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SANDIA REPORT

Autonomous Gas Chromatograph System for Thermal Enhanced Vapor Extraction System (TEVES) Proof of Concept Demonstration

Frank J. Peter, George R. Laguna

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Autonomous Gas Chromatograph System for Thermal Enhanced Vapor Extraction System (TEVES) Proof of Concept Demonstration

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Abstract

An autonomous gas chromatograph system was designed and built to support the Thermal Enhanced Vapor Extraction System (TEVES) demonstration. TEVES is a remediation demonstration that seeks to enhance an existing technology (vacuum extraction) by adding a new technology (soil heating). A pilot scale unit was set up at one of the organic waste disposal pits at the Sandia National Laboratories Chemical Waste Landfill (CWL) in Tech Area III. The responsibility for engineering a major part of the process instrumentation for TEVES belonged to the Manufacturing Control Subsystems Department. The primary mission of the one-of-kind hardware/software system is to perform on-site gas sampling and analysis to quantify a variety of volatile organic compounds (VOCs) from various sources during TEVES operations. The secondary mission is to monitor a variety of TEVES process physical parameters such as extraction manifold temperature, pressure, humidity, and flow rate, and various subsurface pressures. The system began operation in September 1994 and was still in use on follow-on projects when this report was published.

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1.0 Overview

Department 2338 has developed an autonomous gas chromatograph system for Department 6621 to support the Thermal Enhanced Vapor Extraction System (TEVES) experiment. The primary mission of this one-of-kind hardware/software system is to perform on-site gas sampling and analysis to quantify a variety of volatile organic compounds (VOCs) from various sources during TEVES operations. The secondary mission is to monitor a variety of TEVES process physical parameters such as extraction manifold temperature, pressure, humidity, and flow rate, and various subsurface pressures. The system is located in a portable, temperature-controlled building at the chemical waste landfill in Area III and was in continuous operation from September 1994 through June 1995.

1.1 View of TEVES Site
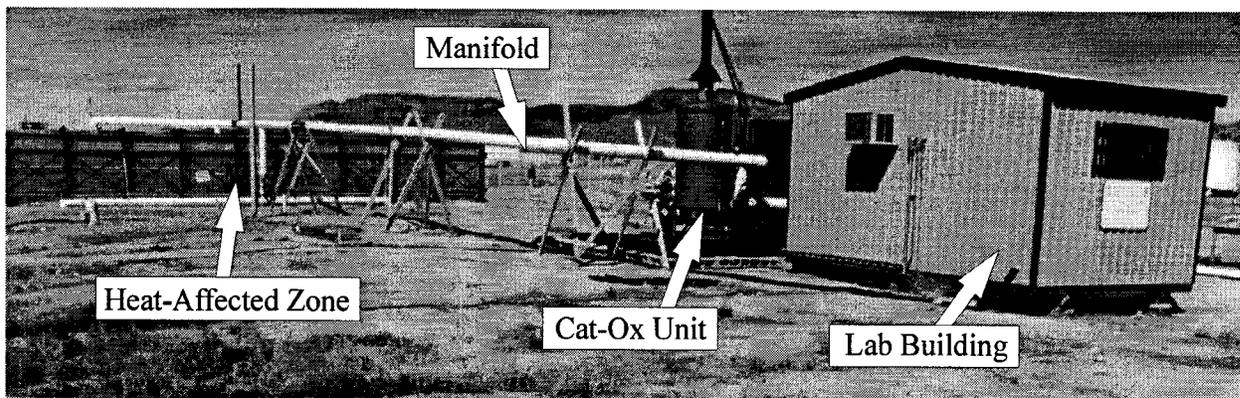
1.2 What is TEVES?

The Thermal Enhanced Vapor Extraction System (TEVES) is a demonstration that seeks to enhance an existing technology (vacuum extraction) by adding a new technology (soil heating). A pilot scale unit was set up at one of the organic waste disposal pits at the Sandia National Laboratories Chemical Waste Landfill (CWL) in Tech Area III. A vacuum blower pulls untreated vapors from the ground via two boreholes into an extraction manifold. The vapors (containing air, a complex mix of volatile organic compounds and water) are dried and then introduced into a catalytic oxidation (cat-ox) unit which converts the vapors into water, carbon dioxide, and simple acids. The treated vapors, rendered non-hazardous are vented into the ambient air. A more detailed description may be found in:

Resource Conservation and Recovery Act, Research Development, and Demonstration Permit for Thermal Enhanced Vapor Extraction System. issued by the New Mexico Environment Department, Santa Fe, New Mexico, May 26, 1994.

1.3 TEVES Block Diagram
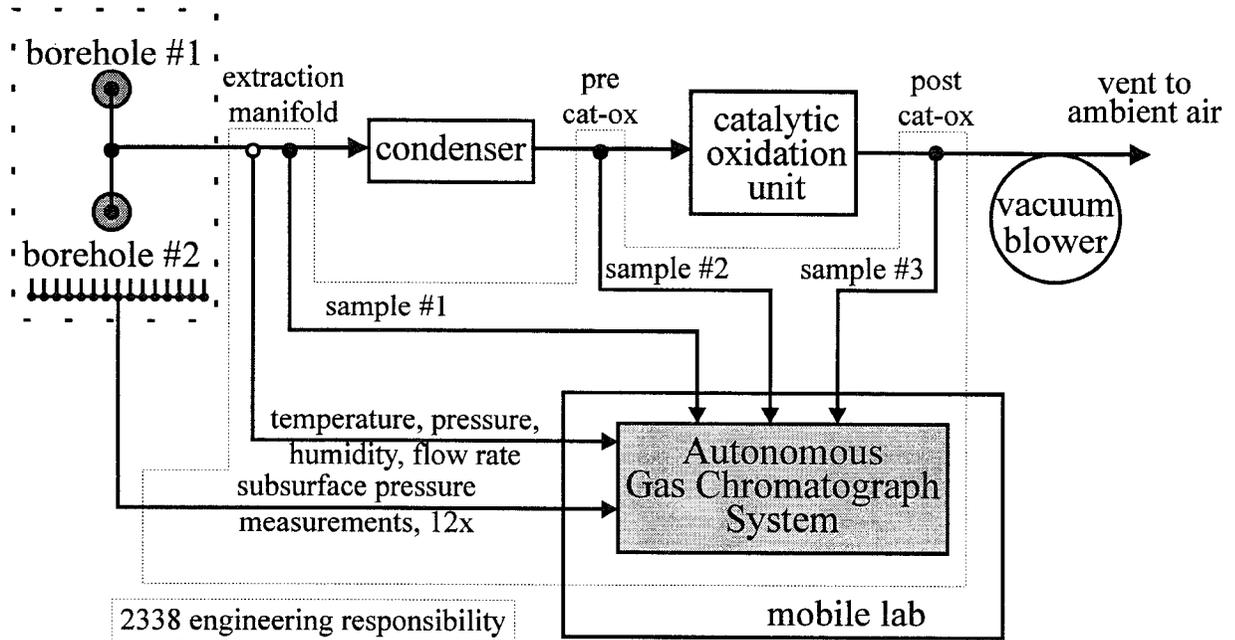
1.4 Manufacturing Control Subsystems Department Contribution

The mission of the autonomous GC system is to collect data to help characterize several aspects of the TEVES experiment. These include:

- VOC concentrations in the untreated borehole effluent
- extraction manifold flow rate
- extraction manifold temperature, pressure, and relative humidity
- mass removal rates for a select list of VOCs
- mass removal rates for water
- efficiency of the catalytic oxidation system
- mass discharge rates of VOCs into the ambient air
- subsurface pressure profile.

1.5 Target Analytes

The gas chromatograph method quantifies the following compounds with nominal detection limits ranging from 2 ppm to 1,000 ppm calibrated, but with the capability to extend lower and higher.

Compound	CAS No.
Dichlorobenzene (1,2-)	95-50-1
Ethyl Benzene	100-41-4
Freon 113	76-13-1
Pentane	109-66-0
Tetrachloroethylene (PCE)	127-18-4
1,1,1-Trichloroethane (TCA)	71-55-6
Trichloroethylene (TCE)	79-01-6
Xylene (o- isomer)	108-38-3
Xylene (m- isomer) *	95-47-6
Xylene (p- isomer) *	106-42-3

* m-Xylene & p-Xylene coelute

1.6 Quality Control Measures

The system is operated in accordance with the QC/QA requirements described in:

Resource Conservation and Recovery Act, Research Development, and Demonstration Permit for Thermal Enhanced Vapor Extraction System. issued by the New Mexico Environment Department, Santa Fe, New Mexico, May 26, 1994.

To this end the following were incorporated:

- twice daily calibration verification with a NIST-traceable calibration gas
- twice daily zero air certification to establish lower detection limits
- periodic measurement of parameters that impact data quality (mobile lab temperature, gas supply pressures, valve states, sample flow rate).

2.0 Hardware Subsystems

The autonomous GC system consists of six hardware subsystems:
- sample transfer lines
- sampler
- gas chromatograph
- extraction manifold instrumentation
- computer and data acquisition hardware
- gas supplies.

2.0.1 View of Autonomous GC inside Lab building
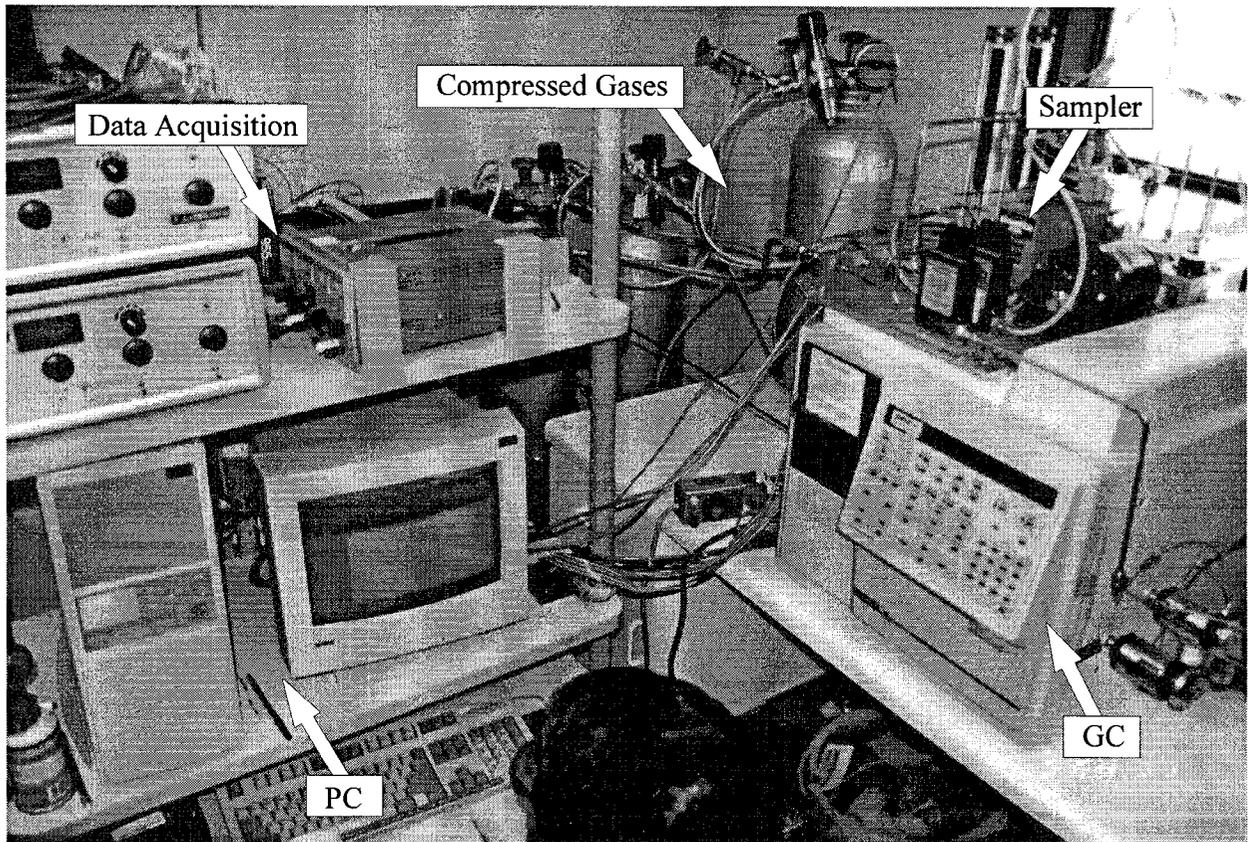
2.0.1 Hardware Subsystem Block Diagram

```
┌──────────────┐     ┌─────────┐     ┌──────────────┐     ┌──────────────┐
│     Gas      │◄────│ Sampler │◄────│   Sample     │◄────│              │
│ Chromatograph│     │         │     │Transfer Lines│     │    TEVES     │
└──────────────┘     └─────────┘     └──────────────┘     │              │
                                                          └──────────────┘
                                                                 │
                                                          ┌──────────────┐
                                                          │  Manifold &  │
                                                          │  Subsurface  │
┌──────────────┐     ┌──────────────────────────┐        │   Pressure   │
│              │     │      ┌──────────┐         │        │Instrumentation│
│ Gas Supplies │     │      │          │         │        └──────────────┘
│              │     │      └──────────┘         │
│   ∩ ∩ ∩      │     │   ▌▌▌▌▌▌▌▌  ▭            │
│              │     │  Computer & Data Acquistion│
└──────────────┘     │     & Control Hardware    │
                     └──────────────────────────┘
```
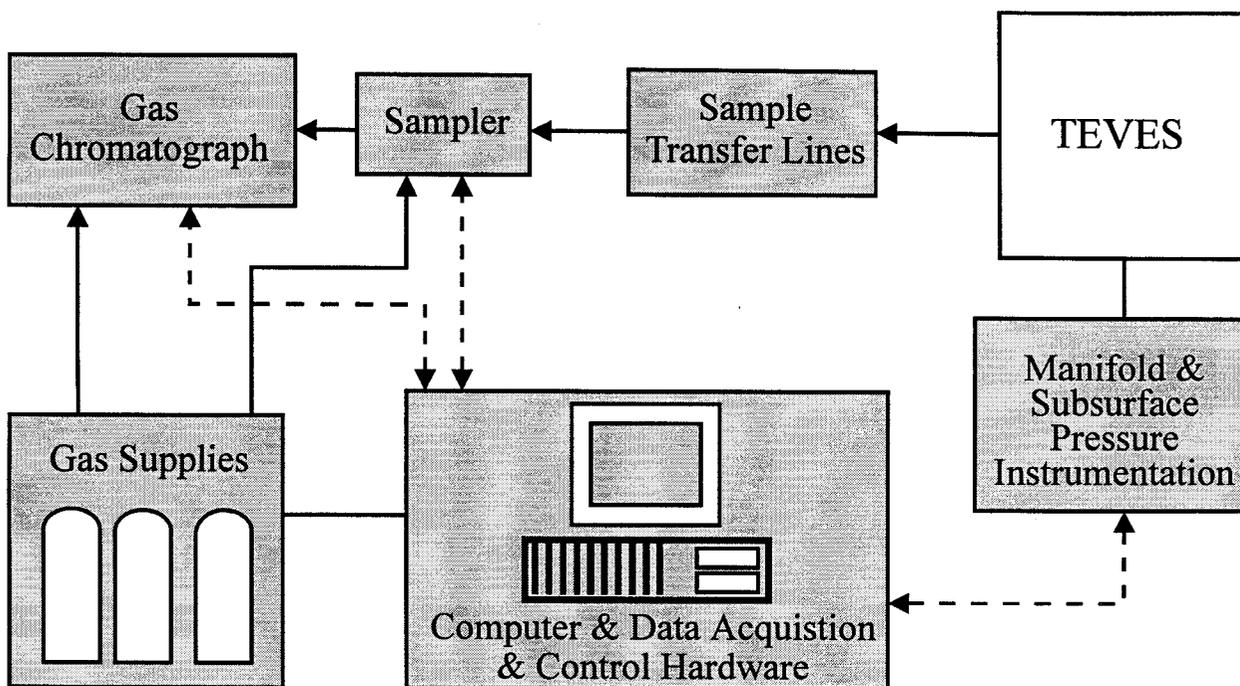
2.1 Sample Transfer Lines

The sample transfer lines (Figure 2.1) are designed to deliver a small fraction (<1%) of TEVES vapors to the mobile lab where the autonomous GC is located. Three TEVES vapor sources are monitored:

- extraction manifold (untreated borehole effluent)
- pre-cat-ox (dried vapors before catalytic oxidation treatment)
- post-cat-ox (vapors after catalytic oxidation treatment)

Each source has it's own independent transfer subsystem with the following major components:
- heated Teflon™ tubing
- pump
- particle filter

A tee between the pump and heated lines is the access point for the sampler subsystem. The 25 foot long Teflon™ lines are heated to 100°C to prevent condensation of VOCs and water vapor. The orientation of the components prevents condensation from entering the sampler and fritted filters prevent particulates from entering the sampler subsystem.. The unsampled portion is vented through a charcoal filter to the outside air.

2.1.1. Sample Transfer Subsystem Design Layout
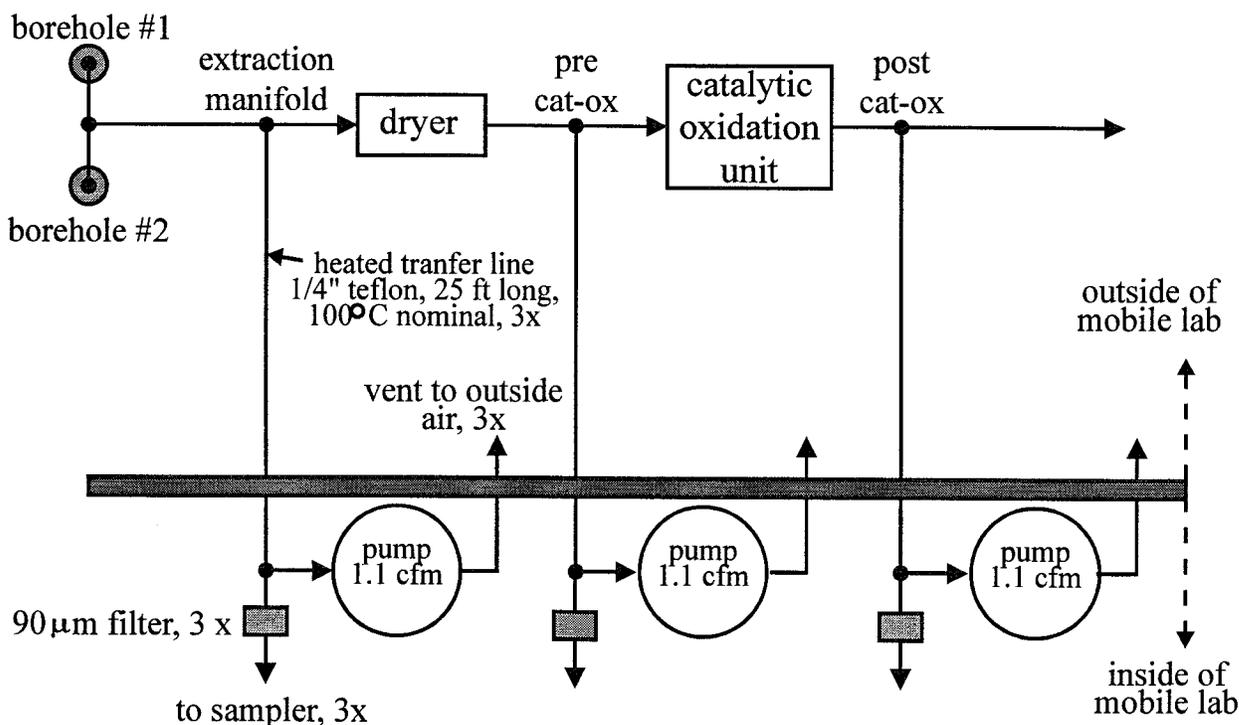
2.2 Sampler

The sampler (Figure 2.2) selects the sample source of interest and conditions the sample for injection onto the column. The major components are

- Valco 6 port switching valve
- Nafion™ dryer
- Tylan FC-260 precision mass flow controller
- rotary vane air pump
- 1 cc sample loop
- 10 port, 2 position injector valve.

The mode of operation is to inject a repeatable volume of sample using constant flow rate sampling through a sample loop. The sample loop volume was carefully selected so that no sample dilution or preconcentration is required to meet the target detection limits for the GC. The sample flow rate was selected to be high enough to eliminate errors due to diffusion effects while keeping pressure drops reasonably low. In addition, a volumetric purge of about 500x is performed between sample changes to minimize carryover. Because of the extremely high relative humidity of the samples, a Nafion™ membrane dryer is used for drying all samples upstream of the mass flow controller and sample loop.

The rotary vane pump continuously circulates whichever sample source is selected in order to purge the lines and minimize carryover between runs. The sample source of interest is selected by the six port valve, which diverts the sample stream through the Nafion™ dryer, mass flow controller, then through a 1 cc sample loop. The mass flow controller regulates flow rate at a

constant, preset level (100 cc/min) independent of source pressure. After a 2 minute purge time (a volumetric purge of 200 times), the 10 port valve changes position, injecting the contents of the sample loop (while flow rate is held constant) onto the chromatographic column. After sample injection, the 6 port switching valve is reset to position 1 to purge the sampler with relatively clean room air).

2.2.1 Sample Sources

There are five vapor sample sources, three from the TEVES site and two used for quality control.
- extraction manifold (untreated borehole effluent)
- pre-cat-ox (dried vapors before catalytic oxidation treatment)
- post-cat-ox (vapors after catalytic oxidation treatment)
- NIST-traceable calibration verification standard (to monitor GC calibration stability)
- UHP zero air (to establish lower detection limits)

2.2.2 Sampler Design Layout
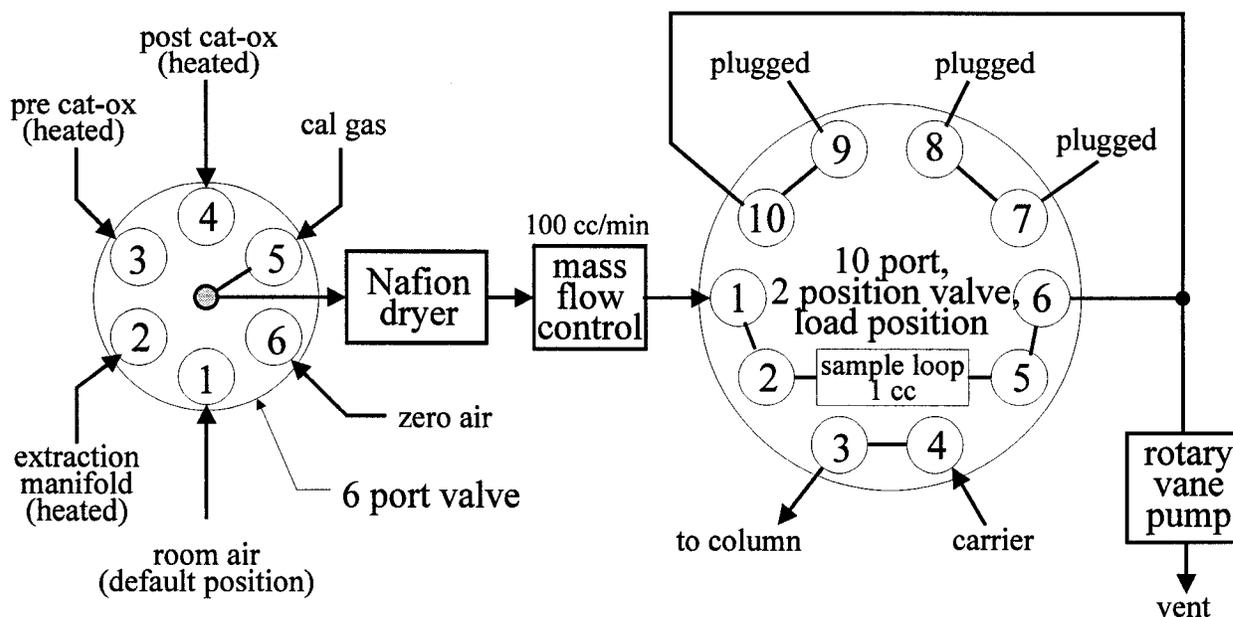
Because of the extremely high relative humidity of the samples, a Nafion™ membrane dryer is used for drying all samples upstream of the mass flow controller and sample loop. In the worst case design condition, the dryer is designed to reduce sample dew point to 0°C or lower. Although we have attempted by design to minimize the potential for condensation of water and or VOCs, we have no means for verifying that condensation does not occur.

2.2.3 Nafion™ Dryer Design Layout

hot, wet zone   transition zone   cool, dry zone
$100°C$, dp $=100°C$ temperature > dp $25°C$, dp $= 0°C$

"wet" sample in ⟶ | NAFION Dryer, Permapure #MD-190-24S | ⟶ 100 cc/min ⟶ "dry" sample out

"wet" air out ⟵ | | ⟵ 200 cc/min (2x sample flow rate)

mass flow control

ultra zero air
thc < 0.1 ppm
dp < -40°C
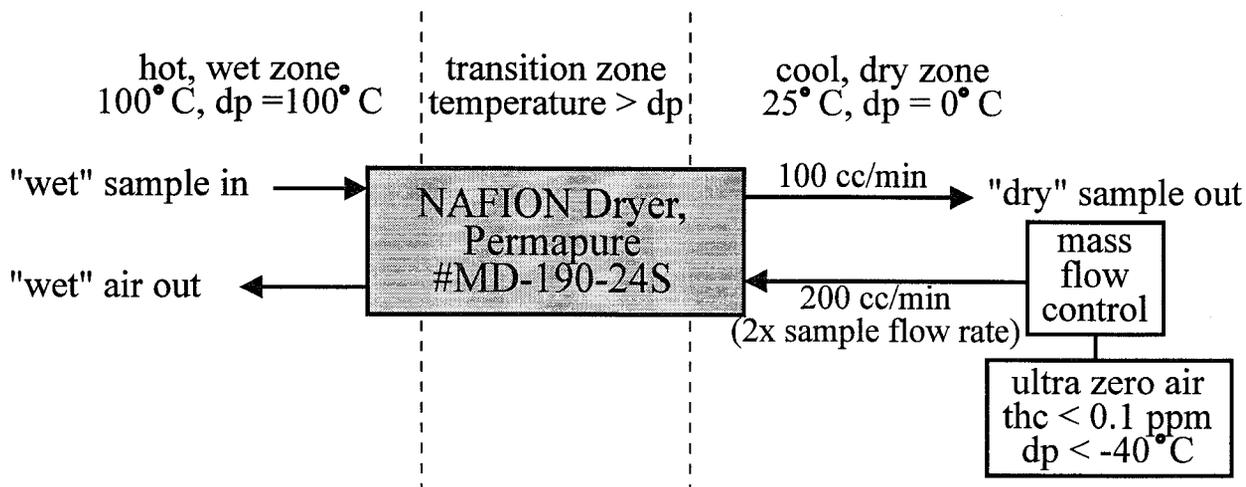
2.2.4 Sample Loop Volume

The sample loop size (1 cc) was selected so that the concentration of any of the target analytes in a 1 cc sample would fall within our target detection limits (10 ppm to 1,000 ppm) and also fall within the range bracketed by the FID minimum detection limit and the maximum column capacity.

Minimum sample volume is driven by the detection limit of the flame ionization detector (FID). The detection limit for the FID is conservatively estimated to be about 1 nanogram, although much less may be possible for some compounds.

Maximum sample volume is limited by the capacity of the column. The capacity of the 0.53 mm ID capillary column is conservatively estimated to be 1000 nanograms per component, but much more is probable for most compounds.

2.2.5 Sample Rate

A sample rate of 100 cc/min was chosen because it is
- low enough to keep pressure drops within reasonable limits
- high enough to eliminate errors due to diffusion
- high enough to keep purge times reasonably short.

2.3 Gas Chromatograph

The gas chromatograph (GC) is a Varian model CX3400 with the following features.
- wide bore capillary column (Restek MXT-vol), designed specifically for volatile organic compound separation.
- flame ionization detector (see below)
- programmable column temperature from ambient to 250°C
- carrier gas = Helium
- makeup gas = Helium

- FID fuel = Hydrogen

The chromatographic method is described in section 3.4.

2.3.1 Flame Ionization Detector

A flame ionization detector (FID) was used because it is responsive to almost all organic compounds, and has more than enough sensitivity for the TEVES application. FID response is greatest to hydrocarbons and decreases with increased substitution of other elements. The FID has the advantages of a wide dynamic range (10^7), low sensitivity to water and most inorganic compounds, and requires essentially no maintenance.

2.4 Extraction Manifold and Subsurface Pressure Instrumentation

In addition to performing its primary mission of quantifying VOCs by gas chromatography, our system also monitors a variety of other parameters needed to characterize the TEVES experiment. These include extraction manifold temperature, pressure, humidity, and flow rate, barometric pressure, and a variety of subsurface pressures. Manifold temperature and relative humidity are measured directly by a Vaisala HMP-235 humidity transmitter. Manifold flow rate is measured indirectly by an averaging pitot tube Omega # FPT-6130. Manifold pressure, barometric pressure, and 12 subsurface pressures are measured by a customized pressure scanning system developed by Science Engineering Associates (SEA).

2.4.1 Extraction Manifold & Subsurface Pressure Instrumentation

computer interface

temperature → temperature/humidity sensor (Vaisala #HMP235)

humidity →

RS232, COM 6

RS232, COM 1

manifold pressure, 4x → pressure scanner

subsurface pressure, 12x →

barometric pressure sensor (Vaisala #PTA427)

datalogger (Campbell Scientific #21X)

flow rate → pitot tube (Omega #FPT-6130)

hi

lo

differential pressure sensor (Setra #264)
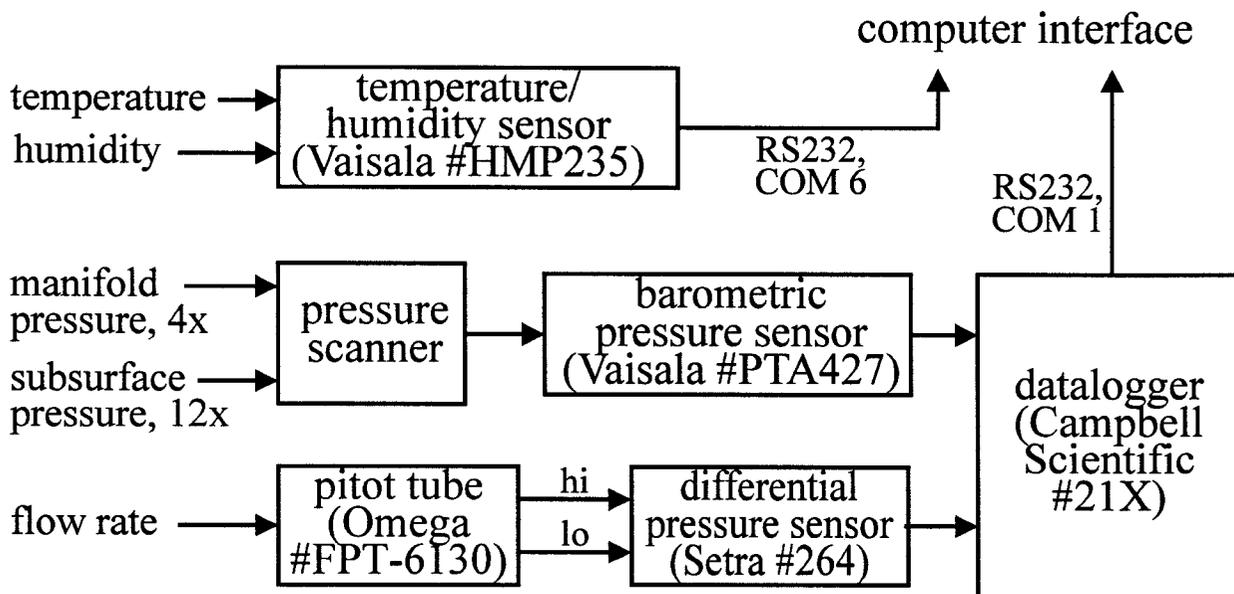
2.5 Computer and Data Acquisition Hardware

All system functions are controlled by a DEC model 466d2 MT computer. To run the software with acceptable response time a 66 MHz 486 with at least 16 MB RAM is required. A National

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Instruments A/D board with signal conditioners and a Hostess 8 channel RS232 port board are used for data acquisition and control. Software is discussed in detail in Section 5.0.

2.5.1 Computer & Data Acquisition Hardware Block Diagram

lab temperature sensor	sampler mass flow controller	dryer mass flow controller

helium pressure gage

hydrogen pressure gage

cal gas pressure gage

zero air pressure gage

signal conditioner

temperature & humidity transmitter

6 port valve

486PC 66 Mhz

A/D-D/A

16 Mb RAM

RS232 serial card

data logger
- manifold pressure
- pitot delta-pressure
- barometric pressure
- subsurface pressures

15"monitor

video

240 Mb harddisk

90 Mbyte Bernoulli

parallel port

mouse

mouse port

GC i/f card

switch

Gas Chromatograph

2.5.2 Computer Electrical Interface

486 PC

5B01 backplane w/ signal conditioners

A/D-D/A MIO 16 F5

A/D ch 0	all 0-5V	5B34 RTD module	Ω	lab temperature, 100 Ω Pt RTD
A/D ch 1		5B32 current module	4-20 mA	hydrogen pressure
A/D ch 2		5B32 current module	4-20 mA	calibration gas pressure
A/D ch 3		5B32 current module	4-20 mA	zero air pressure
A/D ch 4		5B41 voltage module	0-5V	sample mass flow control read
A/D ch 5		5B32 current module	4-20 mA	helium pressure
A/D ch 6		5B41 voltage module	0-5V	dryer mass flow control read

D/A ch 0 — 0-5V → sample mass flow control set
D/A ch 1 — 0-5V → dryer mass flow control set

8 channel RS232 card (COM 2,3,6,7,8 not used).

COM 4 ↔ Vaisala HMP 235 humidity/ temperature transmitter

COM 2 ↔ Valco serial valve interface ↔ 6 port valve

COM 1 ↔ datalogger

COM 5 ↔ GC trigger

GC ADC & serial i/f

serial comm cable
FID A signal (not used)
FID B signal

Varian 3400CX Gas Chromatograph

2.6 Gas Supplies

Five gases are used.

Gas	purpose	source
UHP Helium	carrier & makeup gas for GC	cylinder
UHP Hydrogen	FID fuel	cylinder
Compressed Air	FID air	compressor
UHP Zero Air	calibration blank & NAFION drier	cylinder
Calibration Gas	NIST-traceable calibration verification standard	cylinder

The GC back panel gas hookups are shown in Appendix B. Assembly diagrams for the helium, hydrogen, calibration gas, and zero air supplies are shown in Appendix C. The helium and hydrogen supplies are scrubbed prior to delivery to the GC by water/oxygen/hydrocarbon filters. Compressed air is supplied by an air compressor. All compressed gas cylinder pressures are monitored by the computer to ensure adequate gas supplies. Each manifold was leak tested using Snoop up to the pressure set point (100 psi) of the pressure relief valves.

3.0 Summary of Operation

The autonomous GC system collects data to characterize several aspects of the TEVES experiment. The system operates continuously 24 hours a day, starting a new operating cycle (or task) every two hours. During each task, the following operations occur automatically:

- one of five vapor sources (calibration gas, zero air, extraction manifold, pre catalytic oxidation unit, post catalytic oxidation unit) is selected for sampling
- the sample is prepared for injection into the GC
- the sample is analyzed using a wide bore capillary gas chromatography and 9 specific analytes are quantified
- parameters that impact data quality (trailer temperature, gas supply pressures, valve states, sample flow rate) are monitored.
- extraction manifold physical conditions are monitored (temperature, pressure, relative humidity)
- the mass removal rates for VOCs and water are calculated
- a summary data file is generated. This is designed to be imported into an EXCEL spreadsheet which will provide a quick and easy platform for data analysis and presentation
- a backup copy of the TEVES subdirectory in made onto a Bernoulli disk.

3.1 Installation and Turn-on

Prior to unattended operation, the system needs several manual adjustments, described in detail in Appendix A. Subsequently, all operations run unattended under computer control. Software is discussed in Section 5.0.

3.2 Unattended Operation

Five types of tasks are performed each day. Each task follows the same procedure as any other task with one exception - the choice of sample source. There are five sample sources, three from the TEVES and two used for data quality control. A scheduler program calls one of the five tasks to execute starting at a given time of day according to the following schedule:

3.2.1 TEVES Sampling Schedule

time	task name	sample source	purpose
00:00	cal gas	NIST-traceable cal gas	calibration verification
02:00	zero air	zero air (dp<-40 C, THC<0.1 ppm)	establish lower detection limit & measure carryover
04:00	manifold	extraction manifold	quantify vapors in untreated borehole effluent
06:00	pre cat ox	after condenser	pre cat-ox value
08:00	zero air	zero air (dp<-40 C, THC<0.1 ppm)	establish lower detection limit
10:00	post cat-ox	exhaust stack	destruction verification
12:00	calibrate	NIST-traceable cal gas	calibration verification
14:00	zero air	zero air (dp<-40 C, THC<0.1 ppm)	establish lower detection limit & measure carryover
16:00	manifold	extraction manifold	quantify vapors in untreated borehole effluent
18:00	pre cat-ox	after condenser	pre cat-ox value
20:00	zero air	zero air (dp<-40 C, THC<0.1 ppm)	establish lower detection limit
22:00	post cat-ox	exhaust stack	destruction verification

The sequence of operation for a typical cycle is:
1. initialize valve positions, GC settings, sample flow rate
2. read lab temp, pressures, flow rate
3. select sample source
4. dry the sample
5. purge sample loop
6. inject sample
7. run chromatographic method to measure concentrations of target analytes
8. calculate VOC mass removal rate, water mass removal rate, manifold flow rate
9. integrate and archive data

3.3 Chromatographic Method

The chromatographic method uses a single wide-bore capillary column and flame ionization detection. The column is a Restek model MXT-VOL (30 meters long, 3.0 mm thick film, 0.53 mm ID) designed specifically for volatile organic compound separations. A chromatogram is generated by injecting the sample loop contents directly on column, then reading the FID output while the oven temperature is controlled to a specific temperature versus time profile. The profile was selected to resolve as many VOCs as possible given the following constraints:

- the GC does not have sub-ambient temperature capability
- only a single general purpose column is used
- cycle time must be 2 hours or less.

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After the heaviest *identified* compound (Dichlorobenzene) elutes from the column, the column is baked out to condition the column and to remove any *unidentified* heavy compounds that might otherwise carry over into the next chromatography cycle. This is incorporated into every run by ramping the column temperature to 200°C for a short period of time. A cool down period of approximately 35 minutes is required to allow the oven to return to its initial temperature after the bakeout. The trailer into which the GC is placed must be capable of maintaining the temperature less than 20°C.

3.3.1 Column Oven Temperature Profile

time after injection, minutes (not to scale)
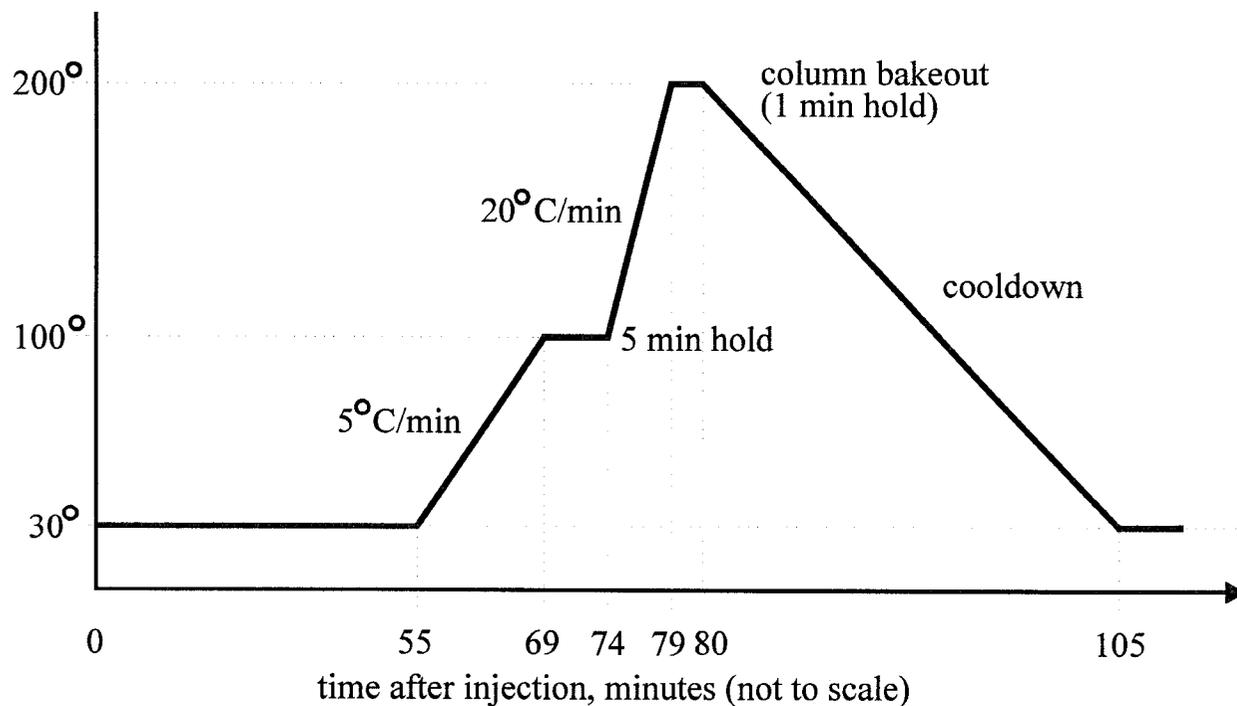
3.3.2 GC gas flow rates

The GC requires helium as a carrier and makeup, hydrogen and air for the FID. The flow rates are:

Helium carrier	7 cc/min
Helium makeup	20 cc/min
FID Hydrogen	30 cc/min
FID air	300 cc/min

3.3.3 GC Results

After a chromatogram is generated, retention time, peak area, and concentration of each compound are calculated by the Varian GC Applications software. A typical report is shown here:

```
Title       : TEVES analysis
Run File    : D:\TEVES\941115\0000.RUN
Method File : C:\STAR\STARTUP1.MTH
Sample ID   : TEVES calibration run

Injection Date: 15-NOV-94 0:02 AM

Operator    : FJ Peter          Detector Type: ADCB (10 Volts)
Workstation: DECPC              Bus Address  : 16
Instrument : Varian Star #1     Sample Rate  : 2.50 Hz
Channel    : B = B              Run Time     : 80.007 min

********** Varian GC Star Workstation *********** Version 3.0 *************

Run Mode        : Analysis
Peak Measurement: Peak Area
Calculation Type: External Standard

                           Retention  Time                         Width
Peak     Peak     Result     Time    Offset     Area      Sep.      1/2
No.      Name     (ppmv)     (min)    (min)    (counts)   Code     (sec)
---   ----------  --------   ------   -------   --------    --      -----
 1                    0.0    3.369                  110              3.2
 2    PEN            17.9    4.561    0.004       11156             5.8
 3    FRE            17.3    5.083    0.001        3767             9.8
 4    TCA            19.3   10.427    0.019        4659            17.9
 5    TCE            18.5   15.378    0.007        4516            17.7
 6    PCE            18.6   37.026   -0.064        4797            39.7
 7    EBZ            20.1   59.790   -0.080       24114            23.5
 8    XMP            54.8   60.897   -0.075       51406            18.9
 9    X-O            21.9   64.297   -0.038       27432            12.5
10    DCB            15.5   75.083   -0.010       18796             8.5
11                    0.0   79.170                  298             0.0
12                    0.0   79.441                  571             0.0
---   ----------  ========   ------   =======   ========    --      -----
      Totals:        204.0           -0.238      151621

Total Unidentified Counts :        979 counts

Detected Peaks: 16    Rejected Peaks: 4      Identified Peaks: 9

Amount Standard: 1.000000   Multiplier: 1.000000   Divisor: 1.000000

Baseline Offset: -7 microVolts

Noise (used): 30 microVolts - monitored before this run

*****
```

4.0 Calibration & Verification

The relatively high expected concentrations (up to 1000 ppm by volume) of some compounds places restrictions on *unattended* calibration of the GC. The problem is that compounds with low vapor pressures cannot be volatilized at even modest cylinder pressures (10s of psi). The consequence is that calibration mixtures that bracket the high end of our concentration range of interest cannot be made in sufficient quantity, practically speaking, to support a long-term unattended application. For this reason, calibration and verification was divided into two groups: **laboratory calibration** and **field verification**.

4.1 Laboratory Calibration

All laboratory GC calibration runs were performed prior to the field tests and used the identical sampling procedure and hardware at the site. Multi-point calibrations (0, 2, 20, 200, 1000 ppm by volume) were performed in order of increasing concentrations with three replicates at each level for each compound. Absolute retention time on the column is used for compound identification and peak area is used for quantitation. All results are expressed as parts per million by volume (ppmv) at 20°C, 760 mm Hg. The calibration procedure and calculations are described in detail in Appendix D.

4.2 Field Verification

To ensure data quality, two types of quality control samples are taken. First, the calibration stability of the GC is verified on 12 hour intervals using a NIST-traceable gas standard (nominally 20 ppm) from Scott Specialty Gases. The certificate of analysis is given in Appendix E. Second, the lower detection limit is measured and carryover quantified by periodically analyzing zero air blanks.

4.3 Typical Calibration Chromatogram

Typical Calibration Chromatogram
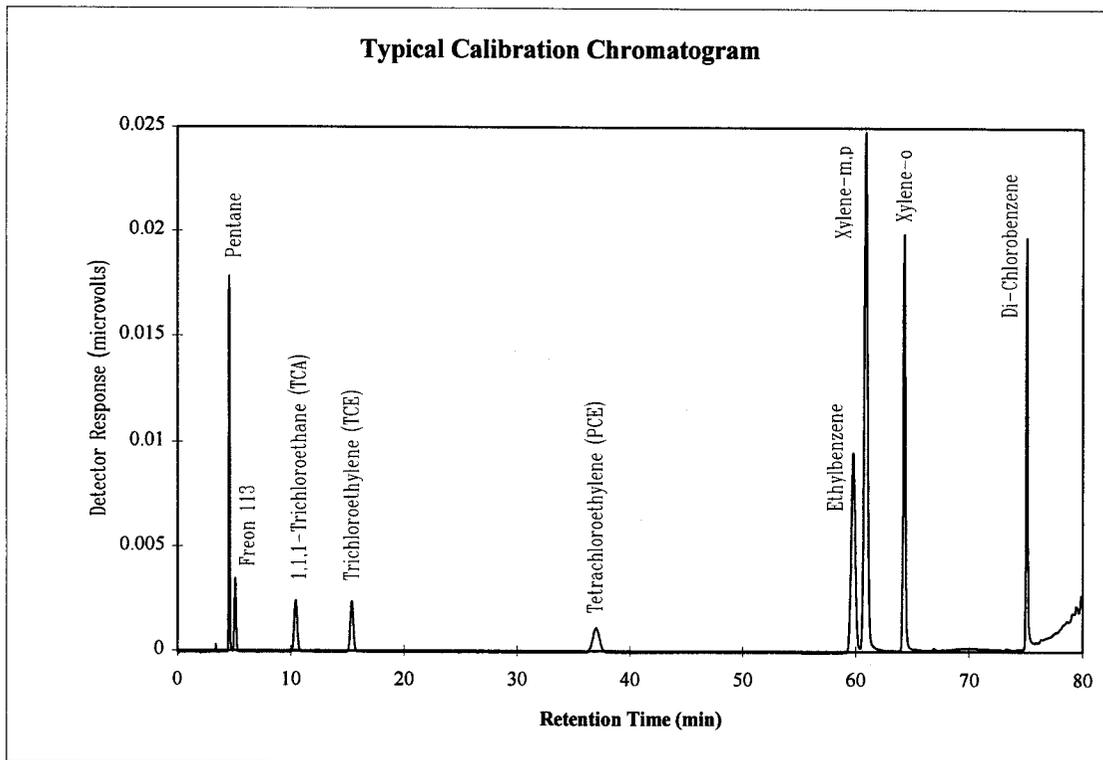
4.4 Typical Calibration Report

```
Title        : TEVES analysis
Run File     : D:\TEVES\941115\0000.RUN
Method File  : C:\STAR\STARTUP1.MTH
Sample ID    : TEVES calibration run

Injection Date: 15-NOV-94 0:02 AM

Operator    : FJ Peter          Detector Type: ADCB (10 Volts)
Workstation : DECPC             Bus Address  : 16
Instrument  : Varian Star #1    Sample Rate  : 2.50 Hz
Channel     : B = B             Run Time     : 80.007 min

*********** Varian GC Star Workstation ************ Version 3.0 **************

Run Mode          : Analysis
Peak Measurement: Peak Area
Calculation Type: External Standard
```

Peak No.	Peak Name	Result (ppmv)	Retention Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)
1		0.0	3.369		110		3.2
2	PEN	17.9	4.561	0.004	11156		5.8
3	FRE	17.3	5.083	0.001	3767		9.8
4	TCA	19.3	10.427	0.019	4659		17.9
5	TCE	18.5	15.378	0.007	4516		17.7
6	PCE	18.6	37.026	-0.064	4797		39.7
7	EBZ	20.1	59.790	-0.080	24114		23.5
8	XMP	54.8	60.897	-0.075	51406		18.9
9	X-O	21.9	64.297	-0.038	27432		12.5
10	DCB	15.5	75.083	-0.010	18796		8.5
11		0.0	79.170		298		0.0
12		0.0	79.441		571		0.0
	Totals:	204.0		-0.238	151621		

```
Total Unidentified Counts :     979 counts

Detected Peaks: 16   Rejected Peaks: 4     Identified Peaks: 9

Amount Standard: 1.000000   Multiplier: 1.000000   Divisor: 1.000000

Baseline Offset: -7 microVolts

Noise (used): 30 microVolts - monitored before this run

*****
```

5.0 Software

The major software elements, all operating under Microsoft Windows, are:

1) Labview virtual instruments for instrument monitoring and control
2) the Varian GC Star Workstation software for controlling the GC method
3) several Visual Basic programs to provide timing synchronization between the Labview VIs and the Star Workstation and for creating the summary data file used by the EXCEL spreadsheet
4) an EXCEL spreadsheet for data manipulation and graphical presentation

5.1 Software Architecture
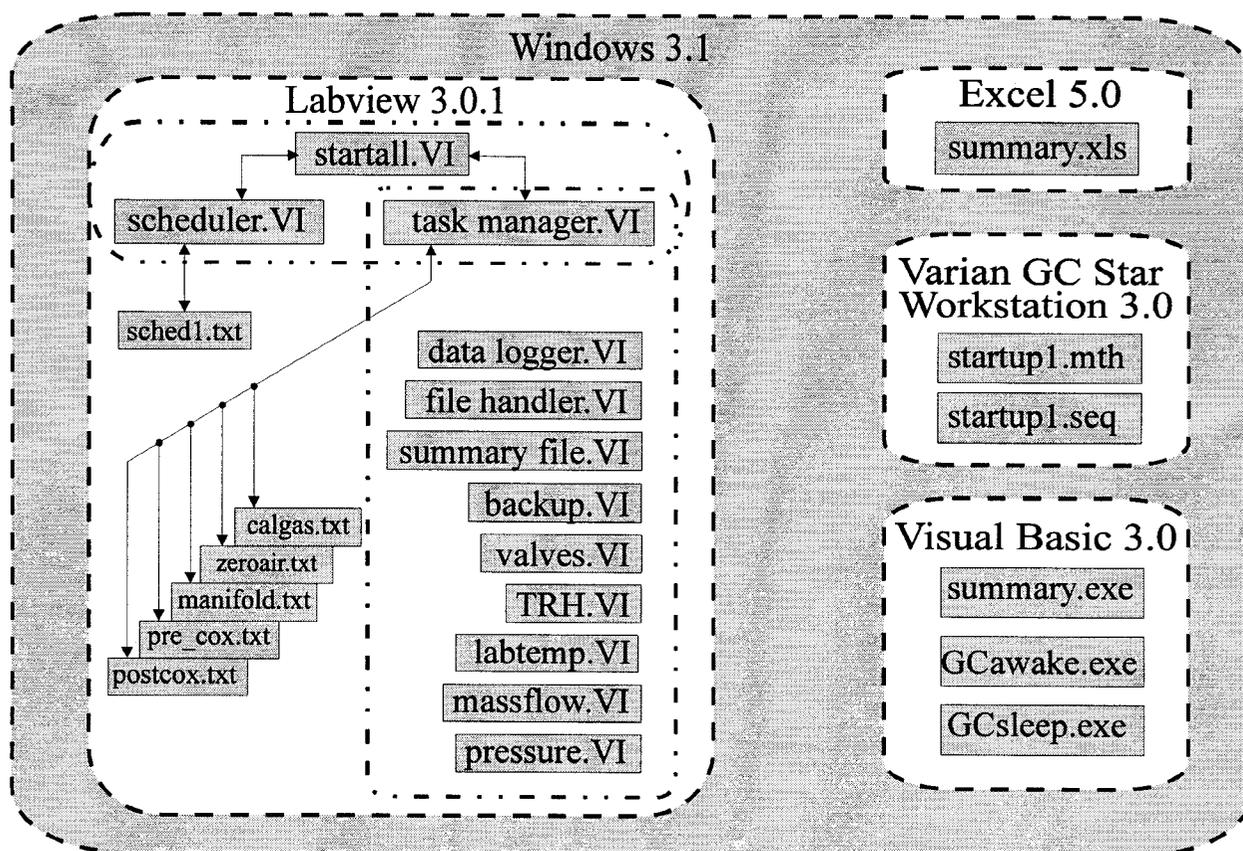
5.1.1 Labview Virtual Instruments

Most instrument control functions are written as Labview virtual instruments (VIs). All VIs and their respective functions are listed below:

virtual instrument name	description
startall.VI	starts the two main controlling VIs: scheduler.VI & task manager.VI.
scheduler.VI	reads a schedule file containing the time of day based sequence files to pass to the task manager and signals the task manager to begin sequence execution.
Task manager.VI	triggers specific events (such as reading temperatures, pressures, actuating valves) based on times contained in task file.
GC.VI	calls GC Star Workstation software
H2P.VI	reads hydrogen gas cylinder pressure
calgas.VI	reads calibration gas cylinder pressure
carrier.VI	reads helium gas cylinder pressure
TRH.VI	reads the temperature and relative humidity from the Vaisala instrument.
RTD.VI	reads lab temperature
mass flow controller.VI	sets and reads sampler flow rate & zero air flow rate for Nafion™ dryer
valves.VI	controls and reads position of Valco electrically actuated valves
datalogger.VI	reads and save datalogger data
file handling.VI	names & stores data files
backup.VI	backup to 90 Mbyte Bernoulli disk

5.1.2 GC Star Workstation Application

The GC is controlled by the Varian Star Workstation. Functions include calibration, column oven temperature control, sample inject valve control, FID output measurement, chromatographic analysis, and report generation.

5.1.3 Visual Basic Applications

There are three Visual Basic applications:

Gcawake.exe	opens and operates GC Star Workstation application
GCsleep.exe	closes Star Workstation application
summary.exe	generates a comma delimited data file, yymmdd.CSV which integrates all data files up to and including the given day into a single ASCII text file for uses by an Excel spreadsheet

5.1.4 EXCEL Spreadsheet

The summary data files, yymmdd.CSV, contain all relevant TEVES data in a form directly importable to a customized EXCEL spreadsheet. The spreadsheet provides a single integrated platform for analysis and presentation of all TEVES data. TEVES data may be accessed at any

time (up to the most recently completed operating cycle) by removing the Bernoulli disk used for backups and importing the summary data file into the EXCEL spreadsheet.

5.2 Software Sequence of Operation

After all the hardware (GC, data acquisition, sampling system, etc.) is turned on (see Appendix A), the software can be run. The sequence of software operation is:
1. the machine boots from the hard disk wherein CONFIG.SYS is executed, AUTOEXEC.BAT is executed.
2. the STARTALL.VI program opens all Labview Virtual instruments
3. the scheduler.VI waits for the system clock to trigger the appropriate task files at the appropriate times.
4. the task manager.VI waits for the system clock to trigger the hardware and data collection events at the appropriate times.
5. the GC method runs
6. at the end of each task, a set of data files containing all data acquired during that task (instrument readings, raw chromatograms, datalogger data, etc.) is saved to hard disk.
7. a summary data file is updated on the hard disk
8. all data files are backed up to the Bernoulli disk
9. wait for next task

5.3 Summary Data File

The summary data file contains the following data:
- date/time of sample collection
- sample location (zero air, calibration gas, extraction manifold, cat-ox inlet, or cat-ox exhaust)
- extraction manifold temperature, pressure, relative humidity, and pitot tube pressure differential
- species concentration for each target analyte (in units of ppm by volume @ STP).
- GC state of health measurements
- data logger pressure scanner data

5.4 Task Files

For the TEVES project, there are five task files, one for each sample source:

task file name	contains
manifold.txt	Extraction Manifold sample sequence
pre_cox.txt	Pre cat-ox sample sequence
postcox.txt	Post cat-ox sample sequence
calgas.txt	Calibration sequence
zeroair.txt	Zero air sequence

5.5 Data File and Data Directory Organization

Each subdirectory named as *yymmdd* is intended to hold the data files (chromatograms and other instrumentation data files) for the day defined by the subdirectory name. The data file name format is *hhmm.ext* where *hhmm* represents military time. The *.ext* is an extension identifying the contents of the datafile.

Subdirectory Name	Filename(s)	file type	description
C:\	autoexec.bat	batch	set PC environment
C:\DOS	DOS 6.2 files	see DOS manual	operating system
C:\WINDOWS	Windows 3.1 files	see Windows manual	operating system
C:\STAR	Star files	see Star manual	GC control
C:\LABVIEW	Labview files	see Labview manual	Labview application
C:\LABVIEW\TEVES	*.VI	*.VI	Virtual instruments
C:\VB	GCawake.exe GCsleep.exe summary.exe	*.exe	GC Star Workstation control creates summary data file
C:\TEVES	sched1.txt manifold.txt pre_cox.txt postcox.txt calgas.txt zeroair.txt	ASCII text	schedule file manifold sample task file pre cat-ox sample task file post cat-ox sample task file cal gas sample task file zero air sample task file
C:\TEVES\yymmdd	*yymmdd.CSV* *hhmm*.RTD *hhmm*.dat *hhmm*.hep *hhmm*.h2p *hhmm*.cg *hhmm*.TRH	ASCII text	summary data thru current day RTD temperature reading chromatogram report Helium pressure Hydrogen pressure reading cal gas pressure reading manifold temperature & ... ...relative humidity readings

6.0 Lessons Learned, Proposed System Improvements

6.1 Hardware

Sample Filtering. The mass flow controller on the post cat-ox sample line needed to be replaced several times because it was fouled by the "dirty" samples downstream of the cat-ox unit. A gravity trap for "heavy" particulates, followed by a graduated filter (multiple step, with finer filtering at each stage) is recommended.

Hydrogen Source. The compressed Hydrogen cylinder should be replaced by a Hydrogen Generator, which generates H_2 from distilled water on demand. This has two benefits:
1. it would enhance fire safety by limiting the volume of stored hydrogen and by eliminating the possibility of introducing a leak during cylinder changeout.
2. there would be no need to interrupt testing to replace empty cylinders.

Air Compressor. The current compressor is extremely loud and has minimal storage tank volume. Investing in a quieter compressor with a larger storage tank would have two benefits:
1. a more comfortable work space by significantly reducing noise.
2. in the event of an electrical power blackout, the larger storage tank would reduce the risk of the FID flaming out due to lack of air flow.

6.2 Software

The system test schedule and methods are currently coded as text files. This requires that the user has some facility with a text editor and requires an understanding of the required text file syntax. A graphical user interface (GUI) schedule editor that insulates the user from the details is highly recommended if frequent changes in test schedule and methods are required.

Appendix A: System Installation & Turn-on

Computer/Electrical System Turn-on

1. make sure all equipment, pumps, computer, and instruments are plugged in
2. turn on power to all instruments
3. turn on the GC, press the RESET button
4. run software (see software section)

Compressed Gas System Turn-on

1. close all valves in the manifold
2. open valve at gas cylinder fully
3. make sure it is open by reading pressure gauge on inlet of regulator
4. adjust regulator output pressure settings (±2 psi) to the following:
   - helium: 80 psi
   - hydrogen: 40 psi
   - zero air: 10 psi
   - cal gas: 10 psi
5. open all shut-off valves
6. at initial turn-on, the excess flow valve on the hydrogen tank will likely trip due to the initial surge of flow, requiring that it be reset. Reset it by simply pressing the red button.
7. leak check visually using "Snoop" leak detection fluid.
8. recheck pressure gauges for proper pressure and adjust regulator if necessary.

Setting GC Flow Rates

All gas flow rates were preset in the laboratory using a bubble flow meter. See the GC manual for instructions. The nominal flow rates are:
- helium carrier = 7 cc/min
- helium makeup = 20 cc/min
- hydrogen = 30 cc/min:
- FID air = 300 ml/min:

Lighting Flame Ionization Detector

1. make sure hydrogen and air flow rates are properly set
2. press *Shift* and *Ignite B* on front panel of GC and hold for 5 seconds.
3. make sure FID is lit by holding a cool shiny object next to exhaust port of FID. If lit, moisture will condense on the object. If not, recheck gas supply and flow rate settings.

Important: If loss of electrical power occurs for more than a few minutes, the FID flame will go out because the air compressor will stop supplying air. Although the software will begin to run when power returns, the FID may need to be relit per above instructions.

Appendix B: Gas Supply Hookups (back panel of GC)

FID AIR	AUX	FID H₂	CARRIER	MAKEUP

300 cc/min   30 cc/min   10 cc/min   20 cc/min

HC trap

H₂O trap

O₂, H₂O, HC trap

O₂, H₂O, HC trap

air compressor >500 cc/min @ 60 psi

UHP Hydrogen @ 40 psi

UHP Helium @ 80 psi
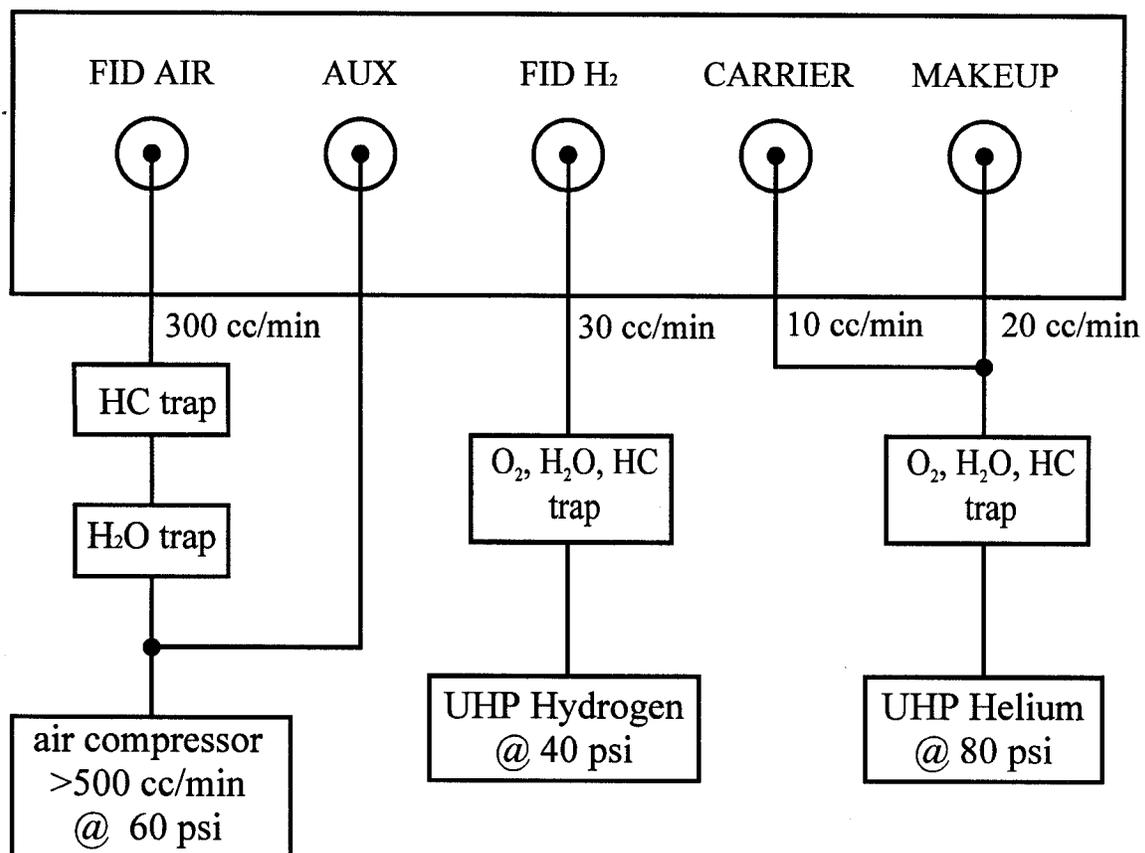
Appendix C: Compressed Gas Assembly Diagrams

Helium
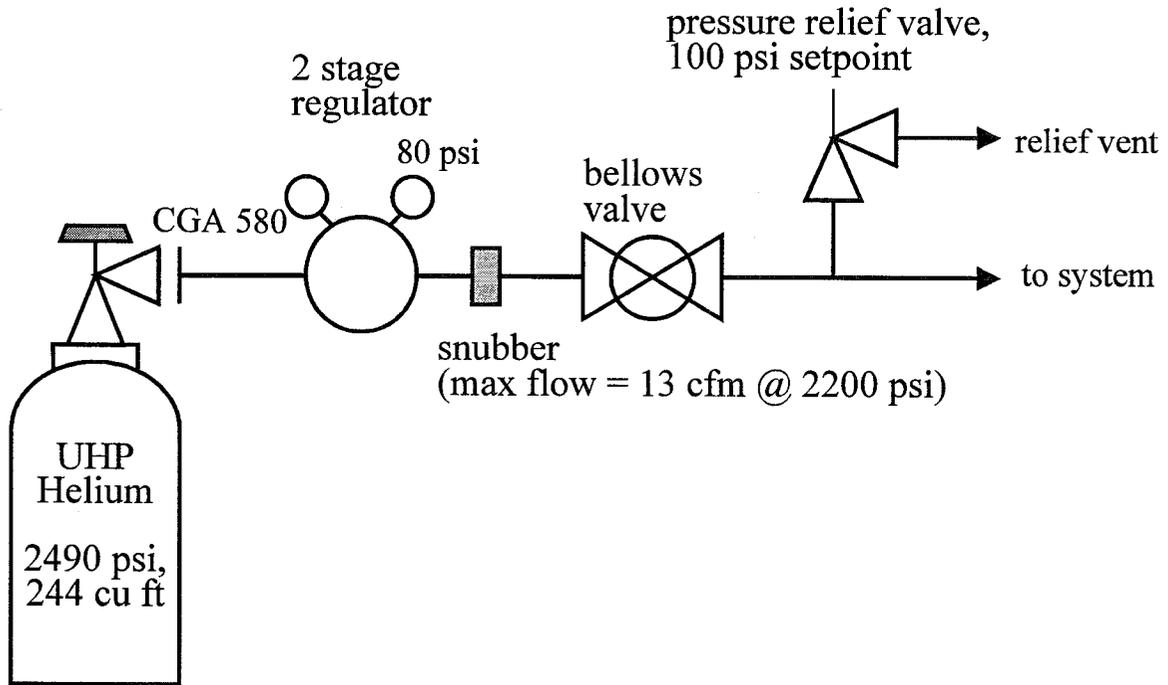
Hydrogen
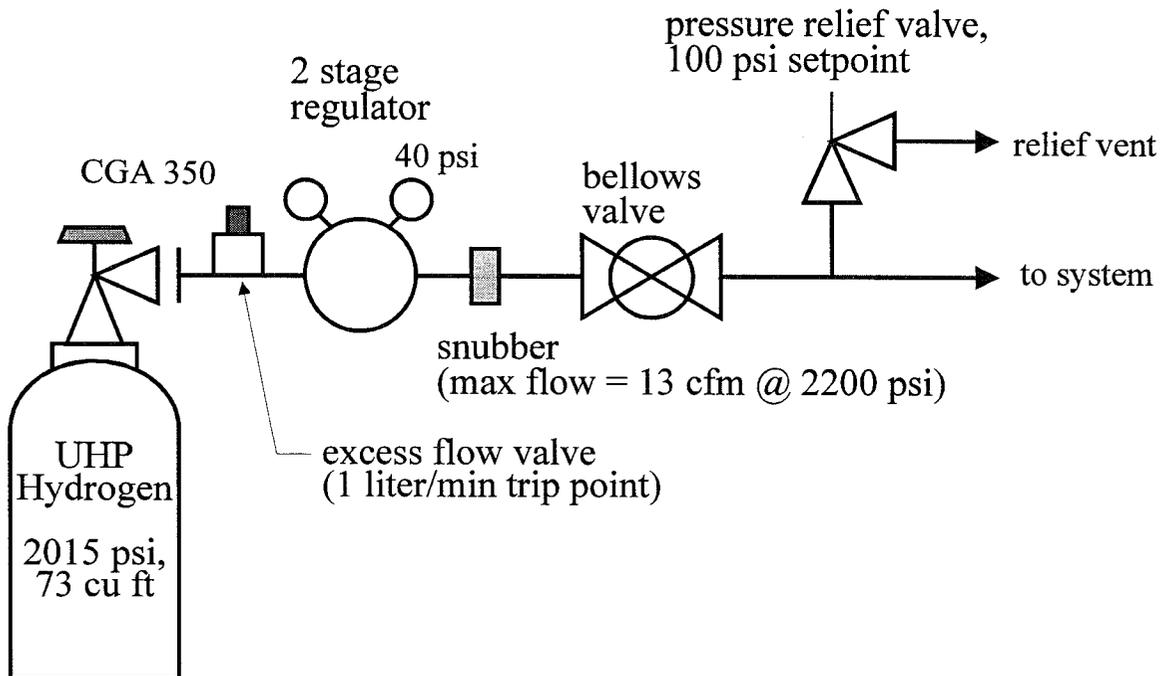
Zero Air
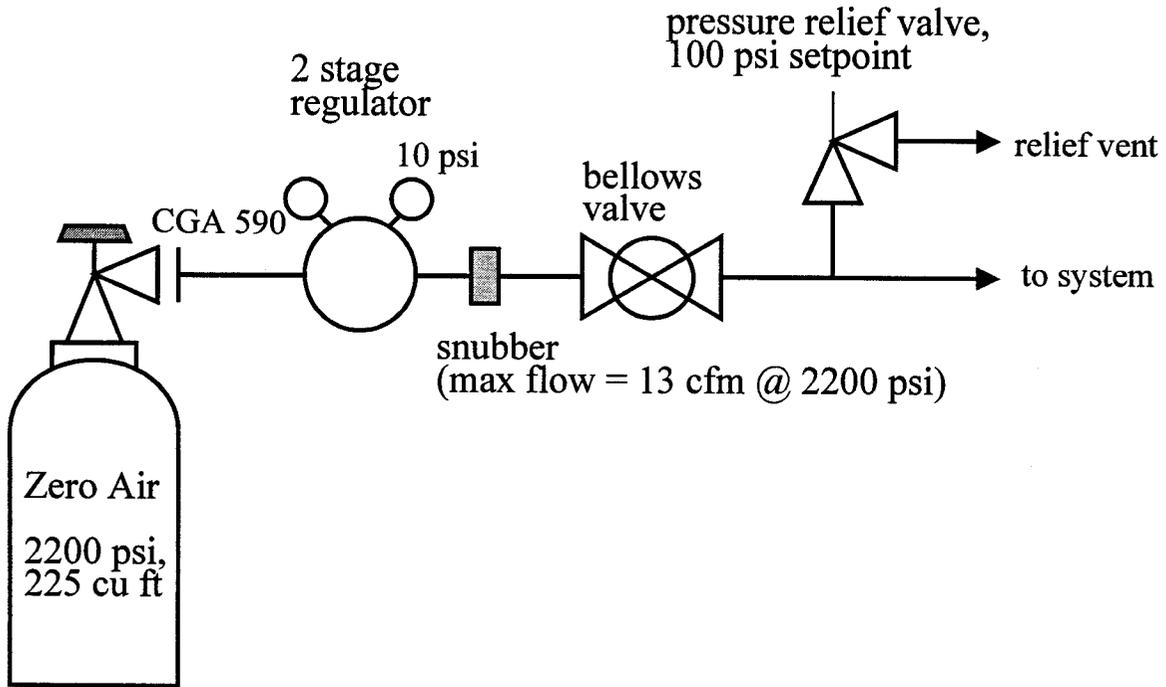
Calibration Gas
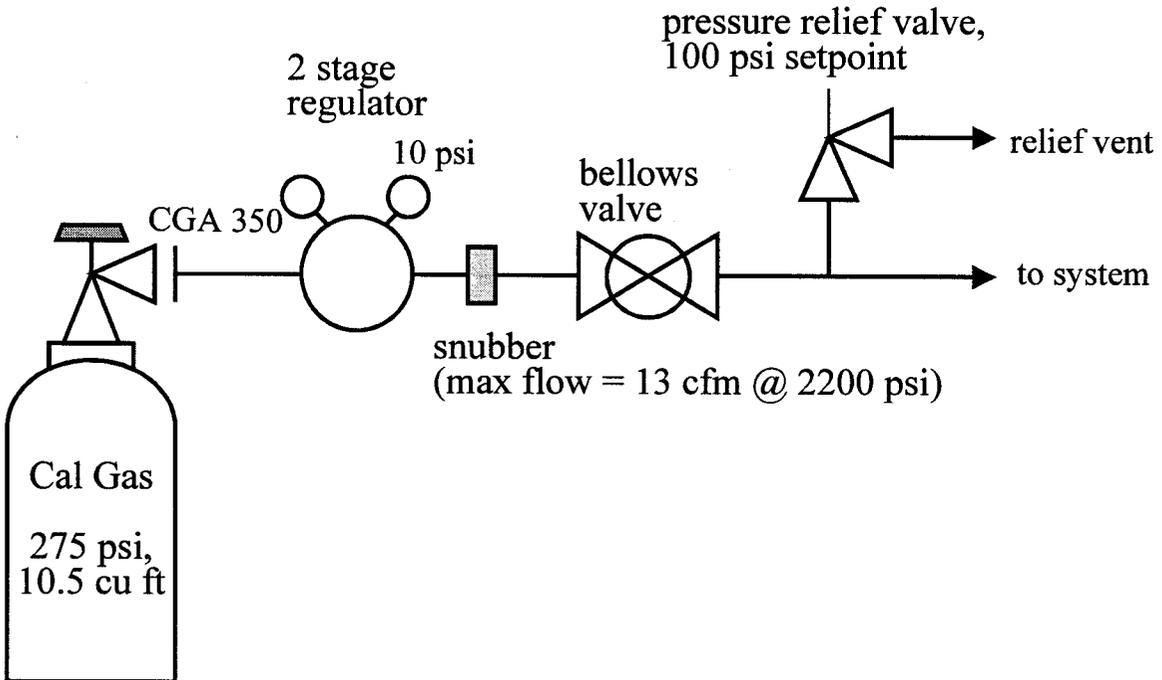
Appendix D: Calibration

Calibration Standard Preparation

Vapor phase calibration standards were prepared using the following procedure:

1. A Scott Specialty Gases Acculife aluminum cylinder (size CL) was cleaned by purging with dry UHP Zero Air, then evacuated to 10^{-4} torr. This process was repeated three (3) times.
2. Each VOC of interest was introduced into the evacuated cylinder by injecting a measured volume of each through a silicone septum at the cylinder valve. A gas-tight microliter syringe was used to inject the compounds of interest, one at a time, in liquid phase. The syringe was cleaned between injections by purging twice with methanol and once with the VOC to be injected next.
3. After all compounds were injected, the cylinder was filled with a metered volume of UHP Zero Air using a precision mass flow controller. Flow rate was 500 cc/min and fill time was dependent on what volume of dilution gas was needed to achieve the desired VOC vapor concentration.

Calculations

All chromatographic results are calculated as parts per million by volume (ppmv) at 20°C, 760 mm Hg. Vapor concentrations for each VOC are calculated as follows:

step 1) calculate mass injected: $m_X = v \times r_X$

step 2) calculate volatilized vapor mass density: $d_X = m_X/V$

step 3) convert mg/m^3 to ppmv: $c_X = d_X \times Z/M$

$c_X =$	concentration of x	ppmv
$d_X =$	concentration of x	mg/m^3
$m_X =$	mass injected	milligrams
$v =$	liquid volume of VOC x injected	mliter
$r_X =$	liquid density of VOC x	g/ml
$V =$	volume of dilution gas (zero air)	cubic meters
$Z =$	molar volume of perfect gas @ 20 °C, 760 mm Hg	24.04 liters/mole
$M =$	molecular weight of x	grams/mole

Calibration Table

Compound	CAS number.	conc* level 1	conc* level 2	conc* level 3	conc* level 4
Dichlorobenzene (1,2-)	95-50-1	2.14	20.4	213.6	------
Ethyl benzene	100-41-4	1.96	20.2	196.3	------
Freon 113	76-13-1	2.01	20.0	201.4	1007.2
Pentane	109-66-0	2.09	21.1	208.6	1042.9
Tetrachloroethene	127-18-4	2.35	19.6	234.8	1174.2
Trichloroethane (1,1,1-)	71-55-6	2.41	20.3	241.1	1205.6
Trichloroethylene	79-01-6	2.67	19.9	267.5	1337.5
Xylene (m-)	108-38-3	1.97	20.6	196.5	------
Xylene (o-)	95-47-6	1.97	19.8	197.0	------
Xylene (p-)	106-42-3	1.96	19.4	196.1	------
UHP Zero Air	n/a	balance	------	balance	balance
UHP Nitrogen	n/a	------	balance	------	------

conc* = ppm by volume @ 20°C, 760 mm Hg

Level 1: made by mixing 0.5 mliter liquid of each compound and 50 liters air
Level 2: NIST-traceable standard from Scott Specialty Gases, Scott #CAL9245
Level 3: made by mixing 10 mliter liquid of each compound and 10 liters air
Level 4: made by mixing 50 mliter liquid of each compound and 10 liters air
         (compounds with VP > 10 mm Hg)

Appendix E: Calibration Standard Certificate of Analysis

Scott Specialty Gases, Inc.

Shipped From:
500 WEAVER PARK RD
LONGMONT   CO 80501
Phone: 303-442-4700   Fax: 303-772-7673

C E R T I F I C A T E   O F   A N A L Y S I S

SANDIA NATIONAL LABS

U.S.O.E. BLDG 957
1515 EUBANK BLVD SE
ALBUQUERQUE   NM 87123

PROJECT #: 08-16356-001
PO#: AK-7118
ITEM #: 0802DA001001AL
DATE: 10/31/94

CYLINDER #: ALM050149   ANALYTICAL ACCURACY: +/- 1%
FILL PRESSURE: 275 PSIG
BLEND TYPE : GRAVIMETRIC MASTER GAS

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
1,2-DICHLOROBENZENE	20.	PPM	19.82	PPM
ETHYLBENZENE	20.	PPM	19.40	PPM
HALOCARBON 113	20.	PPM	19.66	PPM
N-PENTANE	20.	PPM	19.58	PPM
TETRACHLOROETHYLENE	20.	PPM	19.81	PPM
1,1,1-TRICHLOROETHANE	20.	PPM	19.63	PPM
TRICHLOROETHYLENE	20.	PPM	20.16	PPM
M-XYLENE	20.	PPM	19.82	PPM
O-XYLENE	20.	PPM	19.55	PPM
P-XYLENE	20.	PPM	19.68	PPM
NITROGEN		BALANCE		BALANCE

CGA 350   275 PSIG   QC# 24319414
NIST TRACEABLE BY WEIGHT

EXPOSURE TO TEMPERATURES BELOW 32 DEG F MAY CAUSE COMPONENTS
TO LIQUIFY. KEEP CYLINDER ABOVE 70 DEG F FOR 1-2 DAYS OR
HEAT FOR 1-2 HOURS.
ROLL CYLINDER FOR 15 MINUTES BEFOR USING.
****
DO NOT HEAT ABOVE 120 DEG F.
ALWAYS USE ADEQUATE TEMPERATURE CONTROL.
****

ANALYST: _DIANA BEEHLER_

Appendix F: Power Requirements

All instruments operate using 120 VAC. The following is a conservative estimate of amperage required.

Instrument	Current Amps
Gas Chromatograph	20.0
computer	5.0
monitor	1.5
Bernoulli drive	1.0
A/D, digital I/O, etc	2.0
valves	1.0
mass flow controllers	1.0
air compressor	4.0
sample pump	1.4
circulating pumps (2.0 A x 3 each)	6.0
heated sample lines (3.6 A x 3 each)	10.8
Total amperage estimate	53.7

Appendix G: Routine Maintenance

The only maintenance required is periodic replacement of compressed gases and gas filters. Cleaning of the FID electrode is not anticipated, but may be required if the samples are .extremely dirty.

Compressed Gas Replacement

The helium, hydrogen, or zero air cylinders should be replaced when the tank pressure gauge reads 100 psi or less. Life expectancies for the gases are

gas	quantity	use rate cc/min, duty cycle	lifetime
hydrogen	2015 psi, 73 ft^3	30 cc/min, 100%	40 days
helium	2000 psi, 220 ft^3	30 cc/min, 100%	66 days
zero air	2015 psi, 225 ft^3	10 cc, 100% 200 cc/min, 4%	300 days
cal gas	275 psi, 10 ft^3	100 cc/min, 0.002%	150 days

Gas Filters

If the chromatogram baseline starts to look "dirty", the carrier gas filter should be replaced. Filter life expectancy with our system is expected to be many months of continuous usage.

Particle Filters

If a drop in sampler flow rate (as read by the sampler mass flow controller) takes place over time, the cause may be a clogged particle filter. If this is the case, the 2 micron stainless steel frit must be replaced.

FID Detector Cleaning

If a reduction in FID response is noticed over a period of time, as indicated by the twice daily field calibrations, it may be necessary to clean deposits from the FID electrode. See the GC manual for guidance on disassembly and cleaning.

Appendix H: Manifold air flow rate calculations

Extraction manifold flow rate is calculated from three measurements:

- pitot tube differential pressure
- manifold static pressure
- manifold temperature

The calibration curve for the Omega #FPT-6130 pitot tube is:

$$Q = \sqrt{\left\{ \frac{16590 \times Dp \times K^2 \times D^4 \times P}{s \times (T + 460)} \right\}}$$

Q =	flow rate	ft^3/min @ 60°F, 760 mm Hg	(calculated)
Dp =	differential pressure	inches H$_2$O	(measured)
K =	pitot tube flow coefficient	dimensionless	0.665 (known)
D =	pipe diameter	inches	3 (known)
P =	manifold static pressure	psi absolute	(measured)
s =	specific gravity of air	relative to air @ 60°F	1.0 (known)
T =	temperature	°F	(measured)

To convert flow rate Q at 60°F (15.6°C = 288.6 K) to flow rate Q¢ @ 20°C (293 K):

$$Q' = Q \times \frac{293}{288.6}$$

$$Q' = 1.015 \times Q$$

Appendix I: VOC mass removal rate calculations

VOC mass removal rate is simply the product of manifold air flow rate and mass density of VOC per volume air. It is calculated from two parameters:

- extraction manifold air flow rate Q' (calculated per Appendix H)
- VOC concentration as measured by the GC

step 1) convert chromatographic result, parts per million by volume (ppmv) at 20°C, 760 mm Hg to mg/m^3 at 20°C, 760 mm Hg for each VOC:

$$D_X = C_X \times \frac{M_X}{Z} \times \frac{273}{T} \times \frac{P}{760}$$

$C_X =$	concentration of VOC x	ppmv
$D_X =$	concentration of VOC x	mg/m^3
$Z =$	molar volume of perfect gas @ 0°C, 760 mm Hg	22.4 liters/mole
$M_X =$	molecular weight of VOC x	grams/mole
$T =$	local air temperature	°K
$P =$	local air pressure	mm Hg

At 20°C, 760 mm Hg, this reduces to:

$$D_X = \frac{M_X \times C_X}{24.04}$$

VOC mass removal rate converted to lb/hr is:

$$V_X = Q' \times D_X \times \frac{lb}{454,000 \ mg} \times \frac{m^3}{35.71 \ ft^3} \times \frac{60 \ min}{hr}$$

Appendix J: Water mass removal rate calculations

Water mass removal rate is simply the product of manifold air flow rate and mass density of water per volume air. It is calculated from four parameters:

- extraction manifold air flow rate Q' (calculated per Appendix H)
- manifold relative humidity (measured by Vaisala humidity transmitter)
- manifold temperature (also measured by Vaisala humidity transmitter)
- manifold pressure (measured by the pressure scanner)

Relative humidity is defined as the ratio of water vapor pressure to the saturation water vapor pressure at the gas temperature. Total pressure does not enter the definition.

step 1) calculate saturation water vapor pressure: Over the temperature range 0 to 200°C, saturation water vapor pressure (psia) can be approximated (<0.38% error) by:

$$P_{ws} = 0.0885 \times 10^{(7.3354 \times T/(230.5 + T))}$$

T = temperature, °C

step 2) calculate water vapor concentration by volume: Water vapor concentration by volume is equivalent to the ratio of water vapor partial pressure to total (manifold) pressure.

$$C_w = 10^6 \times (H/100) \times P_{ws}/P_t$$

C_w = water vapor concentration, ppmv
H = relative humidity, %
P_{ws} = saturation water vapor pressure, psia
P_t = total (manifold) pressure, psia

step 3) convert ppmv to mg/m^3 at 20°C, 760 mm Hg:

$$D_w = C_w \times \frac{M_w}{Z} \times \frac{293}{T} \times \frac{P}{760}$$

C_w =	concentration of water	ppmv
D_w =	concentration of water	mg/m^3 air
Z =	molar volume of perfect gas @ 20°C, 760 mm Hg	24.04 liters/mole
M_w =	molecular weight of water	18.02 grams/mole
T =	manifold temperature	°K
P =	manifold pressure	mm Hg

step 4) convert water mass removal rate to lb/hr:

$$V_W \; = \; Q' \; \times \; D_W \; \times \; \frac{lb}{454,000 \; mg} \; \times \; \frac{m^3}{35.71 \; ft^3} \; \times \; \frac{60 \; min}{hr}$$

Appendix K: Parts List (arranged by subsystem)

Chromatograph

description	supplier	part number
gas chromatograph	Varian	CX3400
FID	Varian	comes with above
interface card for above	Varian	comes with above
wide bore capillary column, 30 meters long, 3.0 mm thick fil, 0.53 mm ID	Restek	MXT-VOL
liquid calibration standards, 1 ml each	Accu-standard	custom order

Sample Transfer Subsystem

description	supplier	part number
heated sampling line, Teflon, 25 ft long	Technical Heaters	212-4-25
diaphragm air pump, 1.1 cfm, 120 VAC	Fisher Scientific	13-875-226
particle filter, 90 mm SS frit	Nupro	SS-4TF-90

Sampler

description	supplier	part number
6 port valve, electrically actuated	Valco	ESF6P
RS232 Serial valve interface, for above	Valco	SVI
sample loop, 1 cc	Valco	SL1KC10UW
Nafion Dryer	Perma-pure	MD-190-24S
mass flow controller	Tylan	FC-260
readout box for above	Tylan	RO-28
rotary vane air pump, 1.5 cfm, 120 VAC	Thomas	SR-0015-VP

Manifold Instrumentation

description	supplier	part number
Humidity/Temperature transmitter	Vaisala	HMP235
Platinum RTD (100 W)	Omega	PR-13-2-100-1/8-6-E
data logger	Campbell Scientific	21X
pitot tube	Omega	FPT-6130
differential pressure sensor (±5" H_2O)	Setra	264

Compressed Gases & Plumbing

description	supplier	part number
UHP Helium	Tri-Gas	SGUHPHE243M
UHP Hydrogen	Tri-Gas	SGUHPHY73M
UHP Zero air	Tri-Gas	SGUZCA239M
Calibration Verification Standard	Scott Specialty Gases	Cylinder #ALM050149
pressure transmitter, 0-2500 psig, 4-20 mA output	PSI-tronix	PG-4/20
excess flow valve, CGA 350, 1 liter/min trip point	ABQ V&F	6L-E4-HA-350-VR4
pressure regulator	Concoa	432-3301
shut off valve, metal bellows type	ABQ V&F	SS-4BG-V51
pressure relief valve, 100 psi	ABQ V&F	SS-RL3M4-S4-MO-100
gas purifier cartridge	Alltech	81012
air compressor, 0.6 cfm @ 60 psi	Thomas	LGH-210

Computer & Data Acquisition Hardware

description	supplier	part number
computer, 80486, 66 MHz, 16 Mb RAM	DEC	466d2 MT
15' monitor	DEC	PCXBV-DE
RS232, 8 channel expander	Hostess	INHX0835A
Bernoulli drive, 90 Mb	Liberty	90PRO
A/D, D/A I/O board	National Instruments	ADFIO16
16 channel back plane	National Instruments	5B01
RTD to 5 volt module	National Instruments	5B34
±5 V to 5 volt module	National Instruments	5B41
4/20 ma to 5 volt module	National Instruments	5B32

Distribution:

5	MS 0503	F. J. Peter	2338
5	MS 0503	G. R. Laguna	2338
1	MS 0503	S. L. Trauth	2338
5	MS 0719	J. M. Phelan	6621
1	MS 0719	J. E. Nelson	6621
1	MS 9018	Central Technical Files	8523-2
5	MS 0899	Technical Library	4414
2	MS 0619	Review & Approval Desk For DOE/OSTI	12630