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Development and Installation of Continuous Water Monitoring Systems for the AEDC

ES Industries
701 South Route 73
Berlin, NJ 08009-2621

August 1992

Final Report for Period March 1991 through May 1992

Approved for public release; distribution is unlimited.

ARNOLD ENGINEERING DEVELOPMENT CENTER
ARNOLD AIR FORCE BASE, TENNESSEE
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

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A system to sample and analyze water from Rowland Creek at AEDC for hydrocarbon contaminants has been developed under a Small Business Innovation Research (SBIR) program contract. The online continuous water monitoring system involves the combination of two gas chromatographs (GC). The first instrument combines a gas/liquid sparger and a GC. The sparger uses an inert gas, helium, to remove and concentrate volatile organic chemicals which are then sequentially analyzed using a GC. The second gas chromatographic instrument involves the analysis of nonvolatile water samples through direct injection of water.

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PREFACE

The work completed herein was conducted by ES Industries, 701 South Route 73, Berlin, NJ 08009-2621 for Arnold Engineering Development Center (AEDC), Air Force Materiel Command (AFMC), Arnold Air Force Base, TN, under Phase II of a Small Business Innovation Research (SBIR) contract number F40600-91-0005, during the period March 1991 to May 1992. The Air Force Project Managers were Ms. Marjorie S. Collier and Capt (CF) Paul Lacasse. The principal investigator was Dr. M. Przybyciel of ES Industries. The reproducibles used in this report were supplied by the authors.

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1.0 INTRODUCTION

The environmental quality of waterways is of ever-growing concern. One area of particular concern is the presence of organic chemical pollutants contained in waterways. A critical step in assessing these concerns involves the accurate measurement of organic pollutant levels contained in water samples. These critical measurements rely on the laboratory analysis of discrete samples. Samples for water analysis can be obtained via single point grab samples or composite samplers. Unfortunately, these sampling strategies provide little more than historical information. In addition, they suffer from possible sample degradation and require labor-intensive sample preparation techniques and analysis procedures. A more desirable sampling strategy would involve the continuous or semicontinuous online analysis of water samples using fully automated equipment. The automated instrument can provide real-time detection of organic pollutant levels and ensure that a directed response can be initiated.

Unfortunately, reliable automated online instruments for the analysis of water samples have not been commercially available. It is the intention of this project to develop and refine an instrument that continuously analyzes water samples and reports the analysis results rapidly to ensure that corrective action can be taken. In addition, it is critical that this instrument deliver results at part per billion (ppb) level for many contaminants.

The instrument developed for this project will be used to sample and analyze water from Rowland Creek. The instrument, through a rapid analysis of samples from Rowland Creek, will provide information to control diversion gates leading to a retention pond. The system will enable Arnold AFB to monitor and keep their discharges in compliance with NPDES permits.

The system developed for the study is based upon gas chromatography technology. This system involves the combination of two gas chromatographs (GC). The first instrument combines a gas/liquid sparger and a gas chromatograph. The sparger uses an inert gas, such as helium, to remove and concentrate volatile organic chemicals which are then sequentially analyzed using a gas chromatograph.

The second gas chromatographic instrument involves the analysis of nonvolatile water samples through direct injection of water. Using a specially designed injection valve, the direct injection system is rugged, but care must be taken to minimize the deposition of solids.

2.0 RESULTS AND DISCUSSION

2.1 SYSTEM FOR VOLATILE HYDROCARBONS

The system developed for the study is based upon gas chromatography technology. The system involves the combination of two gas chromatographs (GC). The first instrument combines a gas/liquid sparger and a gas chromatograph. The sparger uses an inert gas such as helium to remove and concentrate volatile organic chemicals which are then sequentially analyzed using a gas chromatograph. This GC is a Siemens SiCHROMAT 1-4 temperature-programmable instrument and requires a gas sample for analysis (settings for this instrument are contained in Table 1). This gas sample contains the organic chemicals being analyzed and is delivered to the GC via the sparger shown schematically in Figs. 1 and 2.

Figure 1 shows the path of water into the sparger system. This water sample is delivered to the sparger vessel via a gear pump (a description of the gear pump is contained in the Appendix) installed in the system. During the pumping process the sample is heated to a constant temperature (55 °C). After the sample is delivered to the sparging vessel it overflows into a pressurization vessel which leads to a drain.

Figure 2 shows the path of the inert (helium) sparger gas. The helium is delivered precisely to the sparger using a pressure regulator and a flow control valve. A rotometer is placed in the gas flow path to monitor the rate of gas delivery. The helium is introduced into the sparging vessel through a glass frit. This frit disperses the gas into fine bubbles. These bubbles maximize the interaction of the gas and facilitate the removal of organic chemicals from the water column. The helium containing the volatile organic components is then passed through a loop contained in a gas injection valve. This valve is fitted into a heated compartment on top of the GC. The design of the valve allows the gas sample to continually flow, except during the injection period. During the injection period the gas contained in the sample loop is injected onto the GC for analysis. The volume of the injected sample is fixed by the size of the loop contained in gas injection valve; in the case of the AEDC system this volume is 1 mL.

A schematic diagram of the analytical system contained in the gas chromatograph is shown in Fig. 3. This diagram shows the configuration for the internal plumbing contained in the GC oven and is used to follow the sample flow and gas supplies through the GC oven. A flame ionization detector (FID) is used for the detection of pollutants. This analytical system relies on two types of technology for chemical component separation. The first type of separation technology involves open tubular capillary GC columns (Ref. 2). The interior surface walls of these columns are coated with a thin film (1-micron thickness) of polymer. The polymer coating acts to selectively retard the various chemical components that are passed through the capillary. The internal diameter of capillary tubing used to construct the GC columns is narrow (0.32 mm ID). The combination of the thin uniform polymer coating and the narrow diameter of the capillary GC columns enables the retarded components to travel through the column in tight time bands. These narrow bands allow the GC to separate numerous chemicals in a relatively short period of time. Many of these pollutants have similar molecular structure and physical properties .

The second type of separation technology involves the coupling of capillary columns. This technique is called "live" valveless column switching (Ref. 3). The GC contains a device, the T-piece, that acts both as a capillary column and pressure coupler. This device enables the operation of the "live" valveless column switching system. Using this technology, capillary columns of different lengths, polymer film thickness, and polymer composition can be coupled together. This allows for the complete refinement of the separation. In the case of the Arnold AFB system the "live valveless switching" is used to gain a complete separation of the components of interest in the shortest possible time. Using the valveless switch, trichlorofluoromethane, methylene chloride, and 1,1 dichloroethane are separated only on the first column. The other components of interest are switched to the second column for their separation. In addition to column switching, the "T-piece" enables the backflushing of the first column to prevent the unwanted elution of higher boiling chemicals contained in materials such as JP-8.

Table 2 contains a list of the volatile organic chemicals determined by the sparger system and GC. This table also contains the detection limit (DL) for each of the chemicals analyzed by the sparger system. Figure 4 shows a chromatogram of the Table 2 components separated. Each component shown in the chromatogram is at the 25-ppb level.

This chromatogram represents the "high resolution" scan for the water analyzer system. The total analysis time for the "high resolution" scan is 25 min, including the cooldown of the GC oven. Figure 5 shows a chromatogram of a 10-ppb standards analyzed in the "high resolution" mode, and graphically displays the sensitivity of the system. The conditions for the GC oven and valve timing for the "high resolution" scan are contained in Table 3. Interferences from other chemicals, especially those contained in JP-4, will appear in the sparger analysis. This is particularly true at higher JP-4 levels; however, high levels of JP-4 will appear on direct injection GC, providing a flag for the sparger analysis. Chromatograms showing JP-4 interference on the sparger system were not produced for this study.

Figure 6 shows a high-speed chromatogram ("low resolution" scan) for the components contained in Table 2. Unfortunately, this chromatogram does not represent a separation of all the Table 2 components; however, this chromatogram is completed in 9.5 min. The "low resolution" scan is a viable way of reducing the analysis time for the system. The conditions for this analysis are contained in Table 4. The ultimate viability of the low-resolution scan will be determined when the instrument is installed and actually analyzes water from Rowland Ditch. This high-speed scan has a low resistance to interferences and may trigger a high number of false alarms. Fortunately, the instrument may be switched between low- and high-resolution modes rapidly and easily through the manual input of computer software commands.

Figures 7 - 9 are curves used to check the linearity for each component determined using the "high resolution" scan. These curves vary in concentration from 25 - 100 ppb and display the high degree of accuracy possible using the sparger and GC technology. Unfortunately, a linearity check for trichlorofluoromethane was not performed because an accurate standard of this volatile chemical could not be made at our facility.

2.2 SYSTEM FOR NONVOLATILE COMPONENTS

The second gas chromatographic instrument involves the analysis of nonvolatile water samples through direct injection of water. Using a specially designed injection valve, the direct injection system is rugged, but care must be taken to minimize the deposition of solids.

A Siemens P-101 process type GC is employed in the AEDC system for the analysis of nonvolatile components. A list of these components is contained in Table 5. The nonvolatiles GC relies upon the analysis of water samples using a direct injection technique. Water is continually passed through a liquid injection valve and, at a preset time, the valve is triggered, causing the water to be vaporized and swept onto a capillary GC column for analysis. Figure 10 shows a diagram of the internal plumbing for the nonvolatile system. This diagram shows the configuration for the internal plumbing contained in the GC oven and is used to follow the sample flow and gas supplies through the GC oven. Table 6 contains the operating conditions for this system.

The nonvolatile GC will require extensive maintenance and materials because dissolved salts in the water will deposit/build up in the instrument, causing possible failure of the system. However, the direct injection technology is a viable procedure for the ppm analysis of nonvolatile components such as JP-8. Glass-wool can be placed in the vaporization chamber to protect the system from high salt levels; however, because of the design of the liquid injection valve, extreme care must be taken when installing the glass-wool. Incorrect installation of glass-wool may damage the sample stem of the liquid injection valve.

Figure 11 shows a chromatogram of a blank water sample, and Fig. 12 shows a chromatogram for a 25-ppm standard of ethylene glycol. Figures 13 and 14 show chromatograms of JP-4 and JP-8, respectively. Each material is at the 2-ppm level. The water standards of these two materials contained undissolved components, even at the 1-ppm level. The undissolved fraction of the JP-4 and JP-8 appeared on the water's surface, and samples taken for analysis were below the surface. However, because of the undissolved fraction, a 1-ppm standard, when analyzed by the GC, probably represented a sample of actual lower concentration.

A linearity check for ethylene glycol is shown in Fig. 15. This curve is only linear over a short range (25 - 100 ppm) because of degradation of ethylene glycol in the chromatograph. Linearity checks for JP-4 and JP-8 were not performed, and information on the levels of these components should be obtained from the visual inspection of chromatograms.

2.3 ALARMS

The water analyzer system contains the provisions for alarms. These alarms can be triggered from either the levels of organics contained in a sample or the failure of the instrument. These alarms will output a dry contact closure. The alarms levels should be set at completion of the installation at AEDC.

3.0 SBIR START UP

The following is a list of observations made during the installation and start-up procedures for the Siemens P101 Process Gas Chromatograph and SiCHROMAT 1-4 at AEDC.

1. A complete written checklist detailing requirements of the installation should be distributed to the appropriate personnel involved in the site preparation. This list should include not only the electrical, sample, and

gas requirements, but also extend to the training and personnel to be involved with the installation and operation of the instrument(s). This checklist should be completed prior to the manufacturer's personnel arriving on site.

2. Most instruments of this nature are used to identify specific contaminants as opposed to fuels. That is to say, a fuel such as JP-4 would be injected into the instrument and analyzed for its various chemical components. With the P101, water is injected to identify four different components by virtue of their individual "fingerprints," based on what will mix or dissolve into the water.

3. Although the manufacturer provides detailed written materials on each analyzer, a summary description of their operation (Appendix A) should be created for each custom installation. The advantage of providing this material is a discussion of the specific application and a "quick" reference for the customer.

4. A daily, weekly, and/or monthly maintenance checklist should be provided to the customer for each installation (Appendix B). This list would give the customer the benefit of keeping the instrument(s) in top operating condition based on our experience with the instrument(s).

4.0 CONCLUSIONS

An automatic water analyzer system for determination of organic pollutants has been developed. The system can analyze volatile organic components at ppb levels with a minimum of operational maintenance. This analysis can be completed in less than 10 min; however, the information obtained in this mode is minimal. Using a 25-min analysis sequence, high-resolution information can be obtained for 17 individual chemicals.

The system also contains a GC for the analysis of nonvolatile components such as JP-4 and JP-8 using direct water injections. This system, which is not as rugged as the volatiles system, is able to analyze for chemicals that are difficult to detect using commercially available techniques.

The water analyzer delivered to AEDC is an integration of the two gas chromatographs. The system will transmit alarms at predetermined component threshold levels and will become an important part of the pollution control technology at the AEDC. Hopefully, by using continuous water analyzing technology the AEDC will be able to rapidly discover and eliminate pollution emission sources.

5.0 RECOMMENDATIONS

It is important to the start-up and the ongoing operation of the water analyzer that an "expert" trained by ES Industries be available at the AEDC. In addition, the plant operators should be trained and have a basic understanding of the operation of the water analyzer.

REFERENCES

1. Hoemer, G., Kuehn, W., and Leonhardt, D. "Vom Wasser." 59 Band 1982, pp. 115 - 128.

2. Jennings, W. *Analytical Gas Chromatography*. Academic Press, 1987.

3. Muller, F. and Oreans, M. Chromatographie, Vol. 10, No. 8 (1977), pp. 767 - 779.

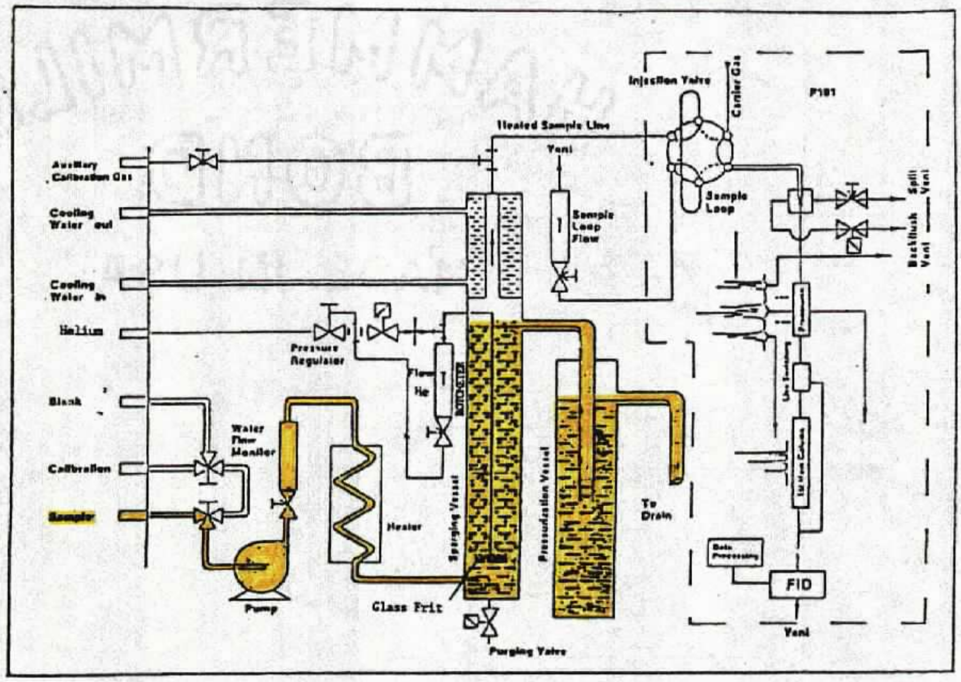


Figure 1. Sample flow path for AEDC water monitoring system.

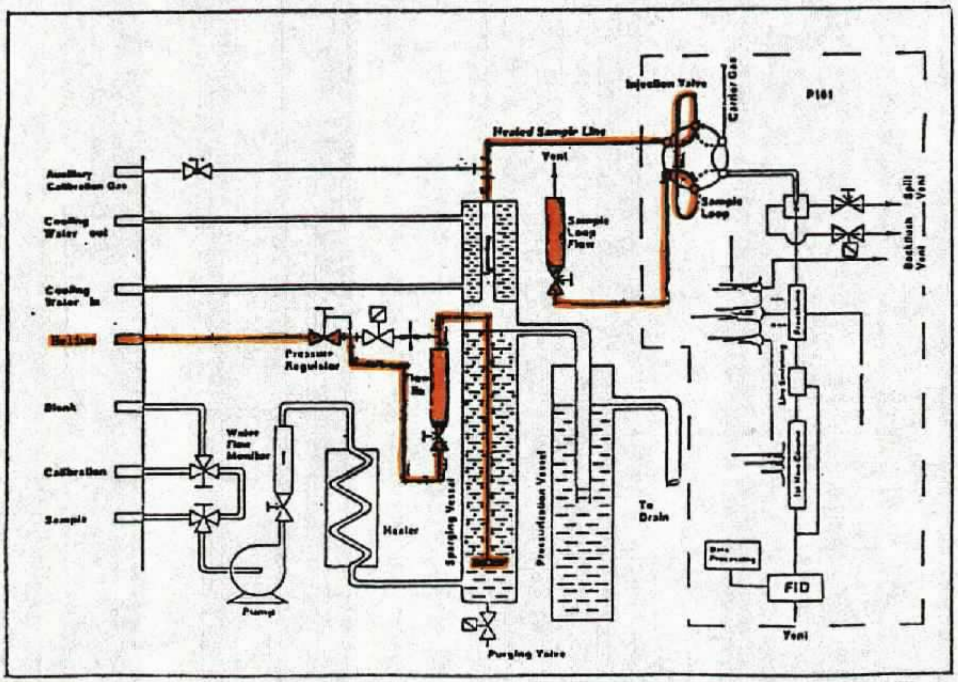


Figure 2. Sparging flow path for AEDC water monitoring system.

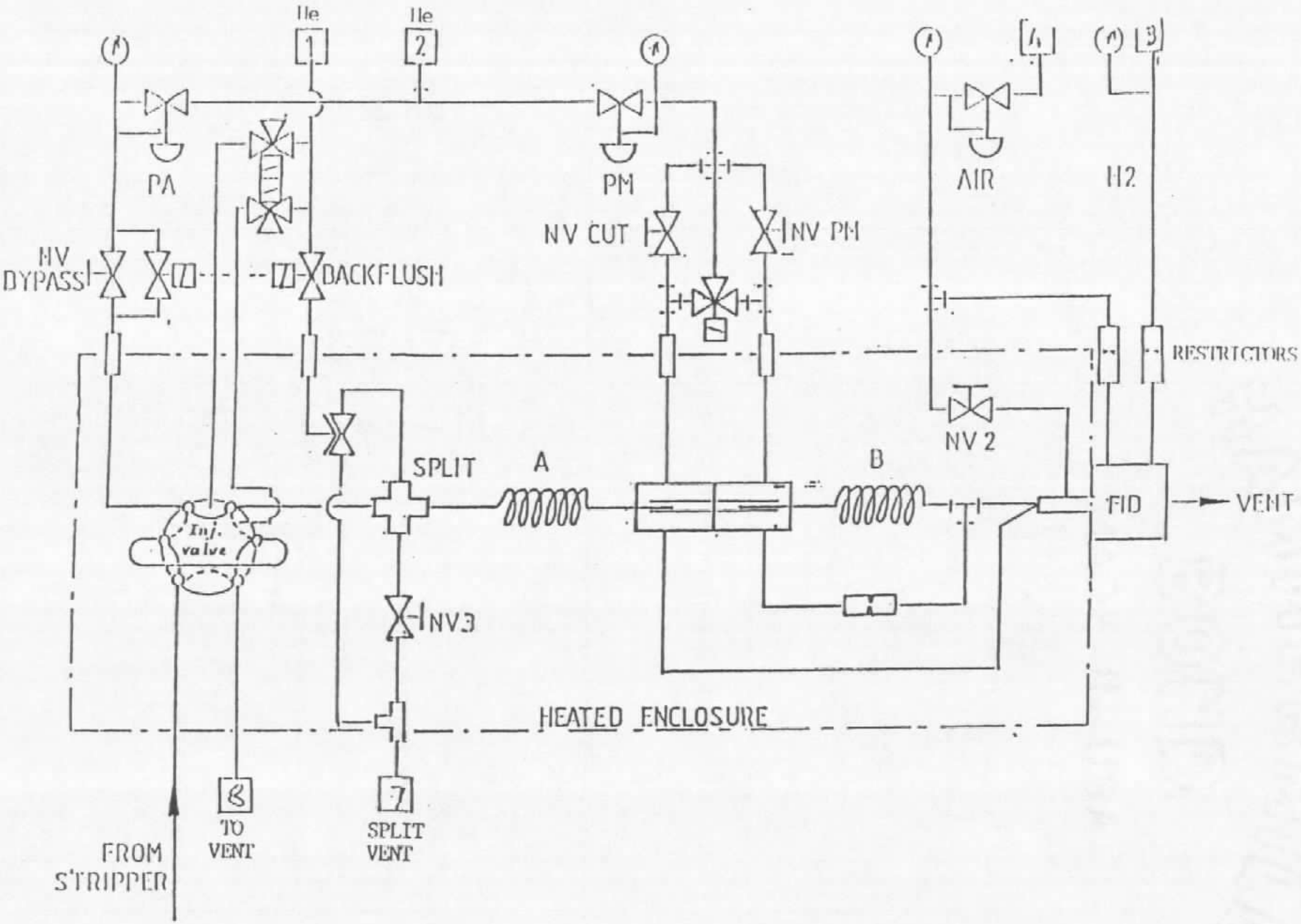
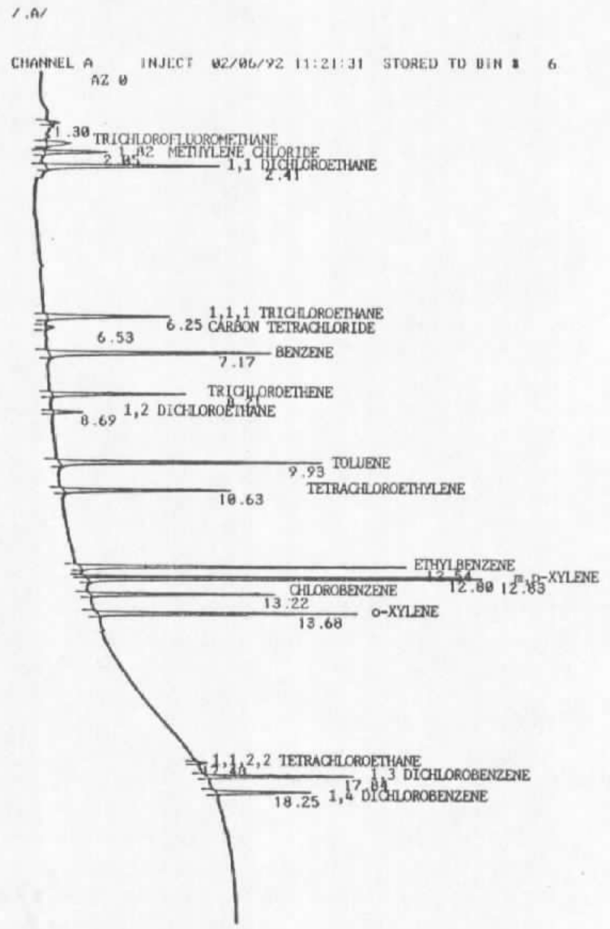


Figure 3. Internal tubing for AEDC water monitoring system.



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ANALYST: JFB

NAME                PPB        RT       AREA BC       RF

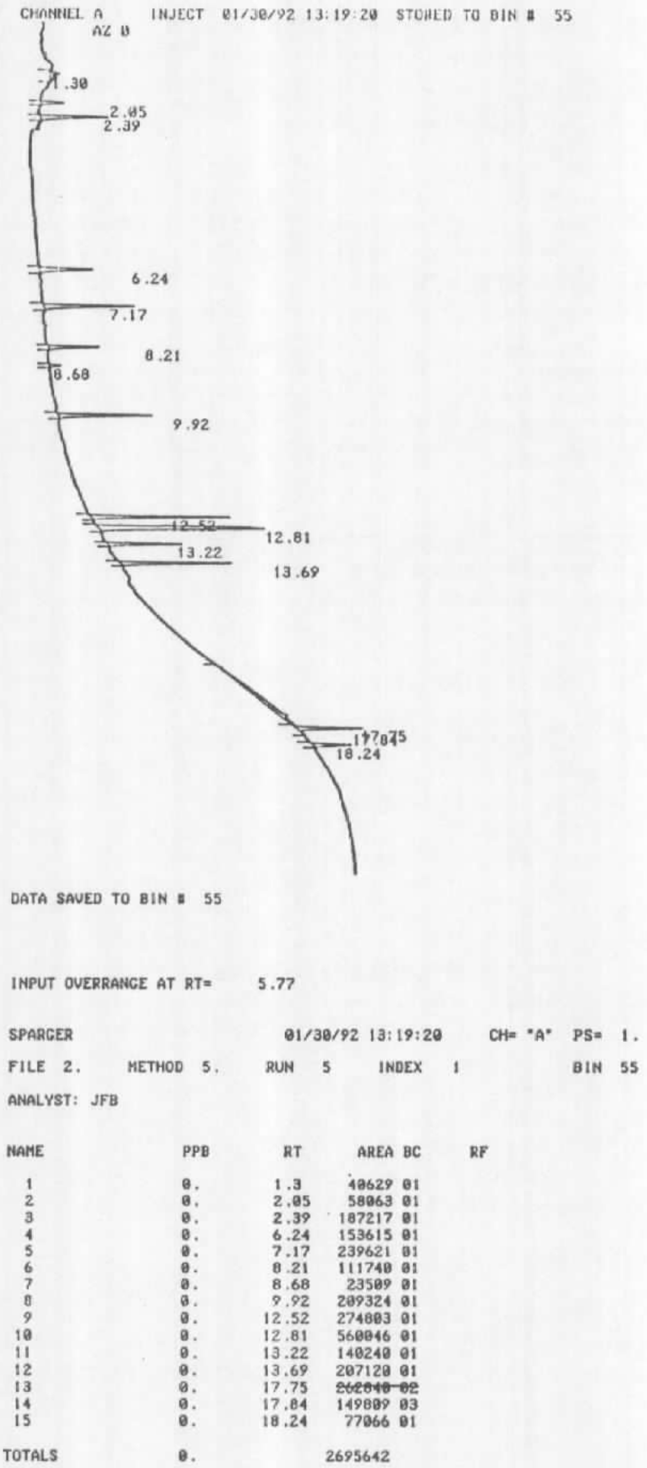
  1                 0.         1.3      20625 01
  2                 0.         1.82     94826 01
  3                 0.         2.05    166438 01
  4                 0.         2.41    480060 01



  5                 0.         6.25    358965 01
  6                 0.         6.53     21250 01
  7                 0.         7.17    593017 01
  8                 0.         8.21    304865 01
  9                 0.         8.69     61641 01
 10                 0.         9.93    600390 01
 11                 0.        10.63    371416 01
 12                 0.        12.54    665789 01
 13                 0.        12.8     578063 02
 14                 0.        12.83    772250 03
 15                 0.        13.22    361850 01
 16                 0.        13.68    521407 01
 17                 0.        17.48     16995 01
 18                 0.        17.84    302705 01
 19                 0.        18.25    191096 01

TOTALS              0.                6484440
```

Figure 4. Chromatogram of a 25-ppb volatiles standard.



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        AZ 0

DATA SAVED TO BIN #  55


INPUT OVERRANGE AT RT=      5.77

SPARGER                     01/30/92 13:19:20      CH= "A"  PS=  1.

FILE  2.     METHOD  5.     RUN   5      INDEX   1               BIN  55

ANALYST:  JFB

NAME                PPB        RT        AREA BC        RF

  1                 0.         1.3      40629 01
  2                 0.         2.05     58063 01
  3                 0.         2.39    187217 01
  4                 0.         6.24    153615 01
  5                 0.         7.17    239621 01
  6                 0.         8.21    111740 01
  7                 0.         8.68     23509 01
  8                 0.         9.92    209324 01
  9                 0.        12.52    274803 01
 10                 0.        12.81    560046 01
 11                 0.        13.22    140240 01
 12                 0.        13.69    207120 01
 13                 0.        17.75    ~~262040 02~~
 14                 0.        17.84    149809 03
 15                 0.        18.24     77066 01

TOTALS              0.               2695642
```

001

Figure 5. Chromatogram of a 10-ppb volatiles standard.

```
CHANNEL A       INJECT  01/29/92 10:29:42  STORED TO BIN #  21
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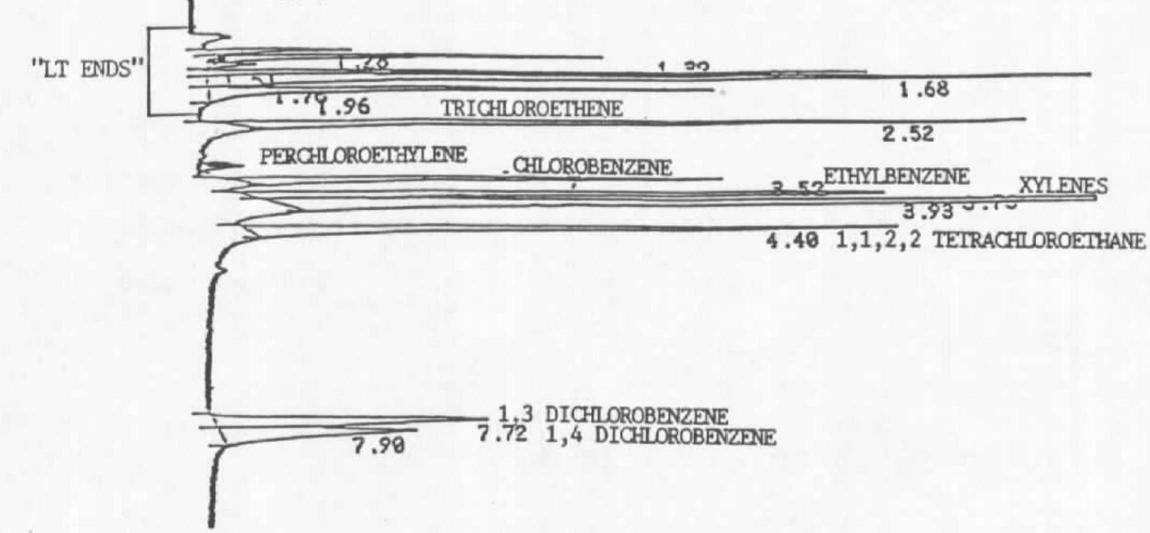

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DATA SAVED TO BIN #  21


SPARGER                         01/29/92 10:29:42      CH= "A"  PS=  1.

FILE  3.      METHOD  5.     RUN  3      INDEX  1               BIN  21

ANALYST:  JFB

NAME                PPB       RT       AREA BC      RF

  1                 0.       1.28     94261 01        "LT ENDS" = TRICHLOROFLUOROMETHANE
  2                 0.       1.39    278163 01                    METHYLENE CHLORIDE
  3                 0.       1.51     29169 02                    1,1 DICHLOROETHANE
  4                 0.       1.68    483534 02                    1,1,1 TRICHLOROETHANE
  5                 0.       1.76    975784 02                    CARBON TETRACHLORIDE
  6                 0.       1.96    445588 03                    BENZENE
  7                 0.       2.52    646320 01                    1,2 DICHLOROETHANE
  8                 0.       3.52    438084 01                    TOLUENE
  9                 0.       3.78    812248 02
 10                 0.       3.93   1817324 03
 11                 0.       4.4     734809 01



 12                 0.       7.72    465098 02
 13                 0.       7.9     389044 03
```

Figure 6. High-speed volatiles chromatogram - 25 ppb.

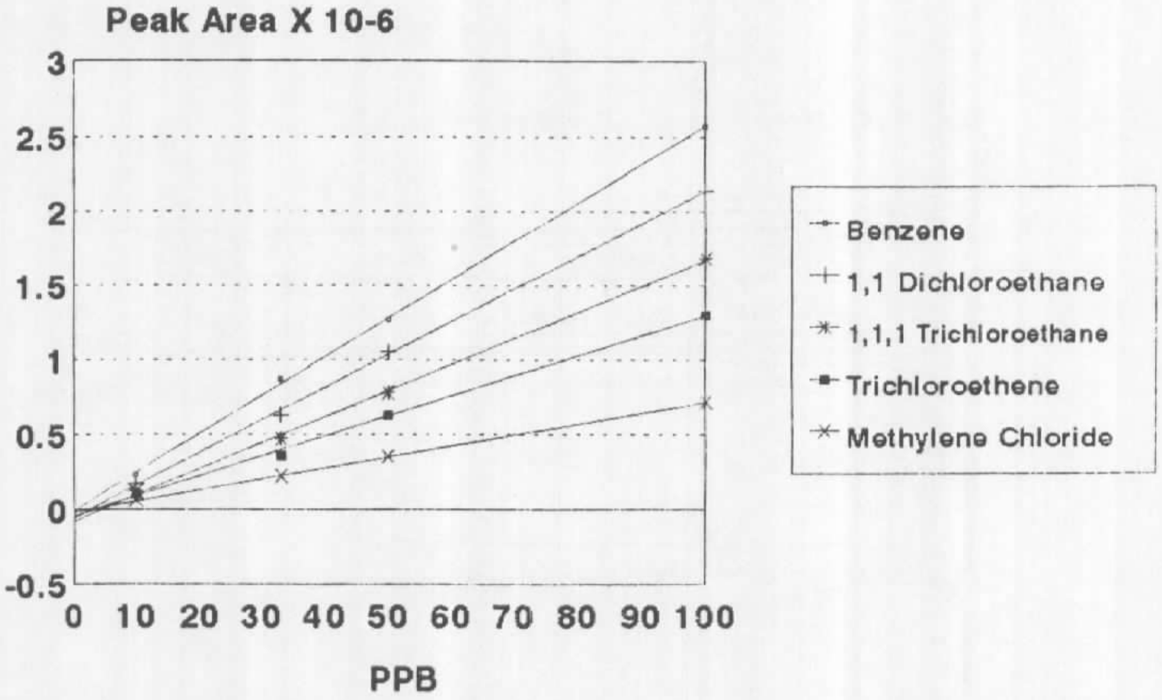

Figure 7. Linearity check for benzene, 1,1 dichloroethane, 1,1,1 trichloroethane, trichloroethylene, and methylene chloride.

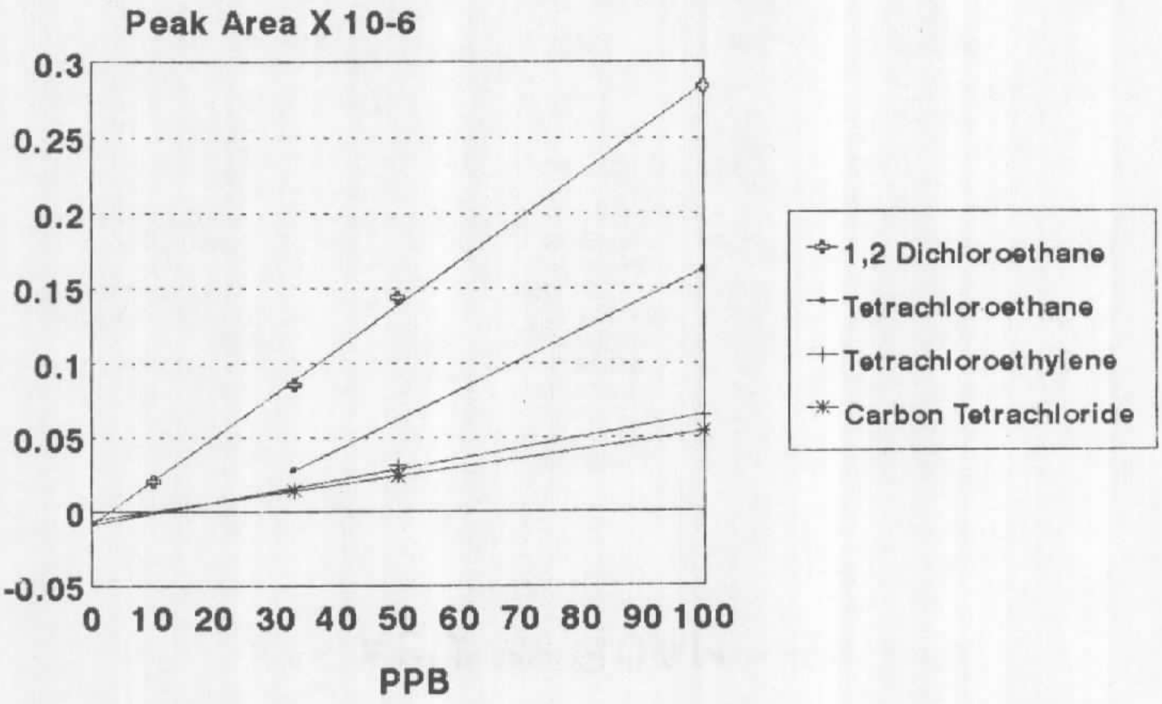

Figure 8. Linearity check for 1,2 dichloroethane, tetrachloroethane, tetrachloroethylene, and carbon tetrachloride.

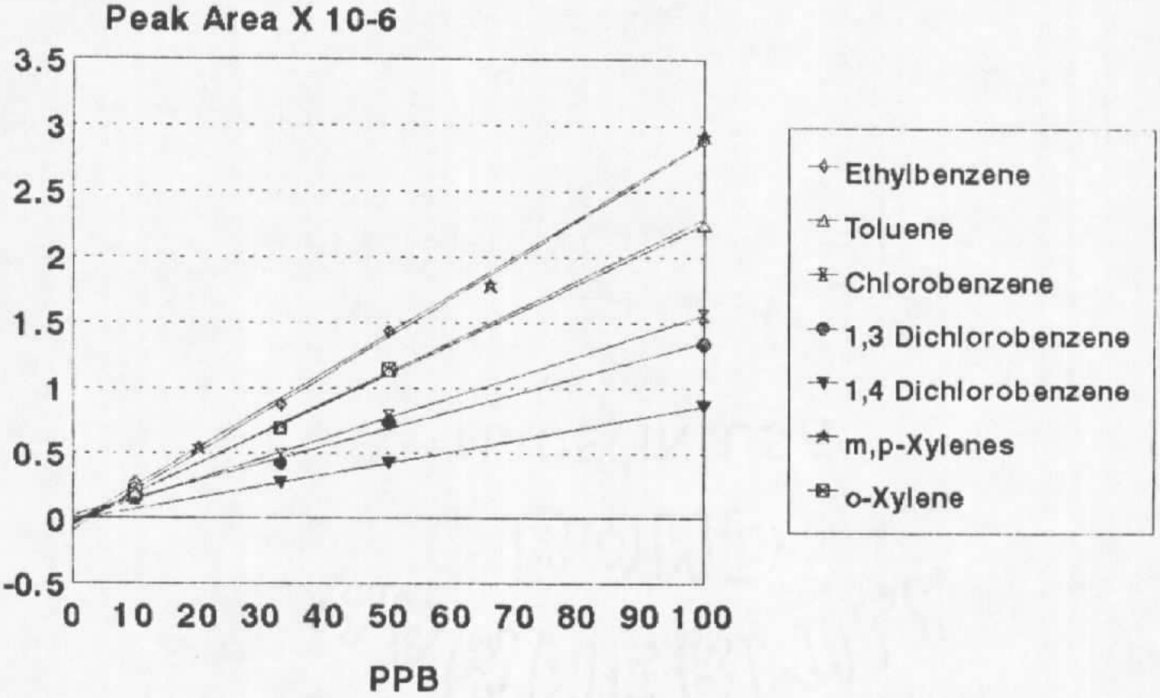

Figure 9. Linearity check for ethylbenzene, toluene, chlorobenzene, 1,3 dichlorobenzene, and 1,4 dichlorobenzene.

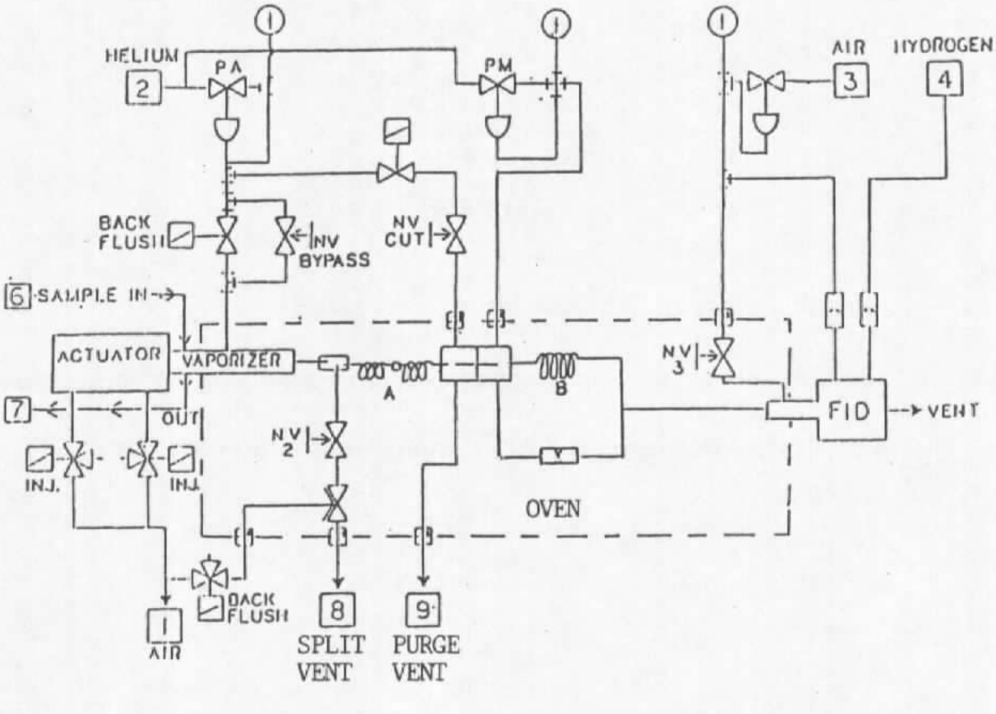

Figure 10. Diagram of internal tubing of gas analyzer to be used for nonspargable components.

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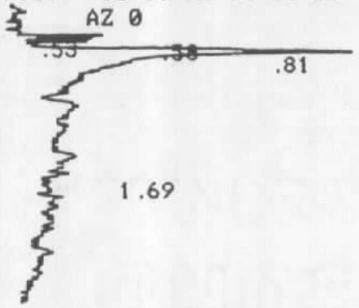

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FILE  1.     METHOD  5.     RUN  42      INDEX   1               BIN 106

ANALYST: JFB


NAME                 PPB         RT       AREA BC       RF

  1                  0.          0.53     47007 02
  2                  0.          0.58     60287 03
  3                  0.          0.81    696497 01
  4                  0.          1.69    606718 01

TOTALS               0.                 1410509



WARNING - MEMORY AT  4. K - UNPROTECTED CHROMATOGRAMS WILL BE REPLACED
```

Figure 11. Chromatogram from direct injection instrument - blank.

```
CHANNEL B       INJECT  02/03/92 09:29:49  STORED TO BIN #    2
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```
DATA SAVED TO BIN #   2


DIRECT INJECT                    02/03/92 09:29:49     CH= "B"  PS=  1.

FILE  1.     METHOD  5.     RUN  65     INDEX   1               BIN   2

ANALYST:  JFB

NAME                PPB        RT       AREA BC      RF

  1                 0.         0.59     53152 01
  2                 0.         0.84    699458 01
  3                 0.         1.07    141668 02
  4                 0.         1.18    498606 03

TOTALS              0.                1392884

WARNING - MEMORY AT  0. K - UNPROTECTED CHROMATOGRAMS WILL BE REPLACED
```

Figure 12. Chromatogram from direct injection instrument - ethylene glycol.

```
CHANNEL B      INJECT  02/01/92 12:09:57  STORED TO BIN # 112
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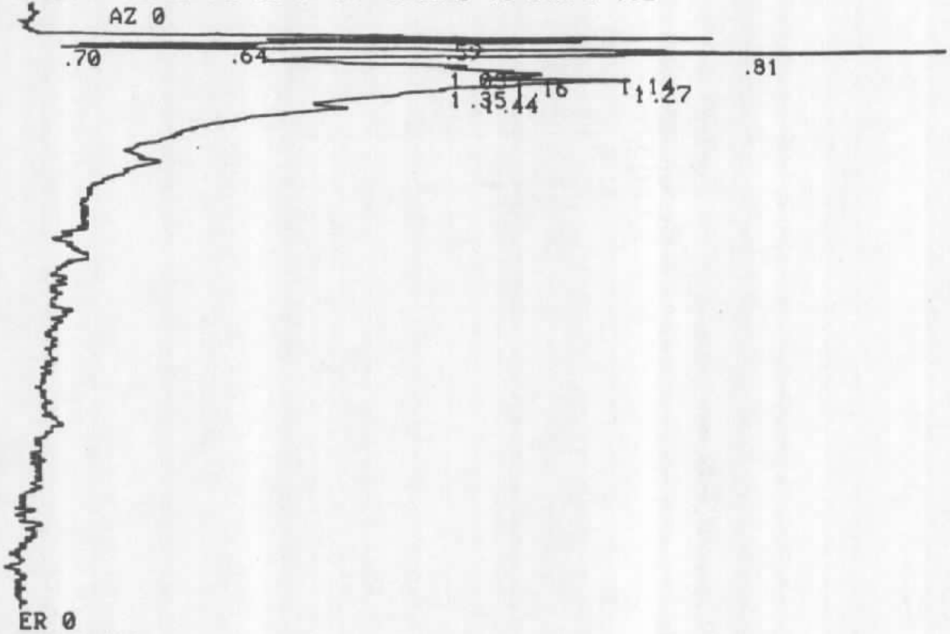

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DATA SAVED TO BIN # 112


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FILE  1.    METHOD  5.    RUN  47    INDEX   1              BIN 112

ANALYST: JFB


NAME                 PPB        RT      AREA BC      RF

  1                  0.        0.59    994458 02
  2                  0.        0.64    437748 02
  3                  0.        0.7     109931 02
  4                  0.        0.81   2672338 02
  5                  0.        1.03   1091275 02
  6                  0.        1.14    786163 02
  7                  0.        1.16   1028351 02
  8                  0.        1.27   1348640 02
  9                  0.        1.35    764765 02
 10                  0.        1.44   4111981 03




TOTALS               0.               13345650

WARNING - MEMORY AT  4. K - UNPROTECTED CHROMATOGRAMS WILL BE REPLACED
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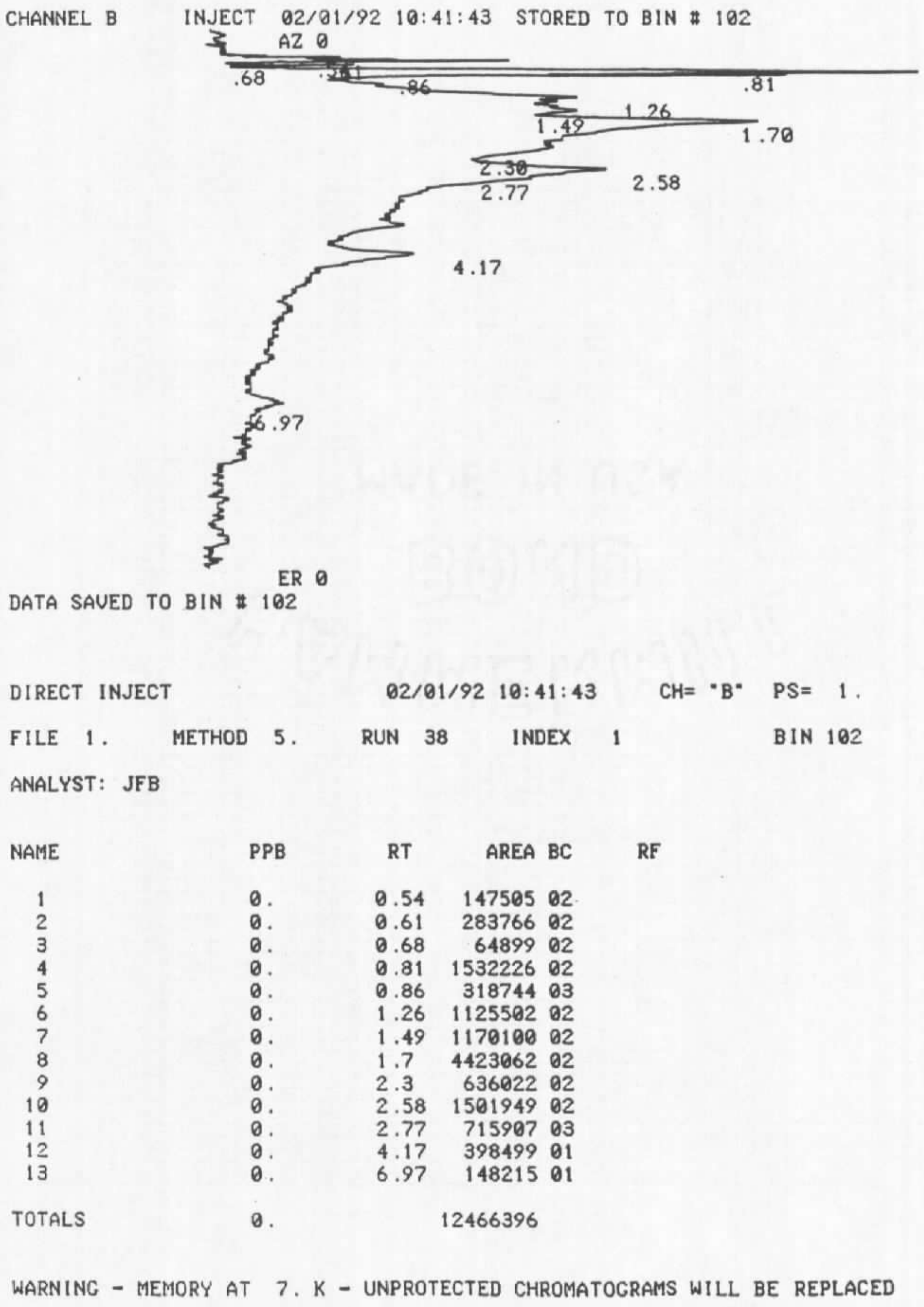
Figure 13. Chromatogram from direct injection instrument - JP-4.



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DIRECT INJECT                  02/01/92 10:41:43     CH= "B"  PS=  1.

FILE  1.      METHOD  5.      RUN  38      INDEX   1             BIN 102

ANALYST:  JFB


NAME                PPB        RT       AREA BC       RF

  1                 0.        0.54    147505 02
  2                 0.        0.61    283766 02
  3                 0.        0.68     64899 02
  4                 0.        0.81   1532226 02
  5                 0.        0.86    318744 03
  6                 0.        1.26   1125502 02
  7                 0.        1.49   1170100 02
  8                 0.        1.7    4423062 02
  9                 0.        2.3     636022 02
 10                 0.        2.58   1501949 02
 11                 0.        2.77    715907 03
 12                 0.        4.17    398499 01
 13                 0.        6.97    148215 01

TOTALS              0.              12466396

WARNING - MEMORY AT  7. K - UNPROTECTED CHROMATOGRAMS WILL BE REPLACED
```

Figure 14. Chromatogram from direct injection instrument - JP-8.

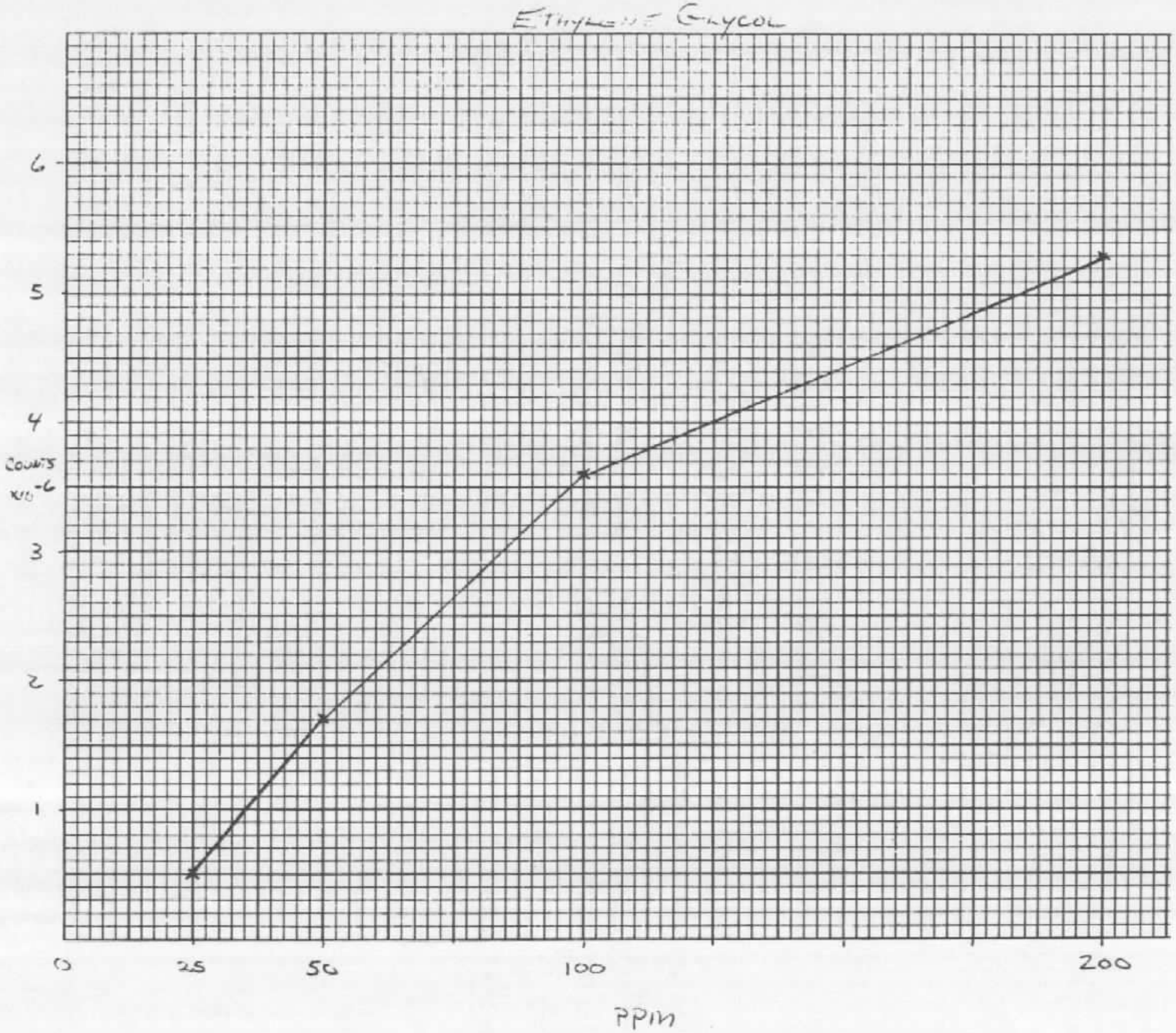


Figure 15. Linearity check for ethylene glycol.

Table 1. Conditions and Settings for Sparger GC

Application Data: SBIR SiCHROMAT 1-4

Gas Supply

Control Medium: AIR
Pressure: 4.0 bar

Carrier gas :
PA-Pressure: 1.52 bar
PM-Pressure: 0.91 bar

Combustion Air:
Pressure: 2.00 bar Consumption: 500 ml/min

Hydrogen
Pressure: 1.41 bar Consumption: 25 ml/min

Admixture Type: AIR
Consumption: 20 ml/min

Injection Type: GIV Volume: 1.0 ml

Columns

	Material	Length (m)	I.D. (mm)	film thickness (micron)
A.	OV101	30	0.32	1
B.	OV225	30	0.32	1

Table 2. Components for Volatile Analysis

CHEMICAL	LIMITS OF DETECTION* (ppb)
Trichlorofluoromethane	15
Methylene Chloride	5
1,1 Dichloroethane	2
1,1,1 Trichloroethane	3
Carbon Tetrachloride	20
Benzene	2
Trichloroethene	3
1,2 Dichloroethane	10
Toluene	1
Tetrachloroethylene	2
Ethylbenzene	1
m-Xylene	1
p-Xylene	1
Chlorobenzene	2
o-Xylene	1
1,1,2,2 Tetrachloroethane	20
1,3 Dichlorobenzene	2
1,4 Dichlorobenzene	3

* = signal to noise of three

Table 3. Conditions for High-Resolution Scan

```
SiCHROMAT               Method 1
========================================================================
OVEN          Initial temperature       60   C
PROGRAM         "     time               4   min.
              Rate                       8   C/min.
              Final temperature        160   C
                "   time                 5   min.
------------------------------------------------------------------------
INJECTOR
1 Gas Sampling Valve                   160  C

------------------------------------------------------------------------
DETECTOR
A   FID                                250   C
Range                                    0
Attenuation                              6
Polarity                               POS
Damping                                  2
Baseline Offset                          0   %

------------------------------------------------------------------------
VALVE
Inj.  Back. Cut   4     5     6     7     8     9     10    11    12
OFF    ON   ON   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF

------------------------------------------------------------------------
TIME EVENTS TABLE
1     0.010         Back                OFF
2     0.010         Cut                 ON
3     0.050         Inject              ON
4     0.300         Inject              OFF
5     3.100         Cut                 OFF
6    14.000         Back                ON
7    21.500         Reset
```

Table 4. Conditions for Low-Resolution Scan

```
SICHROMAT1-4         ACTUAL METHOD              13.03.00  02:23
================================================================
OVEN                                    105   C
----------------------------------------------------------------
INJECTOR
1   Gas Sampl. Valve                    120   C


----------------------------------------------------------------
OPTION
----------------------------------------------------------------
DETECTOR
A   FID                                 200   C
Range                    0
Attenuation              6
Polarity                 POS
Damping                  2
Baseline Offset          0      %

----------------------------------------------------------------
VALVE
Inj. Back Cut   4    5    6      7    8    9    10   11   12
OFF  OFF  ON   OFF  OFF  OFF    OFF  OFF  OFF  OFF  OFF  OFF

----------------------------------------------------------------
TIME EVENTS TABLE
1    .01          Back                    OFF
2    .01          Cut                     ON
3    .05          Inject                  ON
4    .300         Inject                  OFF
5    10.00        Reset
----------------------------------------------------------------
```

Table 5. Components for Nonvolatile GC

COMPONENT	LIMIT OF DETECTION (ppm)
Ethylene Glycol	10
JP-4	1
JP-8	1

Table 6. Conditions for Nonvolatile GC

```
        Application Data: SBIR-Direct Injection


Gas Supply

Control Medium: Air
   Pressure:     4.0  bar  Consumption:   20  ml/min

Carrier gas:    Helium
   PA-Pressure: 0.60 bar
   PM-Pressure: 0.30 bar

Combustion Air:
   Pressure:    2.00 bar  Consumption:  400  ml/min

Hydrogen
   Pressure:    2.00 bar  Consumption:   25  ml/min

Admixture  Type: Air
   Pressure:    2.00 bar  Consumption:   20  ml/min

Oven purge  Type: None


Analyzer Parameters:

Oven Temp.      140  Deg. C  Actual value: 6.80 V  Set value: 7.00 V
Detector Temp. 200  Deg. C  Actual value:10.12 V  Set value:10.00 V
Injector Temp. 350  Deg. C                        Set value: 0.00 V
Detector type: FID
Basic current:(uncompensated) 0.032(*131.4 pA)
or
Bridge current:       mA
Injection Type: LIV         Volume: 2.4 ul


Columns

        Material                 Length  I.D.   film thickness
                                  (m)    (mm)   (micron)
A. Methyl-5% Phenyl Silicone       5     0.25     0.25
B. Methyl-5% Phenyl Silicone      10     0.25     0.25
```

APPENDIX A
OPERATION AND CALIBRATION OF THE SIEMENS WATER ANALYZER

SBIR
OPERATION AND CALIBRATION OF THE SIEMENS P101 PROCESS GAS CHROMATOGRAPH

OPERATION

The P101 is electrically and electronically controlled through the front panel of the instrument. It is protected electrically through a main breaker panel located at the back of the rack in a locked box. All breakers are clearly marked (see drawing # B29000016).

Upon initial startup please insure that breaker "CB3" is in the up (on) position in order to supply power to the P101. In the front of the analyzer's lower left corner is a green button switch. After supplying all gases to the analyzer (helium, air, and hydrogen) at the pressures indicated in the documentation for approximately five (5) minutes press the green button switch to turn the instrument on.

Using a dental mirror or other similar object check to insure the detector has ignited. Do this by holding the mirror by the chimney of the detector and look for condensation. If the gas did not ignite enter the following commands: <Op. mode><3><1><2nd><Alloc.>; listen real close for five clicks coming from the top of the instrument (this would be the ignitor sending a spark to the detector). The format <> means to press the key indicated inside the brackets. Check again for condensation. (If the detector still will not ignite, try reducing the amount of air to the detector by about 1/2 bar.)

Once the detector has been ignited place or leave the instrument in operating mode 31 (as described above) for twelve to twenty four hours to equilibrate. If it has only been shut down for a few hours let it equilibrate for three or four hours, or until the baseline is steady.

When the instrument has equilibrated you may either begin injecting a sample or perform a calibration.

CALIBRATION

It is recommended that a standard be made for each contaminant of interest (ethylene glycol, JP-4, JP-8, or "heavy oil"). Therefore this instrument will require four separate standards each in it's own one gallon glass container. The standard should be fresh (less than four hours old) and kept sealed and cool until ready for use. Just prior to using it should be well mixed in order to simulate the sample that would normally be introduced to the instrument.

On the left side of the rack (as you face the rack), towards the back, are two 1/8 inch plastic tubes. The one that is on the fourth fitting up from the bottom is marked "Standard P101" (refer to drawing # B15000012); it and the plastic tube coming from the liquid injection valve (going to the drain) should be placed into the bottle containing the standard; turn the valve marked "Sample/Standard" to "standard". This will give you a closed system and recirculate the standard.

CALIBRATION P101 (cont.)

When you are ready to inject the standard turn on breaker "CB4" located in the electrical panel box (refer to drawing # B2900016). This will start pump #3 (refer to drawing # D1200013) and supply sample to the liquid injection valve on the P101. Adjust the flow, using the flow meter (Sample Flow 1), to approximately four liters per hour. Let the standard circulate for a few minutes before beginning the analysis. Start the analysis by entering the following command: <Op mode><5><0> <Time>. At this point you should have heard several clicks (the valves) and the clock on the face of the control panel should be counting.

Allow the instrument to do several analyses. When the analyses appear to be consistent enter the following command: <Op mode><5><1> <Time>. Let the analysis continue until you see all zeros in the clock, indicating that the analysis is complete. Now enter <Op mode><6><0><2nd> <Comp>. In the window you will see the number 1, a decimal followed by another number. The number 1 indicates component number 1, which would be ethylene glycol. The number following would be the value calculated by the instrument for the amount of ethylene glycol in the standard. Assuming you are calibrating for ethylene glycol: if this number is correct, then do not change it and consider the instrument calibrated for that component; if this number is incorrect, enter the correct amount and press the <Off> key. (eg. If the instrument gave you an amount of 56.391 (ppb) and you made the standard to 50.250 ppb, press the following keys:<5><0><.><2><5><0><Off>. At this point the instrument will accept the new value and calculate a new factor.

On the other hand, if you were calibrating for JP-8, which is component number 3, you would do the following to read it's value after going to operation mode 60: <Tab><Tab>. Now you should see the number 3 in the window and some value. As before, if the value is correct consider the instrument calibrated. If it is incorrect, enter the correct value as described above.

If you had to enter a corrected value, enter the following commands: <Op mode><5><0>. Perform at least one more analysis to verify the instrument is analyzing correctly. If it isn't, repeat the above steps until it does.

If you did not have to enter new values, or you are satisfied the system is calibrated, turn off the pump "CB4", return the plastic tube from the sample valve to the drain, switch the "Sample/Standard" valve to "sample" and turn on the pump again. After one or two injections the system should be back to normal.

INJECTION

To operate the P101 g.c. in a normal cyclical mode it is imperative that the gases and temperatures (oven, detector and injector) to the instrument be set correctly and in accordance with the latest documentation, and the instrument be calibrated for the components as described above.

INJECTION P101 (cont.)

After setting the gas pressures correctly and turning on the instrument, a standard volt meter is used to insure the temperatures are adjusted correctly. Facing the instrument, to the left is a door, behind the door are several controls and receptacles for measuring temperature. Approximately in the middle of the panel (behind the door) you will see six (6) receptacles for banana plugs, next to which are two (2) potentiometers. Set the volt meter to VDC and place the "common" lead from the volt meter into the top right receptacle; place the "positive" lead from the volt meter into the top middle receptacle. The volt meter should give a reading of 8.0 VDC, or 160°C for the detector (each volt is equal to 20°C). If it isn't correct, adjust it using the potentiometer to the right. Repeat this for the oven using the receptacles just below in the same manner. This time you should get a reading of 6.0 VDC, or 120°C. Pull the instrument out from the rack. On top, towards the left is a computer board with two receptacles marked + and -. Place the leads from the volt meter in the respective receptacles and get a reading of -0.006 VDC. This reading may be adjusted using a small screwdriver on the potentiometer on this card.

Unless there has been a major change to the operating parameters of the instrument, once the above settings are made, they should never have to be adjusted. But it doesn't do any harm to periodically check them (once a year), or if there are problems with the instrument.

If any changes had to be made to the temperatures you **MUST** give the instrument a chance to equilibrate. If they were minor changes, say 3/10 of a volt or less, an hour will be more than sufficient, however anything greater than that and several hours or over night would be recommended.

Assuming all temperatures and pressures are correct, the instrument has had sufficient time to equilibrate, and it is calibrated for all components of interest, make sure there is sample flowing to the sample valve by checking that the "Sample/Standard" valve is in the "Sample" position, pump #3 is on ("CB4") and the flow meter #1 on the front is adjusted to 4 Liters per hour. Now enter the following command: <Op mode><3><1><Time>. If necessary reset the time to 00.000 by entering the following command: <0><Tab>. When the time is set to 00.000 enter the following command: <Op mode><5><0><Time>.

SBIR
OPERATION AND CALIBRATION OF THE SIEMENS SiCHROMAT 1-4

OPERATION

The SiCHROMAT 1-4 is electrically and electronically controlled at the front of the instrument. It is protected electrically through a main breaker panel located at the back of the rack in a locked box. All breakers are clearly marked [see drawing # B2500020].

The analyzer consists of two major components, the gas chromatograph (g.c.) and it's related control cabinet. The main power supply switch is a green button located in the upper right corner of the g.c., next to which is a white switch used to turn the oven fan on and off. The main power switch also controls the power tc the control cabinet.

Before supplying power to the instrument, it is imperative that you provide the gases (helium, hydrogen, and air) to the analyzer at the correct pressures as described in the most current documentation provided.

Main power is provided through the electrical panel located in the back of the rack using breaker "CB5" (refer to drawing # B2500020); place both switches in the on (up) position. Return to the front of the g.c. and press the green button switch. At the same time turn on the oven fan by pressing the white button switch.

The control cabinet contains a small CRT; after power has been initiated to the analyzer and the computer has performed it's self-check a logo will appear on the screen. The computer will have already been pre-programmed with two methods, however it will be necessary for you to tell it which of the two programs you wish to operate.

At the top of the controller, to the right of the CRT is a button labeled "CONFIGURATION", press this key. The screen will now display a message; at the bottom of the screen you will see the definition of four "soft" keys (located under the screen), enter the one for "no change".

Now press the key labeled "METHOD" to display the method directory. In the upper right corner of the screen you will see the "active method" (most likely # 1), below you will see all the methods available.

Method 1 is the short (10 minute) method developed for the "normal" operation of this instrument, while method 2 is a longer (21.5 minute) temperature controlled program designed to be used when you want more definitive answers to a contamination problem.

To select between the two programs, press the soft key labeled "load", the number of the program you wish to run, and the "enter" key. It will also be necessary to turn on the heat to the oven, detector and the injector. This is accomplished by pressing the appropriate key (located in the bottom section of the control panel to the left of the numerical key pad), then pressing the soft key labeled "heating on/off". (eg. To turn on (or off) the heat to the detector, press the key labeled "detector" on the control panel. When the CRT displays the detector screen press the soft key labeled "heating on/off", and the screen will display the appropriate action.)

OPERATION SICHROMAT 1-4 (cont.)

It may also be necessary to ignite the detector. In the lower section of the control panel, to the left of the temperature controls, you will see a key labeled "ignition". Pressing this key will cause the ignitor to trigger five times, sending a spark to the detector. It should be verified, through the use of a dental mirror, or similar object that the detector is lit (the detector is located on top of the g.c.).

It will take several minutes for the temperatures to stabilize. During this time the "not ready" light will be turned on. Until this light goes off and the "ready" light comes on it will not be possible to inject a sample.

This analyzer receives it's sample from a sparging unit located in the lower portion of the rack (refer to drawing # D1200013). The sparger consists of two mirror image halves. Each half consisting of a pump, a flow controller for water, a flow controller for gas (nitrogen), two solenoid valves, glassware, and heat traced sample lines. The latter is common to both halves.

CALIBRATION

As with all instruments, it will be necessary to verify the calibration. To do this you will have to make a standard containing all of the contaminants of interest in a large (5 gallon) glass container. This standard will be used to simulate a sample.

The analyzer uses a "Spectra-Physics Chromjet" integrator to calculate the concentration of each component in the sample. This is a separate piece of equipment connected to the back of the control cabinet. Like the analyzer, it is equipped with a battery to supply power in the event of a power failure; unlike the analyzer, it should NEVER be turned off using the on/off switch as this will cause it to lose it's memory. (If it is necessary to turn it off, simply unplug it.)

With a fresh standard already prepared and well mixed (using a magnetic table and stir bar) insert the plastic tube located on the side of the rack labeled "GC2" into the glass container. On the front of the sparger is a panel housing several valves and flow meters (three valves on top and three valves on the bottom of the panel). Also, above these, on a separate panel are located two rocker switches (white).

The standard must be placed into one of the two sets of glassware. This is done by selecting the appropriate valves and switches. To select the sparger on the right: 1) turn the top-most valve so that it points to the right; 2) next there are a pair of valves located just below; turn the one on the right so that it faces down (turn the other one so that it points to the left); go to the three valves on the bottom of the panel, and (3) turn the valve labeled "Sample/Calibration" to "Calibration"; (4) turn the valve labeled "Standard/Blank" to "Standard"; and (5) turn the valve labeled "Stripper 1/Stripper 2" to "Stripper 1". Now turn on the white rocker switch on the right (you should be able to hear the pump on the right come on).

At this point the standard should begin to replace any water in the front right stripping vessel and you should see gas bubbling through the water. Do not shut this off during the calibration.

CALIBRATION SiCHROMAT 1-4 (cont.)

Check the analyzer control panel to make sure it is "ready", indicated by the "ready" light being lit. Press the key labeled "Sequence"; the CRT will display a screen that will indicate "sample", "inj. no.", "method", etc. It is important that the "method" indicated here is the same method you want to calibrate. If it isn't, use the cursor key(s) to move to the method number; press the soft key labeled "select" to change the method number, and then press "enter".

Since you will want to run several analyses to check the calibration you'll want to set the instrument so that it performs this automatically. Next to the "sequence" key are two lights labeled "sampler" and "autostart". Press the "sequence" key. The soft keys displayed will include one labeled "mode", press it. Next press the soft key labeled "select" until "autostart" appears in the window; press "enter".

The first sample to be injected must be done manually, but only after the standard has had a chance to flow through the sparger for at least twenty (20) minutes at a flow rate of four (4) liters an hour. To initiate the start, press the "start" key. Be patient, it may take a few seconds for it to actually start while the computer checks all systems. At the start of the analysis the "run" light will come on and the system will automatically start the integrator. At the end of the analysis the integrator will print out the results, the analyzer will reset itself (the "not ready" light may come on), and then inject another sample.

At the end of two or three analyses you should be deriving consistent results. If the calibration is acceptable nothing has to be done except switch back to a sample. (See below.)

If the results are unacceptable, press "reset" at the end of the analysis. On the keyboard of the Chromjet is a key labeled "Calib", press it once, type "1" and then press the "enter" key. This will flag the next run as a calibration run. Next press the "start" key on the analyzer controller. Check the results after the second analyses.

Once you have achieved an acceptable calibration you can let the analyzer continue to run, however you must switch the valve labeled "sample/calibration" on the sparger back to "sample". You may also have to adjust the sample flow to four (4) liters per hour.

APPENDIX B
WATER ANALYZER CHECKLIST

SBIR
WATER ANALYZER
CHECK LIST

DAILY

1. Check all compressed gas cylinders.
   - Relplace all "empty" cylinders as required
   - Leak check all fittings at the cylinders replaced

2. Check all pressure regulators for correct pressure as written on the gauges.
   - Adjust as required
   - Replace or repair as needed

3. Check sample flow from creek.
   - Inspect flow back to creek after the split
   - Repair or adjust as required

4. Check gas pressures at each instrument as indicated on each gauge.
   - If incorrect, determine reason and correct the situation

5. Check printer and integrator.
   - Insure that each is printing correctly
   - Insure that each has an adequate supply of paper
   - Correct situation as required

6. Check sample flow to each instrument.
   - P101 should have a water flow of 4 liters per hour
   - SiCHROMAT 1-4 should have a water flow of 4 liters per hour
   - SiCHROMAT 1-4 have a gas flow of 3 liters per hour
   - Correct any discrepancies after determining the cause

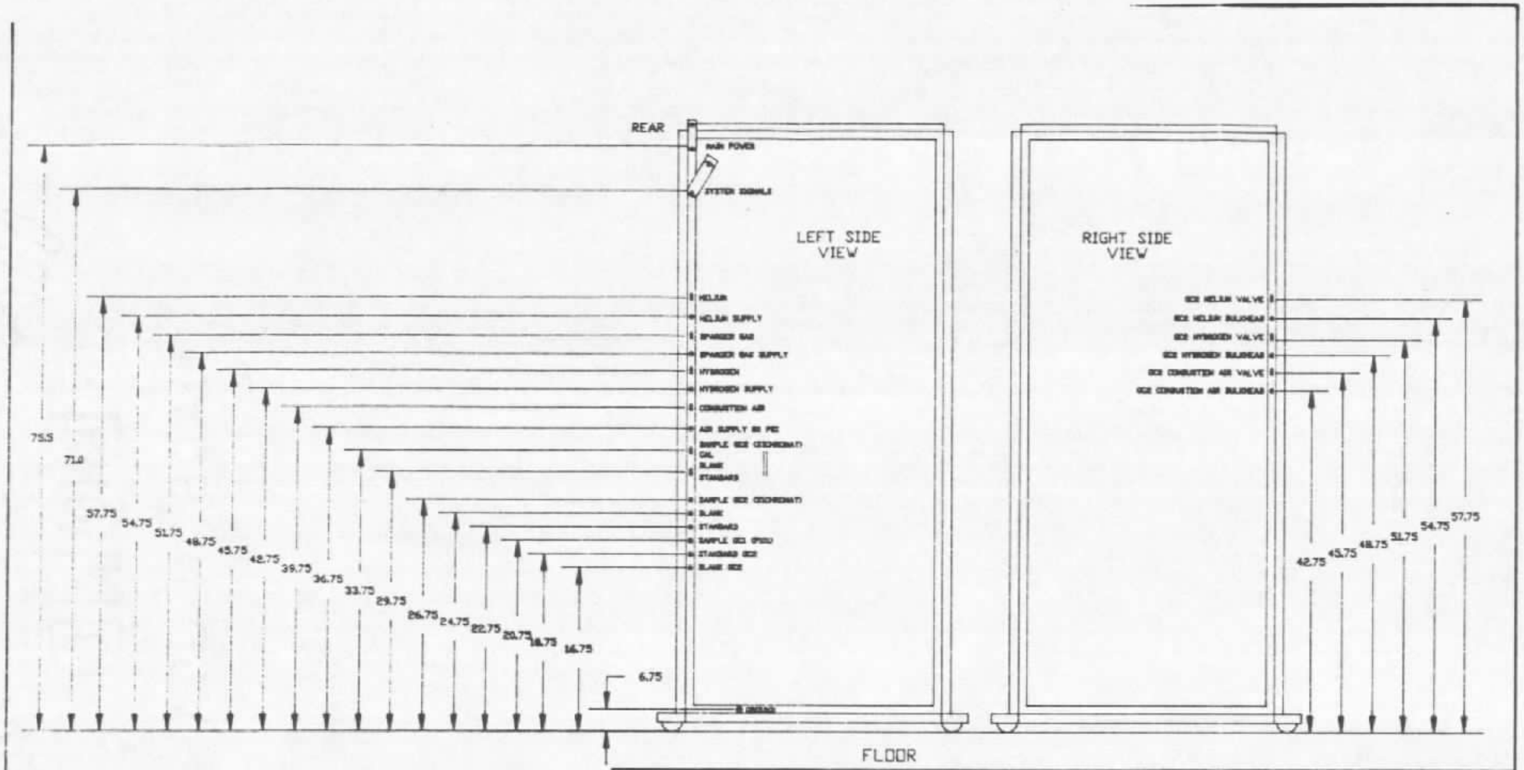
MONTHLY

1. Leak check entire gas system using an appropriate leak detector such as "SNOOP".
   - Correct all leaks to the system

2. Calibration check of each analyzer for components of interest.
   - Make fresh standards for each instrument
   - Perform calibration check as described in operating manual
   - Make corrections as required
   - Record new data on appropriate forms and distribute copies as is appropriate

3. Supplies should be ordered as required for an appropriate period of time.
   - A minimum of two week supply of paper and pens should be available for the printer and the integrator
   - Spare parts should be replaced as soon as possible after being used

APPENDIX C
ENCLOSURE INLET PLUMBING



NOTES:
1. POWER CONNECTION IS 3/4" NPT, RIDGID CONDUIT.
2. SIGNAL CONNECTION IS 1.0" NPT, RIDGID CONDUIT.

LTR	DESCRIPTION	DATE	APPROVED
	RELEASED	03/10/92	

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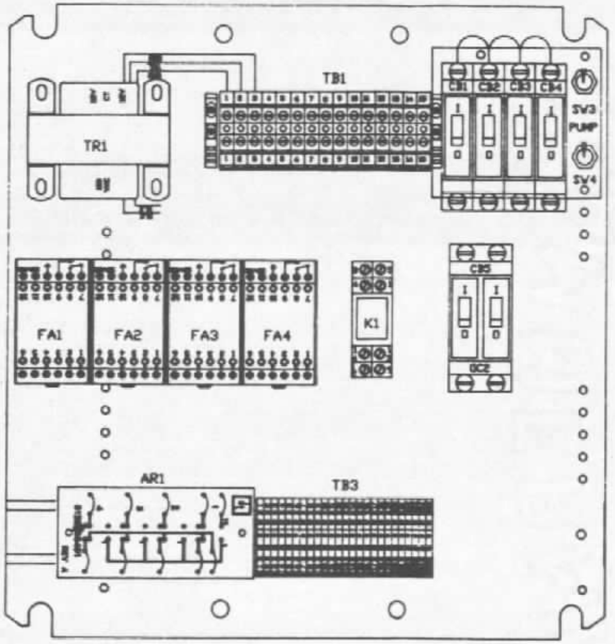
JOB NO. SBIR
REL.
DRAWN BY — DATE 03/10/92
CHECKED BY — DATE
DSGN ACTIVITY APPD D.DAWSON — DATE 03/10/92
ACAD 25

DELAWARE TECHNOLOGIES,INC

ENCLOSURE
INLET PLUMBING

SIZE B
B1500012
SCALE
SHEET 1 OF 8

APPENDIX D
ELECTRICAL PLATE COMPONENT LAYOUT



LTR	DESCRIPTION	DATE	APPROVED
	RELEASED	2/18/91	

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SBIR

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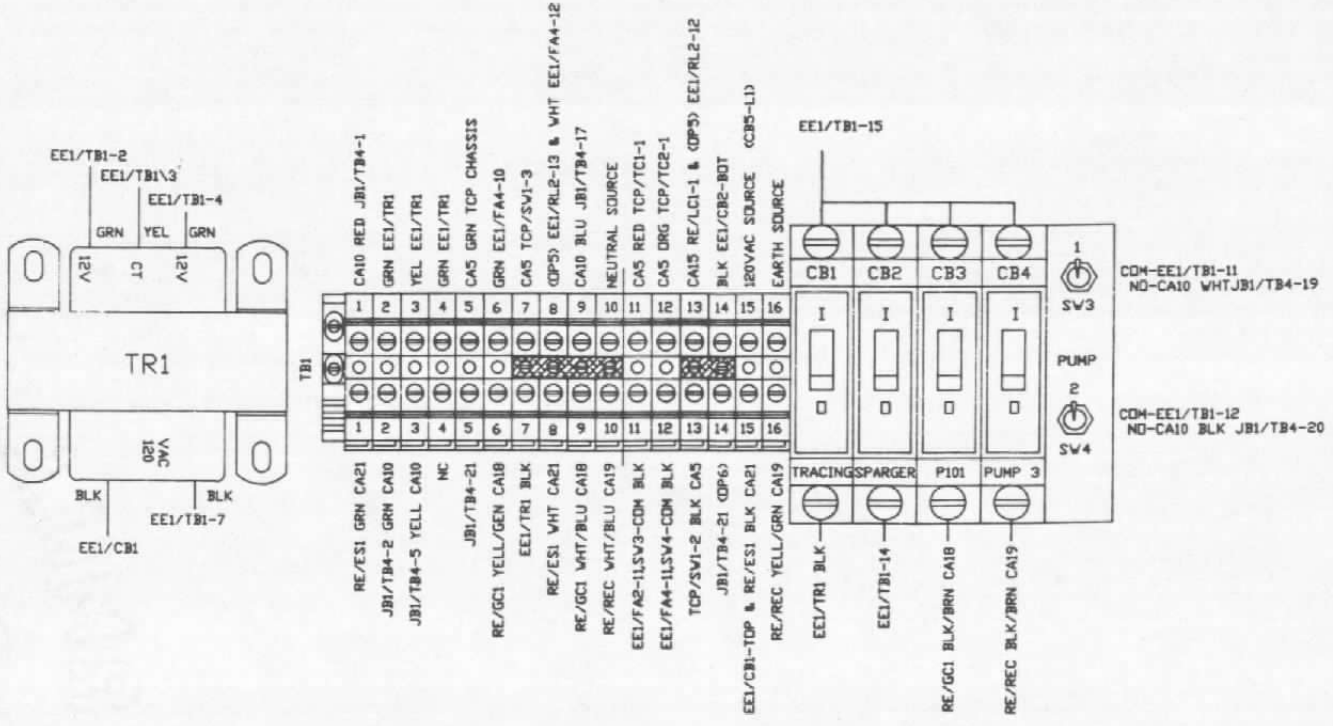
CHECKED BY DATE
DSGN ACTIVITY APPD DATE
D.DAWSON 2/18/91
ACAD 25

DELAWARE TECHNOLOGIES,INC

ELECTRICAL PLATE
COMPONENT LAYOUT

SIZE B
B2500020
SCALE
SHEET 8 OF 8

APPENDIX E
WIRING, POWER EE1/TB1



LTR	DESCRIPTION	DATE	APPROVED
	RELEASED	2/17/91	

REVISIONS

NOTES:

1. TERMINALS 1,5,6,16 = EARTH GROUND
2. TERMINALS 7,8,9,10 = NEUTRAL
3. TERMINAL 15 = 120V AC

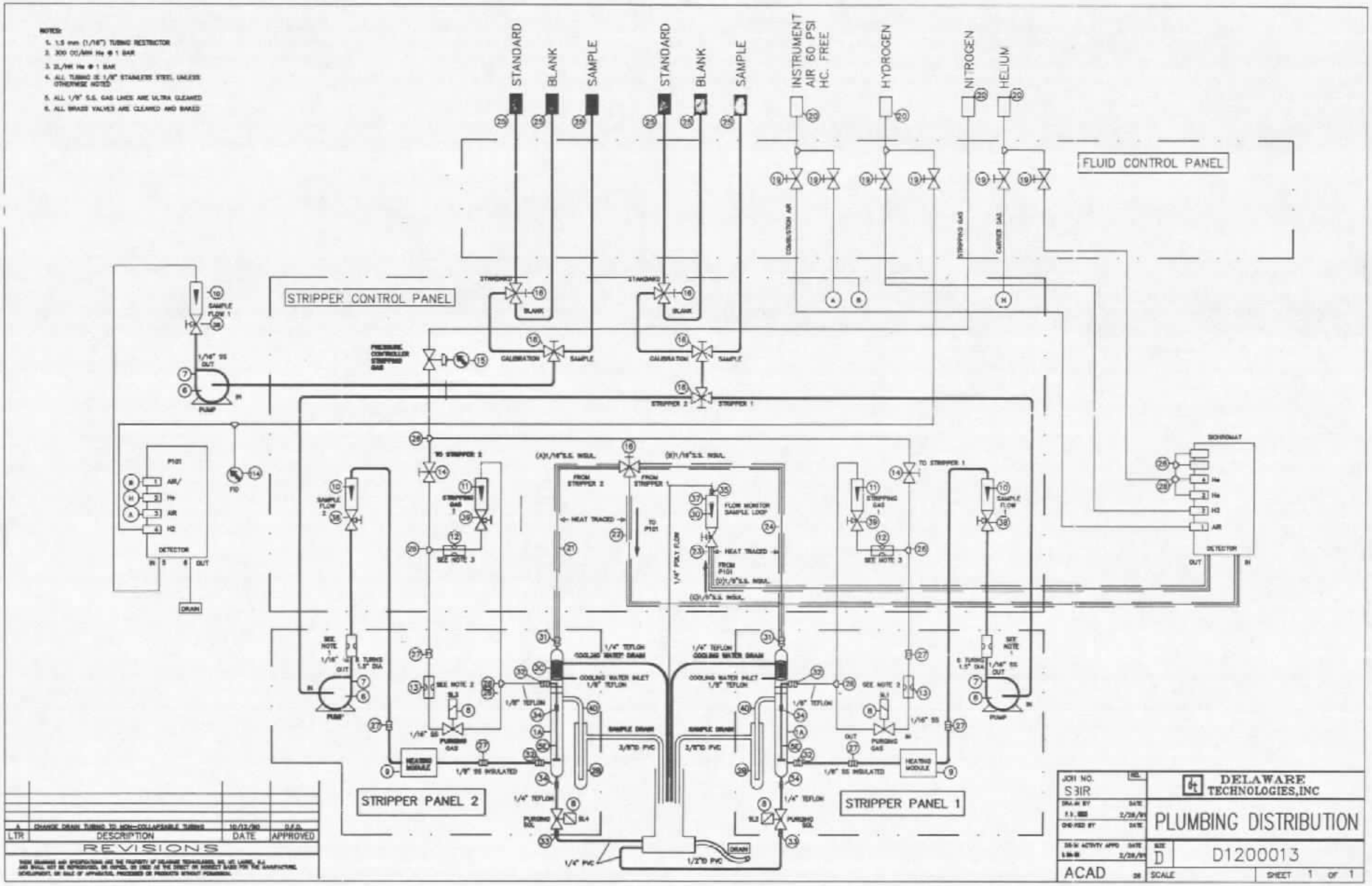
JOB NO.
SBIR
DRAWN BY DATE 2/17/91
CHECKED BY DATE
DSGN ACTIVITY APPD DATE
D.DAWSON 2/17/91
ACAD 25

DELAWARE TECHNOLOGIES,INC

WIRING, POWER
EE1/ TB1

SIZE B
B2900016
SCALE
SHEET 4 OF 8

APPENDIX F
PLUMBING DISTRIBUTION


NOTES:
1. 1.5 mm (1/16") TUBING RESTRICTOR
2. 300 CC/MIN He @ 1 BAR
3. 2L/HR He @ 1 BAR
4. ALL TUBING IS 1/8" STAINLESS STEEL UNLESS OTHERWISE NOTED
5. ALL 1/8" S.S. GAS LINES ARE ULTRA CLEANED
6. ALL BRASS VALVES ARE CLEANED AND BAKED
STANDARD
BLANK
SAMPLE
STANDARD
BLANK
SAMPLE
INSTRUMENT AIR 60 PSI HC. FREE
HYDROGEN
NITROGEN
HELIUM
FLUID CONTROL PANEL
COMBUSTION AIR
STRIPPING GAS
CARRIER GAS
STRIPPER CONTROL PANEL
STANDARD
BLANK
CALIBRATION
SAMPLE
STRIPPER 2
STRIPPER 1
PRESSURE CONTROLLER STRIPPING GAS
SAMPLE FLOW 1
1/16" SS OUT
PUMP
IN
P101
AIR/
He
AIR
H2
DETECTOR
IN
OUT
DRAIN
FID
TO STRIPPER 2
TO STRIPPER 1
SAMPLE FLOW 2
STRIPPING GAS 1
SEE NOTE 3
(A)1/16"S.S. INSUL.
(B)1/16"S.S. INSUL.
FROM STRIPPER 2
FROM STRIPPER 1
HEAT TRACED
TO P101
1/4" POLY FLOW
FLOW MONITOR SAMPLE LOOP
FROM P101
(D)1/8"S.S. INSUL.
(C)1/8"S.S. INSUL.
SICHROMAT
He
He
H2
AIR
DETECTOR
OUT
IN
SEE NOTE 1
1/16" OUT
6 TURNS 1.5" DIA
SEE NOTE 2
1/4" TEFLON COOLING WATER DRAIN
COOLING WATER INLET 1/8" TEFLON
1/8" TEFLON
1/16" SS
PURGING GAS
HEATING MODULE
1/8" SS INSULATED
SAMPLE DRAIN
3/8"OD PVC
1/4" TEFLON
PURGING SOL.
SL4
SL3
1/4" PVC
1/2"OD PVC
DRAIN
STRIPPER PANEL 2
STRIPPER PANEL 1
A
CHANGE DRAIN TUBING TO NON-COLLAPSABLE TUBING
10/02/90
D.F.D.
LTR
DESCRIPTION
DATE
APPROVED
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JOB NO.
S3IR
DRAWN BY
DATE
2/28/91
CHECKED BY
DATE
DESIGN ACTIVITY APPD
DATE
2/28/91
ACAD
DELAWARE TECHNOLOGIES,INC
PLUMBING DISTRIBUTION
SIZE
D
D1200013
SCALE
SHEET 1 OF 1