

The Determination of the Helium Discharge Detector
Response to Fixed Gases

by

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ABSTRACT

The Beckman Helium Discharge Detector has been found to be sensitive to the fixed gases oxygen, nitrogen, and hydrogen at detection levels 10-100 times more sensitive than possible with a Gow-Mac Thermal Conductivity Detector. Detection levels of approximately 1.9×10^{-4} % v/v oxygen, 3.1×10^{-4} % v/v nitrogen, and 3.0×10^{-3} % v/v hydrogen are estimated. Response of the Helium Discharge Detector was not linear, but is useable for quantitation over limited ranges of concentration using suitably prepared working standards. Cleanliness of the detector discharge electrodes and purity of the helium carrier and discharge gas were found to be critical to the operation of the detector. Higher sensitivities of the Helium Discharge Detector may be possible by the design and installation of a sensitive, solid-state electrometer.

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CHAPTER 1

INTRODUCTION

The analysis of fixed, or permanent, gases such as hydrogen, methane, oxygen, nitrogen, carbon monoxide, argon, and carbon dioxide has traditionally posed problems for the analytical chemist. Gas chromatography remains the method of choice due to its ability to separate a gaseous mixture into its component parts: the difficulty arises in the choice of suitable detection methods to quantify the eluting fractions.

Recent advances have seen the development of highly specialized, computer-assisted gas chromatographic systems which incorporate infrared (GC-IR), mass spectrometric (GC-MS), and ultraviolet (GC-UV) detectors. In the latter case, Driscoll, Towns, and Ferioll have just reported the use of a far-UV detector interfaced to a gas chromatograph¹. This system, operating at 120 nm, is reported to be universally sensitive to all gases except the noble gases, with the response predictable from the absorption coefficient, at low to sub-nanogram levels. While such systems have obvious applicability to the analysis of fixed gases, they are, for the most part, beyond the reach of most practical analytic laboratories which must rely on less expensive techniques. It was the intent of this investigation to evaluate the suitability of a relatively inexpensive gas chromatographic detector, the Helium Discharge Detector, for the analysis of fixed gases, and, in particular, for the analysis of hydrogen.

The most common gas chromatographic detector employed in

analytical laboratories for the analysis of fixed gases is the Thermal Conductivity Detector (TCD). The TCD relies for its sensitivity upon the difference in thermal conductivity between the eluting sample component and the carrier gas. Helium is frequently chosen as the carrier gas as its thermal conductivity is substantially greater than that of all other gases except hydrogen. Thus, in a mixture of gases with similar thermal conductivities, the response of the TCD to an individual gas component will be proportional to the weight fraction of the component in the mixture. If, however, hydrogen is one of the component gases, the response with helium as carrier gas will be significantly less sensitive due to comparatively small difference in thermal conductivities of these two gases. At high concentrations of analyte hydrogen, peak reversal resulting in M-shaped peaks is common, and has been attributed² to a minimum in the thermal conductivity curve for hydrogen-helium mixtures. The concentration of hydrogen at which the reversal occurs varies with the particular thermal conductivity detector employed, the carrier gas flow rate, and the filament temperature. It is, of course, possible to substitute a different carrier gas, such as nitrogen or argon, in order to facilitate a greater thermal conductivity difference between an eluting hydrogen peak and the carrier; this, in turn, limits the sensitivity of the detector to other fixed gases if they are present in the sample. In practical terms, while the TCD is sufficiently sensitive to quantitate most fixed gases to a level of about 10-50 ppm³, its sensitivity to hydrogen is limited to around 100-200 ppm in the sample^{4,5}, the actual detection levels depending upon the particular detector and

operating conditions employed. Despite the wide linear dynamic range of the TCD, typically quoted⁶ as 10^4 to 10^5 , and the comparative ease of operation, the application of the TCD to the analysis of fixed gases is generally limited by its inability to quantitate low to sub-ppm levels of such analytes.

Several other detectors, most notably from the family of ionization detectors, have been employed for the analysis of fixed gases with varying degrees of success. The Photoionization Detector (PID) finds application in the analysis of organic compounds, having a sensitivity comparable to that of the Flame Ionization Detector (FID) but displaying somewhat less noise⁷. In its most recent form, the PID is comprised of a discharge compartment, containing a discharge gas such as argon or hydrogen, separated from the detector compartment by an alkali or alkaline earth metal fluoride window. The window is transparent to the passage of high energy photons generated in the discharge zone. Depending upon the composition of the window material, the energy of transmitted photons is limited to a maximum energy of approximately 11.9 eV. Substances eluted from the gc column pass through the detector compartment and are ionized by the high energy photon flux. The ions thus generated are directed through an electric field and the resulting current is monitored. As described, the PID shows no response to fixed gases, nor to common impurities such as water, as these substances have ionization potentials greater than 11.9 eV - hence, the lower noise factor associated with this detector. Earlier versions of this detector, however, were constructed with no window separating the discharge and detector

compartments. In this arrangement, the unattenuated photon flux was targeted on the column effluent and, via mechanisms involving both photon interaction and collisions with metastable atoms with energies higher than 11.6 eV.⁸, the analysis of fixed gases was possible. Despite the obvious value of this detector, it saw limited use due to the requirement that the discharge/detector compartment be operated at pressures less than one atmosphere. Not only did this present problems in connecting the detector to a gc column, but it also resulted in varying partial pressure of the discharge gas and, hence, a variation in the energy distribution of the emitted photons⁹.

A second ionization detector, the Cross Section Detector (CSD), is also capable of detecting fixed gases. Radiation from a beta emitter such as Strontium or Tritium is directed through the gc eluant in a detector cell, producing a steady current of ions and electrons which then pass through an electric field. The denser polyatomic gases tend to be more strongly absorbing than the common carrier gases, hydrogen and helium, thus generating an increase in current when present. The major advantage of this detector lies in the ability to calculate the expected response to any molecule from the values of the molecular cross sections of the individual atoms comprising the substance¹⁰. The CSD has not enjoyed widespread usage, in part due to the restrictions inherent in maintaining a radioactive source, but primarily due to its relatively low sensitivity.

In 1958, Lovelock¹¹ described a radioactive Argon Ionization Detector for the sensitive detection of organic gases. Subsequent investigators, for example, Karmen and

Bowman¹² and Evrard, Thevelin, and Joossens¹³, produced a modification of Lovelock's detector wherein the radioactive source was replaced with a self-sustained direct current discharge. The detector in question was a cylinder of brass, acting as the cathode, and a coaxially mounted platinum wire anode. The detector was purged with the carrier gas, either argon or helium, and the discharge was initiated by polarization of the electrodes at 1000-2000 VDC. As described, the detector was reported sensitive to the permanent gases, nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, and chlorine. There was, however, conflicting evidence regarding the need for pure carrier gas, ie. free of organic and inorganic contaminants, with Karmen and Bowman stressing the need for purified argon or helium.

In 1963, Yamane¹⁴ published an account of a detailed investigation of the electrical operating characteristics of a subsidiary discharge argon ionization detector. In this study, the detector described above was modified by Yamane to include two separate chambers, one the discharge chamber containing the discharge electrodes over which flowed a stream of helium, and the second, the sensing chamber which was flushed with the discharge carrier gas and, simultaneously, with the argon column carrier gas. As shown in Figure 1, the inlet of the column effluent acted as the anode and the cathode was mounted in the center of the sensing chamber.

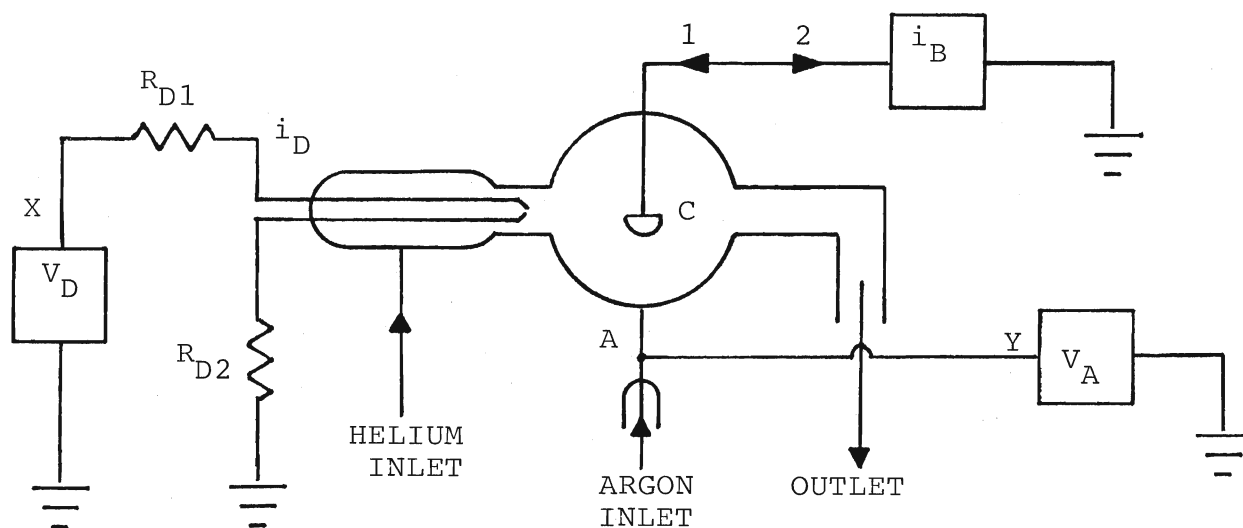


FIGURE 1.14

Subsidiary Discharge Argon Ionization Detector.

He: Discharge Gas; Ar: Carrier Gas;

C - Cathode; A - Anode;

**i_B : Background A-C Current
(Electrometer Amplifier)**

The subsidiary discharge was excited in two ways
(Figures 2,3)

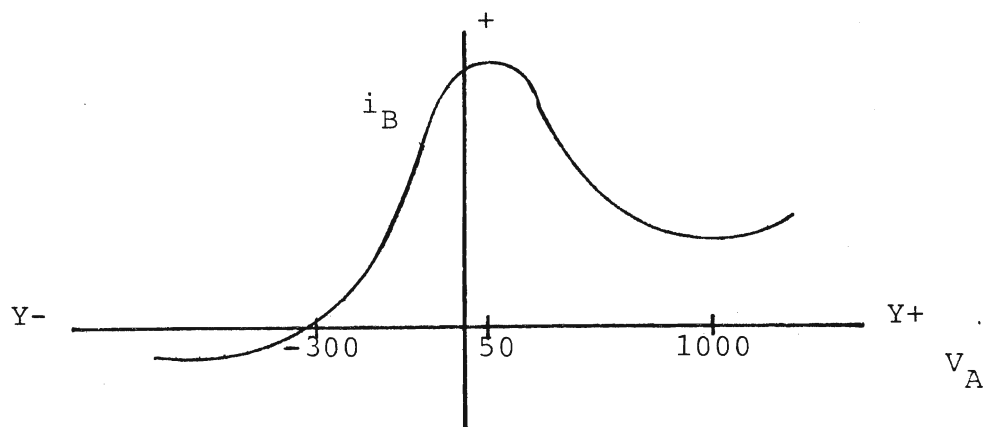


FIGURE 2.

Subsidiary Discharge Argon Ionization Detector.
Background current versus Anode Volts.
 $V_D = +850$ V (X+), $R_{D1} = 20$ M Ω , $R_{D2} = 0$ Ω ,
 $i_D = 30$ μ A, He=Ar=60 ml/min.

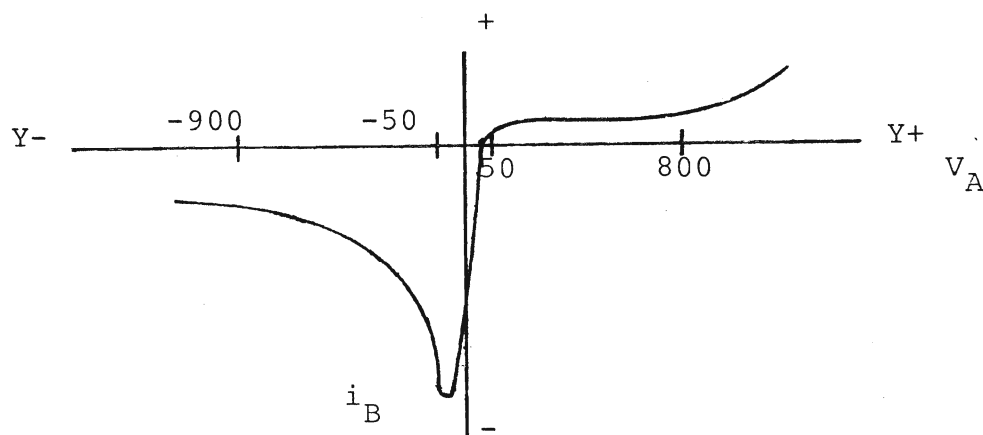


FIGURE 3.

Subsidiary Discharge Argon Ionization Detector.
Background current versus Anode Volts.
Same as Figure 2, except $V_D = -850$ V (X-)

According to Yamane, the subsidiary discharge produces He cations and electrons (by surface ionization) as well as He excited states. These species are swept into the zone containing A and C (the sensing chamber); there they create

Ar cations and electrons as well as Ar excited states.

In Figure 2, a positive current was observed at $V_A = 0$. Ions are captured by C and the electron flow is indicated by 1 (Figure 1). When $V_A = +50$ V, i_B becomes a maximum. For $+50 \text{ V} < V_A < 1000 \text{ V}$, i_B decreases because more electrons than ions have been drawn into the sensing chamber. For $V_A > 1000 \text{ V}$, further ionization by collisions with electrons occurs and i_B begins to increase again. When V_A becomes negative, the positive current declines until $V_A = -300 \text{ V}$ is reached. For $V_A < -300 \text{ V}$, the current becomes negative and the electron flow is indicated by 2 (Figure 1). Yamane suggests that the electrons captured by C for $V_A < -300 \text{ V}$ are photoelectrons.

In Figure 3, a negative current (electron flow 2, Figure 1) was observed at $V_A = 0$. Electrons are now captured by C. As V_A becomes more positive, the electrons are increasingly captured by A and i_B declines. Yamane suggests that for $V_A > +800 \text{ V}$, the increase in positive current which occurs is caused by photoionization. He also suggests that the flat region between $V_A \approx +50 \text{ V}$ and $V_A \approx +800 \text{ V}$ is the desirable operating region for the detector. For $V_A < -50 \text{ V}$ (at which the negative i_B is a maximum), electron flow is said to be inhibited (by undisclosed processes) and i_B declines again but its sign is always negative (i.e. current flow is always depicted by 2, Figure 1).

Yamane showed that with $V_D = -870 \text{ V}$ (Figure 3), the value of i_B is maximized when $R_{D2} = 20 \text{ M}\Omega$ and $R_{D1} = 0 \Omega$, and is minimized when $R_{D1} = 20 \text{ M}\Omega$ and $R_{D2} = 0 \Omega$. There is very little effect on i_B when $V_A > +500 \text{ V}$. Yamane also showed that the characteristic curve shown in Figure 3 is changed

very little when the AC distance is changed (C-fixed, A-moveable), but is markedly changed when the discharge electrode - AC distance is changed (AC-fixed, discharge electrode is moveable). Finally, Yamane demonstrated that an increase in He flow results in an increase in i_B .

Yamane's work provides a valuable insight into the characteristics of the subsidiary discharge ionization detector; as will be discussed later, these characteristics may provide a partial understanding of the workings of the Helium Discharge Detector.

It was at about this period in time, 1964-1966, that Beckman Instruments Inc. incorporated the first commercial Helium Discharge Detector (HDD) in their GC-4 series of gas chromatographs. That the utility of this detector was not widely recognized is illustrated by the distinct lack of literature references to its use. There have, however, been several publications dealing with the operational characteristics of the radioactive Helium Ionization Detector (HID), fashioned in the design previously described by Lovelock¹¹. Hartmann and Dimick¹⁵ described the practical application of the HID to the analysis of fixed gases. Response to argon, oxygen, carbon monoxide, and carbon dioxide was demonstrated, with part per billion sensitivities reported. Lasa and Bros^{16,17} have discussed the effect on the Helium Ionization Detector of both impurities in the helium supply and the concentration of components eluted from the column. The authors noted that above a certain concentration of analyte, the normal near-Gaussian peak changes to an M-shaped curve as the detector appeared to become overloaded. Furthermore, if gaseous impurities were

present in the helium supply, the analyte concentration, at which this peak reversion was observed, was reduced. Experience in the current investigation confirms the observations of Lasa and Bros, as will be discussed later. Other authors,^{18,19,20} report similar observations, suggesting the use of ultrapure helium as the only suitable course of action to ensure reproducible, and sensitive, response.

The lack of user acceptance of Beckman's Helium Discharge Detector may well have its origins in the operating difficulties and type of response described by Lasa and Bros. Nevertheless, the fact that the HID and the HDD differ only in the mechanism of ionization suggests that the HDD may be capable of response and sensitivities comparable to that of the HID and, hence, is worthy of investigation.

CHAPTER 2

EXPERIMENTAL

2.1 INSTRUMENTATION.

A Beckman Instrument Inc. GC-4 gas chromatograph equipped with a Beckman Instrument Helium Discharge Detector was used. A 0-1000 VDC voltmeter and a 0-25 mA ammeter were added to the circuitry of the detector to permit monitoring of its operation. Power supply and electrometer for the Helium Discharge Detector were as provided on-board by Beckman. Connected in series with, and preceeding the Helium Discharge Detector, was a Gow-Mac Filament-type Thermal Conductivity Detector. The TCD was powered by a Gow-Mac Model 40-001 Solid State DC Power Supply. The presence of the TCD provided immediate comparison of the sensitivity of the two detectors and, additionally, acted as a valuable diagnostic tool. Output from both the HDD Electrometer and the TCD Power Supply was directed to a Linear Dual Pen Recorder operated at 10 mV full scale.

2.2 HELIUM DISCHARGE DETECTOR.

The Helium Discharge Detector, as supplied by Beckman Instruments, was assembled as shown in Figure 4. In operation, an auxiliary supply of helium enters the top of the sealed ceramic detector cell, flowing downward over the detector electrodes. High energy species generated as a result of the DC discharge occurring between the discharge electrodes impinge upon a small sensing cell at the base of the detector proper. Mounted in this sensing cell is a polarizing electrode which is maintained, adjustably, at -150

VDC with respect to the discharge anode, which itself is at ground potential. Also entering the sensing cell is the gc column effluent. It is thought that ionizable entities eluting from the column interact with the high energy species; the electrons produced as a consequence of these interactions are collected at the collector electrode and the resulting current is amplified and measured by the electrometer.

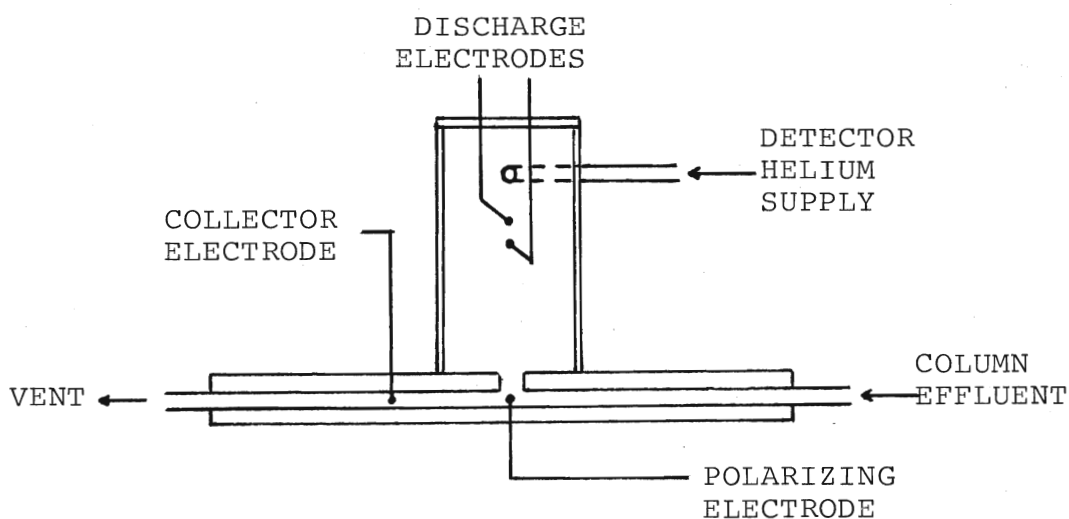


FIGURE 4.

THE HELIUM DISCHARGE DETECTOR

The precise nature of the high energy species generated as a result of the discharge is uncertain, although it is speculated that a metastable helium ion, He^* , may be formed.

2.3 COLUMNS AND COLUMN PACKING.

The analytical column was a 2.13 m X 3.2 mm stainless steel column packed with 5A Carbon Molecular Sieve (60-80 mesh); an identical column was provided as the reference column for the TCD.

2.4 CARRIER GAS.

The carrier gas employed was Matheson certified 99.999% helium. Carrier gas connections to the analytical column were via a Carle six-port gas sampling valve (GSV).

2.5 CHROMATOGRAPHIC CONDITIONS.

Both the analytical and reference columns were operated at room temperature with carrier gas flows of approximately 40 mL/min. The flow of auxiliary helium to the HDD approximated 160 mL/min. The TCD was operated at a voltage and filament current of 10 VDC and 225 mA, respectively. Operating voltage and current for the HDD were typically 210 VDC and 15.5 mA, respectively, while the polarizing voltage and bias voltage were held constant at 1000 VDC and 0 VDC, respectively. Specific analytical conditions are documented on each chromatogram.

2.6 GAS MANIPULATION RACK.

A mercury filled gas manipulation rack consisting of a 50 mL measuring burette and a 1000 mL storage burette was constructed for the preparation of standard gas dilutions. The vacuum source was a Precision Scientific Vacuum pump with pressure indication provided by a Hastings Thermocouple Gauge. Prepared gas samples were transferred under

atmospheric pressure to the analytical column via the Carle gas sampling valve. Details of the gas manipulation rack and the analysis system are depicted in Figure 5.

2.7 PREPARATION OF STANDARD GAS SAMPLES:

In preparing a standard gas sample for analysis, the analyte gas was first measured into the evacuated measuring burette, displacing the mercury contained therein. After adjustment of the measuring burette to atmospheric pressure by manipulation of the mercury level, transfer of a known volume of the analyte gas to the storage burette was undertaken, again by a mercury displacement operation. The measuring burette and connecting tubing up to the storage burette were then evacuated once again. Measured quantities of diluent helium gas were transferred, via the measuring burette, to the storage burette by an identical operation, the number of such cycles required reflecting the desired concentration of analyte gas.

Serial dilutions of a prepared standard analyte gas sample, if required, were made by transferring a volume of the gas sample from the storage burette, after adjustment of the storage burette to atmospheric pressure by manipulation of the mercury level, into the evacuated measuring burette. After evacuation of the storage burette, a measured volume of the gas held in the measuring burette, adjusted to atmospheric pressure, was transferred back to the storage burette. Dilution of this aliquot then proceeded as above. This cyclic process was repeated until the desired standard concentration had been prepared.

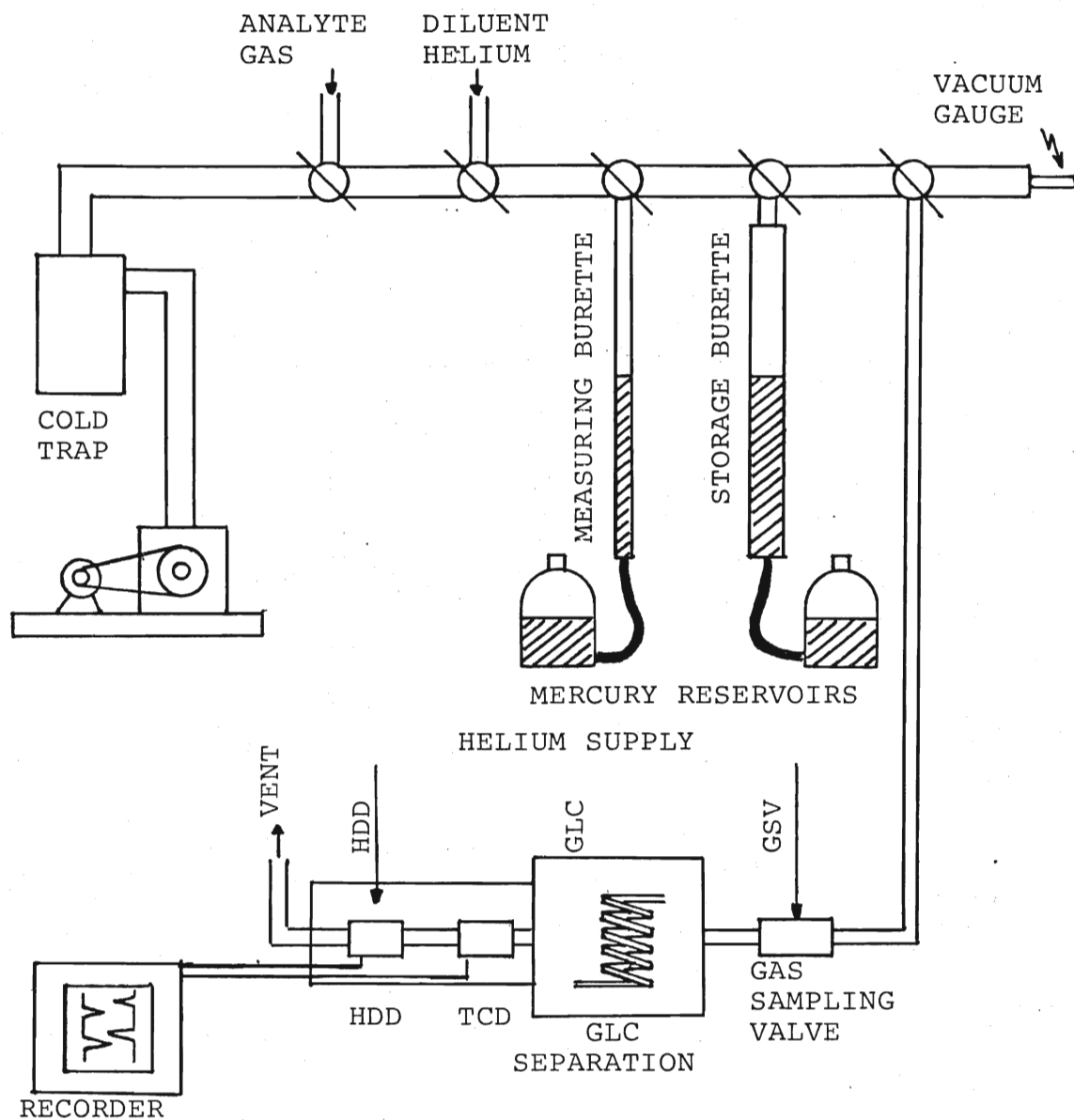


FIGURE 5.

**GAS MANIPULATION RACK
AND
ANALYSIS SYSTEM**

2.8 INJECTION OF STANDARD GAS SAMPLES:

After preparation of the desired calibration gas mixture, the sample contained in the storage burette was adjusted to atmospheric pressure by manipulation of the mercury level. Injection of the sample onto the gas chromatographic column was made via the Carle GSV, using mercury displacement of the gas in the storage burette to transfer the gas sample through the connecting tubing to the sample loop of the GSV. A brief, but definite, purge of the sample loop to the atmospheric vent was included to ensure that all plumbing downstream of the gas sample valve contained the gas sample under analysis, thereby minimizing back diffusion of ambient air into the gas sample valve.

2.9 QUANTITATION OF ANALYTICAL DATA:

Outputs from both the HDD and TCD detectors was directed to a Linear Dual Pen recorder. As indicated earlier, both the HDD and the TCD are prone to generating M-shaped peaks under certain conditions, primarily when high concentrations of analyte are being analysed. This phenomenon leads to distinct problems when attempting to quantitate the observed signal from these detectors, as the traditional methods of triangulation are not applicable. Visual inspection of the tracings in which M-shaped peaks were obtained revealed that these peaks were triangular. The area of these peaks was determined by measuring the total length of pen displacement (t) from the baseline during elution of a component. Division of the length (t) by 2 provides the length (l) of each of two sides of an (assumed) isosceles triangle; measurement of the length of travel along the baseline during

peak elution provides the third side (b) of the triangle.

The area of the triangle is then given by the Heron formula:

$$\text{Area} = \text{SQRT} [s(s-b)((s-l)^2)] \quad \dots\dots (1)$$

where $s = 1/2 * (\text{perimeter length of triangle})$
 $= (t+b)/2$
 $b = \text{base length of triangle}$
 $l = \text{side length of triangle}$
 $= t/2$

For consistency, the area of all chromatographic peaks was determined by this technique.

CHAPTER 3

RESULTS AND DISCUSSION

As a result of this investigation, it can be stated with some certainty that the two most important variables affecting the performance of the HDD are detector cleanliness and carrier gas purity. The initial analyses conducted with the HDD were not reproducible. In fact, the initiation of the discharge became increasingly difficult, to the point at which even a boost voltage from a hand held Tesla coil could not initiate the electrical discharge. The problem was traced to a deposit or layer, of an unknown nature, on the discharge electrodes which could be removed by a rigorous cleaning procedure. Examination of the electrodes at up to 40 X magnification did not show any obvious build up. The Beckman GC-4 gas chromatograph was located in an active, commercial, analytical laboratory and, as such, was in frequent use. The majority of gas chromatographic analyses conducted in this laboratory required the use of the TC detector which, as described earlier, was connected in series with the HDD. Instead of making extensive plumbing modifications to isolate the HDD from the TCD and move the latter to the analytical column required for a particular analysis, the required column was connected to the influent end of the TCD. While satisfactory for the immediate need, this operation apparently resulted in either condensation of eluting components or deposition of liquid phase in the HDD. Baking the HDD for extended periods in the gc oven was not successful in removing the condensed materials, and it became

necessary to subject the HDD to routine ultrasonic cleaning in a mixture of hexane and methylene chloride to ensure electrode cleanliness prior to each use of the detector. The strict need for cleanliness of this detector cannot be overstressed and future versions of this detector must address this problem. It is suggested that the material condensing on the detector electrodes represented not only residues from injected materials, but also bleed from the liquid phase coating the particular analytical columns employed. For analytical purposes, only solid supports such as the Porapak[®] or carbon molecular sieves proved useable with the HDD as they exhibit essentially no bleed. A partial remedy to the contamination problem was found by ensuring that a purge of helium was flushed continuously through the HDD during the occasions when the gas chromatograph was being used for routine, commercial analyses. While this action reduced the severity of the fouling, it did not eliminate the need for ultrasonic cleaning of the electrodes prior to use.

Alleviation of electrode fouling difficulties revealed a second, more subtle problem, however. It was observed that substantial background current changes, manifested as baseline shifts, were apparent in the HDD response, almost on a weekly basis. At that time, the Beckman GC-4 gas chromatograph, together with several other instruments in frequent use, was supplied from a single cylinder of 'pure' helium. Due again to the throughput of the commercial laboratory, the helium cylinder was subject to frequent changes. Armed with the suspicion of carrier gas purity requirements suggested by several authors^{12,16,17,18,19,20}, samples were collected from several spent cylinders of helium

and subjected to mass spectral analysis. The results confirmed that the bottled helium contained variable quantities of trace contaminants such as nitrogen, oxygen, and even argon. The presence in the carrier gas of such impurities, all of which have lower ionization potentials than helium, was apparently causing the variable background currents observed. It is suspected that the contamination of the cylinders is due not to the purity of the helium being bottled, but rather to the misuse of cylinders by previous users and to the lack of good quality control procedures by the vendors. To remedy the situation, a supply of certified ultra high purity helium was connected to the HDD analysis system on a dedicated basis; once installed, the background current was observed to be substantially more stable and reproducible.

After the establishment and confirmation of short and long term reproducibility, the system was employed to produce response data for three fixed gases, oxygen, nitrogen, and hydrogen. The analyses were undertaken by preparing serial dilutions of known concentrations for each gas under consideration, and analysing each by injection onto a 5A carbon molecular sieve column. Ambient air was used as the source of oxygen and nitrogen. Tables 1 - 6 detail the experimental results.

H E L I U M D I S C H A R G E D E T E C T O R R E S P O N S E
O X Y G E N

RUN #	OXYGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	LOG SIGNAL	AVERAGE LOG SIGNAL
72	2.09E+01		265.0	5000	1324827.2	1324453.3	6.1220	
73	2.09E+01	1.320	272.2	5000	1361203.5	1360829.6	6.1338	6.1279
74	2.09E+00		115.5	5000	577390.4	577016.5	5.7612	
75	2.09E+00	0.320	114.7	5000	573639.7	573265.8	5.7584	5.7598
76	2.09E-01		171.5	1000	171497.1	171123.1	5.2333	
77	2.09E-01	-0.680	172.0	1000	171997.1	171623.1	5.2346	5.2339
78	2.09E-02		40.0	500	19993.7	19619.8	4.2927	
79	2.09E-02	-1.680	42.5	500	21244.1	20870.2	4.3195	4.3061
80	2.09E-03		12.7	50	636.9	262.9	2.4198	
81	2.09E-03	-2.680	13.1	50	655.6	281.7	2.4498	2.4348
82	0		7.5	50	373.9	0.0		
83	0		7.5	50	373.9	0.0		

T A B L E 1.

HELIUM DISCHARGE DETECTOR RESPONSE

NITROGEN

RUN #	NITROGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	LOG SIGNAL	AVERAGE LOG SIGNAL
72	7.81E+01		762.9	5000	3814508.3	3813330.3	6.5813	
73	7.81E+01	1.893	785.7	5000	3928272.5	3927094.5	6.5941	6.5877
74	7.81E+00		386.2	5000	1930997.2	1929819.1	6.2855	
75	7.81E+00	0.893	388.1	5000	1940373.4	1939195.4	6.2876	6.2866
76	7.81E-01		378.0	1000	377966.1	376788.1	5.5761	
77	7.81E-01	-0.107	379.1	1000	379091.2	377913.2	5.5774	5.5767
78	7.81E-02		77.9	500	38948.7	37770.7	4.5772	
79	7.81E-02	-1.107	82.9	500	41451.8	40273.8	4.6050	4.5911
80	7.81E-03		44.6	50	2228.2	1050.2	3.0213	
81	7.81E-03	-2.107	45.2	50	2259.7	1081.7	3.0341	3.0277
82		0	23.6	50	1178.0	0.0		
83		0	23.6	50	1178.0	0.0		

TABLE 2.

HELIUM DISCHARGE DETECTOR RESPONSE

HYDROGEN

RUN #	HYDROGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	% REL STD DEV	LOG SIGNAL	AVERAGE LOG SIGNAL
91	1.00E+02		125.1	5000	625306.2	625306.2		5.7961	
92	1.00E+02		131.1	5000	655306.5	655306.5		5.8164	
93	1.00E+02	2.000	134.1	5000	670306.6	670306.6	2.88	5.8263	5.8129
94	1.00E+01		64.1	5000	320622.6	320622.6		5.5060	
95	1.00E+01		72.5	5000	362497.8	362497.8		5.5593	
96	1.00E+01		81.2	5000	406248.1	406248.1		5.6088	
97	1.00E+01	1.000	84.9	5000	424373.2	424373.2	10.64	5.6277	5.5755
98	1.00E+00		20.7	5000	103749.5	103749.5		5.0160	
99	1.00E+00		21.1	5000	105624.5	105624.5		5.0238	
100	1.00E+00	0.000	21.1	5000	105624.5	105624.5	0.84	5.0238	5.0212
101	1.00E-01		52.5	500	26249.7	26249.7		4.4191	
102	1.00E-01	-1.000	52.5	500	26249.7	26249.7		4.4191	4.4191
103	1.00E-02		1.5	25	37.5	37.5		1.5737	
104	1.00E-02	-2.000	1.5	25	37.5	37.5		1.5737	1.5737

TABLE 3.

THERMAL CONDUCTIVITY DETECTOR RESPONSE

OXYGEN

RUN #	OXYGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	LOG SIGNAL	AVERAGE LOG SIGNAL
72	2.09E+01		172.7	8	1382.0	1382.0	3.1405	
73	2.09E+01	1.320	173.0	8	1384.0	1384.0	3.1411	3.1408
74	2.09E+00		26.2	8	210.0	210.0	2.3221	
75	2.09E+00	0.320	26.2	8	210.0	210.0	2.3221	2.3221
76	2.09E-01		82.5	1	82.5	82.5	1.9163	
77	2.09E-01	-0.680	82.5	1	82.5	82.5	1.9163	1.9163
78	2.09E-02		2.4	1	2.4	2.4	0.3732	
79	2.09E-02	-1.680	2.4	1	2.4	2.4	0.3732	0.3732
80	2.09E-03		NA	1	NA			
81	2.09E-03	-2.680	NA	1	NA			
82	0		NA	1	NA			
83	0		NA	1	NA			

TABLE 4.

T H E R M A L C O N D U C T I V I T Y D E T E C T O R R E S P O N S E
N I T R O G E N

RUN #	NITROGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	LOG SIGNAL	AVERAGE LOG SIGNAL
72	7.81E+01		462.5	8	3699.7	3699.7	3.5682	
73	7.81E+01	1.893	460.0	8	3679.7	3679.7	3.5658	3.5670
74	7.81E+00		81.9	8	655.2	655.2	2.8164	
75	7.81E+00	0.893	81.9	8	655.2	655.2	2.8164	2.8164
76	7.81E-01		161.1	1	161.1	161.1	2.2072	
77	7.81E-01	-0.107	157.4	1	157.4	157.4	2.1969	2.2021
78	7.81E-02		13.4	1	13.4	13.4	1.1276	
79	7.81E-02	-1.107	12.9	1	12.9	12.9	1.1104	1.1190
80	7.81E-03		NA	1	NA			
81	7.81E-03		NA	1	NA			
82	0		NA	1	NA			
83	0		NA	1	NA			

T A B L E 5.

THERMAL CONDUCTIVITY DETECTOR RESPONSE

HYDROGEN

RUN #	HYDROGEN %	LOG	PEAK AREA	ATTEN	TOTAL SIGNAL	CORRECTED SIGNAL	% REL STD DEV	LOG SIGNAL	AVERAGE LOG SIGNAL
91	1.00E+02		60.6	2	121.2	121.2		2.0837	
92	1.00E+02		60.5	2	121.0	121.0		2.0828	
93	1.00E+02	2.000	60.0	2	120.0	120.0	0.45	2.0792	2.0819
94	1.00E+01		15.0	1	15.0	15.0		1.1761	
95	1.00E+01		15.0	1	15.0	15.0		1.1761	
96	1.00E+01		15.1	1	15.1	15.1		1.1797	
97	1.00E+01	1.000	15.1	1	15.1	15.1	0.41	1.1797	1.1779
98	1.00E+00		1.5	1	1.5	1.5		0.1757	
99	1.00E+00		1.5	1	1.5	1.5		0.1757	
100	1.00E+00	0.000	1.5	1	1.5	1.5	.00	0.1757	0.1757
101	1.00E-01		NA	1	NA				
102	1.00E-01	-1.000	NA	1	NA				
103	1.00E-02		NA	1	NA				
104	1.00E-02	-2.000	NA	1	NA				

TABLE 6.

DETECTOR RESPONSE FOR OXYGEN HELIUM DISCHARGE & THERMAL CONDUCTIVITY

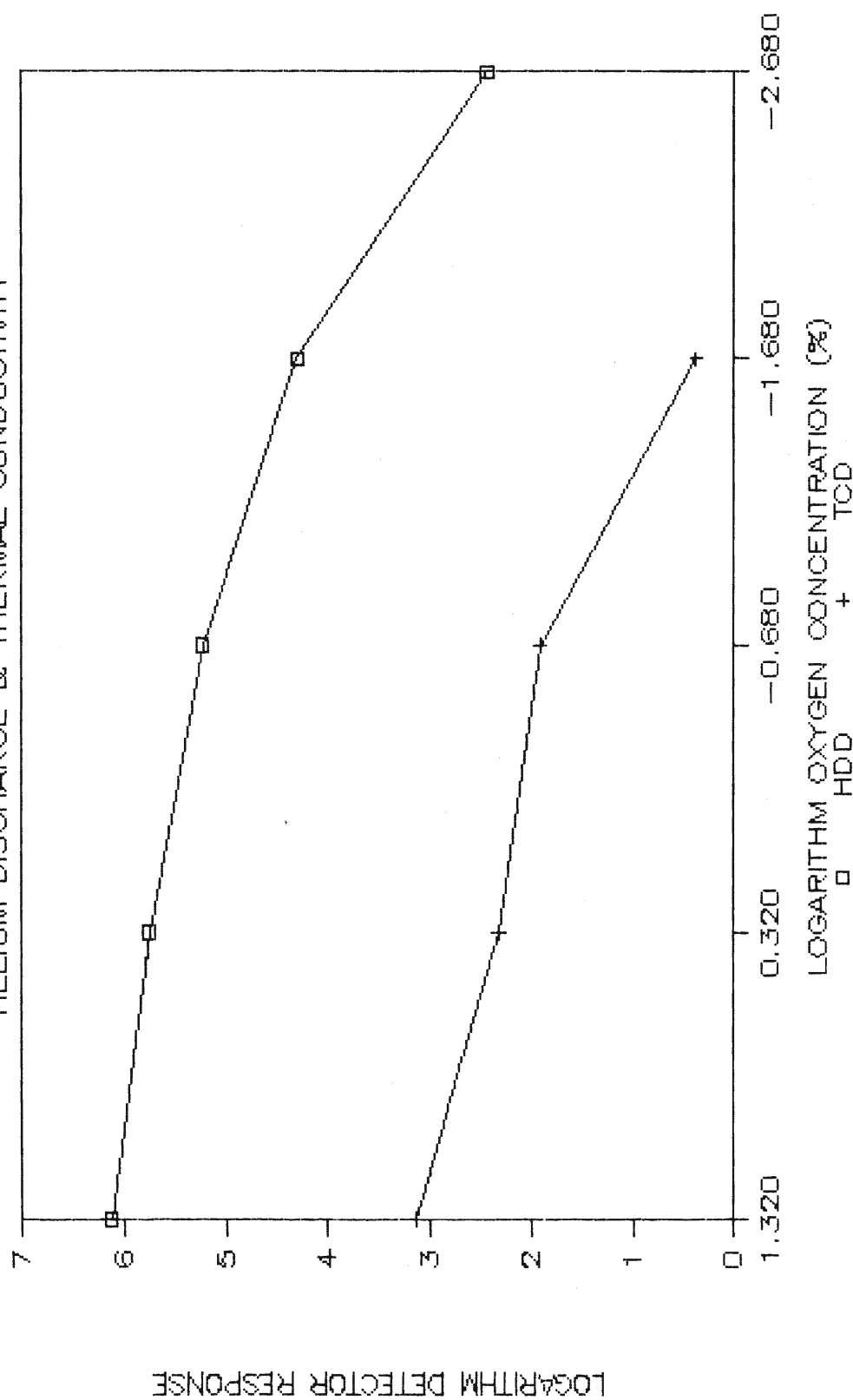


FIGURE 6.

DETECTOR RESPONSE FOR NITROGEN

HELIUM DISCHARGE & THERMAL CONDUCTIVITY

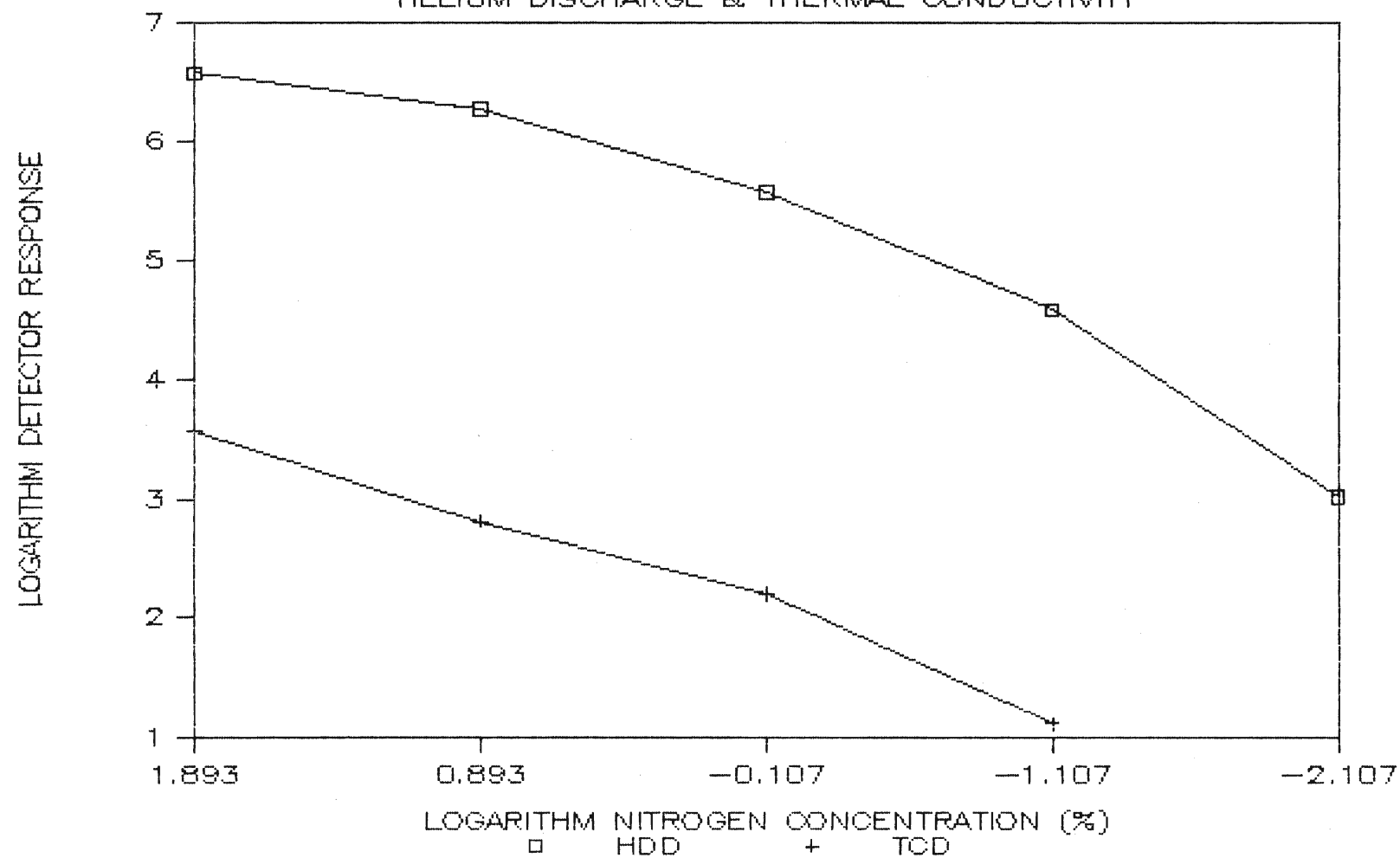


FIGURE 7.

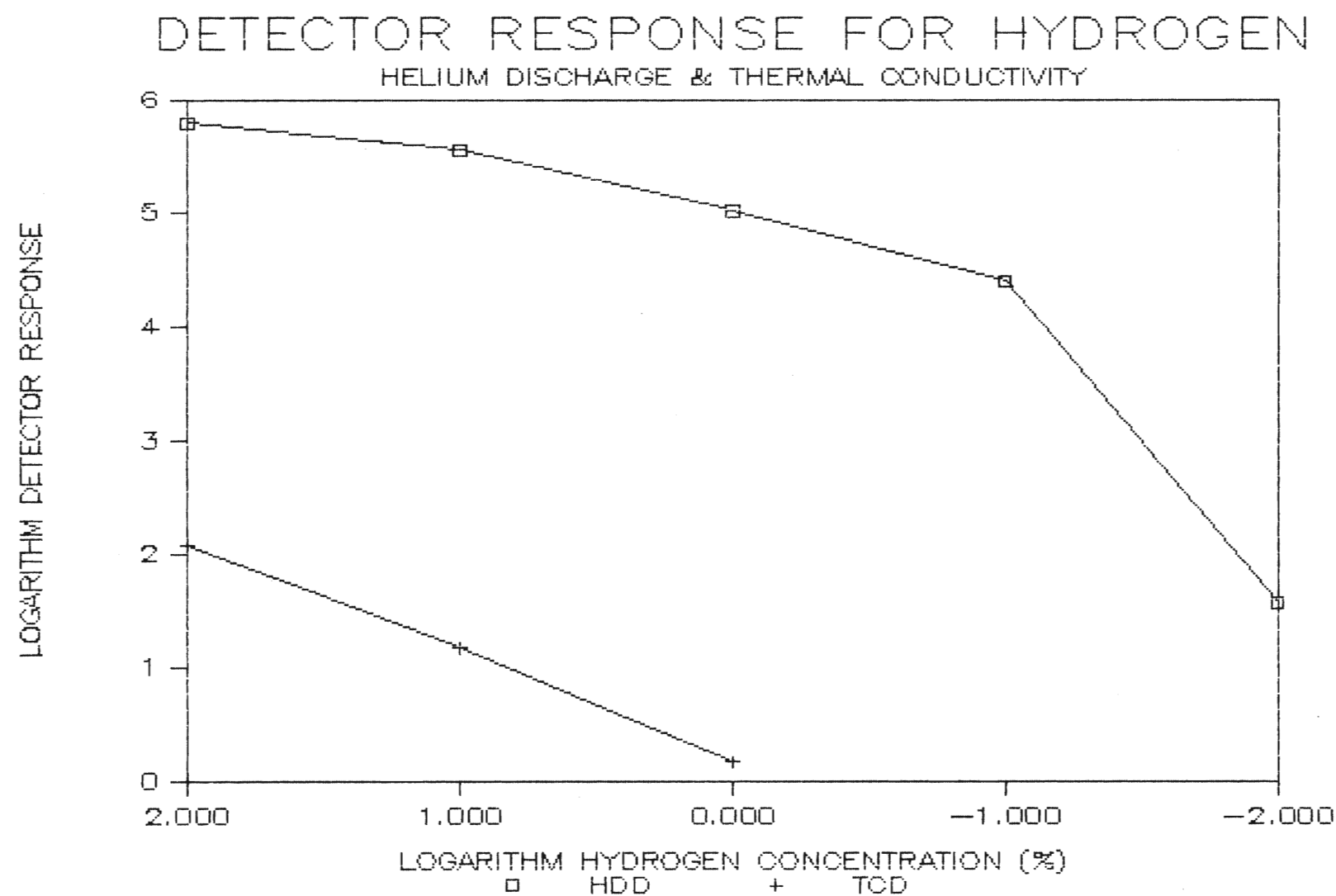


FIGURE 8.

Chromatographic data indicated the presence of a slight air leak in the analysis system; the amount of this leakage was quantitated and appropriate corrections made in the concentration of each oxygen and nitrogen sample. As indicated earlier, estimation of the area of the HDD and TCD signals was performed by a geometric interpretation to manage the M-shaped peaks generated, on occasion, by both detectors. To facilitate data display, logarithms of both the detector response and analyte concentration were calculated and are shown in Figures 6, 7, and 8. The actual chromatographic tracings are included in Appendix A.

Considering first the TCD measurements, typical near-Gaussian response for oxygen, nitrogen, and hydrogen was observed over the range of concentrations studied with the exception of the injections of 100 % hydrogen. In these instances, runs 91, 92, and 93 in Appendix A, an M-shaped peak response was obtained. This phenomenon, as discussed earlier, is attributed to a minimum in the thermal conductivity curve which occurs in a mixture of about 13 % hydrogen - 87 % helium. Inspection of the curves shown in Figures 6, 7, and 8 indicates that the TCD response is essentially linear for the three gases analysed over the range of concentrations studied. Specifically, a TCD response was measured over the concentration ranges 21 - 0.021 % oxygen, 78 - 0.078 % nitrogen, and 100 - 1.00 % hydrogen. As a precaution against filament damage with oxygen in the system, the TCD was operated at much less than maximum current, namely 150 mA. While increasing the operating current to, say, 200 mA may well have extended the analysis range, the potential risk to the detector was not

justified. By linear regression and extrapolation of the response data of Tables 4, 5, and 6, it is possible to estimate the detection limit for each gas analysed with the Gow-Mac Thermal Conductivity Detector as shown in Table 7.

THERMAL CONDUCTIVITY DETECTOR RESPONSE
LINEAR REGRESSION ANALYSIS

for $y = mx + b$

GAS	m	b	CORR. COEFF.	STD. ERROR OF ESTIMATE	DETECTION LIMIT
O ₂	0.8709	2.0949	0.9684	0.4776	8.7E-3%
N ₂	0.7958	2.1134	0.9928	0.2008	5.3E-3%
H ₂	0.9531	0.1921	0.9996	0.0463	1.3 %

TABLE 7.

For the analyses of oxygen and nitrogen with the TCD, only duplicate analyses were performed; however, in the case of hydrogen, the analyses were performed in triplicate. Examination of Table 6 indicates that the peak area response is quite reproducible with a relative standard deviation of less than 0.5 %. Inspection of Tables 4 and 5 suggests that, although insufficient data exists to permit quantitation, a similar reproducibility was achieved.

The HDD was, in general, more sensitive than the TCD for the analyses at hand. M-shaped peaks were encountered, but only at the higher concentrations of analyte gas, namely 21 - 2.1 % oxygen, 78 - 7.8 % nitrogen, and 100 % hydrogen. Below these concentrations, normal near-Gaussian peaks were obtained. Inspection of the Figures 6, 7, and 8 reveals

that, unlike the response of the TCD, the response curves of the HDD are not linear. Detector response was measured for concentrations of 21 - 0.0021 % oxygen, 78 - 0.0078 % nitrogen, and 100 - 0.01 % hydrogen. The plotted curves of HDD response shown in Figures 6 through 8 can be fitted to a simple quadratic function and estimates of the detection limit of each gas analysed with the Beckman Helium Discharge Detector can be made as shown in Table 8.

HELIUM DISCHARGE DETECTOR RESPONSE
CURVILINEAR REGRESSION ANALYSIS

$$\text{for } y = ax^2 + bx + c$$

GAS	a	b	c	STD. ERROR OF ESTIMATE	DETECTION LIMIT
O ₂	-0.2435	0.5529	5.7479	0.2485	1.9E-4%
N ₂	-0.2000	0.8387	5.7060	0.0694	3.1E-4%
H ₂	-0.3162	1.0472	4.9455	0.1312	3.0E-3%

TABLE 8.

As with the TCD analyses, only duplicate analyses of oxygen and nitrogen were undertaken with the HDD. Again however, several of the hydrogen analyses were performed in triplicate. Examination of the data of Table 3 indicates that the reproducibility of the HDD response is considerably more varied, with the relative standard deviation ranging from 0.84 - 10.64 %. Oddly, the most non-reproducible result is not the most sensitive measurement, but rather an intermediate result. The reason for this behaviour is uncertain but may originate in the electronics of the HDD.

As noted earlier, the corresponding peak responses measured with the TCD were quite reproducible, suggesting the problem does not lie with the analysis train. The peak responses tabulated in Tables 1 and 2, while not quantitated, suggest acceptable reproducibility.

Comparison of the data of Tables 1 through 8 indicates that, for oxygen and nitrogen, the Beckman Helium Discharge Detector is 10 times more sensitive than the Gow-Mac Thermal Conductivity Detector. Of more immediate significance, however, is the observation that the HDD is 100 times more sensitive to hydrogen than is the TCD. In addition, the potential exists to realize even greater sensitivity from the HDD by the use of of a solid-state electrometer. Increased sensitivity was not possible with the analysis system utilized in this study due to the substantial noise background inherent in the vacuum tube electrometer employed for this work.

As indicated earlier in this discussion, the Helium Discharge Detector generated M-shaped peaks in the presence of high concentrations of analyte gas. The phenomena occurring within the detector which result in the generation of an M-shaped peak are of interest in understanding the mechanism by which the HDD operates. It is speculated that a mechanism similar to that proposed by Yamane¹⁴ to explain the electronic characteristics of the Helium Ionization Detector may describe the processes occurring within the Helium Discharge Detector. Gaseous components exiting the chromatographic column are ionized in the sensing chamber by high energy species (helium ions, metastable helium atoms, and electrons) generated in the region of the helium

discharge electrodes. The generation of an increased current flow, as measured at the collector electrode, is indicative of the increasing concentration of these ionized species corresponding to the increased concentration of the gaseous effluent in the sensing chamber. At two points (undefined) during the elution of the gaseous component from the chromatograph, the measured current reverses in polarity. Yamane has suggested that the change in current observed with the Helium Ionization Detector may result from photoionization processes occurring within the sensing chamber. It is thought that similar processes may be at work in the HDD. While it is not possible to validate this hypothesis at present, a future study might involve the construction of a working detector cell from quartz, thereby allowing the processes occurring within the detector to be studied spectroscopically.

CHAPTER 4

CONCLUSIONS

The results of this study indicate that the Beckman Helium Discharge Detector is a suitable device for the analysis of the fixed gases oxygen, nitrogen and hydrogen at levels 10-100 times more sensitive than possible with the Gow-Mac Thermal Conductivity Detector. Detection levels of $1.9 \times 10^{-4} \%$ oxygen, $3.1 \times 10^{-4} \%$ nitrogen, and $3.0 \times 10^{-3} \%$ hydrogen are estimated for the HDD. The applicability of this detector to the analysis of fixed gases, and in particular, hydrogen, suggests that the Helium Discharge Detector could represent a relatively inexpensive alternative to the use of sophisticated analytical devices by practical analytic laboratories.

Considerable difficulty was initially encountered in the course of the investigation due to the relative instability of the HDD. The necessity of absolute electrode cleanliness and carrier gas purity have been established as physical prerequisites for reproducible operation of the detector. Contamination of the detector electrodes, traced to column bleed from packed columns inadvertently connected to the HDD, was found to be removable only by ultrasonic cleaning. Trace impurities such as oxygen, nitrogen, and argon in bottled helium were found to cause variable background current in the HDD. The only convenient solution to this problem was the use of certified purity helium.

The appearance of M-shaped peaks at high levels of analyte do not appear to cause any problems in quantitation

of the fixed gases studied when the peaks are integrated by the geometric technique employed; however, the progress of this and future studies would be greatly assisted through the incorporation of electronic integration devices to facilitate the integration of the chromatograms.

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APPENDIX A

CHROMATOGRAPHIC DATA

BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 5000

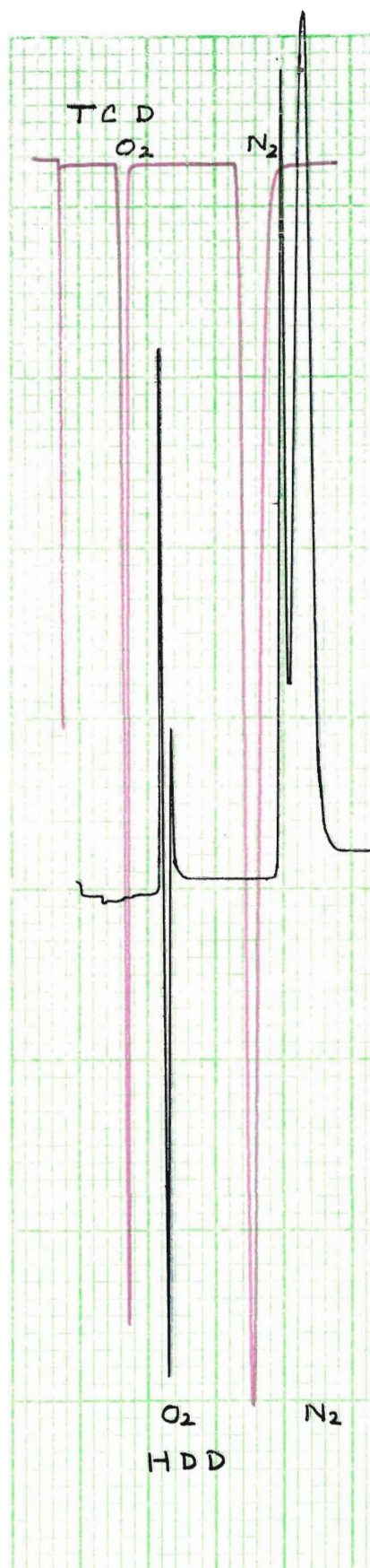
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 8

Recorder: 1 cm/min
 10 mV FSA

RUN # 72

O₂: 209460 ppm
 N₂: 780840 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 8

Recorder: 1 cm/min
10 mV FSA

RUN # 73

O₂: 209460 ppm
N₂: 780840 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

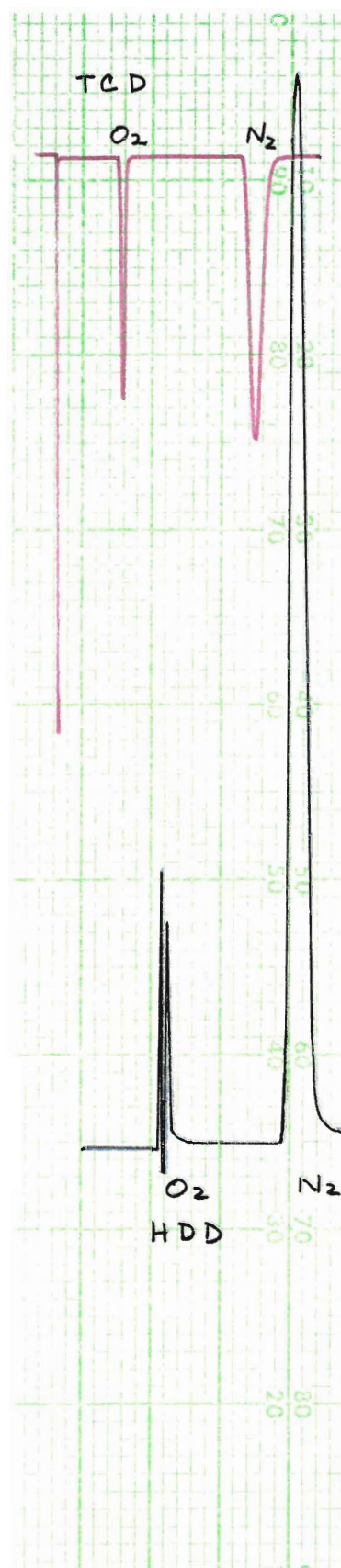
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 8

Recorder: 1 cm/min
10 mV FSA

RUN # 74

O₂: 20946 ppm
N₂: 78084 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

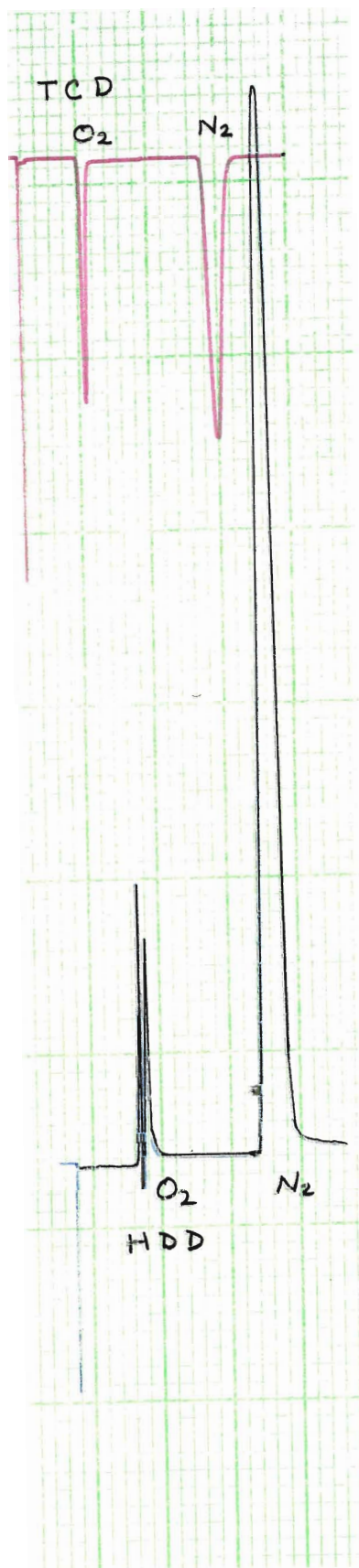
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 8

Recorder: 1 cm/min
10 mV FSA

RUN # 75

O₂: 20946 ppm
N₂: 78084 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 1000

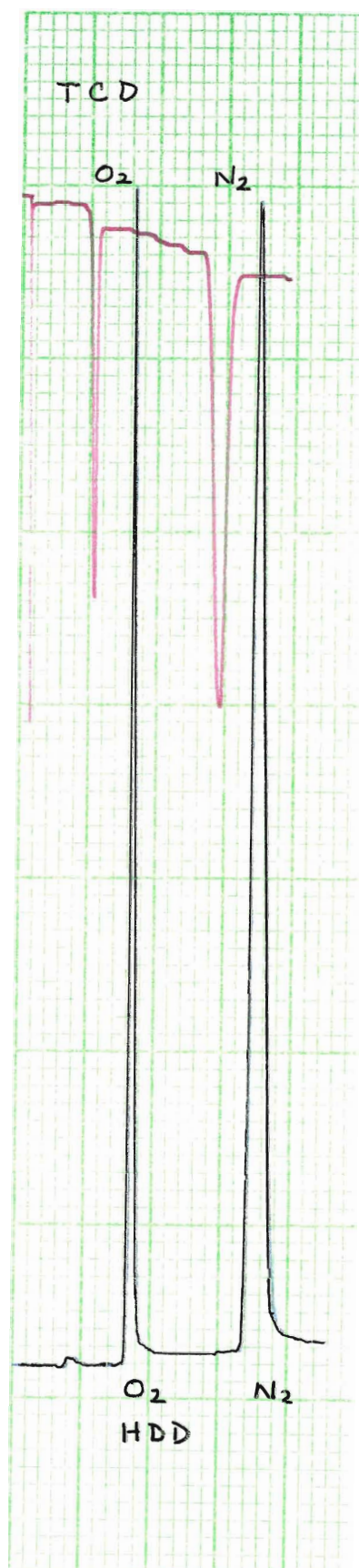
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 76

O₂: 2095 ppm
N₂: 7808 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80)mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 1000

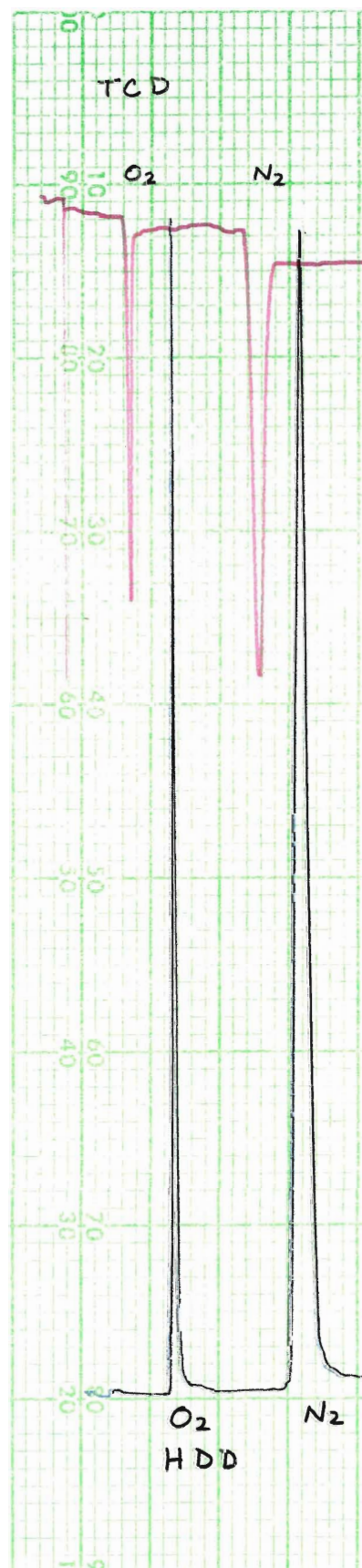
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 77

O₂: 2095 ppm
N₂: 7808 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 500

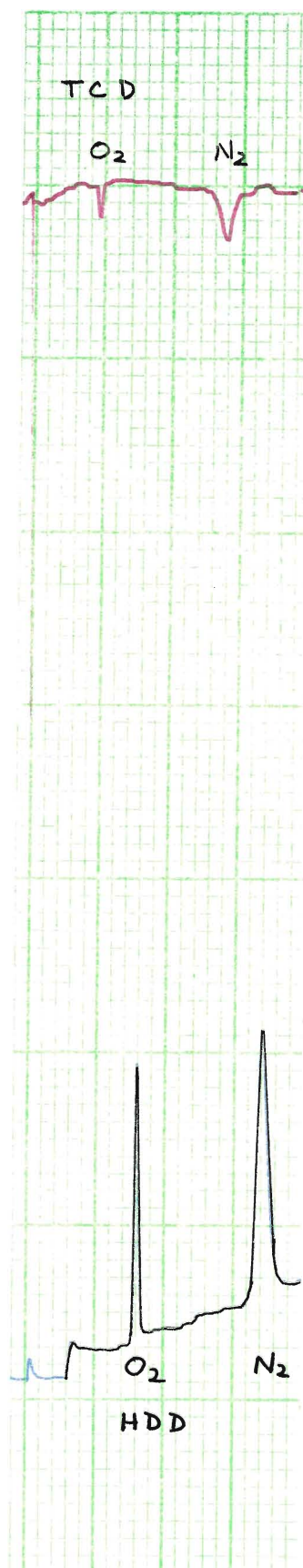
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 78

O₂: 209 ppm
 N₂: 781 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 500

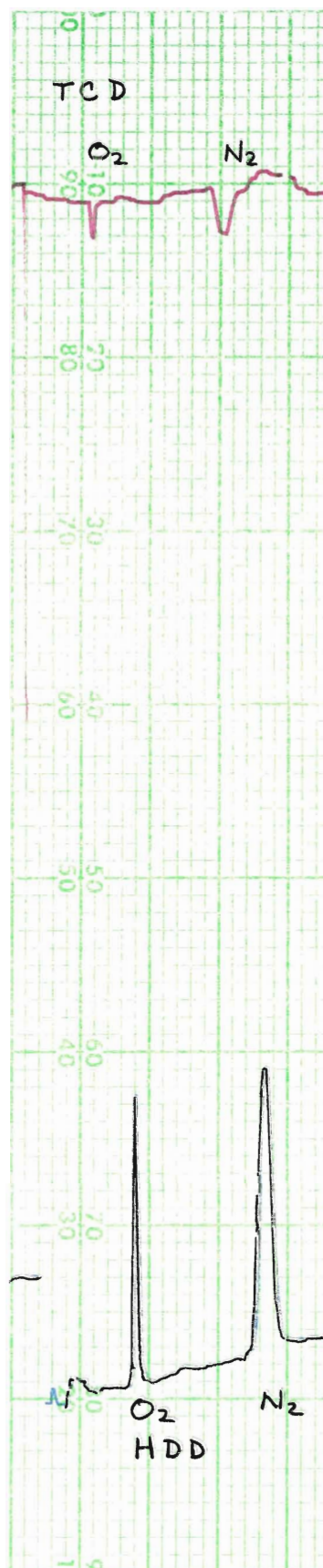
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 79

O₂: 209 ppm
 N₂: 781 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 50

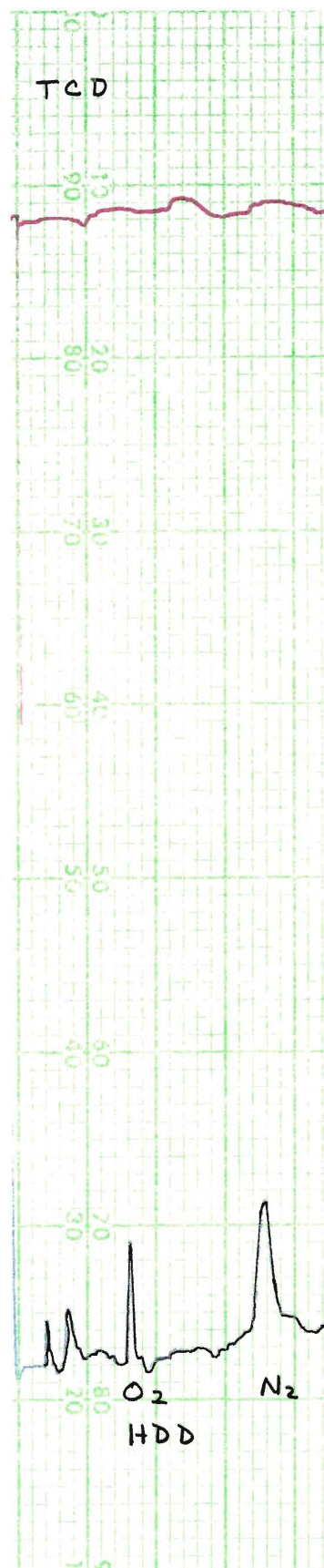
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 80

O₂: 21 ppm
 N₂: 78 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 3A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 50

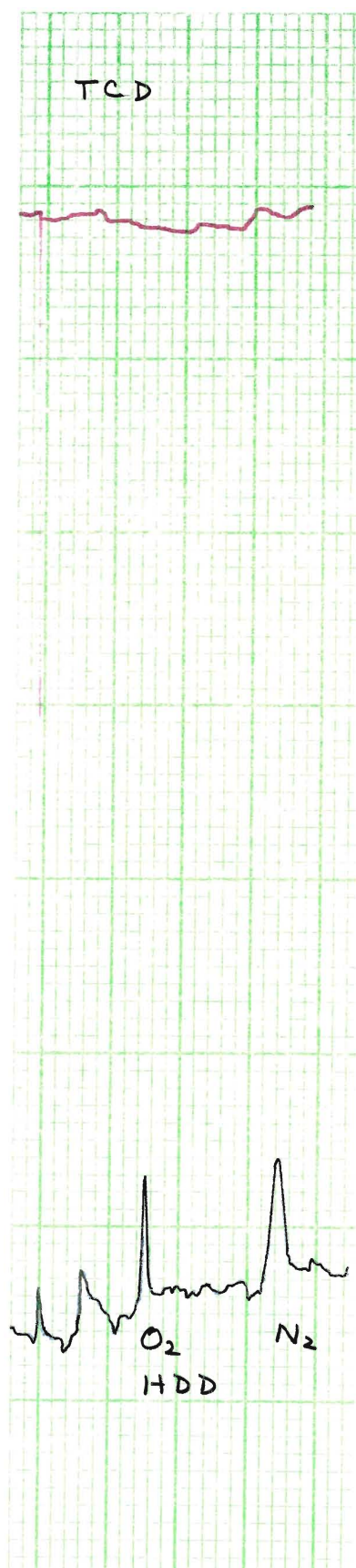
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 81

O₂: 21 ppm
 N₂: 78 ppm



BECKMAN 6C-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 50

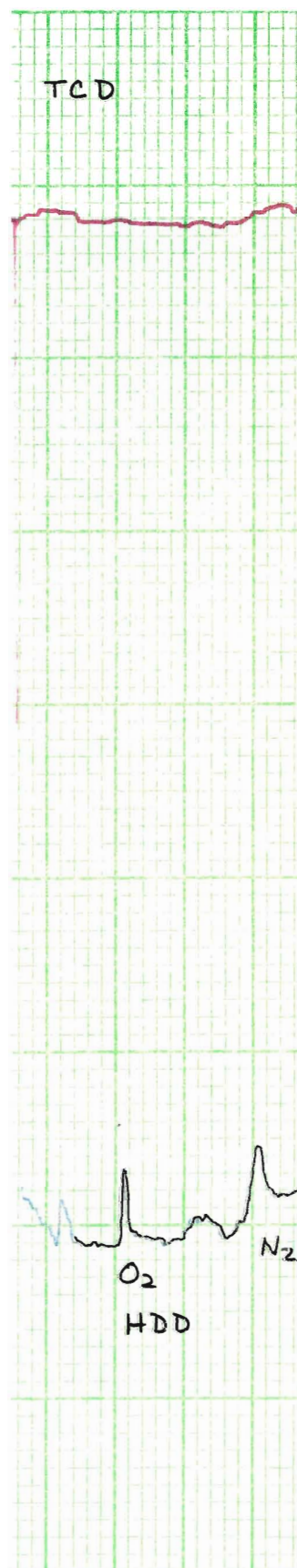
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 82

O₂: 0 ppm
 N₂: 0 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 50

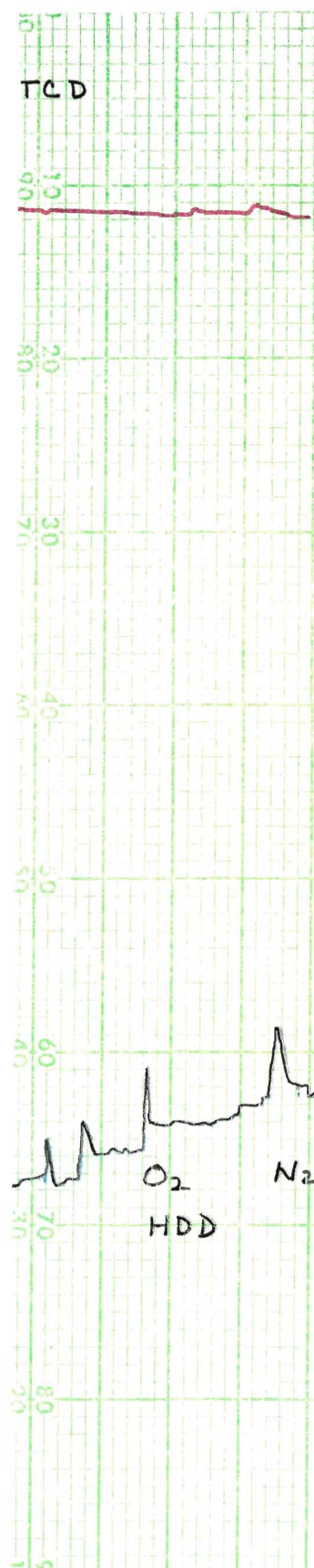
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 83

O₂: 0 ppm
 N₂: 0 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

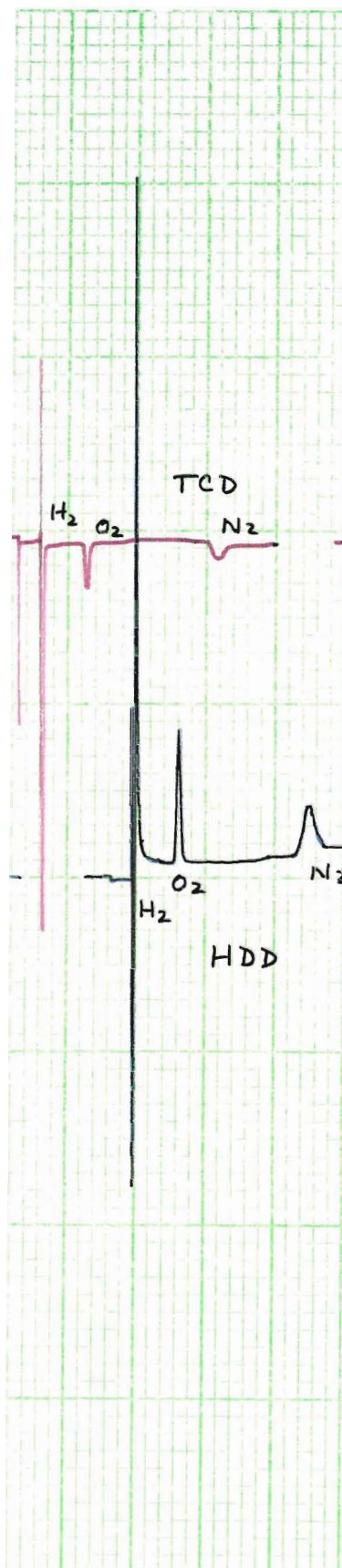
Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 2

Recorder: 1 cm/min
 10 mV FSA



RUN # 91

H₂: 1000000 ppm

BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80)mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 5000

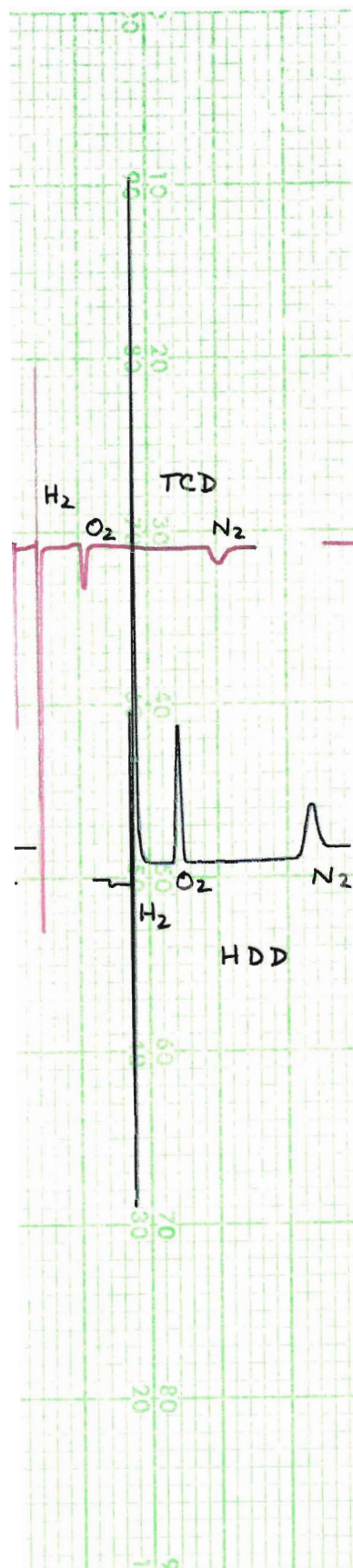
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 2

Recorder: 1 cm/min
 10 mV FSA

RUN # 92

H₂: 1000000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 2

Recorder: 2 cm/min
10 mV FSA

RUN # 93

H₂: 1000000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80)mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

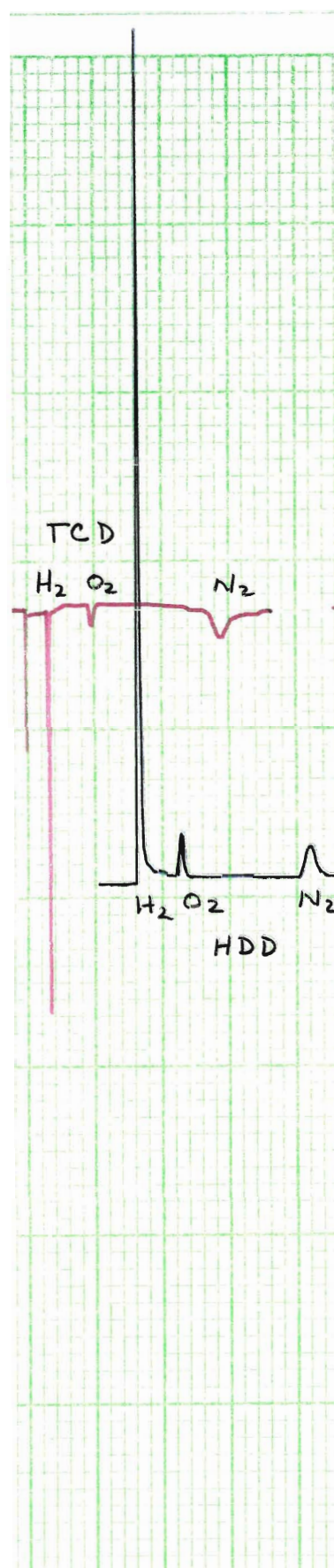
Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA



RUN # 94

H₂: 100000 ppm

BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 5000

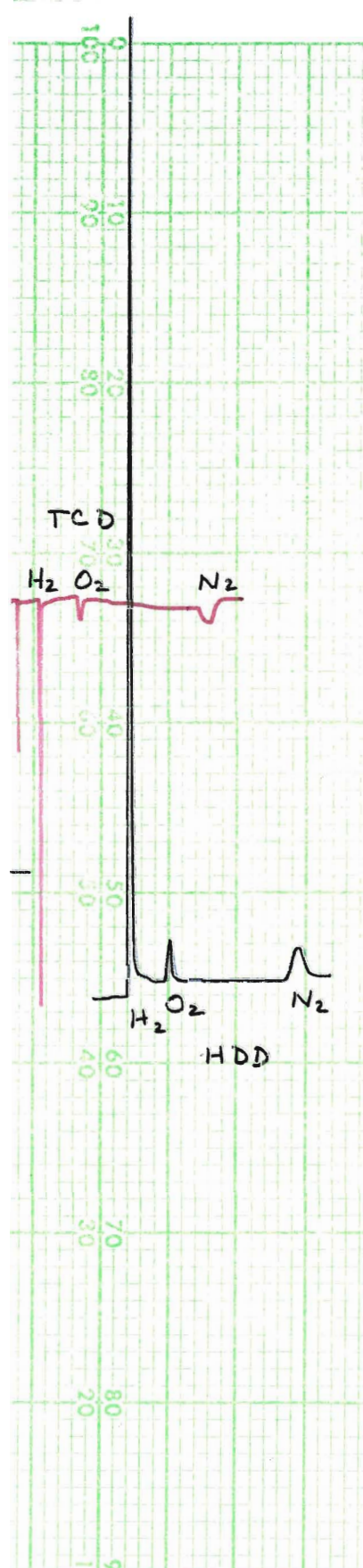
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 95

H₂: 100000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

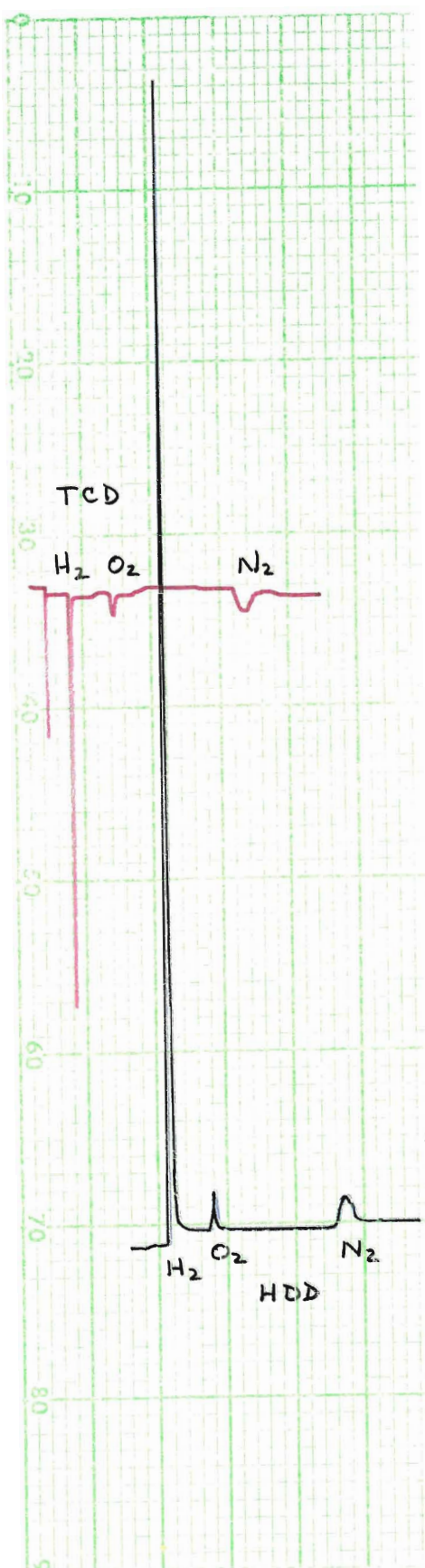
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 97

H₂: 100000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
 Steel packed with 5A Carbon
 Molecular Sieve (60-80)mesh

Carrier Gas:

Column : 40 ml/min
 Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
 Current : 15.5 mA
 Polarizing Voltage: 1000 VDC
 Bias Voltage : 0 VDC
 Attenuation : X 5000

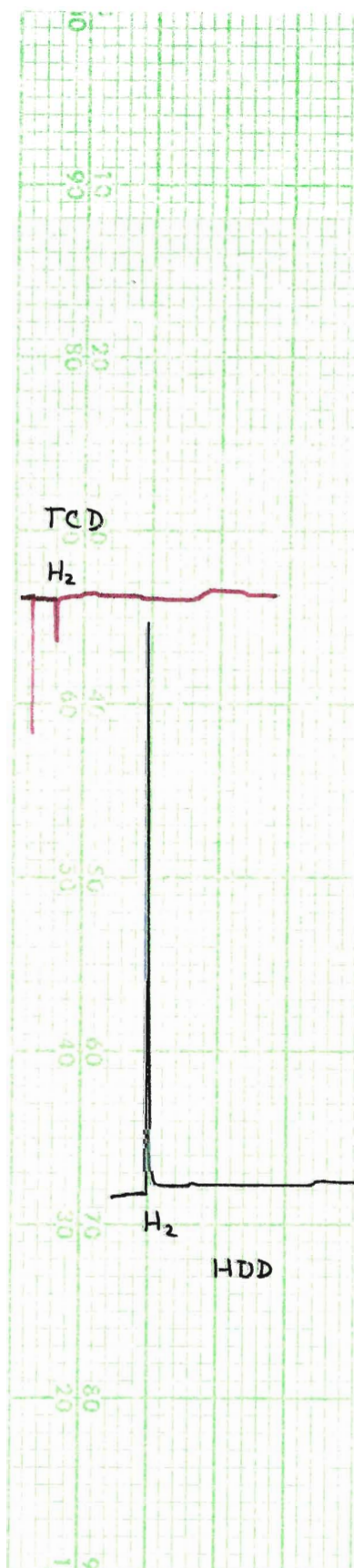
Thermal Conductivity Detector:

Voltage : 10 VDC
 Current : 125 mA
 Attenuation : X 1

Recorder: 1 cm/min
 10 mV FSA

RUN # 98

H₂: 10000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 99

H₂: 10000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 5000

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 100

H₂: 10000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80)mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 500

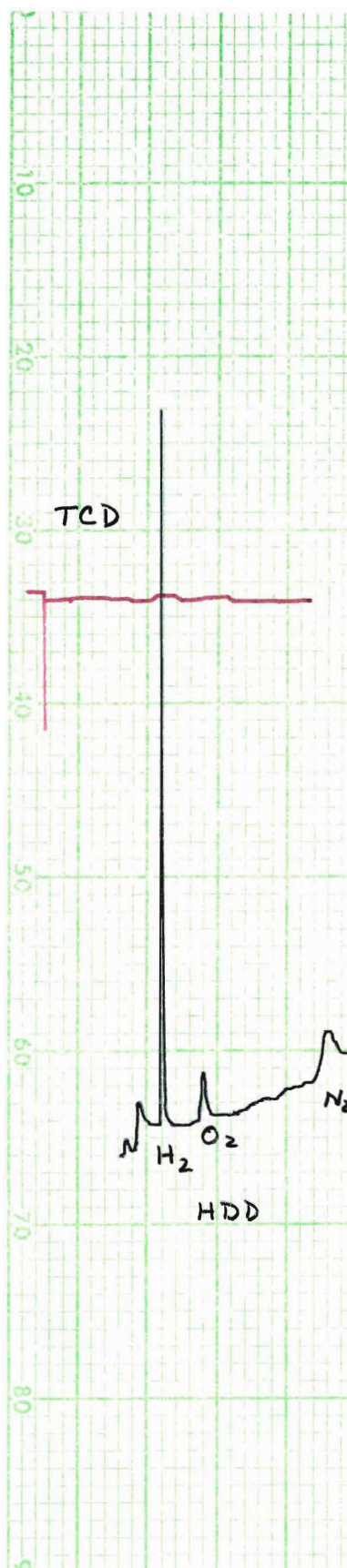
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 101

H₂: 1000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 500

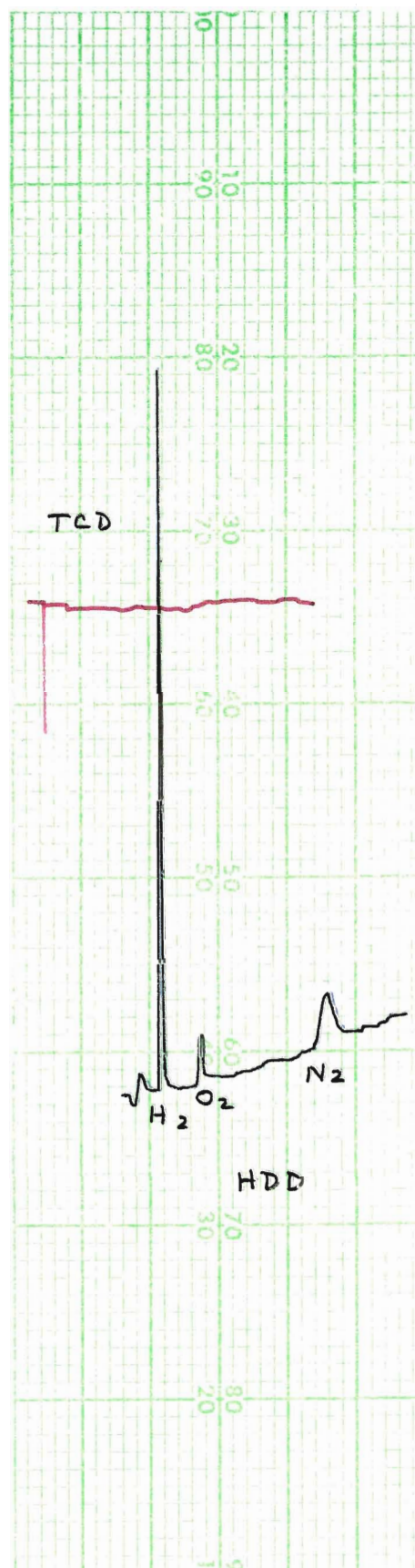
Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA

RUN # 102

H₂: 1000 ppm



BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

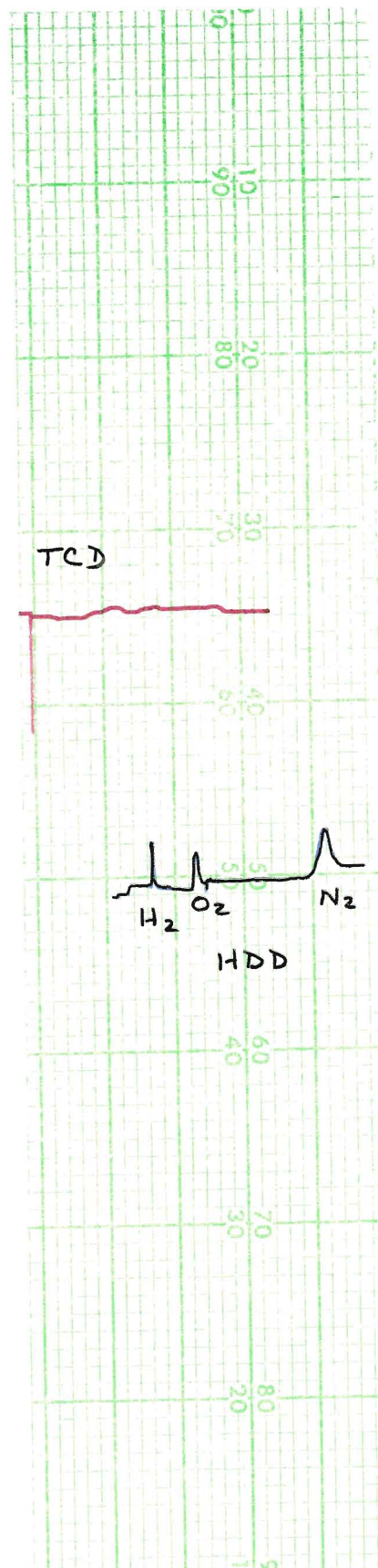
Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 25

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder: 1 cm/min
10 mV FSA



RUN # 103

H₂: 100 ppm

BECKMAN GC-4 GAS CHROMATOGRAPH

Column: 7' X 1/8" Stainless
Steel packed with 5A Carbon
Molecular Sieve (60-80) mesh

Carrier Gas:

Column : 40 ml/min
Discharge : 160 ml/min

Column Temperature : Ambient

Helium Discharge Detector:

Voltage : 210 VDC
Current : 15.5 mA
Polarizing Voltage: 1000 VDC
Bias Voltage : 0 VDC
Attenuation : X 2

Thermal Conductivity Detector:

Voltage : 10 VDC
Current : 125 mA
Attenuation : X 1

Recorder:

1 cm/min
10 mV FSA

RUN # 104

H₂: 100 ppm

