

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

A Chromatographic System for the Analysis of Selected Light
Gases in Geothermal and Volcanic Systems

by

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BACKGROUND

In 1985 an experiment was initiated to test the performance of a hydrogen sensor developed by the USGS, and to study the hydrogen-degassing behavior of fumaroles located in the Casa Diablo area of Long Valley Caldera, California. One portion of the proposed field study involved the collection and analysis of over 200 soil gas samples from the Casa Diablo area. Another portion of the field study involved the collection and analysis of more than thirty fumarole gas samples. During an earlier reconnaissance survey of the area it was determined that hydrogen concentrations in both matrices were low or sub (0.5 - 100 part per million by volume (ppmv)). Compounding the problem, hydrogen gas, with its small molecular size and high diffusivity, might escape from syringes used for sampling soil gas or glass sample bottles used for sampling fumaroles before the analyses could be completed. This led to a search for (and ultimately the development of) a simple analytical instrument that would be capable of determining low or sub ppmv hydrogen in either fumaroles or soil gases along with the added features of high sample throughput and transportability.

INSTRUMENT DESCRIPTION

Analytical Method

Casa Diablo fumarole and soil-gas samples contain varying amounts of nitrogen, argon, methane, carbon dioxide, carbon monoxide, water vapor, hydrogen sulfide, and oxygen (Farrar et al., 1985). In addition to lengthening the analysis time, the presence of these gases is detrimental to columns and detectors. Excess water can pack up on molecular sieve columns and cause deactivation. Carbon dioxide is strongly retained by molecular sieves and can emerge at just the wrong moment as a phantom peak. Sulfur gases attack metal surfaces inside the detector, and also the thermistor elements themselves, in addition to causing premature column deterioration. By backflushing these unwanted species before they reach the analytical separation column, the analysis as well as the downtime necessary to recondition or replace columns and detectors can be shortened. This is accomplished by using a ten port multifunctional valve. This valve is configured for gas sampling, with backflush to vent of the precolumn, using the same carrier to the analytical column in both modes (Valco Inst. Co., 1984). The analytical procedure is shown in steps in figure 1. Step 1 is the fill/backflush mode, where the sample loop is filled. The use of a sample loop assures that the same volume of sample is injected each time, unlike syringe injections which are subject to operator error. Soil-gas samples collected in 50 cc syringes may be used directly to flush and fill the sample loop. Fumarole samples involve pumping down the sample loop, then opening the sample bottle to

fill the loop after the pump has been valved off. Once the loop is filled, the valve may be switched to the inject mode. In this mode, the sample loop, precolumn, and analytical column are placed in series, and the light gases (H₂, He, Ne) separate as a group from the heavier gases, which are more strongly adsorbed on a short precolumn of Porapak Q (Thompson, 1977). After the light gases reach the analytical column, the valve may be switched back to the fill/backflush mode, as shown in step 3. Once the valve has been switched, the unwanted gases are backflushed, while the gases of interest proceed through the long analytical column of Molecular Sieve 5A. Helium, neon, and hydrogen emerge from the analytical column and pass to the detector.

Pneumatics

The pneumatic system is shown schematically in figure 2 and photographically in figure 3. The carrier gas of choice for the analysis is argon, owing to the great difference in thermal conductivity between it and hydrogen, although nitrogen works nearly as well (Cowper and DeRose, 1985). Prepurified (or better) carrier gas is used with an oxygen/water trap to remove residual impurities. A good quality two stage gas regulator provides the stable carrier gas pressure. Flow rates are set using precision micrometering needle valves. Pneumatic balance between the reference and analytical side of the detector is accomplished by placing additional lengths of packed column downstream of the detector on the reference side. This is especially important to minimize switching peaks (McNair and Bonelli, 1969).

Electronics

The detector used for this instrument is a micro volume thermal conductivity cell using two 8 K ohm thermistors. The thermistors constitute two arms of a wheatstone bridge as shown in figure 4 (Gow Mac Inst. Co., 1984). A commercial bridge control unit is used as a constant current source for the cell. The output from the bridge is connected directly to a recording integrator, which records the chromatogram and integrates the peak areas.

OPERATION

Instrument Settings

1. Pneumatic: Adjust regulated pressure to 80 psig. Adjust analyte flow rate to 8 ml/min +/- 3 ml/min. Adjust reference flow rate to a value slightly higher than that of the analyte. The actual values used may vary depending on the pressure imbalance in the system and characteristics of the individual detector. Purge the entire system overnight before activating the bridge for the first time.

2. Electronic: After the system has been purged overnight, set bridge current to 6.5 milliamperes (ma). Allow system to stabilize, and adjust bridge output to a value near 0.0 millivolts (mv). Set bridge attenuator to 1, allowing full output from the bridge to reach the integrator. Settings to start with for HP-

3390, or HP-3392 integrator are as follows:

ZERO	=20,0.1
ATT 2	=3
CHT SP	=1.0
PK WD	=0.04
THRSH	=-3
AR REJ	=0

Integrate functions should be entered into the timed-events table of the HP integrator after peaks of interest are located and evaluated.

Locating Peaks of Interest

1. With column switching valve in fill/backflush position, flush the sample loop with 500 ppmv hydrogen standard. A 50 cc plastic syringe works well for this. The total volume of standard used for flushing is unimportant so long as the sample loop is flushed with a quantity of standard at least ten times that of the sample loop.

2. Set column switching valve to inject position. Mark time. Wait three minutes.

3. Set column switching valve to fill/backflush position. Zero the integrator and watch trace. The helium, neon, and hydrogen peaks should emerge at approximately the five minute mark of the run. Note the exact time, and continue the run for about thirty minutes, allowing oxygen and nitrogen to elute. The helium and neon peaks may not be visible on the trace. The hydrogen peak should be clipping. The oxygen and nitrogen peaks will clip for a period of 1 to 5 minutes each. At the end of thirty minutes, stop the run.

4. Repeat steps 1-3 above, except decrease the injection time by 15 seconds and note differences in chromatograms (if any). The purpose of this procedure is to determine the minimum injection time needed to just get the helium-neon-hydrogen triplet onto the analytical column, without getting the nitrogen and oxygen. Continue reducing the injection time until both the oxygen and nitrogen peaks disappear completely from the chromatogram. Care should be taken not to clip the helium, neon, and hydrogen peaks by reducing the injection time too far.

Analysis

With the peaks of interest located, and retention times defined, proceed with standard calibration and analytical runs. The sequence for analytical run will take the form shown in figure 1 and discussed in the Analytical Method section of this report. A sample chromatogram is presented in figure 5.

CONCLUSION, OPTIMIZING SYSTEM PERFORMANCE

A number of factors are involved in optimizing the performance of the system. Inlet pressure, flow rates, quality of columns, stability of AC line source, and ambient temperature and pressure fluctuations all affect operational characteristics. With a moderate amount of experimentation, analysis times can be reduced to under 10 minutes, and detection limits of 5 ppmv for hydrogen are possible. Depending upon the level of patience and impetus possessed by the analyst, detection limits may be lowered by an order of magnitude. The key to optimizing system performance is a methodical common sense approach, salted with a good dose of patience. An excellent treatment of general GC troubleshooting may be found in McNair and Bonelli (1969). A system that uses long columns, and low flow rates requires extra time to equilibrate between changes in flow rate settings. Care should be taken to protect the integrity of the columns. Deterioration in resolution of the helium-neon-hydrogen triplet indicates that the analytical column need of regeneration. Other advantages to this system include: 1. Prolonged column life: since gases that typically cause columns to deteriorate never reach the analytical column. 2. Rapid deployment, because system is lightweight and easily transportable. If a suitable battery-operated analog integrator is available, the entire system may be battery operated. 3. Versatility. If nitrogen, oxygen and methane (or other gases that are separated on molecular sieve columns) are desired in the analysis, simply omit (or delay) the backflush step and allow all desired species onto the analytical column. 4. Cost. The entire system excluding the integrator and gas supply may be assembled for less than \$1,000 (1986 prices).

ACKNOWLEDGEMENT

I would like to thank Paul Greenland, formerly of the Hawaiian Volcano Observatory, for several stimulating and instructive conversations regarding the design and construction of this instrument. Paul earlier developed a similar instrument for hydrogen and helium trace analysis of fumarole samples from Kilauea and Mauna Loa.

APPENDIX A. CONSTRUCTION NOTES

1. The instrument should be housed in a suitable container with a size at least 0.3 m X 0.2 m X 0.3 m. Smaller containers make maintenance and troubleshooting more difficult. The housing material should be a good thermal insulator. Plastic or fiberglass is recommended.
2. All fittings are 1/8 inch 316 stainless steel (SS) Swagelok. All tubing is 1/8 inch OD, SS, precleaned gas chromatography grade. All tubing ends are reamed out and cleaned following cutting.
3. The precolumn is prepared by packing Porapak Q, 80/100 mesh or another suitable porous polymer into a 1.0 m length of tubing. The ends are packed off with silanized glass wool. The column is wound around a 10 cm mandrel and preconditioned overnight under argon carrier at 180 degrees C.
4. The analytical column is prepared by packing 5 A Molecular sieve, 80/100 mesh into a 5.3 m length of tubing. The first 0.3 meter is packed with silica gel, 80/100 mesh. This portion of the column is to absorb any water vapor that may enter the column during the location of peaks of interest. The ends are packed off as in step 3. The column is wound around a 10 cm mandrel and preconditioned overnight under argon carrier at 250 degrees C. The column ends are sealed until just before instrument assembly.
5. The entire assembled GC is static-leak checked using "Snoop" at a pressure equal to twice the operating pressure. Any leaking fittings are either tightened or replaced.
6. After final assembly, and leak check, the instrument housing is packed with polystyrene packing material to provide good thermal stability.

APPENDIX B. PARTS LIST

Porapak Q, 80/100 mesh
Silica gel, 80/100 mesh
Molecular sieve 5A, 80/100 mesh
Valco 10 port multifunctional gas sampling valve, Valco part number 10P, 1 ea.
Thermal conductivity detector, Gow Mac part number 10-470, 1 ea.
Bridge control unit, Gow Mac part number 40-400, 1 ea.
SS 1/8 inch OD tubing, approximately 20 meters
SS Tee joints, 1 ea.
SS bulkhead unions, 5 ea.
SS micrometering needle valves, 2 ea
SS gate valve, packless, 1 ea.

Accessories

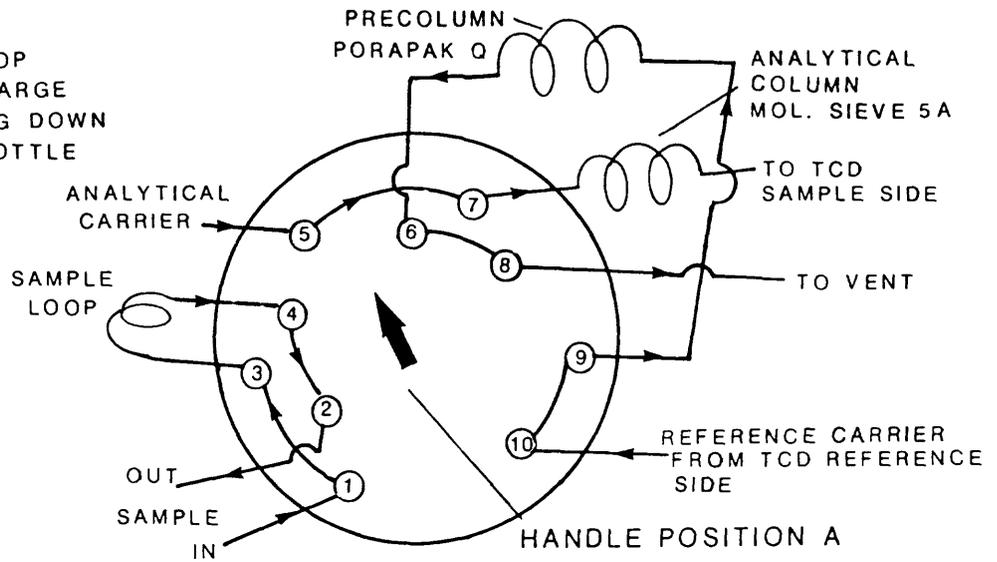
Integrator HP-3390 or HP-3392 computing type or other as desired, carrier gas supply, argon prepurified or better with oxygen/water trap, and 2 stage regulator.

References

- Cowper, C. J. and DeRose, A. J., 1985, The Analysis of Gases by Chromatography: Pergamon Press, Elmsford, New York., p. 53-60.
- Farrar, C. D., Sorey, M. L., Rojstaczer, S. A., Janik, C. J., Mariner, R. H., Winnett, T. L., Clark, M. D., 1985, Hydrologic and Geochemical Monitoring in Long Valley Caldera, Mono County, California, 1982-1984, U.S. Geological Survey Water Resources Investigations Report 85-4183, p. 31.
- Gow-Mac Instrument Co., 1984, Bulletin SB-13, Thermal Conductivity Detector Elements for Gas Analysis from Gow-Mac, 8 p.
- McNair, H. M. and Bonelli, E. J., 1969, Basic Gas Chromatography: Varian Instrument Co., Palo Alto, California, p. 259-282
- Thompson, B., 1977, Fundamentals of Gas Analysis by Gas Chromatography: Varian Instrument Co., Palo Alto, California, 132 p.
- Valco Instruments Co. Inc., 1984, 10 Port Multi-Functional Gas Sampling Valves Bulletin, 20 p.

STEP 1

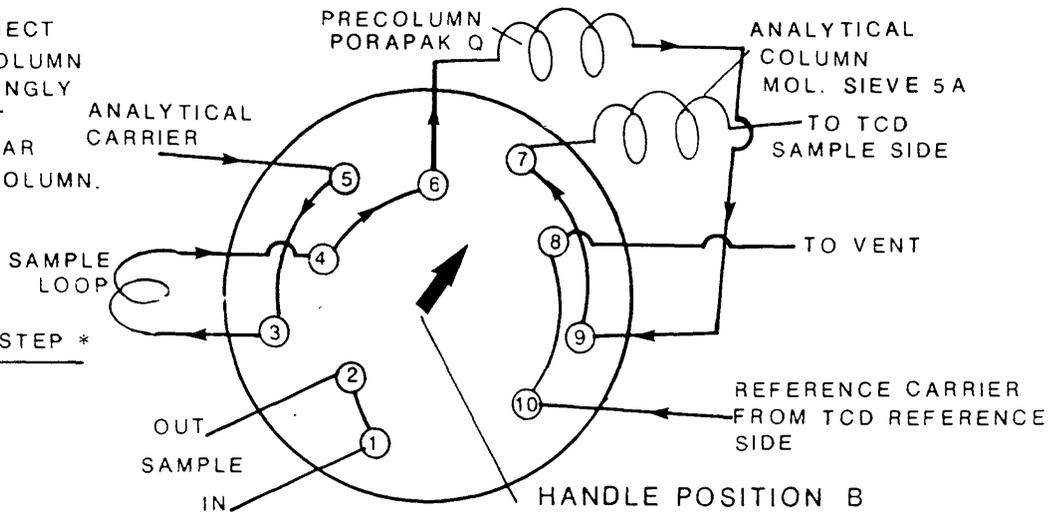
FILL 1CC SAMPLE LOOP
BY FLUSHING WITH LARGE
SYRINGE, OR PUMPING DOWN
AND FILLING FROM BOTTLE



STEP 2

TURN HANDLE TO INJECT
SAMPLE ONTO PRECOLUMN
'HEAVIES' ARE STRONGLY
HELD WHILE 'LIGHTS'
SLIP ONTO MOLECULAR
SIEVE ANALYTICAL COLUMN.

* TIME CRITICAL STEP *



STEP 3

TURN HANDLE BACK TO
BACKFLUSH 'HEAVIES'
FROM PRECOLUMN WHILE
ELUTING AND
INTERGRATING PEAKS
FOR H₂ AND He.

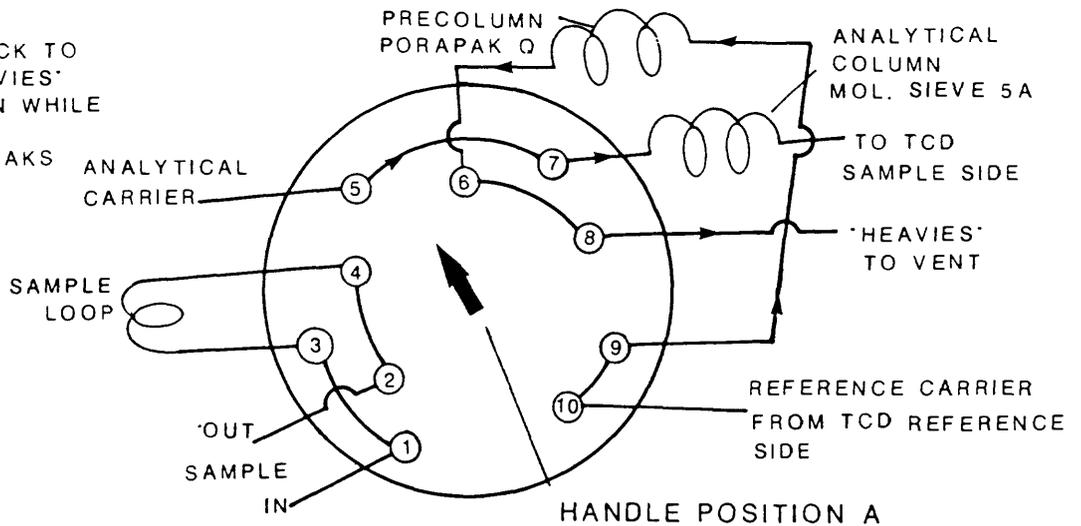


Figure 1. - Analytical sequence for instrument operation.

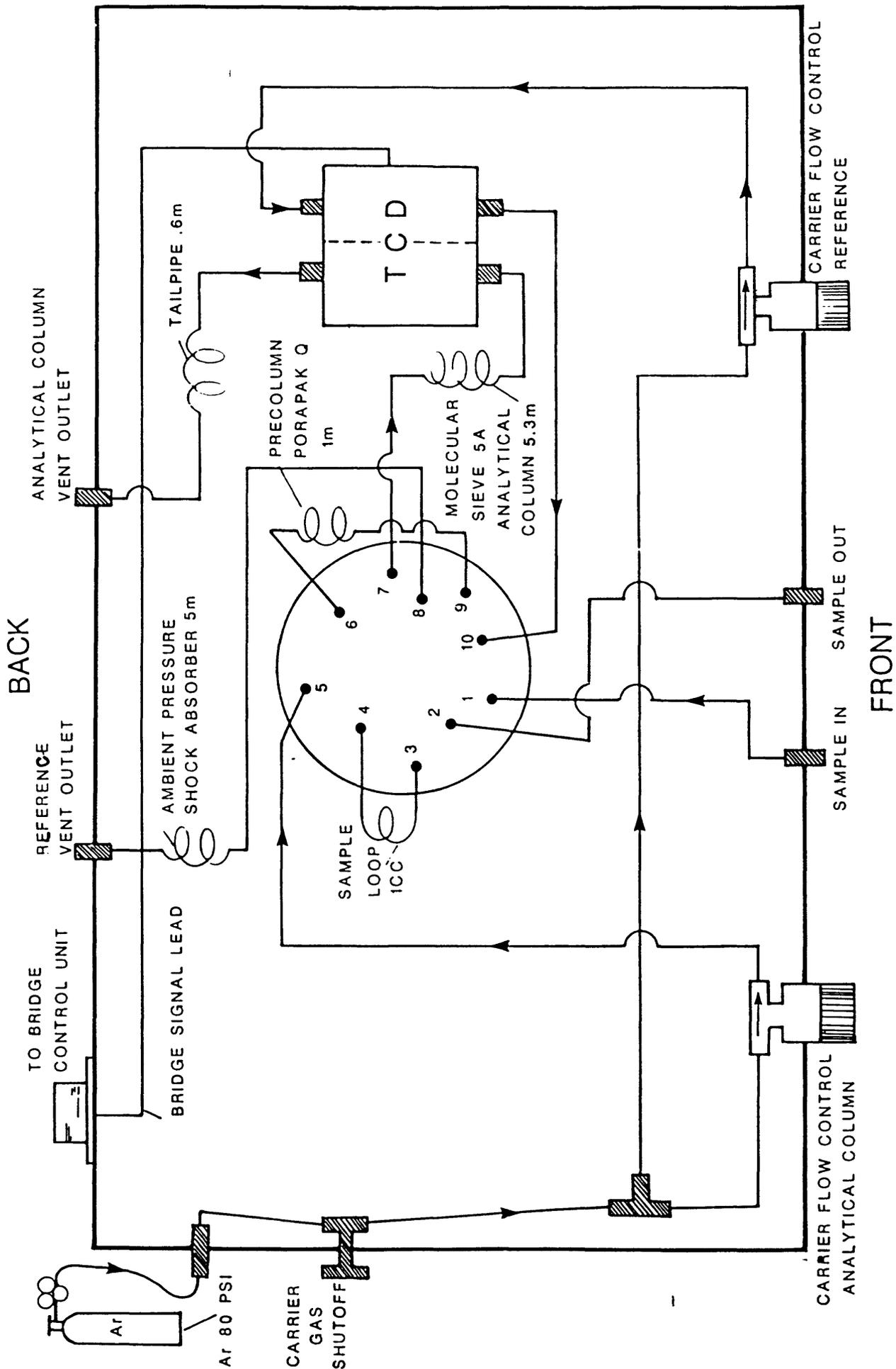


Figure 2. - Schematic of pneumatic layout for instrument.

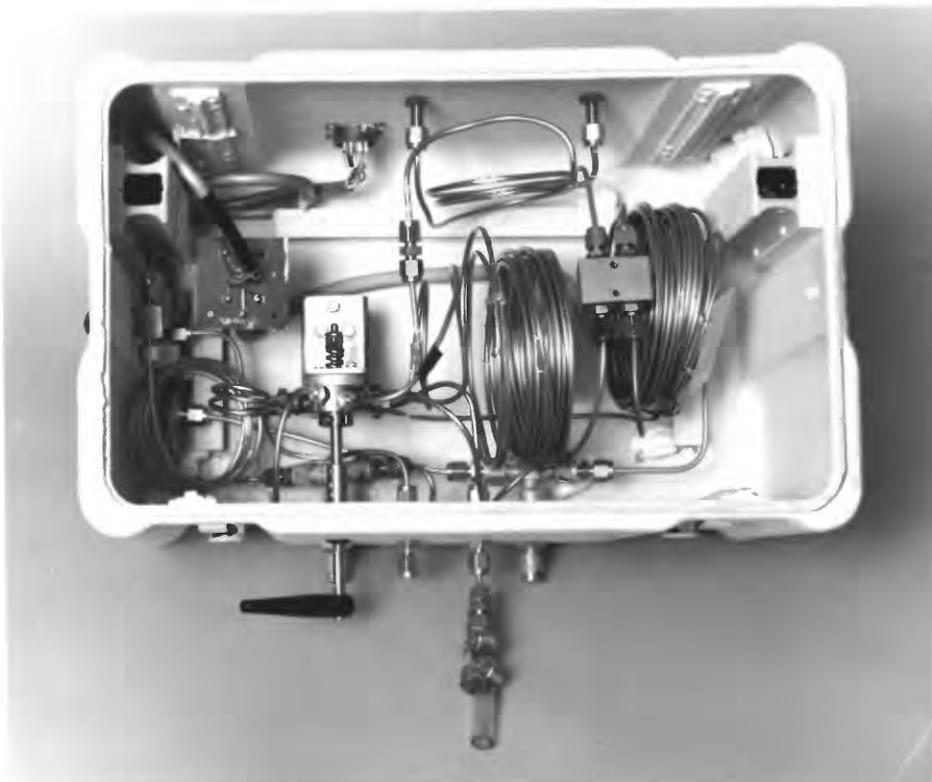
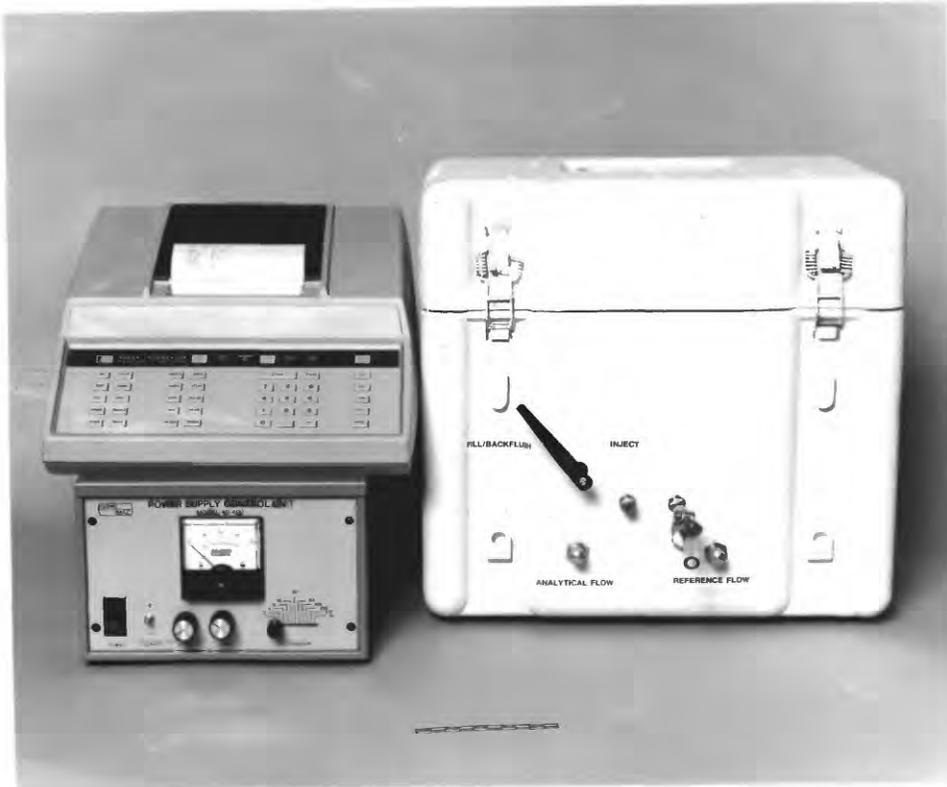
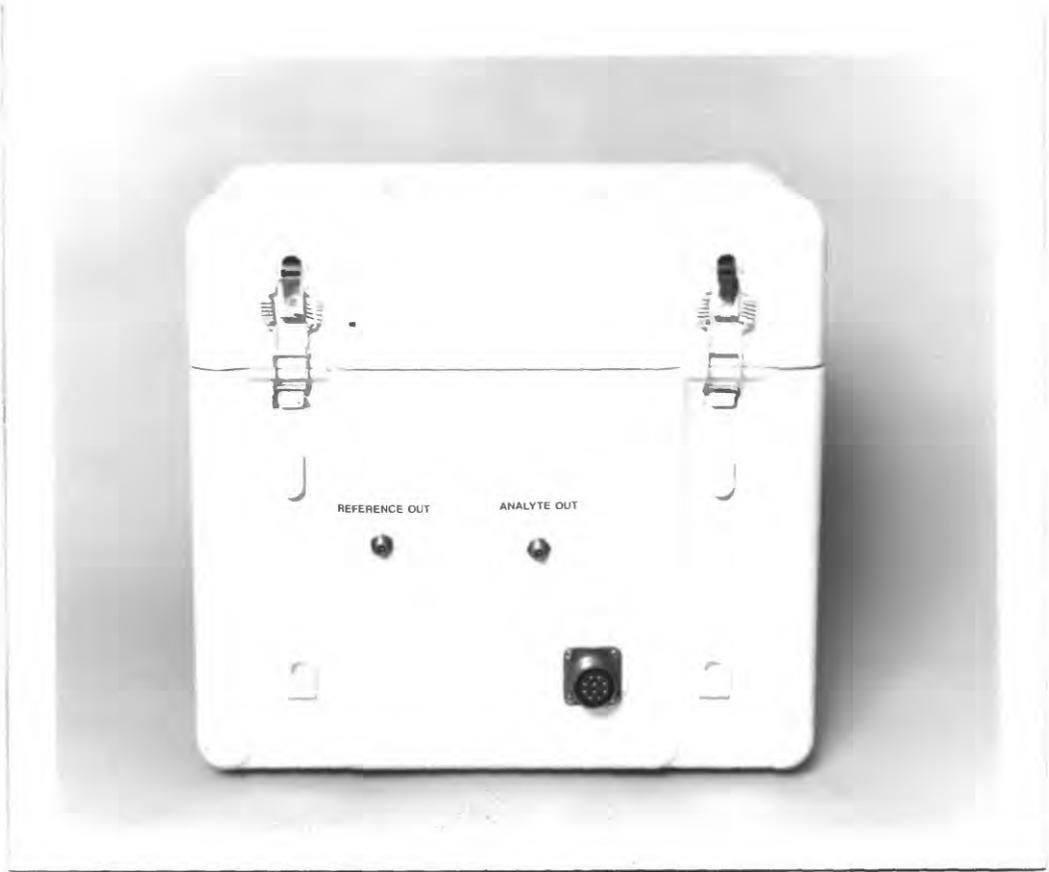


Figure 3.- Photographic views of instrument system showing front, inside, and rear views.



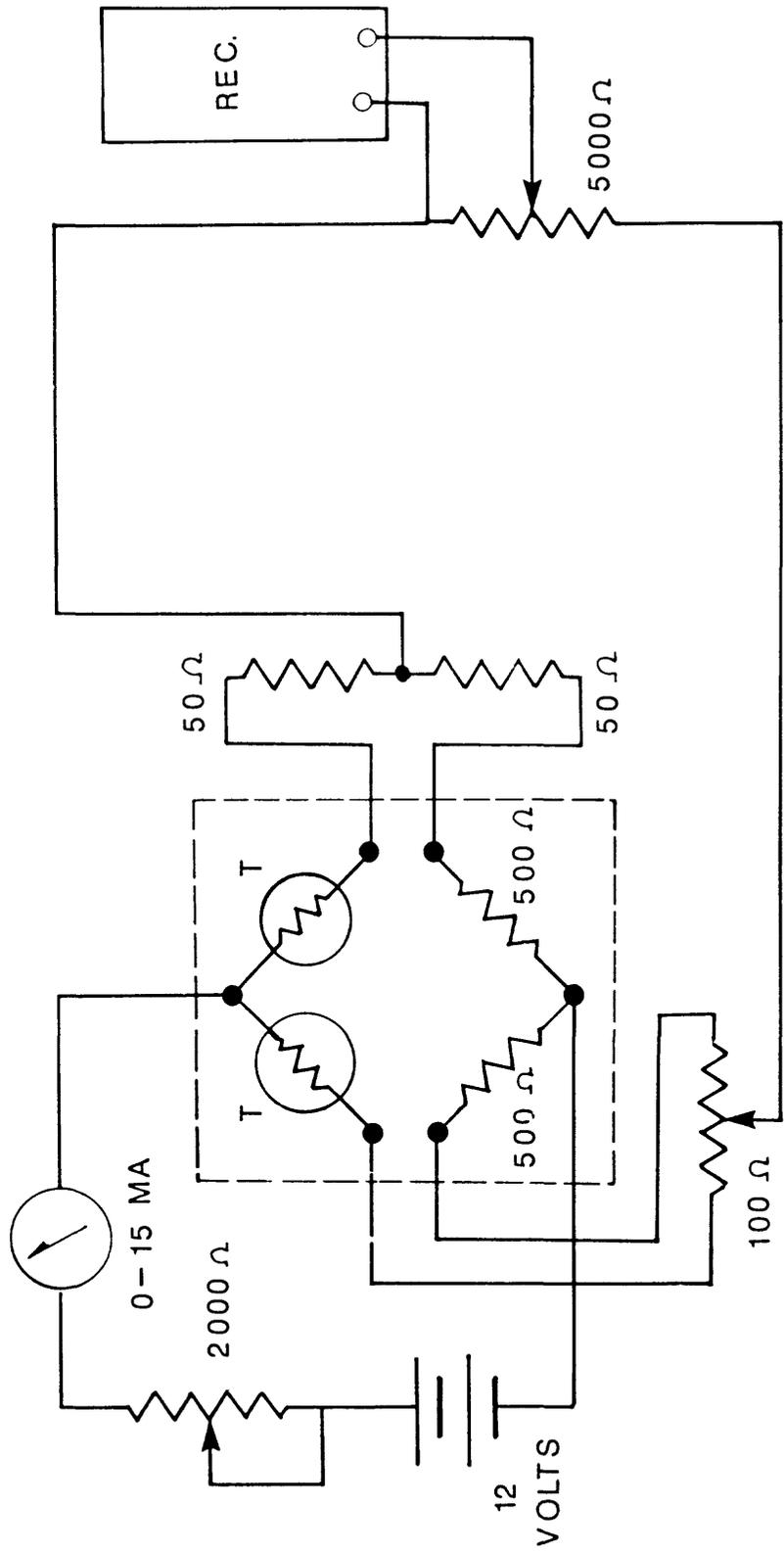
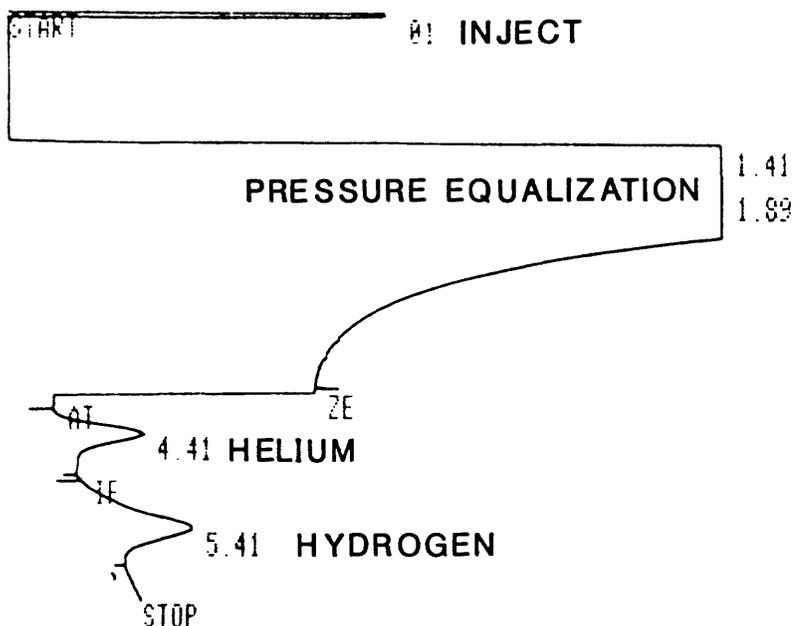


Figure 4. - Schematic of thermal conductivity detector circuit.



RUN # 44 SEP/18/86 21:07:41
 WORKFILE ID: C
 WORKFILE NAME:

RT	AREA	TYPE	AR/HT	AREA%
0.01	0	D BB	0.000	0.000
1.41	5699100	PY	0.308	28.338
1.89	1.4222E+07	YB	0.994	70.718
4.41	54268	PP	0.233	0.270
5.41	135540	BY	0.423	0.674

Figure 5. - Sample chromatogram of an analytical run of mixture of 100 ppmv hydrogen, and 100 ppmv helium in atmospheric air.