Several DME/methanol mixtures were measured for their properties as a transportation fuel. With small amounts of DME added, significant improvements in both flash point and RVP were observed over methanol alone. With a flash point of 7°C and an RVP of 6.4 psi, methanol alone has a cold-start problem when the temperature becomes too low. Adding DME to methanol brings those properties closer to those of M85, an acceptable automobile fuel. These results are encouraging and more tests with DME/methanol mixtures would be worthwhile.

The development work described here on DME synthesis at laboratory scale laid a basis for a demonstration of liquid phase DME technology at DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas.

## FUTURE PLANS

The next logical step in the development of slurry-phase DME synthesis technology is a demonstration at DOE's LaPorte Alternative Fuels Development Unit (AFDU). The AFDU is equipped with a 22.5" ID, 29' tall bubble column reactor. This facility has been used to successfully demonstrate slurry-phase methanol synthesis under previous DOE contracts. Production rates as high as 12 tons per day of methanol were attained, limited only by the capacity of the feed compressor.

In addition to demonstrating the feasibility of mixed DME/methanol synthesis in a single-stage, slurry reactor, the AFDU run would also verify that conclusions drawn in the laboratory are valid for large-scale reactors. While bench-scale reactors are essential in demonstrating reaction feasibility and intrinsic kinetics, they cannot address many of the scale-up issues. Back-mixing in the reactor and mass transfer limitations, for example, are critical factors in commercial designs and cannot be adequately investigated in the lab. It is anticipated that data obtained from the AFDU will demonstrate the magnitude and importance of these two phenomena.

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## APPENDIX I
## Air Products Memorandum from R. A. Byerley to B. Bhatt
## 25 May 1990

# MEMORANDUM

AIR PRODUCTS

To: B. Bhatt — Dept.: PSG Research

From: R. A. Byerley — Dept./Ext.: CRSD-Analytical/6504

Date: 25 May 1990 — Chemical Separations Laboratory

Subject: Documentation for Iron Run Lab 17 Gas Chromatograph

cc: S. Gaul; T. Dahl; J. Frost; P. Clark; R. Mayo

## INTRODUCTION

A Hewlett Packard 5890 gas chromatograph (GC) has been set-up to analyze reactor gas for light gases, methanol, dimethyl ether, methyl formate, and ethanol. The chromatograph, located in Iron Run lab 17, was originally configured by John Booker & Co., Austin, Texas. Modifications were performed to the chromatograph sampling system to improve the analysis of hydrogen in the reactor gas.

## SYSTEM DESCRIPTION

Figure 1 is a block diagram of the chromatograph and integrator system. The original flame ionization (FID)/thermal conductivity detector (TCD) GC configuration was

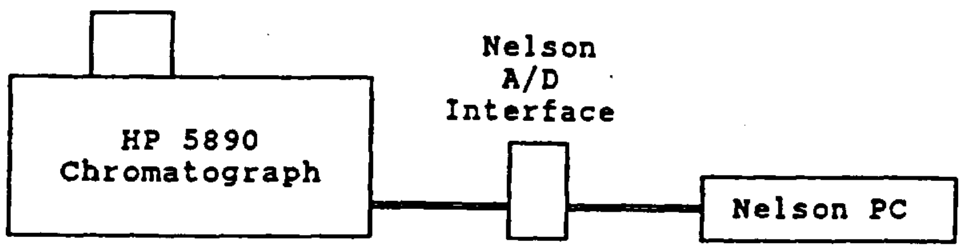


Fig. 1. System Configuration

modified by replacing the FID with a TCD to perform a hydrogen analysis with nitrogen carrier. Both signals from the dual TCD arrangement are sent to the A/D (analog to digital) interface and are processed by the Nelson PC Integrator software.

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## FLOW PATHS

Figure 2 shows a diagram of the chromatograph in its ready state. Gas from th reactor (or calibration standard) enters the system from solenoid valve S4 passing through a 2 micron VALCO filter located inside the VALCO heated valve enclosure. The sample exits the system to vent after passing through a rotometer. All VALCO valves are shown in the load position with the sample stream purging the three 0.5 cc sample loops.

Helium and nitrogen carrier gasses are supplied to the GC from the Iron Run dock. Helium carrier is delivered to mass flow controllers (MFC) B1 and B2 at 50 psig. Nitrogen is supplied to MFC A at approximately 55 psig. Output flow of the three flow controllers is set to 20 ml/min. The B2 MFC regulates the helium carrier flow for VALCO valve V1, maintaining a column head pressure of 8 psig. Helium carrier flow for valve V2 is controlled by MFC B1, maintaining a head pressure of 18 psig. A column head pressure of 11 psig is maintained for valve V3 by MFC A. Figure 3 is a diagram of V1 in the inject mode with V2 and V3 in the load position. Figure 4 is a diagram showing valve V1 returned to the load position and V2 and V3 in the inject positions. V1 must be returned before injecting V2. Timed events for valve control are listed in Table 1 of Appendix A.1.

## CHROMATOGRAPHY

Appendix A.2 lists the columns and conditions for the gas chromatograph system. Figure 5 is a chromatogram and Nelson report table of the V1 and V2 valve injections. Valve V1 with the attached Porapak T/ molecular sieve 13X column set is used for the separation of $H_2$, $O_2$/Ar, $N_2$, $CH_4$, and CO ($H_2$ quantitated on V3). The Porapak column is required to protect the molecular sieve column from heavy non-eluting components. After elution of the CO peak, valve V1 is returned and the Porapak T/ molecular sieve 13X column set is backflushed to vent.

Immediately after V1 is returned V2 is switched to inject. The Hayesep D column connected to V2 separates a composite peak of air, $H_2$, and CO from $CH_4$, $CO_2$, $H_2O$, methanol, dimethyl ether, methyl formate, and ethanol. Valve V2 is returned after elution of ethanol, backflushing the Hayesep column to the detector. The valve switching times and other timed events for valves V1 and V2 are listed in Table 1 of Appendix A.1. Figure 6 is a chromatogram of the hydrogen analysis. Valve V3 is injected after V1 to allow for the V3 sample loop to reach equilibrium. The hydrogen analysis is very selective for hydrogen, giving a minimal response for $O_2$/Ar, $N_2$, CO, etc. Detector B (connected to V3) is used for the quantitation of hydrogen only. Valve switching times and other timed events for valve V3 are listed in Tables 1 and 2 of Appendix A.1.

The dual channel Nelson method naming convention is listed Table 2 of Appendix A.3. By convention, the first character of the second dual channel method must be named with the next logical letter or number. Table 1 of Appendix A.3 lists the Nelson PC Integrator parameters used for both detectors.

## CALIBRATION

Instrument calibration should be checked by running standards as often as possible. Recalibration should be performed when the integrator report differs by more than 3 percent of the accepted standard values. An average of three injections should be used for calibration. The Nelson Integrator method given in Table 1 of Appendix A.3 is the same for all dual channel methods. Table 2 of Appendix A.3 lists the dual channel method names and the corresponding calibration standards. Since methanol and dimethyl ether are common to all process streams, the same methanol/dimethyl ether response factors are used for all methods listed in Appendix A.4. Response factors are also assumed for components that are not present in the calibration standards for a particular process stream. The assumed response factors provide a reasonable quantitative estimate since these components are usually insignificant. Refer to the notes at the bottom of each calibration listing of Appendix A.4 for the assumed response factors. However, if any of these components become significant, then a response factor from an appropriate standard must be substituted into the calibration.

## MAINTENANCE

The system requires minimal maintenance. It may be necessary to occasionally condition the molecular sieve 13X column for 1/2 hour @ 300 °C in order to improve separation. The charcoal column (in the 5890 oven) may also need conditioning for several hours @ 300 °C to remove accumulated material.

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R. A. Byerley

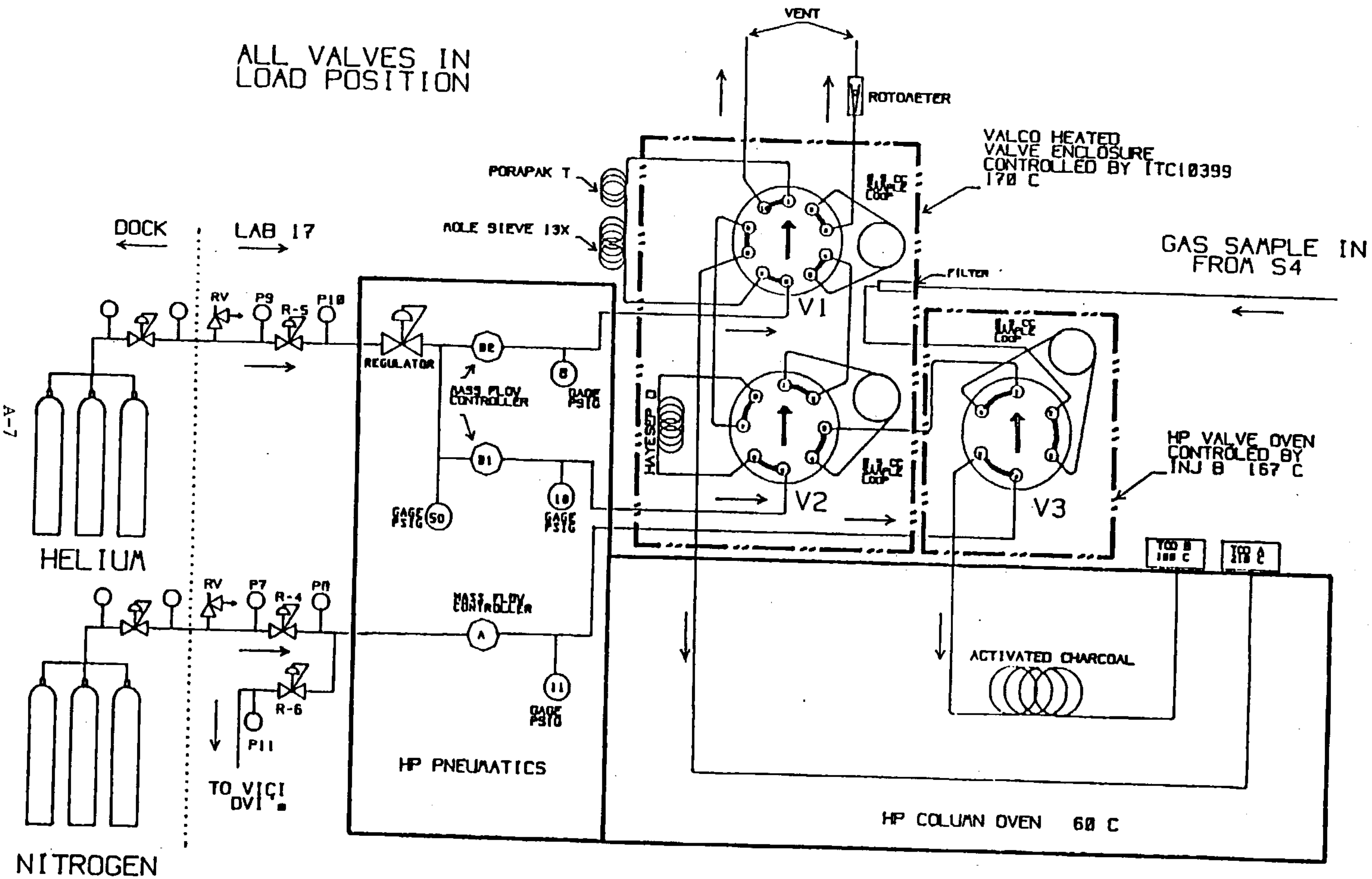



FIG. 2. Flow Diagram of Methanol Reactor GC

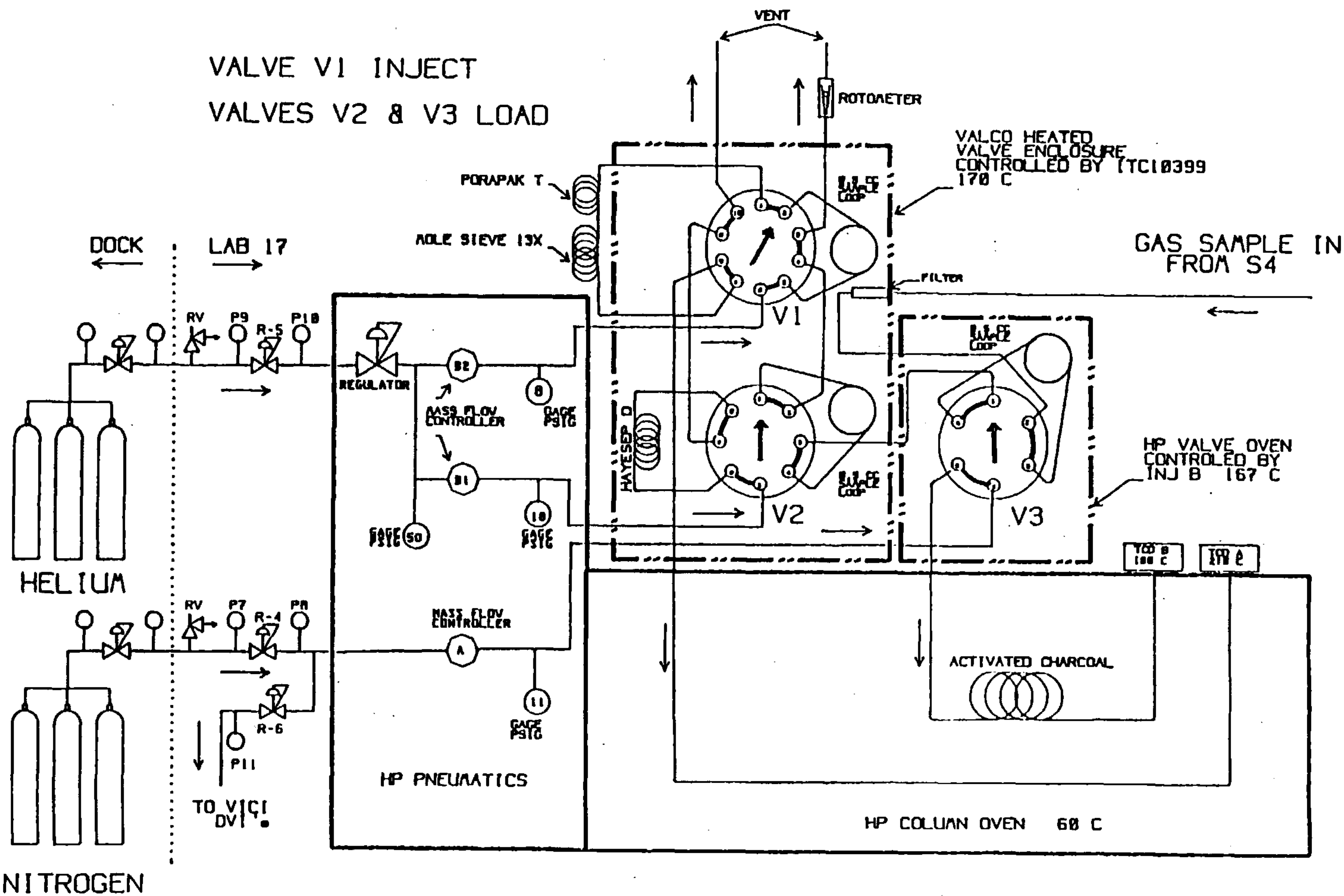



FIG. 3. Flow Diagram of Methanol Reactor GC

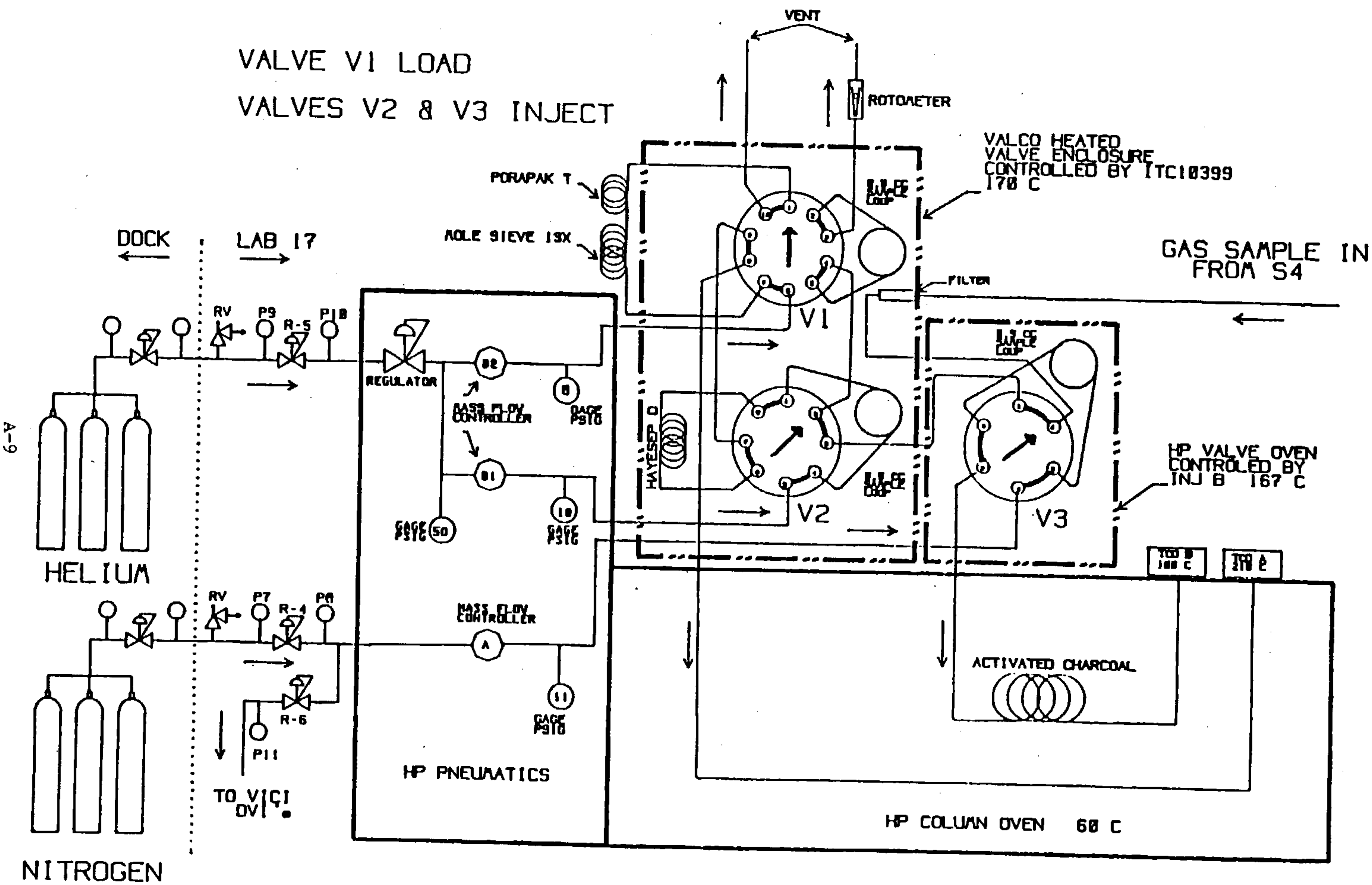
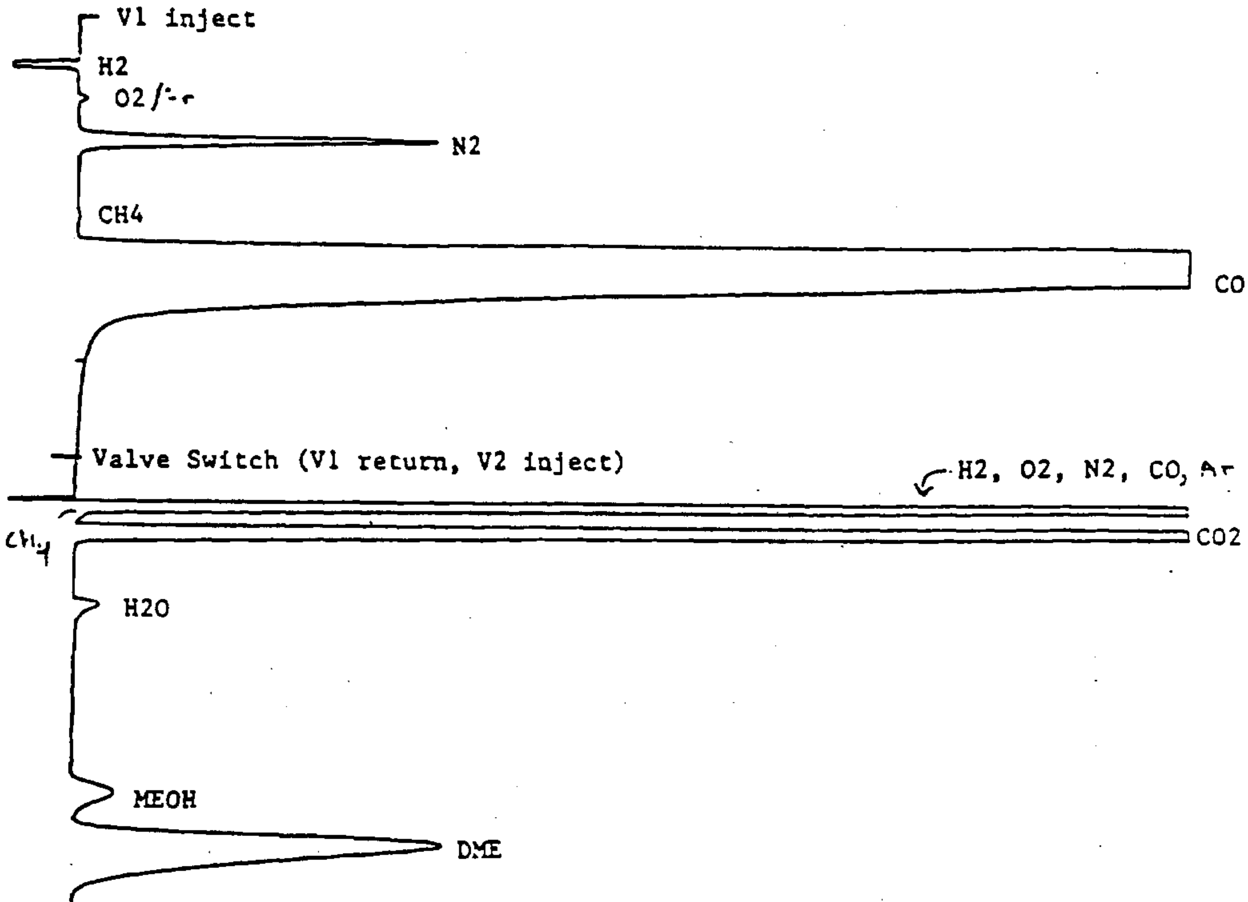



FIG. 4. Flow Diagram of Methanol Reactor GC

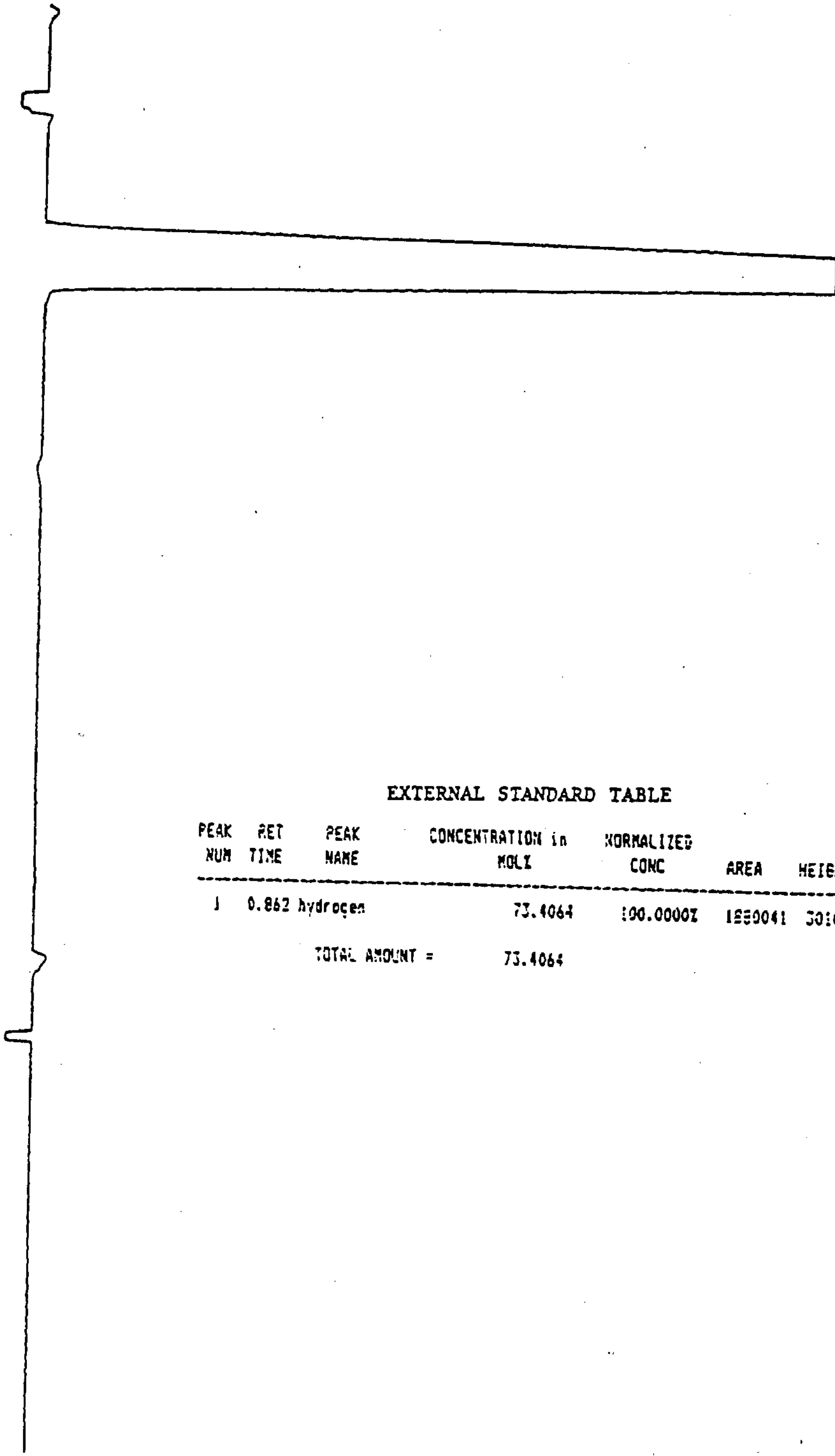



EXTERNAL STANDARD TABLE

| PEAK NUM | RET TIME | PEAK NAME | CONCENTRATION in MOL% | NORMALIZED CONC% | AREA | HEIGHT | AREA/ HEIGHT | BL |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.02 | | 560.4493 | 89.7591% | 560 | 258 | 2.1 | 1 |
| 2 | 0.55 | O2/Ar | 0.0201 | 0.0032% | 1517 | 807 | 1.9 | 2 |
| 3 | 0.52 | N2 | 1.3058 | 0.2068% | 98443 | 30707 | 3.2 | 2 |
| 4 | 1.32 | CH4 | 0.0157 | 0.0025% | 1113 | 258 | 4.3 | 2 |
| 5 | 1.36 | CO | 41.4568 | 6.5556% | 2943768 | 214143 | 13.7 | 2 |
| 6 | 3.37 | CO2 | 21.7903 | 3.4510% | 1134162 | 396577 | 2.9 | 2 |
| 7 | 3.88 | H2O | 0.1361 | 0.0216% | 8709 | 2076 | 4.2 | 1 |
| 8 | 5.12 | MeOH | 0.5960 | 0.0947% | 27958 | 3480 | 8.0 | 2 |
| 9 | 5.46 | DME | 5.6549 | 0.8956% | 361843 | 31595 | 11.5 | 2 |

TOTAL AMOUNT = 631.4271

Fig. 5 Chromatogram of V1 and V2 Injections




EXTERNAL STANDARD TABLE

| PEAK NUM | RET TIME | PEAK NAME | CONCENTRATION in MOL% | NORMALIZED CONC | AREA | HEIGHT | AREA/ HEIGHT | BL |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.862 | hydrogen | 73.4064 | 100.0000% | 1880041 | 301049 | 6.2 | 1 |

TOTAL AMOUNT = 73.4064

Fig. 6. Chromatogram of V3 injection

# APPENDIX A.1

## Table 1

**NELSON TIMED EVENTS FOR VALVES V1, V2, V3,**
(Detector A)

| Ev# | Time | Event | Description | NOTE |
|---|---|---|---|---|
| 1 | 0.01 | 1C | relay (Close) | Inject V1 |
| 2 | 0.05 | PD- | Peak Detection (off) | |
| 3 | 0.06 | 1O | relay (Open) | |
| 4 | 0.30 | 6C | relay (Close) | Inject V3 |
| 5 | 0.40 | 6O | relay (Open) | |
| 6 | 0.45 | PD+ | Peak Detection (on) | |
| 7 | 2.85 | PD- | Peak Detection (off) | |
| 8 | 2.90 | 2C | relay (Close) | Return V1 |
| 9 | 2.90 | 3C | relay (Close) | Inject V2 |
| 10 | 3.20 | 2O | relay (Open) | |
| 11 | 3.20 | 3O | relay (Open) | |
| 12 | 3.35 | PD+ | Peak Detection (on) | |
| 13 | 11.80 | PD- | Peak Detection (off) | |
| 14 | 11.85 | 4C | relay (Close) | Return V2 |
| 15 | 11.85 | 7C | relay (Close) | Return V3 |
| 16 | 11.95 | 4O | relay (Open) | |
| 17 | 11.95 | 7O | relay (Open) | |

## Table 2

**NELSON TIMED EVENTS FOR DETECTOR B**
(hydrogen)

| Ev# | Time | Event | Description |
|---|---|---|---|
| 1 | 0.01 | PD- | Peak Detection (off) |
| 2 | 0.50 | PD+ | Peak Detection (on) |
| 3 | 1.00 | PD- | Peak Detection (off) |

## GAS CHROMATOGRAPHIC CONDITIONS

**Instrument:** Hewlett Packard 5890 Gas Chromatograph

**Columns:**

(1) VALCO Valve V1 - 2' x 1/8" Porapak T 60/80 mesh in series with a 3' x 1/8" mole sieve 13X 40/50 mesh

(2) VALCO Valve V2 - 5' x 1/8" Hayesep D(ip) acid washed 80/100 mesh

(3) VALCO Valve V3 - 6' x 1/8" Activated Charcoal 60/80 mesh

**Column Temperatures:** Isothermal

Column 1 - Ambient temperature

Column 2 - 170 °C VALCO heated valve enclosure

Column 3 - 60 °C HP 5890 oven

**Carrier Gas:**

Column 1 (mass flow cont. B2) - 20 ml/min helium, 8 psig

Column 2 (mass flow cont. B1) - 20 ml/min helium, 18 psig

Column 3 (mass flow cont. A) - 20 ml/min nitrogen, 11 psig

**Injection Volume:** 0.5 cc for all three loops V1 - V3

**Injection Mode:** VALCO gas sampling valve

**Detectors:** Thermal Conductivity
A - 210 °C, refer. flow = 25 ml/min. helium, total flow = 45 ml/min., Low Sensitivity, Range = 0, Zero (typical) = 1.0

B - 100 °C refer. flow = 25 ml/min. helium, total flow = 45 ml/min., Low Sensitivity, Range = 0, Zero (typical) = -9.2 Negative Polarity

**Data System:** Nelson PC Integrator

**Integration Parameters:**

| | | |
|---|---|---|
| Noise Threshold | 5 | microvolts/sec |
| Peak Width | 3 | seconds |
| Area Threshold | 300 | microvolts*sec |
| Sampling Rate | 0.2 | seconds/sample |
| Peak Area Rejection | 0 | microvolt-sec |

**Quantitation Method:** External Standard, mole %

APPENDIX A.3

Table 1

Nelson Integrator Method (Dual Chanel) For Detectors A and B

ACQUISITION PARAMETERS

| | |
|---|---|
| SINGLE OR DUAL CHANNEL (1 OR 2) | 2.00 |
| RUN TIME (minutes) | 12.00 |
| END TIME FOR PLOTS (default=RUN TIME) | 12.00 |
| SOLVENT DELAY TIME (minutes) | 0.00 |
| PEAK DETECTION THRESHOLD (microv/sec) | 5.00 |
| Area Threshold | 300.00 |
| MINIMUM PEAK WIDTH (seconds) | 3.00 |
| TIME FOR ONE SAMPLE (seconds) | 0.20 |
| NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99) | 1.00 |
| REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts) | 50.00 |
| REAL TIME FULL SCALE FOR CH.1 (millivolts) | 50.00 |
| HARD COPY REAL TIME PLOT | NO |
| AUTO ZERO REAL TIME PLOT | YES |
| Pre Version 4 method | NO |
| RECORD AREA TABLES ON DISK | YES |
| RECORD RAW DATA | YES |
| NUMBER OF CRT PAGES FOR REPLOT (1 TO 99) | 1.00 |
| VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak) | 0.00 |
| OFFSET FOR THE REPLOT (millivolts) | 5.00 |
| PUT NAMES ON REPLOT? | YES |
| PRINT AREA PERCENT REPORT | NO |
| PRINT EXTERNAL STANDARD REPORT | YES |
| PRINT INTERNAL STANDARD REPORT | NO |
| FINAL REPORT AREA REJECT (microvolt-sec) | 500.00 |
| LINK TO USER PROGRAM | NO |
| FORCE DROP LINE INTEGRATION | NO |
| FORCE COMMON BASE LINE | NO |
| FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT) | 3.00 |
| AREA REJECT FOR REFERENCE PEAKS? | 0.00 |
| % RET TIME WINDOW FOR REFERENCE PEAKS | 15.00 |
| RET TIME WINDOW IN SECONDS FOR REF. PEAKS | 15.00 |
| AREA OR PEAK HEIGHT QUANTITATION (0 OR 1) | 0.00 |
| PRINT GROUP REPORT | NO |
| NUMBER OF CALIBRATION LEVELS (1 TO 6) | 1.00 |
| LIST COMPONENTS NOT FOUND IN SAMPLE? | YES |
| INCLUDE UNKNOWN PEAKS IN REPORTS? | YES |
| UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1) | 0.00 |
| DEFAULT DILUTION FACTOR | 1.00 |
| DEFAULT SAMPLE WEIGHT | 1.00 |
| DEFAULT AMOUNT INJECTED | 1.00 |
| DEFAULT AMOUNT OF INTERNAL STANDARD | 1.00 |
| PRINT GPC MW DISTRIBUTION | NO |
| PRINT SIMULATED DISTILLATION REPORT | NO |

NOTE: Both methods in a dual chanel configuration must have the same integration parameters and run time. Timed events may be different for each.

Table 2

Method Naming Convention

| Calibration Standards | Detector A | Detector B |
|---|---|---|
| Dakota Syngas | DAKSYN.MET | EAKSYN.MET |
| Unbalanced | UNBAL.MET | VNBAL.MET |
| Balanced | BAL.MET | CAL.MET |
| $H_2$ Rich | H2RICH.MET | I2RICH.MET |

NOTE: First charater of second dual chanel method must be named with the next logical letter or number. Detector B is used for determination of hydrogen only.

APPENDIX A.4
CALIBRATION LISTINGS FOR DETECTOR A
Method: DAKSYN

Response factor for unknowns= 1.0000E+00 Component Units = MOL%

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1 O2/Ar Ret. Time = 0.56 min. Fit.type =1
Ref. peak: CO Int Std: CO Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 930911 | 18.00000000 | 0.00001934 |

2 N2 Ret. Time = 0.96 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 930911 | 18.00000000 | 0.00001934 |

3 CH4 Ret. Time = 1.35 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 930911 | 18.00000000 | 0.00001934 |

4 CO Ret. Time = 1.94 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1311880 | 19.39999960 | 0.00001479 |

5 CO2 Ret. Time = 3.43 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 48720 | 1.00000000 | 0.00002053 |

6 H2O Ret. Time = 3.90 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

7 MeOH Ret. Time = 5.32 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 49024 | 1.10000002 | 0.00002244 |

8 DME Ret. Time = 5.69 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

9 Methylformate Ret. Time = 8.46 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

10 EtOH Ret. Time = 9.80 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

NOTE: Response factors for $N_2$, $O_2$/Ar were taken as $CH_4$ of the DAKSYN STD.
Response factors for $H_2O$, Methyl Formate, and EtOH were taken as DME of the MEOH/DME standard.

Method: UNBAL

Response factor for unknowns= 1.0000E+00 Component Units = MOL%

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1 O2/Ar Ret. Time = 0.54 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 77649 | 1.02999997 | 0.00001326 |

2 N2 Ret. Time = 0.81 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 20.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 77649 | 1.02999997 | 0.00001326 |

3 CH4 Ret. Time = 1.35 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 3491471 | 49.16999800 | 0.00001408 |

4 CO Ret. Time = 1.65 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 20.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 3491471 | 49.16999800 | 0.00001408 |

5 CO2 Ret. Time = 3.38 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 676637 | 13.00000000 | 0.00001921 |

6 H2O Ret. Time = 3.90 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 499098 | 7.80000020 | 0.00001563 |

7 MeOH Ret. Time = 5.06 min. Fit.type = 1
Ref. peak: MeOH Int Std: MeOH Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 168323 | 3.59999990 | 0.00002139 |

8 DME Ret. Time = 5.41 min. Fit.type = 1
Ref. peak: DME Int Std: DME Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 499098 | 7.80000020 | 0.00001563 |

9 Methylformate Ret. Time = 8.46 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 499098 | 7.80000020 | 0.00001563 |

10 EtOH Ret. Time = 9.80 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 499098 | 7.80000020 | 0.00001563 |

NOTE: Response factor for $O_2$/Ar was taken as $N_2$ of the UNBALANCED standard. Response factor for $CH_4$ was taken as CO of the UNBALANCED std. Response factors for H2O, Methyl Formate, and EtOH were taken as DME of the MEOH/DME standard.

Method: BAL

Response factor for unknowns= 1.0000E+00 Component Units = MOL%

1 O2/Ar Ret. Time = 0.56 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 276008 | 21.00000000 | 0.00007608 |

2 N2 Ret. Time = 0.89 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 276008 | 21.00000000 | 0.00007608 |

3 CH4 Ret. Time = 1.35 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1023628 | 19.10000040 | 0.00001866 |

4 CO Ret. Time = 2.06 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1023628 | 19.10000040 | 0.00001866 |

5 CO2 Ret. Time = 3.43 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 7.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 350208 | 5.02000000 | 0.00001433 |

6 H2O Ret. Time = 3.90 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

7 MeOH Ret. Time = 5.32 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 49024 | 1.10000002 | 0.00002244 |

8 DME Ret. Time = 5.69 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

9 Methylformate Ret. Time = 8.46 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

10 EtOH Ret. Time = 9.80 min. Fit.type = 1
Ref. peak: CO Int Std: CO Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

NOTE: Response factor for $O_2$/Ar was taken as $N_2$ of the BALANCED standard. Response factor for $CH_4$ was taken as CO of the BALANCED std. Response factors for H2O, Methyl Formate, and EtOH were taken as DME of the MEOH/DME standard.

Method: H2RICH

Response factor for unknowns= 1.0000E+00    Component Units = MOL%

1 O2/Ar    Ret. Time = 0.56 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 276008 | 4.04000000 | 0.00001464 |

2 N2    Ret. Time = 0.89 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 15.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 276008 | 4.04000000 | 0.00001464 |

3 CH4    Ret. Time = 1.35 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1023628 | 15.10000040 | 0.00001475 |

4 CO    Ret. Time = 2.06 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1023628 | 15.10000040 | 0.00001475 |

5 CO2    Ret. Time = 3.43 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 7.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 350208 | 7.05000020 | 0.00002013 |

6 H2O    Ret. Time = 3.90 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

7 MeOH    Ret. Time = 5.32 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 49024 | 1.10000002 | 0.00002244 |

8 DME    Ret. Time = 5.69 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

9 Methylformate    Ret. Time = 8.46 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

10 EtOH    Ret. Time = 9.80 min.  Fit.type = 1
Ref. peak: CO    Int Std: CO    Window size: 5.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 449767 | 7.80000020 | 0.00001734 |

NOTE: Response factor for $O_2$/Ar was taken as $N_2$ of the H2 RICH standard. Response factor for $CH_4$ was taken as CO of the H2 RICH std. Response factors for H2O, Methyl Formate, and EtOH were taken as DME of the MEOH/DME standard.

HYDROGEN METHODS

METHOD: EAKSYN

Response factor for unknowns= 1.0000E+00
Component Units = MOL%

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1 hydrogen Ret. Time = 0.82 min. Fit.type = 1
Ref. peak: hydrogen Int Std: hydrogen Window size: 10.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1571592 | 61.59999800 | 0.00003920 |

METHOD: VNBAL

Response factor for unknowns= 1.0000E+00
Component Units = MOL%

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1 hydrogen Ret. Time = 0.83 min. Fit.type = 1
Ref. peak: hydrogen Int Std: hydrogen Window size: 20.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 945398 | 36.79999900 | 0.00003893 |

METHOD: CAL

Response factor for unknowns= 1.0000E+00
Component Units = MOL%

---

1 hydrogen Ret. Time = 0.87 min. Fit.type = 1
Ref. peak: hydrogen Int Std: hydrogen Window size: 10.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1890377 | 54.88000100 | 0.00002903 |

METHOD: I2RICH

Response factor for unknowns= 1.0000E+00
Component Units = MOL%

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1 hydrogen Ret. Time = 0.87 min. Fit.type = 1
Ref. peak: hydrogen Int Std: hydrogen Window size: 10.0%

| LEVEL | AREA | AMOUNT | RATIO (amount/area) |
|---|---|---|---|
| 1 | 1890377 | 73.80999800 | 0.00003905 |