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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

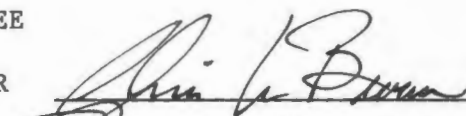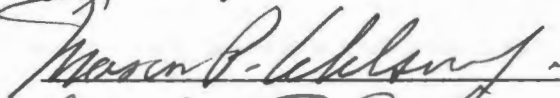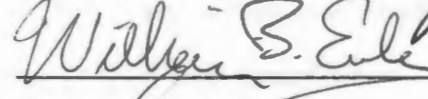
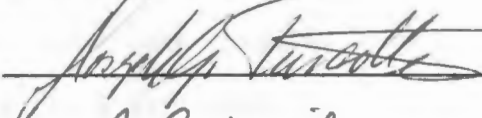UNIVERSITY OF RHODE ISLAND

1987

MASTER OF SCIENCE THESIS

OF

MARK AHMADJIAN

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APPROVED:

THESIS COMMITTEE

MAJOR PROFESSOR

DEAN OF THE GRADUATE SCHOOL

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 instrumention usually involves a gas chomatograph, 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.

My thanks to the U.S. Air Force for providing me with the opportunity to finish this degree and special thanks to Dr. Randall E. Murphy, Director, Infrared Technology Division, AF Geophysics Laboratory, for his support and encouragement.

<div align="right">Mark Ahmadjian</div>

PREFACE

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[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 reconstucted gas
chromatograms. Not until Cooley and Tukey (11) developed their algorithm
for fast processing of interferograms and the ready availablity 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 correspond-
ing 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[12] 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 thermostat-
ically 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,

3

TC DETECTOR

M3

IR SOURCE

GAS CHROMATOGRAPH

SAMPLE
CELL

AMPLIFIER

FILTERS

M2

MI

A/D C

C P U

(NOVA 3)

PLT

CRT

DISK STORAGE

GC/IR COMPUTER SYSTEM

Figure 1. Block diagram of the GC/IR computer system

IR SOURCE

SAMPLE OUTLET

SAMPLE INLET – FROM GC

SAMPLE CELL

CHOPPER

SLIT

FILTER WHEEL

THERMOCOUPLE
DETECTOR

OPTICAL DIAG. BECKMAN IR-102 FAST SCANNING IR

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 recon-
structed 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

AMPLIFIER ← ~~~~~~~~~~~~~~~~~ ← GC/IR

0-10 VDC

ANALOG/DIGITAL
CONVERTER

0-4096

COMPUTER ──────→ DISK
STORAGE

COMPUTER ───→ TOTAL IR PLOT

COMPUTER ───→ SPECTRAL
DISPLAY

SIGNAL AVERAGING

SMOOTHING

SPECTRAL SUBTRACTION

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.

GCIRSPEC: Plots out individual spectra corresponding to peaks from the reconstructed gas chromatograms.

GCIRSUM: Signal averages any number of IR spectra.

<div align="center">RESULTS AND DISCUSSION</div>

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; $\sum A_i$/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:

scan #1 = $A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0}$

scan #2 = $A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0}$

scan #3 = $A_{2.5} + A_{2.6} + A_{2.7} + A_{2.8} + A_{2.9} + A_{3.0}$

.
.
.
.
.

In this actual case the following would be represented:

scan #xxx = $A_{2.5} + A_{2.6} + A_{2.7} + \cdots\cdots A_{14.5}$

or in other words:

$$\text{scan \#xxx} = \sum_{i=2.5}^{14.5} A_i$$

The $\sum A_i$'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_2O. 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 (144seconds), 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 ident- ification 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

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Figure 4. TWIRP (Total Wavelength IR Plot)
A reconstructed gas chomatogram

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 (CS$_2$ vented to atmosphere).

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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, store⁴ 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 aborbance 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

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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 H_2O and CO_2.

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 back-
ground while scans 14, 22, 41, 47, and 55 correspond to the
TWIRP peaks #1, #2, #3, #4, and #5 respectively.

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Figure 8. Infrared spectrum for scan #1 showing instrument background. Absorptions are due to ambient CO_2 and H_2O.

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.

SCAN #55

PEAK #5

% TRANSMISSION

22

2.5   4.5   4.4   8.0   7.9   14.5

WAVELENGTH (UM)

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 —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 um 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 chioce of possible candidates for positive identification.

During this investigation we also conducted a comparision 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 comparision 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.

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GAS CHROMATOGRAM

TWIRP

Figure 14. Comparision 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.

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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 noticable 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 suffient 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.

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APPENDIX

Program Listings and Descripti ns

These computer programs were written for use on a Data General

Corporation (DGC) NOVA 3/12 mini-comuter 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.

3. Signal averaging.

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
                     CONTIGOUS 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.
                           NPLOT.SR
                           FORT.LB

GCIRAVG.FR   : TO SIGNAL AVERAGE SPECTRA
                           FORT.LB

GCIRPLOT.FR   : TO PLOT OUT SPECTRA
                           PLOTTER4NS.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
```

```
1.      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 sore the data
and an ADC sampling rate.

Output: Output are contiguous disk file containing the digitized spectral
data from the GC/IR.

THIS PRG 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 BETWEED 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'
TYPE 'CFILW IER =',IER

CALL OPEN(0,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.

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```
C          SUBROUTINE FOR GCIRAD.FR (ACQUIRING DATA FROM THE GCIR AND
C          STORING THIS DATA IN CONTIGUOUS DATA BLOCKS ON DISK).
C
C          ****************************************************

           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
90         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
115        CONTINUE

           CALL ADGCIR(IARRAY,I4,I3)

           DO 130 I=1,I3
130        JDAT(I)=IDAT(I)

           CALL WRBLK(0,J,JDAT,I6,IER)
           IF (IER.NE.1) TYPE'ERROR ERROR ERROR ERROR'

           J=J+I6

           INFO(21)=IL
           CALL WRBLK(0,1,INFO,1,IER)
140        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.

```
            .TITL ADGCIR
            .NREL
            .TXTM 1
            .ENT ADGCIR
            .EXTU
            .EXTN .I
TTY=10
CLK=14
ADCONV=21
FS.=3
T.=-167
            FS.
ADGCIR:  JSR @.FARL
            STA  0,AC0
            STA  1,AC1
            STA  2,AC2
            LDA  0,T.+0,3
            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,ADCONV
            INTDS
            NIOS ADCONV
            SKPDN ADCONV
            JMP  .-1
            DICC 0,ADCONV
            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)
      I7=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,I3
      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
```

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```
CS:        6
CL:        2
CH:        3
AC0:       0
AC1:       0
AC2:       0
DTIME:     300.
STIME:     0
COUNT:     0
CNTP:      1.
CNTEMP:    0
ARRAY:     0
ERR:       .SYSTM
           .BREAK
           .END
```

Program: TWIRP.FR

Purpose: This program will plot the reconstucted 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,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
          TDAT(K)=KDAT(K)
          TDAT(K)=TDAT(K)*10./4096.+1
          TDAT(K)=(ALOG10(TDAT(K)))*10.
          TDAT(K)=10.-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(YDAT(JV).GE.YDAT(J)) GO TO 9
        JV=J
9       CONTINUE

        XF=4096/YDAT(JV)

        DO 8 J=1,IC
8       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
R
```

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 TOTIOM.FR


         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
         IP=KI(1)-1
         L=0
         IPT=5

         TYPE'# OF SPECTRA =',IP
         ACCEPT'SIGNAL AVG?  00=NO, 01=YES'  ,ISIG
         DO 300 I=1,IP
         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)
```

```
            L=L+1
            ZDAT(L)=YSUM
            IPT=IPT+1050
300         CONTINUE

401         CONTINUE
            L=IC
            DO 402 I=1,L
402         ZDAT(I)=KDAT(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
8           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


            YDAT(IK)=8.-YDAT(IK)+1.0
            YDAT(IK)=(ALOG10(YDAT(IK)))*10.
            YDAT(IK)=10.-YDAT(IK)

            YSUM=YDAT(IK)
            XPLT=IK*XX
            PLTX(IK)=XPLT
600         PLTY(IK)=YSUM
            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)
700       CONTINUE
          CALL  PLOT(0.0,-1.75,-3)
          GO  TO  401
          CALL  RESET
          GO  TO  1

          STOP
          END
```

```
C         THIS PRG IS TO PLOT INDIVIDUAL SPECTRA
C
C         ***************************************r****
          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(S14)

          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
7         YDAT(J)=JDAT(J)*TI

          DO 8 I=5,1046
          YDAT(I-4)=(-YDAT(I-4)*21.+YDAT(I-3)*14.+YDAT(I-2)
1         *54.+YDAT(I)*59.+YDAT(I+1)*54.+YDAT(I+2)*39.+YDAT
2         YDAT(I+4)*21.)/231.
          IF(YDAT(I-4).LT.0.) YDAT(I-4)=0.
8         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(8192),IPT(256)
        DIMENSION YDAT(500),KI(5),KDAT(1051)
        WRITE(10,2)
  2     FORMAT(' SPECTRUM ID?  ')
        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?  '
        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
```

```
             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=4096/YDAT(JV)

      DO 8  J=1,IC
8     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
```