Gas Chromatographic/Infared Spectral Analysis Using a Computer Integrated Circular Variable Filter Spectrometer

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GAS CHROMATOGRAPHIC/INFRARED SPECTRAL ANALYSIS USING A COMPUTER INTERFACED CIRCULAR VARIABLE FILTER SPECTROMETER

BY

MARK AHMADJIAN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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ABSTRACT

Gas chromatography/infrared spectroscopy (GC/IR) is a powerful analytical technique for "on-the-fly" analysis of multi-component mixtures. The gas chromatograph separates the mixture into single components which are then analyzed by the spectrometer as they elute off the gc column and into the spectrometer. Standard instrumentation usually involves a gas chromatograph, a fourier transform infrared spectrometer (FT-IR), and a computer system. The end products are a reconstructed gas chromatogram and a number of infrared spectra for each of the mixture components. These pieces of information often allow the identification of an unknown mixture. A GC/FT-IR/Computer System, however, is an elaborate and expensive laboratory instrument which requires extensive care, maintenance, and a well trained operator. It is not designed for field use and is seldom deployed outside of a laboratory. The objective of this research therefore was to develop a simple and inexpensive GC/IR/Computer System which would be rugged, easy to use, and readily adaptable for field use.

To do this, we interfaced a fast scanning circular variable filter (CVF) infrared spectrometer to a mini-computer and then coupled the spectrometer/computer to a gas chromatograph. The system was configured such that the same end products generated by a GC/FT-IR/Computer System, i.e. reconstructed gas chromatograms and infrared spectra, are also generated by this GC/CVF-IR/ Computer System. A five component mixture of hazardous class type compounds with closely related boiling points was analyzed to demonstrate the feasibility of this new system.
ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. Chris W. Brown, for his guidance, teaching, and most of all his friendship throughout the years.

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Mark Ahmadjian
This thesis was prepared in accordance with the standard thesis plan.
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INTRODUCTION

Since the 1950s infrared spectroscopy has been used to identify components separated by gas chromatography. Early efforts\textsuperscript{1-10} involved grating or prism type spectrometers which, however, lacked the wavelength scanning speed to adequately measure chemical compounds eluting from gas chromatographs in real time, i.e. on-the-fly. It was usually necessary to trap the components and hold them in a trap or matrix until an infrared spectrum of the sample was obtained. This was time consuming and did not provide for generation of reconstructed gas chromatograms. Not until Cooley and Tukey (11) developed their algorithm for fast processing of interferograms and the ready availability of laboratory computers did actual GC/IR "on-the-fly" analysis become practical. For the first time a gas chromatograph could be coupled directly to a Fourier Transform - Infrared instrument (FT-IR) for analysis of multi-component mixtures with results plotted out by computer in the form of reconstructed gas chromatograms with corresponding spectra for the individual gas chromatographic peaks. The ability of the FT-IR system to rapidly acquire interferograms over a broad spectral region revolutionized the analysis of mixtures by gas chromatography. Today there are a number of GC/FT-IR instruments available (Nicolet, Perkin-Elmer, Digilab, IBM, and others); however, they are expensive, complicated (moving mirrors, air bearings, lasers, extensive data processing requirements), and are found only in a limited number of laboratories. In addition, they are not considered to be field type instruments. The objective of this research was to
develop a simple, inexpensive, and transportable GC/IR system using a circular variable filter (CVF) infrared spectrometer controlled by a small mini-computer. This combination could provide facilities with an inexpensive and easy to use survey type instrument for fast characterization of multi-component mixtures.

To do this we used a Beckman IR-102 fast scanning CVF infrared spectrometer to measure gas chromatographic effluents by passing the volatile fractions through a gold plated light pipe in the optical path of the spectrometer while it scanned the 2.5 - 14.5 um region.

History

Analysis of gas chromatographic fraction with an IR-102 is not new. Beckman Instruments developed this instrument in 1965 for this purpose. At that time though there were few laboratory computers in routine use and spectra were recorded by a fast oscillographic recorder which necessitated manually and laboriously examining many feet of heat sensitive chart paper to pick out the infrared spectrum of interest. Needless to say this technique was not accepted by the analytical community and only a few IR-102's were ever sold. There is no evidence at Beckman Instruments or in the literature that this type of fast scanning CVF spectrometer was ever interfaced to a computer to perform the same tasks as a GC/FT-IR (however, the U.S. Air Force did use computerized CVF spectrometers for chemical analysis of the earth's upper atmosphere from sounding rockets and high altitude balloons).
This paper will show how a GC/IR-102 can be interfaced to a Data General Corporation NOVA 3/12 mini-computer and developed the software to perform GC/IR analysis on-the-fly. The system is demonstrated on a one component solution and then on a five component mixture of closely boiling compounds; acetone b.p. 56 C, chloroform b.p. 61 C, methanol b.p. 64 C, carbon tetrachloride b.p. 76 C, and benzene b.p. 80 C. The GC/IR not only provides a reconstructed gas chromatogram comparable to standard flame ionization detection (FID) gas chromatograms but, also generates infrared spectra for each of the chromatographic peaks.

EXPERIMENTAL SECTION

Instrumentation

Figure 1 is a block diagram of the GC/IR computer system. A HP-7100 gas chromatograph with a Supelco 10% SP-2250, 100/120 Supelcoport, 1/8”x10' column was directly coupled to the Beckman IR-102 gold plated 10 cm long light pipe. The interface line was heated to 150° C and was thermostatically controlled. 100% of the g.c. effluent was allowed to pass through the sample cell. The flow rate was varied from 10-15 cc/minute. The optical path and components of the IR-102 were used as designed except it was no longer necessary to use the trap and hold option valves for the sample cell. Figure 2 shows the optical layout. A Nernst glower was used as the IR source and chopped at 120 Hz. The beam is directed through the heated sample cell. A torroidal mirror collected the radiation and reflected it onto a flat mirror and through the CVF wheel,
Figure 1. Block diagram of the GC/IR computer system.
Figure 2. Beckman IR-102 optical diagram (redrawn from Beckman user's manual)
a slit, and onto a thermocouple detector. The filter wheel consists of three wedge shaped segments covering the infrared wavelength range of 2.5 - 4.5 um, 4.4 - 8.0 um, and 7.9 - 14.5 um. The analog output signal from the detector is passed through a signal conditioning channel where it is inverted and amplified to 0 to +10 VDC. The signal is then sampled by the DGC NOVA 3/12 16 bit analog digital converter. The sampling rate is determined by an internal oscillator, 1000 Hz clock, under software control. The digitized signal is then stored in contiguous data blocks on a 5 Megabit cartridge disk subsequent to any additional processing. The data can then be processed and displayed in a variety of ways. Usually a Total Wavelength IR Plot (TWIRP), i.e. the reconstructed gas chromatogram, is first generated to show how many components were in the mixture. The individual spectra for each of the reconstructed g.c. peaks can then be displayed as a function of scan number. The spectra can also be signal averaged, smoothed, and subtracted. Figure 3 shows a typical sequence of events for this analysis.

**Samples**

Mixtures were prepared by mixing equal volumes of reagent grade acetone, chloroform, methanol, carbon tetrachloride, and benzene in carbon disulfide.

**Software**

Eight computer programs were written for this system. By using
Figure 3. Sequence of events for the GC/IR computer analysis.
individual programs we were able to develop, test, and debug the hard­
ware/software one phase at a time. The individual programs are brought
into memory by a main controller program. When not in use, they reside
in one of the user directories on disk. The following is a list of the
programs with a brief description of each. Copies of the programs are
attached as an appendix.

GCIR: This is the main controller program, the executive, and allows
the other programs to be brought into use via swap commands.

GCIRAD: This program and its subroutines samples the IR-102 analog detector
signal through a multiplexer, performs an analog to digital conversion
via the analog digital converter (ADC), and stores the digitized data
into an optimally sized contiguous data file on disk.

GCIRSUB: A subroutine used by GCIRAD to initiate data acquisition and store
data on disk.

ADGCIR: An assembly language subroutine to sample the ADC.

GCIRCAL: Calibrates all the individually acquired IR spectra using the
0 VDC signal between filter elements one and three.

TWIRP: Plots out the reconstructed gas chromatograms.
RESULTS AND DISCUSSION

We want to show that this GC/IR system using a computer interfaced IR-102 infrared circular variable filter spectrometer is able to analyze a multi-component mixture in a manner similar to that of a sophisticated GC/FT-IR/computer system. As in any research endeavor, we started off with a simple feasibility demonstration which involved the measurement of a one component mixture. In this case we used acetone in carbon disulfide. Carbon disulfide was chosen as the solvent because our laboratory was using it on a routine basis for IR analysis of hydrocarbon solutions and because carbon disulfide has a large IR "window" and would therefore present minimal spectral interferences for low boiling compounds. To prevent gross $CS_2$ contamination of the gold plated IR sample cell, the solvent peak was vented via a bypass valve to an exhaust hood. Once the $CS_2$ had eluted from the g.c. column (time as determined from previous flame ionization detection measurements) the g.c. column effluent was rerouted to the Beckman IR-102 sample cell and the analog signal from the IR-102 detector amplifier was digitized via program GCIRAD. After sixty full wavelength scans, data acquisition was terminated and the IR data was transformed from contiguous data.
data blocks to random data files, calibrated, converted to absorbance units, and plotted out in the form of a reconstructed gas chromatogram (figure 4). We call this a Total Wavelength IR Plot (TWIRP). The x-axis is plotted as a function scan number (same as time), i.e. each cycle of the circular variable filter wheel from 2.5 to 14.5 um is one scan. In this case sixty scans are plotted. The y-axis represents the integrated signal of each single scan, i.e. the summation of each data point over the entire spectral region of one scan; \( \sum A_i/\text{scan} \). For example, if each scan covered 2.5 to 3.0 um and a data point was taken at every 0.1 um, the result would be:

\[
\begin{align*}
\text{scan } #1 &= A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0} \\
\text{scan } #2 &= A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0} \\
\text{scan } #3 &= A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0} \\
&\vdots \\
&\vdots \\
&\vdots
\end{align*}
\]

In this actual case the following would be represented:

\[
\text{scan } #xxx = A_{2.5} + A_{2.6} + A_{2.7} + \ldots \ldots + A_{14.5}
\]
or in other words:

\[
14.5 \\
\text{scan } #xxx = \sum A_i \\
i=2.5
\]
The $A_i$'s are then normalized and plotted as a function of increasing scan number and we end up with a reconstructed gas chromatogram or a TWIRP. From this TWIRP, the number of compounds in the injected mixture can be easily seen. Of course the compounds need to have IR active groups to cause a signal on the IR detector. In this initial case, after sixty scans, there is one TWIRP peak starting at scan #25. Figure 5 shows the IR spectra associated with the scan numbers 22, 24, 25, 26, and 28 plotted as a function of IR intensity vs wavenumber. Scan #22 is instrument background and since this is a single beam spectrometer the spectrum is due to ambient CO$_2$ and H$_2$O. At scan #24 however a distinctly different spectrum is seen and its intensity continues to increase at scan #25. At scan #28 the sample has completely eluted from the g.c. column thru the cell and all that is left is ambient background. These two figures would give two significant pieces of information for identification of an unknown sample. From having previously characterized the SP-2250 column, knowing the g.c. oven temperature is at 150°C, and seeing the sample elute after 24 scans (144 seconds), this would identify it as a low boiling compound. Then by examining the IR spectrum and looking up the wavelengths of the absorbance bands a preliminary identification of the eluting compound would be made. Further chemical analysis would confirm that finding. Similar runs were performed for acetone, methanol, carbon tetrachloride, and benzene.

Having thus demonstrated the GC/IR system on one component solutions
Figure 4. TWIRP (Total Wavelength IR Plot) 
A reconstructed gas chromatogram

Figure 5. Spectral plots corresponding to the TWIRP peak in figure 4
Figure 6. TWIRP for a five component mixture consisting of (1) methanol, (2) acetone, (3) chloroform, (4) carbon tetrachloride, and (5) benzene in a carbon disulfide solution (CS2 vented to atmosphere).
the next step was the analysis of a multi-component mixture. Five compounds closely related in boiling points were chosen to provide a test as to whether we could separate and obtain spectra on-the-fly of rapidly eluting compounds. The five components, acetone b.p. 56°C, chloroform b.p. 61°C, methanol b.p. 64°C, carbon tetrachloride b.p. 76°C, and benzene b.p. 80°C were mixed in equal volumes into a carbon disulfide solution. This solution not only provided a stringent test as far as separation and identification but was also typical of compounds found in hazardous waste sites and which must be analyzed in an actual facility prior to the start of any cleanup operations.

The same procedure used for the one component solution was used for this five component analysis. The CS$_2$ was vented and the scan and acquisition initiated. Spectral scans were recorded, stored on disk, calibrated, converted to absorbance units, and the TWIRP displayed on the plotter as shown in figure 6. It is immediately evident that we have a five component mixture as evidenced by the reconstructed g.c. peaks at scan #14,22,41,47, and 55. Even though we had a known solution of equal amounts of compounds, we do not necessarily end up with equal intensity peaks. This is because each component has different IR active groups and absorbance coefficients. For example, CS$_2$ has very little IR absorbance in the 2.5 to 14.5 um region compared to acetone which has strong IR absorbance. Therefore the IR-102 detector would not "see" very much CS$_2$ relative to acetone and the resultant integrated IR signal would be very small. The same is true for all compounds and since the TWIRP is normalized to the strongest integrated signal, the
reconstructed g.c. peaks are all relative in intensity.

Again as done previously the spectra associated with each reconstructed g.c. peak are plotted out as a function of % transmission vs wavelength (figure 7). Scan #1 is the instrument background and the subsequent scans correspond to the five g.c. peaks. Figures 8, 9, 10, 11, 12, and 13 are the spectra displayed for more detailed analysis.

Scan #1: Instrument background. Absorptions correspond to atmospheric H2O and CO2.

Scan #14: Represents TWIRP peak #1 which is due to methanol.

Scan #22: Represents TWIRP peak #2 which is due to acetone.

Scan #41: Represents TWIRP peak #3 which is due to chloroform.

Scan #47: Represents TWIRP peak #4 which is due to carbon tetrachloride.

Scan #55: Represents TWIRP peak #5 which is due to benzene.

For a real world application we would not know apriori what each IR spectrum is due to, but there is significant information contained in the GC/IR TWIRP and spectra to allow an educated selection of possible candidates. In scan #14 there is strong absorption at 3.0 um which is very
Figure 7. Infrared spectra for the five component mixture corresponding to the TWIRP in figure 6. Scan #1 is the instrument background while scans 14, 22, 41, 47, and 55 correspond to the TWIRP peaks #1, #2, #3, #4, and #5 respectively.
Figure 8. Infrared spectrum for scan #1 showing instrument background. Absorptions are due to ambient CO$_2$ and H$_2$O.
Figure 9. Infrared spectrum for scan #14 which corresponds to the first TWIRP peak of figure 6 and is due to methanol.
Figure 10. Infrared spectrum for scan #22 which corresponds to the second TWIRP peak of figure 6 and is due to acetone.
Figure 11. Infrared spectrum for scan #41 which corresponds to the third TWIRP peak of figure 6 and is due to chloroform.
Figure 12. Infrared spectrum for scan #44 which corresponds to the fourth TWIRP peak of figure 6 and is due to carbon tetrachloride.
Figure 13. Infrared spectrum for scan #55 which corresponds to the fifth TWIRP peak of figure 6 and is due to benzene.
characteristic of an \( \sim \text{OH} \) stretch such as in an alcohol. This coupled with the fact that it is a low boiling point compound narrows the search for an unknown compound considerably. For scan #55 an absorption at 3.2 \( \mu \text{m} \) signifies an aromatic compound. Thus, based on very little interpretation the analyst would know the unknown mixture contains five low boiling compounds and that one is an alcohol and one is an aromatic. If only a gc was available, the analyst would know there were five compounds in the mixture and that they were low boiling. The additional IR data provides a great amount of valuable information and significantly narrows the choice of possible candidates for positive identification.

During this investigation we also conducted a comparison between the GC/IR TWIRP and a standard gc flame ionization detector (FID). The same five component mixture used previously was analyzed with the gc column reconnected to the FID as in normal gc operation. Figure 14 shows the comparison between the normal gc output and the TWIRP from the GC/IR. Both plots are similar in that they identify a five component mixture and just as the integrated IR detector signal for each particular compound is different so it is for the FID where the electron rich aromatic ring of benzene gives a much stronger signal than the other compounds. The FID analysis confirms the GC/IR results in regards to the number of components in the mixture.
Figure 14. Comparison of a gas chromatogram (flame ionization detector) to the TWIRP reconstructed gas chromatogram of a five component mixture of acetone, chloroform, methanol, carbon tetrachloride, and benzene.
While checking the reproducibility of the CVF scan and data acquisition we decided to try signal averaging the spectra to decrease the noise in a plotted spectrum. Figure 15 shows the original spectrum and an averaged spectrum where four spectra were added together and then signal averaged. As can be seen there is a noticeable reduction in noise (the original spectra were made noisy on purpose by running at a higher than normal amplifier gain). Also a three point smooth technique was used and again this resulted in noise reduction. As in any case when spectra are digitized and stored in memory a wide variety of signal processing options are possible including expansion, subtraction, and spectral searches to match an unknown to a known. In fact a laboratory which does routine analysis would maintain a spectral library of known compounds as well as a listing of gc elution times for a given gc column at known temperatures and flow rates.

Conclusion

We have demonstrated a simple GC/IR/Computer system to analyze multi-component mixtures "on-the-fly". The system is demonstrated on a five component mixture with closely related boiling points. The resulting reconstructed gas chromatograms and associated IR spectra provide sufficient information to identify each of the five components. This GC/IR consists of a rugged circular variable filter spectrometer and is ideally suited for field use.
Figure 15. Computer processing of Beckman IR-102 spectra demonstrating signal averaging and smoothing techniques.
REFERENCES


APPENDIX

Program Listings and Descriptions

These computer programs were written for use on a Data General Corporation (DGC) NOVA 3/12 mini-computer system with an analog digital converter. The programs were written in Fortran and DGC assembly language.
Program: GCIR.FR

Purpose: This is the main controller program, i.e. executor, for the GC/IR/Computer System.

Method: GCIR.FR allows specific run time programs to be executed via swap commands.

Input: The user needs to specify at the prompt which real time programs are to be run. They are:

1. Data acquisition of the infrared data from the IR-102 signal conditioning electronics.
2. Wavelength calibration of the spectral data.
4. Plotting of the reconstructed gas chromatograms, TWIRPs, and spectra.

Output: User prompts for the above functions.
THIS IS THE MAIN CONTROLLER PROGRAM FOR THE GCIR COMPUTER
SYSTEM. THE RUN TIME PROGRAMS ARE BROUGHT INTO EXECUTION VIA
SWAP COMMANDS. THE FOLLOWING PROGRAMS ALONG WITH THEIR
SUBROUTINES AND LIBRARIES ARE USED:

GCIRAD.FR : TO ACQUIRE DATA AND STORE THIS DATA IN
CONTIGUOUS BLOCKS ON DISK FOR SUBSEQUENT PROCESS
AND DISPLAY.
   GCIRSUB.FR
   ADGCIR.SR
   FORT.LB

GCIRCALIB.FR : TO CALIBRATE THE SPECTRAL DATA ON A FREQUENCY
SCALE
THE CALIBRATION DATA IS THE STORED
FOR SUBSEQUENT USE BY THE PLOTTER PROGRAM.
   NPLAT.SR
   FORT.LB

GCIRAVG.FR : TO SIGNAL AVERAGE SPECTRA
   FORT.LB

GCIRPLOT.FR : TO PLOT OUT SPECTRA
   PLOTTER4ANS.LB
   FORT.LB

20  CALL SWAP('GCIRCALIB,SV',IER)
    GO TO 100

30  CALL SWAP('GCIRAVG,SV',IER)
    GO TO 100

40  CALL SWAP('GCIRPLOT,SV',IER)
    GO TO 100

100  CONTINUE

   WRITE(10,110)
110  FORMAT(' RUN AGAIN? 00=NO, 01=YES ')  
   READ(11,120) JA
120  FORMAT(I2)
   IF(JA.EQ.1) GO TO 1
   STOP
END
CONTINUE

TYPE 'DATA ACQUISITION = 01
TYPE 'CALIBRATION = 02
TYPE 'SIGNAL AVERAGING = 03
TYPE 'PLOTTING = 04

ACCEPT ' ? ' , J

GO TO (10, 20, 30, 40), J

10 CALL SWAP('GCIRAD.SV', IER)
GO TO 100
Program: GCIRAD.FR

Purpose: This program and its subroutines acquire data from the Beckman IR-102 spectrometer.

Method: GCIRAD.FR and its subroutines samples the analog signal from the IR-102 signal conditioning electronics, converts the analog data to digital via the DGC ADC, and stores the digitized data on disk for subsequent processing and display.

Input: The user needs to specify a file name into which to store the data and an ADC sampling rate.

Output: Output are contiguous disk file containing the digitized spectral data from the GC/IR.
THIS PROG AND ITS SUBROUTINES ACQUIRE DATA FROM THE GCIR AT EVERY CLOCK TICK (IF TIME DELAY = 1) A DATA POINT IS TAKEN THE IR DETECTOR ELECTRONICS AND THIS DATA IS STORED IN BLOCKS.

SUBROUTINES: GCIRSUB.FR
ADGCIR.SR

```
DIMENSION JSPEC(10), JDAT(8192)
WRITE(10,2)
2 FORMAT( ' SPECTRUM ID? ' )
READ(11,3) JSPEC(1)
3 FORMAT(S14)
ACCEPT' # OF DISK TRANSFERS TO BE EFFECTED? ',N
ACCEPT' # OF DATA PTS PER DISK TRANSFER? ',I3
ACCEPT' # OF CLOCK PULSES BETWEEN DATA POINTS? ',I4
IF(I3.GT.256) GO TO 5
C
I6=# OF DATA BLOCKS/SCAN
I6=1
GO TO 30
5   D3=I3/256.*
    J3=D3
    R3=D3-I3
    IF(R3) 20,10,20
10   I6=J3
    GO TO 30
20   I6=J3+1
30   CONTINUE
C
IFILE=# OF DATA BLOCKS PER ENTIRE RUN
IFILE=I6*(N+3)
C
I7=SIZE OF DIMENSION DATA ARRAY
I7=256*I6
C
SET UP DATA FILE ON DISK
CALL DFILW(JSPEC,IER)
TYPE' DFILW IER = ',IER
```
CALL CFILW(JSPEC,3,IFILE,IER)
IF(IER.NE.1) TYPE 'ERROR ERROR ERROR ERROR ERROR'
TYPE 'CFILW IER = ' IER

CALL OPEN(O,JSPEC,2,IER)
TYPE 'OPEN IER = ' IER

CALL GCIRSUB(JDAT,I3,I4,I6,I7,N)

CONTINUE
STOP
END
Program: GCIRSUB.FR

Purpose: This is a fortran subroutine used by GCIRAD.FR to initiate data acquisition and write the data onto disk.

Method: Based on the inputs from GCIRAD.FR specifying the file name and the length of time for data acquisition this program will run an assembly language subroutine, ADGCIR.SR, to sample the ADC and write the data out to a disk.

Output: Contiguous data blocks on disk.
SUBROUTINE FOR GCIRAD.FR (ACQUIRING DATA FROM THE GCIR AND 
STORING THIS DATA IN CONTIGUOUS DATA BLOCKS ON DISK).

****************************************************************

SUBROUTINE GCIRSUB (JDAT, I3,I4,I6,I7,N)
DIMENSION JDAT(I7), INFO(256)
COMMON IDAT(8192)
EQUIVALENCE (IDAT(1),IARRAY)
DO 90 I=1,I7
   JDAT(I)=0
   INFO(1)=I3
   INFO(6)=I4
   INFO(11)=I6
   INFO(16)=I7
   INFO(21)=N
WRITE(10,100)
100 FORMAT(' HIT RETURN TO START DATA ACQUISITION ')
READ(11,110) KR
110 FORMAT(I2)
   J=2
   LR=0
   DO 140 IL=1,N
   CONTINUE
   CALL ADGCIR(IARRAY,I4,I3)
   DO 130 I=1,I3
   JDAT(I)=IDAT(I)
   CALL WRBLK(0,J,JDAT,I6,IER)
   IF (IER.NE.1) TYPE 'ERROR ERROR ERROR ERROR ERROR ERROR'
      J=J+I6
   INFO(21)=IL
   CALL WRBLK(0,1,INFO,1,IER)
   LR=LR+1
   CALL WRBLK(0,1,INFO,1,IER)
   TYPE IER
   TYPE 'SET UP FOR CALIBRATION RUN? 00-NO, 01-YES'
   READ(11,110) JCL
   IF (JCL.EQ.0) GO TO 150
   PAUSE HIT RETURN TO START CALIBRATION RUN
   GO TO 115
150 CONTINUE
RETURN
STOP
END
Program: ADGCIR.SR

Purpose: This assembly language subroutine runs the ADC and stores the digitized data into RAM.

Method: ADGCIR.SR samples the ADC channel #0 (multiplexed), stores the data into an accumulator, and then loads the accumulator into a RAM array for subsequent reading and writing by GCIRSUB.FR.

Inputs: No user inputs are required.

Output: Digitized infrared spectral data in RAM storage.
TTY = 10
CLK = 14
A0C0 = 21
FS, = 3
T, = -137

FS,
ADGCIR: JSR @, FARL
STA 0, AC0
STA 1, AC1
STA 2, AC2
LDA 0, T, 40, 3
STA 0, ARRAY
LDA 0, @T, +1, 3 ; GET DELAY
STA 0, STIME
LDA 0, @T, +2, 3 ; GET # OF DATA POINTS
STA 0, COUNT
GO: LDA 0, CNTP
STA 0, CNTEMP
REPT: LDA 1, STIME
\SYSTM
\DELAY
JSR ERR
LDA 0, C5
DOA 0, A0C0
INTDS
NI0S A0C0
SKPDN A0C0
JMP -1
N0CC 0, A0C0
INTEN
LDA 2, ARRAY
STA 0, 0, 2
INC 2, 2
STA 2, ARRAY
SUBZL 0, 0
DSZ COUNT
JMP GO
RET: LDA 0, AC0
LDA 1, AC1
LDA 2, AC2
JSR @, FRET
Program: GCIRCAL.FR

Purpose: This program transforms the digitized infrared data into spectra.

Method: GCIRCAL.FR calibrates the infrared spectra on a wavelength scale using the 0 VDC signal between the circular variable filter elements one and three.

Inputs: The user needs to specify the file name the digitized data is stored in and a new file name to write the calibrated data out to.

Output: Output is a random data file containing calibrated spectra.
THIS PRG IS TO DETERMINE THE ARRAY BOUNDARIES OF INDIVIDUAL SPECTRA ACQUIRED FROM THE GCIR SYSTEM VIA PRG GCIR, AND TO STORE THE INDIVIDUAL SPECTRA IN A RANDOM DATA FILE

DIMENSION JSPEC(10), INFO(256), JDAT(8192), IPT(256)
DIMENSION YDAT(500), KI(5), KDAT(1051), TDAT(1050)
WRITE(10,2)
FORMAT(′ SPECTRUM ID? ′)
READ(11,3) JSPEC(1)
FORMAT(S14)

CALL OPEN(0, JSPEC,2, IER)
TYPE′OPEN IER =′, IER

CALL RDBLK(0,1, INFO,1, IER)
TYPE′RDBLK IER =′, IER

I3=INFO(1)
I6=INFO(11)
17=INFO(16)
N=INFO(21)
TYPE′# OF DATA PTS/TRANSFER =′, I3
TYPE′# OF DISK TRANSFERS =′, N

TYPE′NEW FILE NAME? ′
READ(11,3) JSPEC(1)
CALL DFILW(JSPEC, IER)
TYPE′DFILW IER =′, IER
CALL CFILW(JSPEC,2, IER)
TYPE′CFILW IER =′, IER
CALL OPEN(1, JSPEC,2, IER,2)
TYPE′OPEN IER =′, IER
ACCEPT ′SIGNAL AVG? ′ 00=NO, 01=YES ′, KSIG
IP=5
IC=0
DO 300 JS=1, N
I4=2+(I6*JS)-I6

CALL RDBLK(0, I4, JDAT, I6, IER)
TYPE′RDBLK IER =′, IER

IL=1
DO 10 I=1, 13
IF(JDAT(I).GT.300) GO TO 10

K=I+160
DO 20 J=I, K
IF(JDAT(J).LE.300) GO TO 20
I=J
GO TO 10
CONTINUE
C5: 6
CL: 2
CH: 3
AC0: 0
AC1: 0
AC2: 0
DTIME: 300,
STIME: 0
COUNT: 0
CNTP: 1,
CNTTEMP: 0
ARRAY: 0
ERR: .SYSTM
    .BREAK
    .END
Program: TWIRP.FR

Purpose: This program will plot the reconstructed gas chromatograms.

Method: TWIRP.FR inputs the infrared spectral data from the random files, sums the intensities/spectrum, and plots the sums as a function of scan number.

Inputs: The user needs to specify the file name, noise filtering if desired, and expansion factors for the plotter.

Output: Output is a Total Wavelength IR Plot, TWIRP, i.e. a gas chromatogram.
DO 30 J=I,J3
IF(JDAT(J).GE.1000) GO TO 25
CONTINUE
GO TO 11
25 IF((J+1050).GT.13) GO TO 11
IPT(IL)=J
I=J
IL=IL+1
10 CONTINUE
11 CONTINUE
IL=IL-1
IF(KSIG.EQ.1) IL=IL-1
DO 100 I=1,IL
IPT1=IPT(I)
IPT2=IPT(I)+1050
L=1
DO 200 K=IPT1,IPT2
KDAT(L)=JDAT(K)
200 L=L+1
IF(KSIG.EQ.0) GO TO 202
IPT1=IPT(I+1)
IPT2=IPT(I+1)+1050
L=1
DO 201 K=IPT1,IPT2
KDAT(L)=(KDAT(L)+JDAT(K))/2
201 L=L+1
202 CONTINUE
IC=IC+1
YSUM=0.0
DO 210 K=1,1050
TDAT(K)=KDAT(K)
TDAT(K)=TDAT(K)*10,./4096.01
TDAT(K)=(ALOG10(TDAT(K)))*10.
TDAT(K)=10.0-TDAT(K)
210 YSUM=YSUM+TDAT(K)
YDAT(IC)=YSUM
TYPE IC ="",IC
100 CONTINUE
300 CONTINUE
JV=1
DO 9 J=1,IC
IF(YPD(JV),GE,YPD(J)) GO TO 9
JV=J
9 CONTINUE

XF=4096/YPD(JV)

DO 8 J=1,IC
KD(J)=YPD(J)*XF
KI(1)=IC

CALL WRTR(1,0,KI,5,IER)
TYPE 'IER =' ,IER

CALL WRTR(1,5,KDAT,IC,IER)
TYPE 'IER =' ,IER

TYPE KDAT
CALL RESET
STOP
END
Program: GCIRSPEC.FR

Purpose: This program plots out individual spectra corresponding from the TWIRP.

Method: GCIRSPEC.FR obtains the calibrated spectral data from the data file and plots it as a function of wavelength.

Inputs: The user needs to specify the file name, the spectrum number, plotter expansion factors.

Output: Infrared spectra
THIS PRG IS TO DETERMINE THE ARRAY BOUNDARIES OF INDIVIDUAL SPECTRA ACQUIRED FROM THE GCIR SYSTEM VIA PRG GCIR..., AND TO DETERMINE THE TOTAL WAVELENGTH IR PLOT IN A MANNER ANALOGOUS TO THAT USED FOR THE GC/MS SYSTEM PRG TOTUNFR.

DIMENSION JSPEC(10),KI(5),KDAT(1050),JDAT(1050),YDAT
DIMENSION ZDAT(1000),PLTY(300),PLTX(300)
CALL INITIAL(6,200,10.5,30.0)

1 CONTINUE
CALL PLOT(0.0,2.0,-3)
TI=8.0/4096
WRITE(10,2)

2 FORMAT( ' SPECTRUM ID? ' )
READ(11,3) JSPEC(1)

3 FORMAT(S14)

CALL OPEN(0,JSPEC,2,IER,2)
TYPE'OPEN IER =',IER
CALL RDRW(0,0,KI,5,IER)
TYPE'RDRW IER =',IER

IC=KI(1)
TYPE'IC =',IC
CALL RDRW(0,5,KDAT,IC,IER)
TYPE 'WRTR IER =',IER
GO TO 401
IF=KI(1)-1
L=0
IPT=5

TYPE'$ OF SPECTRA =',IF
ACCEPT 'SIGNAL AVG? NO=0, YES=1 ' ,ISIG
DO 300 I=1,IF
CALL RDRW(0,IPT,JDAT,1050,IER)
TYPE'RDRW IER =',IER

IF(ISIG.EQ.0) GO TO 4
IPT1=IPT+1050
CALL RDRW(0,IPT1,KDAT,1050,IER)
TYPE 'RDRW IER =',IER

4 YSUM=0.0

DO 200 J=1,1050
JDAT(J)=4096-JDAT(J)
IF(ISIG.EQ.0) GO TO 200
KDAT(J)=4096-KDAT(J)
JDAT(J)=(JDAT(J)+KDAT(J))/2

200 YSUM=YSUM+JDAT(J)

48
L=L+1
ZDAT(L)=YSUM
IPT=IPT+1650
300 CONTINUE

401 CONTINUE
L=IC
DO 402 I=1,L
402 ZDAT(I)=KBAT(I)
JM=1
DO 7 I=1,L
IF(ZDAT(JM),LE,ZDAT(I)) GO TO 7
JM=I
7 CONTINUE
ZMIN=ZDAT(JM)
TYPE,'MIN VALUE =''ZMIN

DO 8 I=1,L
YDAT(I)=ZDAT(I)-ZMIN
C SCALE DATA
JV=1
DO 9 IK=1,L
IF(YDAT(JV),GE,YDAT(IK)) GO TO 9
JV=IK
9 CONTINUE
XF=8.0/YDAT(JV)
DO 400 IK=1,L
YDAT(IK)=YDAT(IK)*XF
400 CONTINUE

ACCEPT,'LOW LEVEL DIGITAL FILTER IN PLOTTER UNITS?
DO 500 IK=1,L
YDAT(IK)=YDAT(IK)-XL
IF(YDAT(IK),LT,0.0) YDAT(IK)=0.0
500 CONTINUE

ACCEPT,'Y-EXPANSION FACTOR FOR PLOTTER? 'XY
ACCEPT,'X-AXIS INCREMENT PER SCAN? 'XX
DO 600 IK=1,L
YDAT(IK)=YDAT(IK)*XY
IF(YDAT(IK),GT,8.0) YDAT(IK)=8.0
600 CONTINUE

YDAT(IK)=8.0-YDAT(IK)+1.0
YDAT(IK)=(ALOG10(YDAT(IK)))*10.
YDAT(IK)=10.0-YDAT(IK)
YSUM=YDAT(IK)
XPLT=IK**XX
PLTX(IK)=XPLT
600 CALL LINE(PLTX,PLTY,L,0,1)
CALL PLOT(XPLT,-.25,3)
CALL PLOT(0,0,-.25,-2)

DO 700 I=1,N
X=XX
CALL PLOT(X,1,3)
CALL PLOT(X,-1,2)
CONTINUE
CALL PLOT(0,0,-1.75,-3)
GO TO 401
CALL RESET
GO TO 1

STOP
END
THIS PRG IS TO PLOT INDIVIDUAL SPECTRA

DIMENSION JSPEC(10),INFO(256),JDAT(1280)
DIMENSION XAXIS(4096),YDAT(4096),KI(5)
CALL INITIAL(6,200,10,0,15,0)
WRITE(10,2)
2 FORMAT(' SPECTRUM ID? ')
READ(11,3) JSPEC(1)
3 FORMAT(54)

CALL OPEN(0,JSPEC,2,IER,2)
TYPE'OPEN IER =',IER

CALL PLOT(0,0,0,0,3)
1 ACCEPT'SPECTRUM # TO BE PLOTTED?',IP
ACCEPT'Y-AXIS IN INCHES? ',TY
ACCEPT'X-AXIS/1050 PTS? ',XAX
XY=XAX/1050
TI=TY/4096

IP=IP-1
KF=IP*5+1
CALL RDBLK(0,KF,JDAT,5,IER)
TYPE'RDBLK IER =',IER
DO 7 J=1,1050
XAXIS(J)=J*XY
YDAT(J)=JDAT(J)*TI
7
DO 8 I=5,1046
YDAT(I-4)=(-YDAT(I-4)*21.+YDAT(I-3)*14.+YDAT(I-2)*54.+YDAT(I)*59.+YDAT(I+1)*54.+YDAT(I+2)*39.+YDAT(I+3)*21.)/231.
8 IF(YDAT(I-4).LT.0.) YDAT(I-4)=0.
CONTINUE

X=XAXIS(1)
Y=YDAT(1)
CALL LINE(XAXIS,YDAT,1050,0,1)
X=1070*XY
CALL PLOT(X,0,0,-1)
GO TO 1
CALL RESET
STOP
END
Program: GCIRSUM.FR

Purpose: This program will signal average any number of infrared spectra.

Method: GCIRSUM.FR sums corresponding spectral points for the specified spectra and finds the average.

Inputs: The user needs to specify the file name and the spectra numbers to be signal averaged.

Output: Signal averaged spectra.
THIS PRG IS TO DETERMINE THE ARRAY BOUNDARIES OF INDIVIDUAL SPECTRA ACQUIRED FROM THE GCIR SYSTEM VIA PRG GCIR... AND TO STORE THE INDIVIDUAL SPECTRA IN A RANDOM DATA FILE

```
DIMENSION JSPEC(10),INFO(256),JDAT(3192),IPT(256)
DIMENSION YDAT(500),KI(5),KD(1951)
WRITE(10,2)
2 FORMAT(' SPECTRUM ID? ',I)
READ(11,3) JSPEC(1)
3 FORMAT(S14)

CALL OPEN(0,JSPEC,2,IER)
TYPE 'OPEN IER = ',IER

CALL RDBLK(0,1,INFO,1,IER)
TYPE 'RDBLK IER = ',IER

I3=INFO(1)
I6=INFO(11)
I7=INFO(16)
N=INFO(21)
TYPE '# OF DATA PTS/TRANSFER = ',I3
TYPE '# OF DISK TRANSFERS = ',N

TYPE 'NEW FILE NAME? ',I
READ(11,3) JSPEC(1)
CALL DFILW(JSPEC,IER)
TYPE 'DFILW IER = ',IER
CALL CFILW(JSPEC,2,IER)
TYPE 'CFILW IER = ',IER
CALL OPEN(1,JSPEC,2,IER,2)
TYPE 'OPEN IER = ',IER

ACCEPT SIGNAL AVG? 00=NO, 01=YES , KSIG
IP=5
IC=0
DO 300 JS=1,N
I4=2+(I6*JS)-I6

CALL RDBLK(0,I4,JDAT,I6,IER)
TYPE 'RDBLK IER = ',IER

IL=1

DO 10 I=1,I3
IF(JDAT(I).GT.300) GO TO 10

53
```
K=I+160
DO 20 J=I,K
IF(JDAT(J),LE.300) GO TO 20
I=J
GO TO 10

20 CONTINUE

DO 30 J=I,I3
IF(JDAT(J),GE.1000) GO TO 25
30 CONTINUE
GO TO 11

25 IF((J+1050),GT,I3) GO TO 11
IPT(IL)=J
I=J
IL=IL+1

10 CONTINUE
11 CONTINUE

IL=IL-1
IF(KSIG.EQ.1) IL=IL-1
DO 100 I=1,IL
IPT1=IPT(I)
IPT2=IPT(I)+1050

L=1
DO 200 K=IPT1,IPT2
KDAT(L)=JDAT(K)
200 L=L+1
IF(KSIG.EQ.0) GO TO 202
IPT1=IPT(I+1)
IPT2=IPT(I+1)+1050

L=1
DO 201 K=IPT1,IPT2
KDAT(L)=(KDAT(L)+JDAT(K))/2
201 L=L+1
202 CONTINUE

IC=IC+1
YSUM=0.0

DO 210 K=1,1050
KDAT(K)=4096-KDAT(K)
210 YSUM=YSUM+KDAT(K)
YDAT(IC)=YSUM

TYPE' IC =',IC

100 CONTINUE
300 CONTINUE
JV=1
DO 9 J=1,IC
IF(YDAT(JV).GE.YDAT(J)) GO TO 9
JV=J
9 CONTINUE

XF=4396/YDAT(JV)

DO 8 J=1,IC
KDAT(J)=YDAT(J)*XF
KI(1)=IC

CALL WRTR(1,0,KI,5,IER)
TYPE 'IER = ',IER

CALL WRTR(1,5,KDAT,IC,IER)
TYPE 'IER = ',IER

TYPE KDAT
CALL RESET
STOP
END