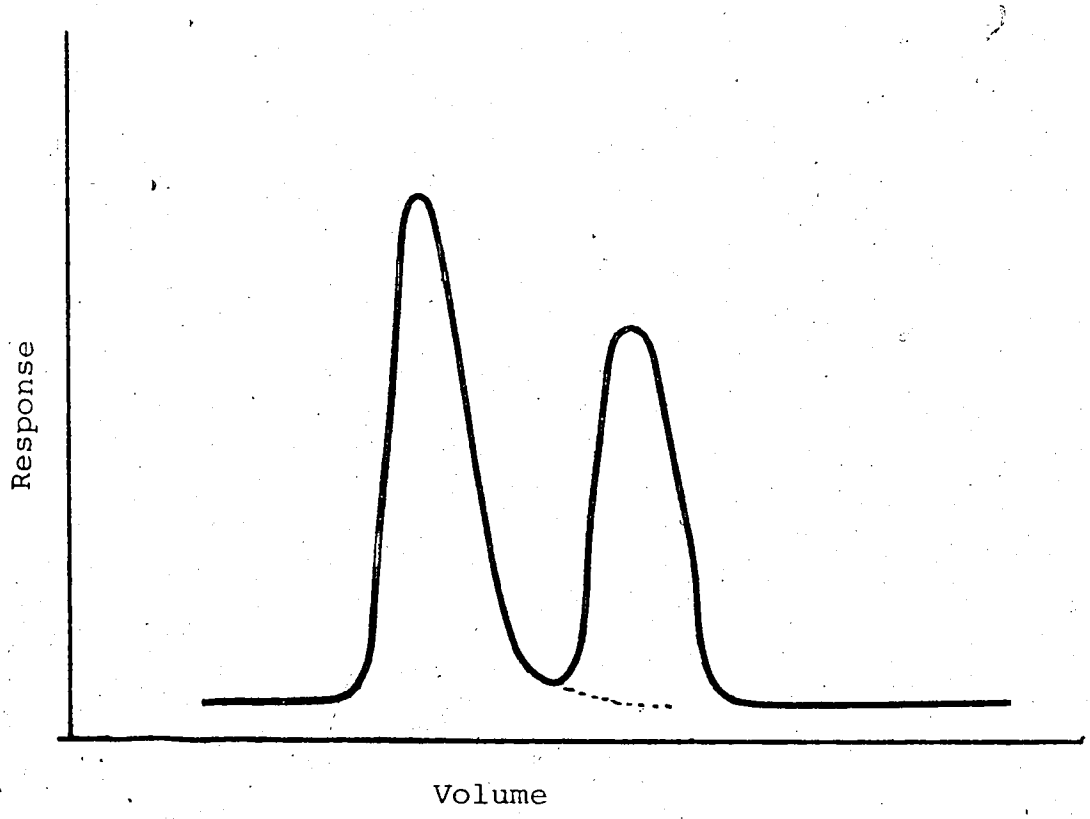


Figure 1.1. Effect of overlapping peaks on height measurements.

to the program for computing the area.

Height measurements are often subject to errors which are insignificant when using area integration. Goedert and Guiochon[22-23] have found that peak height provides superior results if the system has excellent thermal stability even though poorer pressure and flow control. The requirement for thermal stability means that isothermal operation of the column is much preferred over temperature programming, which is difficult to reproduce and requires cooling to the initial temperature after each run. With sensitive, non-cycling temperature controls, large thermal mass and sufficient insulation; thermal stability should be easily maintained. The flow controls, which are difficult to maintain at highly stable values, may then be simplified.

Due to adsorption on various internal surfaces of both the parent hydrocarbon and water produced, the system design must carefully minimize these effects to maintain linearity and reproducibility throughout the sample size range.

Sampling

An on-line system must be attached to and directly sample the system under study, in this case, the outlet of a gas chromatographic system. This

requires a sampling valve, which transfers the contents of a sample loop from one gas stream to the other at the moment of actuation. Depending on the volume of this loop and the flow rate in the primary system, the valve samples a section of the gas stream of known width at a known point on the chromatogram.

Sensitivity

The volume of the sample loop is limited by the width of sharp peaks to approximately 1 cc in most systems. At a flow rate of 30 ml/min, this corresponds to a sample of two seconds on the chromatogram. This typically limits the maximum sample size to one to ten micrograms. The detector of the analytical train must have a high response factor to maintain sufficient signal/noise ratio.

Accuracy and Precision

The system must be able to distinguish between compounds of adjacent carbon numbers and the run to run precision must consistently be within these same limits. The greatest problems will not come in distinguishing between the two highest possible ratios: methane (CH_4) and ethane (C_2H_6) or between the lowest: benzene (C_6H_6) and toluene (C_7H_8), but between adjacent carbon numbers in the higher saturated hydrocarbons.

Decane has a ratio of hydrogen to carbon of 2.20 and nonane a ratio of 2.22. With a relative difference of 1% between these two compounds the system must be accurate to 0.5% if no ambiguity is allowable between these compounds.

Interferences

The presence of sulfur, nitrogen, or halogens in the sample should not affect the carbon/hydrogen ratio.

Sample size range

Response should be linear over the entire sample range from the upper limit, imposed by the response of the voltmeter, to the lower limit, imposed by inadequate signal/noise ratio.

Design simplicity

The above requirements should be met with the minimum number of components in the system. Once assembled and tested, the equipment should require minimal maintenance and be simple to operate. The small sample size of this system will be a major advantage since a large number of samples can be run before the reactor requires recharging or replacement. By using a Porapak column, the direct determination of

water and carbon dioxide should be possible without serious tailing. This allows the system to consist of solely the sampling valve, reactor, column and detector along with the usual pneumatic and temperature controls.

After extensive tests with various instrument configurations, a system has been devised which meets the basic requirements that have just been examined. The following sections describe the instrument and method of analysis as well as the results of analysing 62 different compounds of various types.

II

INSTRUMENT DESIGN AND CONSTRUCTION

2-1 GENERAL DESIGN

To obtain accuracy and precision better than 0.5% for the C/H ratio, (significantly better than that obtained from an ordinary GC) the design of the various components must be carefully examined. Some general design features and criteria follow.

The reactor, which is the heart of the system, is based on oxidation of the samples by cupric oxide. No catalytic agents are present which may become poisoned, requiring replacement of the reactor. The pure cupric oxide can be regenerated by passing air through the hot reactor tube.

The water and carbon dioxide produced from the oxidation of the sample are measured directly after separation on a short column. Conversion or trapping in this critical part of the system can greatly complicate the design. The number of components and the dead volume between the sample valve and detector are held to a minimum. If unnecessary variables affect this basic part of the system, the overall operation of the instrument becomes too cumbersome to be practical.

Control is completely automatic. The only operator action is that of pushing the sequence start switch at the proper moment. The system then produces a printed record of all necessary data with no operator intervention required.

Every major variable is controlled to give roughly the same relative error and the variables are arranged to cancel each other wherever possible. The final system does not possess an observable dependence on any single variable.

Since the system operates isothermally, with only two compounds produced in normal operation, full advantage can be taken of a peak height determination. After all possible sources of error have been identified and minimized, the residual determinate errors can be eliminated by use of small correction factors.

2-2 MAIN SYSTEM CONSTRUCTION

The block diagram shown on the following page can be separated into two principal sections. Column B and detector B with their associated components provide the samples to the main system and would vary with the particular system being sampled. Therefore, the main system components are examined first.

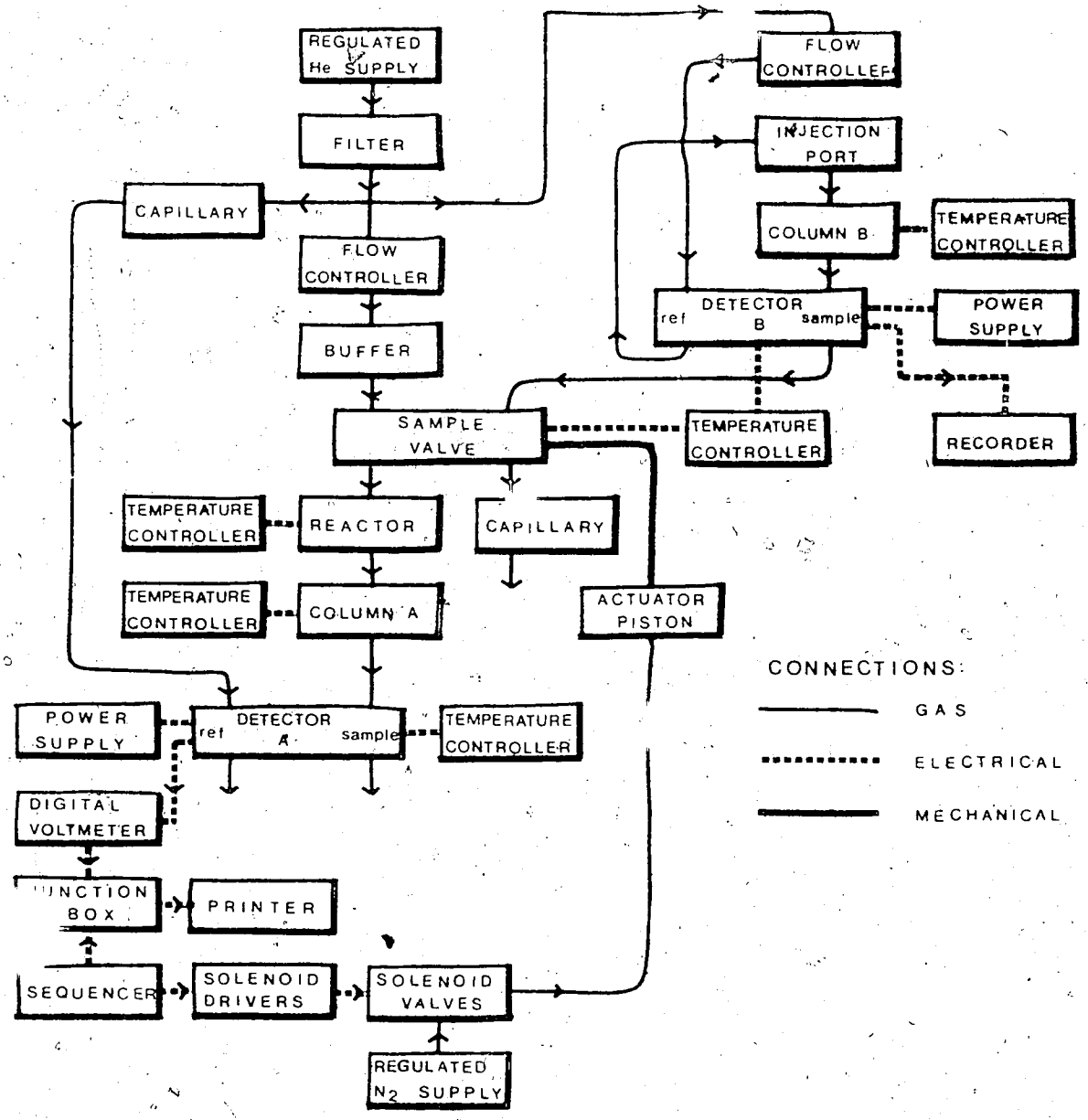


Figure 2.1. Block diagram of analyser.

Regulated Helium Supply

The helium supply consists of a tank of high purity helium (0.001% impurities, Canadian Liquid Air) with a two stage regulator (model 201 oxygen double stage regulator, Canadian Liquid Air Company, Ltd.). The main tank valve and pressure adjusting screw on the regulator are left in their operating positions and not disturbed except when changing tanks. The main gas flow is turned on and off with a valve placed downstream from the regulator.

While this method of shutting down the system results in a slight long-term leakage of helium when the system is idle, it is necessary for system stability. The flow controls in this system require a highly stable upstream pressure which cannot be maintained if the regulating spring and diaphragm of the regulator are unloaded after each session. When the regulator is first activated there is a slow drift in the baseline measured at detector A as the control setting gradually settles toward its equilibrium value. This settling time is typically about 12 hours. With the entire system dependent on the main supply pressure remaining constant, this drift is intolerable.

If the regulator remains under load at all times with only the flow shut off during idle periods,

a slight drop in pressure of approximately 50 mb is observable as the shutoff valve is opened each day. After this initial drop the remaining drift is greatly reduced and the baseline reaches a steady state within the two hour warm-up period allowed.

Filter

The filter used is a model 236 mixed bed trap made by Guild Corporation, Bethel Park, Pennsylvania. It contains a layer of activated carbon to remove residual hydrocarbons and two sections of molecular sieve drying agent, one with indicator.

Flow Controls

The two flow controllers (X-8744 ELF with #1 needle, Brooks Instrument Division, Emerson Electric Company, Hatfield, Pennsylvania) maintain a constant flow rate if the upstream pressure remains constant. Capillary tubes are used for the fixed controls on the reference side of detector A and the outflow from the sample side of the sampling valve. All flow control devices are mounted together away from heat-producing equipment and further isolated by being sandwiched between two large pieces of 5 cm thick fiberglass batting.

Gas connections in the apparatus are made with Swagelok fittings. Copper tubing and brass fittings

are employed in noncritical sections. All sections which operate at elevated temperatures are made of stainless steel quartz (reactor), or teflon (valve mechanism, reactor seals).

Buffer

The buffer tank between the flow controller and the sample valve is necessary to smooth out variations in flow from the controller and also to provide some isolation for the controller from sudden pressure surges during sample valve switching since the controller equilibrates slowly after sudden changes. The buffer tank consists of a 25 mm diameter copper tube 15 cm long with copper end caps soldered in place and 1/8 inch stainless steel tubing attached to each end. Its internal volume of approximately 75 cc is sufficient to buffer flow variations from the flow controller and sampling valve.

Sample Valve Assembly

The sampling valve (Micro-volume Valve model 2014, Carle Instruments, Inc., Fullerton, California) is an 8-ported valve with the gas connections made as in Figure 2.2. In this configuration the sample and reactor gas streams are isolated from one another at all times. Each time the valve is thrown the contents

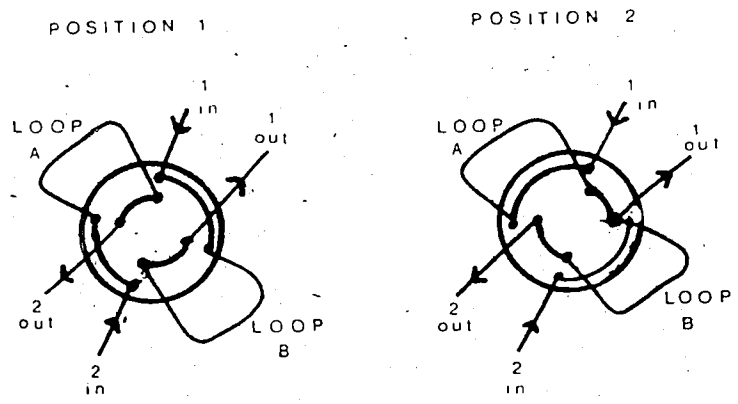


Figure 2.2. Gas connections to sample valve.

of the sample loops are transferred from one stream to the other. If the sample loops are matched, the size of sample will then remain constant regardless of the direction of throw. The sample loops are short sections of 1/8 inch stainless steel tubing with internal volumes of 0.4 cc. For automatic operation the solenoid switched actuator (Carle model 2050) is used for valve switching. This actuator consists of a simple gas-driven piston to rotate the value shaft.

A double solenoid valve actuates the piston by reversing the high pressure and exhaust connections. The valve is mounted in the same oven as detector B as shown in Figure 2.3.

An average sample taken by this valve is ~5 nanoliters, and is measured in the following manner: The internal volume of the sample loop is 0.4 cc, which is equal to 0.41 cc at room temperature and pressure. Since the flow rate is 1 cc/sec at room temperature, measured with a soap bubble flow meter, the contents of the loop represent a width on the chromatogram of 0.41 sec.

A 1 µl sample of n-decane injected onto column B results in a total peak area of 160,000 count-sec. Sampling the peak at a height of 2000 counts results in a sample taken of 820 count-sec which is equal to 0.005 µl or 5 nanoliters. This sample size results in a peak height for the resultant carbon dioxide peak of 15,000 counts or one-half of the maximum digital voltmeter reading.

The stability and accuracy of the system are strongly dependent on proper operation of this valve assembly. Therefore, several important points must be mentioned.

Since some of the sample compounds tested have

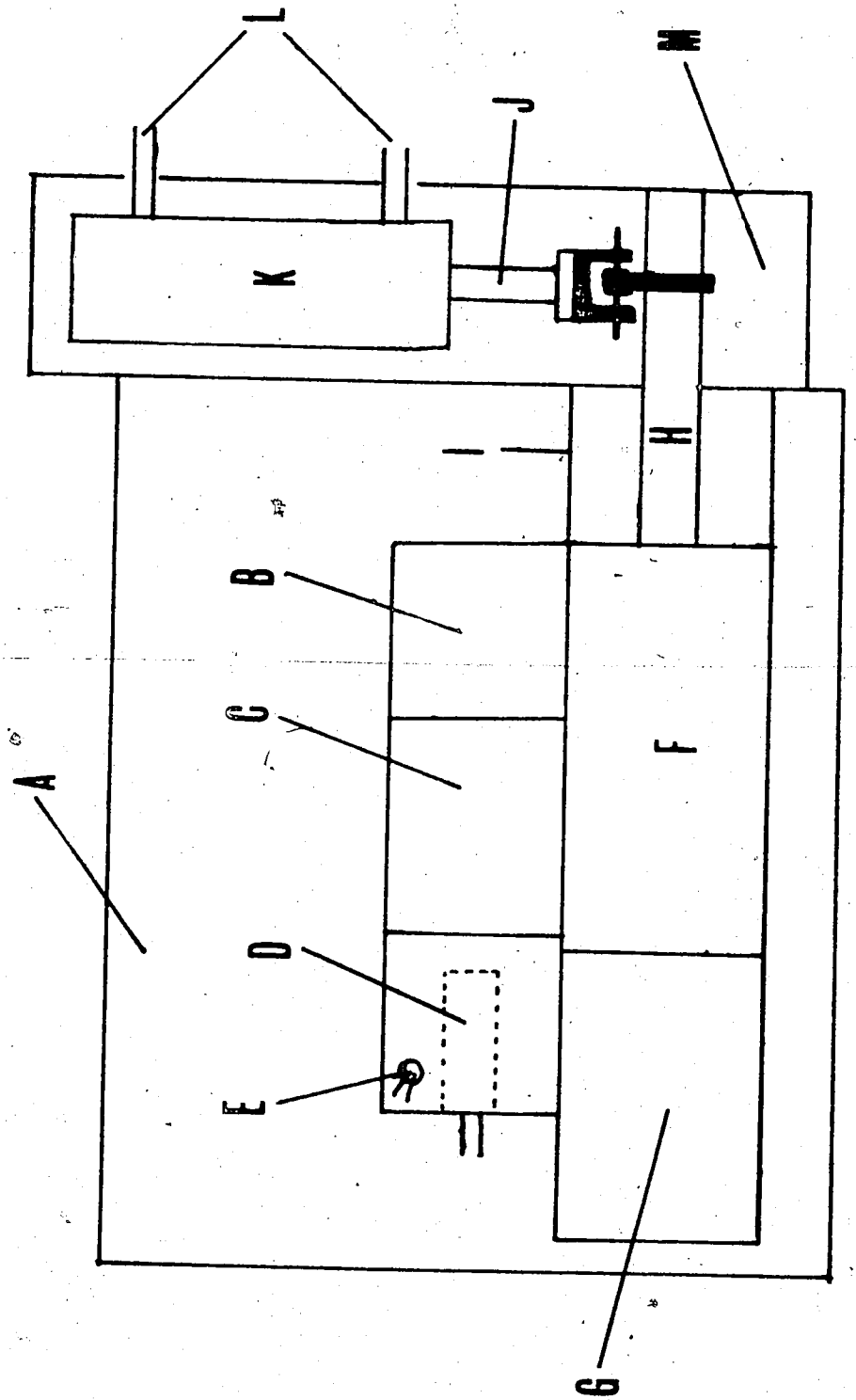


Figure 2.3. Mounting of sample valve and detector A. (top view) A. oven, B. heater block, C. Detector (above block, connected with brass plates on sides), D. Heater cartridge, E. thermistor sensor, F. sample valve, G. open box with sample loops inside, filled with lead shot, H. valve shaft, I. mounting bracket, J. piston, K. cylinder, L. gas connections, M. valve actuator.

boiling points near 200°C, care must be taken to prevent adsorption or condensation inside the valve. As shown in the diagram, the main valve body is directly mounted to the heater block of the detector, which operates at 200°C. Heating the sampling loops is somewhat more difficult and is accomplished by enclosing them within a small metal box which is then filled with lead shot until the loops are completely covered. All lines carrying the sample are wrapped with copper braid which is then looped around the heater block. The remaining space inside the oven is filled with fiberglass wool.

The valve, Figure 2.4, consists of a polished metal disk with inlet and outlet connections drilled through it and a teflon-ceramic disk with grooves cut into its surface to carry the gas streams. A gas-tight seal is maintained by spring pressure on the two disks. The ball bearing maintains even pressure over the entire surfaces of the disks. The spring is normally adjusted for room temperature operation at high pressures. This high tension can result in premature wear of the teflon material at the high temperatures used. Spring tension is reduced to the minimum needed to maintain a gas-tight seal. If this is not done, the teflon crumbles enough to block the gas flow within a few months of operation.

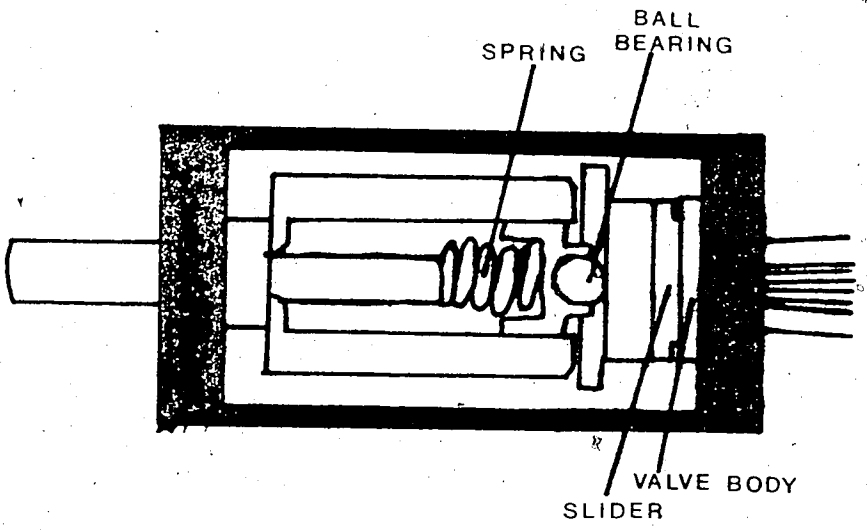


Figure 2.4. Cutaway view of sample valve.

During the valve throw all gas flow is momentarily cut off, which results in pressure surges being transmitted to the detector. The pressure surge also results when the two gas streams operate at different pressures, since the contents of the sample loops are compressed or expanded at the completion of the valve throw. The surge appears as a false peak at a point just before the elution of the carbon dioxide peak on the chromatogram and, if of sufficient magnitude, can cause oscillations in the baseline for several minutes. Because of its position on the chromatogram, this false peak must be rigorously controlled and suppressed to obtain acceptable results.

Operation of the piston at a pressure of 4000 mb from a regulated nitrogen supply minimizes the first cause of error. To keep the valve throw time to a constant value of about 0.1 sec, the piston is lubricated with a commercial molybdenum sulfide oil (Moly-Slip, Slipco Chemicals of Canada, Bowmanville, Ontario) at the start of each day.

The second cause of pressure surges is more complex. With the reactor side of the valve operating at 1250 mb, the minimum spike from detector A is obtained at a sample pressure of 1600 mb. Since the flow controller on the sample side maintains a constant flow rate, a length of capillary tubing on the outlet from the valve can maintain a constant pressure drop to atmosphere.

With the sample stream pressure maintained within 50 mb and the nitrogen supply to the piston within 150 mb, the residual false peak does not exceed 10 counts (50 μv).

Because the several variables affecting the pressure surge cannot be completely equalized for the two directions of valve throw, separate calibrations are necessary for each direction to correct for the slight difference in response.

Reactor

The reactor construction is shown in Figure 2.5. The furnace consists of a quartz tube 33 cm long with an outer diameter of 18 mm. The central 30 cm of the tube are covered with a layer of Fibrefray Insulation #9703 (Carborundum Ltd., Ontario) secured in place by 3M fiberglass tape. The heating element of 1/8 inch wide chromel ribbon with a resistance of 1.06 ohms per foot is then wound around the insulation. The power cord is silver soldered to the ends of the element and the element is secured with more fiberglass tape. Three layers of Fibrefray insulation are then wrapped around the tube. After the completed furnace is baked for 12 hours to remove volatile components it is ready for use. The thermocouples are 20 gauge chromel/alumel wires inserted through notches cut in the transite plugs and extending approximately 10 cm from each end. The transite plugs simply minimize heat losses and provide a guide for centering the reactor tube but are not used to support the reactor because the fragile quartz tubing would shatter when the end fittings are tightened.

The reactor tube is a 28 cm length of 6 mm quartz tubing with short sections of 3 mm quartz tubing fused to each end to minimize dead volume and allow the use of 1/8 inch fittings on both ends. Stainless steel

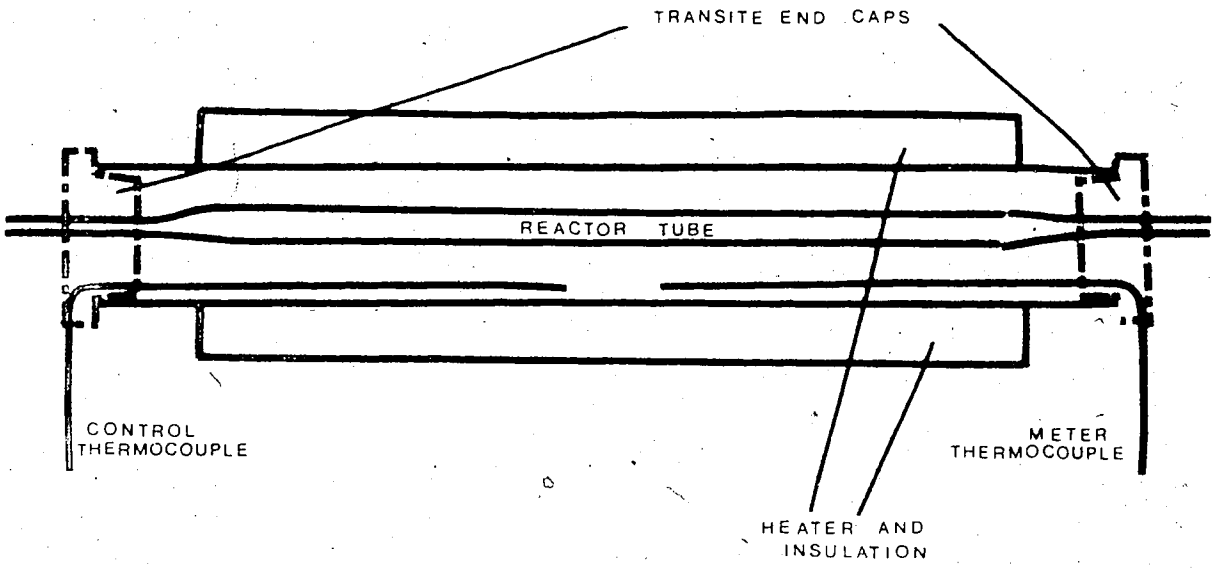


Figure 2.5. Diagram of reactor and furnace.

ferrules are used on the end fittings with a layer of teflon tape first wrapped around the tube to prevent shattering as the fitting is tightened and to provide a better seal.

The reactor packing consists of wire-form cupric oxide (ACS certified, Fisher Scientific Company, Fairlawn, New Jersey) which has been crushed and sieved to a 30/60 mesh size. This provides a uniform packing of the tube without excessive pressure drop. The packing is held in place with short sections of 30 gauge copper wire in each end of the tube.

This reactor design is highly efficient and

has low power consumption. The overall diameter of the furnace is only 4 cm, yet the outside of the insulated portion is not hot to the touch when the unit is in operation at temperatures above 700°C.

The inlet end of the reactor and the end connections are insulated with fiberglass wool to prevent condensation. The reactor is connected directly to the column with an 1/8 inch union.

The temperature profile along the 28 cm central portion of the reactor tube is shown in Figure 2.6. The furnace is slightly hotter near the inlet end due to a slight nonuniformity in the heater winding. The abrupt temperature drop on the outlet end is caused by the absence of insulation between the end of the heating element and the transite plug. This is necessary to prevent an excessive temperature at the column inlet. The column packing is destroyed by temperatures exceeding 200°C. The stainless steel column is a moderately poor heat conductor so that, if excessive heat exists at the union, the first few centimeters of the column will be damaged. The temperature at the inlet connector is approximately 260°C. The outlet connector operates at 130°C.

The upper temperature limit of the reactor is determined by the point at which significant amounts

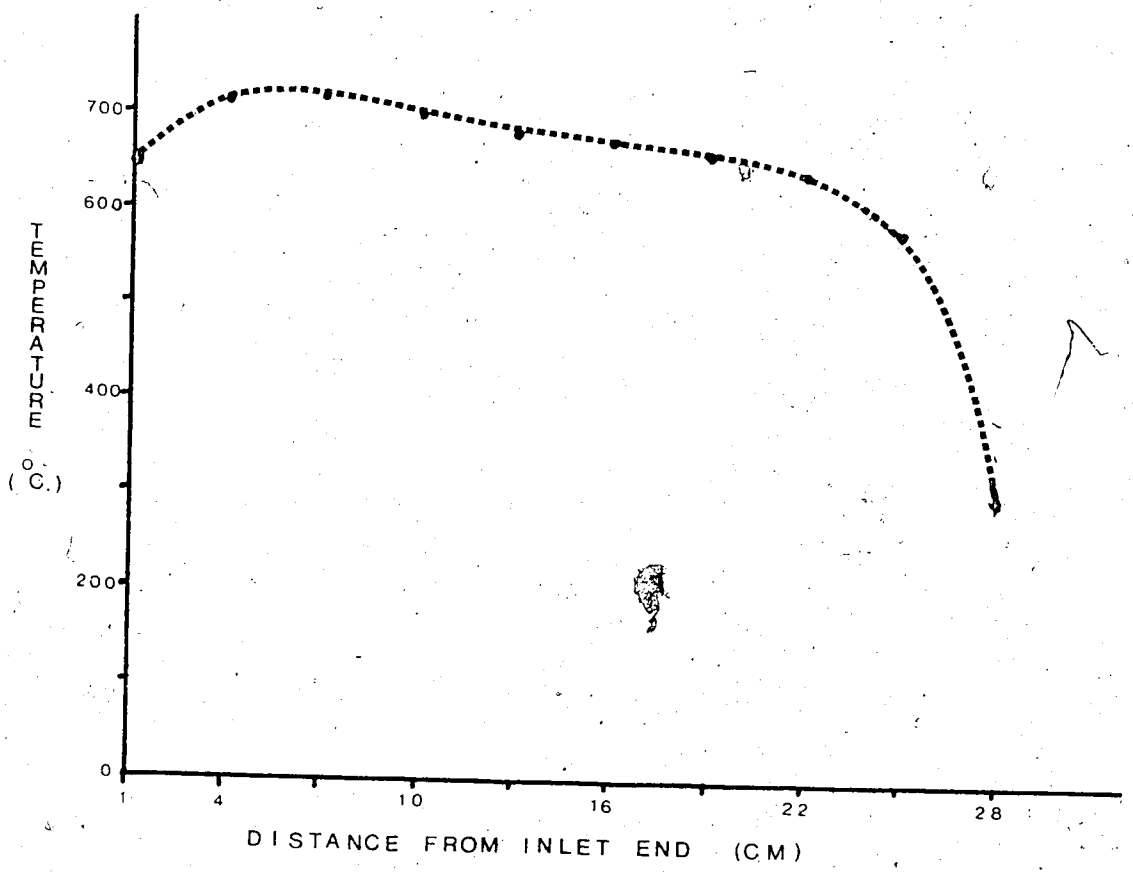


Figure 2.6. Temperature profile along packed portion of reactor tube.

of oxygen are produced by decomposition of the cupric oxide. This is shown by a rapid rise in baseline at detector A as the furnace temperature is raised.

The temperature controller for the furnace is an API 0-1000 degree centrigrade model 226 proportional controller (API Instruments Company, Chesterland, Ohio). The controller maintains the set point within 0.5°C. Its stepless control of temperature by varying the duty cycle of a thyristor prevents observable temperature cycling when properly adjusted.

After analysing 300-400 samples, the reactor is recharged by passing air through it at operating temperature.

The residence time in the reactor is approximately two seconds. The insertion of a bypass tube around the reactor gives the same retention time for an air sample as that obtained with the hot reactor tube in place. Since the flow rate is 20 ml/min and the volume of the bypass is 0.6 cc, the time for the air peak to pass through the bypass must be two seconds. This is then equal to the time necessary to pass through the reactor tube.

Column A

The main separating column is a 30 cm long, 1/8 inch outer diameter stainless steel tube packed with 80/100 mesh Porapak N (Waters Associates, Framingham, Massachusetts). This highly polar Porapak

allows excellent resolution of the water and carbon dioxide peaks with a short column length at a temperature high enough to minimize water peak tailing. The short column length is necessary to minimize the pressure at the sample valve.

Column temperature is controlled by an RFL model 70 proportional temperature controller (RFL Industries, Inc., Boonton, New Jersey) with thermistor sensor and regulation to 0.05°C. Column B and both detectors are controlled by similar controllers, all of which are mounted on a large aluminum sheet which acts as a heat sink.

To stabilize the column temperature, the column is wound around a cylindrical aluminum block approximately 7 cm in diameter and 15 cm long with holes drilled in it to hold the 25 watt cartridge heater and the thermistor sensor. To maintain good thermal contact with the core, the column is covered with a layer of copper wire braid. The entire assembly is then heavily insulated with a 10 cm layer of fiberglass wool.

Detector

The detector oven is a Gow-Mac TR2B (Gow-Mac Instrument Company, Madison, New Jersey) with the original thermal switch replaced by the proportional

controller and the original thermal conductivity cell replaced with a Gow-Mac model 460 detector block. This flow-through cell has low internal volume (0.35 cc), fast response time (0.5 sec) and high sensitivity with W2X filaments installed. Since this cell is much smaller than the cell normally mounted in this oven, copper block spacers are used on each side which also serve as gas preheaters with the 1/16 inch stainless steel inlet tubes passing through the spacers before connecting with the detector. The sample inlet tube is further heated between the spacer and column connection with copper braid. A short length of tubing between spacer and column is used, with heavy insulation to prevent adsorption of the water vapor on the tubing walls.

The bridge power supply is a Lambda model LL903 0-40 volt power supply (Lambda Electronics Corporation, Melville, New York) with ± 4 mv regulation and adjustable current limiting to prevent filament damage. A 1.0 ohm 10-turn potentiometer provides zero control of the bridge circuit. Since the filaments gradually age and shift the balance point, provision for external trimming resistors has been provided on the terminal box which contains the potentiometer.

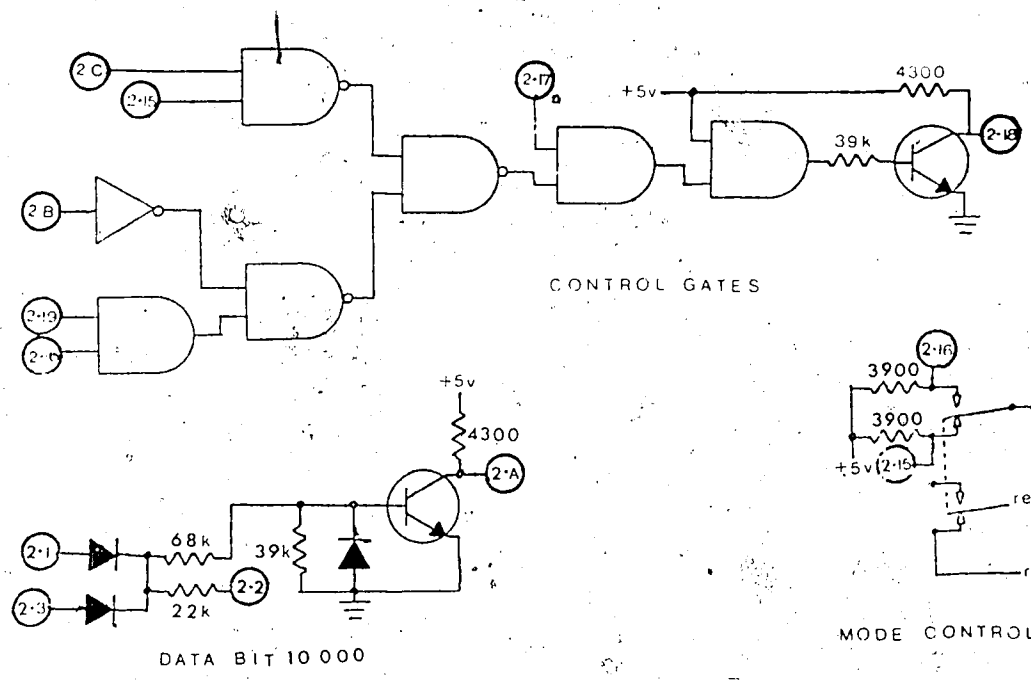
Digital Voltmeter (DVM)

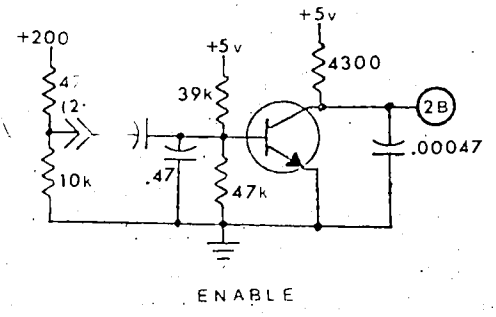
The instrument chosen for peak height sensing is a Solartron LM1440.3 Voltmeter (Solartron Electronic Group Ltd., Farnborough, Hampshire, England). This instrument operates on the successive approximation principle, with a series of precision resistors being switched in and out of parallel at the summing input to an operational amplifier until balance with the input signal is obtained. This type of voltmeter is ideal for peak maxima detection since the voltmeter can be switched to compare the largest previous reading and the present voltage and initiate a new conversion only if the present value exceeds the previous maximum.

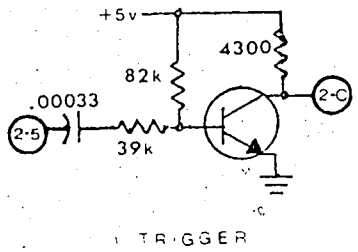
For the present study the system is used in the maximum sensing mode on its most sensitive range of 150 mv full scale with 5 μv resolution so that a full scale reading registers 29,999 counts. Since a slight bias is used in the sensing circuit to prevent false triggering, base line readings are also made in the maximum mode. The instrument has been carefully adjusted to exceed the manufacturers specifications in sensitivity so that the instrument senses a difference of no more than 2 counts (10 μv).

Junction Box and Printer

The output levels of the BCD outputs from the voltmeter are not directly compatible with the TTL inputs to the Model 5100 Printer (Monitor Labs, Inc., San Diego, California). A major portion of the circuitry in the junction box, shown in Figures 2.7a and 2.7b, provides the necessary signal conditioning. A two position switch allows the printer to be operated in an external command mode, with the sequencer providing the print and reset commands; or an automatic mode, with the print command coming from the voltmeter. The automatic mode is useful when continuous interval sampling is needed, as when checking baseline stability. The logic gates and triggering transistors on board 1 provide proper synchronization of the print command signal in both modes. In the external command mode the voltmeter external reset is connected and a print command signal is generated only if ENABLE and EXTERNAL PRINT are ON and the printer BUSY signal is OFF. In the automatic mode the reset is disconnected and the print command signal is generated when the TRIGGER is ON and BUSY is OFF. Power is provided by a zener controlled 5 V supply driven from the +10 V DVM supply line. All inputs for the printer are brought to two terminal strips for easy modification of the data inputs.



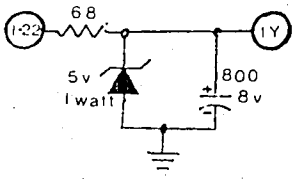




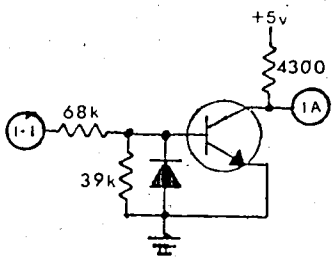
BOARD 2

1.	IN-10,000	A	OUT-10,000
2.	-30 v	B	OUT-ENABLE
3.	IN-$\overline{20,000}$	C	OUT-TRIGGER
4.	IN-ENABLE	E	OUT-4000
5.	IN-TRIGGER	E	OUT-8000
6.	IN-4000	F	OUT-20,000
7.	IN-8000	H	OUT-NEGATIVE POLARITY
8.	IN-20,000	J	
9.	IN-NEGATIVE POLARITY	K	
10.		L	
11.		M	
12.		N	
13.		P	
14.		R	
15.	IN-SWITCH AUTO	S	
16.	IN-SWITCH COMMAND	T	
17.	IN-BUSY	U	
18.	OUT-PRINT	V	
19.	PRINT-EXT	W	
20.		X	COMMON
21.		Y	+5 v
22.			

Figure 2.7a. Junction Box Circuits. Board 2 - print command control circuits and data lines. Resistors in ohms, capacitors in microforads, transistors - 2N 3904, diodes - general purpose silicon. Circled numbers refer to edge connections listed in table. MODE CONTROL SWITCH is shown in the external command position. The 470k and 10k resistors in the ENABLE circuit are mounted inside the DVM to divide down the +200 V. Nixie tube supply which is synchronized to the portion of the sampling cycle when the ring register is holding a stable reading.



POWER SUPPLY



DATA BIT 1

BOARD 1

1.	IN-1	A	OUT-1
2.	IN-2	B	OUT-2
3.	IN-4	C	OUT-4
4.	IN-8	D	OUT-8
5.	IN-10	E	OUT-10
6.	IN-20	F	OUT-20
7.	IN-40	H	OUT-40
8.	IN-80	J	OUT-80
9.	IN-100	K	OUT-100
10.	IN-200	L	OUT-200
11.	IN-400	M	OUT-400
12.	IN-800	N	OUT-800
13.	IN-1000	P	OUT-1000
14.	IN-2000	R	OUT-2000
15.		S	
16.		T	
17.		U	
18.		V	
19.		W	
20.		X	COMMON
21.		Y	+5 v.
22.	+10 v.		

Figure 2.7b. Junction Box Circuits. Board 1 - Power supply and data lines. Resistors in ohms, Capacitors in microforads, Transistors - 2N3904, diodes general purpose silicon. Circled numbers refer to edge connections listed in table. All data bits and negative polarity line, except bit 10,000, are wired as shown for bit 1.

The printer allows any data input column to appear in any of the 21 columns across the paper tape output. The printer is normally fitted with seven data input columns with later expansion possible. Column 0 is connected to the sequencer and identifies the current position of the sampling valve. Column 1 is also connected to the sequencer and identifies the four readings in each cycle with appropriate numbers. Columns 2-6 record the voltmeter reading.

Sequencer

The sequencer is assembled using a Heath EU-801A Analog-Digital Designer (ADD) (Heath Company, Mississauga, Ontario). The various components are supplied on plug-in cards with spring push-in connectors on top of each card. All interconnections are made with standard 22 gauge solid wire. A power supply is provided as well as a number of switches and status lights and a signal generator which provides the master square wave clocking pulses.

A simplified block diagram of the sequencer circuit is shown in Figure 2.8. The complete schematics are shown in Figures 2.9a and 2.9b. The counter and decoding gates control the print-out times during the cycle and the firing order gates determine

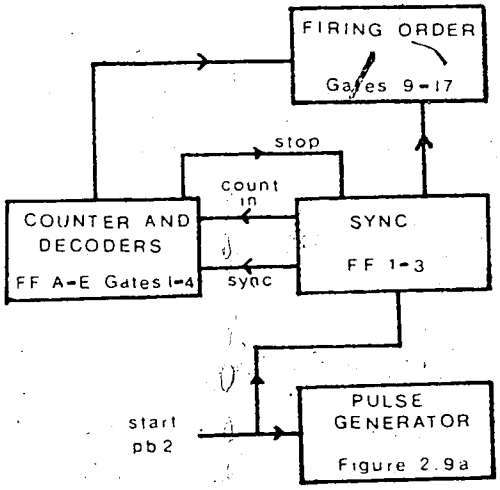


Figure 2.8. Block diagram of sequencer functions.

the order of the print and reset commands. The synchronization flip-flops provide input and control signals to the other two sections of Figure 2.9a. The pulse generator supplies firing pulses for the sample valve.

For a complete description of the operation and theory of digital logic components, see Malmstadt and Enke.(24)

Switch A allows the count to be halted at any point during the cycle. In the event of a misfire, PB1 aborts the cycle and resets all flip-flops. PB2

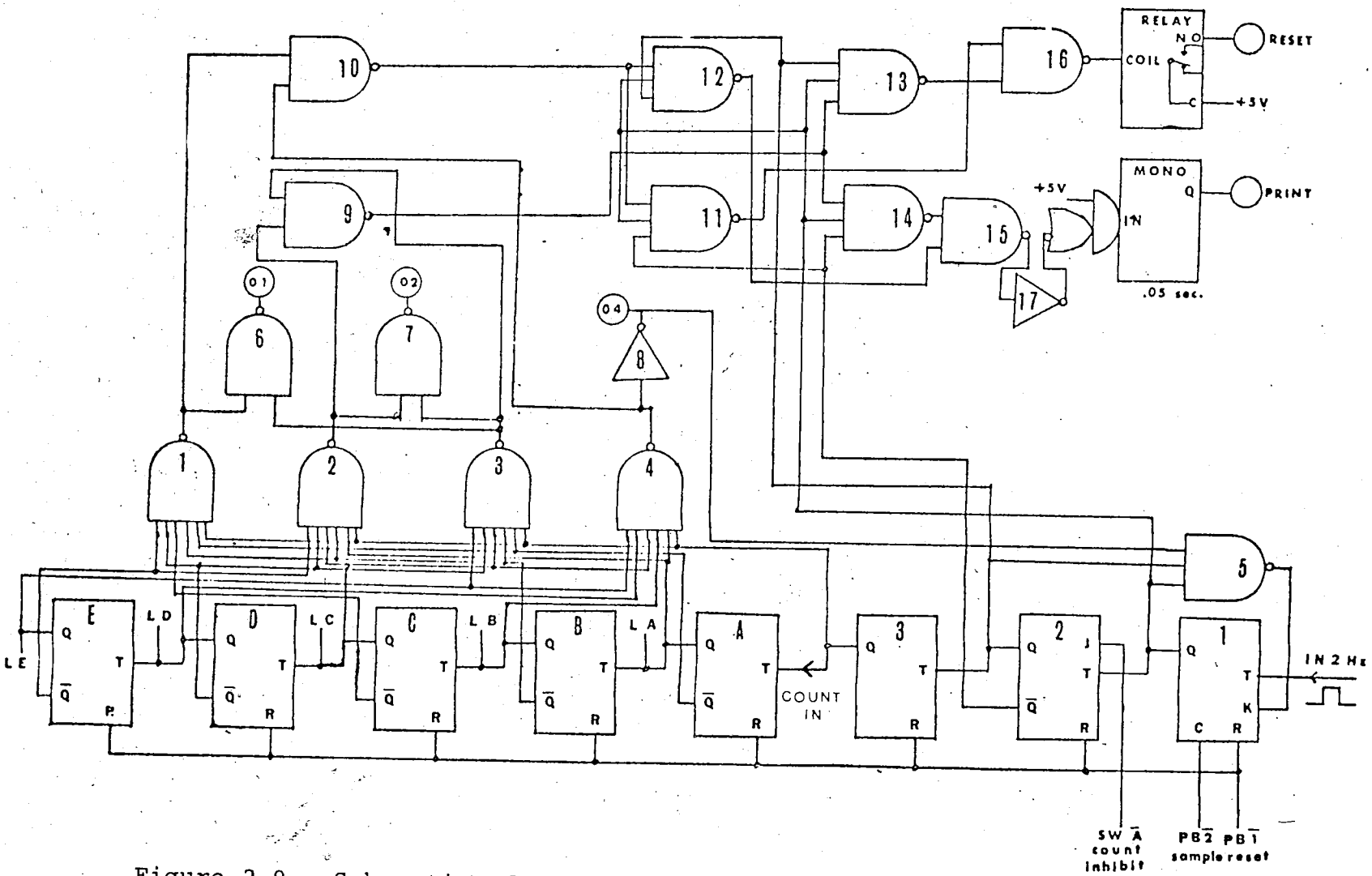


Figure 2.9a. Schematic of master sequencer. Lower row of rectangles are JK flip-flops. Monostable is a Fairchild 960159. Flip-flops A-E, asychronous binary counter; flip-flops 1-2, Synch for gates 11-14; flip flop 3, delay for event gates; gates 1-4, event gates, gates 6-8, output to printer; gates 9 and 10, select order of firing; gates 12 and 14, control print gate 15; gates 11 and 13, control reset gate 16; gate 17, inverts signal for input to monostable gates; gate 5, sequence lock-out gate.

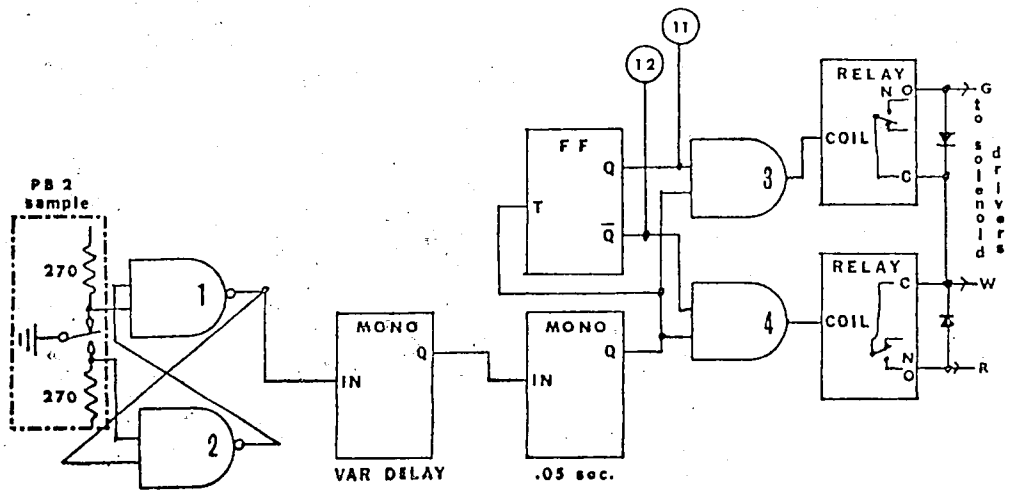


Figure 2.9b. Schematic of master sequencer. Gates 1 and 2, contact bounce eliminator; delay monostable corrects for delay between detector and valve; second monostable generates firing pulse; flip-flop indicates which solenoid is to be fired; gates 3 and 4, transmit firing pulse to proper relay.

starts the delay monostable and begins the count sequence by deactivating the lock-out gate on the first flip-flop.

Figure 2.9b shows the pulse generator for firing the sample valve. It includes a variable delay for correction of the time required for the sample to move from the detector into the sample loop. The necessary outputs for identification of the current valve position are also provided. All switches in the ADD unit are internally wired in the manner shown in the dotted portion of the figure.

The parts of the sequencer shown in Figure 2.9a provide set and print pulses at the proper times during the cycle. Flip-flops A to E and decoder gates 1-4 are the heart of the sequencer. The flip-flops are connected as a simple asynchronous binary divide by 32 counter with a cycle time of two minutes. Thus the sample cycle is broken into 4 second bits. By changing the appropriate connections to the NAND gates, the 11-14 printout times can be selected at will. Flip-flops 1 and 2 provide synchronization signals for gates at top right. Since each flip-flop in the chain cannot change state until after the preceeding flip-flop has completed its transition, the decoding gates could sense false input conditions as the count transition

cascades down the chain. Flip-flop 3 prevents false triggering of decoding gates 1-4 by delaying activation until well after all ripple transitions are completed.

The functions and times of operation of the decoder gates are shown in Table 2.1. Note that after the printout cycle triggered by gate 4 is completed, gate 5 stops the cycle with all flip-flops in logic 1 state until the operator starts the cycle again by pushing PB2.

The remaining parts of the circuit provide identification of peaks for the printer (gates 6-8) and generate the firing pulses for the reset and print commands in the proper sequence (gates 9-17). Printouts one and four require a reset pulse followed by the print command and two and three require the opposite firing order.

Figure 2.10 illustrates the transitions of the various gates and synchronizing flip-flops during the first printout cycle, controlled by gate 1. The three other printouts will occur in the same general manner. If gate 9 opens (logic 0), the reset pulse is to precede the print pulse. If gate 10 opens, the print pulse will occur first. The $\overline{Q}$ condition from flip-flop 2 generates the first pulse, and the second pulse occurs after flip-flop 2 is in the Q state. Note

Table 2.1

Firing Order of Decoding Gates

Gate	Function	Count	Input Logic
1	First baseline measurement	0	$\overline{E}\ \overline{D}\ \overline{C}\ \overline{B}\ \overline{A}$
2	CO_2 peak maximum	5	$\overline{E}\ \overline{D}\ C\ \overline{B}\ A$
3	H_2O peak maximum	20	$E\ \overline{D}\ C\ \overline{B}\ \overline{A}$
4	Second baseline measurement and stop	31	$E\ D\ C\ B\ A$

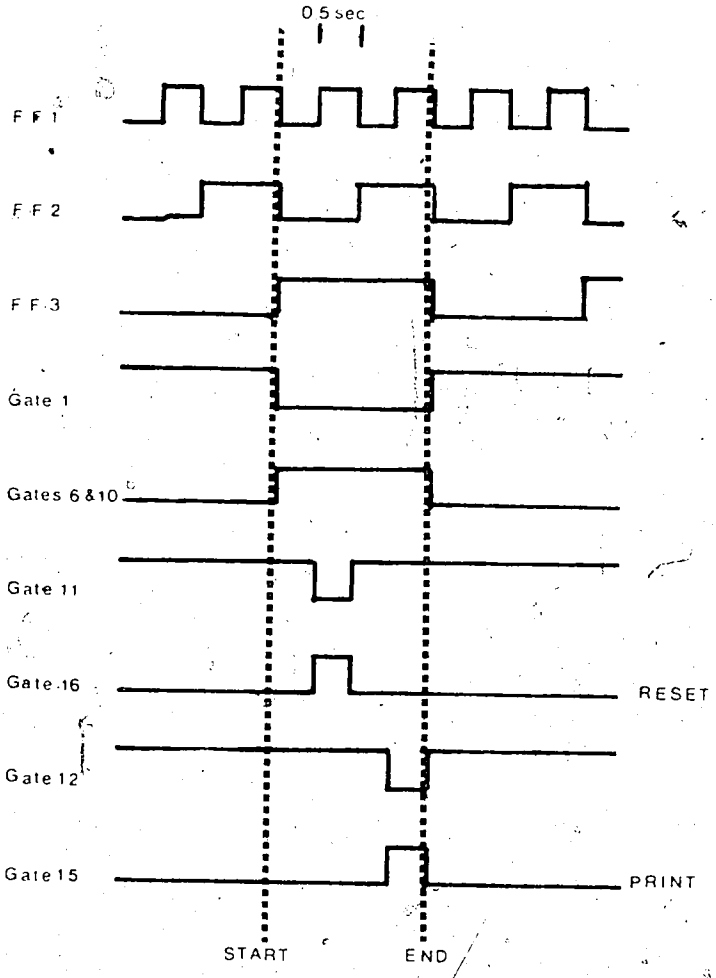


Figure 2.10. Sequence of gate switching during a printout cycle (Printout one shown).

that the output pulses can never occur until flip-flop 1 changes to a logic 1 state. This delay prevents false triggering of the gates as flip-flop 2 changes state and prevents interference between printer and DVM since printer, DVM and sequencer all operate with a common ground.

Solenoid Drivers

The solenoid drivers, shown in Figure 2.11, perform two functions. First, they must amplify the small current capability of the sequencer relays to the level required to fire the line voltage solenoids. Second, they must isolate the sequencer from the high noise levels associated with switching the high inductance solenoids.

The current amplification is accomplished by a transistor driving the coil of a relay (KM110, Potter and Brumfield). The contacts of this relay are capable of carrying the line voltage required by the solenoids. The various diodes and capacitors suppress switching noise. Since the sequencer power supply can not be sufficiently decoupled if it supplies the operating current for the power relays, the separate battery power supply is used instead. The battery supplies significant current only briefly at the moment of firing. The small residual current drain of the filter capacitor and tran-

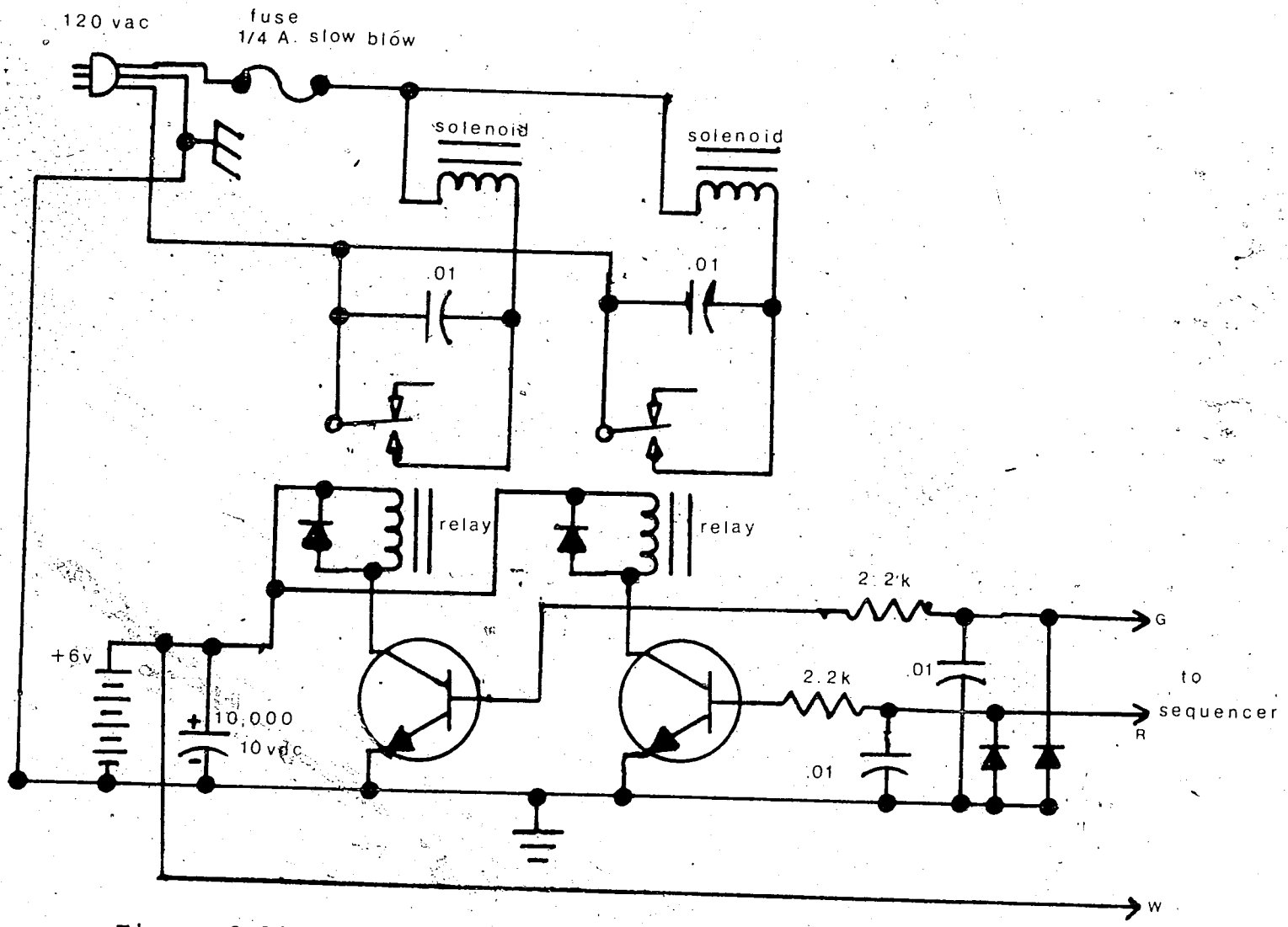


Figure 2.11. Schematic of solenoid drivers.
Resistors in ohms. Capacitors in microfarads
Transistors - 2N3904 Diodes - general purpose germanium
Battery - Eveready #643 Relays - Potter and Brumfield KM110.

sistors gives the battery a life span of more than one year if it is connected at all times. The continuous voltage on th large capacitor keeps it in peak condition so t e leakage current is small.

2-3 SAMPLE SYSTEM CONSTRUCTION

The equipment is designed to obtain its samples from the outlet of a gas chromatograph. The components associated with column B constitute a simple gas chromatograph to provide these samples and also to serve as a check on the purity of the compounds used in testing.

A single gas stream is used in this system. This usually leads to difficulty in zeroing the detector bridge and nonlinear response due to the pressure differential between the two sides of the detector. However, in this system the differential is not great, since the major pressure drop occurs across the capillary and not across the column as with an ordinary system.

Sample Injector

After flowing through the reference side of the detector, the carrier gas enters the injection port. The injector used is a modified Swagelok 1/4 inch tee connector shown in Figure 2.12. This arrangement recovers rapidly from accidental overloading and effec-

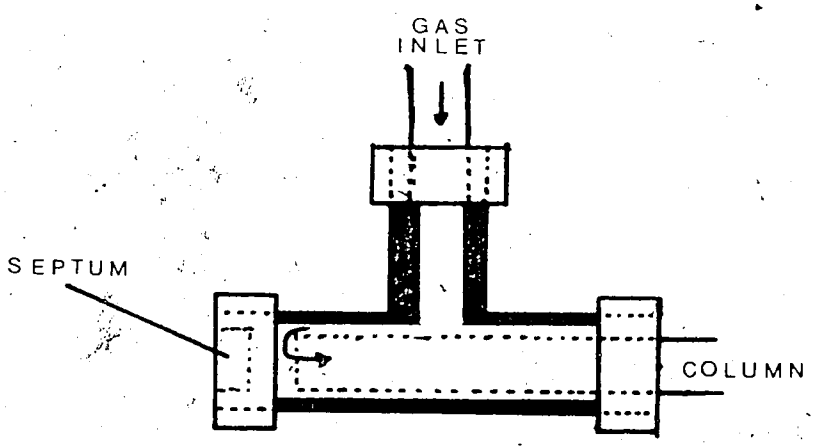


Figure 2.12. Sample injection port. Modified Swagelok Tee Joint.

tively prevents serious diffusion before the sample enters the column. A length of heating tape powered by an autotransformer is wrapped around the outside of the injector to maintain a high temperature for rapid volatilization of the samples.

Column B

The column is a two meter stainless steel 3/16 inch diameter tube filled with 80/100 mesh Durapak (Carbowax 400 on Porasil C, Waters Associates). By chemically bonding the Carbowax to the silica support, the upper temperature limit of the column is significantly extended. Carbowax was chosen because of the

wide range of substances separable on it. It is especially well-suited for separations of the hydrocarbons which provide most of the samples for this study.

The column is wound on an aluminum core similar to that of column A and insulated in like manner.

Detector B

The detector is a standard Gow-Mac 9285 semi-diffusion cell with W2 filaments. The normal 3/16 inch copper tubing connections are replaced by 1/8 inch stainless steel tubing wrapped with copper braid for efficient heating. A Lambda LL903 power supply supplies current to these filaments.

Recorder

Sargent model SR recorder (E. H. Sargent and Company, Chicago, Illinois) is used for readout from the detector. A simple resistive divider chain added to its input allows stepwise control of sensitivity between 1 and 100 mv full scale.

2-4 SUMMARY

To provide a clearer picture of the operation of the equipment, a timed sequence of events for one full sample cycle follows:

0.0 sec- Start. When the recorder chart shows a peak

to be sampled, the sample pushbutton PB2 is pushed when the peak has reached a suitable height. The delay monostable and binary divider chain begin operation.

~1 sec- Sampling. The sample which was in the detector when the sequence started has now reached the sample loop. The delay monostable now fires the second monostable which in turn causes the proper solenoid to fire. This reverses the pressure on the piston, causing the sample valve to rotate to its other position. The contents of the loop are thus transferred to the reactor side of the valve.

2.5 sec-First Reading. Nand gate one activates for the first baseline reading. The voltmeter is first reset and the result is printed out one second later. The sample is now entering the reactor and is being oxidized to carbon dioxide and water.

10 sec-Carbon dioxide peak maximum. The carbon dioxide passes rapidly through the column into the detector. The voltmeter senses the first increase in voltage from the detector and keeps sampling the height of the peak every sixtieth of a second until it senses no further increase in magnitude. The maximum reading is held by the voltmeter until reset.

22 sec-Second reading. The maximum reading is printed out and the voltmeter reset. The carbon dioxide peak

has returned to near the baseline and the water peak is just beginning to elute from the column.

30 sec- Water peak maximum. The maximum of the water peak is reached and the voltmeter again holds this reading.

80 sec- Third reading. The sequencer prints out the reading of the water peak maximum and resets the voltmeter. The voltmeter should now show a value near the baseline.

120 sec- Fourth reading. The tailing from the water peak has now stopped and the system is again at equilibrium. The voltmeter is reset for the second baseline reading and this value is printed out. The sequencer then locks out the first flip-flop and all systems are now ready for a new sample.

III

RESULTS AND DISCUSSION

3-1 EFFECT OF VARIOUS SOURCES OF ERROR ON PRECISION.

The contributions of the major sources of error for peak heights are shown in Table 3.1. The proportionality coefficients are from Goedert and Guiochon.[22]

The measurement error is determined primarily by the error in reading the water peak. Assuming a H_2O peak height of 3000 counts and a reading error of two counts, two readings, baseline and maximum, are necessary, so the total error is four counts. The errors for bridge current and column temperature are taken from the manufacturers specifications of the power supply and the proportional controller. A 4 mb variation in outlet pressure is assumed[22] at an atmospheric pressure of 700 mb. The error in the column inlet pressure can only be estimated but should not exceed 1 mb with the flow controls used.

The error resulting from these factors, $\varepsilon = \sqrt{\Sigma \varepsilon_i^2}$, is equal to 5.7×10^{-3} or 0.57% relative error. The relative standard deviation for the 31 hydrocarbons analysed is 0.23% or 0.45% at the 95% confidence limit used in the proportionality coefficients. The higher precision found experimentally

Table 3.1

Contributions of the Major Sources of Error for Peak Heights.

Source	Variation (ppt)	Proportionality Coefficient	Contribution (ppt)
Column inlet pressure	1.0	-2.1	2.1
Column outlet pressure	5.7	0.9	5.1
Column temperature	0.1	3.3	0.4
Bridge current	0.1	3.0	0.4
Measurement	1.3	1.0	1.3

indicates that the assumptions made for the variations, especially the column outlet pressure, are conservative since the ratios are subject to additional errors, such as the blank corrections and sample size, which are difficult to estimate.

The effect of atmospheric pressure variations on precision can be seen clearly in Figure 3.1. The results with open windows show a significantly higher random scatter. If a least squares linear plot is made for the two sets of data, the relative standard deviations are: 0.89% with the windows open, 0.43% with the windows closed. A relative standard deviation of 0.16% is obtained for the fit of the smooth curve shown for closed windows. The curvature in the graph is probably caused by the temperature rise after the windows closed. Even when the equipment is operated in a closed room at a stable temperature, passing storm fronts or periods of high gusting winds cause a serious increase in the scatter of the results.

3-2 METHOD OF ANALYSIS

To start up the equipment for operation, helium flow is first established. All other components, except the gauge power supplies are then activated. The filaments are not turned on until a few minutes

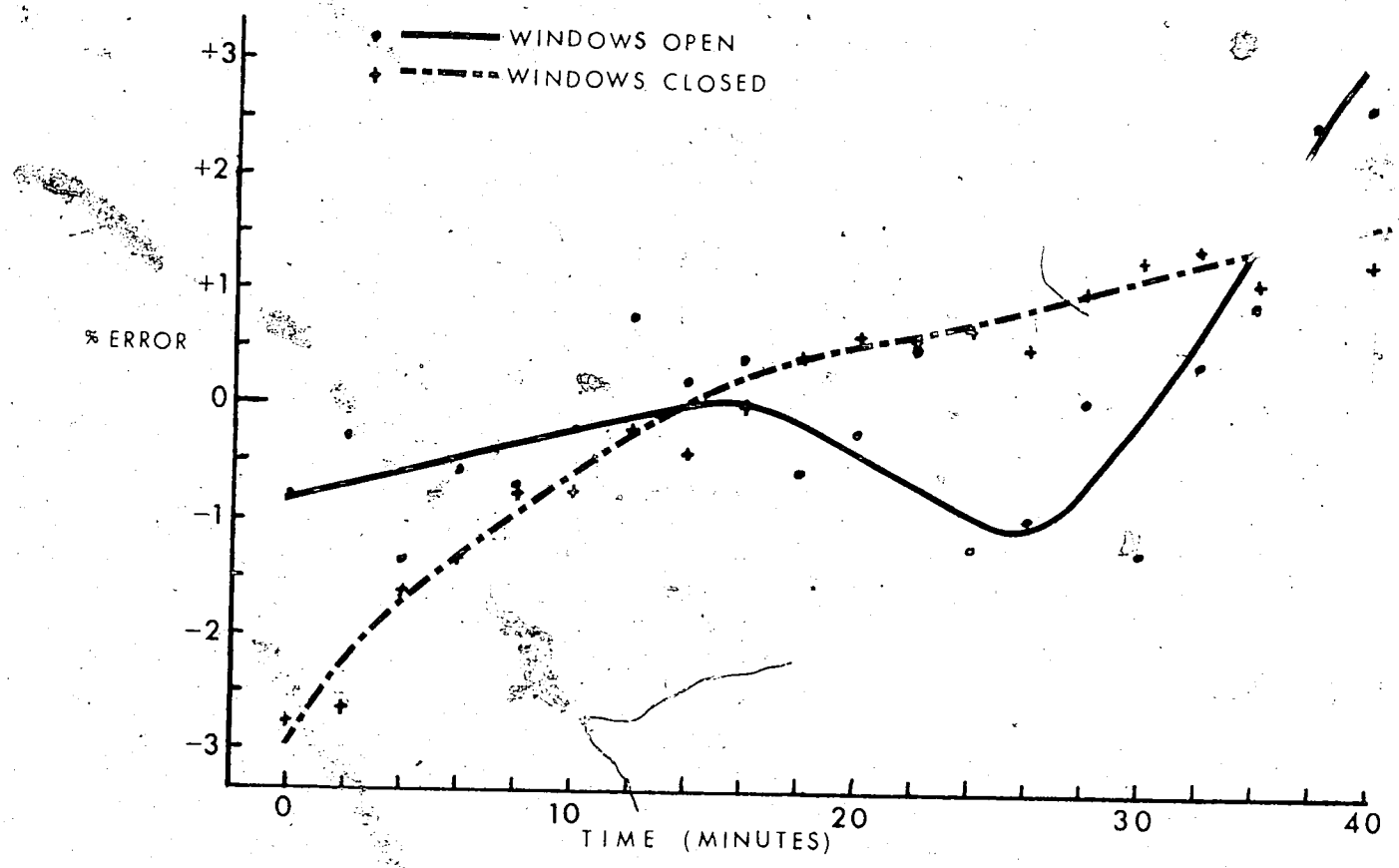


Figure 3.1. Comparison of stability with laboratory windows open and closed. 20 samples of 2,2-dimethylbutane analysed with windows open. The windows were then closed and 20 samples were run again after a 20 minute stabilization period. All conditions constant except for the windows. Measurements made on a mild summer day with stable weather and low wind velocity.

have elapsed to allow the carrier gas to flush out most of the air. The system is allowed to equilibrate for two hours before beginning analysis. During this time the sequencer time delay can be set by injecting a sample with reasonably symmetrical peaks from column B and sampling at a constant point on the recorder chart for the leading and trailing edges of the peak. The time delay is adjusted until the CO_2 peaks are constant for both edges. Just before beginning analysis, the standard compound is sampled three times to check system functions and stabilize response. These test samples are not valid for inclusion as standard runs since the peak ratios are unstable for the first one or two samples after system start up. When the equipment is operating, but not sampling, only normal long-term drift is found.

Standardization

Ideally, the equipment could be calibrated once and then used for a day or more with no further checks or corrections necessary to maintain the required accuracy. Due to the exacting operating conditions of the analysis, frequent standardizations are required to correct for the various factors that cause long-term drift in the results.

Because the two valve positions show slightly different H/C ratios, the standards are run in pairs, one standard for each position. To correct for drift a pair of standards is run every 30-40 minutes during normal analysis. Thus, each unknown sample can be compared with two standards, one from the preceding pair of standards and the other from the succeeding pair. The average of the two results is reported. Since the reference standard ratios normally drift to the same extent as the unknown samples, the effect of the drift is removed.

The standard chosen must have no known determinate error in its analysis and should be of high purity. Because the necessary correction for adsorption effects may change for compounds of widely varying structure, the standard should be similar in structure to most of the unknown samples to be analysed. The sample and standards should also have similar peak heights to minimize errors arising from drift in the linearity factors.

Since most of the samples analysed are hydrocarbons, 2,2-dimethylbutane is the standard compound chosen. It has a known purity of 99.94% and has a H/C ratio similar to that of most hydrocarbons, particularly the saturated hydrocarbons, which are the most difficult

to analyse because of the small H/C ratio differences between adjacent members of the series.

Calculation of Results

Baseline and blank corrections:

The first two corrections applied to the peak heights of the carbon dioxide and water peaks are those to subtract the baseline and blank. The two baseline measurements made during each run are averaged and this average value for the baseline is subtracted from both peaks. The difference in the two baseline readings is not more than eight counts if the system is operating properly.

The blank correction is made by firing the sample valve when no sample peak is being eluted from column B. The primary contribution to the blank is bleeding of the liquid phase from column B. The blank normally remains constant for a full day's runs unless the column temperature or flow rate are changed or the column becomes contaminated with a severely tailing sample. Since the blank is dependent on column temperature, the determination of the blank would be difficult if temperature programming is used. To make temperature programming of column B practical, the liquid phase used in such cases must have a known zero blank value over the temperature range used. In isothermal work

the only requirement is that the blank value be constant and a few percent of the smallest sample peaks to maintain high precision. Most of the runs made for this thesis have a blank correction of approximately 60 counts for the CO_2 peak and 20 counts for the H_2O peak. The blank values are subtracted from their respective peaks.

Linearity of response:

The relation between relative error and sample size is shown in Figure 3.2. The graph cannot show whether the nonlinearity is due to the CO_2 or the H_2O peak, but only the overall effect of both contributions, if any.

To determine which peak is causing the nonlinearity, a comparison is made between two hydrocarbons with widely differing ratios of hydrogen to carbon. The two compounds chosen are benzene and 3-methylhexane. Both are available in high purity and show no secondary peaks from combustion even at temperatures well below the normal operating point of the reactor.

Measuring samples of each compound with identical CO_2 peaks, the H_2O/CO_2 ratio for benzene is compared with the ratio for 3-methylhexane:

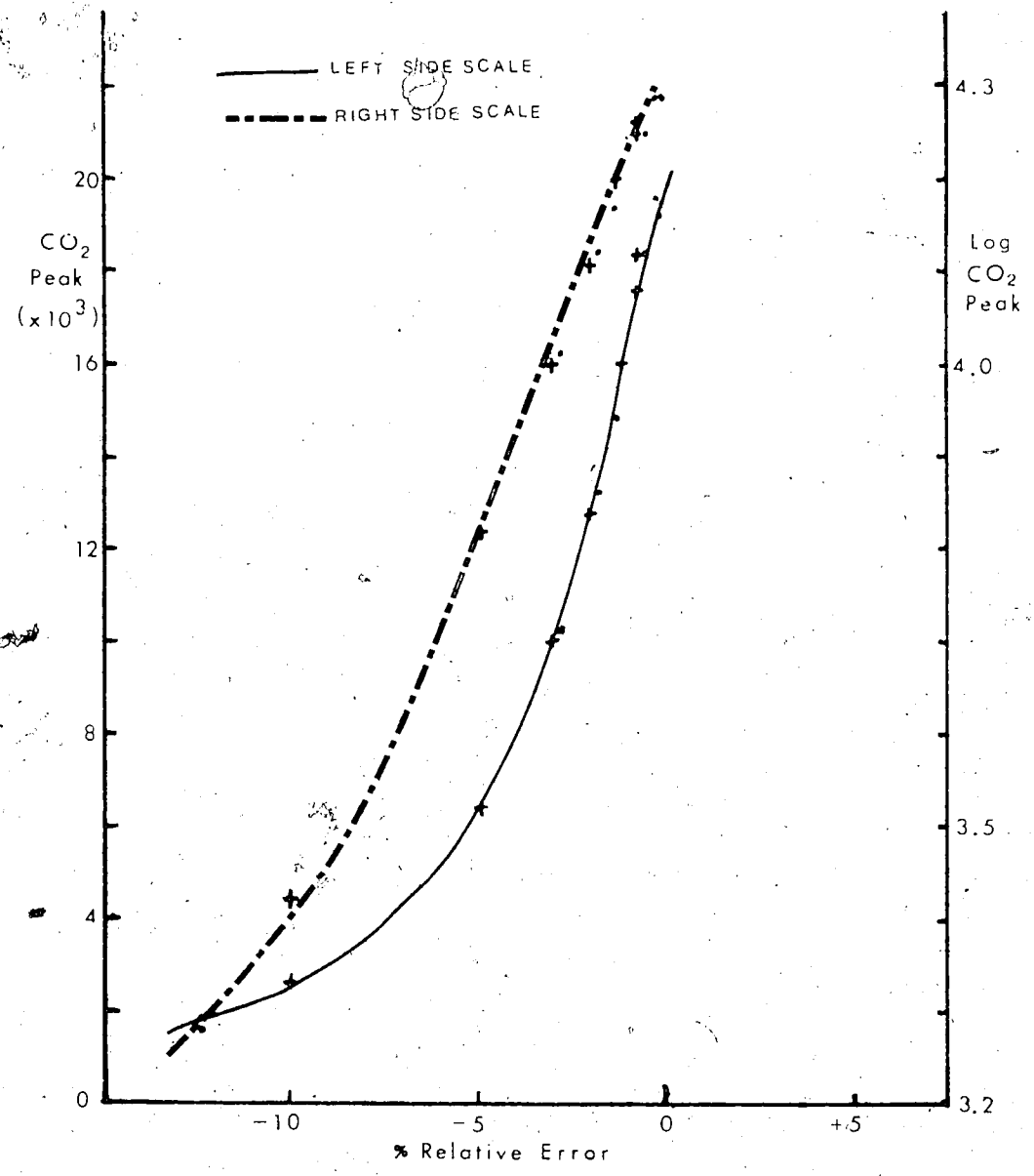


Figure 3.2. Plot of % relative error in H/C ratio of 2,2-dimethylbutane versus sample size (measured as CO_2 peak height). Dots represent position 2, pluses represent valve position 1.

$$ratio_b = \frac{ratio_m}{r_{mt}/r_{bt}}$$

If the H_2O peak response is linear, the calculated and observed values for $ratio_b$, H_2O/CO_2 ratio for benzene, should agree. $Ratio_m$ is the H_2O/CO_2 ratio measured for 3-methylhexane, r_{bt} is the theoretical H/C ratio for benzene and r_{mt} is the theoretical H/C ratio for 3-methylhexane. The following values were measured for valve position 1:

benzene peaks: 2592-H_2O; 19116-CO_2,

3-methylhexane peaks: 6180-H_2O; 19552-CO_2,

$ratio_b$ (calculated) = 0.1383,

$ratio_b$ (observed) = 0.1356,

difference in ratios = 1.99%.

Repeating the calculations for position 2:

$Ratio_b$ (calculated) = 0.1397,

$ratio_b$ (observed) = 0.1374,

difference in ratios = 1.71%

Choosing samples with equal H_2O peaks, the linearity for the CO_2 peak is also checked:

Position 1:

$ratio_b$ (calculated) = 0.1342,

$ratio_b$ (observed) = 0.1359,

difference in ratios = 1.24%

Position 2:

$ratio_b$ (calculated) = 0.1357,

$ratio_b$ (observed) 0.1374,

difference in ratios = 1.21%

From the above calculations, both peaks show nonlinearity and require separate corrections for both size and valve position. Assuming that both peaks are linear when plotted as log peak height versus error, the apparent ratio of H_2O/CO_2, R, can be corrected as follows:

$$R(\text{corrected}) = \frac{R(\text{observed})}{f_C \cdot f_H}$$

f values are determined by the following equation:

$$f = 1\text{-}C \cdot \log(\text{standard peak/unknown peak})$$

The values for C for each position and the two different peaks are:

$$C = \left(\frac{\text{Ratio}_b \text{ (observed)}}{\text{Ratio}_b \text{ (calculated)}} - 1 \right) / \log \text{ (benzene/3-methylhexane)}$$

The log term is CO_2 peak heights for H_2O corrections and H_2O peak heights for CO_2 corrections. If the correction is made for the H_2O peak first, the CO_2 peaks should be within 1-2% of each other to eliminate non-

linearity corrections for the CO_2 heights. Wider limits are then allowed in calculating the correction for the CO_2 peak since the H_2O peaks can be equalized exactly using the H_2O peak correction factor. After correcting the runs used in plotting Figure 3.2, the residual error is shown in Figure 3.3. Using 20,000 counts for the CO_2 peak and 7,000 counts for H_2O as nominal references, the resulting ratios are within 0.25% for the range from the reference points to half their values and the error reaches 1% at about 25% of the reference points. The data used to compute the linearity factors was measured more than two months after the runs in Figures 3.2 and 3.3 were determined. The system had been idle during most of this period. The small residual error shows that the linearity factors remain constant for long periods if the experimental conditions are not changed. The factors have to be redetermined only if major changes are made in the system, such as changing the reactor tube or changing the temperature of reactor, column, detector or the connections, or if the cumulative error becomes significant.

Peak height measurements are sensitive to column overloading and changes in the shape of the sample peak as it enters the analytical column.

The base width of both peaks does change with

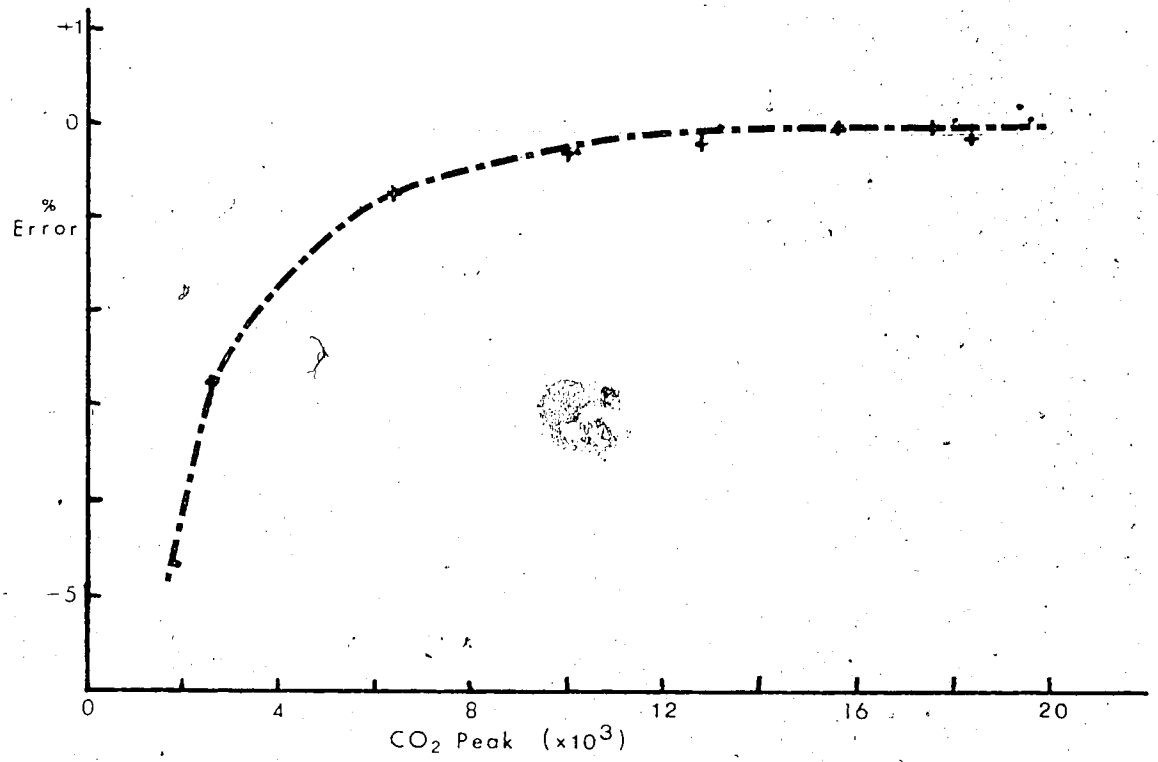


Figure 3.3. Graph of residual error after applying linearity corrections to data from Figure 3.2. Dots are position 2 and pluses are valve position 1.

sample size, which shows that column loading is affecting the results somewhat. Also, the ability of the water to adsorb on almost every surface, particularly with small sample sizes, means that some nonlinearity will always be present.

Correction for adsorption of the sample before combustion:

After the H_2O/CO_2 ratio has been corrected for linearity, the H/C ratio can be determined with the equation

$$\text{H/C ratio} = \frac{H_2O/CO_2 \text{ ratio(unknown)} \cdot \text{H/C ratio(theoretical of standard)}}{H_2O/CO_2 \text{ ratio(standard)}}$$

The experimental errors for several hydrocarbons are shown in Table 3.2. A systematic error still remains in the results. Within the group of the straight chain hydrocarbons the change in ratio can be clearly seen. The problem is to determine a reliable method of correcting for the error. When analysing unknown peaks, the only information available in addition to the H/C ratio is the retention time on column B, which is easily converted to k, the partition ratio. From the data shown in the table, log k is more nearly linear, with regard to % error, than k. The use of log k in the correction is advantageous because

different column temperature alter the slope, but the plot remains linear.

Using the method of least squares, log k versus % error in the observed ratio gives a slope of 1.320. The residual errors remaining after correcting for this phenomenon are shown in the last column of Table 3.2.

The correction is made according to the following equations:

$$\text{Ratio (corrected)} = \frac{\text{H/C ratio}}{f_a},$$

$$f_a = 1.0 - (C_a \cdot (\log k(\text{standard}) - \log k(\text{unknown})),$$

$$C_a = S/100 \text{ where } S = \frac{\Delta \text{\% error}}{\Delta \log k} \text{ from the plot.}$$

The errors remaining after corrections are within the limits of normal experimental precision for hydrocarbons.

A lower limit is necessary when using log k for corrections. The log goes rapidly negative for compounds with short retention times and reaches $-\infty$ for peaks with the retention time of the air peak. A small error in measuring the retention time results in a large error in log k. Because the % error does not change further for compounds eluted before n-pentane,

Table 3.2

Table of compounds, corrected for nonlinearity, showing effect of sample adsorption on the experimental ratios. k is the partition ratio on a 3/16" diameter, 2 m Durapak (Carbowax 400 on Porasil C) column at 120°C and a flow-rate of 60 cc/min.

Compound	% Error in H/C Ratio	k	Log k	Error after Correction for Sample Adsorption
n-pentane	-0.52	0.8	-0.10	-0.20
n-hexane	0.02	1.5	0.18	-0.04
n-heptane	0.57	2.9	0.46	0.15
n-octane	0.78	5.4	0.73	0.16
n-nonane	0.94	9.7	0.99	-0.18
n-decane	1.25	17.5	1.24	-0.20
2,3,4-trimethylpentane	0.82	4.2	0.62	0.18
2,2,4-trimethylpentane	0.45	3.5	0.54	-0.08
2,2,5-trimethylhexane	0.89	6.1	0.78	0.04
3-methylhexane	0.51	2.6	0.42	0.14
2-methylpentane	-0.24	1.4	0.14	-0.24
2,3-dimethylbutane	0.04	1.4	0.14	0.04
cyclohexane	0.43	1.6	0.20	0.35
cyclooctane	1.15	6.6	0.82	0.25
benzene	0.12	2.3	0.36	-0.17
toluene	0.85	2.7	0.43	0.46

the retention time for n-pentane is the lower limit chosen.

Because peak height measurements are sensitive to changes in the injection function, many possible reasons for the systematic error could be suggested. The cause of the error must be in either the reactor or the tubing connecting the sample valve to the reactor since the sample is in contact with only these components. The most probable reason is an adsorption effect from the walls of the tubing. The interior walls of the tubing become coated with a layer of pyrolytic carbon from decomposition of the compounds passing over them. The result can be that the connecting tubing with its layer of deposited carbon, acts as a small capillary column which broadens the sample peaks as their boiling points increase.

To be useful the correction should also hold with non-hydrocarbon compounds. As the results from the next section show, the H/C ratio for non-hydrocarbons varies in approximately the same fashion. Problems of sample purity with the hetero atom compounds obscure the results somewhat, but the evidence seems clear that most hetero compounds show the same relation and the value of C_a may be nearly identical to that of the hydrocarbons. C_a may change with columns other than the Carbowax column used, but the

relation should hold for other nonspecific, nonpolar liquid phases which separate primarily in order of the boiling points. Columns which separate by polarity or other specific effects will probably give a reliable plot only for a restricted type of sample.

3-3 ANALYSIS RESULTS FOR 62 COMPOUNDS

To sample a compound the sample pushbutton PB2 must be pushed when the recorder pen deflection is sufficient to yield carbon dioxide and water peaks within the limits of good linearity correction. For the conditions used in this study, most compounds are sampled at approximately 10 mv recorder deflection. If the first sample does not give peaks of convenient size, subsequent samples were taken at a point which will give a resonable sample size. Triplicate samples are determined with no results rejected except those from obvious equipment or operator errors. The formulas shown in the tables which follow are computed by multiplying the H/C ratio found by the integers from 1 to 12. The product which is nearest to a whole number is then reported in the table. The program rejects any result with more than 2n + 2 hydrogen atoms, where n is the number of carbon atoms. The result of this calculation is that the most probable formula will be

the lowest even multiple of the correct formula. Benzene C_6H_6 will show C_1H_1 and all singly unsaturated noncyclic alkenes will have a formula of CH_2.

Table 3.3 shows the results of a variety of saturated hydrocarbons and Table 3.4 shows results for various other types of hydrocarbons. Table 3.5 lists a representative sampling of compounds containing oxygen as a hetero atom and Table 3.6 lists the results of analysis for compounds containing nitrogen, sulfur or halogens. The reference standard for all runs is 2,2-dimethylbutane. The complete data are listed in the tables in the appendix to this thesis.

Since a few of the compounds shown in the tables show determinate errors, the average error or standard deviation are not reliable indicators of the error between predicted and experimental ratios. The median error is used instead. Table 3.3 has a median error of 0.18%; Table 3.4, 0.22%; and Table 3.5, 0.88%.

Summary

The difference in the median error for the two sets of hydrocarbons is probably not significant. The method works well for all hydrocarbon samples, with none of the samples showing an error sufficient to result in an incorrect formula. Most of the small

Table 3.3

Results for Various Saturated Hydrocarbons

Compound	Formula	Ratio Found	Percent Error	Most Probable Formula
Methane	CH_4	3.7647	-5.88	CH_4
Ethane	C_2H_6	2.9879	-0.40	CH_3
Propane	C_3H_8	2.6659	-0.03	C_3H_8
n-Butane	C_4H_{10}	2.5083	0.33	C_2H_5
n-Pentane	C_5H_{12}	2.395[illegible]		C_5H_{12}
n-Hexane	C_6H_{14}	2.3325	[illegible]	C_3H_7
2,3-Dimethylbutane	C_6H_{14}	2.3342	[illegible]	C_3H_7
2-Methylpentane	C_6H_{14}	2.3276	-0.24	C_3H_7
3-Methylpentane	C_6H_{14}	2.3344	0.05	C_3H_7
n-Heptane	C_7H_{16}	2.2892	0.15	C_7H_{16}
3-Methylhexane	C_7H_{16}	2.2889	0.14	C_7H_{16}
n-Octane	C_8H_{18}	2.2536	0.16	C_4H_9
2,2,4-Trimethylpentane	C_8H_{18}	2.2482	-0.08	C_4H_9
2,3,4-Trimethylpentane	C_8H_{18}	2.2541	0.18	C_4H_9
n-Nonane	C_9H_{20}	2.2183	-0.18	C_9H_{20}
2,2,5-Trimethylbenzene	C_9H_{20}	2.2231	0.04	C_9H_{20}
n-Decane	$C_{10}H_{22}$	2.1956	-0.20	C_5H_{11}
Cyclohexane	C_6H_{12}	2.0070	0.35	CH_2
Methylcyclohexane	C_7H_{14}	2.0026	0.13	CH_2
Cyclooctane	C_8H_{16}	2.0050	0.25	CH_2

Table 3.4

Results for Various Unsaturated and Aromatic Hydrocarbons

Compound	Formula	Ratio Found	Percent Error	Most Probable Formula
2-Methylbutene-1	C_5H_{10}	2.0033	0.17	CH_2
Pentene-2	C_5H_{10}	2.0090	0.45	CH_2
2-Methylpentene-1	C_6H_{12}	2.0043	0.22	CH_2
cis-4-Methylpentene-2	C_6H_{12}	2.0045	0.23	CH_2
Cyclohexene	C_6H_{10}	1.6711	0.26	C_3H_5
Benzene	C_6H_6	0.9983	-0.17	CH
Toluene	C_7H_8	1.1482	0.46	C_7H_8
Ethylbenzene	C_8H_{10}	1.2515	0.12	C_4H_5
n-Propylbenzene	C_9H_{12}	1.3362	0.22	C_3H_4
Isopropylbenzene	C_9H_{12}	1.3332	-0.01	C_3H_4
t-Butylbenzene	$C_{10}H_{14}$	1.3989	-0.08	C_5H_7

Table 3.5

Results for Various Oxygen-containing Compounds

Compound	Formula	Ratio Found	Percent Error	Most Probable Formula
Isopropyl Acetate	$C_5H_{10}O_2$	2.0168	0.84	CH_2
n-Propyl Butyrate	$C_7H_{14}O_2$	2.0229	1.15	CH_2
Butyl Formate	$C_5H_{10}O_2$	2.0247	1.24	CH_2
Allyl Propionate	$C_6H_{10}O_2$	1.6806	0.84	C_3H_5
Methanol	CH_4O	4.0348	0.87	CH_4
Ethanol	C_2H_6O	3.0591	1.97	CH_3
2-Propanol	C_3H_8O	2.7066	1.50	C_3H_8
Allyl Alcohol	C_3H_6O	2.0342	1.71	CH_2
t-Butyl Alcohol	$C_4H_{10}O$	2.4970	-0.12	C_2H_5
t-Amyl Alcohol	$C_5H_{12}O$	2.3949	-0.21	C_5H_{12}
Allyl Ether	$C_6H_{10}O$	1.6803	0.82	C_3H_5
n-Butyl Ether	$C_8H_{18}O$	2.2491	-0.04	C_4H_9
Allyl Phenyl Ether	$C_9H_{10}O$	1.1406	2.66	C_7H_8
bis(2-Methoxyethyl)Ether	$C_6H_{14}O_3$	2.3145	-0.81	C_3H_7
Dioxane	$C_4H_8O_2$	2.0093	0.46	CH_2
Propionaldehyde	C_3H_6O	2.0599	3.50	CH_2
Valeraldehyde	$C_5H_{10}O$	2.0307	1.54	CH_2
Acetone	C_3H_6O	2.0256	1.28	CH_2
3-Pentanone	$C_5H_{10}O$	2.0179	0.90	CH_2
4-Heptanone	$C_7H_{14}O$	2.0124	0.62	CH_2

Table 3.6

Results for Various Compounds Containing Nitrogen, Sulfur, and the Halogens

Compound	Formula	Ratio Found	Percent Error	Most Probable Formula
Pyridine	C_5H_5N	1.0137	1.37	CH
Acetonitrile	C_2H_3N	1.4390	-4.07	C_9H_{13}
Nitromethane	CH_3NO_2	2.7977	-6.74	CH_3
Dimethyl Formamide	C_3H_7NO	2.2031	-5.58	C_5H_{11}
Carbon Disulfide	CS_2	4.1418	-	CH_4
Dichloromethane	CH_2Cl_2	2.0243	1.22	CH_2
1,2-Dichloroethane	$C_2H_4Cl_2$	2.0339	1.69	CH_2
Dibromomethane	CH_2Br_2	1.9316	-3.42	CH_2
Diiodomethane	CH_2I_2	2.0354	1.77	CH_2
Tetrachloroethylene	C_2Cl_4	CO_2 peak only		
Monofluorotrichloromethane	$CFCl_3$	CO_2 peak only		

deviations remaining are attributable to normal scatter of the results. The only hydrocarbon to exceed the 0.5% error limit stated in the introduction is methane, which is known to be extremely difficult to oxidize. Since there is no other possible similar ratio the error observed is acceptable. The H/C ratio of methane shows any malfunction causing incomplete combustion and is the preferred check compound for adjusting reaction conditions. Increasing the flow rate through the reactor by 50% results in a 50% error in the methane ratio.

The oxygen-containing compounds show somewhat poorer results. Yet only one compound, allyl phenyl ether, gives the wrong formula. Like many other compounds in this table, a high impurity level is known to be present in this compound even though no definite secondary peaks are observed on the Carbowax column. Where the impurity peaks coincide with the primary sample peak or overlap it closely, the equipment cannot be expected to give the proper results. The lower molecular weight alcohols have observable water peaks which partially overlap the main peak and probably cause the high results for these compounds. Many of the alcohols show severe tailing on the Carbowax column with the blank corrections being so large that the accuracy of the results

suffers.

The results for compounds having hetero atoms other than oxygen show that a reactor with pure cupric oxide is subject to definite systematic errors from such compounds. Nitrogen-containing compounds can be identified by a carbon dioxide peak which begins rising from the baseline earlier than normal. The nitrogen peak is resolvable at lower column A temperatures. Sulfur probably appears as SO_2 which has a retention time nearly identical to the water peak but tails severely. The halogens give no observable secondary peaks, but do cause the system to give unstable readings for some time after running compounds containing them.

3-4 LIMITATIONS OF THE METHOD AND SUGGESTIONS FOR FURTHER WORK

For hydrocarbon analysis the instrument meets essentially all of the requirements for on-line analysis of C/H ratios stated in the introduction except for the interferences of sulfur, which is often found as an impurity in petroleum, nitrogen, and halogens. The accuracy of the system is sufficient for the demands placed on it, if the interferences can be eliminated. Many reagents have been studied for removing these interferences.[25,26] The reactor can be easily modified to

include a short section of one or more of these reagents to eliminate this problem. The reagents will probably not be amenable to regeneration. This will place an upper limit on the life expectancy of the reactor tube dependent on the number of sample runs containing these interfering elements. For nitrogen it is more practical to correct for the presence of the nitrogen peak than to attempt its removal. Better resolution between the nitrogen peak and the CO_2 peak is obtainable at lower column temperatures, but this adversely affects the analysis time. Similarly, increasing the length of the column requires a slower analysis or much higher column temperature. Since no detectable peaks in addition to the peak which precedes CO_2 appear when analysing nitrogen compounds, all of the nitrogen in the compound is probably present in this peak. By determining the shape of the leading edge of the CO_2 peak with and without the nitrogen peak present, an additional electronic circuit can measure the height at a known point on this edge and obtain an approximate measure of the nitrogen present. While the determination of the nitrogen/carbon ratio by this method cannot approach the accuracy of the C/H ratio, it should be satisfactory for most compounds, since few compounds contain more than one nitrogen atom. More

important, it should be possible to subtract the contribution of the nitrogen peak from the peak height of the carbon dioxide peak with appropriate calculations and improve the precision of the H/C ratio for compounds which contain nitrogen.

The corrections for linearity and the sample adsorption effect make the computations of the ratios moderately difficult, but well within the capabilities of even a small computer. While it is possible that a set of experimental conditions exist for which these factors are unnecessary, a more practical approach is adopted in the present method by minimizing the factors and then holding them constant. It is much easier to correct for a known constant error than to attempt to eliminate it entirely, especially at the required accuracy. The constancy of the factors is proved by the fact that the experimental values used in computing the linearity factors were determined two months after most of the runs were made. The resulting errors in the H/C ratio are within the experimental limits for an acceptable range of sample sizes.

The correction for sample adsorption uses the experimental values from the main set of experimental runs. Yet it also remains constant over the week required to complete the analyses and still appears to fit for

several compounds which were reanalysed five months later. Of course, changes in the conditions of the analysis probably change the factors to a varying extent. Changing the reactor tube, which does have a finite life - even with recharging, shows the greatest effect. While replacing the reactor changes all of the factors, recharging a reactor tube does not seem to affect the results. Changing column B, its temperature or flow-rate usually requires a change in the log k correction. Thus, the factors can normally be expected to remain constant for considerable periods of time.

The remaining possible difficulty is the slight change in the ratios found for compounds other than simple hydrocarbons. Even if high purity samples show a change in behavior for these compounds, the error can be greatly reduced by using a standard for these compounds which is more similar in structure to the unknowns. This should be the normal procedure for an analysis, since the effect of the various corrections can be minimized by using a similar standard with a similar sample size so that the residual error from the corrections will be as small as possible.

The results of an analysis are always dependent on the basic requirements that (1) the same compounds have sufficient vapor pressure at the 200°C operating

temperature of the sample valve, (2) sufficient sample must be present to give reasonable carbon dioxide and water peaks after combustion, (3) the peak being sampled must be a pure compound or have a constant H/C ratio for all species present, and (4) the sample peaks must not tail severely or the large blank corrections required will cause considerable inaccuracy in the final results.

APPENDIX

DATA

Conditions: All runs were made under identical conditions:

Reactor temperature-700°

Column A temperature-150°

Detector A temperature-160°

Flow rate, reactor side-20 ml/min.

Bridge current, detector A-200 ma

Sample valve temperature-200°

Column B temperature-120°

Sample side of valve-1600 mb

Reactor side of valve-1250 mb

Flow rate, sample side-60 ml/min.

Bridge current, detector B-140 ma

Recorder-30 mv full scale

Standard compound-2,2-dimethylbutane H/C ratio = 2.3333, log K = 0.14

Explanation of data: Number at left of each run indicates order of analysis. Note that for standards the standard for valve position one always appears first in the listing. The standard ratios are H_2O peak/CO_2 peak. Due to limitations of the computer printout, subscripts in formulas are not offset and chemical symbols and terms such as cis, n, are in upper case.

All peak heights shown are corrected for only baseline and blank as explained in section 3-2.

The first line for each sample shows the compound name, source of supply, formula, H/C ratio, and the log of the partition ratio, as measured on the Carbowax column. The first column labelled values lists the H/C ratio calculated from the preceeding standard for the corresponding valve position; and the second column, the ratio using the standard following the sample. The ratio column shows the average of these two values and the average of all runs for that compound appears at the bottom. Spread is calculated by the formula

$$\%\,\text{SPREAD} = \frac{(\text{largest value} - \text{smallest value}) \times 100}{\text{average}}$$

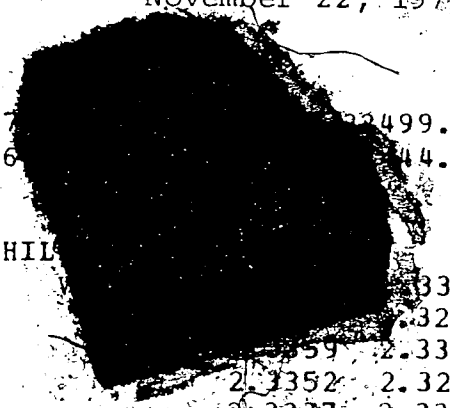
The appearance of three question marks after a run indicate that this run is of doubtful validity. The value exceeds the 90% confidence limits determined by the Pierce-Chauvenet method.[27]

The three most probable formulas appear last in the listing. The method of determination appears in section 3-3 and the sign after the formula indicates the direction of deviation from the formula. A plus sign indicates that the hydrogen number given is higher than the value calculated. A minus sign indicates the hydrogen number is lower.

Comments: Amyl alcohol, propionaldehyde and allyl phenyl ether showed interfering peaks in the November

runs. The alcohols all showed severe tailing in the November runs. These compounds were redetermined in April with individual blank corrections to obtain greater accuracy. The April values are reported in the tables in this thesis.

November 22, 1972



2 STANDARD H2O PEAK=7 499.0 RATIO=0.31246
1 6 44.5 0.31484

2,2-DIMETHYLBUTANE PHIL C6H14 2.3333 LOG K=0.14

3	H2O=6165.5	CO2=19623.5		3334	RATIO=1:2.3344	VALVE POS=2
4	5452.5	17589.5		3276	2.3314	1
5	5622.0	17944.0		3339	2.3349	2
6	4909.0	15894.0	2.3352	2.3275	2.3314	1
7	4591.5	14766.5	2.3337	2.3317	2.3327	2
8	5689.5	18347.5	2.3326	2.3249	2.3288	1
9	4075.5	13159.5	2.3335	2.3315	2.3325	2

AVERAGE=2.3323 ERROR= -0.04% SPREAD= 0.26%
MOST PROBABLE FORMULAS: C 3H 7+, C 6H14+, C 7H16-,

2,2-DIMETHYLBUTANE PHILLIPS 99.94% C6H14 2.3333 LOG K=0.14

10	H2O=3921.0	CO2=12809.0	VALUES=	2.3326	2.3249	RATIO=1:2.3287 VALVE POS=1
11	6088.5	19358.5		2.3389	2.3368	2.3378 2
12	3048.5	10057.5		2.3300	2.3223	2.3262 1
13	3148.0	10279.0		2.3272	2.3252	2.3262 2
14	1945.5	6548.5		2.3200	2.3123	2.3161 1
15	521.0	1888.0		2.2261	2.2242	2.2252 2???
16	732.5	2605.5		2.2726	2.2650	2.2688 1

AVERAGE=2.3041 ERROR= -1.25% SPREAD= 4.89%
MOST PROBABLE FORMULAS: C 3H 7+, C 7H16-, C 6H14+,

18 STANDARD H2O PEAK=6788.0 CO2 PEAK=21680.0 RATIO=0.31310
17 6798.5 21570.5 0.31518

```
BENZENE                              FISHER CERT.                          C6H6    1.0000   LOG K=0.36
  19    H2O=2941.5    CO2=22100.5    VALUES=  0.9988   0.9970    RATIO=1:0.9979    VALVE POS=2
  20          2908.5        22076.5              0.9982   1.0002             0.9992              1
  21          2833.5        21321.5              0.9985   0.9967             0.9976              2
AVERAGE=0.9983     ERROR= -0.17%    SPREAD=  0.16%
MOST PROBABLE FORMULAS: C 1H 1+, C 2H 2+, C 3H 3+,

N-PENTANE                            PHILLIPS 99%                          C5H12  2.4000   LOG K=0.10
  22    H2O=2969.0    CO2= 9586.0    VALUES=- 2.3834   2.3881    RATIO=1:2.3858    VALVE POS=1???
  23          6629.0        20533.0              2.4004   2.3961             2.3983              2
  24          6716.0        20944.0              2.3988   2.4036             2.4012              1
AVERAGE=2.3951     ERROR= -0.20%    SPREAD=  0.65%
MOST PROBABLE FORMULAS: C 5H12+, C 3H 7-, C 2H 5+,

        26   STANDARD H2O PEAK=6813.0    CO2 PEAK=21800.0    RATIO=0.31252
        25                 7048.0              22296.0           0.31611

2-METHYLPENTENE-1                    PHILLIPS 99%                          C6H12  2.0000   LOG K=0.21
  27    H2O=5727.0    CO2=21203.0    VALUES=  2.0014   2.0017    RATIO=1:2.0016    VALVE POS=2
  28          5551.0        20709.0              2.0101   2.0098             2.0100              1???
  29          4378.5        16355.5              2.0012   2.0015             2.0014              2
AVERAGE=2.0043     ERROR=  0.22%    SPREAD=  0.43%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

2-METHYLPENTANE                      PHILLIPS 99%                          C6H14  2.3333   LOG K=0.14
  30    H2O=5999.5    CO2=19313.5    VALUES=  2.3294   2.3291    RATIO=1:2.3292    VALVE POS=1
  31          7006.0        22339.0              2.3151   2.3155             2.3153              2
  32          5964.5        19130.5              2.3385   2.3382             2.3384              1
AVERAGE=2.3276     ERROR= -0.24%    SPREAD=  0.99%
MOST PROBABLE FORMULAS: C 3H 7+, C 6H14+, C 7H16-,
```

```
N-HEXANE                          PHILLIPS 99%                          C6H14   2.3333  LOG K=0.18
  33   H2O=6450.0   CO2=20464.0   VALUES=  2.3320  2.3323   RATIO=1:2.3322   VALVE POS=2
  34        6082.0        19537.0           2.3321  2.3318          2.3320              1
  35        6348.0        20141.0           2.3332  2.3335          2.3333              2
AVERAGE=2.3325    ERROR= -0.04%   SPREAD=  0.06%
MOST PROBABLE FORMULAS: C 3H 7+, C 6H14+, C 7H16-,

     36   STANDARD H   EAK=6172.5   CO2 PEAK=19815.5   RATIO=0.31150
     37                     6854.0            21705.0         0.31578

CIS-4-METHYLPENTENE-2             PHILLIPS 99%                          C6H12   2.0000  LOG K=0.20
  38   H2O=5587.0   CO2=20895.0   VALUES=  2.0046  2.0028   RATIO=1:2.0037   VALVE POS=1
  39        5466.5        20227.5           2.0062  2.0100          2.0081              2
  40        3293.5        12557.5           2.0026  2.0008          2.0017              1
AVERAGE=2.0045    ERROR=  0.23%   SPREAD=  0.32%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

3-METHYLHEXANE                    PHILLIPS 95%                          C7H16   2.2857  LOG K=0.42
  41   H2O=6188.5   CO2=19984.5   VALUES=  2.2868  2.2912   RATIO=1:2.2890   VALVE POS=2
  42        5894.0        19261.0           2.2869  2.2849          2.2859              1
  43        6205.5        20013.5           2.2896  2.2939          2.2918              2
AVERAGE=2.2889    ERROR=  0.14%   SPREAD=  0.26%
MOST PROBABLE FORMULAS: C 7H16-, C 3H 7+, C 4H 9-,

2,3-DIMETHYLBUTANE                PHILLIPS 99%                          C6H14   2.3333  LOG K=0.14
  44   H2O=5704.0   CO2=18345.0   VALUES=  2.3354  2.3333   RATIO=1:2.3344   VALVE POS=1
  45        4378.0        14080.0           2.3315  2.3359          2.3337              2
  46        6458.0        20679.0           2.3357  2.3336          2.3346              1
AVERAGE=2.3342    ERROR=  0.04%   SPREAD=  0.04%
MOST PROBABLE FORMULAS: C 3H 7-, C 6H14-, C 5H12+,
```

```
      48   STANDARD H2O PEAK=6240.5   CO2 PEAK=20008.5   RATIO=0.31189
      47                 6918.0             21942.0         0.31529

3-METHYLPENTANE                  PHILLIPS 99%                    C6H14  2.3333  LOG K=0.14
  49   H2O=6232.5   CO2=19793.5   VALUES=  2.3383  2.3324   RATIO=1:2.3353   VALVE POS=2
  50        3959.0       12910.0            2.3305  2.3300          2.3302              1
  51        6587.0       20862.0            2.3405  2.3346          2.3375              2
AVERAGE=2.3344    ERROR=  0.05%   SPREAD=  0.31%
MOST PROBABLE FORMULAS: C 3H 7-, C 6H14-, C 5H12+,

CYCLOHEXANE                      PHILLIPS 99%                    C6H12  2.0000  LOG K=0.20
  52   H2O=6074.0   CO2=22395.0   VALUES=  2.0103  2.0052   RATIO=1:2.0077   VALVE POS=2
  53        5271.0       19750.0            2.0031  2.0026          2.0029              1
  54        6296.0       23156.0            2.0129  2.0078          2.0104              2
AVERAGE=2.0070    ERROR=  0.35%   SPREAD=  0.37%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

      55   STANDARD H2O PEAK=6690.5   CO2 PEAK=21394.5   RATIO=0.31272
      56                 7280.0             22994.0         0.31660

N-DECANE                         PHILLIPS 99%                    C10H22 2.2000  LOG K=1.24
  57   H2O=5065.5   CO2=17175.5   VALUES=  2.1887  2.1879   RATIO=1:2.1883   VALVE POS=1
  58        6387.0       21178.0            2.1989  2.2051          2.2020              2
  59        5620.0       18918.0            2.1968  2.1960          2.1964              1
AVERAGE=2.1956    ERROR= -0.20%   SPREAD=  0.63%
MOST PROBABLE FORMULAS: C 5H11+, C10H22+, C11H24-,
```

```
METHYLCYCLOHEXANE                EASTMAN
  60   H2O=5247.0   CO2=19412.0   VALUES=  2.0014  2.0070
  61        5961.0        22201.0          1.9996  1.9989
  62        5228.5        19343.5          2.0016  2.0072
AVERAGE=2.0026    ERROR=  0.13%   SPREAD=  0.26%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

C7H14  2.0000  LOG K=0.45
RATIO=1:2.0042   VALVE POS=2
       1.9993             1???
       2.0044             2

       63   STANDARD H2O PEAK=7203.0   CO2 PEAK=22966.0   RATIO=0.31364
       64                 6395.0          20341.0         0.31439

N-NONANE                         PHILLIPS 99%
  65   H2O=5511.5   CO2=18482.5   VALUES=  2.2131  2.2160
  66        6307.0        20822.0          2.2230  2.2157
  67        6189.0        20613.0          2.2195  2.2223
AVERAGE=2.2183    ERROR= -0.18%   SPREAD=  0.29%
MOST PROBABLE FORMULAS: C 9H20+, C 5H11-, C 4H 9+,

C9H20  2.2222  LOG K=0.99
RATIO=1:2.2145   VALVE POS=1
       2.2194             2
       2.2209             1

2,2,5-TRIMETHYLHEXANE            EASTMAN
  68   H2O=6846.5   CO2=22570.5   VALUES=  2.2264  2.2190
  69        5992.5        20020.5          2.2211  2.2240
  70        6836.5        22523.5          2.2279  2.2205
AVERAGE=2.2231    ERROR=  0.04%   SPREAD=  0.07%
MOST PROBABLE FORMULAS: C 9H20-, C 4H 9+, C 5H11-,

C9H20  2.2222  LOG K=0.78
RATIO=1:2.2227   VALVE POS=2
       2.2225             1
       2.2242             2

       71   STANDARD H2O PEAK=6645.5   CO2 PEAK=21274.5   RATIO=0.31237
       72                 7371.5          23262.5         0.31688

PENTENE-2                        PHILLIPS 99%
  73   H2O=5601.0   CO2=20946.0   VALUES=  2.0107  2.0122
  74        5185.5        19266.5          2.0058  2.0058
  75        5220.5        19586.5          2.0091  2.0105
AVERAGE=2.0090    ERROR=  0.45%   SPREAD=  0.28%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

C5H10  2.0000  LOG K=0.05
RATIO=1:2.0114   VALVE POS=1
       2.0058             2
       2.0098             1
```

```
N-HEPTANE                          PHILLIPS 99%                          C7H16   2.2857  LOG K=0.46
  76   H2O=6057.0    CO2=19579.0    VALUES=   2.2824   2.2825    RATIO=1:2.2825    VALVE POS=2
  77        6063.0         19750.0              2.2903   2.2920              2.2911              1
  78        5548.0         17897.0              2.2938   2.2939              2.2939              2
AVERAGE=2.2892     ERROR=  0.15%    SPREAD=  0.50%
MOST PROBABLE FORMULAS: C 7H16-, C 3H 7+, C 4H 9-,


TOLUENE                            FISHER                                C7H8    1.1429  LOG K=0.43
  79   H2O=3550.5    CO2=23325.5    VALUES=   1.1480   1.1489    RATIO=1:1.1484    VALVE POS=1
  80        3421.0         22246.0              1.1462   1.1462              1.1462              2
  81        2976.5         19650.5              1.1494   1.1503              1.1499              1
AVERAGE=1.1482     ERROR=  0.46%    SPREAD=  0.32%
MOST PROBABLE FORMULAS: C 7H 8-, C 6H 7+, C 1H 1-,


       83    STANDARD H2O PEAK=7779.5    CO2 PEAK=24787.5    RATIO=0.31385
       82                      6871.0             21734.0          0.31614


2,3,4-TRIMETHYLPENTANE             PHILLIPS 99%                          C8H18   2.2500  LOG K=0.62
  84   H2O=5521.0    CO2=18107.0    VALUES=   2.2514   2.2565    RATIO=1:2.2540    VALVE POS=2
  85        6291.0         20751.0              2.2554   2.2590              2.2572              1
  86        6833.5         22282.5              2.2487   2.2537              2.2512              2
AVERAGE=2.2541     ERROR=  0.18%    SPREAD=  0.27%
MOST PROBABLE FORMULAS: C 4H 9-, C 8H18-, C 7H16+,


N-OCTANE                           PHILLIPS 99%                          C8H18   2.2500  LOG K=0.73
  87   H2O=5563.0    CO2=18418.0    VALUES=   2.2534   2.2570    RATIO=1:2.2552    VALVE POS=1
  88        5405.0         17735.0              2.2487   2.2537              2.2512              2
  89        6130.5         20235.5              2.2527   2.2562              2.2544              1
AVERAGE=2.2536     ERROR=  0.16%    SPREAD=  0.18%
MOST PROBABLE FORMULAS: C 4H 9-, C 8H18-, C 7H16+,
```

```
      91   STANDARD H2O PEAK=6753.5   CO2 PEAK=21657.5   RATIO=0.31183
      90                    7428.0             23488.0         0.31625


2,2,4-TRIMETHYLPENTANE          EASTMAN                          C8H18  2.2500  LOG K=0.54
  92   H2O=6685.5   CO2=21899.5   VALUES=  2.2473  2.2416   RATIO=1:2.2445   VALVE POS=2
  93        6925.0        22850.0           2.2531  2.2448          2.2489            1
  94        6954.5        22683.5           2.2541  2.2484          2.2513            2
AVERAGE=2.2482    ERROR= -0.08%   SPREAD=  0.30%
MOST PROBABLE FORMULAS: C 4H 9+, C 8H18+, C 9H20-,


CYCLOOCTANE                     MATHESON                         C8H16  2.0000  LOG K=0.82
  95   H2O=5531.5   CO2=20555.5   VALUES=  2.0061  1.9987   RATIO=1:2.0024   VALVE POS=1
  96        5737.0        21053.0           2.0118  2.0007          2.0033            2
  97        6206.0        22893.0           2.0130  2.0056          2.0093            1???
AVERAGE=2.0050    ERROR=  0.25%   SPREAD=  0.34%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,


      99   STANDARD H2O PEAK=6484.5   CO2 PEAK=20748.5   RATIO=0.31253
      98                    7296.0             23026.0         0.31686
```

November 25, 1972

```
        1   STANDARD H2O PEAK=6943.5    CO2 PEAK=22147.5    RATIO=0.31351
        2                    6884.0                21756.0          0.31642


ISOPROPYL ACETATE                EASTMAN              C5H10-O2       2.0000  LOG K=0.68
   3   H2O=4017.5   CO2=15000.5   VALUES=  2.0137  2.0115   RATIO 1: 2.0126   VALVE POS=1
   4       4133.5       15204.5            2.0205  2.0200            2.0202            2
   5       4732.0       17526.0            2.0186  2.0164            2.0175            1
AVERAGE=2.0168    ERROR=  0.84%   SPREAD=  0.38%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,


N-PROPYL BUTYRATE                EASTMAN              C7H14-O2       2.0000  LOG K=1.24
   6   H2O=5092.0   CO2=18453.0   VALUES=  2.0222  2.0217   RATIO=1: 2.0220   VALVE POS=2
   7       5015.5       18392.5            2.0200  2.0178            2.0189            1
   8       4739.5       17166.5            2.0281  2.0276            2.0279            2
AVERAGE=2.0229    ERROR=  1.15%   SPREAD=  0.44%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,


        9   STANDARD H2O PEAK=6962.5    CO2 PEAK=22182.5    RATIO=0.31387
       10                    6630.0                20974.0          0.31611


BUTYL FORMATE                    MATHESON             C5H10-O2       2.0000  LOG K=0.77
  11   H2O=4243.0   CO2=15747.0   VALUES=  2.0176  2.0176   RATIO=1: 2.0176   VALVE POS=1
  12       4228.5       15422.5            2.0335  2.0297            2.0316            2
  13       4544.0       16764.0            2.0249  2.0249            2.0249            1
AVERAGE=2.0247    ERROR=  1.24%   SPREAD=  0.69%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,
```

```
ALLYL PROPIONATE                EASTMAN                    C6H10-O2      1.6667  LOG K=0.99
  14   H2O=3894.0   CO2=17098.0   VALUES=  1.6847  1.6816   RATIO=1:1.6832   VALVE POS=2
  15        3932.0       17461.0            1.6823  1.6823          1.6823            1
  16        2137.0        9609.0            1.6780  1.6749          1.6765         2???
AVERAGE=1.6806    ERROR=  0.84%   SPREAD=  0.40%
MOST PROBABLE FORMULAS: C 3H 5-, C 6H10-, C 9H15-,

      17   STANDARD H2O PEAK=6691.5   CO2 PEAK=21348.5   RATIO=0.31344
      18                    7026.5          22145.5         0.31729

ETHANE                          PHILLIPS RESEARCH          C2H6   3.0000  LOG K=0.10
  19   H2O=6627.5   CO2=16621.5   VALUES=  2.9871  2.9859   RATIO=1:2.9865   VALVE POS=1
  20        7882.0       19487.0            2.9821  2.9815          2.9818            2
  21        6587.0       16475.0            2.9960  2.9948          2.9954            1
AVERAGE=2.9879    ERROR= -0.40%   SPREAD=  0.45%
MOST PROBABLE FORMULAS: C 1H 3+, C 2H 6+,

PROPANE                         PHILLIPS RESEARCH          C3H8   2.6667  LOG K=0.10
  22   H2O=7697.0   CO2=21267.0   VALUES=  2.6666  2.6660   RATIO=1:2.6663   VALVE POS=2
  23        7385.5       20595.5            2.6730  2.6719          2.6725            1
  24        8121.5       22462.5            2.6592  2.6586          2.6589            2
AVERAGE=2.6659    ERROR= -0.03%   SPREAD=  0.51%
MOST PROBABLE FORMULAS: C 3H 8+, C 2H 5-, C 1H 3+,

METHANE                         MATHESON RESEARCH          CH4    4.0000  LOG K=0.10
  25   H2O=5143.0   CO2=10351.0   VALUES=  3.7653  3.7637   RATIO=1:3.7645   VALVE POS=1
  26        5108.5       10204.5            3.7550  3.7542          3.7546            2
  27        5548.0       11106.0            3.7758  3.7743          3.7751            1
AVERAGE=3.7647    ERROR= -5.88%   SPREAD=  0.54%
MOST PROBABLE FORMULAS: C 1H 4+,
```

```
        29   STANDARD H2O PEAK=6440.0   CO2 PEAK=20565.0   RATIO=0.31315
        28                    6723.0           21215.0         0.31690

N-BUTANE                          PHILLIPS RESEARCH                    C4H10  2.5000  LOG K=0.10
  30   H2O=7606.0   CO2=22367.0   VALUES=  2.5039  2.5055   RATIO=1:2.5047   VALVE POS=2???
  31        6507.0       19386.0            2.5101  2.5108            2.5104              1
  32        6917.5       20363.5            2.5091  2.5107            2.5099              2
AVERAGE=2.5083    ERROR=  0.33%   SPREAD=  0.23%
MOST PROBABLE FORMULAS: C 2H 5-, C 4H10-, C 3H 8+,

CYCLOHEXENE                       PHILLIPS 99%                         C6H10  1.6667  LOG K=0.27
  33   H2O=5150.5   CO2=22939.5   VALUES=  1.6765  1.6770   RATIO=1:1.6768   VALVE POS=1
  34        1850.0       8516.0             1.6588  1.6598            1.6593              2???
  35        5281.5       23496.5            1.6770  1.6774            1.6772              1
AVERAGE=1.6711    ERROR=  0.26%   SPREAD=  1.07%
MOST PROBABLE FORMULAS: C 3H 5-, C 6H10-, C 9H15-,

2-METHYLBUTENE-1                  MATHESON 95%                         C5H10  2.0000  LOG K=0.05
  36   H2O=5864.5   CO2=21705.5   VALUES=  1.9992  2.0005   RATIO=1:1.9999   VALVE POS=2
  37        6429.5       23881.5            2.0076  2.0082            2.0079              1
  38        5279.0       19583.0            2.0015  2.0029            2.0022              2
AVERAGE=2.0033    ERROR=  0.17%   SPREAD=  0.40%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

        39   STANDARD H2O PEAK=5754.5   CO2 PEAK=18452.5   RATIO=0.31185
        40                    6615.5           20900.5         0.31652
```

DIOXANE MCB SPECTRA C4H8-O2 2.0000 LOG K=0.67

41	H2O=2973.5	CO2=11266.5	VALUES=	2.0029	2.0049	RATIO=1:2.0039	VALVE POS=1
42	4125.5	15235.5		2.0094	2.0184	2.0139	2
43	4980.0	18479.0		2.0090	2.0109	2.0100	1

AVERAGE=2.0093 ERROR= 0.46% SPREAD= 0.50%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

PROPIONALDEHYDE EASTMAN C3H6-O 2.0000 LOG K=0.05

44	H2O= 816.0	CO2= 3246.0	VALUES=	1.9872	1.9961	RATIO=1:1.9917	VALVE POS=2???
45	3935.5	14710.5		2.0298	2.0318	2.0308	1
46	3248.0	12039.0		2.0372	2.0464	2.0418	2

AVERAGE=2.0214 ERROR= 1.07% SPREAD= 2.48%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

PROPIONALDEHYDE EASTMAN C3H6-O 2.0000 LOG K=0.18

47	H2O=1849.5	CO2= 7110.5	VALUES=	2.0200	2.0221	RATIO=1:2.0211	VALVE POS=1
48	1277.5	4954.5		2.0019	2.0109	2.0064	2
49	2804.5	10601.5		2.0248	2.0268	2.0258	1

AVERAGE=2.0178 ERROR= 0.89% SPREAD= 0.96%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

51	STANDARD H2O PEAK=6452.0	CO2 PEAK=20627.0	RATIO=0.31279	
50	6692.0	21228.0	0.31524	

ACETONE MALLINKRODT C3H6-O 2.0000 LOG K=0.27

52	H2O=2449.5	CO2= 9233.5	VALUES=	2.0223	2.0173	RATIO=1:2.0198	VALVE POS=2
53	4025.0	1501(		2.0256	2.0213	2.0234	1
54	4389.5	1612		2.0362	2.0311	2.0336	2

AVERAGE=2.0256 ERROR= 1.2[illegible] SPREAD= 0.68%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

```
VALERALDEHYDE                    ALDRICH                    C5H10-O    2.0000  LOG K=0.71
  55   H2O=4749.0   CO2=17493.0   VALUES=  2.0282  2.0239   RATIO=1:2.0260   VALVE POS=1
  56        5298.5       19214.5            2.0379  2.0327          2.0353            2
  57        4451.0       16394.0            2.0330  2.0286          2.0308            1
AVERAGE=2.0307    ERROR=  1.54%   SPREAD=  0.46%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,


       59   STANDARD H2O PEAK=6907.5   CO2 PEAK=21984.5   RATIO=0.31420
       58                      7862.0            24746.0         0.31771


BIS(2-METHOXYETHYL) ETHER     MATHESON SPECTRO      C6H14-O3       2.3333  LOG K=1.56
  60   H2O=1076.0   CO2= 3610.0   VALUES=  2.2954  2.2953   RATIO=1:2.2954   VALVE POS=2
  61        1243.5        4153.5            2.3177  2.3183          2.3180            1
  62        1640.5        5346.5            2.3301  2.3303          2.3302            2
AVERAGE=2.3145    ERROR= -0.81%   SPREAD=  1.51%
MOST PROBABLE FORMULAS: C 3H 7+, C 6H14+, C 7H16-,


ALLYL PHENYL ETHER            EASTMAN              C9H10-O      1.1111  LOG K=1.62
  63   H2O=1730.5   CO2=10506.5   VALUES=  1.2501  1.2505   RATIO=1:1.2503   VALVE POS=1???
  64        2620.5       17164.5            1.1298  1.1299          1.1298            2
  65        2078.5       13888.5            1.1272  1.1276          1.1274            1
AVERAGE=1.1692    ERROR=  5.23%   SPREAD= 10.51%
MOST PROBABLE FORMULAS: C 6H 7-, C12H14 , C11H13+,


       67   STANDARD H2O PEAK=5763.5   CO2 PEAK=18466.5   RATIO=0.31211
       66                      5963.0            18944.0         0.31477
```

```
METHANOL                          MACARTHUR99.5%                    CH4-O  4.0000  LOG K=0.06
  68   H2O=3804.0   CO2= 7184.0   VALUES=  4.0159  4.0111  RATIO=1:4.0135   VALVE POS=2
  69        5158.5        9732.5             4.0071  3.9927         3.9999            1
  70        5665.0       10548.0             4.0204  4.0155         4.0180            2
AVERAGE=4.0105   ERROR=  0.26%   SPREAD=  0.45%
MOST PROBABLE FORMULAS: C 1H 4-,

ETHANOL                           95%                               C2H6-O 3.0000  LOG K=0.32
  71   H2O=5415.5   CO2=13 29.5   VALUES=  3.0932  3.0820  RATIO=1:3.0876   VALVE POS=1
  72        5270.0       12799.0             3.0683  3.0646         3.0664            2
  73        3270.0        8169.0             3.0544  3.0435         3.0489            1
AVERAGE=3.0676   ERROR=  2.25%   SPREAD=  1.26%
MOST PROBABLE FORMULAS: C 1H 3-, C 2H 6-,

2-PROPANOL                        FISHER                            C3H8-O 2.6667  LOG K=0.46
  74   H2O=5059.0   CO2=13789.0   VALUES=  2.7285  2.7252  RATIO=1:2.7268   VALVE POS=2
  75        4583.5       12659.5             2.7218  2.7120         2.7169            1
  76        5364.0       14605.0             2.7261  2.7228         2.7244            2
AVERAGE=2.7227   ERROR=  2.10%   SPREAD=  0.37%
MOST PROBABLE FORMULAS: C 3H 8-, C 1H 3+, C 2H 5-,

ALLYL ALCOHOL                     FISHER                            C3H6-O 2.0000  LOG K=0.63
  77   H2O=3275.5   CO2=11757.5   VALUES=  2.1078  2.1003  RATIO=1:2.1041   VALVE POS=1
  78        4187.5       15031.5             2.0726  2.0701         2.0714            2
  79        4237.5       15832.5             2.0059  1.9986         2.0023            1
AVERAGE=2.0592   ERROR=  2.96%   SPREAD=  4.94%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,
```

T-BUTYL ALCOHOL MCB C4H10-O 2.5000 LOG K=0.55

80	H2O=5530.0	CO2=16931.0	VALUES=	2.4153	2.4124	RATIO=1:2.4138	VALVE POS=2
81	5498.0	[illegible]		2.3809	2.3722	2.3766	1
82	6397.5	[illegible]		2.4977	2.4946	2.4961	2

AVERAGE=2.4288 ERROR= [illegible] SPREAD= 4.92%
MOST PROBABLE FORMULAS: C 2H 5-, C 5H12-, C 4H10+,

84	STANDARD H2O PEAK=6474.0	CO2 PEAK=20586.0	RATIO=0.31449	
83	6044.0	19170.0	0.31528	

T-AMYL ALCOHOL FISHER C5H12-O 2.4000 LOG K=0.84

85	H2O=3449.0	CO2=12780.0	VALUES=	2.0246	2.0246	RATIO=1:2.0246	VALVE POS=1
86	3239.5	11930.5		2.0288	2.0288	2.0288	2
87	3427.0	11378.0		2.2630	2.2630	2.2630	1
88	2983.5	10977.5		2.0363	2.0363	2.0363	2
89	3421.0	11235.0		2.2882	2.2882	2.2882	1
90	2846.0	8952.0		2.3907	2.3907	2.3907	2

AVERAGE=2.1719 ERROR= -9.50% SPREAD= 16.86%
MOST PROBABLE FORMULAS: C 6H13-, C12H26-, C11H24+,

92	STANDARD H2O PEAK=6474.0	CO2 PEAK=20586.0	RATIO=0.31449	
91	6044.0	19170.0	0.31528	

```
        2   STANDARD H2O PEAK=6887.0   CO2 PEAK=21890.0   RATIO=0.31462
        1                  7073.0             22258.0         0.31777

N-BUTYL ETHER                    BRITISH DRUG HOUSE    C8H18-O        2.2500  LOG K=1.08
   3   H2O=5319.5   CO2=17333.5   VALUES=  2.2459  2.2459   RATIO=1:2.2459   VALVE POS=2
   4       4835.5       15938.5            2.2491  2.2490            2.2490            1
   5       5373.5       17452.5            2.2525  2.2526            2.2525            2
AVERAGE=2.2491    ERROR= -0.04%   SPREAD=  0.30%
MOST PROBABLE FORMULAS: C 4H 9+, C 8H18+, C 9H20-,

ALLYL ETHER                      EASTMAN               C6H10-O     1.6667  LOG K=0.65
   6   H2O=4246.0   CO2=18863.0   VALUES=  1.6798  1.6797   RATIO=1:1.6798   VALVE POS=1
   7       3982.5       17555.5            1.6789  1.6789            1.6789            2
   8       3581.5       15982.5            1.6823  1.6822            1.6822            1
AVERAGE=1.6803    ERROR=  0.82%   SPREAD=  0.20%
MOST PROBABLE FORMULAS: C 3H 5-, C 6H10-, C 9H15-,

       10   STANDARD H2O PEAK=6817.5   CO2 PEAK=21675.5   RATIO=0.31453
        9                  5384.5             17096.5         0.31495

3-PENTANONE                      MATHESON              C5H10-O     2.0000  LOG K=0.73
  11   H2O=4155.5   CO2=15252.5   VALUES=  2.0162  2.0156   RATIO=1:2.0159   VALVE POS=2
  12       4551.5       16793.5            2.0199  2.0169            2.0184            1
  13       5124.5       18648.5            2.0198  2.0191            2.0194            2
AVERAGE=2.0179    ERROR=  0.90%   SPREAD=  0.17%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,
```

```
4-HEPTANONE                    ALDRICH                          C7H14-O     2.0000  LOG K=1.17
  14   H2O=4684.5   CO2=17267.5   VALUES=  2.0083  2.0053   RATIO=1:2.0060   VALVE POS=1
  15        4355.0        15855.0          2.0182  2.0016            2.0117           2
  16        4614.5        16969.5          2.0107  2.0111            2.0126           1
AVERAGE=2.0124    ERROR=  0.62%   SPREAD=  0.44%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

      18   STANDARD H2O PEAK=6116.0   CO2 PEAK=19490.0   RATIO=0.31380
      17                 6614.0           20853.0         0.31717

ETHYLBENZENE                   EASTMAN                          C8H10   1.2500  LOG K=0.94
  19   H2O=3716.0   CO2=21851.0   VALUES=  1.2516  1.2510   RATIO=1:1.2513   VALVE POS=2
  20        3064.5        18333.5          1.2507  1.2522            1.2514           1
  21        3226.0        19050.0          1.2521  1.2516            1.2518           2
AVERAGE=1.2515    ERROR=  0.12%   SPREAD=  0.04%
MOST PROBABLE FORMULAS: C 4H 5-, C 8H10-, C12H15-,

T-BUTYLBENZENE                 MATHESON                         C10H14  1.4000  LOG K=1.31
  22   H2O=4238.5   CO2=22401.5   VALUES=  1.3950  1.3967   RATIO=1:1.3958   VALVE POS=1???
  23        4491.5        23382.5          1.4003  1.3997            1.4000           2
  24        4210.0        22178.0          1.3999  1.4016            1.4008           1
AVERAGE=1.3989    ERROR= -0.08%   SPREAD=  0.36%
MOST PROBABLE FORMULAS: C 5H 7+, C10H14+, C 8H11-,

      26   STANDARD H2O PEAK=6433.0   CO2 PEAK=20489.0   RATIO=0.31397
      25                 6574.5           20723.5         0.31725
```

```
ISOPROPYLBENZENE                BRITISH DRUG HOUSE              C9H12  1.3333  LOG K=1.13
  27   H2O=4158.0   CO2=22894.0   VALUES=  1.3289  1.3339   RATIO=1: 1.3314   VALVE POS=2
  28        3890.0       21654.0            1.3324  1.3357            1.3341              1
  29        3893.5       21439.5            1.3317  1.3367            1.3342              2
AVERAGE=1.3332    ERROR= -0.01%   SPREAD=  0.21%
MOST PROBABLE FORMULAS: C 3H 4+, C 6H 8+, C 9H12+,


N-PROPYLBENZENE                 EASTMAN                         C9H12  1.3333  LOG K=1.18
  30   H2O=3946.5   CO2=21910.5   VALUES=  1.3344  1.3378   RATIO=1: 1.3361   VALVE POS=
  31        3804.5       20937.5            1.3326  1.3376            1.3351              4
  32        4032.0       22347.0            1.3357  1.3391            1.3374              1
AVERAGE=1.3362    ERROR=  0.22%   SPREAD=  0.17%
MOST PROBABLE FORMULAS: C 3H 4-, C 6H 8-, C 9H12-,

       34   STANDARD H2O PEAK=6091.5   CO2 PEAK=19486.5   RATIO=0.31260
       33                    6369.5          20172.5         0.31575


PYRIDINE                        MCB SPECTRO                     C5H5N  1.0000  LOG K=1.02
  35   H2O=1039.5   CO2= 7923.5   VALUES=  1.0066  1.0039   RATIO=1: 1.0052   VALVE POS=2
  36        1784.5       13318.5            1.0220  1.0222            1.0221              1
AVERAGE=1.0137    ERROR=  1.37%   SPREAD=  1.66%
MOST PROBABLE FORMULAS: C 1H 1-, C 2H 2-, C 3H 3-,

       37   STANDARD H2O PEAK=6732.5   CO2 PEAK=21466.5   RATIO=0.31363
       38                    6596.0          20811.0         0.31695


ACETONITRILE                    MCB SPECTRO                     C2H3N  1.5000  LOG K=0.39
  39   H2O=2106.0   CO2=11248.0   VALUES=  1.4375  1.4406   RATIO=1: 1.4391   VALVE POS=1
  40        3403.5       17655.5            1.4365  1.4368            1.4366              2
  41        3326.5       17459.5            1.4396  1.4427            1.4412              1
AVERAGE=1.4390    ERROR= -4.07%   SPREAD=  0.32%
MOST PROBABLE FORMULAS: C 9H13+, C 7H10-, C 2H 3+,
```

```
      42   STANDARD H2O PEAK=6385.5   CO2 PEAK=20441.5   RATIO=0.31238
      43                   6438.0           20334.0          0.31661

NITROMETHANE                    MCB SPECTRO                    CH3NO2 3.0000  LOG K=0.59
  44   H2O=2834.0   CO2= 7737.0   VALUES=  2.8038  2.8038    RATIO=1:2.8038   VALVE POS=1
  45        5140.0       13685.0           2.7785  2.7785          2.7785              2???
  46        3644.0        9837.0           2.8109  2.8109          2.8109              1
AVERAGE=2.7977    ERROR= -6.74%   SPREAD=  1.16%
MOST PROBABLE FORMULAS: C 1H 3+, C 3H 8-, C 2H 6+,

DIMETHYL FORMAMIDE              BDH 99%
  47   H2O=1136.5   CO2= 4042.5   VALUES=  2.1913  2.1913    C3H7NO 2.3333  LOG K=1.46
  48        2627.0        8844.0           2.2149  2.2149    RATIO=1:2.1913   VALVE POS=1
AVERAGE=2.203     ERROR= -5.58%   SPREAD=  1.07%                    2.2149              2
MOST PROBABLE FORMULAS: C 5H11-, C10H22-, C 9H20+,

      49   STANDARD H2O PEAK=6385.5   CO2 PEAK=20441.5   RATIO=0.31238
      50                   6438.0           20334.0          0.31661
```

November 30, 1972

2 STANDARD H2O PEAK=5527.5 CO2 PEAK=18011.5 RATIO=0.30689
1 5401.0 17448.0 0.30955

DICHLOROMETHANE MCB CH2CL2 2.0000 LOG K=0.10
3 H2O=1204.0 CO2= 4768.0 VALUES= 1.9971 2.0243 RATIO=1:2.0107 VALVE POS=2???
4 5210.0 19650.0 2.0176 2.0397 2.0287 1
5 4913.5 18367.5 2.0199 2.0473 2.0336 2
AVERAGE=2.0243 ERROR= 1.22% SPREAD= 1.13%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

1,2-DICHLOROETHANE FISHER C2H4CL2 2.0000 LOG K=0.48
6 H2O=2681.5 CO2=10283.5 VALUES= 2.0205 2.0426 RATIO=1:2.0316 VALVE POS=1
7 3351.5 12615.5 2.0213 2.0487 2.0350 2
8 4044.0 15263.0 2.0240 2.0461 2.0350 1
AVERAGE=2.0339 ERROR= 1.69% SPREAD= 0.17%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

10 STANDARD H2O PEAK=5719.5 CO2 PEAK=18816.5 RATIO=0.30396
9 6028.5 19664.5 0.30657

DIBROMOMETHANE EASTMAN CH2BR2 2.0000 LOG K=0.53
11 H2O=3217.0 CO2=13174.0 VALUES= 1.8979 1.9334 RATIO=1:1.9156 VALVE POS=1
12 3952.5 15867.5 1.9075 1.9843 1.9459 2
13 3244.0 13161.0 1.9154 1.9511 1.9333 1
AVERAGE=1.9316 ERROR= -3.42% SPREAD= 1.57%
MOST PROBABLE FORMULAS: C 1H 2+, C 2H 4+, C12H23-,

```
        15   STANDARD H2O PEAK=6328.0   CO2 PEAK=21128.0   RATIO=0.29951
        14                    7173.0            24189.0         0.29654


DIIODOMETHANE                    FISHER                          CH2I2  2.0000  LOG K=1.13
  16   H2O=1196.5   CO2= 4761.5   VALUES=  2.0680  1.9984   RATIO=1:2.0332   VALVE POS=2
  17        2273.0        8864.0            2.0405  2.0191          2.0298              1
  18        2260.0        8763.0            2.0780  2.0082          2.0431              2
AVERAGE=2.0354    ERROR=  1.77%   SPREAD=  0.65%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,


        19   STANDARD H2O PEAK=5709.0   CO2 PEAK=18932.0   RATIO=0.30155
        20                    5810.5            19077.5         0.30457


CARBON DISULFIDE                 MALLINCKRODT                    CS2    0.0001  LOG K=0.00
  21   H2O=6714.0   CO2=12487.0   VALUES=  4.1731  4.1104   RATIO=1:4.1418   VALVE POS=1
AVERAGE=4.1418    ERROR=653.00%   SPREAD=  0.00%
MOST PROBABLE FORMULAS: C 1H 4-,


        23   STANDARD H2O PEAK=5146.5   CO2 PEAK=16873.5   RATIO=0.30500
        22                    8002.5            27113.5         0.29515
```

April 18, 1973

1	STANDARD H2O PEAK=6110.0	CO2 PEAK=19079.0	RATIO=0.32025			
2	5880.0	18115.0	0.32459			

PROPIONALDEHYDE EASTMAN C3H6-O 2.0000 LOG K=0.05

3	H2O=2914.0	CO2=10561.0	VALUES=	2.0648	2.0917	RATIO=1:2.0782 VALVE POS=1
4	4215.5	15200.5		2.0486	2.0753	2.0620 1
5	4381.5	15720.5		2.0562	2.0830	2.0696 1

AVERAGE=2.0699 ERROR= 3.50% SPREAD= 0.79%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C12H25+,

7	STANDARD H2O PEAK=6291.5	CO2 PEAK=19878.5	RATIO=0.31650
6	6843.0	21543.0	0.31764

ALLYL PHENYL ETHER EASTMAN C9H10-O 1.1111 LOG K=1.62

8	H2O=3253.0	CO2=20398.0	VALUES=	1.1671	1.1367	RATIO=1:1.1519 VALVE POS=2???
9	3116.5	20071.5		1.1411	1.1290	1.1351 1
10	2869.0	18333.0		1.1498	1.1199	1.1348 2

AVERAGE=1.1406 ERROR= 2.66% SPREAD= 1.50%
MOST PROBABLE FORMULAS: C 7H 8+, C 8H 9-, C 1H 1-,

11	STANDARD H2O PEAK=6202.5	CO2 PEAK=19402.5	RATIO=0.31968
12	6247.5	19220.5	0.32504

April 19, 1973

```
        1   STANDARD H2O PEAK=6571.0   CO2 PEAK=20528.0   RATIO=0.32010
        2                  5688.0             17709.0         0.32119

METHANOL                          MACARTHUR99.5%                    CH4-O  4.0000  LOG K=0.06
   3   H2O=5734.0   CO2=10491.0   VALUES=  4.0328  4.0202   RATIO=1:4.0265   VALVE POS=1
   4       6032.0       10888.0            4.0500  4.0707          4.0604            2???
   5       5853.0       10725.0            4.0237  4.0112          4.0174            1
AVERAGE=4.0348    ERROR=  0.87%   SPREAD=  1.06%
MOST PROBABLE FORMULAS: C 1H 4-,

        6   STANDARD H2O PEAK=5824.5   CO2 PEAK=18215.5   RATIO=0.31976
        7                  6158.0             19219.0         0.32041

ETHANOL                           95%                       C2H6-O 3.0000  LOG K=0.32
   8   H2O=4540.0   CO2=10812.0   VALUES=  3.0926  3.0396   RATIO=1:3.0661   VALVE POS=2
   9       5000.0       12052.0            3.0457  3.0418          3.0437            1???
  10       4964.5       11782.5            3.0941  3.0411          3.0676            2
AVERAGE=3.0591    ERROR=  1.97%   SPREAD=  0.78%
MOST PROBABLE FORMULAS: C 1H 3-, C 2H 6-,

       12   STANDARD H2O PEAK=6166.5   CO2 PEAK=19222.5   RATIO=0.32080
       11                  6648.0             20346.0         0.32675
```

```
2-PROPANOL                          FISHER                                  C3H8-O 2.6667  LOG K=0.46
  13   H2O=4678.0   CO2=12673.0   VALUES=  2.7040  2.6944   RATIO=1:2.6992   VALVE POS=1
  14        4871.0        12955.0           2.7064  2.7290            2.7177            2???
  15        4940.0        13339.0           2.7078  2.6982            2.7030               1
AVERAGE=2.7066    ERROR=  1.50%   SPREAD=  0.68%
MOST PROBABLE FORMULAS: C 3H 8-, C 1H 3+, C 2H 5-,

      16   STANDARD H2O PEAK=6862.0   CO2 PEAK=21237.0   RATIO=0.32312
      17                    6053.5            18736.5         0.32300

ALLYL ALCOHOL                       FISHER                                  C3H6-O 2.0000  LOG K=0.63
  18   H2O=3348.0   CO2=11990.0   VALUES=  2.0395  2.0298   RATIO=1:2.0347   VALVE POS=2
  19        3717.5        13421.5           2.0267  2.0253            2.0260               1
  20        3965.5        14073.5           2.0467  2.0370            2.0419               2
AVERAGE=2.0342    ERROR=  1.71%   SPREAD=  0.78%
MOST PROBABLE FORMULAS: C 1H 2-, C 2H 4-, C 3H 6-,

      22   STANDARD H2O PEAK=5880.5   CO2 PEAK=18284.5   RATIO=0.32161
      21                    5917.0            18242.0         0.32436

T-BUTYL ALCOHOL                     MCB                                 C4H10-O     2.5000  LOG K=0.55
  23   H2O=4569.0   CO2=13322.0   VALUES=  2.4986  2.5190   RATIO=1:2.5088   VALVE POS=1???
  24        5158.5        14921.5           2.4868  2.4998            2.4933               2
  25        4853.0        14232.0           2.4789  2.4990            2.4889               1
AVERAGE=2.4970    ERROR= -0.12%   SPREAD=  0.80%
MOST PROBABLE FORMULAS: C 2H 5+, C 4H10+, C 5H12-,

      26   STANDARD H2O PEAK=6818.0   CO2 PEAK=21261.0   RATIO=0.32068
      27                    6760.5            20858.5         0.32411
```

T-AMYL ALCOHOL FISHER C5H12-O 2.4000 LOG K=0.84

28	H2O=5348.5	CO2=16164.5	VALUES=	2.3792	2.3699	RATIO=1:2.3746	VALVE POS=2???
29	5323.5	16045.5		2.4136	2.4004	2.4070	1
30	5359.0	16175.0		2.4097	2.3964	2.4031	1

AVERAGE=2.3949 ERROR= -0.21% SPREAD= 1.35%

MOST PROBABLE FORMULAS: C 5H12+, C 3H 7-, C 2H 5+,

32	STANDARD H2O PEAK=5917.5	CO2 PEAK=18442.5	RATIO=0.32086	
31	6807.5	20917.5	0.32545	

A COMPUTER PROGRAM FOR THE CALCULATION OF RESULTS FROM THE ANALYSIS

The program which appears at the end of this section is written in PL1 and gives a printed output similar to th data tables in the preceeding section of this appendix.

Requirements for data input:

The input data can be broken down into three separate sections. The first five cards are the program prologue. They provide information concerning the run and supply data to the program concerning the standard compounds and the various corrections to be used.

The experimental data follows, grouped into sets containing two standards and the data for several unknown compounds. This grouping is repeated until the batch of runs is completed.

The end of the data is signaled by two standards followed by a blank card. This clears the computer and, if desired, resets the computer for additional data sets.

A sample data set is provided on the following page.

NOV2572-PORAPAKN-150C-120C-705C-20 ML/MIN FLOW

DATE COLUMN COL A COLB REAC COMMENTS

2,2-DIMETHYLBUTANE PHILLIPS 99.94% C6H14 .14 2.3333

61 15

0.0530 0.0458 0.0272 0.0303 0.0132

98 22312 7062 109 1

108 21922 7004 102 2 2 8

ISOPROPYL ACETATE EASTMAN C5H10-02 .68 3 2.0000

N-PROPYL BUTYRATE EASTMAN C7H14-02 1.243 2.0000

93 15159 4130 102 1

98 15161 4244 93 2

92 17682 4842 98 1

102 18618 5211 106 2

100 18557 5134 107 1

106 17332 4859 103 2

94 22342 7076 103 1

102 21136 6746 100 2 1 2

blank card

Prologue:

Cards 1 and 2 - These cards are for identifying information the user wishes to provide. The first card contains the conditions, and the second card the headings to be printed immediately above the conditions.

Card 3 - Standard compound. Columns 1-66: compound name; columns 67-70:log k for standard; columns 71-80: theoretical H/C ratio of standard.

Card 4 - Blank corrections. Columns 1-5:CO_2 peak blank; columns 6-80:H_2O peak blank.

Card 5 - Correction factors. Columns 1-16:linearity factor for position one CO_2 peak; columns 17-32: linearity factor, position two CO_2 peak; columns 33-48: linearity factor, position one H_2O peak; columns 49-64: linearity factor, position two H_2O peak; columns 65-80: log k value correction factor.

Data Sets:

Each group consists of a card for each of the two standards, followed by heading cards for each compound between this set of standards and the next, followed by the individual run values. All three sets of cards must be in the order of determination.

Data cards for standards and unknown runs follow the same format: Columns 1-16:first baseline reading; columns 17-32:CO_2 peak height; columns 33-48:

H_2O peak height; columns 49-64:second baseline reading; columns 65-80:valve position. All values are reported as integers anywhere within the column limits. No decimal point is necessary.

The second standard card must have the valve position appear in columns 65-66. Columns 67-68 show the number of heading cards to follow (maximum 10) and the remaining columns indicate the total number of data cards (maximum 20) appearing in this group, including the two standards.

Next come the compound identification cards; one per compound. There are two compounds in the example. Columns 1-66 contain the compound name; columns 67-70, the log k; columns 71-74, the number of determinations for this compound (maximum 10); columns 75-80, the theoretical H/C ratio.

The sample determinations then follow in order.

Epilogue:

The last three cards in the example demonstrate the format for the epilogue. Two standards appear, followed by a blank card. The last standard must have a 1 punched in columns 67-68 and a 2 in columns 69-80 for the program to exit properly and be reset for a new data batch concatenated after the blank card.

The printed output from the program lists

the comment cards followed by information concerning the standard. The data sets then follow as shown in the data tables except that two sets of average and formula data are provided. The correction for log k is applied only to the second set of average and formulas. This arrangement allows the data for computing the log k correction to be taken from the printout if a value of zero is inserted for log k on card five. The output ends with the relative standard deviation for the batch of data.

A Program for the Calculation of H/C Ratios

```
   5      REPST:PROCEDURE OPTIONS(MAIN);
   6      DCL(Z,R,SRATIO,B1(20),B2(20),CO2(20),H2O(20),RATIO(10),X(20),Y(20),
   7      LIN(4),STX(4),STY(4),STR(4),CMR(20),SX(40),SY(40),CB,     SBX(10),SBY(10)
   8      ,AV(2),T(10),S(2,10),W,WA,CORR,SK,SIG,ER(2),LOW,HIGH,DP,HONE,HN(2,12),
   9      HFOR,RES(2,12),  BL(2),CK(10),CMK(20)) DEC FLOAT,
  10      SIGT(8) DEC FLOAT INITIAL(1.38,1.53,1.65,1.73,1.80,1.86,1.92,1.96),
  11      (POS(20), V,     M,N,P,I,J,Q,ND(10),STO(4),STC(2),K,L,K1,JA,CHK,CMN(20),
  12      SP(40),SO(40),SBP(10),SBO(10),CN(2,12),IND(2),INDEX,CC,U,A,B,TEM,ETFO)
  13      FIXED BINARY(15,0),   (CMT,HDR)CHAR(80),TESTR(10) CHAR(3),
  14      (STNRD,COMPOUND(10),CMC(20)) CHAR(66),(SIGN(2,12),CD) CHAR(1);
  15      ON ENDFILE(SCARDS) GO TO E;
  16      D:GET FILE(SCARDS) EDIT(CMT,HDR,STNRD,SK,SRATIO,BL,LIN,CORR) (2 A(80),
  17      A(66),F(4),F(10),F(5),F(75),5 F(16));
  18      PUT FILE(SPRINT) EDIT(HDR,CMT,'STANDARD IS  ',STNRD,'  SRATIO=',SRATIO,
  19      '  LOG K=',SK)  (PAGE,2(A(80),SKIP),A,A(66),A,F(5,4),A,F(4,2));
  20      K=1;L=1;K1=0;Q=1;CHK=0;STO=0;W=0;WA=0;
  21      F:GET FILE(SCARDS) EDIT(B1(1),CO2(1),H2O(1),B2(1),POS(1),      B1(2),
  22      CO2(2),H2O(2),B2(2),POS(2),M,N,(COMPOUND(I),CK(I),ND(I),RATIO(I) DO I=1
  23      TO M),(B1(J),CO2(J),H2O(J),B2(J),POS(J) DO J=3 TO N))
  24      (5 F(16),            4 F(16),2 F(2), F(12),(M)(A(66),2 F(4),F(6)),
  25      (N-2)(5 F(16)          ));   K1=K1+2;
  26      DO I=1 TO N;
  27      X(I)=H2O(I)-BL(2)-(B1(I)+B2(I))/2;
  28      Y(I)=CO2(I)-BL(1)-(B1(I)+B2(I))/2;END;
  29      DO I=1 TO 2;
  30      IF POS(I)=1 THEN P=K1-1;ELSE P=K1;  STY(P)=Y(I);STR(P)=X(I)/Y(I);
  31      STO(P)=L;L=L+1       ;STX(P)=X(I); END;STC(K1/2)=M;
  32      IF RATIO(1)=0 THEN DO;CHK=1; GO TO G;END;ELSE;
  33      DO I=1 TO M;
  34      CMC(K)=COMPOUND(I);CMN(K)=ND(I);CMR(K)=RATIO(I);CMK(K)=CK(I);K=K+1;END;
  35      DO I=3 TO N;
  36      SX(Q)=X(I);SY(Q)=Y(I);              SP(Q)=POS(I);SO(Q)=L;L=L+1;
  37             Q=Q+1;END;
  38      IF CHK=0 THEN IF K1<4 THEN GO TO F;ELSE;ELSE;
  39      G:PUT FILE(SPRINT) EDIT(STO(1),'   STANDARD H2O PEAK=',STX(1),
  40      '   CO2 PEAK=',STY(1),'   RATIO=',STR(1),      STO(2),STX(2),STY(2),
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41      STR(2)) (SKIP(3),F(10), 2(A,F(8,1)),A,F(8,5),SKIP,F(10)  ,X(21),F(8,1),
42      X(12),F(8,1),X(9),F(8,5));
43      IF K1=2 THEN GO TO H;ELSE;P=0;
44      DO I=1 TO STC(1);   TESTR='   ';AV=0;
45      DO J=1 TO CMN(I);  P=P+1;TEM=SP(P);R=SX(P)*SRATIO/SY(P);
46      S(1,J)=R/(STR(TEM)*(1.0-(LIN(TEM)*LOG10(STX(TEM)/SX(P))))*
47        (1.0-(LIN(TEM+2)*LOG10(STY(TEM)/SY(P)))));
48      S(2,J)=R/(STR(TEM+2)*(1.0-(LIN(TEM)*LOG10(STX(TEM+2)/SX(P))))*
49      (1.0-(LIN(TEM+2)*LOG10(STY (TEM+2)/SY(P)))));
50      T(J)   =(S(1,J)+S(2,J))/2;
51      SBX(J)=SX(P);SBY(J)=SY(P);SBP(J)=SP(P);SBO(J)=SO(P);
52       AV(1)=AV(1)+T(J);END;
53      N=CMN(I);
54      Z=0;AV(1)=AV(1)/N;
55      IF N>2 THEN DO;
56      DO J=1 TO N;
57      R=AV(1)-T(J)  ;Z=Z+R*R;W    =W    +(R/AV(1))**2;WA    =WA    +1;END;
58      WA=WA-1;
59      SIG=(Z/N)**0.5;  DO J=1 TO N;R=T(J)  -AV(1);IF R<0 THEN R=-R; LSE;
60      IF SIG>0.002 THEN IF R/SIG>SIGT(N-2) THEN TESTR(J)='???';
61      ELSE;ELSE;END;END;
62      AV(2)=AV(1)/(1.0-CORR*(SK-CMK(I)));
63      LOW=T(1);HIGH=LOW;
64      DO A=2 TO N;
65      IF T(A)<LOW THEN LOW=T(A);
66       ELSE IF T(A)  >HIGH THEN HIGH=T(A)  ;ELSE;END;
67      DP    =(HIGH-LOW)*100.0/AV(1);SIGN='-';
68       DO J=1 TO 2;
69       ER(J)=(AV(J)-CMR(I))*100.0/CMR(I);
70       DO B=1 TO 12;
71      HONE=B*AV(J);HTWO=HONE;
72      HFOR=HONE-HTWO;
73      IF HFOR>0.5 THEN DO;HFOR=1-HFOR;HONE=HONE+HFOR;SIGN(J,B)='+';END;
74      ELSE HONE=HONE-HFOR;
75      CN(J,B)=B;HN(J,B)=HONE;RES(J,B)=HFOR;
76      IF(B*2)+2<HONE THEN DO;IND(J)=B-1;GO TO CA;END;ELSE;END;IND(J)=12;CA:
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 77      END;  DO J=1 TO 2;IF IND(J)~=1 THEN DO;INDEX=IND(J);
 78      CE:DO B=2 TO INDEX;
 79      IF RES(J,B)<RES(J,(B-1))  THEN DO;
 80      CB=RES(J,B);RES(J,B)=RES(J,(B-1));RES(J,(B-1))=CB;
 81      CB=HN(J,B);HN(J,B)=HN(J,(B-1));HN(J,(B-1))=CB;
 82      CC=CN(J,B);CN(J,B)=CN(J,(B-1));CN(J,(B-1))=CC;
 83      CD=SIGN(J,B);SIGN(J,B)=SIGN(J,(B-1));SIGN(J,(B-1))=CD;END;ELSE;
 84      END;INDEX=INDEX-1;IF INDEX=1 THEN GO TO CF;ELSE GO TO CE;
 85      END;ELSE;CF:END;
 86      PUT FILE(SPRINT) EDIT(CMC(I),CMR(I),'  LOG K=',CMK(I),(SBO(J),'H2O=',
 87      SBX(J),'CO2=',SBY(J),'VALUES=',S(1,J),S(2,J),    'RATIO=1:',T(J),
 88      'VALVE POS=',SBP(J),TESTR(J)  DO J=1 TO N),'AVERAGE=',AV(1),'  %ERROR=',
 89      ER(1),'   %SPREAD=',DP , 'PROBABLE FORMULAS' ,(';C' ,CN(1,U),'H',HN(1,U)
 90      ,SIGN(1,U)  DO U=1 TO IND(1)),  'AVERAGE2=',AV(2),'  %ERROR=',ER(2),
 91      'PROBABLE FORMULAS' ,(';C' ,CN(2,V),'H',HN(2,V),SIGN(2,V) DO V=1 TO IND
 92      (2)))    (SKIP(2),A(66),F(6,4),A,F(6,2),
 93                              (N)(SKIP,F(4),2(X(3),A,F(7,1)),X(3),A,2 F(8,4),
 94            X(3),A,F(6,4),X(3),A,F(2),A(3)),SKIP,A,F(6,4),2(A,F(6,2)),SKIP,A,
 95      (IND(1))(A,F(2),A,F(2),A(1)),
 96       SKIP,A,F(6,4),  A,F(6,2) ,SKIP,A,
 97      (IND(2))(A,F(2),A,F(2),A(1)));
         END;
         DO I=3 TO K1;
100      STX(I-2)=STX(I);STY(I-2)=STY(I);STR(I-2)=STR(I);STO(I-2)=STO(I);END;
101      K1=K1-2;
102      IF CHK=1 THEN GO TO G; ELSE;
103      DO I=1 TO K-STC(1)-1;  J=I+STC(1);
104      CMC(I)=CMC(J);CMN(I)=CMN(J);CMR(I)=CMR(J);CMK(I)=CMK(J);END;K=K-STC(1);
105      DO I=1 TO Q-P-1;J=I+P;
106      SX(I)=SX(J);SY(I)=SY(J);              SP(I)=SP(J);SO(I)=SO(J);END;Q=Q-P;
107      STC(1)=STC(2);
108      GO TO F;
109      H:W=((W/WA)**0.5)*100;
110      PUT FILE(SPRINT)  EDIT('%REL STD DEV=',W)
111                        (SKIP,A,F(6,2));
112      GO TO D;  E:END REPST;
```

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