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DEVELOPMENT OF SRC-I PRODUCT ANALYSIS: DOCUMENTATION OF PROCEDURES

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International Coal Refining Company
Allentown, Pennsylvania

and

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

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DEVELOPMENT OF SRC-I PRODUCT ANALYSIS. VOLUME 3.

DOCUMENTATION OF PROCEDURES

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Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

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VOLUME 3

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VII. DOCUMENTATION OF WILSONVILLE SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY (GCSD) COMPUTATION

Summary

This section documents the BASIC computer program that was written to simulate Wilsonville's GC-simulated distillation (GCSD) results at APCI-CRSD Trexlertown. The GC conditions used at APCI for the Wilsonville GCSD analysis of coal-derived liquid samples were described in an article by I. S. Kingsley and F. K. Schweighardt in the SRC-I Quarterly Technical Report, April-June 1981. The approach used to simulate the Wilsonville GCSD results is also from an SRC-I Quarterly Technical Report and is reproduced in Appendix VII-A. The BASIC computer program is described in the attached Appendix VII-B.

INTRODUCTION

As discussed in detail in previous reports (Kingsley et al., 1981; Kingsley and Schweighardt, 1981; Lamb and Kingsley, 1981), Wilsonville's method of determining the boiling-point distribution of process-stream samples for SDGC differs from the ASTM method (D-2887). The key differences can be categorized as follows:

- The type of boiling-point calibration standard used
- Whether response factors are used (empirical ratios of weight percent to area percent)
- The mode of integration

The Wilsonville method uses aromatic compounds to calibrate the gas chromatographic retention times for boiling points, whereas the ASTM D-2887 method employs aliphatic compounds (n-C_5 through n-C_{44}).

The Wilsonville method uses response factors established for an aromatic calibration standard to report the boiling-point distribution in weight percent. Response factors for selected aromatic compounds have been established from experimental weight percent/area percent ratios. Using these experimental ratios, Wilsonville generated a fifth-order polynomial equation to determine the response factors for unknown peaks (Lewis et al., 1977, 1979). In contrast the ASTM D-2887 method does not use response factors; instead, the boiling-point distribution is reported in gas chromatographic (GC) area percent, which correlates to volume percent for petroleum-derived materials.

The Wilsonville method integrates by peak areas, whereas the ASTM method uses a time-slicing mode of integration. In time-slicing integration, the boiling-point cutoff is defined at a specific retention time and, therefore, can fall in a valley between two peaks or on the slope or apex of a peak. However, in peak-area integration, the boiling-point cutoff is defined by a specific peak and always falls in the valley following that peak.

Methodology

To establish the Wilsonville GCSD procedure at APCI, 21 Wilsonville process-stream samples were analyzed and compared with the results obtained at Wilsonville for the same samples. The following four-step approach was used:

- Conversion of retention time to boiling point
- Conversion of area percent to weight percent
- Screening for heavy or light distillates
- Determination of initial and final boiling points

Conversion of Retention Time to Boiling Point

Wilsonville converts GC retention times to boiling points by using boiling points of selected aromatic compounds documented in the literature. Selected peaks in the chromatogram of a process stream are assigned specific boiling points based on their retention times. Boiling points for unknown peaks are then inter- or extrapolated, based on their respective retention times.

In APCI's method, retention times were converted to boiling points by converting APCI retention times to Wilsonville retention times, and then applying the Wilsonville retention time to the boiling-point conversion. To convert the APCI retention times to Wilsonville retention times, a relationship was established between the two retention times (RT), as expressed by the following linear equations:

$$RT_{WV} = 0.963RT_{APCI} - 8.073 \quad (RT_{APCI} \leq 2{,}050 \text{ sec}) \quad (1)$$

$$RT_{WV} = 0.342RT_{APCI} + 1.243 \quad (RT_{APCI} > 2{,}050 \text{ sec}) \quad (2)$$

These equations allow peak-by-peak conversion of APCI retention times to Wilsonville retention times in a sample analyzed on APCI's GC system.

Application of the Wilsonville GC retention time to boiling-point conversion is effected by three distinct linear transformations:

$$BP\ (^\circ F) = 1.48RT_{WV} - 39.25 \qquad (RT_{WV} \leq 120\ sec) \tag{3}$$

$$BP\ (^\circ F) = 0.341RT_{WV} + 126.5 \qquad (RT_{WV} > 120\ sec\ and \leq 2,560\ sec) \tag{4}$$

$$BP\ (^\circ F) = 0.049RT_{WV} + 893.9 \qquad (RT_{WV} > 2,560\ sec) \tag{5}$$

where BP is boiling point. Using equations 1-5, a boiling point based on the Wilsonville method is assigned to a retention time obtained from APCI's GC system.

Conversion of Area Percent to Weight Percent

Bulk response factors were established by computing the ratio WV weight percent/APCI area percent for 100°F boiling-point cuts from data on 21 SRC-I process stream samples:

BP Cut	Response Factor
<350°F	0.624
350-450°F	1.074
450-550°F	1.004
550-650°F	1.165
650-750°F	1.156
750-850°F	1.444
>850°F	1.800

Multiplying the respective area percents of gas chromatographic peaks by the response factor for the appropriate boiling range and then normalizing the results generates weight percent results from the area percent data.

Screening Process-Stream Samples for Heavy and Light Distillates

Wilsonville assigns a 3% residue to heavy process streams and no residue to light process streams. Thus, the total amount of sample eluting from the GC column in the GCSD analysis for heavy process streams is assumed to represent 97% of the sample.

Because APCI's main objective was to simulate the Wilsonville GCSD method, which distinguishes between heavy and light process streams, a way to identify the streams was devised. Evaluation of Wilsonville's process-stream samples showed that all heavy distillates contain >5 wt % material in the >850°F cut, whereas all light distillates contain <5 wt % material in the >850°F cut. Thus, the computer program that APCI developed was modified so that a sample could be identified as heavy or light distillate by the weight percent of material in the >850°F cut.

Define Initial and Final Boiling Points

The initial boiling point (IBP) and final boiling point (FBP) of a sample are determined as 0.5 and 99.5 weight percent of sample, respectively.

BASIC Programs

Two programs were written to convert APCI gas chromatographic data into WV-GCSD results:

- a program to transfer gas chromatographic data onto magnetic tape,
- a program to calculate WV-GCSD results using the GC data from the magnetic tape.

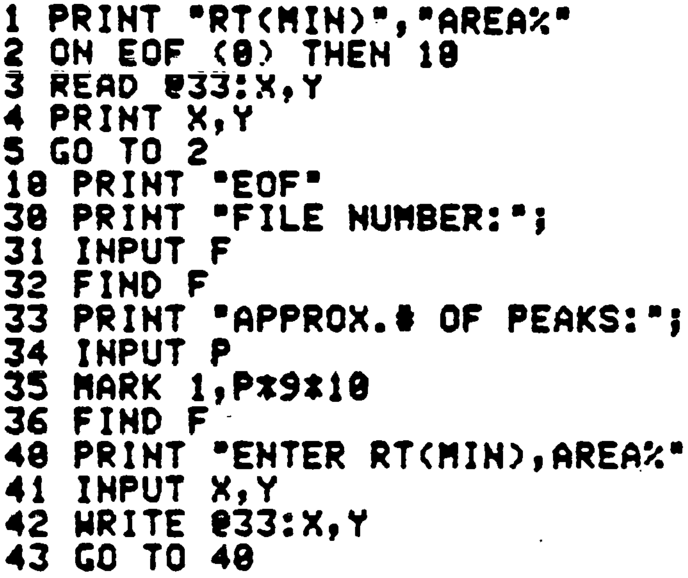
Entering GC Data onto GC Data Tape

The program to enter GC data is listed in Exhibit 1. To enter GC data into the computer and store them in a designated data file on a GC data tape, follow these steps:

Step 1. Load the program into the computer:
  a) Insert program tape.
  b) FIN 4 return (file #4 contains the program listed in Exhibit A).
  c) OLD return loads program from file into computer.
  d) Eject program tape.

Step 2. List last data entered from GC data tape:
  a) Insert GC data tape.
  b) TLIST return will list all data files used on the GC data tape. The files will be labeled as "binary data". The file labeled "last" will be used for new data. For example, if 47 GC data files are used, the new data will be entered into file #48.
  c) FIN 47 return RUN return will list the previously entered GC data in file #47 and position the tape reader at the beginning of file #48. An example is shown in Exhibit 2.

Exhibit 1. Data Is Entered onto Magnetic Tape



```
1 PRINT "RT(MIN)","AREA%"
2 ON EOF (0) THEN 10
3 READ @33:X,Y
4 PRINT X,Y
5 GO TO 2
10 PRINT "EOF"
30 PRINT "FILE NUMBER:";
31 INPUT F
32 FIND F
33 PRINT "APPROX.# OF PEAKS:";
34 INPUT P
35 MARK 1,P*9*10
36 FIND F
40 PRINT "ENTER RT(MIN),AREA%"
41 INPUT X,Y
42 WRITE @33:X,Y
43 GO TO 40
```

Step 3. Format new file for approximate numbers of peaks from the chromatogram and enter data:

a) 48 return 10 return, which will format file #48 for approximately 10 GC data pairs.

b) The screen will show ENTER RT(MIN), AREA %. Enter the GC data and press return after each entry.

c) After last data is entered, press break twice, then type CLOSE return. The screen will show
PROGRAM ABORTED IN LINE 41
CLOSE. An example is shown in Exhibit 3.

Step 4 To relist the just entered data, type FIN 48 return RUN return. This step is only for proofreading the data entry and is not needed in order to execute the program. A listing from file 48 is shown in Exhibit 4.

Exhibit 2. Listing of GC Data Last Entered

```
FIN47
RUN
RT(MIN)                 AREA%
 3.07                    0.814
 11.83                   0.34
 12.11                   0.245
 13.29                   0.242
 13.54                   0.26
 13.95                   1.573
 14.65                   1.148
 15.28                   0.956
 15.52                   0.783
 16.03                   2.433
 16.37                   1.645
 17.3                    5.763
 17.57                   1.717
 17.96                   4.317
 18.95                   2.415
 19.22                   2.199
 19.58                   4.633
 20.25                   3.294
 21.09                   3.874
 21.41                   1.692
 21.82                   1.103
 21.97                   1.754
 22.62                   2.438
 23.2                    5.79
 24.02                   1.791
 24.26                   2.254
 25.18                   5.537
 25.95                   2.788
 26.62                   4.856
 27.41                   3.399
 28.43                   3.324
 28.83                   1.409
 29.16                   1.212
 30.19                   2.92
 30.83                   2.717
 31.52                   0.764
 31.73                   1.549
 32.21                   0.985
 32.69                   1.15
 33.27                   2.29
 33.88                   1.018
 34.49                   1.529
 35.16                   1.817
 36.58                   1.94
 38.27                   1.703
 40.26                   0.832
 42.64                   1.055
 45.51                   0.615
 EOF
```

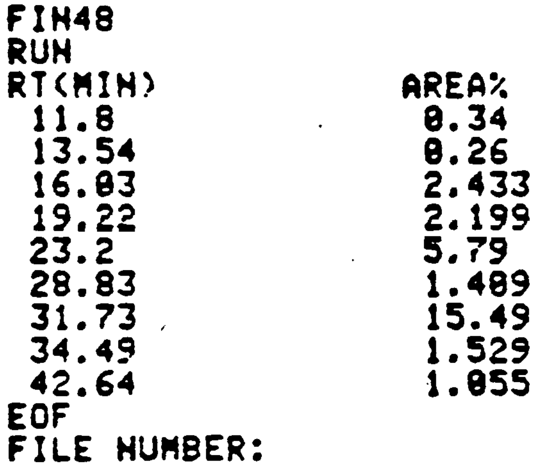
Exhibit 3. Entry of GC Data into File #48

```
EOF
FILE NUMBER:48
APPROX.# OF PEAKS:10
ENTER RT(MIN),AREA%
11.8
.34
ENTER RT(MIN),AREA%
13.54
.26
ENTER RT(MIN),AREA%
16.03
2.433
ENTER RT(MIN),AREA%
19.22
2.199
ENTER RT(MIN),AREA%
23.2
5.79
ENTER RT(MIN),AREA%

28.83
1.409
ENTER RT(MIN),AREA%
31073
15.49
ENTER RT(MIN),AREA%
34.49
1.529
ENTER RT(MIN),AREA%
42.64
1.055
ENTER_RT(MIN),AREA%

PROGRAM ABORTED IN LINE 41
CLOSE
```

Exhibit 4. Listing of Data in File #48



```
FIN48
RUN
RT(MIN)            AREA%
 11.8               0.34
 13.54              0.26
 16.03              2.433
 19.22              2.199
 23.2               5.79
 28.83              1.489
 31.73              15.49
 34.49              1.529
 42.64              1.055
EOF
FILE NUMBER:
```

<u>Note</u>: When a brand new GC data tape is used, follow this procedure:

1. Insert the new GC data tape.
2. Press rewind.
3. Type RUN 33 return.
4. Enter the approximate number of peaks.
5. Proceed from step 3b.

2. Calculating WV-GCSD Results from GC Data

The program used to perform the calculations that generate WV-GCSD results from APCI-CRSD GC data is listed in Appendix VII-A. To understand the various steps in the program and how they relate to the concepts described in the methodology section, the program was dissected as follows:

A. Initialize the program and read APCI retention time and area percent from the GC data file tape into the first and second columns of matrix A:

```
100 INIT
110 PAGE
120 REM:TT RT CUT-OFFS,WV LINEAR REGRESSIONS AS IN QUARTERLY REPORT
130 PRINT "INSERT DATA TAPE AND ENTER FILE# FOR DATA:";
140 INPUT F
150 DIM A(150,7)
160 DIM B(7)
170 R=0
180 B=0
190 T2=0
200 FIND F
210 T1=0
220 A=0
230 S=0
240 T=0
250 FOR I=1 TO 150
260 ON EOF (0) THEN 290
270 READ @33:A(I,1),A(I,2)
280 NEXT I
290 N=I-1
300 FOR I=1 TO N
```

B. Convert APCI retention time to WV retention time and put into column 7 of matrix A, using equations 1 and 2.

```
310 REM conversion of TT RT TO WV RT INTO A(I,7)
320 IF A(I,1)*60=>2050 THEN 350
330 A(I,7)=0.9634*A(I,1)*60-8.073
340 GO TO 360
350 A(I,7)=0.342*A(I,1)*60+1243
```

C. Convert the calculated WV retention time to boiling points and put into column 3 of matrix A, using equations 3, 4, and 5 .

```
360 REMARK DETERMINATION OF BOILING POINTS INTO A(I,3)
370 IF A(I,7)=>120 THEN 400
380 A(I,3)=1.48*A(I,7)-39.25
390 GO TO 430
400 IF A(I,7)=>2560 THEN 430
410 A(I,3)=0.341*A(I,7)+126.5
420 GO TO 430
430 REMARK
```

D. Multiply area percents of peaks with appropriate response factors. Use APCI retention times as boiling range criteria:

Boiling Range (°F)	APCI Retention Time (min)	Response Factor
<350	<10.9	0.624
350-450	≥10.9 to 16.0	1.074
450-550	≤16.0 to 22.5	1.004
550-650	≤22.5 to 27.2	1.165
650-750	≤27.2 to 32.2	1.156
750-850	≤32.2 to 36.3	1.444
>850	≤36.3	1.800

The retention time cutoffs are based on Table A-3 of Appendix VII-A.

The response factors are based on Table A-6 of Appendix VII-A.

```
440 REMARK
450 REMARK DETERMINATION OF AREA% *RF INTO A(I,4)
460 REMARK AREA%*RF FOR EACH DIST. CUT INTO B(1 TO 7)
470 IF A(I,1)=>10.9 THEN 500
480 A(I,4)=A(I,2)*0.624
490 GO TO 660
500 IF A(I,1)=>16 THEN 530
510 A(I,4)=A(I,2)*1.074
520 GO TO 660
530 IF A(I,1)=>22.5 THEN 560
540 A(I,4)=A(I,2)*1.004
550 GO TO 660
560 IF A(I,1)=>27.2 THEN 590
570 A(I,4)=A(I,2)*1.165
580 GO TO 660
590 IF A(I,1)=>32.2 THEN 620
600 A(I,4)=A(I,2)*1.156
610 GO TO 660
620 IF A(I,1)=>36.3 THEN 650
630 A(I,4)=A(I,2)*1.444
640 GO TO 660
650 A(I,4)=A(I,2)*1.8
660 REMARK
670 NEXT I
```

E. Normalize the area percent times response factor to generate weight percent, which is in column 4 of matrix A, and put the weight into column 5, matrix A:

```
680 REMARK SUM OF ALL AREA % * RF (S)
690 FOR I=1 TO N
700 S=S+A(I,4)
710 NEXT I
720 FOR I=1 TO N
730 A(I,5)=A(I,4)/S*100
740 NEXT I
```

F. Determine cumulative weight percent boiling point cuts for the assigned boiling ranges. Put into B(1) through (7):

```
750 FOR I=1 TO N
760 IF A(I,3)=>350 THEN 790
770 B(1)=B(1)+A(I,5)
780 GO TO 950
790 IF A(I,3)=>450 THEN 820
800 B(2)=B(2)+A(I,5)
810 GO TO 950
820 IF A(I,3)=>550 THEN 850
830 B(3)=B(3)+A(I,5)
840 GO TO 950
850 IF A(I,3)=>650 THEN 880
860 B(4)=B(4)+A(I,5)
870 GO TO 950
880 IF A(I,3)=>750 THEN 910
890 B(5)=B(5)+A(I,5)
900 GO TO 950
910 IF A(I,3)=>850 THEN 940
920 B(6)=B(6)+A(I,5)
930 GO TO 950
940 B(7)=B(7)+A(I,5)
950 REM
960 NEXT I
```

G. Generate cumulative weight percents and put into column 6 of matrix A:

```
970 REMARK
980 A(1,6)=A(1,5)
990 FOR I=2 TO N
1000 A(I,6)=A(I-1,6)+A(I,5)
1010 NEXT I
```

H. Determine initial (T1) and final (T2) boiling points. See discussion in Appendix VII-A:

```
1020 FOR I=1 TO N
1030 IF A(I,6)=>0.5 THEN 1050
1040 GO TO 1070
1050 T1=A(I,3)
1060 GO TO 1080
1070 NEXT I
1080 FOR I=1 TO N
1090 IF A(I,6)=>99.5 THEN 1110
1100 GO TO 1130
1110 T2=A(I,3)
1120 GO TO 1200
1130 NEXT I
```

I. Determine if sample is heavy distillate; if so, assign a 3% residue (R). Renormalize the boiling-point cut data accordingly:

```
1140 REM:DETERMINATION OF HEAVY DISTILLATE
1150 IF B<=0.05 THEN 1190
1160 R=3
1170 FOR I=1 TO 7
1180 B(I)=B(I)*0.97
1190 REM
```

Note: If no residue calculation is desired, delete line statements #1140-1190 and #1530.

J. Print out long version of results:

```
1200 REMARK CHROMATOGRAM WITH CALC. BP, WT% AND CUM. WT% PRINT OUT
1210 PRINT "TAPENUMBER:";
1220 INPUT X$
1230 PRINT "SAMPLE NUMBER : ";
1240 INPUT C$
1250 PRINT "DATE:";
1260 INPUT D$
1270 PRINT "APCI GC-SIMULATED DISTILLATION BY WV METHOD"
1280 PRINT
1290 PRINT
1300 PRINT USING 1580:"RT(MIN)","AREA%","BP(F)","WEIGHT%","CUM. WT%"
1310 PRINT
1320 FOR I=1 TO N
1330 PRINT USING 1570:A(I,1),A(I,2),A(I,3),A(I,5),A(I,6)
1340 NEXT I
1350 INPUT Y$
```

<u>Note</u>: Input Y$ allows copying before screen is cleaned for summarized version of results. Press return.

K. Print out summarized or short version of results:

```
1360 REMARK
1370 REMARK BOILING POINT DISTRIBUTION BY WU METHOD
1380 PRINT
1390 PAGE
1400 PRINT "TAPENUMBER:";X$;"   FILENUMBER:";F
1410 PRINT "SAMPLE NUMBER:";C$
1420 PRINT "DATE:";D$
1430 PRINT
1440 PRINT USING 1600:"DISTILLATION CUT","WEIGHT%"
1450 PRINT
1460 PRINT USING 1590:"   <350(F)",B(1)
1470 PRINT USING 1590:"350-450(F)",B(2)
1480 PRINT USING 1590:"450-550(F)",B(3)
1490 PRINT USING 1590:"550-650(F)",B(4)
1500 PRINT USING 1590:"650-750(F)",B(5)
1510 PRINT USING 1590:"750-850(F)",B(6)
1520 PRINT USING 1590:"   >850(F)",B(7)
1530 PRINT USING 1590:"RESIDUE   ",R
1540 PRINT
1550 PRINT USING 1610:"    IBP   ",T1,"(F)"
1560 PRINT USING 1610:"    FBP   ",T2,"(F)"
1570 IMAGE 2D.2D, 4X, 2D.2D, 4X, 4D.1D,6X,2D.2D,4X,3D.2D
1580 IMAGE 7A, 4X, 6A, 3X, 5A, 4X, 7A, 4X, 9A
1590 IMAGE 16A, 6 X, 3D.2D
1600 IMAGE 16A, 4X, 14A
1610 IMAGE 16A,6X,4D,3A
1620 REMAR: THIS WU SIMULATION OF GC-SIM.DIST. DISCRIMINATES
1630 REMAR:BP-CUTS BY RETENTION TIME CUT OFFS.
1640 END
```

Instructions to the WV-GCSD Program User

To use the program, follow these steps:

Step 1. Load the program into the computer:

- a) insert program tape.
- b) FIN 19 return (File #19 contains the program listed in Appendix 2).
- c) OLD return loads the program from the file into the computer.
- d) Eject program tape.

Step 2. Perform WV-GCSD calculation:

- a) Insert GC data tape.
- b) RUN return. The screen will show "Insert data tape and enter file# for data".
- c) Enter GC data file number return

  Enter tape name and or number return

  Enter date return

  The screen will show the first page of the GC results.
- d) Press copy , press home page

  The screen will show the second page of the GC results.
- e) Press copy , press home page

  Repeat until the screen is blank, except for a flashing ? in the upper right-hand corner.
- f) Press return , press copy

  This will copy the summary page for the WV-GCSD results.

<u>Note</u>: To calculate the WV-GCSD results for the next data set, follow from Step 2b.

An example of a typical result is shown in Exhibit 5.

Acknowledgment

Special thanks to Jeff Bauer (Corporate R&D) and Mike Rusak (MID) for their help in writing and debugging this program.

Exhibit 5

```
INSERT DATA TAPE AND ENTER FILE# FOR DATA:47
TAPENUMBER:GC1
SAMPLE NUMBER : 82-4533
DATE:8-16-82
APCI GC-SIMULATED DISTILLATION BY WV METHOD

RT(MIN)     AREA%     BP(F)     WEIGHT%     CUM. WT%

 3.07       0.01      184.3       0.01        0.01
11.83       0.34      356.9       0.31        0.32
12.11       0.25      362.4       0.23        0.55
13.29       0.24      385.7       0.22        0.77
13.54       0.26      390.6       0.24        1.01
13.95       1.57      398.7       1.45        2.46
14.65       1.15      412.5       1.06        3.53
15.28       0.96      424.9       0.88        4.41
15.52       0.70      429.7       0.65        5.06
16.03       2.43      439.7       2.10        7.16
16.37       1.65      446.4       1.42        8.58
17.30       5.76      464.8       4.98       13.56
17.57       1.72      470.1       1.48       15.04
17.96       4.32      477.8       3.73       18.77
18.95       2.42      497.3       2.09       20.85
19.22       2.20      502.6       1.90       22.75
19.58       4.63      509.7       4.00       26.75
20.25       3.29      522.9       2.84       29.60
21.09       3.87      539.5       3.35       32.94
21.41       1.69      545.8       1.46       34.40
21.82       1.10      553.8       0.95       35.36
21.97       1.75      556.8       1.51       36.87
22.62       2.44      569.6       2.44       39.31
23.20       5.79      581.0       5.80       45.11
24.02       1.79      597.2       1.79       46.91
24.26       2.25      601.9       2.26       49.17
```

Exhibit 5

25.18	5.54	620.1	5.55	54.72
25.95	2.79	635.3	2.79	57.51
26.62	4.86	648.5	4.87	62.38
27.41	3.40	664.0	3.38	65.75
28.43	3.32	684.1	3.30	69.06
28.83	1.41	692.0	1.40	70.46
29.16	1.21	698.5	1.21	71.67
30.19	2.92	718.8	2.90	74.57
30.83	2.72	731.4	2.70	77.27
31.52	0.76	745.0	0.76	78.03
31.73	1.55	749.2	1.54	79.57
32.21	0.99	758.6	1.22	80.79
32.69	1.15	768.1	1.43	82.22
33.27	2.29	779.5	2.84	85.07
33.88	1.02	791.6	1.26	86.33
34.49	1.53	791.7	1.90	88.23
35.16	1.82	796.4	2.26	90.49
36.58	1.94	806.3	3.00	93.49
38.27	1.70	818.2	2.64	96.13
40.26	0.83	832.1	1.29	97.41
42.64	1.06	848.7	1.63	99.05
45.51	0.62	868.8	0.95	100.00

Exhibit 5

```
TAPENUMBER:GC1   FILENUMBER:47
SAMPLE NUMBER:82-4533
DATE:8-15-82

DISTILLATION CUT    WEIGHT%

   <350(F)              0.81
350-450(F)              8.57
450-550(F)             25.82
550-650(F)             27.97
650-750(F)             17.20
750-850(F)             19.48
   >850(F)              0.95
RESIDUE                 0.00

     IBP               362(F)
     FBP               869(F)
```

Appendix VII-A

Development of SRC-I Product Analysis

from the

SRC-I Quarterly Technical Report

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DEVELOPMENT OF SRC-I PRODUCT ANALYSIS

Because several research programs are generating data that will be used in SRC-I Demonstration Plant design, standardization of the different analytical work-up methods is critical. Straightforward correlation of the data is essential before a meaningful data base can be established. Therefore, APCI has been evaluating analytical methods used for product studies, in particular by comparing methods used by APCI to analyze products from the coal process development unit (CPDU) to methods used at Wilsonville Pilot Plant.

During this quarter, APCI focused on one of four key analytical procedures used at Wilsonville, simulated distillation by gas chromatography (SDGC). In earlier work, APCI identified differences between Wilsonville's SDGC technique and that used by the American Society for Testing and Materials (ASTM), method D-2887. APCI duplicated Wilsonville's procedure and determined that the results using the integrators from both Wilsonville and APCI differed. APCI has established a mathematical simulation that permits conversion of APCI SDGC results to those obtained at Wilsonville.

APCI analyzed 21 samples from seven different process streams at Wilsonville and compared the results with Wilsonville's analytical data. Conclusions from this comparison are summarized below.

Comparison of the boiling-point distributions obtained using Wilsonville's SDGC method at both Wilsonville and APCI revealed that:

- APCI duplicated Wilsonville's SDGC boiling-point distribution with excellent results.
- APCI's initial and final boiling points are about 5% lower than Wilsonville's.

Comparison of boiling-point distributions of a CPDU sample and Wilsonville process-stream samples determined by Wilsonville SDGC indicated that: duplication of the Wilsonville SDGC method at APCI is adequate for comparing results from all samples based on boiling-point distribution; the single CPDU sample and the Wilsonville process-solvent product had similar boiling-point distributions.

Comparison of boiling-point distributions determined by Wilsonville SDGC and the ASTM SDGC method (D-2887) showed that: ASTM boiling-point distributions correlate poorly with those from Wilsonville SDGC; ASTM initial and final boiling points differ from Wilsonville's (aliphatic vs. aromatic boiling-point standards); ASTM boiling-point distributions are more precise than Wilsonville's (time slicing vs. peak area integration).

Comparison of the results from ASTM and Wilsonville SDGC methods with results from actual distillation will establish the accuracy of these methods.

INTRODUCTION

As discussed in detail in previous reports (Kingsley et al., 1981; Kingsley and Schweighardt, 1981; Lamb and Kingsley, 1981), the Wilsonville approach to determining the boiling-point distribution of process-stream samples differs from the ASTM D-2887 method for SDGC. The key differences are as follows:

- Choice of boiling-point calibration standard
- Use of response factors: empirical ratios of weight percent to area percent
- Mode of integration

The Wilsonville method employs aromatic compounds to calibrate the gas chromatographic retention times for boiling points, whereas the ASTM D-2887 method employs aliphatic compounds (n-C_5 through n-C_{44}). The effect of calibrating with different types of boiling-point standards, as discussed in previous reports, is illustrated in Figure 1. The solid line indicates the relationship of retention time to aromatic boiling points, while the broken line shows this relationship for aliphatic boiling points. For compounds with boiling points of less than 500°F, the results obtained employing aromatic or aliphatic standards will be similar. However, for compounds with boiling points above 500°F, the simulated boiling point determined with the aliphatic standard will be lower than the simulated boiling point determined with the aromatic standard.

The Wilsonville method uses response factors established for an aromatic calibration standard to report the boiling-point distribution in weight percent. The ASTM D-2887 method, which does not use response factors, reports the boiling-point distribution in gas chromatographic (GC) area percent, which correlates to volume percent for petroleum-derived materials.

The Wilsonville method integrates by peak areas, whereas the ASTM method uses the time-slicing mode of integration. In time-slicing integration, the boiling-point cutoff is defined at a specific retention time and, therefore, can fall in a valley between two peaks or on the slope or apex of a peak. However, in peak-area integration, the boiling-point cutoff is defined by a specific peak and always falls in the valley following that peak. Figure 2 (a chromatogram of a Wilsonville recycle solvent) illustrates the differences in these integration modes. Four boiling-point cuts are depicted: <450, 450-550, 550-650, and >650°F. Line A shows the cutoffs for the four boiling-point cuts by the ASTM D-2887 method. For this example, the assigned cut point for two of the cutoff temperatures falls within the area of a peak rather than in a valley between two peaks. Line B shows the same aliphatic boiling-point calibration, but with peak area integration. In this case, the boiling-point cutoffs fall in the valleys between peaks, and the entire area of the peak preceding the cutoff is assigned to the lower boiling fraction. Line C shows peak area integration as in line B; however, the boiling-point axis is calibrated using aromatic standards. The Wilsonville procedure uses peak area integration and aromatic standards. In addition, the peak area is multiplied by a GC response factor, which is calculated from the peak's retention time by the relationship illustrated in Figure 3. Response factors for selected aromatic compounds have been established from experimental weight percent/area percent ratios. Based upon these experimental ratios, a fifth-order polynomial equation was generated by Wilsonville to determine response factors for unknown peaks (Lewis et al., 1977, 1979). APCI observed that with increasing retention time, i.e, increasing boiling point, the response factor increases.

Figure 4 shows that different modes of integration and calibration, when applied to a single chromatogram, will yield different boiling-point distributions. Bar A represents boiling-point distributions derived from the integrated areas of Figure 2, line A (time-slicing, aliphatic standards, ASTM D-2887). Bar B represents boiling-point distributions derived from the integrated areas of Figure 2, line B (peak area, aliphatic standards). Bar C represents boiling-point distributions derived from the integrated areas of Figure 2, line C (peak area, aromatic standards). Bar D represents boiling-point distributions derived from the integrated areas of Figure 2, line C, after applying the response factors shown in Figure 3 (peak area, aromatic standards, response factors, Wilsonville method). Comparison of bars A and B shows the effect of using peak-area and time-slicing integration. The effect of using aliphatic and aromatic standards is shown by comparing bars B and C, and comparison of bars C and D shows the effect of using response factors. A comparison of SDGC results from the ASTM D-2887 method and the Wilsonville method (bars A and D) shows that the Wilsonville method yields a higher product distribution in the higher boiling ranges than does ASTM D-2887.

METHODOLOGY

To establish the Wilsonville simulated distillation procedure at APCI, 21 Wilsonville process-stream samples were analyzed and compared with the results obtained at Wilsonville for the same samples. The following four-step approach was used:

- Conversion of retention time to boiling point
- Conversion of retention time to response factor
- Screening for heavy or light distillate
- Determination of initial and final boiling points

Conversion of Retention Time to Boiling Point

Wilsonville converts GC retention times to boiling points by using documented boiling points of selected aromatic compounds in the literature, as described previously (Kingsley et al., 1981; Kingsley and Schweighardt, 1981; Lamb and Kingsley, 1981). Based on their retention times, selected peaks in the chromatogram of a process stream are assigned specific boiling points. A computer program is then used to inter- and extrapolate boiling points for unknown peaks based on their respective retention times. A plot for this conversion, as practiced at Wilsonville, is illustrated in Figure 5.

APCI's approach for the conversion of retention times to boiling points employs aromatic boiling-point standards by comparing APCI retention times to Wilsonville retention times on an identical sample, by converting APCI retention times to Wilsonville retention times, if necessary, and by applying the Wilsonville retention time to the boiling-point conversion (Figure 5).

Wilsonville and APCI retention times were found to differ (Figure 6). Therefore, in order to convert APCI retention times to Wilsonville retention times, a relationship had to be established (see Figure 7). Figure 7 shows that the relationship between the two retention times (RT) can best be expressed by two linear equations:

$$RT_{WV} = 0.963RT_{APCI} - 8.073 \qquad (RT_{APCI} \leqq 2{,}050 \text{ sec}) \qquad (1)$$

$$RT_{WV} = 0.342RT_{APCI} + 1{,}243 \qquad (RT_{APCI} > 2{,}050 \text{ sec}) \qquad (2)$$

These equations allow peak-by-peak conversion of APCI retention times (RT_{APCI}) to Wilsonville retention times (RT_{WV}) in a sample analyzed on APCI's GC system.

Application of the Wilsonville GC retention time to boiling-point conversion (Figure 5) can be effected by three distinct linear transformations:

$$BP\ (°F) = 1.48RT_{WV} - 39.25 \qquad (RT_{WV} \leqq 120\ \text{sec}) \tag{3}$$

$$BP\ (°F) = 0.341RT_{WV} + 126.5 \qquad (RT_{WV} > 120\ \text{sec and} \leqq 2{,}560\ \text{sec}) \tag{4}$$

$$BP\ (°F) = 0.049RT_{WV} + 893.9 \qquad (RT_{WV} > 2{,}560\ \text{sec}) \tag{5}$$

where BP is boiling point. Using equations 1-5, one can now assign a boiling point based on the Wilsonville method to a retention time obtained from APCI's GC system.

Conversion of Retention Time to Response Factor

Wilsonville's approach for establishing response factors for peaks in a chromatogram involves setting up response factors for selected aromatic compounds, fitting a fifth-order polynomial equation through these response factors, and extrapolating for unknown peaks. For the analysis of an actual process-stream sample, peaks corresponding to the retention time of the selected aromatic compounds are identified as those compounds and assigned the experimental response factors. Response factors for all peaks not identified are computed based on the fifth-order polynomial equation. A plot relating Wilsonville retention times to response factors is shown in Figure 3. (The fifth-order polynomial equation is described in Lewis et al., 1977, 1979.)

APCI's objective is to develop a procedure that will simulate the boiling-point distribution determined by the Wilsonville SDGC method. Wilsonville employs a sophisticated computer program to examine each individual peak in an unknown chromatogram to determine whether an experimentally established or a calculated response factor should be used for that peak. To accomplish APCI's objective without necessitating extensive computer hardware and software development, the following approach has been selected:

- Obtain APCI GC and Wilsonville SDGC data for 21 discrete samples from seven different Wilsonville process streams.
- Use Wilsonville's boiling-point definition to divide APCI data into 100°F boiling-point cuts for each sample.

- Determine APCI area percents for each 100°F boiling-point cut for each sample.
- Obtain Wilsonville weight percents for corresponding boiling-point cuts for each sample.
- Calculate a hybrid response factor for each boiling-point cut by computing the ratio Wilsonville weight percent/APCI area percent for each sample.
- Compute a single "bulk response factor" for each 100°F boiling-point cut.

Table 1 lists the 21 samples used to establish the bulk response factors. These samples, consisting of three distinct samples from seven different process streams routinely tested at Wilsonville for material-balance analysis, vary from light to heavy distillates. They were analyzed by GC at APCI using Wilsonville conditions (as detailed in Kingsley et al., 1981; Kingsley and Schweighardt, 1981; Lamb and Kingsley, 1981).

The resultant chromatograms were compared to those generated at Wilsonville. Boiling-point cuts were defined by Wilsonville. The retention times at the defined cut points are listed in Table 2 for the Wilsonville results and in Table 3 for the APCI results. Means ($\bar{x}$) and standard deviations (SD) are also listed in these tables. The SD reflects the gas chromatographic reproducibility at both laboratories.

Table 4 lists the area percents of the boiling-point cuts for each of the APCI-generated and -analyzed chromatograms, and Table 5 lists the weight percents of the same boiling-point cuts for each of the Wilsonville-generated and -analyzed chromatograms. The results for the heavy oils (Table 5), which as calculated at Wilsonville include a 3 wt % residue value, were normalized to 100% to eliminate the residue value in order to better compare the gas chromatographic results. From the data in Tables 4 and 5, a series of hybrid response factors (Wilsonville weight percent/APCI area percent) for each boiling-point cut was calculated; these are listed in Table 6. Examination of these data reveals a greater scatter in the hybrid response factor for boiling-point cuts containing a low concentration of material. This scatter is due to experimental error, caused by the radically different chemical compositions of the sample streams. To correct this error, a weighted response factor (bulk response factor) was computed for each boiling-point cut as follows:

- Divide the Wilsonville weight percent for each boiling-point cut by the sum of the Wilsonville weight percent for that particular cut.
- Multiply the hybrid response factor by the weighted factor (bulk response factor) for each boiling-point cut for each sample.
- Sum the weighted hybrid response factors for each boiling-point cut.

The bulk response factor (BRF) was calculated with the following equation:

$$\mathrm{BRF} = \Sigma \left(\frac{\mathrm{WV\ wt\ \%}}{\mathrm{APCI\ area\ \%}} \right) \left(\frac{\mathrm{WV\ wt\ \%}}{\Sigma\ \mathrm{WV\ wt\ \%}} \right)$$

The bulk response factors for each boiling-point cut, computed this way, are shown in Table 6 and in Figure 8.

Screening Process-Stream Samples for Heavy and Light Distillates

In 1974, Wilsonville established that some process streams (light process streams) were completely laboratory distillable by ASTM method D-1160, whereas under the same conditions other samples (heavy process streams) left about a 3% residue. The seven process streams tested here (listed in Table 1) consist of three heavy and four light process streams.

The 1974 experiment prompted Wilsonville to assign a 3% residue to the three heavy process streams and no residue to the light process streams. Based on this information, the total amount of sample eluting from the GC column in the SDGC analysis for the heavy process streams was assumed to represent 97% of the sample. The final Wilsonville analytical report is adjusted accordingly to account for the 3% residue.

APCI's main objective is to simulate the Wilsonville SDGC method, which distinguishes between heavy and light process streams. To accomplish this objective, APCI devised a means of distinguishing between heavy and light streams. Rather than conducting an extensive distillation study for CPDU samples, APCI's approach was to examine the Wilsonville data to determine distinguishing characteristics of both heavy and light streams. Evaluation showed (Table 5) that all heavy distillates contain >5 wt % material in the >850°F cut, whereas all light distillates contain <5 wt % material in the >850°F cut. Thus, the computer program APCI developed was modified so that a sample could be distinguished as heavy or light distillate from the weight percent material in the >850°F cut.

Examples of Wilsonville's analyzed light distillate (stream no.'s 20 and P171) and heavy distillate (stream no.'s 3 and V110 dist) are shown in the chromatograms in Figures 9 and 10, respectively. In both figures, the boiling-point calibration is indicated along the base line. Observe that the chromatogram in Figure 9 has reached the base line at the end of the analysis (right side of graph), whereas in Figure 10 it has yet to reach the base line. This last phenomenon was observed for all heavy distillate samples (by Wilsonville definition) and implies that some very high boiling material is still eluting from the column, but the GC integrator is unable to differentiate any peaks. Therefore, the integrator assumes the base line is present in this outer region of a heavy distillate. The addition of 3 wt % residue value is, therefore, justified for the sake of the material balance. An absolute value of nondistillable residue, however, would be much more acceptable.

Define Initial and Final Boiling Points

ASTM method D-2887 defines the initial and final boiling points of a sample as the temperatures calculated from the retention times at the initial 0.5 area % and the final 0.5 area % of the sample's chromatogram. Wilsonville employs a similar procedure: the initial boiling point (IBP) and final boiling point (FBP) of a sample are determined as 0.5 wt % and 99.5 wt % of a sample, respectively, calculated using the previously described reponse factors. APCI used the same approach to simulate the Wilsonville procedure.

REPRODUCING WILSONVILLE'S RESULTS

A computer program was written incorporating all previously described computations. Data from each SDGC analysis performed at APCI on the 21 Wilsonville samples were then run through the computer to obtain weight percents of 100°F distillate cuts, initial and final boiling points, and percent residue. These results were compared with those obtained at Wilsonville.

Initial and Final Boiling Points

Table 7 compares the initial and final boiling points and Figure 11 correlates the APCI and Wilsonville boiling points. The linear regression equation is as follows:

$$BP_{APCI} = 0.949BP_{WV} - 6.115 \ (r = 0.991)$$

This shows better agreement than the IBP and FPB separately. The dotted line in Figure 11 represents a slope of 1.0 and an intercept of zero, which would be the line for perfectly matching results. The overall trend is that the APCI initial and final boiling points are approximately 5% lower than the Wilsonville boiling points. This discrepancy could stem from the different criteria at which the Wilsonville or APCI integrators calculate the initial and final 0.5 area % of the chromatogram, which defines the initial and final boiling points.

Screening for Heavy and Light Distillates

The results of APCI's screening for heavy and light distillates are shown in the residue column of Table 8. Observe that the three heavy distillate process streams (no's. 17, 29, and 3) were identified correctly via the previously described computation. A perfect agreement with the Wilsonville results was achieved and APCI's method for distinguishing heavy and light distillates was considered valid.

Weight Percents for 100°F Distillate Cuts

Results from APCI's simulation of Wilsonville SDGC for 21 process stream samples are also shown in Table 8. These results are then compared to Wilsonville's SDGC results (Table 5) in Figure 12, which shows a plot of the weight percents for each 100°F boiling-point cut from the two laboratories. A similar comparison was performed for the 100°F steps of cumulative weight percents (Figure 13).

A linear regression was performed to compare the APCI and Wilsonville SDGC results on a stream-by-stream basis. The Wilsonville results were treated as the independent variable (x), whereas the APCI results were the dependent variable (y). Analysis of the individual weight percents and cumulative weight percents of 100°F boiling-point cuts for three distinct samples of each process stream generated the data shown in Table 9. Perfect agreement between the two methods would result in a slope of 1.0 and an intercept of 0.0. A comparison of APCI and Wilsonville data indicates the following:

- Cumulative weight percents agree better than individual weight percents.
- For cumulative and individual weight percents, all slopes are near one, all intercepts are small, and weight percents fluctuate close to the values for all streams combined.
- For cumulative and individual weight percents, the data for stream no. 17 show the greatest amount of scatter as reflected in the low correlation coefficient.

Based on the above linear regression analysis, it is clear that APCI can duplicate the Wilsonville SDGC results with excellent agreement in all aspects, for the 21 samples analyzed.

Cumulative Weight Percents for 100°F Distillate Increments

To provide additional insight into the comparison, means and standard deviations from the cumulative weight percents of the 100°F boiling-point cuts of the 21 samples were determined (see Table 10). A comparison of APCI and Wilsonville data indicates the following:

- The means for 100°F boiling-point cuts are very similar in all cases.

- Standard deviations of the means are generally low and comparable.
- Sums of the standard deviations (Σ SD), a measure of the sample-to-sample variation in composition, for each process stream are also generally low and comparable, except for stream no. 17.
- Totals of the Σ SD's are similar and reflect comparable precision.

It was noted during the APCI SDGC analysis that three samples from process stream no. 17 contained some water; even after careful sampling, the results were less reproducible than those for other process stream samples. Therefore, the increased scatter (higher SD) and lower correlation (r) of the APCI and Wilsonville results for process stream no. 17 were attributed to sample composition, not analytical method.

ANALYSIS OF CPDU SAMPLES BY WILSONVILLE SDGC

The objective of this portion of the program was to analyze CPDU-generated samples by using the Wilsonville SDGC method at APCI. This allows direct comparison of CPDU and Wilsonville process streams with respect to boiling point-distribution.

A total-product-liquid (CPDU) sample, obtained during a demonstration-plant-condition run (HCL 43-149), was extracted with n-pentane by solvent separation to obtain the "oils" fraction. This sample was then analyzed at APCI by the Wilsonville SDGC method and the results of the boiling-point distribution were compared to the Wilsonville SDGC results for light (Figure 14) and heavy process streams (Figure 15) The boiling-point distributions for the CPDU sample and the seven Wilsonville process streams are compared numerically for the 100°F boiling-point cuts in Table 11.

Figure 14 shows that the boiling-point distribution for the CPDU sample differs from that for the four light Wilsonville process streams. Figure 15 shows that the boiling-point distribution for the CPDU sample is similar to that for the three heavy process streams; it appears to be most similar to that of process stream no. 29, the Wilsonville process solvent.

COMPARISON OF WILSONVILLE SDGC RESULTS TO ASTM D-2887 RESULTS

The same 21 Wilsonville samples were analyzed by the ASTM SDGC method, D-2887. The results of this method and the Wilsonville SDGC method were compared for the following:

- Initial- and final-boiling-point determination
- ASTM area percent vs. Wilsonville weight percent of 100°F boiling-point cuts
- Analysis reproducibility

Initial and Final Boiling Points

The ASTM D-2887 results for initial and final boiling points are compared with the Wilsonville results in Table 12 and in Figure 16. This comparison is described by the linear regression curve as follows:

$$BP_{ASTM} = 0.847BP_{WV} + 35.643 \qquad (r = 0.994) \qquad (6)$$

It is clear from this comparison that the correlation of the two methods is good (r = 0.994). While the ASTM D-2887 method does not duplicate the Wilsonville results, it is possible to interconvert ASTM D-2887 boiling points to Wilsonville SDGC boiling points using equation 6.

The deviation of the Wilsonville results from the ASTM results is indicated by the dotted line in Figure 16, which is the line for perfect agreement. This deviation is similar to that in Figure 1, which shows the effect of using aliphatic vs. aromatic standards for retention-time calibration. Figure 16, therefore, illustrates the major difference between ASTM D-2887 and the Wilsonville method, that is, the selection of the boiling-point calibration standards.

ASTM Area Percent vs. Wilsonville Weight Percent

The GC area percents for 100°F boiling-point cuts obtained by ASTM D-2887 analysis are listed in Table 13, and Figure 17 compares the ASTM individual area percents with the individual Wilsonville weight percents. A correlation coefficient of 0.863 indicates that results from both methods correlate poorly. This poor correlation precludes the establishment of an equation to allow for direct interconversion of ASTM individual area percents to Wilsonville individual weight percents. The ASTM cumulative area percent is compared with the Wilsonville cumulative weight percent in Figure 18. The best-fit linear regression line is also shown. The linear correlation coefficient for these data is improved to 0.979. Visual inspection of the data in Figure 18 indicates that throughout the majority of the distillation range most data points fall above the best fit of the data. Thus, this equation could then be used to interconvert ASTM and Wilsonville cumulative SDGC results.

Analysis Reproducibility

To describe the analytical reproducibility of ASTM D-2887, means and standard deviations of the cumulative area percent of the 100°F boiling-point cuts were obtained. These results are compared to the Wilsonville cumulative weight percent results in Table 14 and indicate the following:

- The means for the 100°F boiling-point cuts are not consistently similar.
- Standard deviations of the means are generally lower for the ASTM method.
- Sums of the standard deviations (Σ SD) for the ASTM method are much lower, reflecting better precision.
- As found previously (Table 10), process stream no. 17 showed less reproducible results than the other process streams.

The consistently lower standard deviation for the ASTM method can be explained by the difference in modes of integration. APCI concludes that the mode of integration used in the ASTM procedure, time slicing, is a more precise method than the Wilsonville mode of integration, peak area integration.

CONCLUSIONS

The data presented in this report provide the basis for three comparisons. The following conclusions have been drawn:

Boiling-point distribution from the Wilsonville SDGC methods at APCI and Wilsonville:

- Wilsonville SDGC boiling-point distributions can be duplicated at APCI with excellent agreement.
- APCI's method of identifying heavy and light distillates duplicates Wilsonville's results.
- APCI's initial and final boiling points are about 5% lower than Wilsonville's.
- Wilsonville SDGC at APCI and at Wilsonville allows recognition of inconsistencies in process stream composition.

Boiling-point distribution from Wilsonville SDGC of a CPDU sample and of Wilsonville process streams:

- Duplication of Wilsonville's SDGC results at APCI provides the methodology necessary to compare CPDU samples to Wilsonville's process streams on the basis of boiling-point distribution.
- The single CPDU sample analyzed, when compared with the process streams, was found to be similar to the Wilsonville process solvent product.

Boiling-point distribution from Wilsonville SDGC and ASTM D-2887:

- ASTM boiling-point distributions correlate poorly with those from Wilsonville SDGC.
- ASTM initial and final boiling points are different from Wilsonville's (aliphatic vs. aromatic boiling-point standards).

- ASTM initial and final boiling points can be converted to Wilsonville's boiling points by a linear equation.
- ASTM boiling-point distributions are more precise than Wilsonville's (time slicing vs. peak area integration).

The accuracy of the results obtained by the ASTM and Wilsonville SDGC methods needs to be established by comparison to actual distillation results.

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Table 1

Samples of Seven Different Wilsonville Process Streams

Wilsonville process stream	Stream no.	Wilsonville sample no.	APCI sample no.	Distillate type
V164	34	67190	21	Light
		67368	22	
		67292	23	
T104 btm	35	67198	24	Light
		67371	25	
		67285	26	
P171	20	67293	27	Light
		67191	28	Light
		67369	29	
V177	17	67288	30	Heavy
		67195	31	
		67364	32	
V105 oil	11	67204	33	Light
		67192	34	
		67294	35	
V131A	29	67289	36	Heavy
		67189	37	
		67375	38	
V110 dist	3	67290	39	Heavy
		67188	40	
		67366	41	

Table 2

Retention Times (Seconds) of Peaks before and after the Wilsonville Cut Points

Wilsonville process stream	Stream no.	APCI sample no.	350°F		450°F		550°F		650°F		750°F		850°F	
V164	34	21	630	653[a]	894	922	1253[b]	1275	1522[c]	1559	1840[d]	1871	2055	2133
		22	628	648	890	917	1250	1272	1520	1557	1838	1858	2053	2104
		23	626	646	890	916	1249	1272	1518	1556	1838	1871	2054	2131
I104 btm	35	24	641	666	888	911	1242	1277	1511	1571	1845	1871	2108	2141
		25	619	661	900	921	1254	1275	1524	1561	1893	1864	2103	2133
		26	609	669	891	918	1249	1272	1519	1558	1837	1861	2053	2098
P171	20	27	629	645	894	921	1252	1275	1532	1500	--	--	--	--
		28	625	654	891	927	1263	1312	1545	1569	--	--	--	--
		29	626	642	892	918	1249	1274	1523	1597	--	--	--	--
V177	11	30	--	--	862	903	1249	1330	1524	1555	1843	1869	2109	2136
		31	--	--	843	915	1236	1270	1516	1540	1806	1846	2058	2137
		32	--	--	885	913	1255	1329	1522	1558	1839	1872	2131	2187
V105 oil	11	33	627	544	891	917	1251	1276	1522	1554	1815	1843	2082	2137
		34	629	653	892	920	1250	1273	1520	1558	1838	1876	2053	2130
		35	630	648	895	919	1254	1279	1524	1558	1819	1846	2087	2140
V131A	29	36	627	658	892	918	1254	1278	1531	1558	1819	1848	2113	2140
		37	--	578	895	910	1257	1333	1533	1575	1834	1870	2128	2176
		38	613	667	895	918	1251	1278	1525	1557	1818	1848	2116	2140
V110 dist	3	39 40 41	618	654	901	915	1258	1302	1534	1572	1833	1885	2100	2136
		Ranges	609- 641	642- 678	843- 901	903- 927	1236- 1263	1270- 1333	1511- 1545	1540- 1600	1806- 1845	1846- 1885	2053- 2131	2098- 2176
Seconds		$\bar{x}$	625	655	888	917	1251	1287	1524	1563	1831	1862	2088	2137
		SD	8	10	14	5	6	22	8	15	12	13	29	21
Minutes		$\bar{x}$	10.42	10.92	14.80	15.28	20.85	21.45	25.40	26.05	30.52	31.03	34.80	35.62
		SD	0.13	0.17	0.23	0.08	0.10	0.37	0.13	0.25	0.20	0.22	0.48	0.35

Peaks identified at Wilsonville as:

[a] Indan, BP 350°F.

[b] Dibenzofuran, BP 549°F.

[c] Phenanthrene, BP 643°F.

[d] Pyrene, BP 740°F.

Table 3

Retention Times (Minutes) of Peaks before and after the APCI Cut Points

Wilsonville process stream	Stream no.	APCI sample no.	350°F		450°F		550°F		650°F		750°F		850°F	
		21	10.50	11.24	15.67	16.23	22.06	22.42	26.72	27.09	31.91	32.25	35.70	37.22
V164	34	22	10.68	11.42	15.83	16.41	22.23	22.58	26.88	27.25	32.04	32.41	35.89	37.45
		23	10.81	11.56	16.02	16.58	22.44	22.79	27.10	27.47	31.81	32.30	36.19	37.80
		24	10.15	11.08	15.40	16.01	21.78	22.12	26.43	26.83	31.64	31.94	35.38	36.80
T104 btm	35	25	10.19	11.07	15.89	15.94	21.84	22.19	25.88	26.52	31.71	32.02	35.44	36.93
		26	10.03	10.98	15.34	15.93	21.76	22.11	26.42	26.82	31.56	32.29	35.35	36.81
		27	10.79	11.29	15.38	16.58	21.86	22.24	26.08	27.54	--	--	--	--
P171	20	28	10.82	11.11	15.54	16.24	21.69	22.09	26.02	27.51	--	--	--	--
		29	10.79	11.08	15.53	16.27	21.75	22.14	26.05	27.53	--	--	--	--
		30	—	--	15.67	16.34	22.34	23.02	26.66	27.03	31.50	32.34	35.92	37.08
V177	13	31	—	--	15.76	16.43	22.38	23.08	26.71	27.07	31.58	32.33	35.60	37.07
		32	—	--	15.73	16.38	22.38	23.04	26.65	27.03	31.55	32.31	35.59	36.54
		33	10.24	10.98	15.36	15.95	21.75	22.11	26.43	26.82	31.67	31.96	35.37	36.84
V105 off	11	34	10.24	10.00	15.40	16.00	21.82	22.16	26.51	26.68	31.63	32.00	35.40	36.86
		35	10.30	11.04	15.40	15.97	21.75	22.13	26.42	26.83	31.68	31.97	35.39	36.85
		36	9.49	11.19	15.47	15.90	21.85	22.19	26.71	27.07	31.89	32.26	35.65	36.54
V131A	29	37	9.42	11.08	15.34	15.85	21.72	23.23	26.62	26.97	31.75	32.15	35.50	36.39
		38	10.29	11.14	15.37	15.85	21.70	22.05	26.53	26.90	31.72	32.07	35.46	36.32
		39	10.19	11.10	15.34	15.77	21.60	21.96	26.55	26.92	31.78	32.16	35.53	36.47
V110 dist	3	40	10.13	11.05	15.32	15.76	21.63	21.97	26.62	26.98	31.[illegible]	32.22	35.52	36.48
		41	10.17	11.08	15.31	15.74	21.58	21.94	26.51	26.89	31.78	32.12	35.49	36.39
		Ranges	9.42- 10.82	10.98- 11.56	15.31- 16.02	15.74- 16.58	21.58- 22.44	21.94 23.23	25.88- 27.10	26.52- 27.54	31.[illegible]- 32.0[illegible]	31.94- 32.41	35.35- 36.19	36.39- 37.80
Seconds		$\bar{x}$	618	668	933	967	1315	1342	1591	1623	1904	1931	2135	2211
		SD	24	9	13	16	17	25	17	16	5	9	13	24
Minutes		$\bar{x}$	10.30	11.14	15.55	16.11	21.91	22.36	26.51	27.05	31.73	32.18	35.58	36.85
		SD	0.40	0.15	0.22	0.27	0.28	0.41	0.29	0.27	0.[illegible]	0.15	0.22	0.40

Table 4

APCI-Generated Area Percents for 100°F Boiling-Point Cuts of Seven Different Process Streams

Wilsonville process stream	Stream no.	APCI sample no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	>850°F
V164	34[1]	21	7.90	14.71	45.44	20.13	9.13	2.30	0.42
		22	8.19	14.74	44.65	20.44	9.03	2.49	0.46
		23	8.22	15.08	44.67	20.25	8.50	2.85	0.44
T104 btm	35	24	0.34	10.02	53.24	23.13	10.23	2.58	0.45
		25	0.49	6.66	52.23	21.17	16.16	2.63	0.66
		26	0.39	9.40	53.87	23.69	9.99	2.15	0.50
P171	20	27	5.13	33.17	57.00	4.22	0.48	0	0
		28	5.33	34.60	55.94	3.69	0.44	0	0
		29	5.01	31.27	58.96	4.26	0.50	0	0
V177	17	30	0	2.77	9.00	25.67	35.14	17.09	10.34
		31	0	1.03	9.50	31.46	36.95	12.87	8.20
		32	0	1.10	9.56	28.51	36.86	15.19	8.80
V105 oil	11	33	8.94	12.69	43.08	22.09	9.56	2.77	0.87
		34	7.79	12.92	45.22	21.13	9.34	2.24	1.36
		35	9.61	21.88	44.43	20.75	9.23	2.28	0.84
V131A	29	36	0.07	4.76	36.59	26.91	18.64	7.63	5.39
		37	0.35	4.81	35.38	27.20	19.87	8.37	4.03
		38	0.47	4.81	38.03	28.58	17.89	6.46	3.76
V110 dist	3	39	0.34	3.20	23.14	28.46	24.11	12.13	8.62
		40	0.21	3.16	24.71	29.64	23.81	11.22	7.26
		41	0.18	2.89	24.46	29.37	24.25	11.38	7.48

Table 5

Wilsonville-Generated Weight Percents and Sums for 100°F Boiling-Point Cuts of Seven Different Wilsonville Process Streams

Wilsonville process stream	Stream no.	APCI sample no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	>850°F	Distillate type
V1164	34	21	3.95	13.90	44.42	23.75	10.69	2.92	0.37	Light
		22	5.20	14.98	43.90	22.53	10.22	2.62	0.54	
		23	5.16	14.98	44.72	22.81	9.81	2.29	0.21	
T104 btm	35	24	0.34	8.43	47.28	26.60	11.26	4.14	1.95	Light
		25	0.33	5.92	48.87	27.99	12.70	3.32	0.88	
		26	0.13	8.06	49.41	27.05	11.92	2.82	0.60	
P171	20	27	2.35	38.58	54.43	4.59	0.04	0	0	Light
		28	4.50	38.45	52.84	3.80	0.39	0	0	
		29	1.98	36.25	56.41	5.09	0.22	0.55	0	
V177	17	30	--	0.32	7.56	27.33	37.95	15.25	12.11	Heavy
		31	--	0.12	5.79	24.20	30.30	17.35	22.24	
		32	--	0.19	7.56	27.19	38.16	17.74	9.16	
V105 oil	11	33	6.01	12.34	42.30	24.09	10.21	3.68	0.76	Light
		34	4.74	11.39	45.62	25.75	10.96	1.52	0.02	
		35	5.84	12.14	42.23	24.06	11.01	1.40	0.32	
V131A	29	36	0.04	4.09	32.93	28.52	19.65	7.09	7.68	Heavy
		37	--	3.29	32.16	27.95	20.63	7.95	8.02	
		38	0.01	3.16	32.89	29.12	19.59	9.01	7.25	
V110 dist	3	39	0.04	2.93	20.69	27.94	25.07	15.82	7.52	Heavy
		40	0.01	1.99	22.86	27.47	24.75	13.51	9.41	
		41	0.02	2.33	20.68	28.07	25.59	16.11	7.20	
		S	40.65	233.84	755.56	485.90	341.72	147.59	96.24	

Table 6

Hybrid Response Factors (HRF) and Bulk Response Factors (BRF) for Seven 100°F Boiling-Point Cuts

	Wilsonville process stream	Stream no.	APCI sample no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	>850°F
HRF	V164	34	21	0.500	0.945	0.975	1.180	1.170	1.268	0.887
			22	0.635	1.016	0.983	1.132	1.132	1.051	1.182
			23	0.628	0.993	1.001	1.127	1.154	0.804	0.482
	T104 btm	35	24	1.003	0.841	0.888	1.150	1.101	1.607	4.22
			25	0.671	0.888	0.936	1.322	0.786	1.260	1.33
			26	0.333	0.858	0.917	1.142	1.193	1.310	1.195
	P171	20	27	0.458	1.162	0.955	1.087	0.083	--	--
			28	0.845	1.111	0.945	1.029	0.895	--	--
			29	0.395	1.159	0.957	1.195	0.441	--	--
	V177	17	30	--	0.112	0.815	1.033	1.048	0.856	1.136
			31	--	0.117	0.592	0.756	0.795	1.308	2.630
			32	--	0.164	0.767	0.925	1.004	1.133	1.011
	V105 oil	11	33	0.672	0.973	0.982	1.091	1.31	1.329	1.136
			34	0.609	0.882	1.009	1.219	1.173	0.677	0.015
			35	0.607	1.061	0.950	1.160	1.194	1.193	0.381
	V131A	29	36	0.541	0.234	0.873	1.028	1.023	0.901	1.382
			37	--	0.664	0.882	0.997	1.007	0.921	1.930
			38	0.021	0.639	0.839	0.988	1.062	1.353	1.871
	V110 dist	3	39	0.118	0.916	0.894	0.982	1.041	1.304	0.872
			40	0.048	0.630	0.925	0.927	1.040	1.204	1.296
			41	0.111	0.806	0.846	0.956	1.055	1.416	0.693
BRF				0.624	1.074	1.004	1.165	1.156	1.444	1.800

Table 7

Comparison of Initial and Final Boiling Point (IBP and FBP) Determination at Wilsonville and APCI

Wilsonville process stream	Stream no.	APCI sample no.	IBP (°F)		FBP (°F)	
			Wilsonville	APCI	Wilsonville	APCI
V164	34	21	156	91	838	811
		22	133	98	857	812
		23	97	100	838	815
T104 btm	35	24	350	351	905	808
		25	355	351	866	821
		26	360	349	867	808
P171	20	27	281	268	624	667
		28	291	274	630	637
		29	291	273	634	674
V177	17	30	462	324	937	901
		31	466	413	1019	875
		32	463	411	937	854
V105 oil	11	33	67	82	866	835
		34	133	117	809	873
		35	117	809	866	837
V131A	29	36	396	353	961	903
		37	397	350	908	853
		38	396	352	925	852
V110 dist	3	39	372	351	937	875
		40	398	350	949	874
		41	384	360	937	853

Table 8

APCI-Generated Weight Percent of 100°F Boiling-Point Cuts of Seven Different Wilsonville Process Streams

Wilsonville process stream	Stream no.	APCI sample no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	>850°F	Residue
V164	34	21	4.7	15.2	45.8	21.5	8.9	3.2	0.7	0
		22	4.9	15.2	42.9	22.8	10.0	3.5	0.8	0
		23	4.9	14.0	44.4	22.6	9.4	3.9	0.8	0
T104 btm	35	24	0.2	10.0	52.0	24.0	10.0	3.1	0.8	0
		25	0.3	9.4	48.2	27.3	10.6	3.2	1.1	0
		26	0.2	12.4	49.6	24.4	9.4	2.9	0.8	0
P171	20	27	3.4	38.7	53.5	3.8	0.5	0	0	0
		28	3.3	40.2	52.5	3.3	0.5	0	0	0
		29	3.1	36.6	56.0	3.8	0.6	0	0	0
V177	17	30	0.5	1.5	7.0	26.7	27.9	19.1	14.4	3.0
		31	0	0.8	7.5	32.7	29.7	14.6	11.6	3.0
		32	0.1	0.8	7.5	29.8	29.4	17.1	12.4	3.0
V105 oil	11	33	5.4	16.0	40.5	23.5	9.6	3.5	1.5	0
		34	4.6	13.2	45.3	22.5	9.3	2.8	1.5	0
		35	5.2	13.4	45.4	22.3	0.4	2.8	1.5	0
V131A	29	36	0	6.1	30.0	27.2	16.5	9.2	8.1	3.0
		37	0.2	6.1	28.4	29.4	17.7	9.0	6.1	3.0
		38	0.3	6.3	32.2	28.9	16.6	6.9	5.8	3.0
V110 dist	3	39	0.2	3.7	19.2	28.0	20.9	12.5	12.5	3.0
		40	0.1	3.8	20.6	29.3	19.5	13.1	10.6	3.0
		41	0.1	3.6	29.9	29.7	21.5	12.1	9.2	3.0

Table 9

Linear Regression Analysis of APCI vs. Wilsonville Simulated Distillation by Gas Chromatography Cuts

Wilsonville process stream	Stream no.[1]	Individual weight percents: Slope (m)	Individual weight percents: Intercept (b)	Individual weight percents: Correlation coefficient (r)	Cumulative weight percents: Slope (m)	Cumulative weight percents: Intercept (b)	Cumulative weight percents: Correlation coefficient (r)
V164	34	0.986	0.182	0.9976	0.989	0.355	0.9994
T104 btm	35	1.006	-0.074	0.9921	0.991	2.255	0.9986
P171	20	0.999	0.015	0.9994	0.995	0.671	0.9998
V177	17	0.872	1.808	0.9334	0.993	1.530	0.9865
V105 oil	11	0.981	0.272	0.9866	0.982	1.316	0.9988
V131A	29	0.934	0.909	0.9869	0.987	1.739	0.9987
V110 dist	3	0.917	1.183	0.9666	0.974	1.581	0.9980
All streams combined		0.971	0.405	0.9871	0.986	1.457	0.9970

APCI wt % = m x WV wt % + b

Table 10

Means and Standard Deviations of Cumulative Weight Percents for Three Distinct Samples from Seven Process Streams: APCI vs. Wilsonville Analysis

Wilsonville process stream	Stream no.	APCI sample no.		<350°F		350-450°F		450-550°F		550-650°F		650-750°F		750-850°F		Σ SD	
				$\bar{x}$[a]	SD[b]	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	ASTM[c]	Wilsonville
V164	34	21-23	APCI	4.8	0.1	19.6	0.6	64.0	1.5	86.3	0.8	95.7	0.4	99.2	0.1	3.5	4.7
			WV	4.8	0.7	19.7	1.3	67.8	1.3	80.8	0.8	97.0	0.4	99.6	0.2		
1104 btm	35	24-26	APCI	0.2	0.1	10.9	1.7	60.8	2.5	86.0	0.8	95.6	0.2	99.1	0.1	5.4	6.2
			WV	0.2	0.1	7.7	1.3	56.2	1.3	83.7	1.1	95.6	1.5	99.0	0.9		
P171	20	27-29	APCI	3.3	0.2	41.8	1.9	95.9	0.4	99.5	0.1					2.6	4.5
			WV	3.0	1.3	40.8	2.4	95.9	0.6	99.8	0.2						
V177	17	30-32	APCI	0.2	0	1.3	0.2	6.5	7.2	38.8	3.4	69.4	3.7	86.8	1.4	12.8	18.5
			WV	0	0	0.2	0.1	7.2	1.1	33.4	2.9	68.9	7.4	85.7	7.0		
V105 oil	11	33-35	APCI	5.1	0.4	19.3	1.9	63.0	1.1	85.8	0.5	95.2	0.4	98.2	0.4	4.7	6.4
			WV	5.5	0.4	17.4	1.2	60.8	0.8	85.5	1.8	96.4	1.8	99.6	7.0		
V131A	29	36-38	APCI	0.2	0.2	6.5	0.3	37.7	2.1	67.1	2.4	84.5	2.3	93.1	1.3	8.6	3.9
			WV	0	0	3.5	0.5	36.2	0.8	45.7	1.1	84.7	0.6	92.7	0.9		
V110 dist	3	29-41	APCI	0.1	0.1	3.9	0.1	24.8	0.9	54.7	1.8	76.0	2.0	88.0	1.5	6.4	5.5
			WV	0	0	2.4	0.5	23.8	1.0	51.7	0.7	76.8	0.3	90.9	3.0		
															Total	44.0	49.7

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[a] $\bar{x}$, mean.

[b] SD, standard deviation.

[c] ASTM, American Society for Testing and Materials.

Table 11

Cumulative Weight Percents of 100°F Distillate Cuts of Seven Wilsonville Process Streams and a Coal Process Development Unit Sample by the Wilsonville Simulated Distillation by Gas Chromatography Method

Wilsonville process stream	Stream no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F	>850°F
V165	34	5	20	65	86	96	99	100
T104 btm	35	0	11	61	86	96	99	100
P171	20	3	42	96	100			
V105 oil	11	5	19	63	86	95	98	100
V177	17	0	1	7	39	69	87	97
V131A	29	0	7	38	67	85	93	97
V110 dist	3	0	4	25	55	76	88	97
APCI CPDU sample		0	6	29	54	76	83	97

Table 12

Comparison of Initial and Final Boiling Point (IBP and FBP) Determination by Wilsonville Simulated Distillation by Gas Chromatography and ASTM D-2887

Wilsonville process stream	Stream no.	APCI sample no.	IBP (°F) ASTM D-2887	IBP (°F) Wilsonville	FBP (°F) ASTM D-2887	FBP (°F) Wilsonville
V164	34	21	100	156	769	838
		22	97	133	765	857
		23	98	97	757	838
		24	370	350	774	905
T104 btm	35	25	372	355	772	866
		26	368	360	769	867
P171	20	27	301	281	571	624
		28	306	291	571	630
		29	307	291	574	634
V177	17	30	370	462	834	937
		31	390	466	824	1019
		32	400	463	829	937
V105 oil	11	33	87	67	761	866
		34	137	133	762	809
		35	96	97	761	866
V131A	29	36	387	396	830	961
		37	391	397	826	908
		38	391	396	822	925
V110 dist	3	39	388	372	841	937
		40	389	398	828	949
		41	391	384	834	937

Table 13

ASTM D-2887 Area Percent of 100°F Boiling-Point Cuts of Seven Different Wilsonville Process Streams

Wilsonville process stream	Stream no.	APCI sample no.	<350°F	350-450°F	450-550°F	550-650°F	650-750°F	750-850°F
V164	34	21	6	27	41	20	5	1
		22	6	28	41	19	5	1
		23	6	29	41	18	5	1
T104 btm	36	24	0	25	47	21	6	1
		25	0	20	50	23	6	1
		26	0	24	48	21	6	1
P171	20	27	4	62	32	2		
		28	4	63	31	2		
		29	4	60	34	2		
V177	17	30	0	7	15	43	27	8
		31	0	3	14	43	27	7
		32	0	2	12	48	30	8
V105 oil	11	33	6	26	42	20	5	1
		34	5	26	43	20	5	1
		35	6	25	43	20	5	1
V131A	29	36	0	15	37	30	14	4
		37	0	13	37	31	14	5
		38	0	13	39	30	14	4
V110 dist	3	39	0	7	29	35	21	8
		40	0	8	29	35	21	7
		41	0	7	28	36	22	7

Table 14

Means and Standard Deviations of Cumulative Weight Percents for Three Distinct Samples from Seven Process Streams: APCI vs. Wilsonville Analysis

Wilsonville process stream	Stream no.	APCI sample no.		<350°F		350-450°F		450-550°F		550-650°F		650-750°F		750-850°F		Σ SD	
				$\bar{x}$[a]	SD[b]	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	ASTM[c]	Wilsonville
V164	34	21-23	ASTM	6.0	0.0	34.0	1.0	75.0	1.0	94.0	0.0	99.0	0.0	100.0	0.0	2.0	4.7
			WV	4.8	0.7	19.7	1.3	67.8	1.3	80.8	0.8	97.0	0.4	99.6	0.2		
T104 btm	35	24-26	ASTM	0.0	0.0	23.0	2.6	71.3	1.2	93.0	0.0	99.0	0.0	100.0	0.0	3.0	6.2
			WV	0.2	0.1	7.7	1.3	56.2	1.3	83.7	1.1	95.6	1.5	99.0	0.9		
P171	20	27-29	ASTM	4.0	0.0	65.7	1.5	98.0	0.0	100.0	0.0					1.5	4.5
			WV	3.0	1.3	40.8	2.4	95.9	0.6	99.8	0.2						
V177	17	30-32	ASTM	4.0	0.0	4.0	2.6	17.7	4.0	64.3	2.1	92.3	0.6	100.0	0.0	9.3	10.5
			WV	0	0	0.2	0.1	7.2	1.1	33.4	2.9	66.9	7.4	85.7	7.0		
V105 oil	11	33-35	ASTM	5.7	0.7	31.13	0.6	74.0	0.0	94.0	0.0	99.0	0.0	100.0	0.0	1.3	6.4
			WV	5.5	0.4	17.4	1.2	60.8	0.8	85.5	1.8	96.4	1.8	99.6	7.0		
V131A	29	36-38	ASTM	0	0	15.7	1.2	51.3	1.2	81.7	0.6	95.7	0.6	100.0	0.0	3.6	3.9
			WV	0	0	3.5	0.5	36.2	0.8	45.7	1.1	84.7	0.6	92.7	0.9		
V110 dist	3	29-41	ASTM	0	0	7.4	0.6	35.0	1.0	71.3	0.6	92.7	0.6	100.0	0.0	2.0	5.5
			WV	0	0	2.4	0.5	23.8	1.0	51.7	0.7	76.8	0.3	90.9	3.0		
															Total	24.3	49.7

[a] $\bar{x}$, mean.

[b] SD, standard deviation.

[c] ASTM, American Society for Testing and Materials.

Figure 1
Retention Time vs. Boiling Point for Aromatic and Aliphatic Compounds

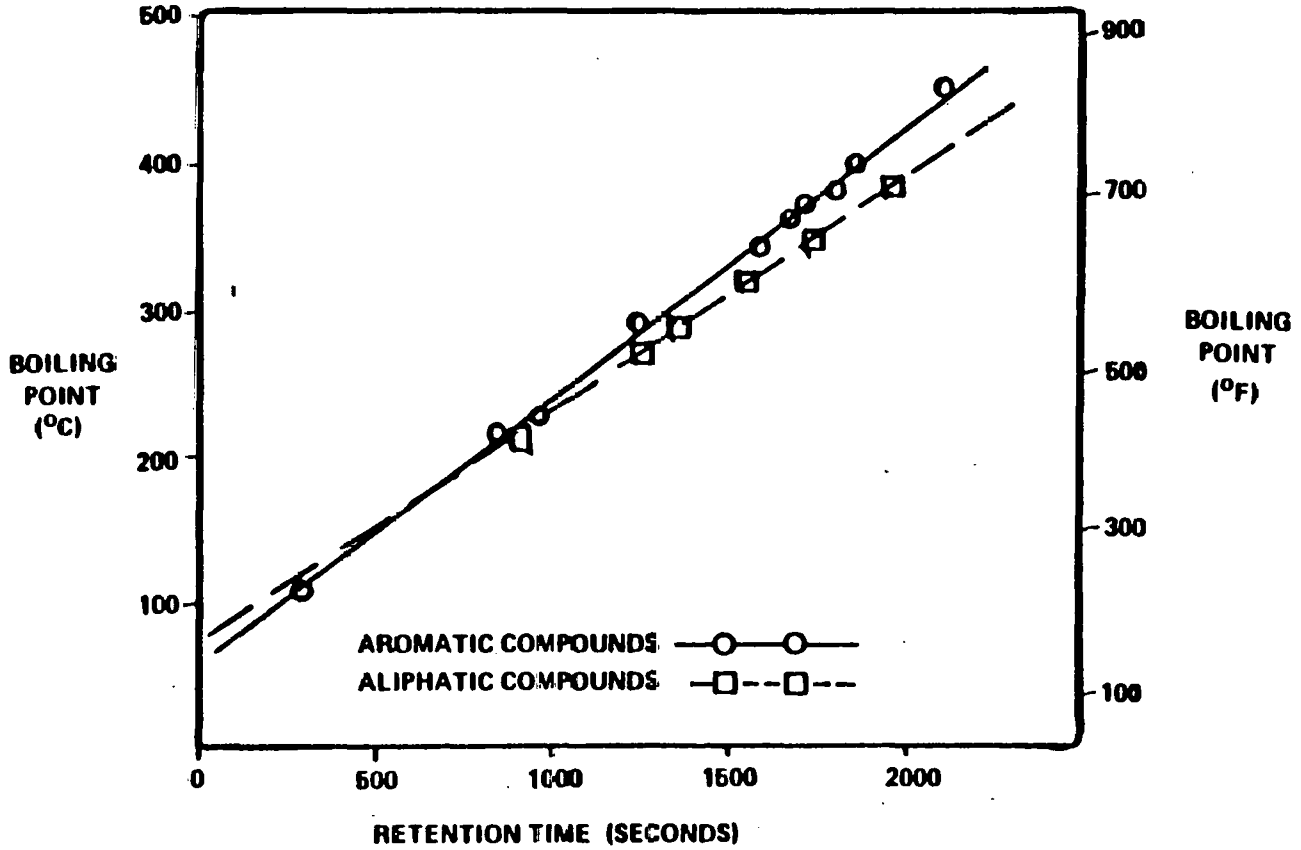


Figure 2
Modes of Integration and Calibration for Boiling Point Distribution of a Wilsonville Recycle Solvent.

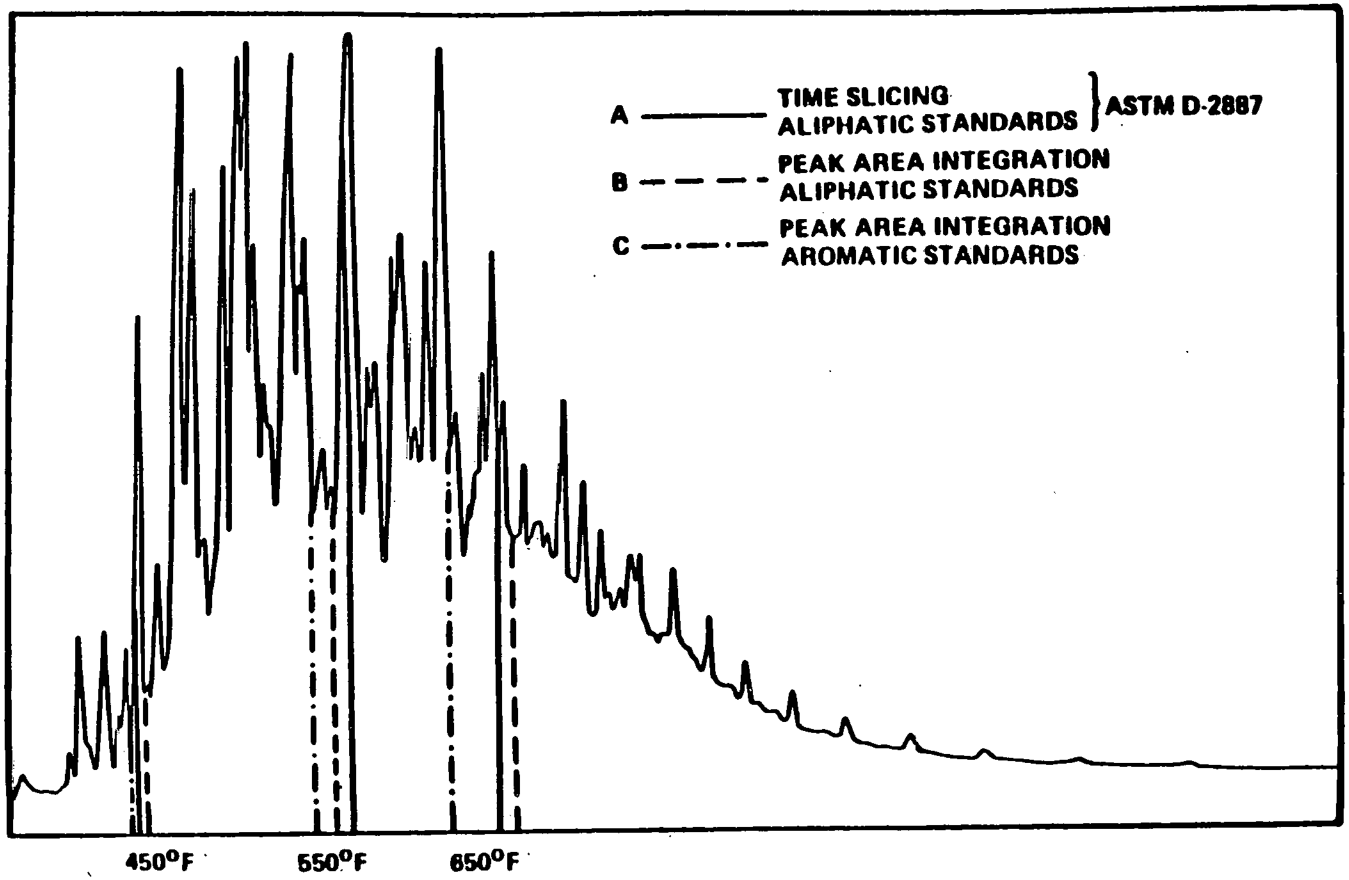


Figure 3
Wilsonville Conversion of Gas Chromatograph-Retention Time to Response Factor

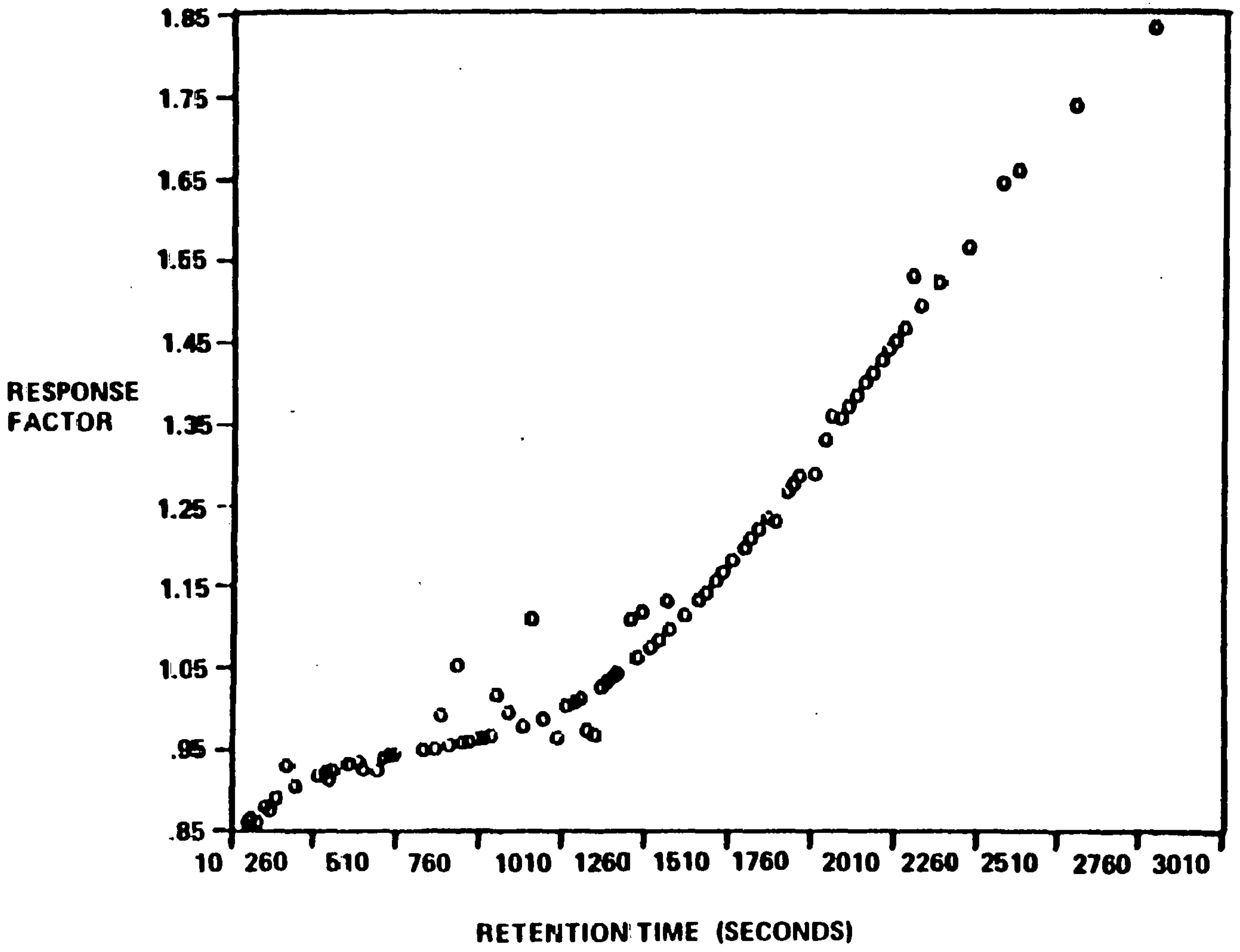


Figure 4
Boiling Point Distribution of Wilsonville Recycle Solvent

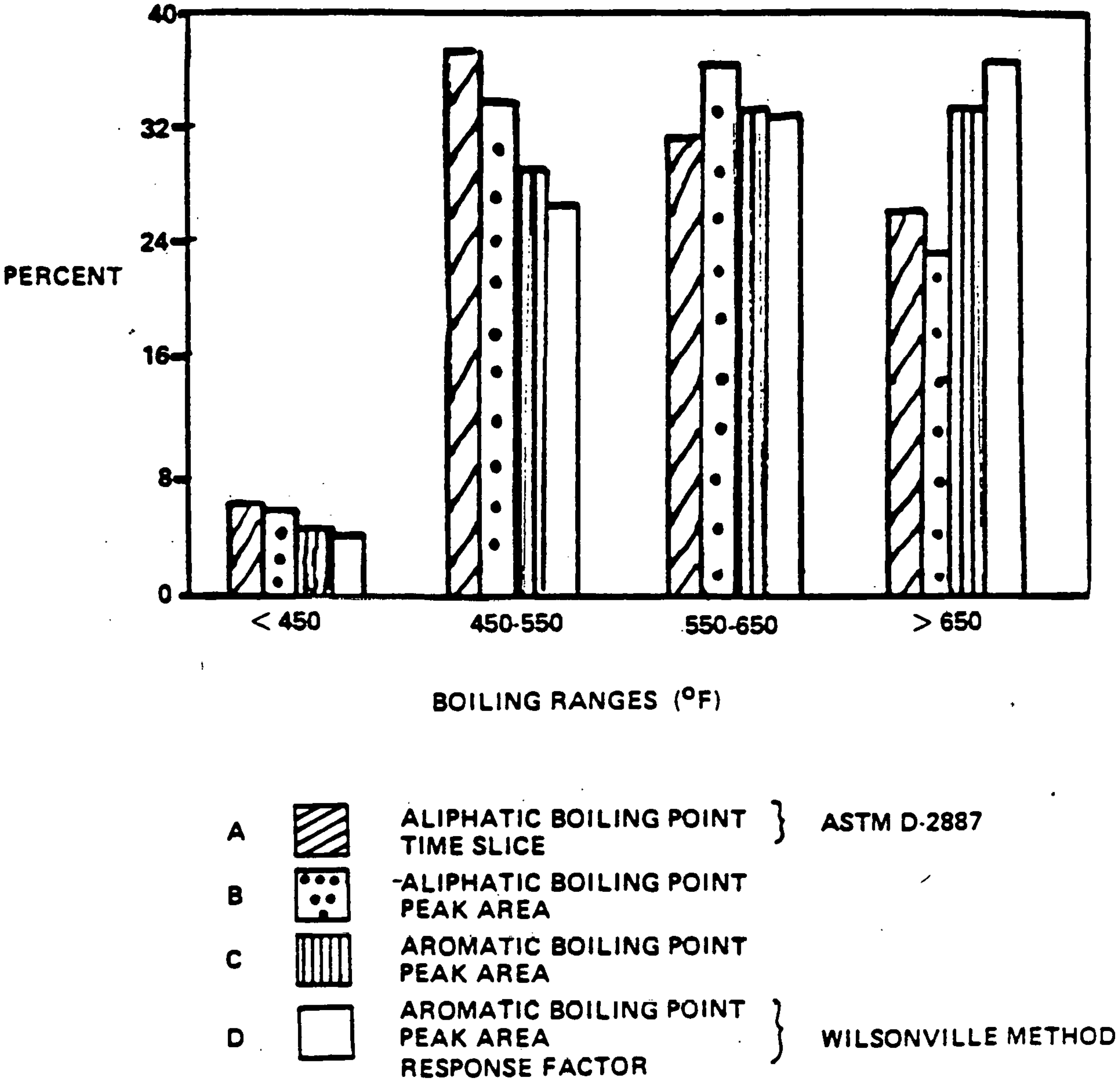


Figure 5
Wilsonville's Conversion of Gas Chromatograph-Retention Time to Boiling Point

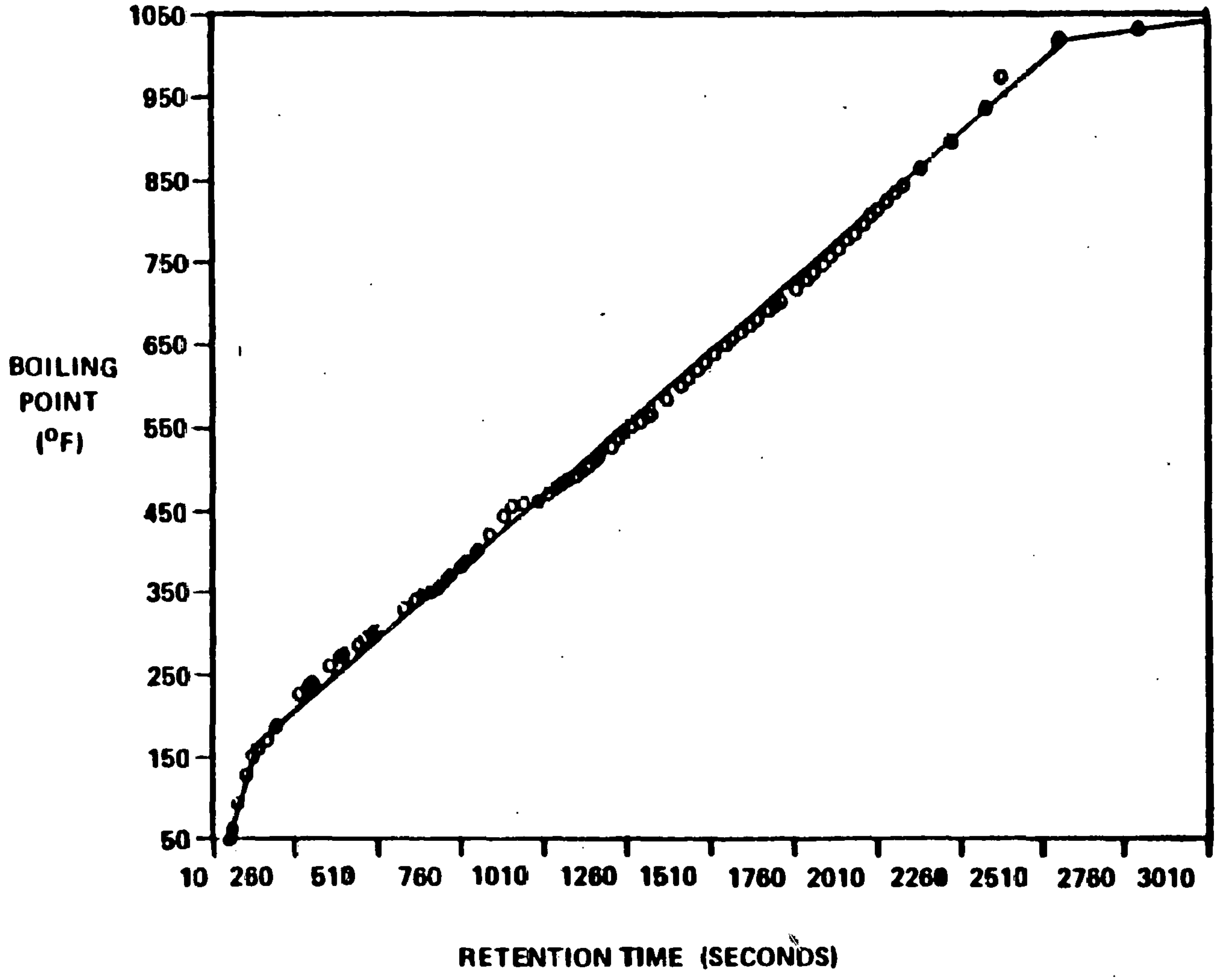
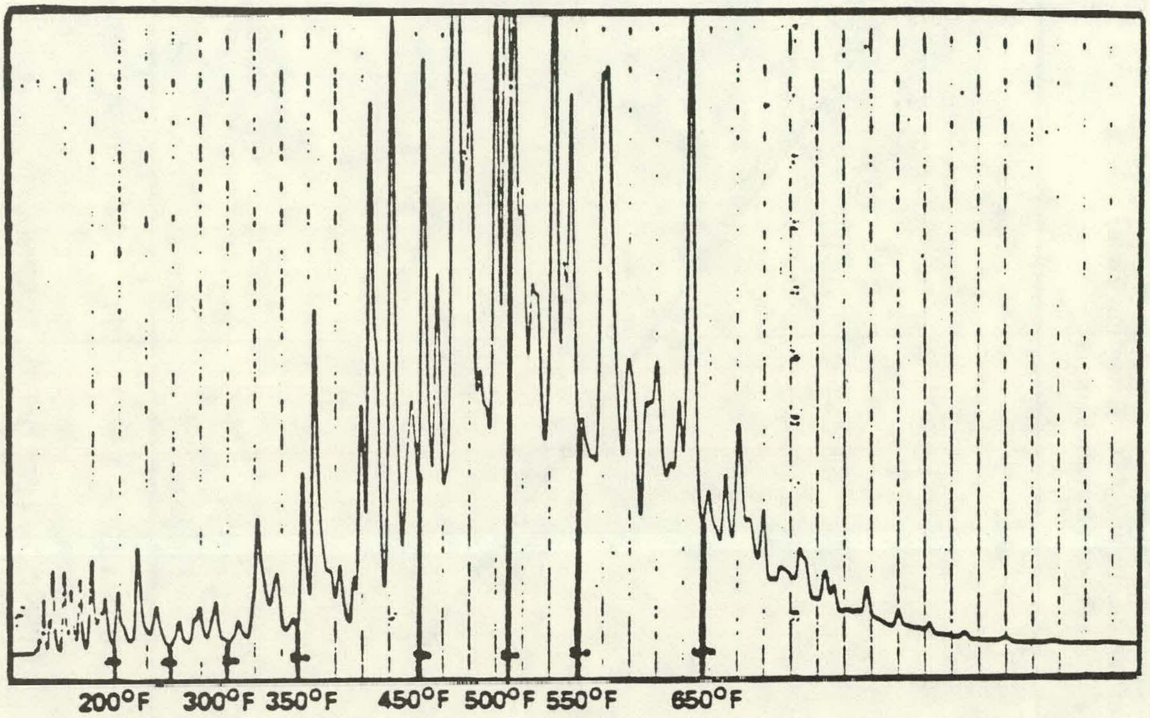


Figure 6
Chromatograms of V164 Process Stream

a. Wilsonville Analysis



b. APCI Analysis

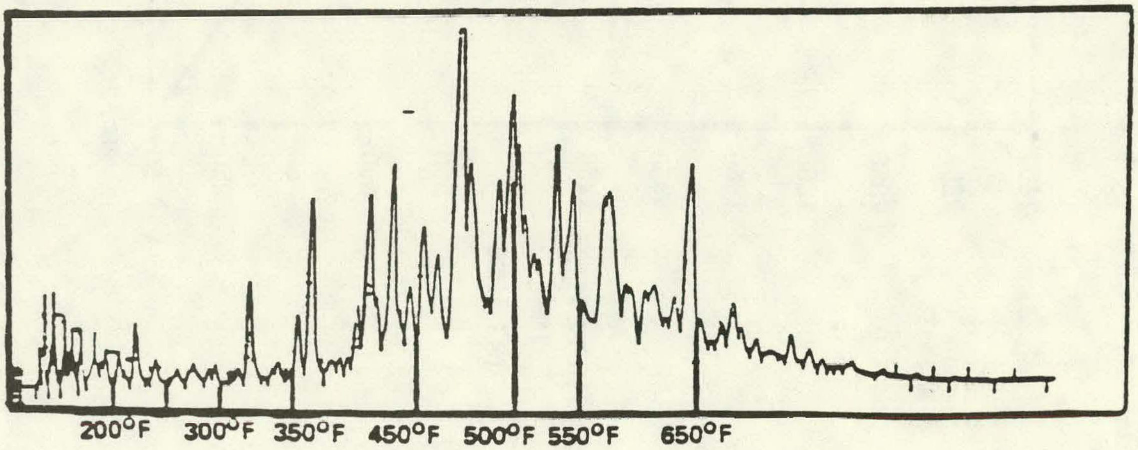


Figure 7
Comparison of Wilsonville and APCI Retention Times
of a V164 Process Stream Sample

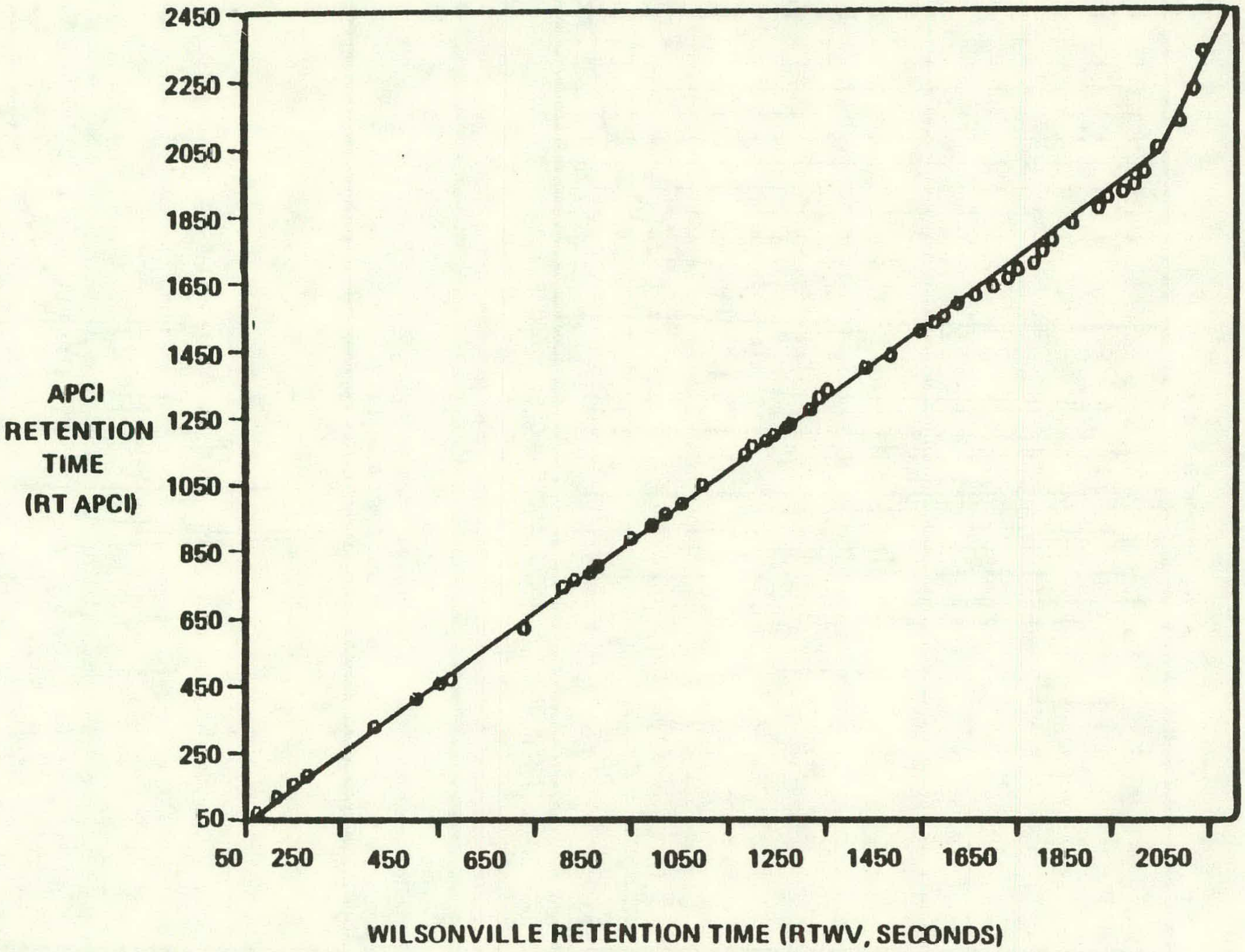


Figure 8

Calculated Bulk Response Factors for 100°F Distillate Fractions for Conversion of Gas Chromatograph Area Percent into Wilsonville Weight Percent

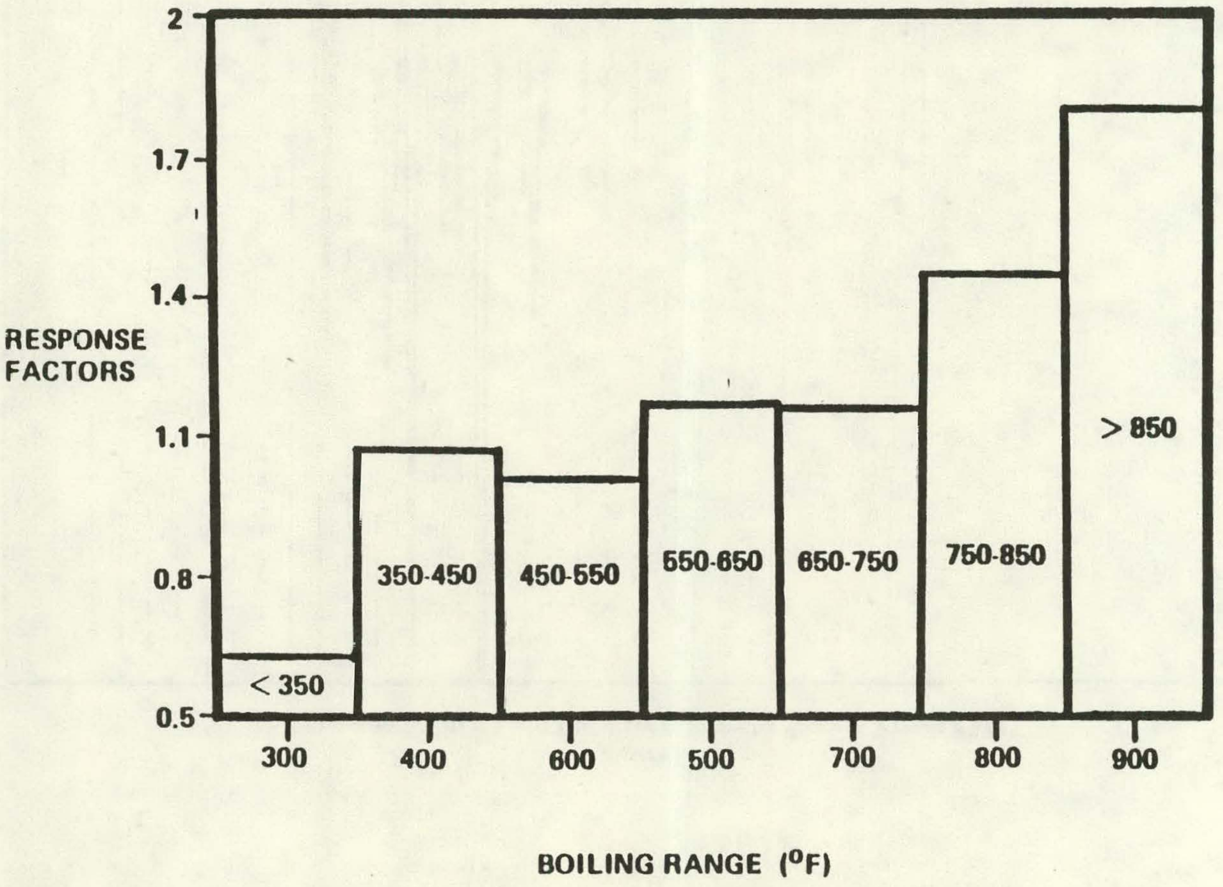


Figure 9
Chromatogram of a Light Distillate Wilsonville Process Stream P171

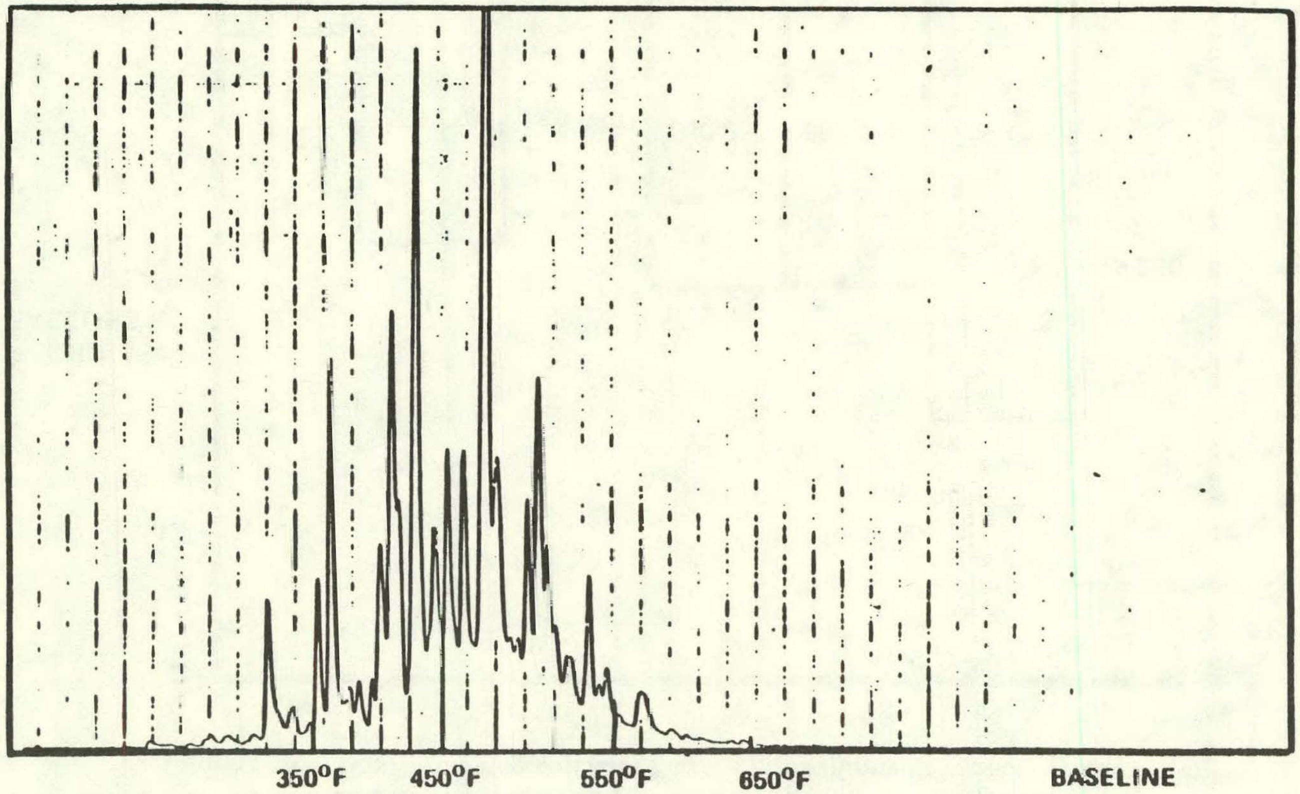


Figure 10

Chromatogram of a Heavy Distillate Wilsonville Process Stream V110

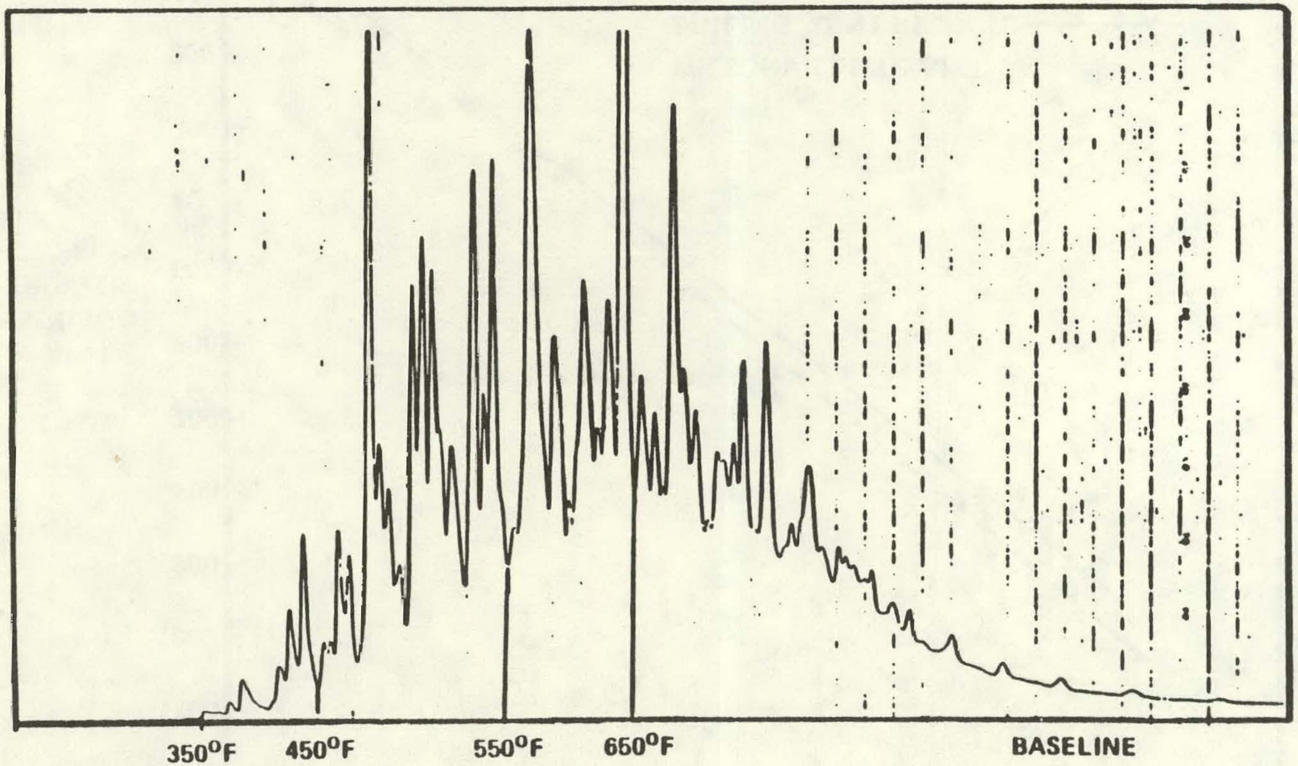


Figure 11
APCI Boiling Point Determination on Seven Wilsonville Process Stream Samples

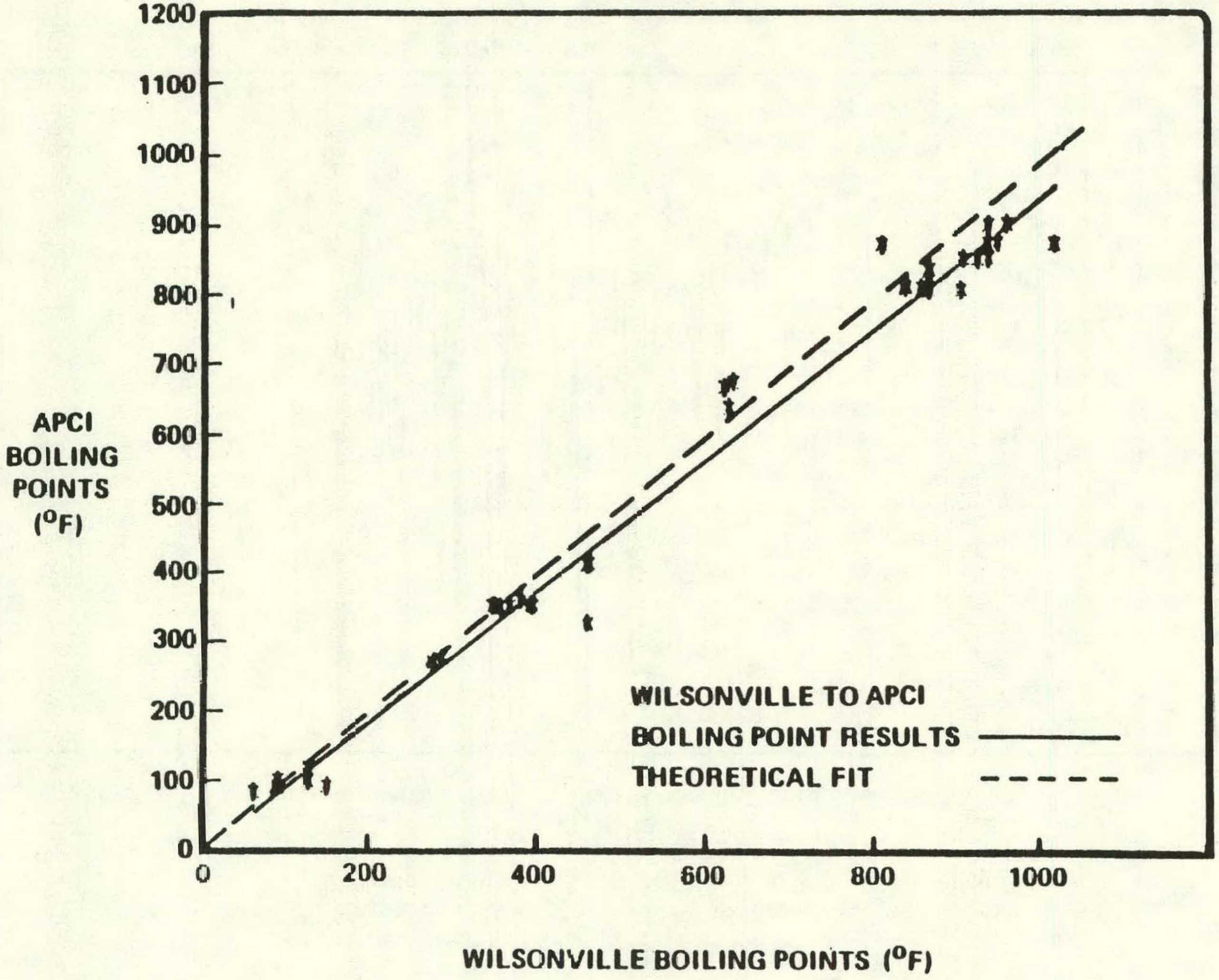


Figure 12
Weight Percents of 100°F Distillate Cuts of Seven Wilsonville Process Stream Samples; Analysis at APCI Compared to Wilsonville Analysis

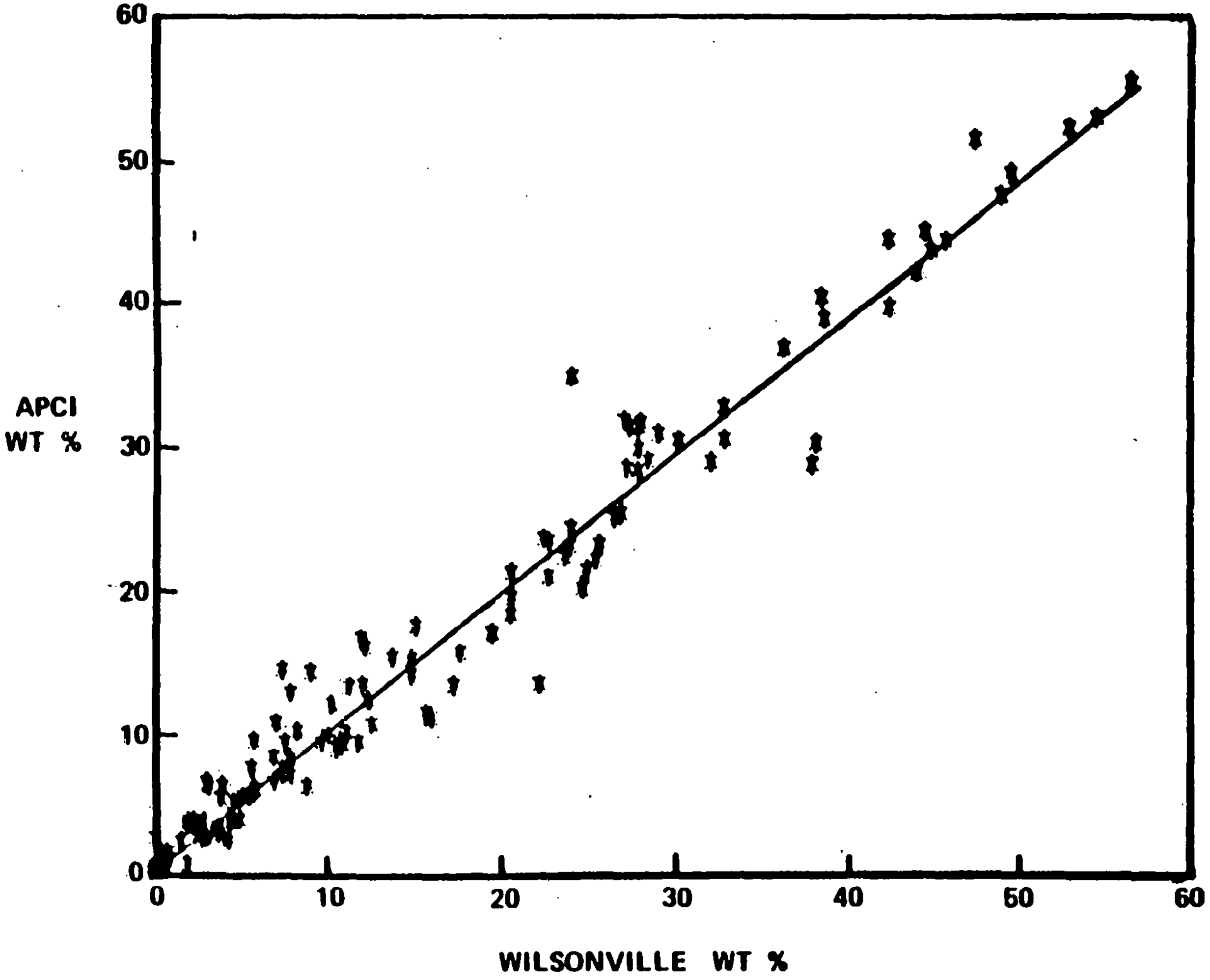


Figure 13
Cumulative Weight Percents of 100°F Distillate Cuts; APCI vs. Wilsonville

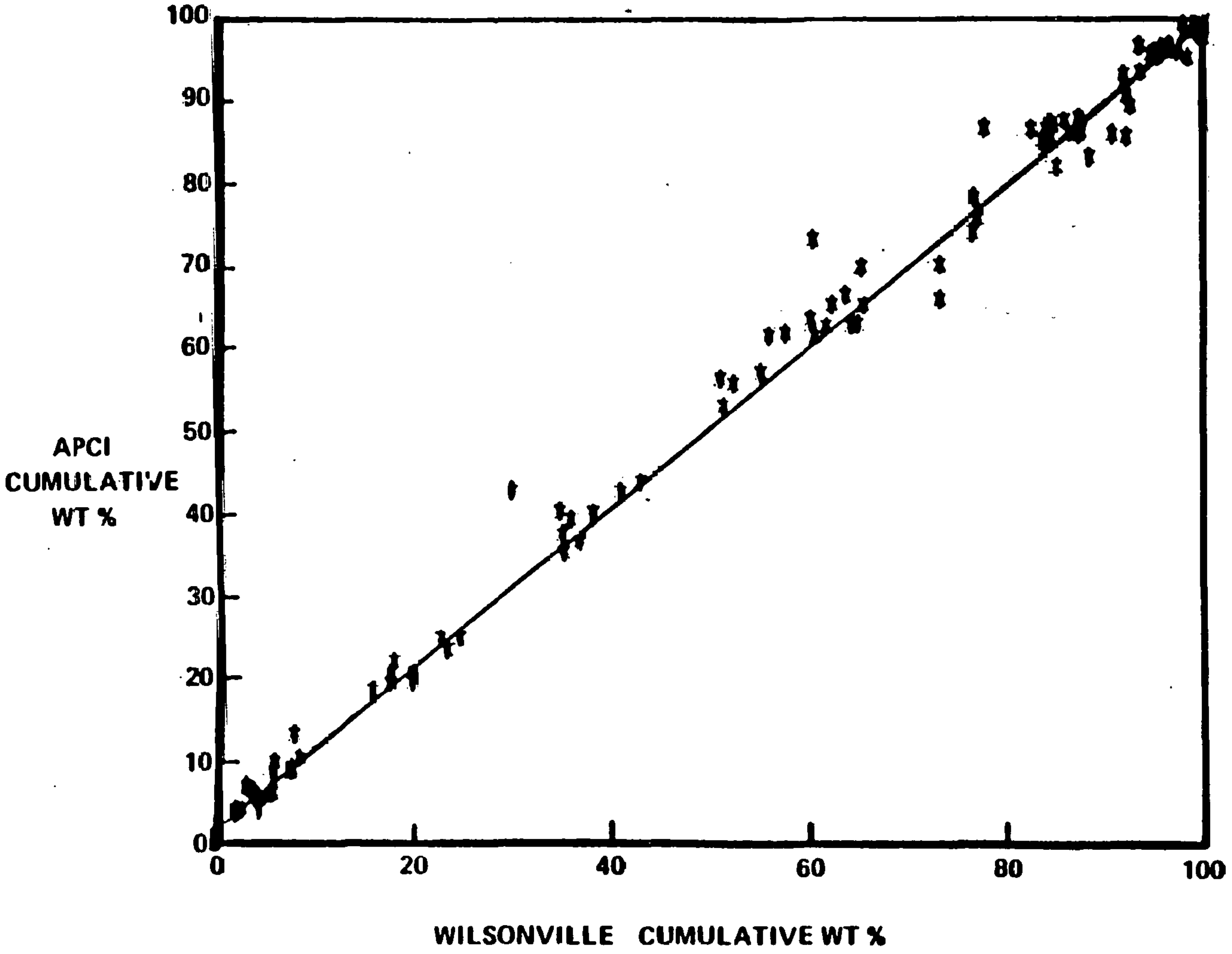


Figure 14
Boiling Point Distribution of Wilsonville Light Process Streams and Continuous Process Development Unit Sample by Wilsonville Simulated Distillation by Gas Chromatography

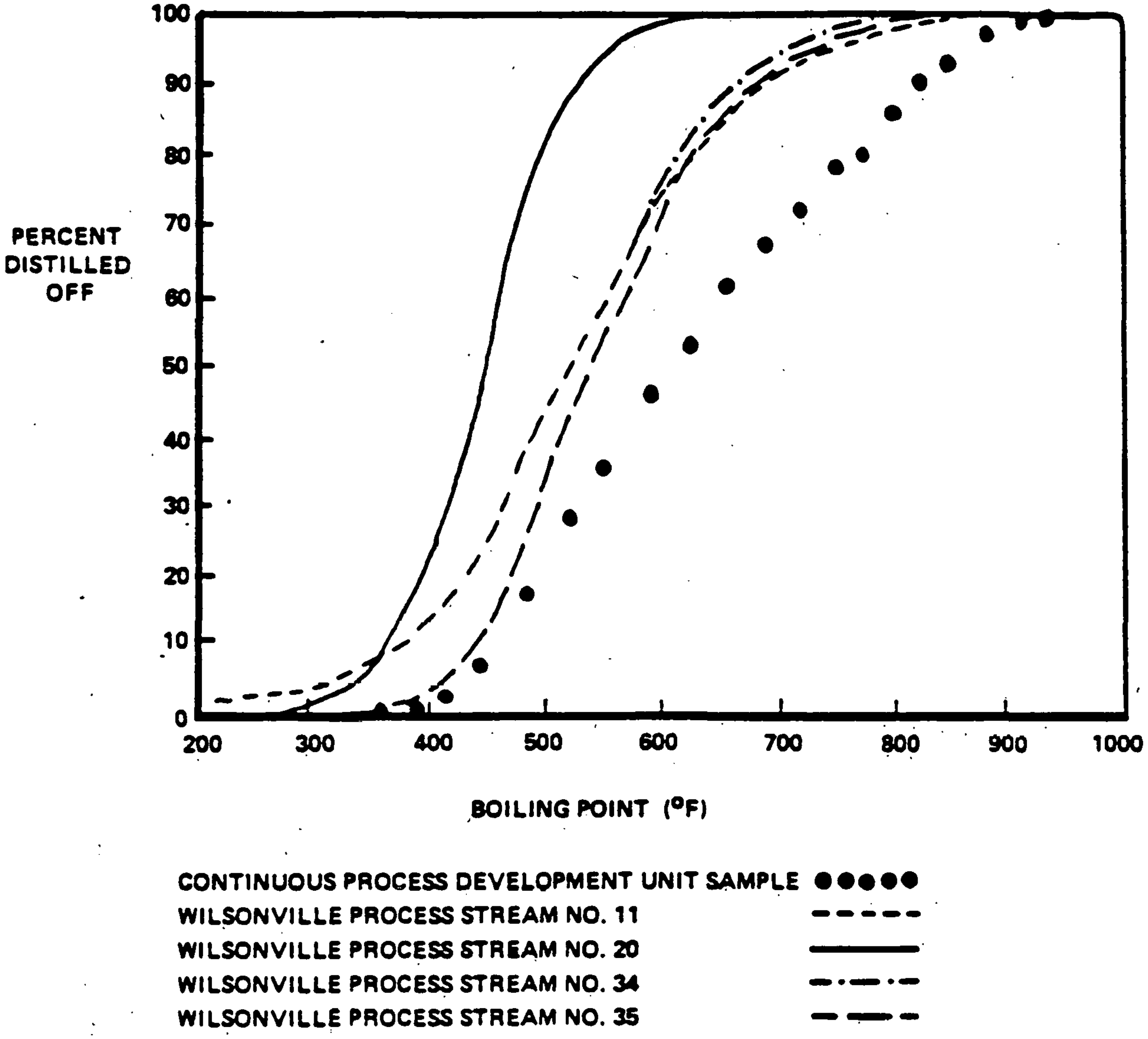


Figure 16
Boiling Point Distribution of Wilsonville Heavy Process Streams and Continuous Process Development Unit Sample by Wilsonville Simulated Distillation by Gas Chromatography

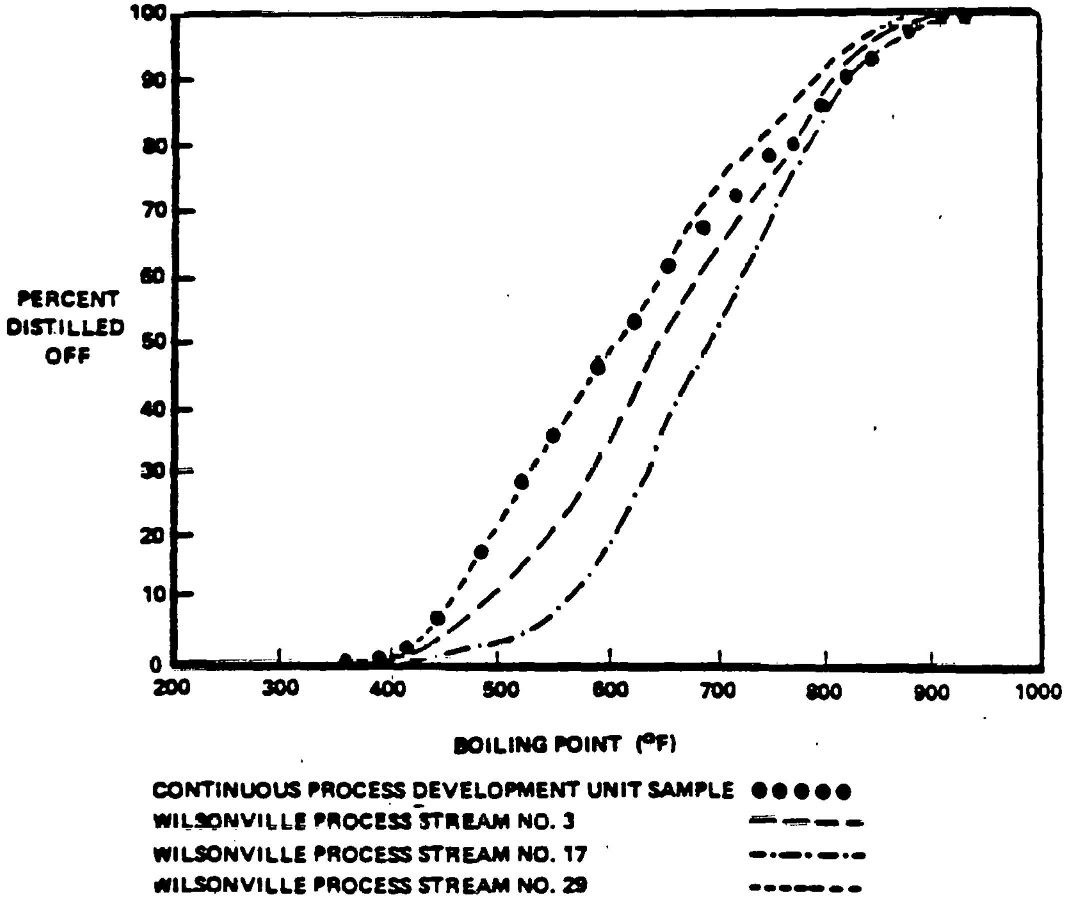


Figure 16
Boiling Point Determination on Seven Wilsonville Process Streams;
ASTM D-2887 vs. Wilsonville Method

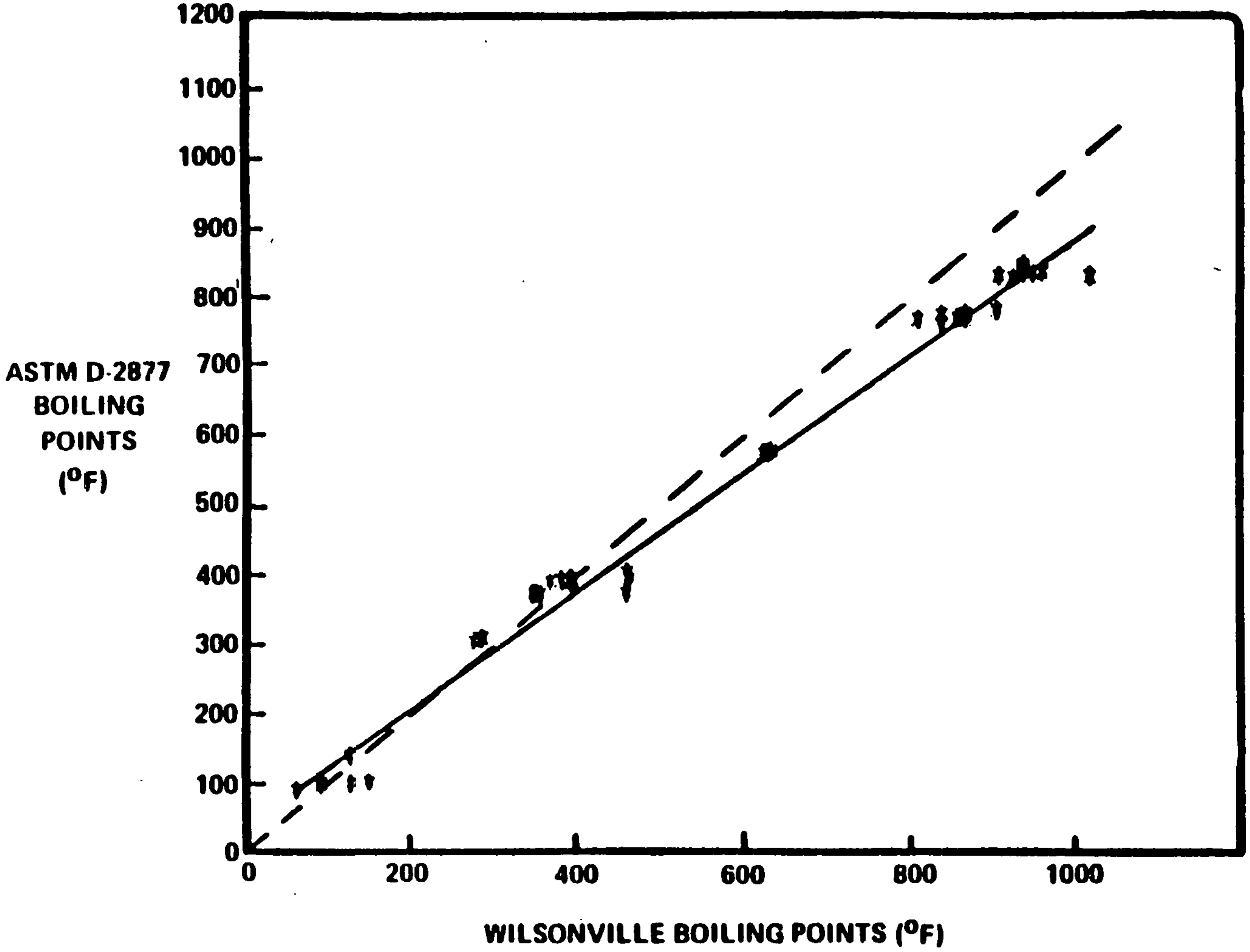


Figure 17
ASTM Area Percent vs. Wilsonville Weight Percent of 100°F Distillate Cuts From 21 Wilsonville Process Stream Samples

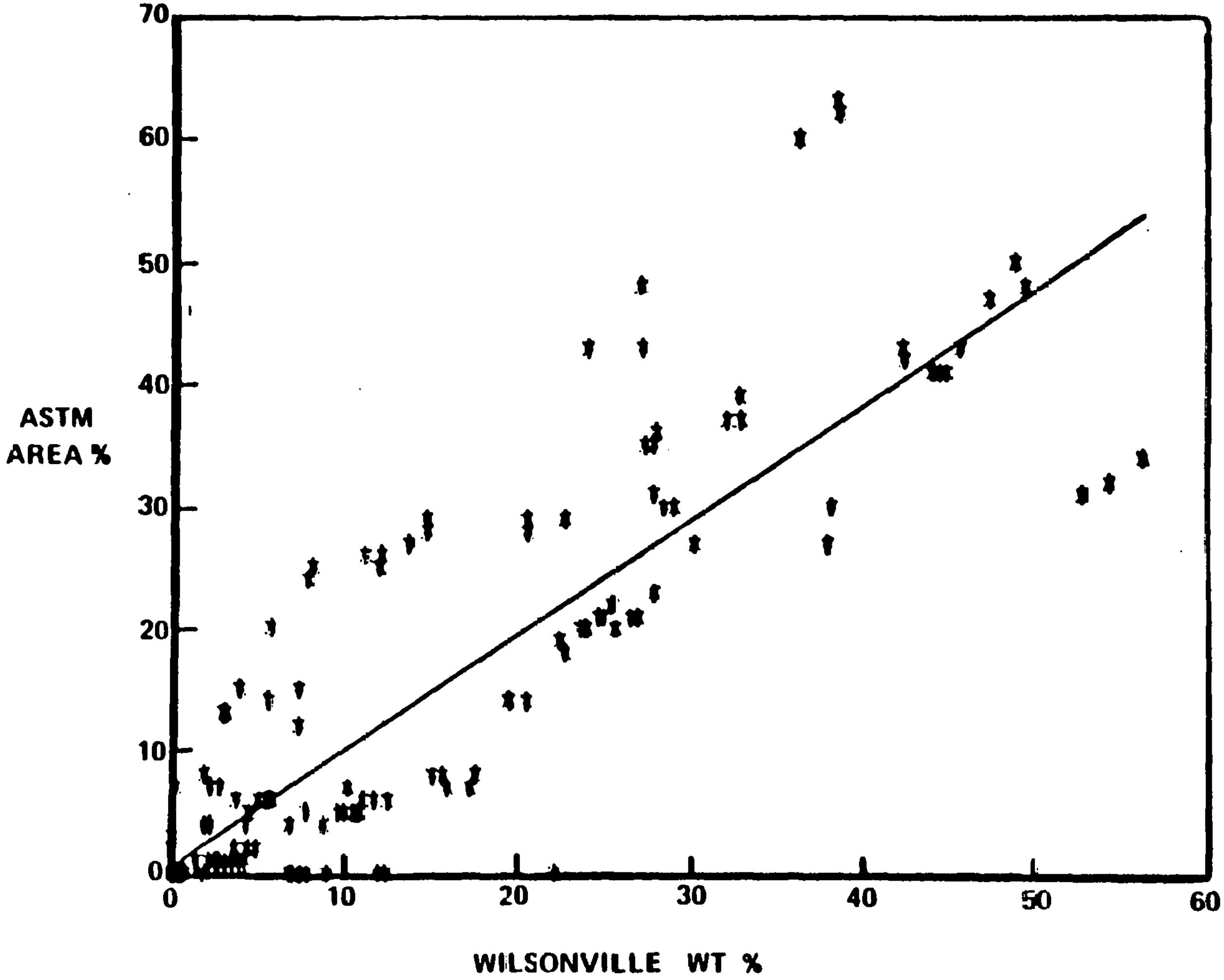
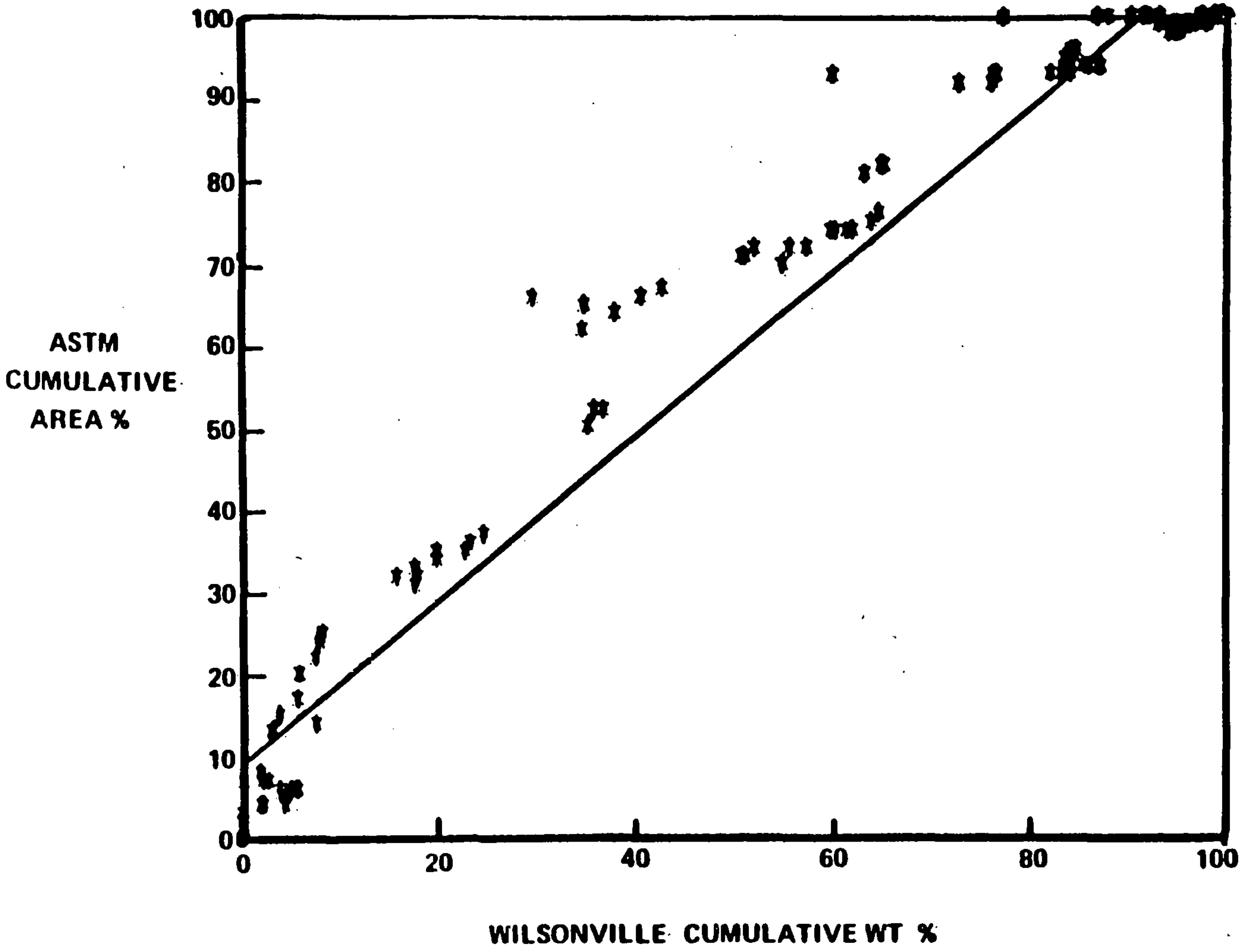


Figure 18
Cumulative Distillate Cuts ASTM D-2887 vs. Wilsonville
Simulated Distillation by Gas Chromatography



Appendix VII-B

BASIC Computer Program

WV-GCSD Calculation from APCI-CRSD Trexlertown GC Data

Exhibit B-1

BASIC Computer Program

```
100 INIT
110 PAGE
120 REM:TT RT CUT-OFFS,WV LINEAR REGRESSIONS AS IN QUARTERLY REPORT
130 PRINT "INSERT DATA TAPE AND ENTER FILE# FOR DATA:";
140 INPUT F
150 DIM A(150,7)
160 DIM B(7)
170 R=0
180 B=0
190 T2=0
200 FIND F
210 T1=0
220 A=0
230 S=0
240 T=0
250 FOR I=1 TO 150
260 ON EOF (0) THEN 290
270 READ @33:A(I,1),A(I,2)
280 NEXT I
290 N=I-1
300 FOR I=1 TO N
310 REM conversion of TT RT TO WV RT INTO A(I,7)
320 IF A(I,1)*60=>2050 THEN 350
330 A(I,7)=0.9634*A(I,1)*60-8.073
340 GO TO 360
350 A(I,7)=0.342*A(I,1)*60+1243
360 REMARK DETERMINATION OF BOILING POINTS INTO A(I,3)
370 IF A(I,7)=>120 THEN 400
380 A(I,3)=1.48*A(I,7)-39.25
390 GO TO 440
400 IF A(I,7)=>2560 THEN 440
410 A(I,3)=0.341*A(I,7)+126.5
420 GO TO 440
430 A(I,3)=0.049*A(I,7)+893.9
```

Exhibit B-1 (Continued)

```
440 REMARK
450 REMARK DETERMINATION OF AREA% *RF INTO A(1,4)
460 REMARK AREA%*RF FOR EACH DIST. CUT INTO B(1 TO 7)
470 IF A(I,1)=>10.9 THEN 500
480 A(I,4)=A(I,2)*0.624
490 GO TO 660
500 IF A(I,1)=>16 THEN 530
510 A(I,4)=A(I,2)*1.074
520 GO TO 660
530 IF A(I,1)=>22.5 THEN 560
540 A(I,4)=A(I,2)*1.004
550 GO TO 660
560 IF A(I,1)=>27.2 THEN 590
570 A(I,4)=A(I,2)*1.165
580 GO TO 660
590 IF A(I,1)=>32.2 THEN 620
600 A(I,4)=A(I,2)*1.156
610 GO TO 660
620 IF A(I,1)=>36.3 THEN 650
630 A(I,4)=A(I,2)*1.444
640 GO TO 660
650 A(I,4)=A(I,2)*1.0
660 REMARK
670 NEXT I
680 REMARK SUM OF ALL AREA % * RF (S)
690 FOR I=1 TO N
700 S=S+A(I,4)
710 NEXT I
720 FOR I=1 TO N
730 A(I,5)=A(I,4)/S*100
740 NEXT I
750 FOR I=1 TO N
760 IF A(I,3)=>350 THEN 790
770 B(1)=B(1)+A(I,5)
780 GO TO 950
```

Exhibit B-1 (Continued)

```
790 IF A(I,3)=>450 THEN 820
800 B(2)=B(2)+A(I,5)
810 GO TO 950
820 IF A(I,3)=>550 THEN 850
830 B(3)=B(3)+A(I,5)
840 GO TO 950
850 IF A(I,3)=>650 THEN 880
860 B(4)=B(4)+A(I,5)
870 GO TO 950
880 IF A(I,3)=>750 THEN 910
890 B(5)=B(5)+A(I,5)
900 GO TO 950
910 IF A(I,3)=>850 THEN 940
920 B(6)=B(6)+A(I,5)
930 GO TO 950
940 B(7)=B(7)+A(I,5)
950 REM
960 NEXT I
970 REMARK DETERMINATION OF IBP(T1),FBP(T2)(AND CUM.WEIGHT% (A(I,6))
980 A(1,6)=A(1,5)
990 FOR I=2 TO N
1000 A(I,6)=A(I-1,6)+A(I,5)
1010 NEXT I
1020 FOR I=1 TO N
1030 IF A(I,6)=>0.5 THEN 1050
1040 GO TO 1070
1050 T1=A(I,3)
1060 GO TO 1080
1070 NEXT I
1080 FOR I=1 TO N
1090 IF A(I,6)=>99.5 THEN 1110
1100 GO TO 1130
1110 T2=A(I,3)
1120 GO TO 1200
1130 NEXT I
```

```
1140 REM:DETERMINATION OF HEAVY DISTILLATE
1150 IF B<=0.05 THEN 1190
1160 R=3
1170 FOR I=1 TO 7
1180 B(I)=B(I)*0.97
1190 REM
1200 REMARK CHROMATOGRAM WITH CALC. BP, WT% AND CUM. WT% PRINT OUT
1210 PRINT "TAPENUMBER:";
1220 INPUT X$
1230 PRINT "SAMPLE NUMBER : ";
1240 INPUT C$
1250 PRINT "DATE:";
1260 INPUT D$
1270 PRINT "APCI GC-SIMULATED DISTILLATION BY WV METHOD"
1280 PRINT
1290 PRINT
1300 PRINT USING 1580:"RT(MIN)","AREA%","BP(F)","WEIGHT%","CUM. WT%"
1310 PRINT
1320 FOR I=1 TO N
1330 PRINT USING 1570:A(I,1),A(I,2),A(I,3),A(I,5),A(I,6)
1340 NEXT I
1350 INPUT Y$
1360 REMARK
1370 REMARK BOILING POINT DISTRIBUTION BY WV METHOD
1380 PRINT
1390 PAGE
1400 PRINT "TAPENUMBER:";X$;"   FILENUMBER:";F
1410 PRINT "SAMPLE NUMBER:";C$
1420 PRINT "DATE:";D$
1430 PRINT
1440 PRINT USING 1600:"DISTILLATION CUT","WEIGHT%"
1450 PRINT
1460 PRINT USING 1590:"   <350(F)",B(1)
1470 PRINT USING 1590:"350-450(F)",B(2)
1480 PRINT USING 1590:"450-550(F)",B(3)
```

Exhibit B-1 (Continued)

```
1490 PRINT USING 1590:"550-650(F)",B(4)
1500 PRINT USING 1590:"650-750(F)",B(5)
1510 PRINT USING 1590:"750-850(F)",B(6)
1520 PRINT USING 1590:"   >850(F)",B(7)
1530 PRINT USING 1590:"RESIDUE    ",R
1540 PRINT
1550 PRINT USING 1610:"    IBP   ",T1,"(F)"
1560 PRINT USING 1610:"    FBP   ",T2,"(F)"
1570 IMAGE 2D.2D, 4X, 2D.2D, 4X, 4D.1D,6X,2D.2D,4X,3D.2D
1580 IMAGE 7A, 4X, 6A, 3X, 5A, 4X, 7A, 4X, 9A
1590 IMAGE 16A, 6 X, 3D.2D
1600 IMAGE 16A, 4X, 14A
1610 IMAGE 16A,6X,4D,3A
1620 REMAR: THIS WV SIMULATION OF GC-SIM.DIST. DISCRIMINATES
1630 REMAR:BP-CUTS BY RETENTION TIME CUT OFFS.
1640 END
```

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VIII. DOCUMENTATION OF GAS ANALYSIS COMPUTATION BY THE CARLE GAS CHROMATOGRAPHY SYSTEM (GC) (BASIC PROGRAM ON TEKTRONIX)

Summary

Analysis of gases produced during coal liquefaction generates key information that is needed to determine product yields for material balance and process control. Gas samples from the coal process development unit (CPDU) and tubing bombs are the primary samples analyzed. A Carle gas chromatographic system was used to analyze coal liquefaction gas samples; the setup is described in Appendix VIII-A. Appendix VIII-B documents the BASIC Computer program to calculate Carle gas analysis. Appendix VIII-C is a user guide to enter raw GC data onto a tape.

A BASIC computer program was written to calculate the gas chromatographic peak area results into mole percent results. This report documents the integrator settings on the gas chromatograph, the BASIC program necessary to enter the gas chromatographic data into the computer and the BASIC program necessary to convert the gas chromatographic results into mole percent results.

Calculation of Results

1. Integration

The gas chromatograph generates integrated area and retention time data for each peak detected in a chromatogram. The mode of integration depends on the integrator settings, which allow either valley-to-valley integration or a forced horizontal base line and no integration settings during valve switching.

The SIGMA15 integrator settings as well as the valve switchings are shown in Exhibit 1.

Exhibit 1. Integrator Settings

```
METHOD    4
ANALYZER CONTROL

INJ TEMP       25
DET ZONE 1,2       50     25
AUX TEMP       25
FLOW A,B     20     0
INIT OVEN TEMP,TIME      53   43

DATA PROC

STD WT,SMP WT       1.0000     1.0000  0
FACTOR,SCALE         1 - 2
TIMES     43.00     2.00  327.67  327.67  327.67  327.67
SENS-DET RANGE      200   20     0.00     2    0    0
UNK,AIR     1.000     0.00
TOL       0.0000    0.050     1.0
REF PK    20.000    37.39   38.89   38.39
STD NAME

  RT      RF       CONC      NAME
   3.30   1.000     0.0000 BACKFLUSH
   6.52   1.000   881.0496 HYDROGEN
   8.24   1.000    49.0000 PROPANE
   9.51   1.000    11.0000 PROPYLENE
  11.00   1.000    69.2000 HYDROGEN SULFIDE
  11.90   1.000    17.6000 I-BUTANE
  13.52   1.000    17.1000 N-BUTANE
  17.25   1.000    17.0000 I-BUTYLENE
  22.91   1.000     6.8000 I-PENTANE
  31.63   1.000    64.9984 CARBON DIOXIDE
  32.89   1.000     8.5000 ETHYLENE
  34.05   1.000   124.9984 ETHANE
  35.42   1.000     3.3000 OXYGEN
  36.56   1.000   299.9952 NITROGEN
  38.39   1.000   585.9840 METHANE
  39.91   1.000    62.9984 CARBON MONOXIDE

EVENT CONTROL

ATTN-CHART-DELAY       3     5     0.01

  TIME  DEVICE     FUNCTION NAME
   0.01 EXT     X    1          SAMPLE INJECT
   2.25 EXT     X   -1          VALVE 1 CLOSE
   2.35 NO INT NI    0          START INT
   6.92 EXT     X    2          VALVE 2 OPEN
   7.00 EXT     X    3          VALVE 3 OPEN
  29.00 NO INT NI    1          STOP INT
  29.50 EXT     X   -2          VALVE 2 CLOSE
  30.75 NO INT NI    0          START INT
  34.75 NO INT NI    1          STOP INT
  35.17 EXT     X   -3          VALVE 3 CLOSE
  35.30 NO INT NI    0          START INT
```

The end-of-analysis time was set at 43.00 min. All peaks of interest were identified by their respective retention times, which had been determined by analyzing a standard gas mixture. The timetable at the end of Exhibit 1 includes integration inhibition during valve switches. The integration mode was from base line to base line.

2. Mole Percent Calculation

In order to determine the concentration of compounds in an unknown mixture, the detector response of the gas chromatograph must be determined for each compound of interest. The detector response is obtained by first analyzing a mixture of compounds of known concentrations and then calculating the ratio of mole percent to integrated area for each compound of interest. This ratio, which is called the response factor, is then multiplied by the integrated area of the respective peak in the chromatogram of an unknown mixture to generate the mole percent results.

Response factors are determined daily by analyzing a standard gas mixture. Mole percent results for an unknown sample are calculated using each day's response factors.

BASIC Computer Program

A BASIC computer program was written to (1) calculate response factors for a standard gas mixture and (2) calculate the mole percent results for an unknown gas sample.

To allow a comprehensive understanding of the steps involved in calculating the analytical results, the program (detailed in Appendix 2) can be broken down as follows:

1 Initialize the program and enter sample analysis information:

```
1 INIT
9 IMAGE 19A,2X,13A,2X,6A,2X,10A,2X,15A
10 IMAGE 16A,2X,13A,2X,6A,2X,10A,2X,15A
70 PAGE
80 PRINT "RESPONSE FACTORS FOR STANDARD GAS MIXTURE"
100 REM:THIS PROGRAM CALCULATES RESPONSE FACTORS FOR THE GAS MIXTURE
110 REM:AND CALCULATES THE MOLE% FOR AN UNKNOWN GAS SAMPLE
120 DIM D(16)
130 DIM E(16)
140 DIM B(16,2)
150 DIM A(16,2)
160 DIM L(16)
170 M=0
180 E=0
190 PRINT "DATE:";
200 INPUT C$
210 PRINT "TIME:";
220 INPUT E$
230 PRINT "ANALYST:";
240 INPUT D$
```

2. Locate GC data file on GC data tape for the standard gas chromatogram:

```
250 PRINT "INSERT DATA TAPE AND ENTER FILE# FOR ";
260 PRINT "GC DATA OF STANDARD GAS:";
270 INPUT F
280 FIND F
```

3. Known concentrations of compounds in gas standard (label values):

```
290 REM: MOLE% CONCENTRATION OF COMPOUNDS IN GAS STANDARD
300 DATA 1.0E-5,88.109,0.49,0.118,0.692,0.176,0.171,0.17
310 DATA 0.088,0.65,0.085,1.25,0.093,2.91,5.06,0.63
```

If these label values change, be sure to change line statements 300 and 310 accordingly. However, be sure to keep the same order of compounds listed in lines 510 through 540.

Note: The first data point refers to the backflush peak, which is assigned a concentration of 0.00001 mol %. This backflush concentration calculates a response factor of zero for the backflush peak in the sample analysis (see lines 420 and 440). The actual concentration of backflush (the C_6 and larger fraction in a coal liquefaction gas sample) can be determined from the difference of the sum of mole percents to 100.

4. Print heading of report page for standardized gas mixture data:

```
320 PRI USI 9:"JJJCOMPOUND","RET.TIME","AREA","MOLE %","RESP.FACTORJ"
```

5. Read label values for standard gas mixture (D), read the retention time and area integration data from GC data tape, read compound names (D$), calculate the response factor (line 400), and then print the information for each compound:

```
330 READ D
340 FOR I=1 TO 16
350 READ @33:A(I,1),A(I,2)
360 REM: CALCULATION OF RESPONSE FACTOR
370 IF A(I,2)=0 THEN 390
380 GO TO 400
390 A(I,2)=1
400 E(I)=D(I)/A(I,2)
410 READ D$
420 IF E(I)>999 THEN 440
430 GO TO 450
440 E=0
450 REM
460 PRINT USING 870:D$,A(I,1),A(I,2),D(I),E(I)
470 NEXT I
480 DATA "BACKFLUSH","HYDROGEN","PROPANE","PROPYLENE"
490 DATA "HYDROGEN SULFIDE","I-BUTANE","N-BUTANE","I-BUTYLENE"
500 DATA "I-PENTANE","CARBON DIOXIDE","ETHYLENE","ETHANE"
510 DATA "OXYGEN","NITROGEN","METHANE","CARBON MONOXIDE"
```

Note: Should any additional compounds be included in this analysis, change the program as follows:

(1) Determine the retention time of the new compound with respect to the order of compounds already identified.

(2) Enter the known concentration of the standard into the appropriate location in line statements 300 and 310.

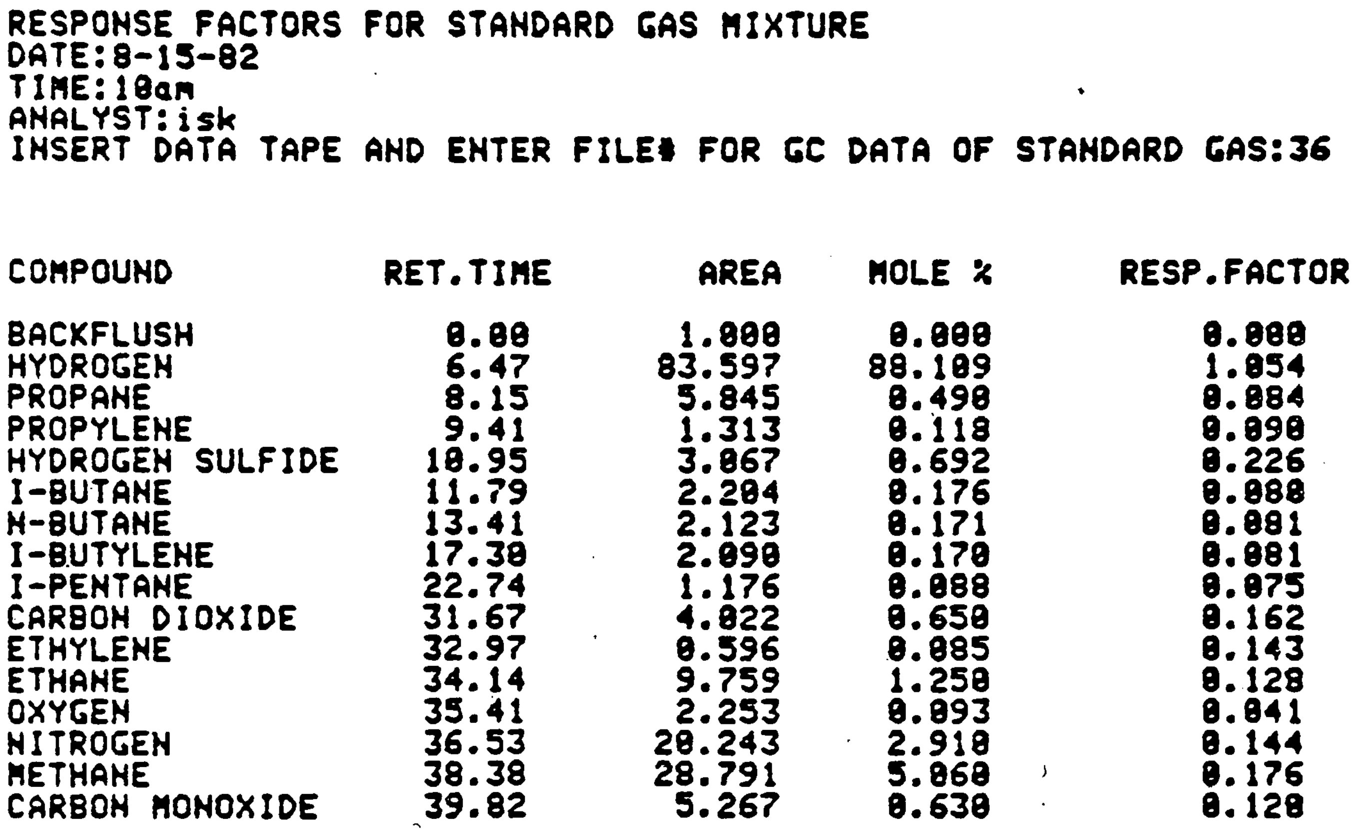
(3) Enter the compound name into the appropriate location in lines 480 to 510. Be sure to enter the name in quotes.

(4) Enter the compound name into the appropriate location in lines 830 to 860.

An example of the printout for the response factor determination from standard gas analysis is shown in Exhibit 2.

6. Initialize that part of the program used to calculate the mole percent concentration of specified compounds in an unknown gas sample. Enter sample information:

Exhibit 2. Printout of Response Factor Determination



```
RESPONSE FACTORS FOR STANDARD GAS MIXTURE
DATE:8-15-82
TIME:10am
ANALYST:isk
INSERT DATA TAPE AND ENTER FILE# FOR GC DATA OF STANDARD GAS:36


COMPOUND              RET.TIME        AREA      MOLE %        RESP.FACTOR

BACKFLUSH                0.00        1.000       0.000              0.000
HYDROGEN                 6.47       83.597      88.109              1.054
PROPANE                  8.15        5.845       0.490              0.084
PROPYLENE                9.41        1.313       0.118              0.090
HYDROGEN SULFIDE        10.95        3.067       0.692              0.226
I-BUTANE                11.79        2.204       0.176              0.080
N-BUTANE                13.41        2.123       0.171              0.081
I-BUTYLENE              17.30        2.090       0.170              0.081
I-PENTANE               22.74        1.176       0.088              0.075
CARBON DIOXIDE          31.67        4.022       0.650              0.162
ETHYLENE                32.97        0.596       0.085              0.143
ETHANE                  34.14        9.759       1.250              0.128
OXYGEN                  35.41        2.253       0.093              0.041
NITROGEN                36.53       20.243       2.910              0.144
METHANE                 38.38       28.791       5.060              0.176
CARBON MONOXIDE         39.82        5.267       0.630              0.120
```

```
520 REM:THIS PORTION OF THE PROGRAM CALCULATES MOLE% FOR AN UNKNOWN GAS
530 INPUT X$
540 PAGE
550 PRINT "ANALYSIS DATE AND TIME:";
560 INPUT G$
570 PRINT "SAMPLE NAME,SAMPLING DATE,SAMPLING TIME:";
580 INPUT I$
590 PRINT "ANALYSIS REQUESTED BY:";
600 INPUT H$
610 PRINT "SAMPLED BY:";
620 INPUT J$
630 PRINT "GC ANALYST:";
640 INPUT K$
650 PRINT "DATA TAPE NAME:";
660 INPUT L$
670 PRINT "INSERT DATA TAPE AND ENTER FILE# OF SAMPLE'S GC DATA:";
680 INPUT K
690 PRINT "CHARGE NUMBER:";
700 INPUT N$
710 PRINT "FOR ANALYSIS REPORT PRESS RETURN"
720 INPUT Y$
730 PAGE
```

7. Set up report page for gas analysis of the hydrocarbon sample:

```
740 PRINT "GASANALYSIS OF HYDROCARBON GAS MIXTUREJJ"
750 PRINT "SAMPLE DESCRIPTION:J";I$
760 PRINT "SAMPLED BY:";J$
770 PRINT "ANALYSIS REQUESTED BY:";H$
780 PRINT "CHARGE NUMBER:";N$
790 PRINT "ANALYSIS DATE:";G$
800 PRINT "GC ANALYST:";K$
810 PRINT "DATA TAPE AND FILE NUMBER:";L$;",";K;"JJ"
820 PRINT USING 10:"COMPOUND","RET.TIME","AREA","RESP.FACT.","MOLE %J
830 DATA "BACKFLUSH","HYDROGEN","PROPANE","PROPYLENE"
840 DATA "HYDROGEN SULFIDE","I-BUTANE","N-BUTANE","I-BUTYLENE"
850 DATA "I-PENTANE","CARBON DIOXIDE","ETHYLENE","ETHANE"
860 DATA "OXYGEN","NITROGEN","METHANE","CARBON MONOXIDE"
870 IMAGE 16A,4X,2D.2D,6X,2D.3D,4X,2D.3D,9X,2D.3D
880 IMAGE 16A,4X,2D.2D,5X,3D.3D,5X,2D.3D,5X,2D.2D
890 IMAGE 46X,5A,2X,3D.2D,2X
```

8. Read GC data for the unknown gas sample from the GC data tape. Calculate the mole percent concentration for the specified peaks, print results, calculate the sum (M) of the mole percent results, and print:

```
900 FIND K
910 FOR I=1 TO 16
920 READ @33:B(I,1),B(I,2)
930 REM: CALCULATION OF MOLE% FROM AREA USING RF(E)
940 L(I)=B(I,2)*E(I)
950 READ D$
960 M=L(I)+M
970 PRINT USING 880:D$,B(I,1),B(I,2),E(I),L(I)
980 NEXT I
990 PRINT USING 890:"J̲SUM:",M
1000 RESTORE
1010 COPY
```

An example of a CPDU gas sample analysis is shown in Exhibit 3.

Note: The program used to enter GC data onto a GC data tape is reproduced below. A description of how to use this program is detailed in the documentation for the Wilsonville simulated distillation by gas chromatography program. The user guide for this program is attached in Appendix 3.

```
1 PRINT "RT(MIN)","AREA%"
2 ON EOF (0) THEN 10
3 READ @33:X,Y
4 PRINT X,Y
5 GO TO 2
10 PRINT "EOF"
30 PRINT "FILE NUMBER:";
31 INPUT F
32 FIND F
33 PRINT "APPROX.# OF PEAKS:";
34 INPUT P
35 MARK 1,P*9*10
36 FIND F
40 PRINT "ENTER RT(MIN),AREA%"
41 INPUT X,Y
42 WRITE @33:X,Y
43 GO TO 40
```

Exhibit 3. Printout of Gas Analysis Result from a CPDU Gas Sample

```
GASANALYSIS OF HYDROCARBON GAS MIXTURE

SAMPLE DESCRIPTION:
                        HCL58-123 8-10-82 21:10
SAMPLED BY:JRR
ANALYSIS REQUESTED BY:D.HOOVER
CHARGE NUMBER:87-7-3003.10
ANALYSIS DATE:8-16-82
GC ANALYST:ISK
DATA TAPE AND FILE NUMBER:JR01,37


COMPOUND                RET.TIME          AREA     RESP.FACT.  MOLE %

BACKFLUSH                  3.32         10.492          0.000    0.00
HYDROGEN                   6.46         82.895          1.054   87.37
PROPANE                    8.13          7.965          0.084    0.67
PROPYLENE                  9.40          0.736          0.090    0.07
HYDROGEN SULFIDE          10.93          4.767          0.226    1.08
I-BUTANE                  11.77          1.043          0.080    0.08
N-BUTANE                  13.39          3.196          0.081    0.26
I-BUTYLENE                17.27          0.064          0.081    0.01
I-PENTANE                 22.71          0.801          0.075    0.06
CARBON DIOXIDE            31.61          3.560          0.162    0.58
ETHYLENE                  32.89          0.262          0.143    0.04
ETHANE                    34.06         11.259          0.128    1.44
OXYGEN                    35.41          2.467          0.041    0.10
NITROGEN                  36.51         17.402          0.144    2.50
METHANE                   38.38         21.381          0.176    3.76
CARBON MONOXIDE           40.05          2.836          0.120    0.34

                                                  SUM:     98.34
```

Appendix VIII-A

Gas Analysis Using Carle GC

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Performance of the Carle GC

Introduction

Our objective was to assemble the Model 111 Carle GC and run samples of carrier gas, pure gases, and a standard gas mixture. Results desired were retention times and response factors for the 14 known compounds in the standard gas mixture, reproducibility, and standard deviation of the results. The retention time of a compound identifies that compound by eluting at a specific time. Response factors for a given compound, which are a function of the detector response for a given quantity of that compound, are determined by dividing the known concentration of a component by its peak area.

Procedure

All gases in this study were handled as stated in the sample loading section of the Procedure for Gas Sample Analysis (see Exhibit A-1). Each gas was analyzed in triplicate using an attenuation of 1 and chart speed of 0.5 cm/min. The flow rates, analysis temperature, valve timings, and other parameters were set according to Carle's specifications(see Figure A-1). Gases used in this study were helium, hydrogen, nitrogen, zero-grade air, and a standard gas mixture (Table A-1).

Ultra Pure Carrier Helium (UPC Grade) was the carrier used. Analysis of the helium carrier identified the detector response due to background or valve switchings and established the base line. This chromatogram is shown in Figure A-2.

Zero-grade hydrogen, nitrogen (house bleed-off from the liquid nitrogen), and zero-grade air were chromatographed to determine the retention times of H_2, N_2, and O_2. The chromatograms (Figures A-2 and A-3) show that the valve-switching sequence of the Carle GC does not cause any of these peaks to split. Reproducibility of the triplicate analysis was calculated as the standard deviation and is listed in Table A-1.

The standard gas mixture, used in the High Bay for calibrating the on-line GC, was analyzed next; Table A-2 lists the composition. The resulting chromatogram is shown in Figure A-4. Compounds were identified by their retention times using the Carle chromatogram (see Figure A-5). Differences in retention times between similar peaks are due to differences in flow rates.

Table A-2 and Figure A-6 compare the retention times of standard compounds from our chromatogram with the retention times generated by the manufacturer. The retention times are comparable, except for those for isopentane and isobutylene, which may be due to a leak in the internal plumbing; this will be investigated further.

Table A-2 identifies background peaks that are due to valve switching. It is up to the discretion of the operator using this table to subtract background peaks that are overlapped by identified peaks.

The response factors were determined by calculating the ratio of concentration to the area counts obtained by electronic integration from the chromatogram in Figure A-4:

$$\text{response factor} = \frac{\text{mol percent}}{\text{area counts}}$$

Table A-2 lists typical response factors for the 14 compounds in the standard gas mixture. These response factors have been normalized for methane.

Exhibit A-1 shows an excerpt from the SIGMA15 integrator operating manual, which is a summary of operating conversations necessary to build an integrator method.

Conclusion

The retention times of hydrogen, nitrogen, and oxygen compared to within ±0.5 min of their retention times in the standard gas mixture. Also, the retention times of the known compounds in the standard gas mixture compared to within ±0.5 min of the retention times of those compounds shown in the Carle chromatogram, except for isopentane and isobutylene. The reproducibility of the retention times was established in triplicate. This lends credibility to the identification of the standard gas peaks and shows that the system works correctly.

Because of day-to-day differences in the gas chromatographic system, the standard gas mixture must be run daily, once in the morning before any unknowns have been run and again in the evening after all other runs have been completed. The results from the standard gas mixture will be used to determine the retention times and the response factors for that day, which are then to be used to identify and quantify compounds in a process stream gas sample.

*Known concentration is provided with standard gas mixture cylinder.

Table A-1

Reproducibility of Retention Times of Hydrogen, Nitrogen, and Oxygen

	Mean	Standard Deviation
Hydrogen	6.93	0.0000 *
Nitrogen	36.33	0.0153
Oxygen	35.71	0.0100

* Triplicate samples

Table A-2

Retention Times and Response Factors of Standard Gas Mixture Using Carle GC

	Peak #	Retention Time 1	Retention Time 2	Integrate Area Counts	Known Conc. Mole %	Response Factor 3
Background		3.0	2.60	1.2773	--	--
Hydrogen	1	6.5	6.43	6.0675	88.109	7.86
(V1) noise*		7.0	7.16	0.0653	--	--
Propane	2	8.25	8.06	0.4999	0.490	0.533
Acetylene		8.75	--	--	--	--
Propylene	3	9.5	9.31	0.1111	0.118	0.627
Hydrogen sulfide		11.5	--	--	--	--
Isobutane	4	12.0	11.64	0.2203	0.176	0.475
Propadiene		13.0	--	--	--	--
N-Butane	5	13.75	13.21	0.2176	0.171	0.473
Butene		17.5	--	--	--	--
Isobutylene	6	18.5	17.06	0.1979	0.170	0.505
N-trans-Butene-2		19.75	--	--	--	--
cis-Butene-2		21.25	--	--	--	--
1,3-Butadiene		22.75	--	--	--	--
Isopentane	7	24.0	22.36	0.1216	0.088	0.412
N-Pentane		27.5	--	--	--	--
Background		29.25	29.62	0.2225	--	--
(V2) noise*		29.5	29.83	0.2848	--	--
Carbon dioxide	8	31.25	31.49	0.5912	0.650	0.707
Ethylene	9	32.5	32.73	0.2243	0.085	0.275
Ethane	10	33.75	33.89	1.4422	1.25	0.542
Oxygen	11	35.25	35.41	0.2470	0.093	0.229
Nitrogen	12	36.25	36.36	2.1213	2.91	0.822
Methane	13	38.25	38.36	3.0275	5.06	1.000
Carbon monoxide	14	40.5	40.07	0.4973	0.630	0.805

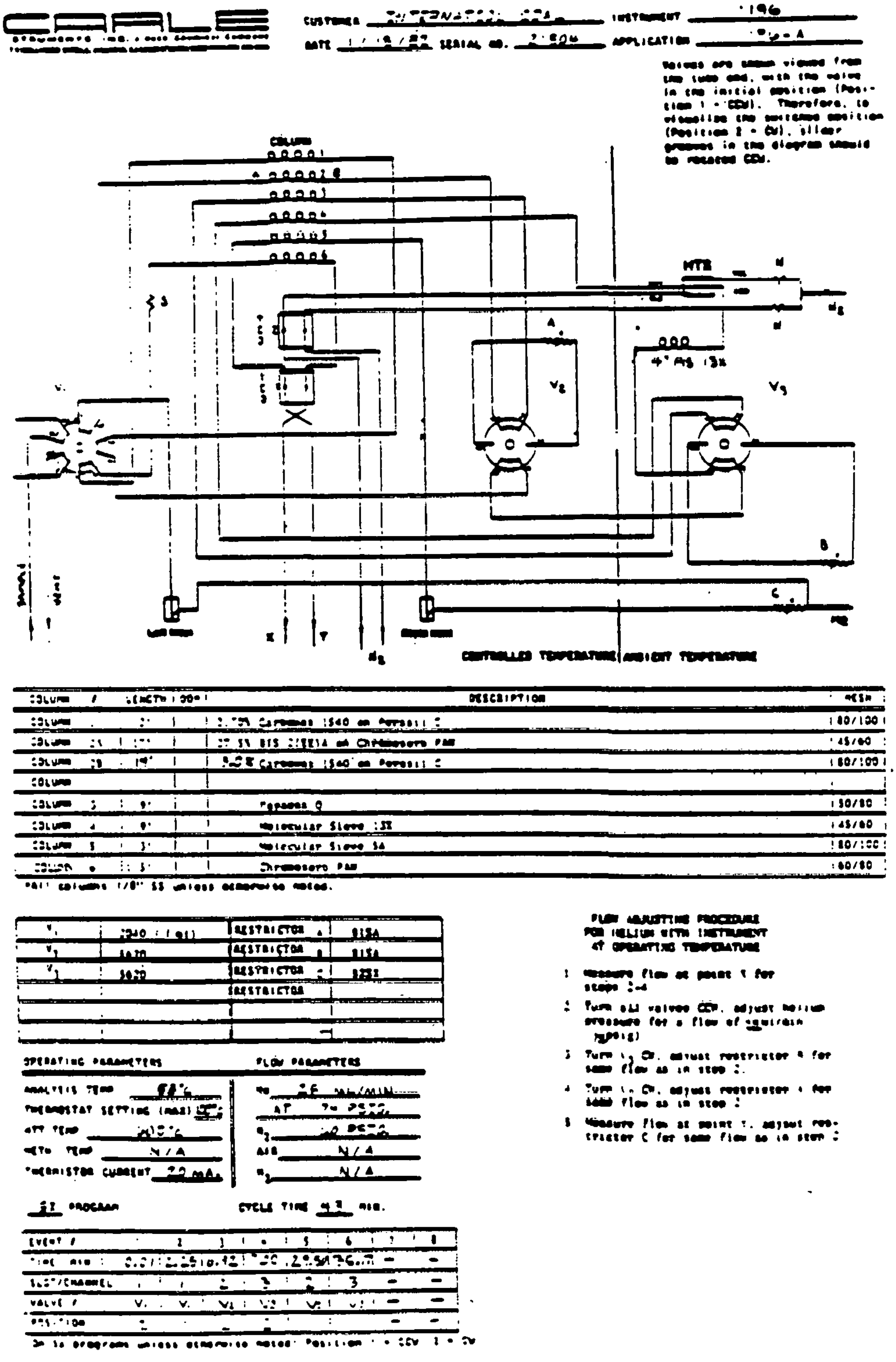
1 Determined by Carle

2 Determined at ICRC

3 Normalized to methane

* Valve closing

Figure A-1 Flow Diagram of GC and Carle's Specifications



CUSTOMER [illegible] INSTRUMENT 196

DATE [illegible] SERIAL NO. [illegible] APPLICATION [illegible]

Valves are shown viewed from the tube end, with the valve in the initial position (Position 1 = CCW). Therefore, to visualize the switched position (Position 2 = CW), slider grooves in the diagram should be rotated CCW.

COLUMN #	LENGTH	OD*	DESCRIPTION	MESH
COLUMN 1	2'		2.75% Carbowax 1540 on Porasil C	80/100
COLUMN 2A	17'		27.5% BIS 2EEEA on Chromosorb PAW	45/60
COLUMN 2B	19'		[illegible] Carbowax 1540 on Porasil C	80/100
COLUMN				
COLUMN 3	9'		Porapak Q	50/80
COLUMN 4	9'		Molecular Sieve 13X	45/60
COLUMN 5	3'		Molecular Sieve 5A	80/100
COLUMN 6	3'		Chromosorb PAW	60/80

*All columns 1/8" SS unless otherwise noted.

V1	2940 [illegible]	RESTRICTOR A	815A
V2	5620	RESTRICTOR B	815A
V3	5620	RESTRICTOR C	[illegible]
		RESTRICTOR	

OPERATING PARAMETERS

ANALYSIS TEMP 68°C
THERMOSTAT SETTING (MAX) [illegible]
ATT TEMP [illegible]
METH TEMP N/A
THERMISTOR CURRENT 22 mA.

FLOW PARAMETERS

He 25 ml/MIN
AT 70 PSIG
H2 [illegible] PSIG
AIR N/A
H2 N/A

[illegible] PROGRAM

CYCLE TIME 43 MIN.

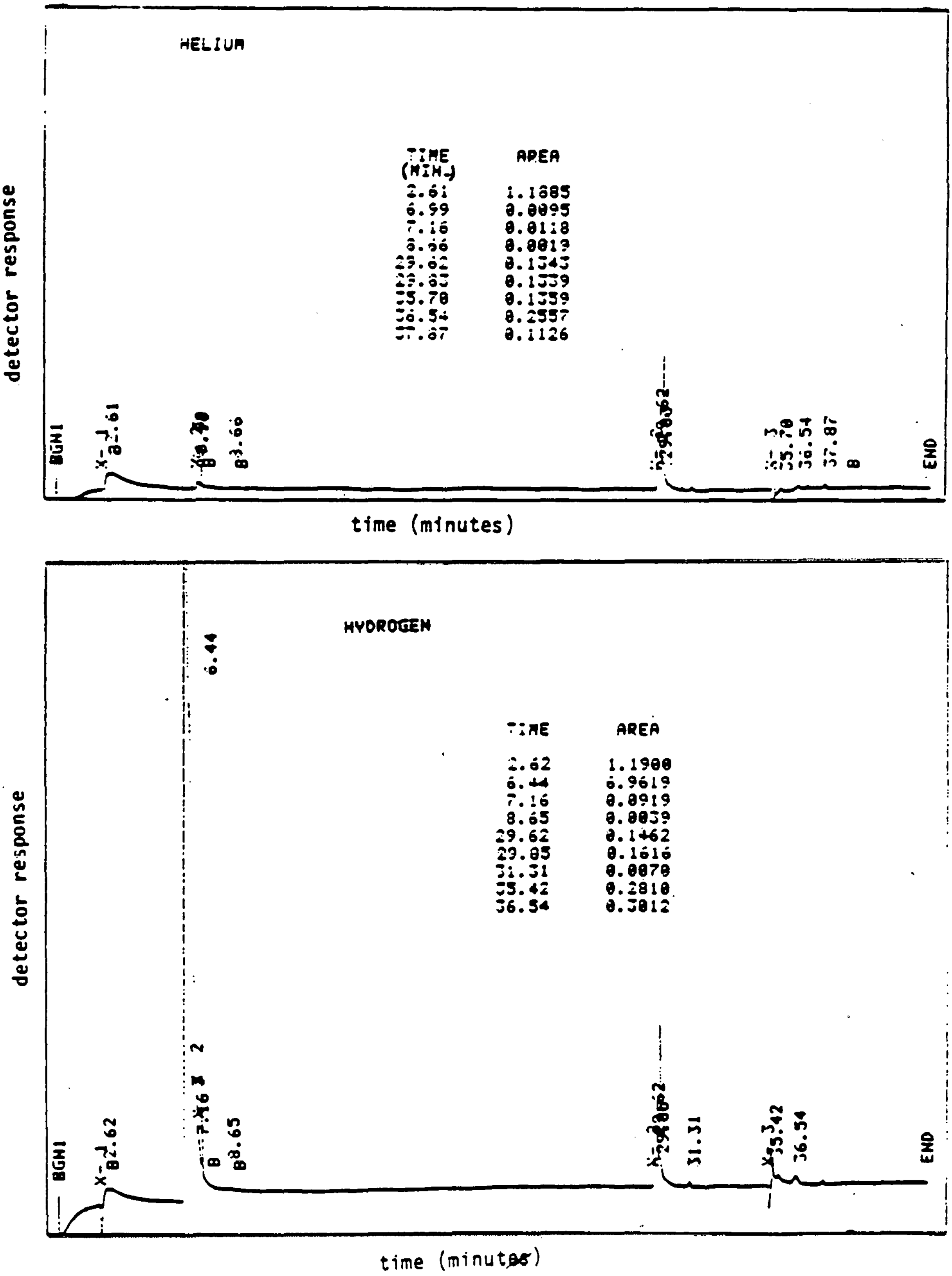
EVENT #	1	2	3	4	5	6	7	8
TIME MIN	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—
SLOT/CHANNEL	1	1	2	3	2	3	—	—
VALVE #	V1	V1	V2	V2	V2	V2	—	—
POSITION	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—

On is programs unless otherwise noted. Position 1 = CCW 2 = CW

FLOW ADJUSTING PROCEDURE
FOR HELIUM WITH INSTRUMENT
AT OPERATING TEMPERATURE

1. Measure flow at point X for steps 2-4
2. Turn all valves CCW, adjust helium pressure for a flow of [illegible]
3. Turn V1 CW, adjust restrictor A for same flow as in step 2.
4. Turn V2 CW, adjust restrictor B for same flow as in step 2
5. Measure flow at point Y, adjust restrictor C for same flow as in step 2

Figure A-2 Chromatograms of Helium and Hydrogen



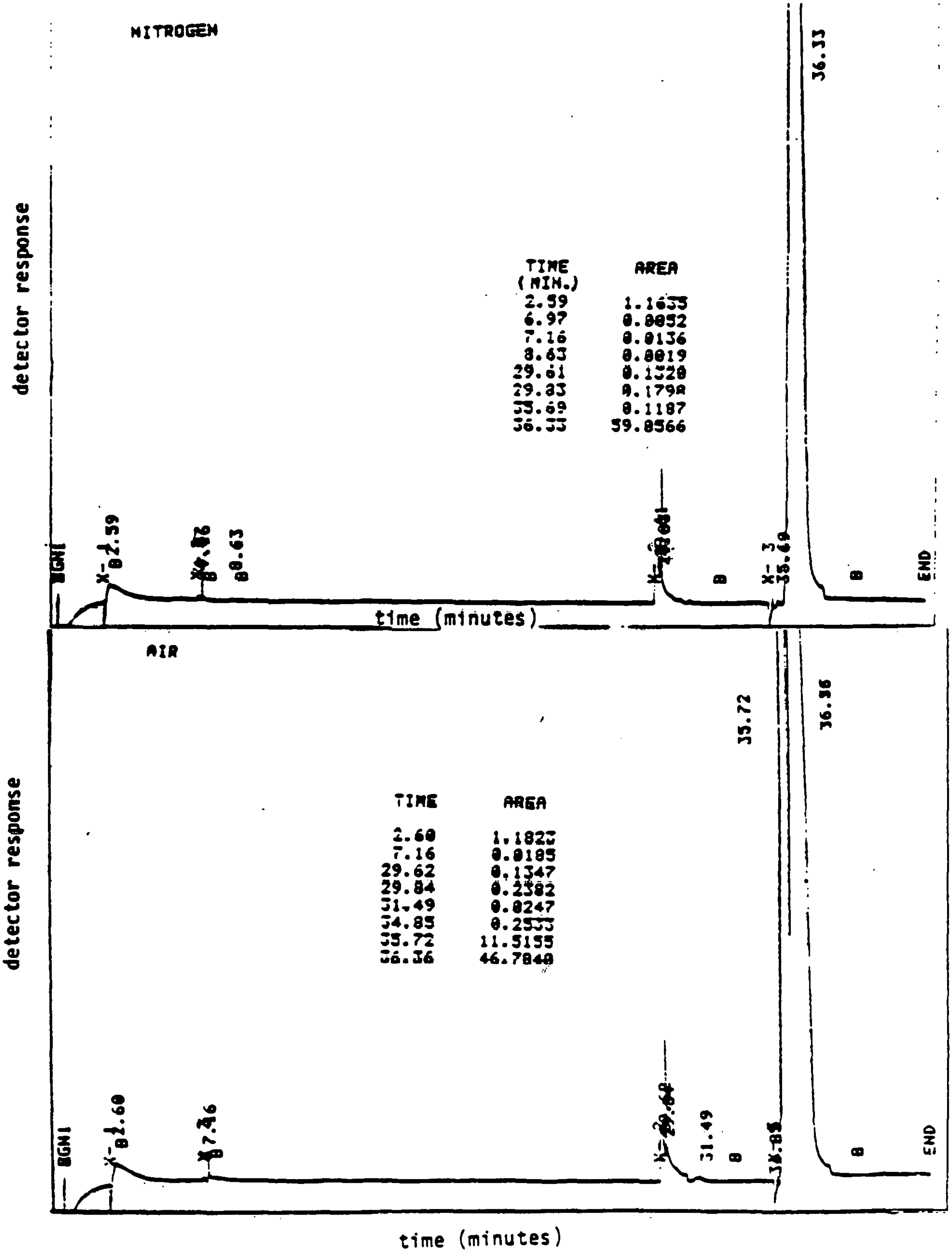
HELIUM

TIME (MIN.)	AREA
2.61	1.1685
6.99	0.0095
7.16	0.0118
8.66	0.0019
29.62	0.1343
29.83	0.1339
35.70	0.1359
36.54	0.2557
37.87	0.1126

HYDROGEN

TIME	AREA
2.62	1.1900
6.44	6.9619
7.16	0.0919
8.65	0.0039
29.62	0.1462
29.85	0.1616
31.31	0.0070
35.42	0.2810
36.54	0.3012

Figure A-3 Chromatograms of Nitrogen and Air



NITROGEN

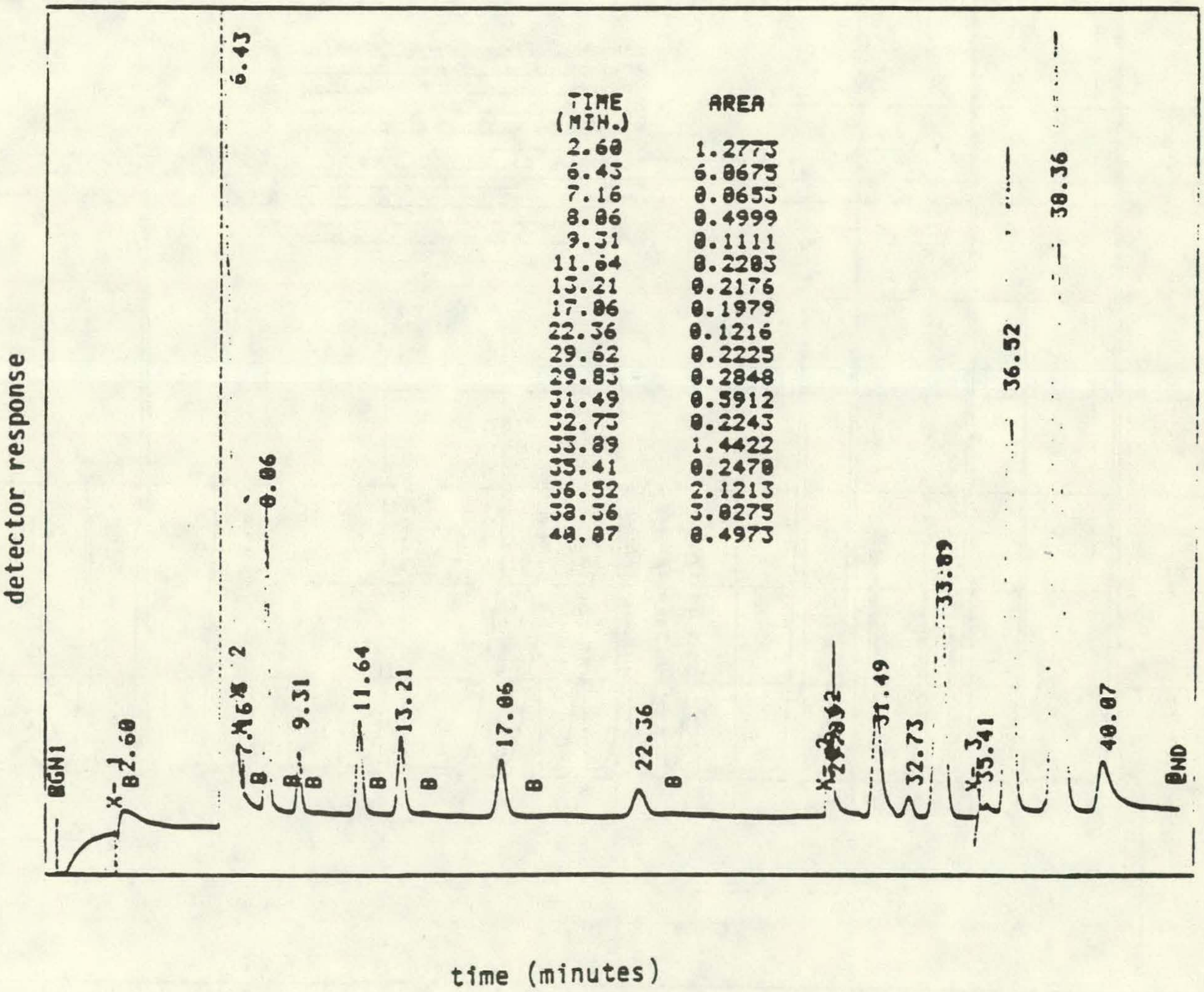
TIME (MIN.)	AREA
2.59	1.1633
6.97	0.0052
7.16	0.0136
8.63	0.0019
29.61	0.1520
29.83	0.1798
33.69	0.1187
36.33	59.8566

AIR

TIME	AREA
2.60	1.1823
7.16	0.0185
29.62	0.1347
29.84	0.2382
31.49	0.0247
34.85	0.2533
35.72	11.5155
36.36	46.7840

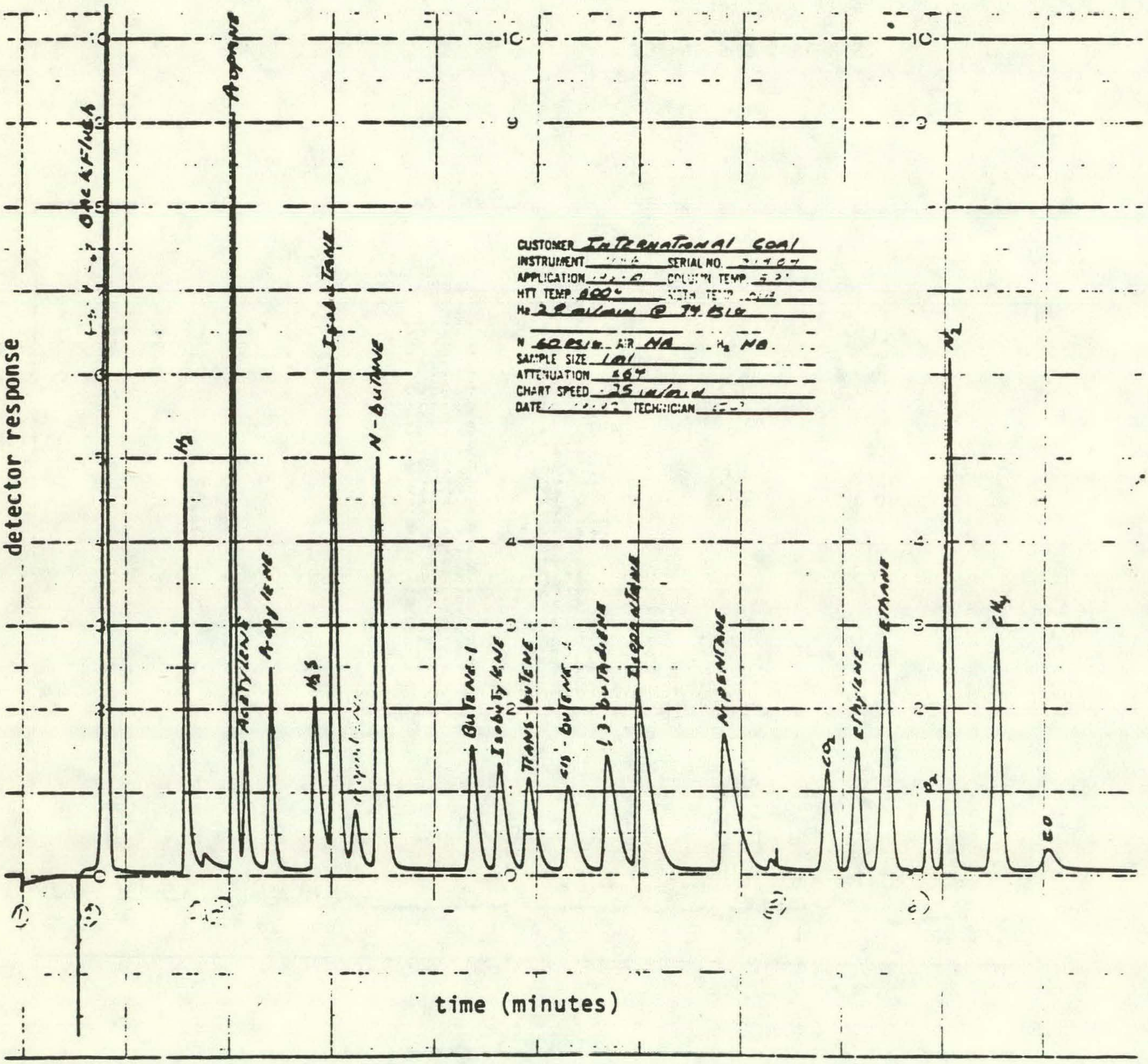
Figure A-4 Chromatogram of Standard Gas Sample

STANDARD GAS SAMPLE



TIME (MIN.)	AREA
2.60	1.2773
6.43	6.0675
7.16	0.0653
8.06	0.4999
9.31	0.1111
11.64	0.2203
13.21	0.2176
17.06	0.1979
22.36	0.1216
29.62	0.2225
29.83	0.2848
31.49	0.5912
32.73	0.2243
33.89	1.4422
35.41	0.2470
36.52	2.1213
38.36	3.0275
40.07	0.4973

Figure A-5 Chromatogram from Carle



CUSTOMER INTERNATIONAL COAL
INSTRUMENT [illegible] SERIAL NO. [illegible]
APPLICATION [illegible] COLUMN TEMP. [illegible]
HTT TEMP. 600° [illegible] TEMP [illegible]
He 28 cc/min @ 34 PSIG
N 60 PSIG AIR NA H2 NA
SAMPLE SIZE 1 cc
ATTENUATION ×64
CHART SPEED .25 in/min
DATE [illegible] TECHNICIAN [illegible]

Figure A-6 Comparison of Retention Times of Compounds in Carle's Chromatogram and ICRC's Chromatogram

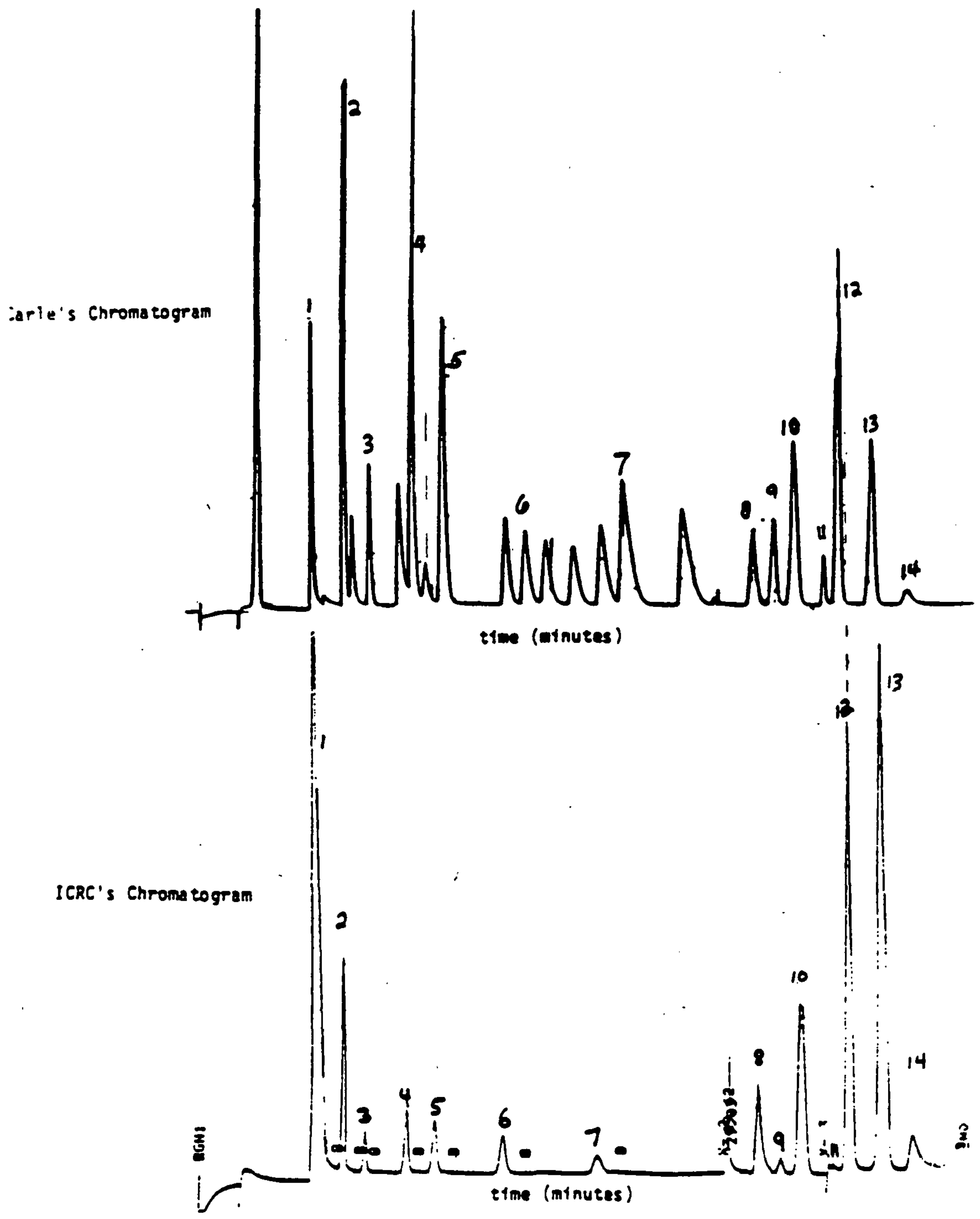


Exhibit A-1. SIGMA15 Integrator Operating Conversations and Directives

LEGEND

Push buttons, console panel displays, and terms printed out on the Printer / Plotter:

Labeled push buttons - ENTER, [illegible], [illegible]
Unlabeled push buttons - [illegible]
Display panel indications - [illegible] [illegible] [illegible]
Print-out, Printer/Plotter - <u>INJ TEMP</u>, <u>FLOW A,B</u>, <u>TOL</u>
User entry, Printer/Plotter - HYDROCARBON RUN, SAMPLE 1

Entries to be made by user from keyboard:

$\overset{\text{Default Value}}{\underset{\text{Range}}{(\text{Item Description})}}$

ERRORS

If [illegible] is displayed, push CANCEL ENTRY, then enter correct value and push ENTER

Operating Conversations

1 SETTING SYSTEM CLOCK

Use for Initial Startup

[1] / C

<u>0 : 28.7 0 / 0 / 0</u> (System prints out current clock reading.)

[3] If clock setting OK: CANCEL

[3a] If hour and minutes not OK, but month, day, year OK:

$\overset{0}{\underset{0\text{ to }23}{(\text{Hour})}}$ ENTER $\overset{0.0}{\underset{0\text{ to }59.9}{(\text{Minutes})}}$ ENTER ENTER

[3b] If month, day, or year not OK:

$\overset{0}{\underset{0\text{ to }23}{(\text{Hour})}}$ ENTER $\overset{0.00}{\underset{0\text{ to }59.9}{(\text{Minutes})}}$ ENTER $\underset{1\text{ to }12}{(\text{Month})}$ ENTER $\overset{0}{\underset{1\text{ to }31}{(\text{Day})}}$ ENTER $\overset{0}{\underset{76\text{ to }99}{(\text{Year})}}$ ENTER

2 SETTING MAXIMUM OVEN TEMPERATURE

OVEN ANALYZER $\overset{\text{No Default}}{\underset{1,2}{(\text{Analyzer No.})}}$ ENTER [illegible] $\overset{\text{Present Max.}}{\underset{-100\text{ to }450}{(\text{Max. Oven Temp. °C})}}$ ENTER

Operating Conversations (Cont'd)

3 METHOD GENERATION
(A) ANALYZER CONTROL

No Default
GEN **GEN** (Method No.) ENTER
1 to 255

ANALYZER CONTROL

25
INJ TEMP (Injector Temp., °C) NEXT LINE
25 to 450

65 / 25
DET ZONE 1,2 (Detector Temp. Except TCD, °C) ENTER (TCD Temp., °C) NEXT LINE
25 to 450 / 25 to 450

25
AUX TEMP (Aux. Device Temp., °C) NEXT LINE
25 to 450

Note:
Valve settings on "Read-a-Flow" units must be entered or "Ready" indicator won't light.

5 / 5
FLOW A,B (Flow, Channel A, cc/min.) ENTER (Flow, Channel B, cc/min.) NEXT LINE
0 to 90 / 0 to 90

75 / 999
INIT OVEN TEMP, TIME (Initial Oven Temp., °C) ENTER (Initial Time, min.) NEXT LINE
-100 to 450 / 0 to 999

TEMP		**RATE**		**TIME**	
		No Default		999	
(Oven Temp., °C)	ENTER	(Temp. Change Rate, °C/min.)	ENTER	(Time at Temp., min.)	NEXT LINE
-99 to 450		0.1 to 40.0		0 to 999	

[Repeat TEMP, RATE, TIME entries as required.]

ACCEPT SECTN

END TIME MAX XXX.XX

[End time max = maximum allowable data end time in Data Processing section.]

3 METHOD GENERATION
(B) DATA PROCESSING

DATA PROC

0 / 1 / 0
STD WT, SMP WT (Standard Weight) ENTER (Sample Weight) ENTER (File Disposition Code) NEXT LINE
0.0000 to 999.9999 / 0.0000 to 999.9999 / 0,1

File Disposition Code:
0 = Save Fil
1 = Delete F

1 / 0
FACTOR, SCALE (Concentration Conv. Factor) ENTER (Exponential Multiplier, Conc.) NEXT LINE
1 to 10,000 / -4 to +4

Operating Conversations (Cont'd)

3 METHOD GENERATION

(B) DATA PROCESSING (Cont'd)

	327.67		0		327.67		327.67		327.67	
TIMES	*(Data Stop Time, min.)	ENTER	(Data Start Time, min.)	ENTER	(Forced Base Point, min.)	ENTER	(Forced Base Point, min.)	ENTER	(Forced Base Point, min.)	ENTER
	0 to 327.67		0 to DET		DST to DET		PBP to DET		PBP to DET	

327.67	
(Forced Base Point, min.)	NEXT LINE
PBP to DET	

[DET = Data End Time
DST = Data Start Time
PBP = Previous Forced Base Point Time]

	10		4		0		2		0	
SENS-DET RANGE	(Area Sensitivity)	ENTER	(Base Sensitivity)	ENTER	(Slum Sensitivity)	ENTER	(Baseline Correction)	ENTER	(Detector Range)	ENTER
	1 to 1023		1 to 255		0 to 100.00		0, 1, 2		0 to 4	

0	
(Multiplier Det. Range)	NEXT LINE
0 to 4	

[Baseline (B.L.)
Correction Code

0 = Draw B.L. to next valley
1 = Project B.L. horizontally
2 = Draw B.L. to next base point

	1.000		0	
UNK, AIR	(Response Factor, Unknowns)	ENTER	(Air Peak Time)	NEXT LINE
	0 to 32,767		0 to 327.67	

	0		0.030		1.00	
TOL	(Peak Tolerance)	ENTER	(RRT Tolerance)	ENTER	(% Tolerance)	NEXT LINE
	0 to 9999.9999		0 to 32.767		0 to 100.00	

	0		0		0		0	
REF PK	(RRT Ref. Pk.)	ENTER	(Ref. Pk. Start Time, min.)	ENTER	(Ref. Pk. End Time, min.)	ENTER	(Reten. Time Ref. Pk., min.)	NEXT LINE
	0 to 32,767		DST to DET		RPS to DET		RPS to RPE	

[RPS = Ref. Pk. Start Time
RPE = Ref. Pk. End Time]

	No Name	
STD NAME	(Name of Standard Compound)	NEXT LINE
	30 characters	

RT		**RF**		**CONC**		**NAME**	
		1		0		No Name	
(RT, Component 1)	ENTER	(Response Factor, Component 1)	ENTER	(Concentration, Component 1)	ENTER	(Name, Component 1)	NEXT LINE
0 to 327.67		0 to 32,767		0 to 9999.9999		30 characters	

[Repeat RT, RF, CONC, NAME entries as required.]

→ ACCEPT SECTN

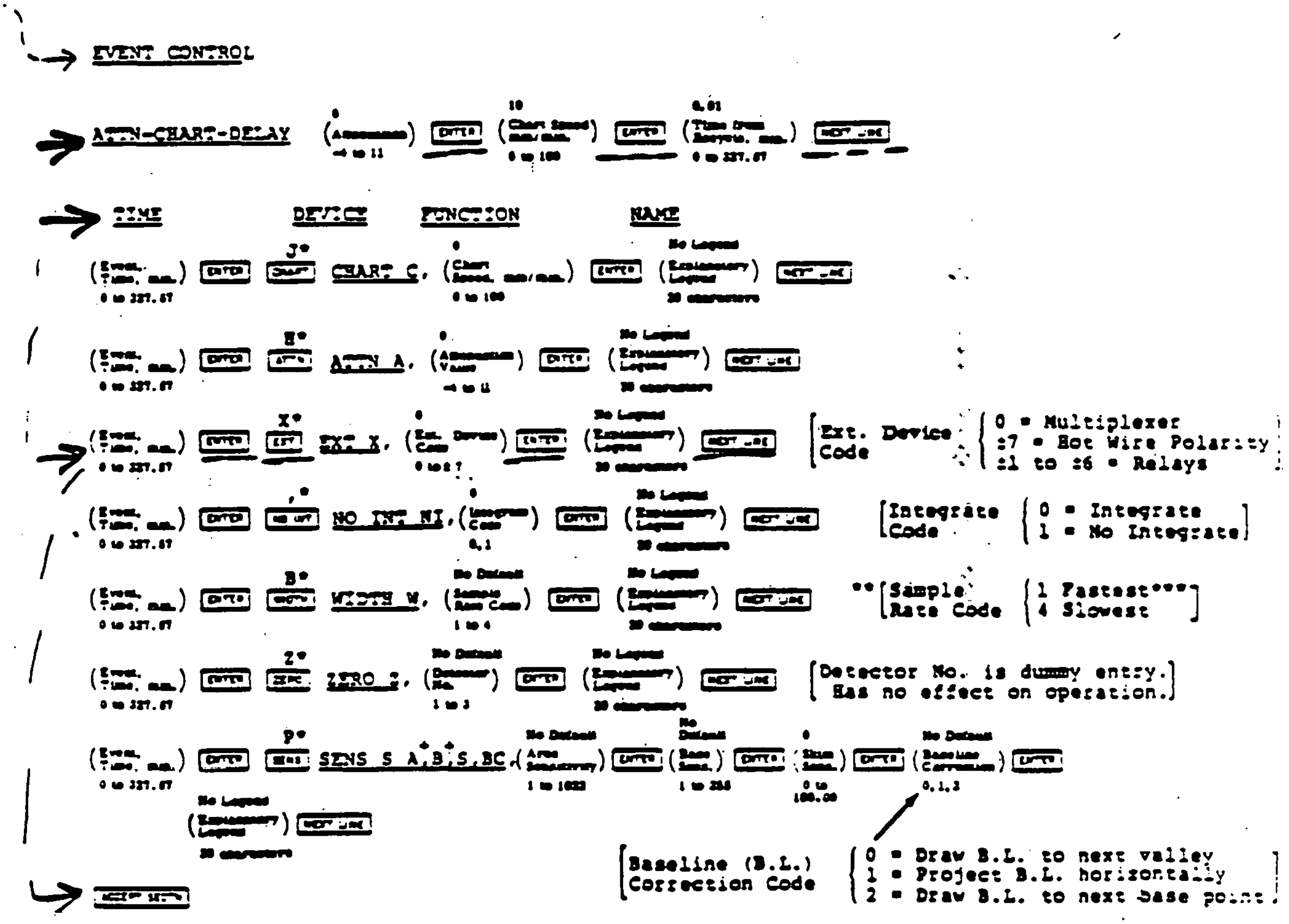
---

* Data end time must be equal to or less than total run time required for temperature program designated in Analyzer Control Section, above.

Operating Conversations (Cont'd)

3 METHOD GENERATION

(C) EVENT CONTROL



---

*Letter or symbol above Device push button represents equivalent key on auxiliary keyboard.

**Change in WIDTH must be entered when NO INT is in effect so System is on baseline. Otherwise, WIDTH may not change.

***Entry of WIDTH 1 for a time of 0.00 results in data collection at the maximum rate throughout a run. Automatic rate reductions to slower, optimum rates at appropriate intervals are suspended.

^Changes to A and B occur when NO INT is in effect or System is on baseline.

Operating Conversations (Cont'd)

4 LINKING PRINTER/PLOTTER TO ANALYZER OR INSTRUMENT

[1] PLOT CURRENT LINKAGE ____ [Current linkage = 0 if Printer/Plotter is not linked.]

[2] If link OK: CANCEL

[3] If plotter is linked to another device, push space bar and answer questions displayed*

[Mode Code {
0 = integration marks, peak crest times
1 = peak crest times only (default)
2 = integration marks only
3 = no integration marks, no peak crest times]

[4] To return to print mode (break link between Plotter and Analyzer or Instrument: PLOT [illegible]

---

*To change link from Analyzer to Instrument, enter 0 for Analyzer number.

5 POSITIONING PRINTER/PLOTTER BASELINE

[1] [illegible] [illegible]

[2] If baseline location displayed (as percent of full scale) is OK: ENTER

[3] If baseline location displayed is not OK:
Current Value
(Baseline Location, % F.S.) ENTER
0 to 100

6 SETUP PROCEDURE

[1] SETUP

[2] ANALYZER (Analyzer No.) ENTER
0
0 to 2

[3] If Analyzer No. entered is 1 or 2, go to step 4a. .If 0, go to step 4b.

Operating Conversations (Cont'd)

6 SETUP PROCEDURE (Cont'd)

[4a] DETECTOR (Detector No. — No Default, 1 to 3) ENTER → [4b] INSTRUMENT (Instrument No. — No Default, 1 to 4) ENTER

→ [5] METHOD (Method No. — No Default, 1 to 255) ENTER

→ [6] MODE (Mode Code — 0; 0,1) ENTER [Mode Code { 0 = short report / 1 = long report }]

[7] DETECTOR [Not requested when Analyzer no. is 0. Push ENTER if no other detector is to be used; otherwise, enter next detector no., then repeat steps 5 and 6.] .

→ [8] SAMPLE #/ID (Sample No. — 1; 1 to 32767) ENTER (Sample ID — No ID; Up to 18 Characters) ENTER [Sample no. is run no. in report]

→ *[9] PTR REQD (Printer No. — 1; 1,2) ENTER [Printer No. 1 = Printer/Plotter]

[10] [NOT READY appears unless Analyzer is at flows and temperatures required by method, all specified detectors and any external devices are "ready". When all conditions required by Method are established at Analyzer, NOT READY goes out and Analyzer temperatures stabilize 2 minutes. Then READY at Analyzer lights.]

[11] Inject sample, push START

[12] RUNNING 1 or RUNNING 2

[13] When analysis end time occurs repeat steps 10 through 12 to run another sample by the same Method.

*Step 9 omitted if Printer/Plotter is only terminal on System.

ATTENUATION VALUES

Value Entered	Attenuation	Value Entered	Attenuation
-4	X16*	4	16
-3	X 8*	5	32
-2	X 4*	6	64
-1	X 2*	7	128
0	1	8	256
1	2	9	512
2	4	10	1024
3	8	11	2048

---

*Expansion factor

Operating Conversations (Cont'd)

7 CALIBRATE CONVERSATION

No Default No Default 0
[1] CAL.B CAL (File No.) ENTER (Method No.) ENTER (Modify Code) ENTER
1 to 32767 1 to 255 0,1

Modify Code
0 = calculate response factors, report, do not change stored Method
1 = calculate response factors, modify stored Method

1
[2] RUN NO. (Run No.) ENTER
1 to 100

Run no. is used to calculate average response factors based on current and previous runs of standard sample.

SIGMA 15 PROCEDURE FOR GAS SAMPLE ANALYSIS

This procedure is used to process unknown samples.

☐ represents actual keys on Sigma 15 keyboard.

⬚ represents messages given on Sigma 15 console.

A. Pre-Run

1. Flow rates are taken daily by J. Rabe.
2. Check gas pressure; nitrogen should be 60-65 psi.
3. To list method to be used, press List key, method #[a], and Enter
4. To get system ready to run:

Setup

Instrument 3 Enter

Method #[a] Enter

Mode 0 Enter

Sample ID Number[b] Enter NAME[c] Enter

PTR REQD! 1 Enter

Note: After setup is completed and entered, then green ready light on instrument labeled "Interface 3" should come on.

[a] Check which method (1-255) is appropriate for your specific analysis.

[b] 1-3000.

[c] Up to 38 characters.

B. Sample Loading

The sample should be contained under pressure in a gas sample cylinger mounted on the ring stand provided. Connect the sample cylinder with an appropriate Swagelock connector (provided) to the stainless steel tubing, which runs to the sample loop. After the cylinder is connected, place the copper tubing that comes from the VENT (outlet side) of the sample loop into a beaker with mineral oil to detect flow. Slowly open the outlet valve on the sample cylinder to bleed sample through the loop. The loop can hold 15 ml, and 40 bubbles should be bled through the loop for a sufficient sample size. Close the sample valve, remove copper tubing from the mineral oil, and press the green ready button on the instrument labeled "Interface 3" to start the run.

C. Run

Check pressures to make sure they are constant; nitrogen should be 60-65 psi.

To communicate with the Sigma 15 console:

1. H displays the actual attenuation.
2. Diaplay Actual Instrument 3 Enter T displays the actual run time.
3. Print Actual prints the current run time and attenuation on chromatogram in progress.

Short Tips

- To list a method, press List , method number , and Enter .
- Tick marks are available for peak crest times and integration times. See Appendix 2, p. A2-3, for further details.
- To get rid of PTR REQD when generating a method, press VOID INSTRUMENT 3 Enter Also, to get Interface 3 out of the ready mode, press VOID INSTRUMENT 3 Enter ; these two actions to remove Interface 3 from the ready mode actually break the linkage between the printer/plotter and the interface.
- ZONE 1 message (for an explanation, see Jeff Rabe).

Delete and Modify Tips

The following tips are to be used with extreme caution. Delete only those methods that you, the user, have benerated.

- To detele a method, press Del , method number , and Enter .
- To modify a method, press Mod , method number , and Enter ; as the method is printed press either accept section if the entire section is acceptable, or next line if changes are needed throughout a section. Follow the Method Generation Procedures in Appendix 2.

Trouble-Shooting

1. Noisy Base Line

   Things to check:

   - Check helium and nitrogen pressures.
   - Check to make sure that the tubing used to connect the X or Y outlets to the bubbler is disconnected.
   - If these things don't work, consult Jeff Rabe.

2. Strange Chromatogram

   If the chromatogram peaks or base line characteristics are not whay you anticipated, allow the GC to ge through all valve switches and complete the entire run. Prematurely stopping a run will cause problems in the GC.

3. If the nitrogen pressure drops noticeably below 60 psi, immediately notify staging of the problem and determine the status of house nitrogen.

Appendix VIII-B

BASIC Computer Program to Calculate Carle Gas Analysis

Exhibit B-1

BASIC Computer Program

```
1 INIT
9 IMAGE 19A,2X,13A,2X,6A,2X,10A,2X,15A
10 IMAGE 16A,2X,13A,2X,6A,2X,10A,2X,15A
70 PAGE
80 PRINT "RESPONSE FACTORS FOR STANDARD GAS MIXTURE"
100 REM:THIS PROGRAM CALCULATES RESPONSE FACTORS FOR THE GAS MIXTURE
110 REM:AND CALCULATES THE MOLE% FOR AN UNKNOWN GAS SAMPLE
120 DIM D(16)
130 DIM E(16)
140 DIM B(16,2)
150 DIM A(16,2)
160 DIM L(16)
170 M=0
180 E=0
190 PRINT "DATE:";
200 INPUT C$
210 PRINT "TIME:";
220 INPUT E$
230 PRINT "ANALYST:";
240 INPUT D$
250 PRINT "INSERT DATA TAPE AND ENTER FILE# FOR ";
260 PRINT "GC DATA OF STANDARD GAS:";
270 INPUT F
280 FIND F
290 REM: MOLE% CONCENTRATION OF COMPOUNDS IN GAS STANDARD
300 DATA 1.0E-5,88.109,0.49,0.118,0.692,0.176,0.171,0.17
310 DATA 0.088,0.65,0.085,1.25,0.093,2.91,5.06,0.63
320 PRI USI 9:"JJJCOMPOUND","RET.TIME","AREA","MOLE %","RESP.FACTORJ"
330 READ D
340 FOR I=1 TO 16
350 READ @33:A(I,1),A(I,2)
360 REM: CALCULATION OF RESPONSE FACTOR
370 IF A(I,2)=0 THEN 390
380 GO TO 400
```

```
390 A(I,2)=1
400 E(I)=D(I)/A(I,2)
410 READ D$
420 IF E(I)>999 THEN 440
430 GO TO 450
440 E=0
450 REM
460 PRINT USING 870:D$,A(I,1),A(I,2),D(I),E(I)
470 NEXT I
480 DATA "BACKFLUSH","HYDROGEN","PROPANE","PROPYLENE"
490 DATA "HYDROGEN SULFIDE","I-BUTANE","N-BUTANE","I-BUTYLENE"
500 DATA "I-PENTANE","CARBON DIOXIDE","ETHYLENE","ETHANE"
510 DATA "OXYGEN","NITROGEN","METHANE","CARBON MONOXIDE"
520 REM:THIS PORTION OF THE PROGRAM CALCULATES MOLE% FOR AN UNKNOWN GAS
530 INPUT X$
540 PAGE
550 PRINT "ANALYSIS DATE AND TIME:";
560 INPUT G$
570 PRINT "SAMPLE NAME,SAMPLING DATE,SAMPLING TIME:";
580 INPUT I$
590 PRINT "ANALYSIS REQUESTED BY:";
600 INPUT H$
610 PRINT "SAMPLED BY:";
620 INPUT J$
630 PRINT "GC ANALYST:";
640 INPUT K$
650 PRINT "DATA TAPE NAME:";
660 INPUT L$
670 PRINT "INSERT DATA TAPE AND ENTER FILE# OF SAMPLE'S GC DATA:";
680 INPUT K
690 PRINT "CHARGE NUMBER:";
700 INPUT N$
710 PRINT "FOR ANALYSIS REPORT PRESS RETURN"
720 INPUT Y$
730 PAGE
```

Exhibit B-1 (Continued)

```
740 PRINT "GASANALYSIS OF HYDROCARBON GAS MIXTUREJJ"
750 PRINT "SAMPLE DESCRIPTION:J";I$
760 PRINT "SAMPLED BY:";J$
770 PRINT "ANALYSIS REQUESTED BY:";H$
780 PRINT "CHARGE NUMBER:";N$
790 PRINT "ANALYSIS DATE:";G$
800 PRINT "GC ANALYST:";K$
810 PRINT "DATA TAPE AND FILE NUMBER:";L$;",";K;"JJ"
820 PRINT USING 10:"COMPOUND","RET.TIME","AREA","RESP.FACT.","MOLE %J"
830 DATA "BACKFLUSH","HYDROGEN","PROPANE","PROPYLENE"
840 DATA "HYDROGEN SULFIDE","I-BUTANE","N-BUTANE","I-BUTYLENE"
850 DATA "I-PENTANE","CARBON DIOXIDE","ETHYLENE","ETHANE"
860 DATA "OXYGEN","NITROGEN","METHANE","CARBON MONOXIDE"
870 IMAGE 16A,4X,2D.2D,6X,2D.3D,4X,2D.3D,9X,2D.3D
880 IMAGE 16A,4X,2D.2D,5X,3D.3D,5X,2D.3D,5X,2D.2D
890 IMAGE 46X,5A,2X,3D.2D,2X
900 FIND K
910 FOR I=1 TO 16
920 READ @33:B(I,1),B(I,2)
930 REM: CALCULATION OF MOLE% FROM AREA USING RF(E)
940 L(I)=B(I,2)*E(I)
950 READ D$
960 M=L(I)+M
970 PRINT USING 880:D$,B(I,1),B(I,2),E(I),L(I)
980 NEXT I
990 PRINT USING 890:"JSUM:",M
1000 RESTORE
1010 COPY
```

Appendix VIII-C

User Guide to Enter Raw GC Data onto a GC Data Tape Prior to Data Analysis

1. <u>Enter GC Data onto GC Data Tape</u>

This program is listed in Exhibit C-1. To enter GC data into the computer and store them in a designated data file on a GC data tape, follow these steps:

Step 1. Load the program into the computer

a) Insert program tape.

b) FIN 4 `return` (file #4 contains the program listed in Exhibit A).

c) OLD `return` loads program from file into computer.

d) Eject program tape.

Step 2. List last data entered from GC data tape:

a) Insert GC data tape.

b) TLIST `return` will list all data files used on the GC data tape. The files will be labeled as "binary data". The file labeled "last" will be used for new data. For example, if 92 GC data files are used, the new data will be entered into file #93.

c) FIN 92 `return` RUN `return` will list the previously entered GC data in file #92 and position the tape reader at the beginning of file #93. An example is shown in Exhibit C-2.

Exhibit C-1 Data Is Entered onto Magnetic Tape

```
 1 PRINT "RT(MIN)","AREA%"
 2 ON EOF (0) THEN 10
 3 READ @33:X,Y
 4 PRINT X,Y
 5 GO TO 2
 10 PRINT "EOF"
 30 PRINT "FILE NUMBER:";
 31 INPUT F
 32 FIND F
 33 PRINT "APPROX.# OF PEAKS:";
 34 INPUT P
 35 MARK 1,P*9*10
 36 FIND F
 40 PRINT "ENTER RT(MIN),AREA%"
 41 INPUT X,Y
 42 WRITE @33:X,Y
 43 GO TO 40
```

Exhibit C-2 Listing of Last GC Data Entered

```
FIN92
 RUN
 RT(MIN)                AREA%
  3.34                   9.1372
  6.44                   81.9635
  7.98                   0.0297
  9.15                   0.4287
  10.63                  2.0636
  11.55                  1.0232
  13.12                  3.023
  16.82                  0.057
  22.26                  0.5257
  31.45                  3.2995
  32.76                  0.2118
  33.95                  12.064
  35.41                  2.1787
  36.48                  4.2337
  38.36                  26.5126
  39.69                  2.9209
 EOF
 FILE NUMBER:
```

Step 3. Format new file for numbers of peaks from the chromatogram and enter data:

a) 93 return 16 return, which will format file #93 for 16 data pairs.

b) The screen will show ENTER RT(MIN), AREA %. Enter the GC data and press return after each entry.

Note: be sure to enter the 16 identified compound-peak data pairs in the correct order and always include a data point for the backflush peak at the beginning.

c) After last data is entered, press break twice, then type CLOSE return. The screen will show

```
PROGRAM ABORTED IN LINE 41
CLOSE.
```

An example is shown in Exhibit C-3.

Step 4 a) Relist the just-entered data by typing FIN 48 return RUN return. This step is only for proofreading the data entry and is not needed in order to execute the program. After listing, the next file is readied for the subsequent set of data.

b) If Step 4a is bypassed, enter the next data set by typing RUN return.

__Note__: When a brand new GC data tape is used, follow this procedure:

1. Insert the new GC data tape.
2. Press rewind.
3. Type RUN 33 return.
4. Enter the approximate number of peaks.
5. Proceed from step 3b.

Exhibit C-3 Entry of GC Data Into File #48

```
FILE NUMBER:93
APPROX.# OF PEAKS:16
ENTER RT(MIN),AREA%
3.34
9.1372
ENTER RT(MIN),AREA%
6.44
81.9635
ENTER RT(MIN),AREA%
7.98
8.0297
ENTER RT(MIN),AREA%
9.15
.4287
ENTER RT(MIN),AREA%
10.63
2.0636
ENTER RT(MIN),AREA%
11.55
1.0232
ENTER RT(MIN),AREA%
13.12
3.023
ENTER RT(MIN),AREA%
16.82
.057
ENTER RT(MIN),AREA%
22.26
.5257
ENTER RT(MIN),AREA%
31.45
3.2995
ENTER RT(MIN),AREA%
32.76
.2118
ENTER RT(MIN),AREA%
33.95
12.604
ENTER RT(MIN),AREA%
35.41
211787
ENTER RT(MIN),AREA%
36.48
4.2337
ENTER RT(MIN),AREA%
38.36
26.5126
ENTER RT(MIN),AREA%
39.69
2.9289
ENTER RT(MIN),AREA%
PROGRAM ABORTED IN LINE 41
CLOSE
```

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IX. DOCUMENTATION OF THE AUTOMATED SEQUENTIAL EXTRACTION (ASE) PROCEDURE

SUMMARY

ICRC has employed several analytical workup procedures to determine the amount of distillate, oils, asphaltenes, preasphaltenes, and residue in SRC-I process streams. However, these procedures are time-consuming and are not always reliable in terms of the material balances of the fraction generated around specific units, e.g., the Kerr-McGee Critical Solvent Deashing (CSD) unit. In order to minimize turnaround time and maximize reliability, ICRC has developed the automated sequential extraction or ASE procedure, which is described in this section.

The ASE procedure was developed using Conoco's liquid column fractionation (LC/F) method as a model. Although LC/F has the shortest turnaround time of those methods commonly used, it requires distillation of oils before analysis. In developing the ASE procedure, ICRC was able to eliminate distillation, and therefore quantify the oils fraction in one extraction step. Furthermore, ASE results were shown to be reproducible within ±2 wt %, and to yield acceptable material balances. Finally, the ASE method proved to be the least affected by sample composition.

It was therefore determined that the ASE procedure can be used to analyze SRC-I streams of varying composition.

INTRODUCTION

Various analytical workup procedures are commonly used to describe the SRC-I process streams with respect to their composition of distillate, oils, asphaltenes, preasphaltenes, and residue. Some procedures also determine sums of fractions, such as asphaltenes + preasphaltenes =

SRC, and preasphaltenes + residue = benzene/toluene insolubles. The relative composition of these fractions reflects specific process conditions and characterizes the SRC-I product streams.

It has been shown that four commonly used distillation procedures yield different amounts of distillate from the same sample (Kingsley and Schweighardt, 1982) Due to thermal degradation, distillation may alter the product distribution of preasphaltenes and residue (Kingsley et al., 1981). Laboratory vacuum distillation must therefore be carried out under well-defined conditions, and should only be used to generate a distillate and not a distillate bottoms for subsequent analysis, such as the determination of asphaltenes, preasphaltenes, and residue.

Various extraction techniques will generate different amounts of oils, asphaltenes, preasphaltenes, and residue. These techniques include beaker extractions, Soxhlet extraction, beaker precipitations, solvent separation filtration (routine workup method used for ICRC CPDU samples), and liquid column fractionation (LC/F), developed by Conoco (Kingsley and Schweighardt, 1982). Most of these procedures are very time-consuming and demand great operational skill. Table 1 compares these procedures with respect to analysis time and types of fractions obtained.

The turnaround time for these procedures is a very important factor in process monitoring and in cost. The fastest is the LC/F procedure:

1 hr for oils/asphaltenes/preasphaltenes
\+ 4 hr for THF beaker extraction
\+ 4 hr for sample distillation
9 hr turnaround time

The Soxhlet and beaker extractions in combination with the beaker precipitation method for the oils/asphaltenes separation require about 5 hr of analysis time; however, the turnaround time is 2 days. The sequential solvent extraction method takes about 12 hr and the turnaround time is also 2 days.

Another difference between the workup methods listed in Table 1 is that all except the LC/F method are preparative procedures, whereas the

LC/F method is an analytical procedure. A preparative procedure is defined as one that generates a fraction large enough for further analysis, such as elemental analysis; the analytical method generates only the weight percent value for the fractions obtained because the fraction size is too small for further analysis.

In addition to analysis time, another criterion for a reliable product workup procedure is the material balance of the weight percents from the fractions generated. If two different samples are analyzed for fraction composition, and an equal mixture (by weight) of the samples is prepared and analyzed to determine its fraction composition, the fractions obtained should match the arithmetic average of the fractions from the two initial samples. It has been shown (Kingsley and Schweighardt, 1982) that beaker extractions, Soxhlet extractions, beaker precipitation, and sequential solvent extraction do not generate all fractions in the same additive manner, which has an effect on the closing of the material balance. Conoco's LC/F yields the best material balance of fractions.

In developing ICRC's automated sequential extraction (ASE) procedure, the following were considered:

- reproducibility of results (precision)
- analysis time (man-hours, elapsed time)
- material balance of fractions around a unit

Conoco's LC/F procedure was used as a model because of its short time requirement and its good reproducibility. However, with this procedure, a sample containing J50% oils must be distilled before analysis. In other words, two procedures are required to yield one result. Due to changes in instrumentation, column configuration, and mode of packing for the ASE procedure, ICRC was able to eliminate the distillation step, and therefore quantify the oils fraction directly in one extraction step.

PRINCIPLES OF THE ASE PROCEDURE

The ASE procedure (detailed in Appendix IX-A) uses a fluidized bed of 100-120-mesh glass beads contained in a glass column; this setup allows the injected THF-soluble sample fraction to be rapidly dispersed in n-heptane, thereby precipitating heptane-insoluble material (asphaltenes and preasphaltenes) on the glass beads. A solvent-metering pump delivers heptane through the column, eluting the oils fraction from the sample. Pumping 90 mL of heptane at a 10 mL/min flow rate through the column is followed by pumping 90 mL each of benzene and pyridine, thereby eluting the asphaltene and preasphaltene fractions, respectively. After the three fractions are collected, the solvent is evaporated in a dry bath at 70°C under a nitrogen stream, and then weighed to obtain the weight percent distribution of oils, asphaltenes, and preasphaltenes in the THF-soluble portion of the sample. The total product distribution of the sample, including the THF-insoluble residue, is calculated from this result. The column is regenerated with heptane before the next sample is analyzed.

EVALUATION OF ASE ANALYSIS RESULTS

Approach

Six different SRC-I process streams were analyzed by the ASE procedure, and the results were evaluated for reproducibility and material balance (MB) of the fractions. The samples were generated at the Wilsonville Advanced Coal Liquefaction Facility during run no. 220 (B-MB); sampling sites are illustrated in Figure 1, a schematic of the SRC-I process.

To evaluate the MB of the analyzed fractions, two mixtures of the samples were prepared; the first was a 50/50 vol % mixture of 20 wt % solutions of V131A and LSRC in THF; the second was a 50/50 vol % mixture of 20 wt % solutions of LSRC and THF solubles of KMAC in THF. The mixed samples were analyzed, and the results were compared to the arithmetic mean of the individually analyzed samples.

Results

Reproducibility. ASE analysis averages ($\bar{x}$) for the weight percent results and standard deviations (s) of the six SRC-I process streams are shown in Table 2. The analysis results for samples V110, T102B, and KMAC were normalized to include the THF-insoluble residue. Standard deviations, which indicate the expected reproducibility of the procedure, were calculated from the results of six replicate assays. The largest standard deviation was determined to be ±1.6 wt %.

Material Balance. LSRC and V131A, as well as THF solubles from the KMAC sample, were combined into 50/50 vol % mixtures. The analysis results for the mixed samples are shown in Table 3, along with the theoretical results based on the arithmetic mean for each 50/50 mixture. The agreement between the analytical and the calculated results is quite good. This study therefore shows that a material balance within 2 wt % can be obtained with the ASE method in the analysis of SRC-I process streams of varying compositions.

Recovery. The analysis of Wilsonville process streams by the ASE procedure yields from 90 to 117 mg of the sum of the three fractions. Theoretically, recovery based on the injection of a 0.500-mL sample from a 20% (weight per volume in THF) solution should yield 100 mg. The range in yields was traced to variations in the 0.500-mL sample injection loop sizes. These loops were calibrated using a 20.0% solution (weight per volume in THF) of eicosane. The recoveries, given in Table 4, reflect the 10% variation in loop size. However, the variation in recovery seemed to have no effect on the distribution of oils, asphaltenes, and preasphaltenes in an SRC-I sample, as shown in Table 5. The recovery for each fraction by ASE analysis, performed six times, was found to be within 1 wt %.

In the ASE analysis of ICRC CPDU process stream samples, the sum of ASE fractions gave consistently lower recoveries (after correction for sample loop size). A material loss of light ends from the oils fraction on these CPDU samples was determined. This discovery warranted a modification of the ASE procedure to be used when analyzing SRC-I process streams containing low-boiling material. To prevent the loss of low-boiling material, the procedure for heptane removal described in Appendix IX-A was modified as follows:

1. After collection of the oils fraction, the fraction contained in the preweighed vial is placed in the 70°C dry bath under a steady nitrogen stream. Vial walls are washed periodically with small amounts of toluene to generate a homogeneous oils concentrate.
2. The vial is removed just before solvent evaporation is completed.
3. A small amount of toluene (not exceeding 0.5 mL final volume) is added to redissolve any oils deposited on the vial walls.
4. The vial is capped, swirled to mix content, cooled to room temperature, and the sample vial is weighed.
5. A sample is withdrawn from the oils solution and injected into a GC to determine heptane and toluene concentrations.
6. The oils weight is adjusted by subtracting the heptane and toluene content.

Oils analysis of any sample containing potentially volatile material (i.e., CPDU and tubing bomb samples) should be carried out as outlined above.

For comparison of the modified (M-ASE) and the unmodified (U-ASE) ASE method, a CPDU sample showing only 75 wt % recovery of the ASE fractions was analyzed by both methods. The ASE fractions by M-ASE showed 103 ± 4 wt % recovery (after sample loop size adjustment). The oils fractions from each of the two methods were compared for their respective boiling point distribution. The chromatograms obtained are shown in Figures 2 and 3 and the boiling point distribution calculated from the chromatograms is given in Table 6. Comparison of the two chromatograms shows more peaks on the left side (light ends) of the chromatogram in Figure 2 than in Figure 3, indicating losses of lights by heptane removal. This is confirmed by the results in Table 6, which show the oils fraction by U-ASE to contain less light material than the oils from the M-ASE procedure.

COMPARISON OF ASE WITH OTHER METHODS

In addition to ASE analysis, the six previously described Wilsonville SRC-I process streams were analyzed by solvent separation (FILT), Wilsonville Soxhlet extraction (SOX) and the Conoco LC/F method (LC/F); weight percent results were obtained for the oils, asphaltenes, preasphaltenes, and residue fraction in each of the six streams. The results are listed in Table 7. Previous studies (Kingsley and Schweighardt, 1982) have shown that the sum of oils and asphaltenes, benzene solubles, describe a fraction that is less dependent on sample composition and procedure. Therefore, the benzene-soluble fraction was calculated for the four different work-up procedures. Figure 4 shows that the ASE results compare closely with the LC/F results for the oils and asphaltenes, and thus for the total benzene-insoluble fraction as well. Otherwise, the results show large variations among the four analytical techniques. This is especially true of the correlation between ASE and solvent separation results. For example, comparison of oil yields of the process streams by these two procedures (Figure 5) shows a poor correlation. Since these data points represent specific oil concentrations in defined SRC-I process streams, the results derived from different analytical procedures will be affected by sample composition. Therefore, it is necessary to evaluate the composition dependency of a procedure. One method is to calculate the material balance of the analysis-generated fractions from a set of SRC-I samples.

The mass balance of the fractions (ϕ) of four SRC-I process streams can be calculated based on known flow rates. The streams for this calculation are the feed (T102B) and products (LSRC, SRC, and KMAC) from the CSD unit, and the material balance can be calculated using the following equation:

$$\phi \mathrm{T102B} = 0.149\ \phi\ \mathrm{LSRC} + 0.532\ \phi\ \mathrm{SRC} + 0.319\ \phi\ \mathrm{KMAC} \qquad (1)$$

With the results from Table 7, equation 1 generated a material balance (recovery) for each fraction as analyzed by each separation method. Table 8 shows that all extraction procedures are sample-composition-dependent. That is, they do not consistently yield 100% recovery in the sum of fractions from the products compared to the amount of fraction in the feed. Presently, there is no explanation for the large difference in weight percent oils and asphaltenes in the CSD feed T102B and the CSD products as determined by the FILT method; this is reflected in the 179% oils and 86% asphaltenes recovery in Table 8. Preasphaltene recovery of under 100% for each method shows that all methods can extract more preasphaltenes from the feed sample than from the products. In contrast, residue recovery is over 100% for all methods; that is, the methods consistently determined more residue in the CSD products than in the feed. This consistency may indicate that regressive reactions are taking place.

To quantify the sample composition dependency of each method, that is, its ability to yield reliable material balance of fractions, a comparison was made by calculating the average recovery and standard deviation for each procedure (bottom of Table 8). The ASE method's low standard deviation of 16 wt % for the recovery indicates that this procedure is not as strongly affected by sample composition as the other procedures. Therefore, the ASE method can be used to reliably determine oils, asphaltenes, preasphaltenes, and residue in SRC-I process streams of varying composition.

RESPONSE FACTORS

Work was done to establish response factors of the respective ASE fractions using a Pye-Unicam moving wire defector. This was an effort to use Conoco's LC/F approach. The work and results are described in Appendix IX-B. The response factor for a fraction of a process stream sample may change with run conditions and/or feed material. This means that response factors must be re-established for each different type of sample. Therefore, using response factors is a viable approach for the analysis of the same types of process streams, but it can be very cumbersome with varying types of process stream samples, because response factors need to be established each time.

LITERATURE CITED

Kingsley, I. S., and F. K. Schweighardt. 1982. Round-robin study of methods used to characterize SRC-I products. Pages 125-174 *in* SRC-I quarterly technical report, January-March 1982. DOE/OR/03054-7. International Coal Refining Company, Allentown, PA.

____________, A. Z. Kamzelski, D. M. Parees, and F. K. Schweighardt. 1981. Development of SRC-I product analysis. Pages 139-149 _in_ SRC-I quarterly technical report, January-March 1981. DOE/OR/03054-3. International Coal Refining Company, Allentown, PA.

Table 1

Comparison of Product Work-Up Procedures

Method	Analysis time (man-hours)	Turnaround time (days)	Fractions obtained
Distillation	2	1/2	distillate, bottoms
Solvent separation	12	2	oils, asphaltenes, preasphaltenes, residue
Beaker extraction	3 each	1/2 each	benzene/toluene, THF, and pyridine solubles and insolubles
Soxhlet extraction	3 each	1/2[c]	oils[d], asphaltenes, preasphaltenes, residue
Beaker precipitation[a]	2	1/2 each	oils, asphaltenes
LC/F[b]	1	1/6	oils, asphaltenes, preasphaltenes

[a] On benzene/toluene-soluble fraction.

[b] On THF-soluble distillate bottoms, i.e., perform distillation and beaker extraction on sample before LC/F analysis.

[c] If fractions are generated in parallel.

[d] Not reliable on a sample containing more than 30 wt % oils.

Table 2

ASE and THF Extraction Weight Percent ($\bar{x}$)

and Standard Deviation (s) Results of SRC-I Process Stream Analyses

Process stream		THF insolubles[a]	Oils[b]	Asphaltenes[b]	Preasphaltenes[b]
V110	$\bar{x}$	10.2	56.7	14.7	18.4
	$\bar{x}^c$		63.1	16.4	20.5
	s		0.5	0.3	0.3
T102B	$\bar{x}$	22.1	24.8	22.7	30.4
	$\bar{x}^c$		31.8	29.2	39.0
	s		1.2	0.5	1.5
SRC	$\bar{x}$	0	33.6	31.2	35.3
	s		1.2	1.0	1.1
V131A	$\bar{x}$	0	99.2	0.8	0.1
	s		0.9	0.9	0.2
LSRC	$\bar{x}$	0	66.4	28.3	5.3
	s		1.6	1.5	1.0
KMAC	$\bar{x}$	80.6	3.3	4.3	11.8
	$\bar{x}^c$		17.1	21.9	61.0
	s		0.1	0.3	0.4

[a] By beaker extraction.
[b] By ASE analysis.
[c] Excluding THF insolubles.

Table 3
ASE Analysis Results for Mixtures of SRC-I Samples

	Wt %		
Mixture	Oils	Asphaltenes	Preasphaltenes
LSRC/V131A			
Analyzed	84.4	12.7	2.9
Calculated	82.8	14.6	2.7
LSRC/KMAC			
Analyzed	42.3	25.6	32.0
Calculated	41.8	25.1	33.2

Table 4
ASE Sample Loop Calibration

	Loop A	Loop B	Loop C
Mg recovered	103.1	111.3	100.8
s[a]	1.1	1.8	1.6
Loop size (½l)	515.5	556.5	504.0

[a] Standard deviation.

Table 5
Reproducibility of Weight Percent and Recovery by ASE Analysis of the THF-Soluble and V110 Samples

Run no.	1	2	3	4	5	6	$\bar{x}^a$	s^b
% oils	63.5	63.5	62.7	62.5	62.6	63.8	63.1	0.6
% asphaltenes	16.3	16.4	16.4	16.8	16.7	16.0	16.4	0.3
% preasphaltene	20.2	20.1	20.9	20.7	20.7	20.2	20.5	0.3
Mg recovered	111	104	113	117	115	117	112.8	4.9

[a] Using sample loop B.
[b] Standard deviation.

Table 6

Comparison of Boiling Point Distribution (by GC) of Two Oils Fractions Obtained by U-ASE and M-ASE Method

Area %	Boiling point distribution (°F)				
	<400	400-500	550-650	650-750	>750
M-ASE	2.3	16.1	44.4	19.7	176
U-ASE	0.4	10.4	47.9	24.4	16.9

Table 7

Comparison of Analytical Techniques

	Tech-	Wt %					
Fraction	nique	V110	T102B	SRC	V131A	LSRC	KMAC
Oils	ASE	56.7	24.8	33.6	99.2	66.4	3.3
	FILT	61.5	6.9	8.9	98.1	47.4	1.8
	SOX	63.5	19.4	20.2	99.7	39.4	1.5
	LC/F	67.8	31.4	41.0	100.0	71.9	4.2
Asphaltenes	ASE	14.7	22.7	31.2	0.8	28.3	4.3
	FILT	16.5	48.4	62.2	1.6	47.2	2.3
	SOX	17.2	39.3	58.8	0.3	60.3	1.2
	LC/F	10.5	22.7	33.9	0	22.1	4.9
Preasphaltenes	ASE	18.4	30.4	35.3	0.1	5.3	11.8
	FILT	13.6	28.5	28.9	0.3	4.1	34.3
	SOX	11.9	25.5	20.5	0	0.3	30.3
	LC/F	11.0	24.3	25.1	0	6.0	10.9
Residue	ASE	10.2	22.1	0	0	0	80.6
	FILT	8.3	16.0	0	0	0	61.6
	SOX	7.4	15.8	0.5	0	0	67.0
	LC/F	10.7	21.6	0	0	0	80.6
Benzene solubles	ASE	71.4	47.5	64.8	99.9	94.7	7.6
	FILT	78.0	55.3	71.1	99.7	94.6	4.1
	SOX	80.7	58.7	79.0	100	99.7	2.7
	LC/F	78.3	54.1	74.9	100	94.0	9.1

Table 8

Material Balance for Fractions as Determined by Four Extraction Procedures

			Wt %			
Fraction	Stream		ASE	FILT	SOX	LC/F
Oils	T102B		24.8	6.9	19.4	31.4
	SRC		17.88	4.73	10.75	21.81
	LSRC		9.89	7.06	5.87	10.71
	KMAC		1.05	0.57	0.48	1.34
		Σ[a]	28.82	12.36	17.10	33.86
		Recov.	116%	179%	88%	108%
Asphaltenes	T102B		22.7	48.4	39.3	22.7
	SRC		16.60	33.09	31.28	18.03
	LSRC		4.22	7.03	8.98	3.29
	KMAC		1.37	0.73	0.38	1.56
		Σ	22.19	41.75	40.64	22.98
		Recov.	98%	86%	103%	101%
Preasphaltenes	T102B		30.4	28.5	25.5	24.3
	SRC		18.78	15.37	10.91	13.35
	LSRC		0.79	0.61	0.04	0.89
	KMAC		3.76	10.94	9.67	3.48
		Σ	23.33	26.92	20.62	17.72
		Recov.	77%	94%	81%	72%
Residue	T102B		22.1	16.0	15.8	21.6
	SRC		0	0	0.27	0
	LSRC		0	0	0	0
	KMAC		25.71	19.65	21.37	25.71
		Σ	25.71	19.65	21.64	25.71
		Recov.	116%	123%	137%	119%
Benzene solubles	T102B		47.5	55.3	58.7	54.1
	SRC		34.47	37.86	42.03	39.85
	LSRC		14.11	14.10	14.86	14.01
	KMAC		2.42	1.31	.86	2.90
		Σ	51.00	53.27	57.75	56.75
		Recov.	107%	96%	98%	105%
All recoveries	$\bar{x}$		102.8	115.6	101.4	101.3
	s[b]		16.2	38.1	21.7	19.8

[a] Σ is the sum of SRC, LSRC, and KMAC streams.
[b] Standard deviation.

Figure 1
Wilsonville Pilot Plant Sampling
Sites for ASE Analysis

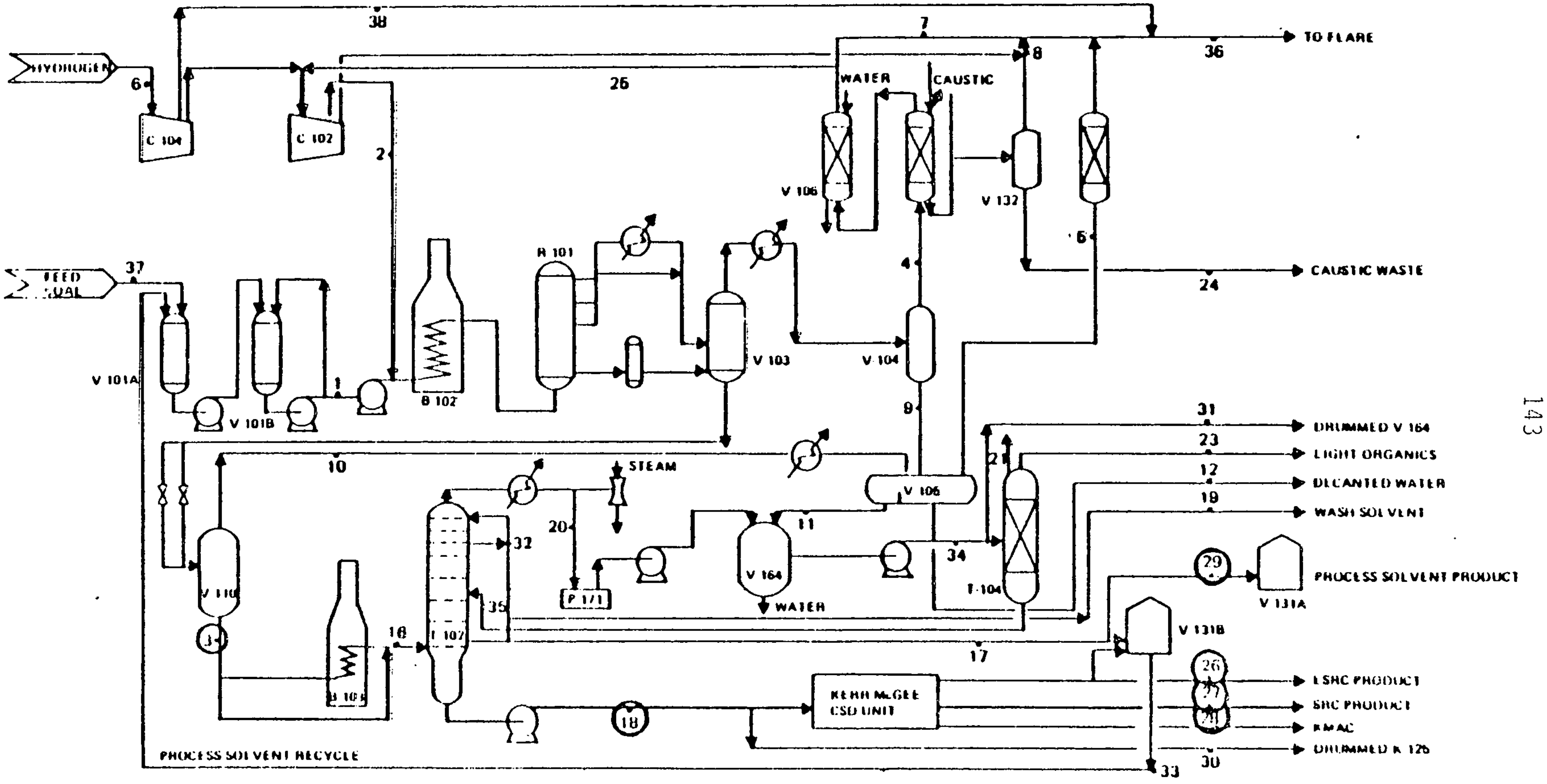


Figure 2
Chromatogram of Oils Determined by M-ASE

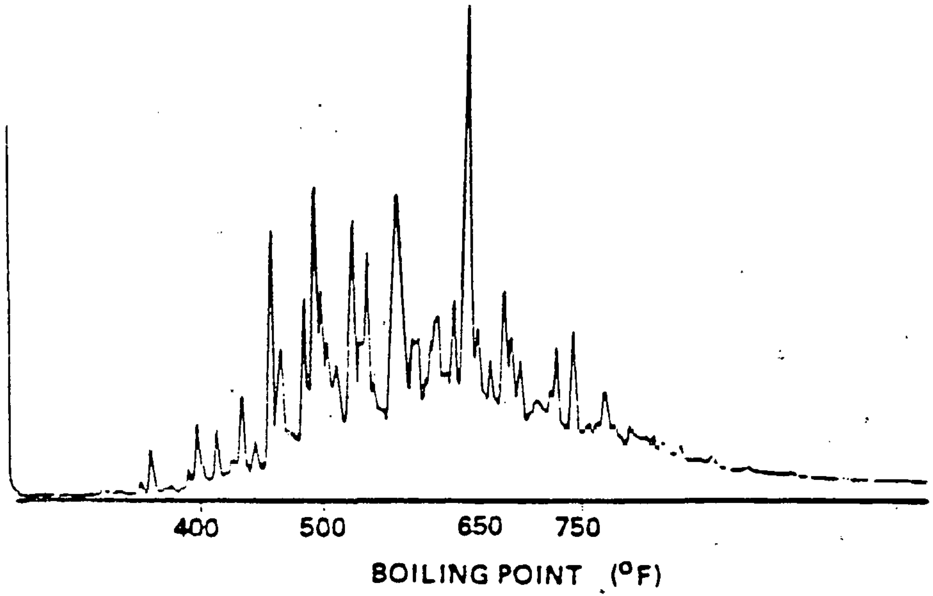


Figure 3
Chromatogram of Oils Determined by U-ASE

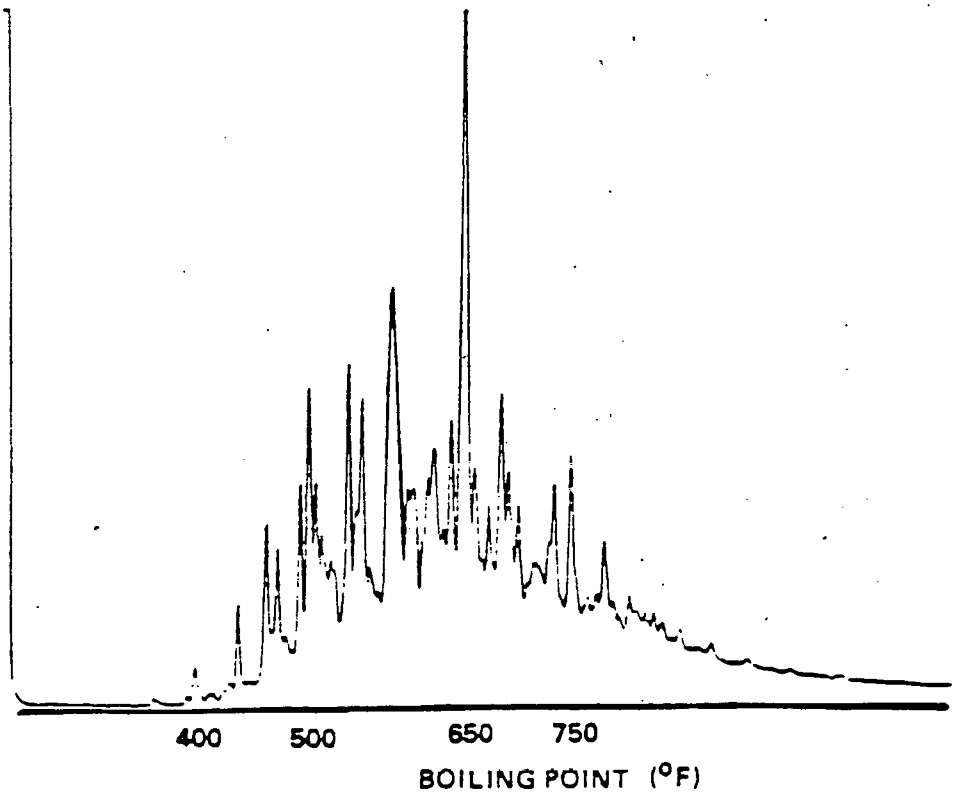


FIGURE 4
COMPARISON OF ANALYTICAL TECHNIQUES

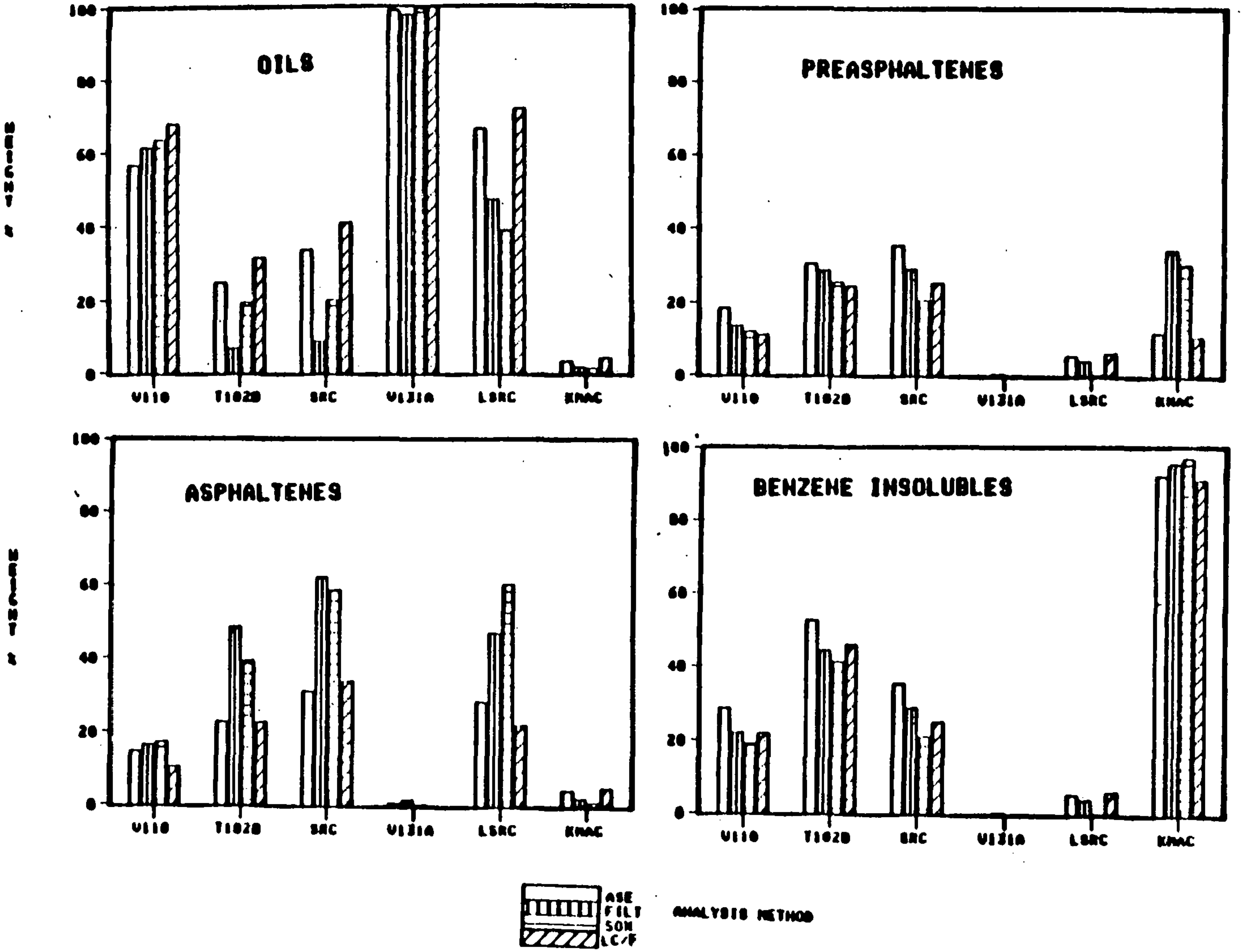
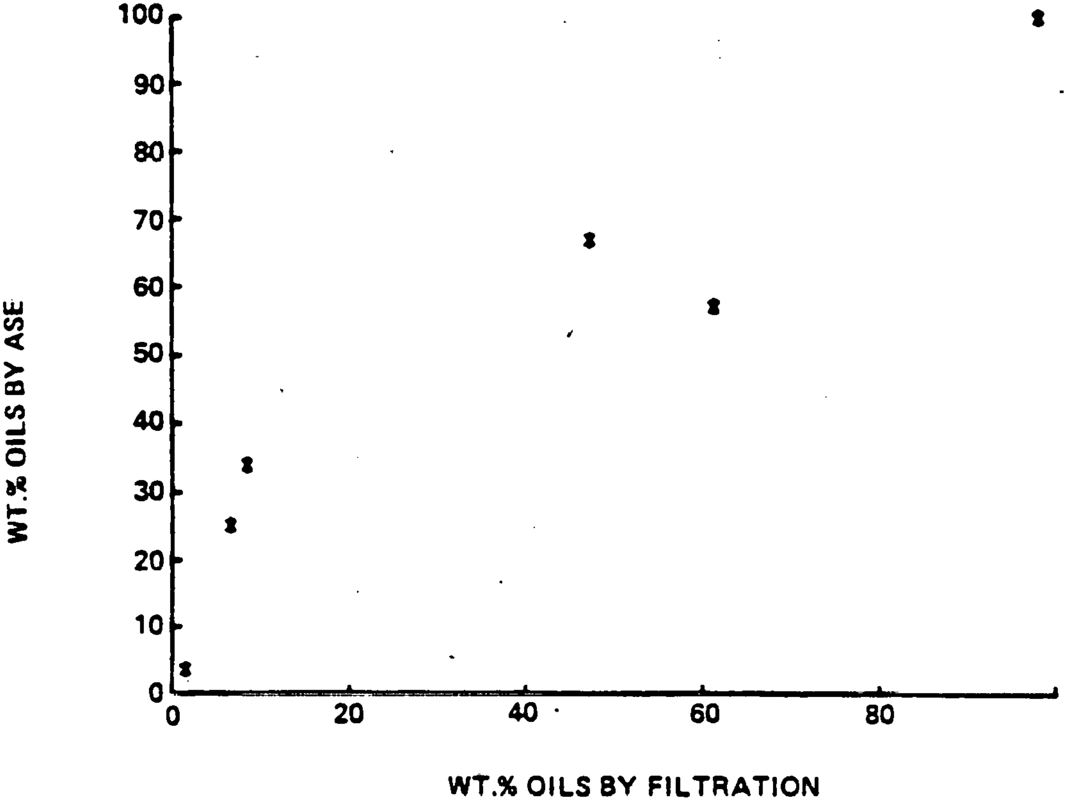


Figure 5
Comparison of Weight Percent Oils Obtained
by Two Different Analytical Methods



Appendix IX-A

ASE Procedure

1. Scope

This method is intended to determine the weight percent fractions of oils, asphaltenes, and preasphaltenes in the residue-free portion of an SRC-I product sample.

2. Principle

This procedure is based on the fractional solubility of the increasingly polar fractions, e.g., oils, asphaltenes, and preasphaltenes, in solvents of increasing polarity such as heptane, benzene, and pyridine. The sample is injected onto a column containing a fluidized bed of glass beads, which allows optimal sample mixing and dilution of the heptane solubles with the sample solvent (THF) in the first solvent, heptane. The oils of the sample are then eluted with heptane, followed by elution of the asphaltenes with benzene, and elution of the preasphaltenes with pyridine. After reconditioning with heptane, the fluidized bed column is ready for a new sample.

Strict adherence to all specific conditions and timing is essential due to the empirical nature of the test.

3. Apparatus

(1) rotary four-way switching valve
(2) sample injection valve, loop size 0.5 mL
(3) metering pump capable of pumping precisely (± 0.01 mL/min) and accurately (± 0.01 mL/min) at a flow rate of 10 mL/min
(4) glass column 250 x 9 mm with end fittings for 1/8-in. thick wall Teflon tubing (suggested supplier: Altex)
(5) stopwatch
(6) collection vials, 120 mL each, glass (suggested supplier: Wheaton Cat. No. 225546)
(7) dry bath, temperature controllable at 80 ± 1°C and 30 ± 1°C

(8) Nitrogen at 9 psig
(9) analytical balance capable of weighing 120 g ± 0.1 mg
(10) 10-mL glass syringe

4. Reagents

(1) n-heptane, HPLC-grade
(2) benzene, pesticide-grade
(3) pyridine, analytical-grade
(4) glass beads, 90 - 120 mesh (suggested supplier: Arthur H. Thomas, Cat. No. 5663R20)
(5) THF for cleaning of injection valve

5. Procedure

Note: It is necessary to obtain a residue-free sample, prepared as tetrahydrofuran-solubles, before analysis by this ASE procedure.

(A) Preparation of Fluidized Bed

Note: This is only necessary if a new ASE column is to be used. After preparation, the ASE column can usually be used for 100 - 200 samples before changing.

(1) Fill glass column with 13.4 g of glass beads.
(2) Connect tubing to inlet and outlet column, inlet is connected to the outlet of the sample injection valve, and the outlet is connected to the inlet of the fraction collector.
(3) Mount the column vertically in the bracket provided, such that the inlet is on the bottom and the outlet is on top.
(4) Wash the glass beads at a flow rate of 10 mL/min, pump n-heptane for 10 min, then benzene for 10 min, then pyridine for 10 min, followed by heptane for 15 min.
(5) Turn flow rate to zero. The glass beads have now been washed and conditioned, and the column is ready for sample injection.

(B) Sample Fractionation by ASE

(1) Weigh three collection vials for each sample on an analytical balance and record weight within 0.1 mg.

(2) Fill glass syringe with 20% solution of sample in tetrahydrofuran and load into sample injection loop.

(3) Turn heptane flow to 10 mL/min with upward flow (fluidizing the bed of glass beads).

(4) At time zero, inject sample onto column and start collecting effluent in first collection vial.

(5) At time 1.5 min, turn column 180° clockwise, thereby switching from a fluidized to a packed bed.

(6) At time 9.0 min, switch to benzene at 10 mL/min flow rate.

(7) At time 9.2 min, switch effluent from first to second collection vial; first vial contains oils fraction.

(8) At time 17.0 min, turn column 180° counterclockwise.

(9) At time 18.0 min, switch to pyridine at 10 mL/min flow rate.

(10) At time 18.2 min, switch effluent from second to third collection vial; second collection vial contains asphaltenes fraction.

(11) At time 21.5 min, turn column 180° clockwise.

(12) At 23.5 min, switch to heptane at 10 mL/min flow rate.

(13) At time 27.2 min, switch effluent from third vial to waste; third vial contains preasphaltenes fraction.

(14) At time 31 min, turn column 180° counterclockwise; column is now reconditioned with heptane and ready for injection of new sample.

(C) <u>Solvent Removal</u>

Note: This procedure should be carried out in a well-ventillated hood.

(1) After the three fractions are collected in procedure B, place vials in a constant-temperature dry bath at 80°C and remove solvents by blowing nitrogen over the surface of the sample, not exceeding 9 psig; avoid any splashing.

(2) Solvent has been removed if the vial content appears dry (or oily for the oils fraction).

(3) Place vials into dry bath at 30°C for 30 min, blowing a stream of nitrogen into the vial; then cap and weigh vial.

Repeat this step as many times as necessary to reach a constant weight; the weight obtained should be within 0.1 mg precision.

6. Calculation

(1) Determine the weight of each fraction by subtraction of the weight of the empty collection vial from the weight of the sample-containing vial. Add the weight of all three fractions to determine the total weight recovered.

(2) Normalize the weights to weight percents:

$$\text{wt \% oils} = \frac{\text{mg oils}}{\text{total mg recovered}}$$

$$\text{wt \% asphaltenes} = \frac{\text{mg asphaltenes}}{\text{total mg recovered}}$$

$$\text{wt \% preasphaltenes} = \frac{\text{mg preasphaltenes}}{\text{total mg recovered}}$$

(3) If THF-insoluble residue was present in the original sample, normalize the weight percents to total fractional distribution:

(a) Determine weight of residue (obtained in procedure for preparation of THF or pyridine solubles before FBF analysis)

(b) Calculate the factor $\frac{(100 - \text{wt \% residue})}{100}$

(c) Multiply each wt % obtained in step (2) with this factor to obtain a total fractional distribution.

Appendix IX-B

Determination of Pye-Unicam Response Factors for the ASE Procedure

INTRODUCTION

Conoco performs the LC/F analysis using response factors obtained with a Pye Unicam (P-U) moving wire detector, thereby allowing determination of oils, asphaltenes, and preasphaltenes without gravimetric analysis. The response factor for a given type of process stream must be determined by preparative analysis of a representative sample to yield weight percent fractions; these fractions are then related to the chromatographic area generated by performing a scaled-down analysis of the same sample using the P-U detector. Once the response factor is established, this approach allows rapid sample analysis. ICRC used a similar approach for the ASE analysis; however, response factors for different types of SRC-I process streams were established with a combined preparative/analytical method.

METHOD

The process stream samples shown in Figure 1 were run through the ASE column, as described in the procedure in Appendix IX-A. The effluent was dropped onto the moving wire of a P-U detector, which, after evaporation of the lighter compounds such as the solvent, continually carried a miniscule amount of representative effluent to a flame ionization detector located in the P-U detector; this generated a response relatable to the amount of carbon-containing compounds in the effluent. The effluent was then collected in three preweighed vials, and the fractions were weighed after evaporation. A schematic of the procedure is shown in Figure B-1. The P-U response was quantified using 20-sec time-slice integration over the 27-min analysis time. Results of integrated areas, area percents, and standard deviations are provided in Table B-1.

REPRODUCIBILITY

Reproducibility of the respective detector responses is described by the standard deviation, which was calculated from six replicate assays. The reproducibility was in the same range as that determined with the gravimetric approach (Table 2), excepting recycle solvent sample V131A. However, the total response for that sample was only about 1/4 of the responses of all other process streams, which decreases the sensitivity and precision of response for that process stream.

Typical chromatograms obtained for these SRC-I process streams are shown in Figure B-2. The recorder was set at identical attenuation for all of the ASE samples, which allowed an overall comparison of the samples' relative detector responses. The V131A process solvent sample again showed significantly lower detector response than all of the other process stream samples.

RESPONSE FACTOR CALCULATION

The response factor (RF) was calculated two ways:

(1) absolute response factor

$$RF = \frac{\text{peak area}}{\text{weight \%}}$$

(2) relative response factor

$$RF = \frac{\text{area \%}}{\text{weight \%}}$$

Dividing the peak area or area % of a fraction from an unknown sample by the respective response factor can then generate the weight percent of that specific fraction after normalization.

Table B-2 shows that the absolute and relative response factors for each of the three SRC-I process stream fractions vary significantly, which reflects the differing composition of oils in different process streams. The absolute response factors show greater variation, i.e., more sensitivity to changes in the fraction composition, than the relative response fractions. The values in parentheses in Table B-2 signify those response factors calculated from a <5 wt % fraction, which renders the value less precise. Preasphaltenes show the smallest variation in RF, indicating that the composition with respect to FID response is very similar for a preasphaltene from any SRC-I process stream.

CONCLUSION

Applying response factors in the ASE analysis of CPDU process streams is cumbersome, since these RF values must be re-established for each different type of sample; in addition, with changes in run conditions or feed materials, the response factors for the three fractions may also change. Therefore, the chromatographic approach was temporarily discontinued, and the gravimetric approach was used exclusively.

Table B-1

Pye Unicam Detector Response in the ASE Analysis of SRC-I Process Streams

		Oils		Asphaltenes		Preasphaltenes		Total
Stream		pk area[a]	area %	pk area	area %	pk area	area %	pk area
V110	$\bar{x}$	1,230	39.9	1,449	47.0	364	13.1	3,043
	s[b]		0.9		1.3		1.6	
T102B	$\bar{x}$	1,384	36.2	1,669	46.1	733	17.7	3,786
	s		0.8		0.2		0.6	
SRC	$\bar{x}$	1,585	38.3	1,903	46.7	540	14.9	4,028
	s		1.1		0.8		1.0	
V131A	$\bar{x}$	415	73.0	139	23.3	21	4.6	575
	s		2.8		2.2		1.9	
LSRC	$\bar{x}$	1,906	49.9	1,658	44.3	231	5.8	3,795
	s		1.4		0.9		1.2	
KMAC	$\bar{x}$	743	27.4	1,259	47.8	617	24.8	2,619
	s		0.6		1.2		1.5	
V131A/LSRC	$\bar{x}$	1,358	50.1	1,176	43.8	140	6.1	2,674
	s		0.8		0.3		0.7	
LSRC/KMAC	$\bar{x}$	1,189	41.2	1,262	43.6	397	15.3	2,848
	s		0.8		0.4		0.7	

[a] Integration units.

[b] Standard deviation.

Table B-2

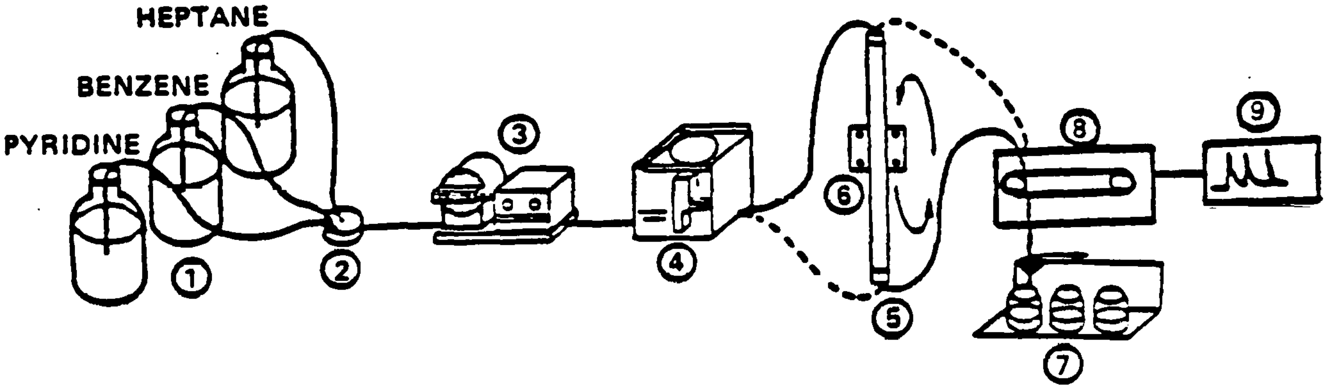
Response Factors for SRC-I Process Streams

Stream	Oils		Asphaltenes		Preasphaltenes	
	abs.	rel.	abs.	rel.	abs.	rel.
V110	19.49	0.63	88.35	2.87	17.76	0.64
T102B	43.52	1.14	57.16	1.59	18.79	0.45
SRC	47.17	1.14	60.00	1.50	15.30	0.42
V131A	4.18	0.74	(173.70)	(29.13)	(210.00)	(46.0)
LSRC	28.70	0.75	58.59	1.66	43.58	1.09
KMAC	(43.45)[a]	(1.60)	(57.49)	(2.18)	(10.12)	0.41
V131A/LSRC	16.09	0.59	92.59	3.45	48.28	2.10
LSRC/KMAC	28.11	0.97	49.30	1.703	12.41	0.48

[a] Parenthetical values were calculated from a F5 wt % fraction.

Figure B-1

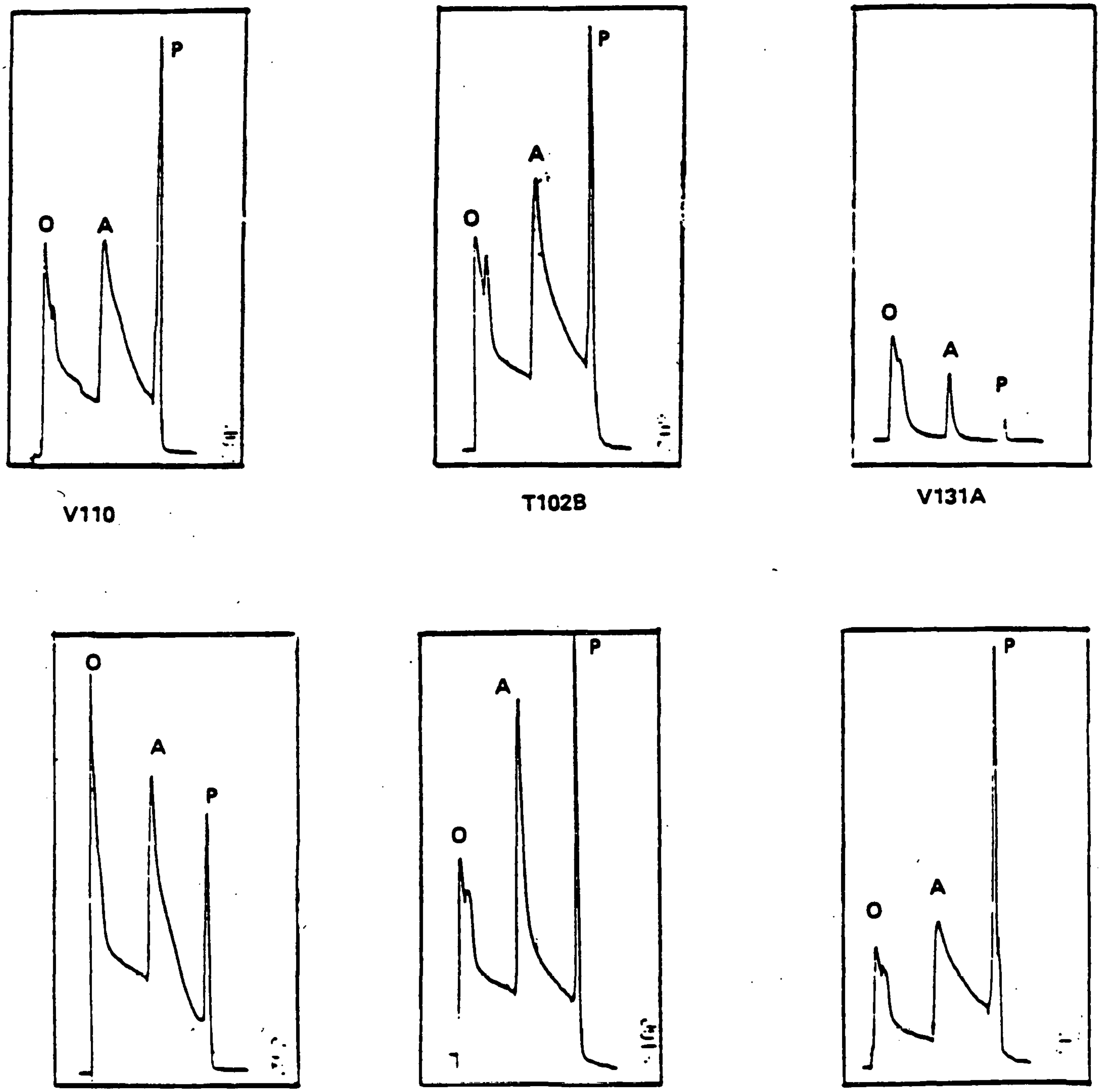
Schematic of ASE Procedure for Response Factor Determination



(1) Eluting Solvents
(2) Solvent Switching Valve
(3) Solvent Metering Pump
(4) Autosampler
(5) ASE Column
(6) Column Turning Valve
(7) Fraction Collector
(8) Pye-Unicam Detector
(9) Recorder

Figure B-2

ASE Chromatograms Using Pye Unicam Detector
(O = Oils, A = Asphaltenes, P = Preasphaltenes)



V110

T102B

V131A

LSRC

SRC

KMAC

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