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FINAL REPORT

TRACE MATERIAL GENERATION RATE SIMULATOR
(TRACE GAS SIMULATOR)

HONEYWELL SYSTEMS & RESEARCH DIVISION

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TRACE MATERIAL GENERATION RATE SIMULATOR (TRACE GAS SIMULATOR)

NASA Manned Spacecraft Center
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CONTENTS

ILLUSTRATIONS

TABLES

SECTION I
INTRODUCTION

In January, 1965, NASA and Honeywell negotiated a contract NAS9-3998 in which the Systems and Research Division of Honeywell, Inc. undertook to develop and deliver a trace material generation rate simulator and to conduct a study of generation rate patterns. The two parts of the program were identified as follows:

Part A - The objective of Part A is to develop a trace material introduction rate control unit capable of producing selected introduction rates for a minimum of ten compounds over the range of 1.0×10^{-6} mole per hour to 1.00×10^{-2} mole per hour into test chambers. The compounds are to be introduced simultaneously and continuously in the gaseous state into test chambers that operate at temperatures between 65°F and 100°F; atmospheres of 100 percent oxygen at 5 psia pressure, or 50 percent oxygen - 50 percent nitrogen at 7 psia pressure, and a relative humidity that varies over the range of 50 percent to 100 percent. The ten compounds are to be introduced into the test chambers without affecting the chamber operating conditions.

Part B - Part B objective is to consist of a study of generation rate patterns of trace materials as they may actually occur during flight in the habitable area of a spacecraft and a feasibility study of simulation devices for demonstrating these generation rate patterns.

The trace material introduction rate control unit, identified as the TRACE GAS SIMULATOR, Honeywell model number DUG1930A1, was completed and shipped to the NASA Manned Spacecraft Center, Houston, Texas, in January of 1966. The development program has been described in six monthly progress reports and is summarized in this document, along with results of the test program.

The results of Part B are contained in a report entitled "Task B: Study of Generation Rate Patterns", prepared for Honeywell, Inc. by the North Star Research and Development Institute, Minneapolis, Minnesota, dated May 29, 1965. The document presents the methods and results of studies on trace-material generation rate patterns anticipated in the habitable area of a spcae-craft on a 14-day mission. The chief objective of the research was to provide programs for operation of a trace material control unit (TMCU) which would simulate both actual generation rates and equivalent rated modified to account for the presence of trace material sinks. A second objective was to disclose any inadequacies in the inventory of a space capsule, in the identification and characterization of trace materials, and in the kinetics of gas evolution which should be remedied to permit a more reliable study of generation rate patterns. Recommendations for additional work growing out of the study are repeated in the concluding section of this report.

SECTION II
BACKGROUND AND PROGRAM SUMMARY

The projection of long-term manned space flights stimulates inquiry into the effects of contamination on crew and equipment in closed atmospheres. Such contamination can occur in normal spacecraft operation from gassing of organic materials used in the construction of equipment and from human effluent. As a result, a trace material generation simulator has been developed for use with closed test chambers at the Manned Spacecraft Center. Trace material introduction to an atmosphere can be programmed on an arbitrary basis, useful in the development of atmospheric purification devices and in toxicological or behavioral studies. Or, given information on the design and operating characteristics of equipments used aboard the spacecraft, programs may be evolved for the introduction of trace materials as they might occur from these sources during a mission.

In this connection a study was made to project a trace material generation rate pattern for a typical 14-day mission. While kinetic gassing data for organic spacecraft materials is not abundant, gas chromatograph recordings of oxygen atmospheres in which organic materials had been exposed were available. These were analyzed to seek a definition of the rate-controlling mechanism for materials gassing. A diffusion-controlled mechanism provided the mathematical model for calculation of gassing rates for components of a typical electronic system. Findings were correlated with atmospheric data taken from Mercury spacecraft flights which led to estimates of the gassing rates of electronic and non-electronic equipments. Volatile materials of biological origin were also taken into account. Finally, a rationale was developed for substitution of trace materials according to chemical classification and toxicological criteria. Such a substitution process may be considered for carrying out a simulation with fewer trace materials involved.

A partial answer to the question of what trace materials will be evident in a closed atmosphere containing equipment constructed partially of organic materials was sought in the gas chromatograph recordings taken when approximately 180 organic material samples were exposed to oxygen atmospheres at elevated temperatures. A list of compounds, which appeared upon such exposure, are shown in Table 1.* This list includes a number of chemical families: alcohols, aldehydes, esters, hydrocarbons, ketones, and inorganic gases. Additional materials found in Mercury spacecraft atmospheres include: Freon-114, vinylidene chloride, methylene chloride, and ethylene dichloride.

Estimates of contributions to atmospheric contamination by materials of biological origin are postulated in Table 2. These estimates are on a per-man basis and assume that: (1) all flatus and respiratory gases reach the atmosphere, (2) feces, urine, and food are well contained and therefore are not significant contamination sources, and (3) skin secretions reach the atmosphere except as limited by their volatility.

The Manned Spacecraft Center's requirement for simulation of trace material generation is for the accommodation of any of 86 compounds. These compounds represent a number of chemical families and have boiling points from -253°C (hydrogen) to 266°C (skatole). The trace material control unit will deliver up to ten of the 86 compounds listed by NASA in any given simulation, and provision has been made for installing ten additional delivery channels. A list of ten representative compounds which were selected is shown in Table 3. This list contains materials having boiling points as low as that of hydrogen (-253°C) to as high as that of n-propyl acetate (102°C) and with molecular weights from 2 for hydrogen to 171 for Freon-114. Both gas and liquid-phase materials are included; the latter, which are liquids at room temperature and near-atmospheric pressure, are marked "L". As might be seen, this listing is in recognition of several factors: (1) it includes trace materials which are prevalent in atmospheres containing organic engineering materials and human beings, (2) it contains materials with a variety of physical and chemical characteristics, (3) it is relatively short to reduce equipment needs and to simplify test procedures.

*See Reference No. 2 in Appendix.

Table 1. Prevalent Compounds Outgassed in Oxygen Atmospheres by Organic Engineering Materials

Carbon Monoxide	Benzene
Carbon Dioxide	Ethylbenzene
Acetone	Trichloroethylene
Ethyl Formate	Carbon Disulfide
Methyl Acetate	Acetaldehyde
n-Butyl Alcohol	n-Valeraldehyde
Methyl Isobutyl Ketone	n-Butyraldehyde
m-, o-, p-Xylene	Methyl Ethyl Ketone
Ethyl Alcohol	tert-Butyl Alcohol
iso-Propyl Alcohol	Heptane
Toluene	iso-Butyl Alcohol
Propionaldehyde	Mesitylene

Table 2. Man-Generated Contaminants Estimated* to Reach the Atmosphere

Substance	Hourly Production (μ Moles)	Sources
Methane	40 to 490	Flatus and Breath
Hydrogen	24 to 240	Flatus and Breath
Carbon Monoxide	18 to 53	Breath
Hydrogen Sulfide	7×10^{-3} to 6.8×10^{-2}	Flatus
Ammonia	2×10^{-2}	Sweat
Ammonia	8.9×10^{2} to $7. \times 10^{3}$	Potential from Sweat Urea Decomposition by Bacteria
Phenol	2 to 17	Sweat
Unidentified Gases	3 to 28	Flatus

*Based on data presented in Table 12 of "Final Report on Trace Material Generation Rate Simulator, Task B: Study of Generation Rate Patterns", 12503-FR1

Table 3. Compounds Presently Delivered by the Trace Material Control Unit

Acetone	L	Hydrogen	
Ammonia		Hydrogen Sulfide	
Benzene	L	iso-Propyl Alcohol	L
Carbon Monoxide		Methane	
Freon - 114	L	n-Propyl Acetate	L

L - Liquid phase at ordinary temperatures and pressures.

During the development of the trace material control unit, a study was made to determine how contaminant introduction could be programmed to simulate generation rate patterns in spacecraft. This study was hampered by lack of data, but it is of interest since it points up the possibilities for pre-flight simulations, given sufficient data on organic material gassing rates and specific inventories of these materials in spacecraft components.

When the partial pressure of trace materials in the atmosphere is low, the rate-controlling factor in the gassing of organic materials is the mechanism by which these volatiles are released. Newly manufactured devices can be expected to contribute more rapidly to atmospheric contamination as surface materials volatilize. But spacecraft devices will have had extensive run-in histories prior to their operation in the sealed atmosphere of the spacecraft (in this study a 1000-hour history was assumed). After this "aging" period trace materials will evaporate more slowly from the surfaces of the solid as they diffuse from within the solid. It is some modification of this simple diffusion process which will govern the gassing of spacecraft organic materials because of the slow, continuous generation of new contaminants by thermal degradation and oxidation within them.

Diffusion-controlled gassing will react to temperature variation because of the changes in magnitude of the diffusion constant and the production rates of trace materials by thermal degradation and oxidation. For a given temperature the trace materials will be lost according to a particular solution of Fick's law of diffusion. A solution, shown in Equation 1, is adapted to empirical data from the investigation of organic gassing already mentioned.

$$\log\left(\frac{Q_t}{Q_o}\right) \cong \log\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 Dt}{9.2a^2} \qquad \text{(Equation 1)}$$

where:

Q_t = average concentration remaining at time t

Q_o = initial uniform concentration

a = thickness

D = diffusion constant

t = time

This solution is an approximation based on the geometry variation between test samples and material configurations in spacecraft components. However, it will define the exponential decline with time of trace contaminant content of a material. Equation 1 was used to derive an estimate of trace material contributions from a spacecraft control system for which organic material content was known. Table 4 gives this estimate for a 14-day period occurring after run-in history. The contributions of each material have been apportioned according to the gas chromatograph records available for that material. This accounts for a combined estimate for acetone, ethyl formate, and methyl acetate which were not separated in the chromatograph analysis, and for the presence of "unknowns" which were not identified in that analysis.

Table 4. Trace Material Estimates for a Given Spacecraft Control System - 14-day Mission

Material	Amount (μ Moles)
iso-Propyl Alcohol	7,510
Carbon Monoxide	5,465
Acetone, Ethyl Formate, Methyl Acetate *	3,109
Methyl-n-Butyl Ketone	1,044
o-, m-, p-Xylene	720
Toluene	672
Heptane	480
Ethyl Alcohol	203
n-Butyl Alcohol	134
Cumene	105
Ethyl Benzene	102
Methyl Ethyl Ketone	90
Methyl Methacrylate	40
Unknowns	1,180

* Not distinguished in gas chromatograph data base.

Since the number of trace materials to be dealt with in a generation rate simulation is large, a scheme was considered to reduce the number by substitution of materials within chemical families according to an arbitrarily derived "relative toxicity" rating. This rating is evolved from a summation of factors as follows:

$$\text{"Relative Toxicity" Rating} = \frac{10,000}{\text{TLV}} \sum \frac{\text{Toxicity x Site x Speed}}{\text{Route}}$$

where:

TLV = Threshold Limit Value

* Toxicity Factor:

0 - No harm

1 - Slight reversible damage

2 - Moderate reversible or irreversible but not causing permanent injury.

3 - Severe (possibility of death or permanent injury upon short exposure to small quantities).

Site Factor:

1 - Local

2 - Systemic

Speed Factor:

1 - Chronic

3 - Acute

Route Factor:

1 - Inhalation, or irritant

5 - Absorption

10 - Ingestion

A substitution process in which trace materials were substituted within chemical families in proportions according to their relative toxicity ratings was used to reduce the number of materials given in the previous estimate for the space-craft control system. An abbreviated listing of materials and generation rates after substitution involves fewer than one half the original number of materials and is shown in Table 5.

Table 5. Trace Material Abbreviated Estimate for a Given Spacecraft Control System - (After Substitution)

Material	Amount (μ Moles)
Acetone	38,000
Carbon Monoxide	5,465
n-Butyl Alcohol	2,064
Heptane	480
Benzene	98
Unknown	(1,180)

The Trace Gas Simulator developed during this program is shown in Figure 1. It is designed for use adjacent to a closed chamber whose atmosphere is circulated through the unit. The unit requires only the connections to the closed chamber atmosphere and 115/230 volt power for its operation. Atmosphere circulation is maintained by a diaphragm pump whose wetted surfaces are constructed of inert, low-vapor pressure materials to avoid flow-stream contamination. A circulation rate of several liters per minute gives high enough dilutions of the trace materials to avoid their condensing at room temperature operation.

Trace materials are stored in cylinders in the lower part of the unit. These cylinders are contained in a ventilated enclosure within the console, thus

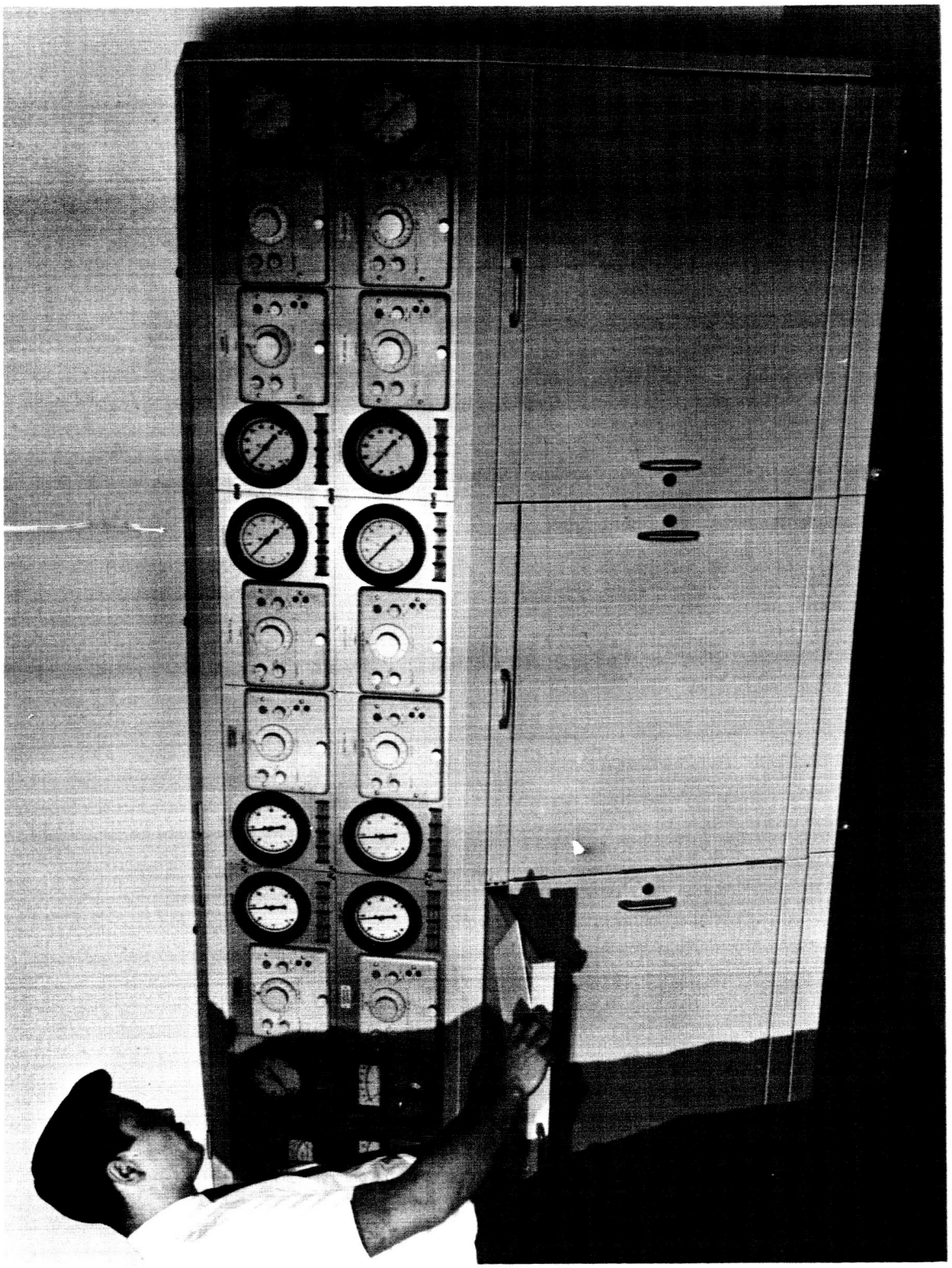


Figure 1. Trace Material Generation Simulator

providing isolation of the temperature-controlled cylinders and any leakage of stored materials. Materials are delivered to the metering devices at constant pressure, maintained by pressure regulators for the gases and by temperature controlling for those stored in the liquid-phase. Delivery pressures in the order of 1 to 2 atmospheres are sufficient to assure the required sonic flow velocities in the metering devices.

A service compartment is located in the lower section of the unit's console, and contains:

- Atmosphere circulation (diaphragm) pump
- Vacuum purge pump
- Regulated source of dry-nitrogen purge gas
- Two sparkless blowers for ventilating the storage enclosure.

The circulation manifold and connecting plumbing wetted by trace materials is constructed of stainless steel tubing with connections made by heli-arc welds or precision-ground fittings. Plumbing quality is comparable to that of high-performance vacuum equipment with leakage not exceeding 10^{-8} standard cubic centimeters of air per second. The use of stainless steel and vacuum-quality standards minimizes the possibilities for inadvertent contamination by chemical reaction with the flow stream and by leakage from the surroundings. The circulation manifold is provided with electrical heating tape, thermostats, and insulation so that purging can be facilitated by the application of heat.

A key function in the simulator is that of the metering system. A separate metering system is provided for each of the ten delivery channels. Metering is accomplished in a digital fashion in which trace material delivery takes place as a series of minute flow pulses. The metered quantity depends upon the frequency and duration of these pulses since without pulsing there is positive closure of the delivery channel. Duration of a pulse is normally set to deliver one micro-mole of trace material. Electrical pulses whose operating

frequency can be adjusted to provide a continuous range of pulse rates from 1 to 10,000 per hour control the metering valves. The use of digital metering provides precise flow control over a wide throttling range through the accuracy and versatility of performance available with digital circuitry.

The Trace Gas Simulator provides a control unit which is capable of introducing controlled and programmable amounts of trace contaminants to a closed atmosphere system. The control unit may be programmed on an arbitrary basis for evaluating the performance of atmosphere purification devices and for conducting toxicological and behavioral studies. The control unit may also be programmed to simulate the presence of equipment in a spacecraft atmosphere upon the availability of kinetic data for the organic materials involved.

SECTION III
TECHNICAL REQUIREMENTS

Consideration of the over-all problem of investigating the effects of trace materials in closed atmospheres, and of determining the extent to which they can be controlled or removed, led to the formulation of technical requirements for the Trace Gas Simulator. The following requirements are based on those initially specified by the Manned Spacecraft Center, NASA, Houston, and are modified only slightly by the results of studies conducted during the development program.

Salient design requirements were as follows:

- The unit is to operate with closed test chambers having 5 psia oxygen or 7 psia oxygen-nitrogen atmospheres;
- Test chamber conditions must not be affected by the operation of the control unit;
- Each delivery channel must permit trace material metering anywhere in the range of 10^{-6} to 10^{-2} gram moles per hour;
- Delivery accuracy is to be ± 10 percent except at higher deliveries it is to be ±5 percent;
- Delivery channels must operate independently of one another and for periods up to 14 days at maximum delivery;
- Vacuum system leakage requirements are applicable; i.e. leakage must not exceed 10^{-8} standard cubic centimeters of air per second;
- The unit must be mobile with all controls easily accessible and with its own provisions for vacuum and dry-nitrogen purging;
- The unit must be versatile to accommodate changes in metering range and the addition of ten more materials.

Additional and more detailed requirements which governed the design and development are given below:

- The unit shall be capable of accommodating any ten of the compounds listed in Table 6, although materials with normal boiling points in excess of 260°F require a higher temperature pulsed leak valve.
- The control unit shall provide for introduction rates for ten compounds. The ten compounds selected for the control unit are listed in Table 3.
- The control unit shall have a minimum of ten individually controlled storage containers and the required metering mechanisms. There shall be provisions for installation of another ten storage containers. Metering mechanisms provided with the control unit shall be capable of being used with any of the compounds in the list attached to this document.
- The control unit shall provide the following control switches that are to be manually operated for control of introduction rates:

  Master Switch - The master switch shall be capable of being set to turn all introduction rates of the control unit on or off simultaneously.

  Course Adjustment Control - Each metering mechanism on the control unit shall have a course adjustment control. Each control shall be capable of being set to select the range of introduction rates to be delivered in order of magnitude of ten (10), between 1×10^{-6} and 1×10^{-2} moles per hour (see Table 7), and turning each metering mechanism off.

  Fine Adjustment Control - Each metering mechanism on the control unit shall have a fine adjustment control and it shall be slaved to the course adjustment control. Each fine adjustment control shall be capable of being set to

Table 6. List of Compounds Required to be Accommodated by the Trace Material Control Unit

1. Acctaldehyde	44. Formaldehyde
2. Acetone	45. n - Hexane
3. Acetylene	46. Hexamethylcycletrisiloxane
4. Allyl Alcohol	47. Hexene - 1
5. Ammonia	48. Hydrogen
6. Amyl Alcohol	49. Hydrogen Chloride
7. Benzene	50. Hydrogen Fluoride
8. H - Butene	51. Hydrogen Sulfide
9. Butene - 1	52. Indole
10. cis - Butene - 2	53. Isopropyl Alcohol
11. trans - Butene - 2	54. Isobutyl Alcohol
12. Butyraldehyde	55. Methylene Chloride
13. Butyric Acid	56. Methyl Alcohol
14. Carbon Disulfide	57. Methyl Chloroform
15. Carbon Monoxide	58. Methyl Ethyl Ketone
16. Caprylic Acid	59. Methyl Isopropyl Ketone
17. Chlorine	60. Methane
18. Chloroacetone	61. 3 - Methyl Pentane
19. Chlorobenzene	62. Methyl Mercaptan
20. Chloropropane	63. Monomethylhydrazine
21. Cyclohexane	64. Nitric Oxide
22. Cyclohexanol	65. Nitrous Oxide
23. Cyanamide	66. Nitrogen Tetraoxide
24. 1,1 - Dimethylcyclohexane	67. Phenol
25. trans - 1,2 - Dimethylcyclohexane	68. Propane
26. 2,2 - Dimethylbutane	69. n-Pentane
27. Dimethylhydrazine	70. Iso-Pentane
28. 1,4 - Dioxene	71. n-Propylacetate
29. p - Dioxene	72. Propylene
30. Ethyl Acetate	73. Propyl Mercaptan
31. Ethyl Alcohol	74. Skatole
32. Ethylene Dichloride	75. Sulfur Dioxide
33. Ethylene	76. Tetrachloroethylene
34. 1, 3 - Methylethylcyclohexane	77. Tetrafluroethylene
35. Ethyl Mercaptan	78. Toluene
36. Ethyl Sulfide	79. Trichloroethylene
37. Freon-11	80. Trichlorofluromethane
38. Freon-12	81. 1,1,3 - Trimethylcyclohexane
39. Freon-22	82. Vinyl Chloride
40. Freon-23	83. Vinylidene Chloride
41. Freon-114	84. m-Xylene
42. Freon-114 Unsym.	85. o-Xylene
43. Freon-125	86. p-Xylene

Table 7. Introduction Rate Controls and Accuracies *

Master Switch	Course Adjustment Control Selection Ranges (moles-hour^{-1})	Fine Adjustment Selection Scale (units)	Control Introduction Rate (moles-hour^{-1})	Accuracy (percent)
OFF	OFF			
ON	1.0×10^{-6} to 1.0×10^{-5}	1 to 10	(1 to 10) $\times 10^{-6}$	±10%
ON	1.0×10^{-5} to 1.0×10^{-4}	1 to 10	(1 to 10) $\times 10^{-5}$	±10%
ON	1.0×10^{-4} to 1.00×10^{-3}	1 to 10	(1 to 10) $\times 10^{-4}$	±10%
ON	1.00×10^{-3} to 1.00×10^{-2}	1 to 10	(1 to 10) $\times 10^{-3}$	± 5%

* Minimum rates for Hydrogen delivery may be higher than minimum specified by a factor of two.

select introduction rates over a continuously selective scale between one (1) and ten (10) within each range set by the course adjustment control. The accuracies of the introduction rates shall be as indicated in Table 7 for each range selected by the course adjustment control.

- There shall be provisions for modifications on the control unit to increase or decrease introduction rates of each compound by a factor of 10.
- It shall be possible to change introduction rates with either the course adjustment control or the fine adjustment control for any of ten metering mechanisms without interrupting the control unit operation.
- The control unit shall be provided with a storage container for each trace material selected. Each storing container shall have a capacity to provide enough trace material for continuous operation at maximum introduction rate for a minimum period of fourteen days.
- There shall be provisions on the control unit for introducing the compounds from a mixing chamber or manifold into test chambers, without affecting test chamber operating conditions and without affecting introduction rate into the test chamber.
- There shall be provisions on the control unit to prevent condensation of any of the trace materials in the metering mechanisms and manifolding parts.
- Provisions shall be made on the control unit to permit filling of storage containers without interrupting the control unit operation.
- There shall be provisions on the control unit for purging the system by vacuum and with dry nitrogen.

- There shall be provisions on the control unit for a gas sampling port in an easily accessible position on the outlet line of the control unit leading to the test chamber.
- The control unit shall not have any leaks greater than 1×10^{-8} standard cubic centimeters of air per second at a pressure of 10^{-6} Torr. or less on the delivery manifold.
- The control unit shall be mobile with all automatic controls located on one panel in an easily accessible position, and shall indicate on the control panel the ranges of introduction rates in moles-hour^{-1}.

SECTION IV
KEY AREAS IN CONFIGURATION DEVELOPMENT

The basic design approach for the Trace Material Control Unit (or Trace Gas Simulator) was based on digital metering techniques. The digital approach was selected because it offered precision, repeatability and versatility, with the wide range of deliveries for various materials as specified by the requirements.

The implementation, as it was originally proposed, is shown in Figure 2. As shown, liquids and gases would be delivered through the metering valves (pulsed leaks) into a low pressure manifold, and delivered to the circulation manifold by means of a diaphragm pump. The valves would be pulsed by electronic controllers whose dwell (or pulse width) and frequency could be adjusted to yield the desired delivery rates.

Several changes were made to the original configuration during the course of the development program. These changes resulted in the configuration indicated in simplified form in Figure 3. The final design is described in greater detail in the next section. The more significant changes and the rationale behind them are reviewed in the following pages.

DELIVERY MANIFOLD PUMPING

The original concept for delivering trace material gases and vapors to the closed chamber atmosphere (shown schematically in Figure 2) called for a delivery manifold pressure of about 1 Torr. The use of such a low pressure would make it possible to store and deliver the liquid-phase materials at lower pressures and temperatures. The requirement for scrupulous avoidance of contamination from outgassing and leakage virtually dictated the use of a diaphragm-type pump for circulating the chamber atmosphere. When it became apparent that a 1-Torr

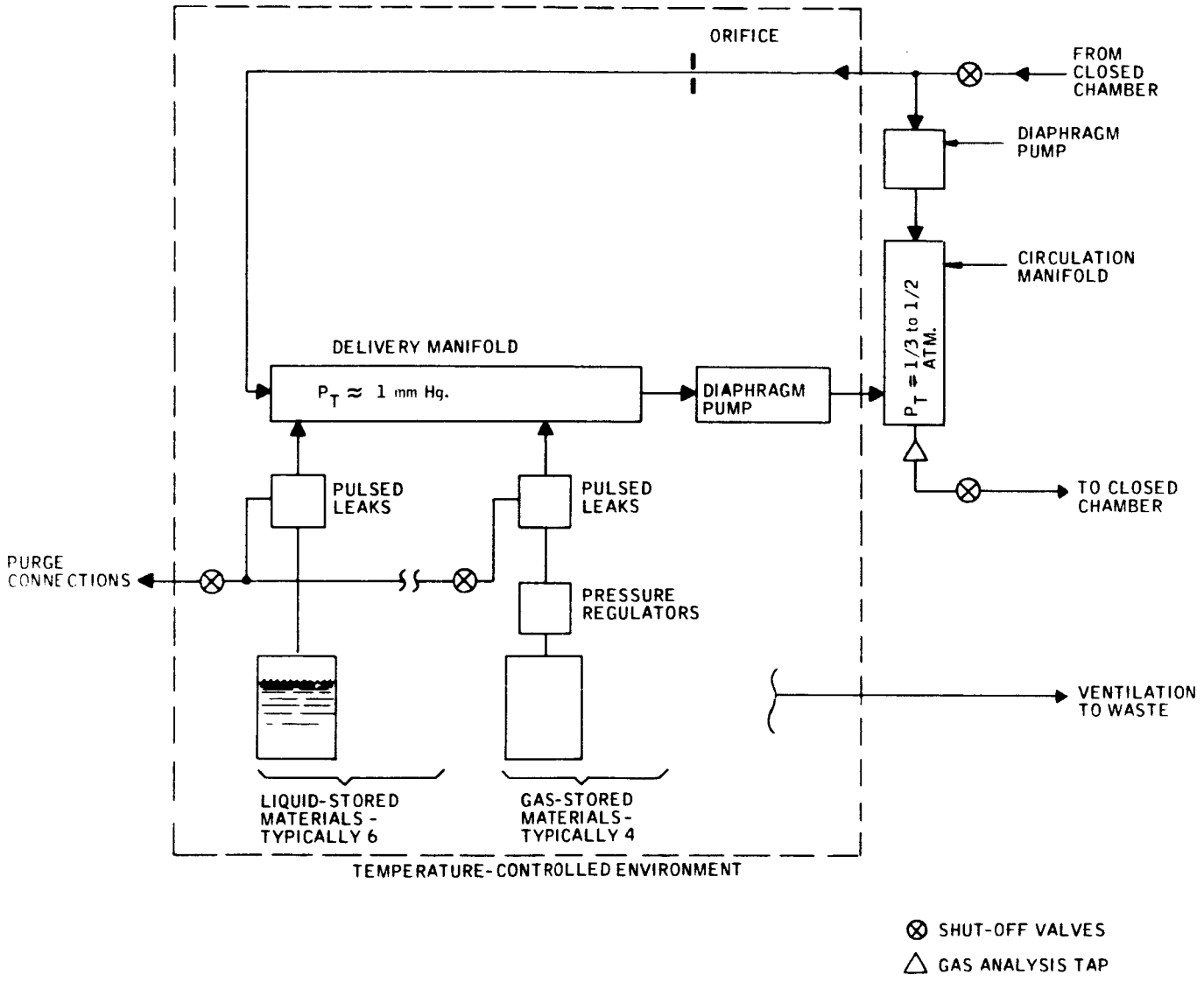


Figure 2. Flow Processes for Trace Material Control Unit -- Proposed Configuration

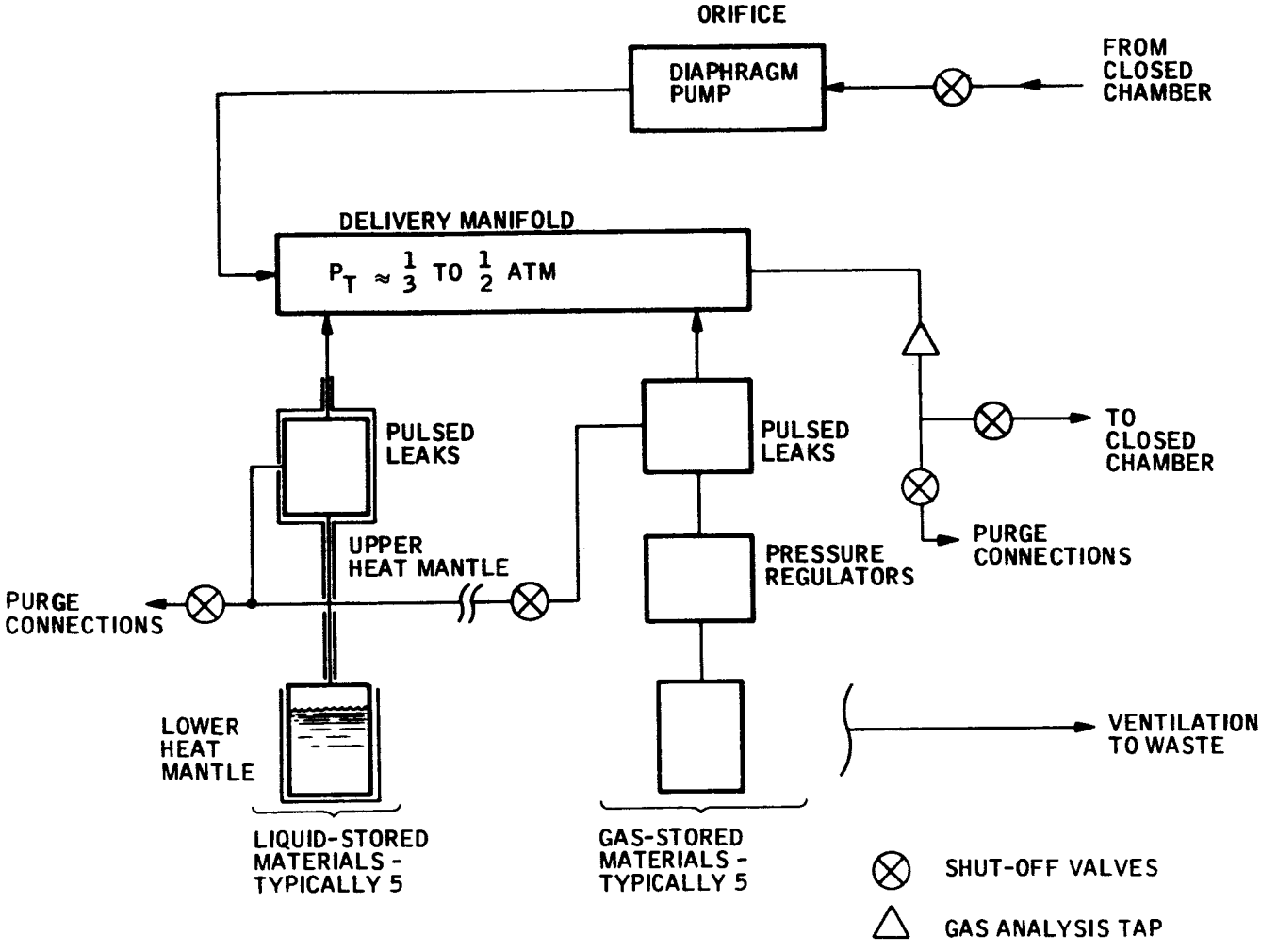


Figure 3. Flow Processes for Trace Material Control Unit -- Revised Configuration

suction pressure could not be achieved in a single pump stage, other possibilities were examined. The complication of multi-staging with attendant compromise of enclosure tightness did not seem warranted. Ejector designs were then considered as a means of obtaining lower delivery pressures. Ejectors seemingly offer an advantage for mixing of trace materials and manifold atmosphere because all wetted surfaces are non-moving parts; however, there is a distinct possibility that insufficient pressure ratio would be obtained.

Untimately the decision was made to operate the delivery manifold at closed chamber pressure even though this meant operating the liquid-phase pulsed leaks at higher temperatures. Advantages to be gained by this decision were 1) the elimination of all pressure changing devices in the delivery manifold (orifice, pump, ejector) with less possibility for condensation of delivered trace materials, and 2) the elimination of the circulation manifold and its pump. It appeared that the critical part of the device (the solenoid) could operate at these new conditions on all channels except the so-called "high boiler" channel. Trace material delivery pressures of 1 1/2 atmospheres at the pulsed leak would assure sonic delivery velocities, and hence flow metering independent of delivery manifold pressure, for the highest expected chamber pressure of 7 psia. Delivery temperatures corresponding to 1 1/2 atmosphere vapor pressure for the liquid-phase materials are:

	°F	°C
Acetone	158°	70°
Isopropyl Alcohol	205°	96°
n-Propyl Acetate	240°	116°
Benzene	201°	94°
*Freon-114	55°	13°

*The higher vapor pressure of Freon-114 requires that a higher delivery temperature be used to give metering control at room temperature. The nominal control point is 100°F with a corresponding pressure of about 46 psia. In actual practice the prevailing temperature in the storage compartment has been permitted to determine delivery pressure.

DELIVERY OF HIGHER BOILING POINT TRACE MATERIALS

At program initiation NASA stipulated that one channel have the capability of delivering higher boiling point trace materials. Specifically, caprylic acid was substituted for p-xylene, the highest boiling point material of the ten suggested (See Table 8). As the project progressed, it became apparent that the amount of design work for this "high boiler" channel was of considerable magnitude. Modification of the pulsed leak required a new magnetic circuit and higher temperature rated materials. Either delivery manifold heating or reduced delivery quantities was necessary to avoid condensation. Permission was then given by NASA to substitute benzene as the tenth material. Of the 86 materials specified in the NASA Exhibit (See Table 6), eight have a boiling point higher than the xylenes, m-, o - and p- (approximately 140°C.), while only three have a boiling point higher than caprylic acid (238° C.). Benzene added an aromatic hydrocarbon to the list of ten materials and was more toxic than xylene. Both xylene and benzene were often found in gassing tests conducted by Honeywell in a related project dealing with the selection of organic materials for constructing electronic equipments for spacecraft.

Design possibilities, other than a pulsed leak, which were considered for a high temperature metering device included: vapor compression and analog metering mechanisms; liquid delivery mechanisms; and inert carrier gas. Liquid delivery mechanisms, such as a motorized syringe, require very small displacements (10^{-6} mole of caprylic acid is equivalent to 1.58×10^{-4}cc at 20°C. Comparable figures for its vapor are 4.0×10^{-2}cc at 238°, and 7.6×10^{-2}cc at 214° C). Additional disadvantages are the limitations of delivery flow range and leak tightness. Use of an inert carrier gas would cause contamination of the closed chamber atmosphere. The high temperature pulsed leak appeared to be the best method of delivering "high boilers", and it would require least change to the trace material control unit.

Table 8. **Suggested List of Compounds.**

NAME	A - Primary List T_{760mm} (°C)	T_{100mm} (°C)	MOLECULAR WEIGHT	POLARITY*	TOXICITY**
Hydrogen	-253		2	N. P.	A
Carbon Monoxide	-192		28	N. P.	100
Methane	-162		16	N. P.	A
Hydrogen Sulfide	-60		34	P.	20
Ammonia	-33		17	P.	100
Freon 114	4		171	N. P.	1000
Acetone	56	8	58	P.	1000
Isopropyl Alcohol	82	40	60	P.	400
n-Propyl Acetate	102	48	102	P.	200
p-Xylene	138	76	106	N. P.	200

NAME	B - An Expanded List T_{760mm} (°C)	T_{100mm} (°C)	MOLECULAR WEIGHT	POLARITY*	TOXICITY**
Sulfur Dioxide	-10		64	P.	5
Methyl Mercaptan	6		48	P.	50
Carbon Disulfide	46	-5	76	N. P.	200
Methyl Alcohol	65	21	32	P.	200
Methyl Ethyl Ketone	80	25	72	P.	200
Benzene	80	26	78	N. P.	25
Trichloroethylene	87	31	131	P.	100
p-Dioxane	101	45	88	N. P.	100
trans-1, 2, Diemethylcyclohexane	123	61	112	N. P.	400
Butyric Acid	164	108	88	P.	S

*P - Polar; N. P.- Non-Polar.

Numbers are parts per million threshold limit values according to the American Council of Governmental Industrial Hygienists.
"A" means simple asphyxiant and "S" means slight toxicity.

This pulsed leak design would be similar to that used for the other channels with these exceptions:

- The solenoid would be further separated from the valve body for thermal isolation;
- A gold insert would most likely be substituted for Teflon in the valve poppet.

Further isolation of the solenoid from the higher temperature parts of the pulsed leak would be accomplished by lengthening the magnetic circuit. Little performance degradation would be expected since most of the circuit reluctance is in the air gap which would not be changed. The lengthened magnetic circuit would increase the thermal path length and the heat radiation surface allowing the use of standard parts in the solenoid coil. Substitution of gold for Teflon in the valve poppet might degrade the leak rate of the device. This possibility, and verification of the thermal characteristics of the elongated magnetic circuit design, were not determined by testing before the decision to eliminate the "high boiler" channel.

An early decision in the design of the trace material control unit provided for high dilutions of the delivered materials in the delivery manifold flow stream to avoid condensation. The alternative of heating the manifold and flow stream during delivery was avoided because of the requirement that chamber operating conditions not be affected. These considerations were reviewed in regard to caprylic acid delivery. Table 9 shows delivery rate data for higher boiling materials assuming perfect mixing and transport of the delivered materials in the manifold flow stream. The data are for the most likely condition for condensation; namely, when delivery manifold flow is least. This will be the case when the closed chamber pressure is lowest (1/3 atmosphere).

The higher boiling materials are the most critical in determining delivery manifold flow rate because of their high saturation volumes (low vapor pressures). These data show that n-propyl acetate could be delivered without condensation 117 times faster than the maximum required delivery rate of 10^{-2} moles per hour,

Table 9. Delivery Rate Data for Higher Boiling Materials - Least Manifold Flow Condition (1/3 Atmospheric Pressure)

	n-Propyl Acetate	p-Xylene	Caprylic Acid
1 - Vapor Pressure at 65° F (mm Hg)	23.5	6.2	6.3×10^{-3}
2 - Boiling Point (° C)	102	138	238
3 - Saturated Vapor Volume of 10^{-6} mole (cm^3. $pulse^{-1}$)	0.772	2.925	2.88×10^{-3}
4 - Delivery Manifold Pump Flow at 1/3 Atmosphere	← 250 cm^3 sec^{-1} →		
5 - Maximum Pulses/Second Without Condensation (Item 4 ÷ Item 3)	324	85.5	.0869
6 - Required Pulses/Second for Maximum (10^{-2} moles $hour^{-1}$) Delivery	← 2.78 →		
7 - Ratio of $\frac{\text{Item 5}}{\text{Item 6}}$	117	31	.0312

and p-xylene 31 times faster. However, caprylic acid can be delivered without condensation only up to .0869 pulses per second (313 micromoles per hour). To deliver unsaturated caprylic acid vapor would require (1) limiting maximum delivery to 313 micromoles per hour; or (2) increasing manifold flow at least 32-fold; or (3) increasing manifold temperature to at least 140°F. Since manifold flow is fixed by pumping capacity, consideration was given to what would be involved in manifold heating. The manifold was considered to be insulated and electrically heated under thermostatic control downstream of caprylic acid entry (the last entry into the manifold). Manifold flow was assumed to be oxygen at 5 psia and 65°F. The manifold Reynolds number is considerably less than 1000 and laminar flow was assumed in computing a convection heat transfer coefficient. With a good grade of insulation 1" thick, the heat flow through the insulation about equals the heat flow into the manifold flow stream. The outlet temperature of the oxygen stream is nearly that of the manifold inner wall. Assuming 140°F control of the manifold outer wall approximately 14 BTU per hour go to the oxygen flow stream and a like amount to insulation loss. At the rated flow of the delivery manifold pump the outlet temperature of the oxygen is about 136°F.

Manifold heating would also be used during purging when a vacuum would be applied to the manifold. Less heating would be required in this mode since there would then be no heat flow to the oxygen stream. For purging, a higher temperature would be used than in the foregoing example.

TRACE MATERIAL STORAGE AND DELIVERY

As originally proposed, trace materials were to be stored in a constant-temperature enclosure within the control unit. This scheme of collective temperature control was changed to give greater versatility in the selection of delivery pressures for the materials stored in the liquid phase, and to minimize the possibility for temperature upset to several channels while exposing one channel to ambient conditions for servicing. Instead, each storage cylinder and its pulsed leak were made individually temperature controlled using a heating mantle. Each cylinder is fitted

with an upper and a lower mantle which are removable and contoured to the cylinder. The mantles provide insulation and contain resistance elements so dispersed as to provide even heating. The upper and lower mantles are slightly separated providing a heat leak at the mid-section of the cylinder to assure heat control dominance in the lower mantle. Heating of the lower mantle is controlled proportionally in response to a thermister sensor immersed in the stored liquid. Heating of the upper mantle is constant with heater voltage set at the factory by a variable auto transformer. This is a relatively permanent setting which may have to be changed if a different trace material is delivered from the channel.

A further advantage in the use of mantles with two-zone heating became apparent later in the program when the pulsed leaks were bench calibrated. Occasionally, calibration loss occurred which it was suspected resulted from some liquid-phase delivery. This difficulty was corrected by superheating the vapor in the delivery line and pulsed leak. The superheating serves only to dry the vapor while the delivery pressure remains a function of the evaporating liquid temperature. This dependence of delivery pressure upon liquid temperature has been demonstrated using vapor superheats up to 40°F.

Storage capacity of the trace material control unit was predicated on the ultimate use of 10 liquid-phase and 10 gas-phase channels. Individual channels have a capacity for delivering at the maximum delivery rate for 14-day periods. Liquid-phase materials are stored in 1-liter stainless steel cylinders. Cylinders are filled only half way to assure sufficient vapor volume for dry vapor delivery. Gas-phase materials use No. 4 commercial cylinders. Storage data are given in Table 10.

PULSED LEAK VALVES

The decision to use a higher delivery manifold pressure required that the pulsed leaks operate at higher pressures to assure sonic velocity in flow/metering.

Table 10. Relation of Trace Material Storage Capacity to Maximum Consumption

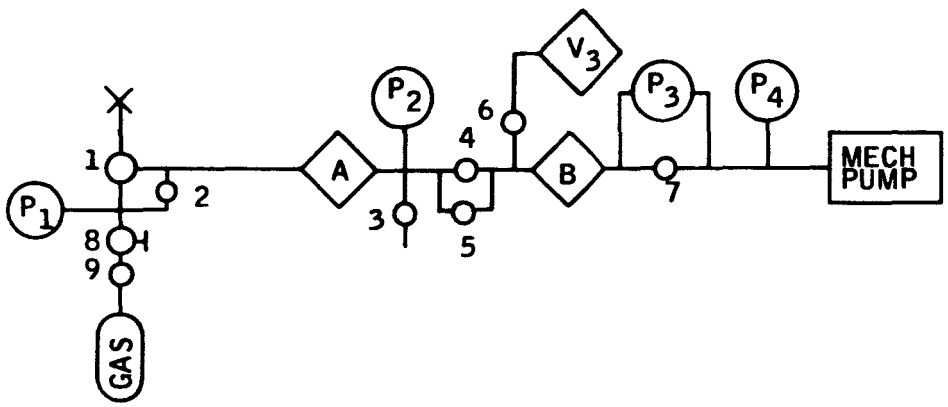
Trace Material	Weight of 3.36 Gram moles		Volume (ml) 3.36 gram-moles (liquid at 20 °C)	No. 4 Cylinder		Storage Margin	
	Grams	Lbs.		Pressure (psig)	Capacity (lbs)	One-liter Cylinder	No. 4 Cylinder
Liquids							
Acetone	195	0.43	246			4 X	
Benzene	262	0.58	298			3.4X	
Freon-114	575	1.27	399 (30°C)			2.5X	
Isopropyl Alcohol	202	0.45	255			3.9X	
n-Propyl Acetate	343	0.76	387			2.6X	
Gases							
Ammonia	57	0.13		114	2		15 X
Carbon Monoxide	94	0.21		1500	0.65		3.1X
Hydrogen	7	0.015		2000	0.05		3.3X
Hydrogen Sulfide	114	0.25		250	3		12 X
Methane	54	0.12		2000	0.54		4.5X

For those trace materials delivered from the liquid phase, these higher pressures required about 40 percent higher liquid temperatures. An existing pulsed leak design was reviewed in the light of the new requirements. Materials suitable for the construction of wetted parts included: Teflon, 300- and 400-series stainless steels, gold, and sapphire. Existing metallic solenoid surfaces which were wetted were to be covered with a Teflon barrier. Later the Teflon was replaced with .006" stainless steel sheet to eliminate bonding anomalies which could interfere with proper opening of the pulsed leak.

At the beginning of the program, experience has been gained with pulsed leaks using valve poppets both contoured and flat, with guided fits and spring mounted. The leak performance and durability of the flat-faced, spring-mounted valve poppet was found superior and this type was chosen for use in the control unit. The poppet is supported on a diaphragm which acts as a bellville spring and provides the closing force. The poppet valve face is flat against the sapphire seat containing the orifice. Lift of the poppet is nominally .004". A pulsed leak of this design operated without failure for 10.4 million cycles when the test was arbitrarily terminated. During this test the greatest leak rate at closure was 5×10^{-7} standard cc per second at 2 million operations. The final leak rate was 4.3×10^{-8} standard cc per second.

Heat rise tests were conducted on the pulsed leak while cycling at 10^4 pulses per hour, and with one-inch fiber glass insulation covering the device to simulate the presence of a heating mantle. These tests resulted in a conclusion to heat sink the solenoid to ambient rather than to the plumbing thereby lowering solenoid temperature. The heating mantles were made, therefore, to expose the solenoid to the surrounding atmosphere.

Flow tests were conducted on the pulsed leaks to determine the effects of the following variables on flow rate: orifice diameter, poppet lift, pulse amplitude and duration, operating frequency, upstream pressure, upstream/downstream pressure ratio, temperature, and molecular weight of the gas. The flow test set up is shown schematically in Figure 4; a photograph of the test is shown in Figure 5. This flow test set up was later used to provide bench calibration data



P_1 - UPSTREAM PRESSURE (HG MANOMETER)
P_2 - DOWNSTREAM PRESSURE (HG MANOMETER)
P_3 - CHAMBER B PRESSURE (OIL MANOMETER)
P_4 - VACUUM PRESSURE GAUGE (THERMOPILE)
A - CHAMBER A
B - CHAMBER B
V_3 - ADDITIONAL VOLUME (ADDED TO CHAMBER B)

1 - PULSED LEAK
2 - PULSED LEAK BYPASS
3 - DOWNSTREAM RELIEF
4 - VARIABLE FLOW VALVE
5 - VARIABLE FLOW VALVE BYPASS
6 - ADDED VOLUME VALVE
7 - DIFFERENTIAL MANOMETER BYPASS
8 - GAS REGULATOR
9 - GAS SHUT-OFF

Figure 4. Pulsed Leak Flow Test Schematic

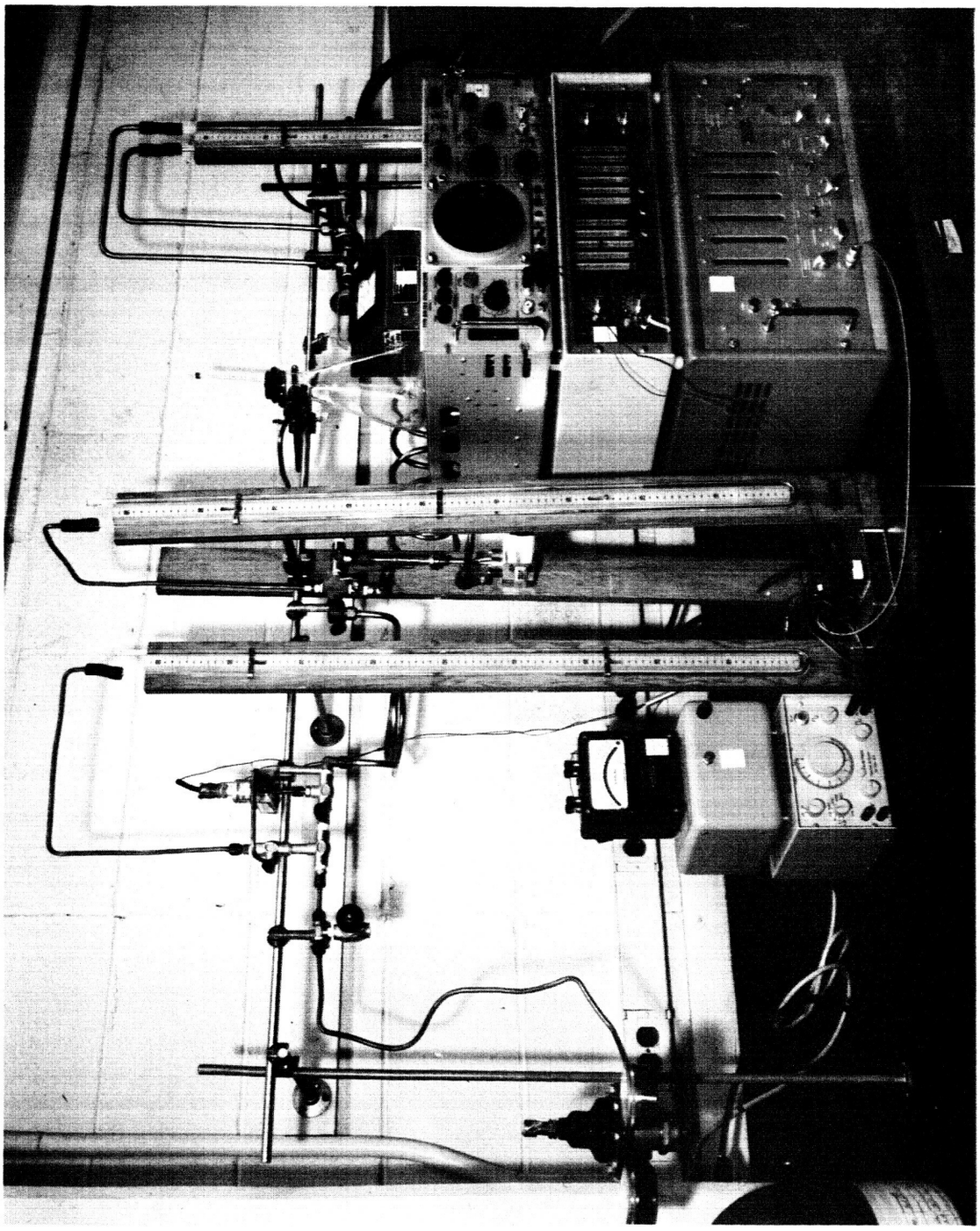


Figure 5. Pulsed Leak Flow Test Apparatus

on each pulsed leak and its associated pulse generator prior to assembly in the control unit.

A detailed account of the flow testing was submitted to NASA as Appendix A of the May 1965 monthly progress report. Basically the delivery rate of the pulsed leak was found by measuring the pressure rise in a hermetic chamber of known capacity. The tests were run as follows (refer to Figure 4):

1) Chamber B was evacuated. (Chamber A and upstream of the pulsed leak were evacuated if necessary.)
2) With the pulsed leak closed the upstream pressure was established.
3) With the variable flow valve closed the downstream pressure was established, usually by pulsing the pulsed leak briefly.
4) The pulsed leak was pulsed at the desired rate by dialing the appropriate cycles per second on the pulse generator.
5) The upstream pressure was readjusted when necessary.
6) The variable flow valve was adjusted to maintain the desired downstream pressure.
7) The levels of the upstream, downstream and differential manometers were noted.
8) The differential manometer bypass was closed and a timer started.
9) The timer was stopped and the upper levels of the upstream and downstream manometers were noted when the rising level of the differential manometer (the vacuum side) reached a desired height.

The time and pulse rate were used to determine the number of pulses. The initial and final height of the upper level of the downstream pressure was used to determine the pressure change in Chamber A. The initial level heights in

the differential manometer were used to determine the initial pressure in chamber B. The height of the vacuum-side level of the differential manometer when the timer was stopped was used to determine the pressure in chamber B at the end of the run.

The range of variables used in the tests was as follows:

Orifice diameter: .0025", .004", .006"

Poppet lift: .0008", .0019", .0025", .004", .006"

Pulse amplitude: 16 to 26 volts

Pulse duration: 80 to 160 milliseconds

Pulse frequency: 30 to 520 pulses per minute

Upstream pressure: 1 to 2 atmospheres

Pressure ratio: 1.3 to 7.5

Molecular weight: 2, 14, and 40

Conclusions:

- For upstream/downstream pressure ratios greater than about 2.5, the pulsed leak delivery at room temperature is given by:

$$D = 0.02\ P\ d^2\ t\ M^{-1/2} \qquad \text{(micromoles)}$$

where:

P - Upstream pressure in atmospheres

d - Orifice diameter in mils

t - Open time in milliseconds

M - Molecular weight of gas

- The delivery per pulse is unaffected by the pulsing rate up to a rate corresponding to 50 percent of time utilization.

- The pulsed leak open time is dependent on the pulse generation circuitry operating characteristics.
- Under the operating constraints anticipated, a delivery of 1 micromole of gas per pulse can be obtained with all required gases except hydrogen.
- Delivery per pulse is relatively independent of poppet lift.
- Temperature dependence, as indicated by nitrogen delivery, showsthat the flow is inversely proportional to the absolute temperature of the pulsed leak. Limited tests with vapors confirm the inverse temperature dependence.

PURGING AND VENTILATION

The Trace Gas Simulator incorporates certain purging and ventilation functions. These include vacuum and dry nitrogen purging of delivery channels and delivery manifold and, ventilation of trace material storage section. As first conceived, purging and ventilating connections were to be provided for the unit; but to provide greater mobility and versatility of use in the laboratory, provisions for these functions were built into the unit. A No. 4 cylinder provides 33 cubic feet (STP) of dry nitrogen for purging; a 21-liter (free air) mechanical vacuum pump exhausts purged trace materials and dry nitrogen. The line of this pump is fitted with an oil separator and a molecular filter, but since trace materials with lighter molecules are not as readily trapped, some odor may be emitted when purging channels such as ammonia and hydrogen sulfide. A 200-cfm centrifugal blower ventilates the trace material storage section - a sheet steel enclosure occupying two-thirds of the lower part of the console. Exhaust from this enclosure will ordinarily not contain contamination.

Heating provision for the delivery manifold was added later in the program. This provision facilitates purging and can be used if higher boiling materials are to be

delivered in large concentrations in the future. Heat is applied with electrical heating tape under control of manifold-mounted thermostats set at 200°F.

PULSE GENERATION

The control unit contains ten pulse generators which operate the pulsed leaks at the prescribed pulse frequency and duration for metering the trace material delivery. Initially, these generators were equipped with reed relays as a means to accommodate more variation of an output load then not completely specified. During the pulsed leak flow tests relay failure occurred after 10^4 to 10^5 cycles. Heavy duty tungsten relays were installed to replace the failed gold relays. The tungsten relay was rated for 3 amp, 50-watt service as opposed to the 1 amp, 15-watt rating of the gold relay. Subsequently, it was noted that although the tungsten relays gave better performance, they were also prone to failure. The contacts appeared to have a welding tendency after repeated operations. A transistor driven circuit was then evaluated and subsequently installed. Requirements on the output circuit were basically those of reproducing the sharp onset and termination of the voltage delivered to the solenoid to give operation similar to that obtained with the reed relays. It had been noticed that valve open time (dwell), as compared to the contact closure time, was significantly greater when diode suppression was used on the solenoid. When adequate protection was provided for the reed relay contacts, minimum delivery rates could not be achieved due to the long solenoid current decay times experienced. The more important requirements on the transistor switching circuit, consequently, were of achieving rapid turn-on and turn-off while providing a long operating life.

The circuit finally evolved is shown in Figure 6, and the associated waveforms in Figure 7. The output transistor is switched ON and OFF by the output stage in the pulse generator described more completely in Section V. The inductive voltage generated when the output transistor is switched off is limited to approximately -65 volts by the zener diode placed across the solenoid coil. With this

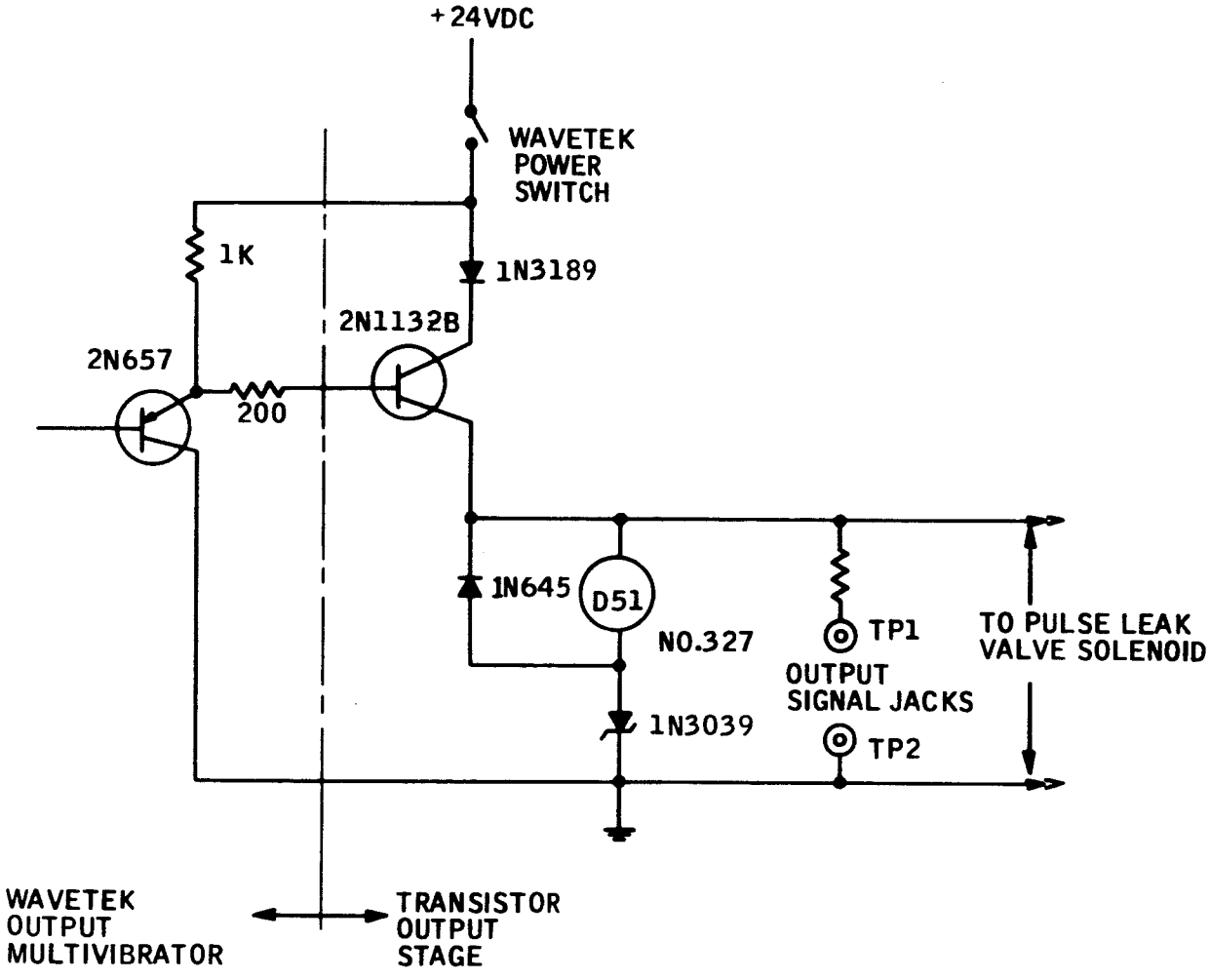


Figure 6. Final Output Circuit for Pulse Controller

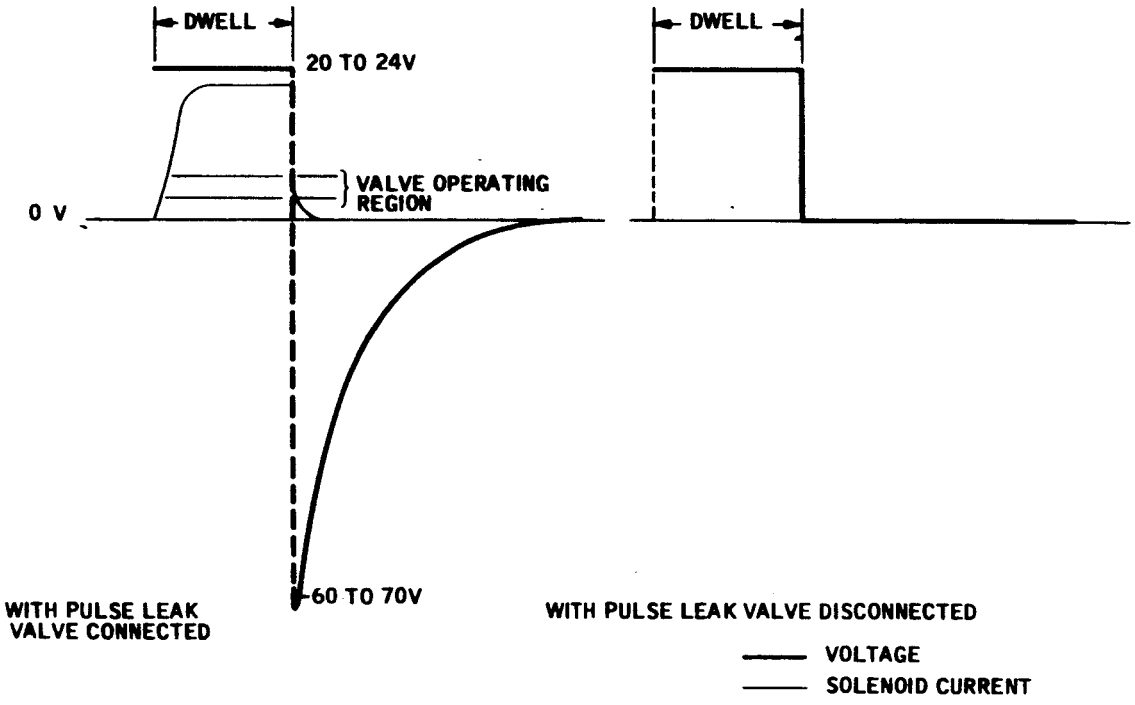


Figure 7. Waveforms

circuit it was found that the coil current decayed to less than 10 percent in approximately 2.5 milliseconds. Over-all performance of the metering system was similar to that obtained with the unsuppressed reed relay switches. No heating problem in the switching circuit was noticed after prolonged operation at maximum dwell and pulsing frequencies, so the circuit can be expected to have an indefinite life expectancy.

SECTION V

DESCRIPTION OF TRACE GAS SIMULATOR

The Simulator is designed to introduce predetermined amounts of trace materials into a vacuum-quality manifold leading to external connections which can be joined to an external system or test chamber. Controls and devices to accomplish introduction of the trace materials, circulation of the atmosphere (diluent) from the external system, and purging of the delivery system are contained in the console shown in Figure 8.

The Trace Gas Simulator has been designed for use with closed test chambers operating under these conditions:

- Atmosphere compositions
  - 100 percent oxygen at 5 psia pressure (258 mm Hg)
  - 50 percent oxygen -50 percent nitrogen at 7 psia total pressure (363 mm Hg) (includes humidity).
- Temperature: between 65 and 100°F.
- Relative humidity: 50 to 100 percent (8 to 49 mm Hg partial pressure)

The unit is placed adjacent to the test chamber, and its two connections provide for circulation of chamber atmosphere through the delivery manifold where trace materials are added.

The trace material control unit provides for the storage and delivery of the following 10 compounds:

- Benzene
- n - Propyl Acetate
- Isopropyl Alcohol
- Acetone
- Freon-114

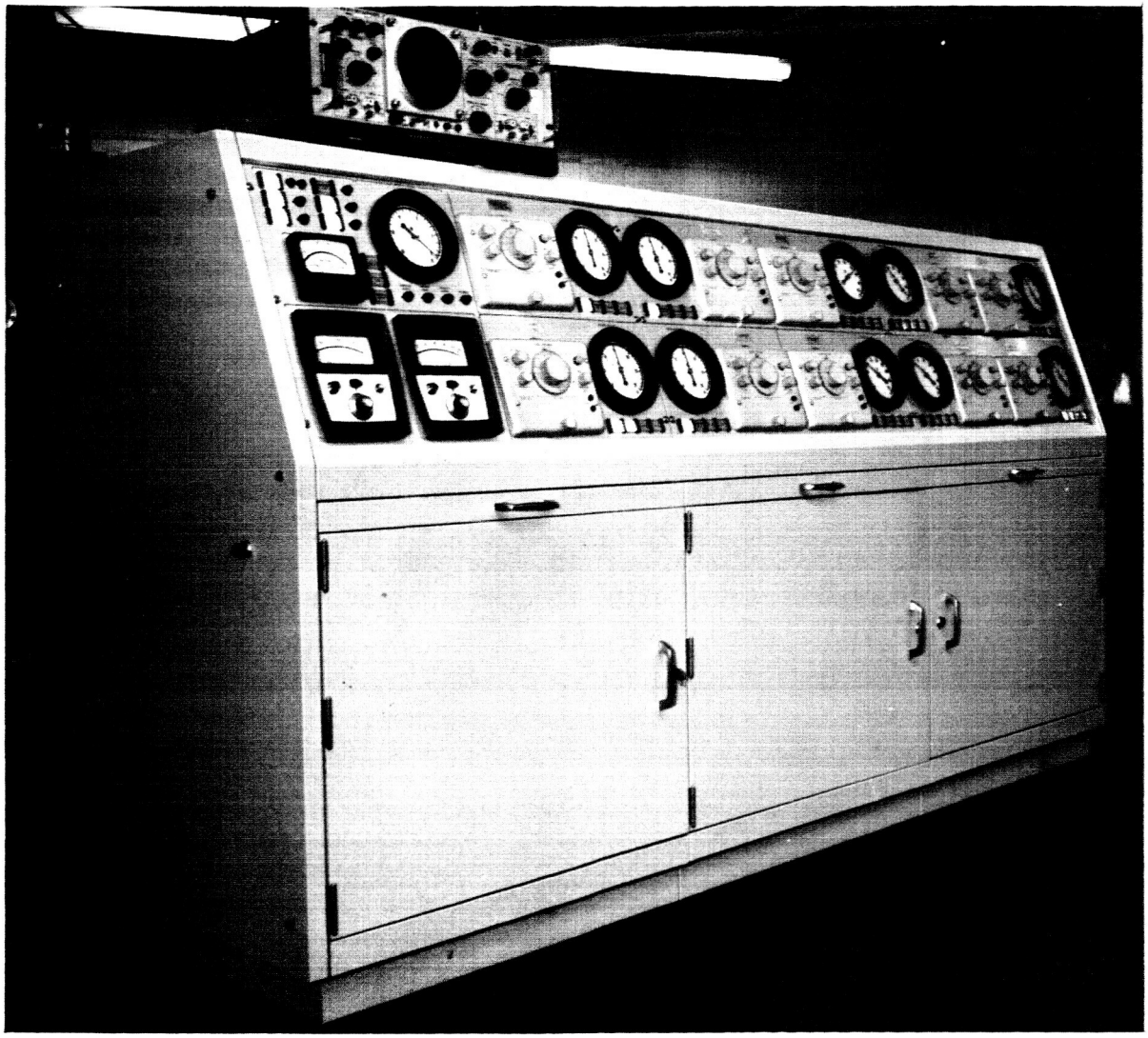


Figure 8. Trace Gas Simulator

- Hydrogen
- Carbon Monoxide
- Methane
- Hydrogen Sulfide
- Ammonia

Storage space and delivery manifold connections for 10 additional compounds is provided.

The unit is capable of accommodating any 10 of the compounds listed in Table 11, although materials with boiling points in excessof 260°F require a higher temperature rated pulsed leak.

The unit requires no electrical or pneumatic service connections except for 115/230-volt, single-phase, a-c power. Discharge gases and vapors from the unit's ventilating and purging systems are normally discharged to the surrounding laboratory atmosphere but may be directed to an exhauster system.

The unit contains an instrument panel where delivery rates may be individually controlled and where operating conditions may be monitored. Compounds are introduced without affecting test chamber conditions.

The delivery manifold of the unit is provided with a gas sampling port (1/4-inch tubing) to permit analysis of the delivered flow stream. It is provided with vacuum and nitrogen sources for use in purging individual delivery channels and the delivery manifold.

The control unit is capable of producing selected introduction rates over the range of 1.0×10^{-6} to 1.0×10^{-2} moles per hour for the 10 compounds noted above. Introduction rates are normally varied by changing the operating frequency

Table 11. **List of Trace Material Characteristics**

TYPE	NASA ITEM NO.	COMPOUND	FORMULA	TOXICITY	T 760mm (°C)	MOLECULAR WEIGHT	POLARITY
NON-CARBON	5	Ammonia	NH_3	100	-33	17	P
	17	Chlorine	Cl_2	1	-35	71	NP
	48	Hydrogen	H_2	---	-253	2	NP
	49	Hydrogen chloride	HCl	5	-85	36	P
	50	Hydrogen fluoride	HF	3	19	20	P
	51	Hydrogen sulfide	H_2S	20	-60	34	P
	64	Nitric oxide	NO	H	-152	30	NP
	66	Nitrogen tetraoxide	NO_2	5	21	46	NP
	65	Nitrous oxide	N_2O	S	-88	44	NP
	75	Sulfur dioxide	SO_2	5	-10	64	P
CARBON-HYDROGEN	3	Acetylene	$CH{\equiv}CH$	S	(-84)	26	NP
	8	n-Butane	$CH_3(CH_2)_2CH_3$	S	0	58	NP
	9	Butene-1	$CH_3CH_2CH{=}CH_2$	U	-5	56	NP
	10	cis-Butene-2	$CH_3CH{=}CHCH_3$	U	1	56	NP
	11	trans-Butene-2	$CH_3CH{=}CHCH_3$	U	2	56	NP
	26	2, 2 - Dimethylbutene	$CH_3CH_2C(CH_3)_3$	U	50	86	NP
	33	Ethylene	$CH_2{=}CH_2$	S	-104	28	NP
	45	n-Hexane	$CH_3(CH_2)_4CH_3$	500	69	86	NP
	47	Hexene-1	$CH_3(CH_2)_3CH{=}CH_2$	M	63	84	NP
	60	Methane	CH_4	---	-162	16	NP
	61	3 - Methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	U	64	86	NP
	70	iso-Pentane	$CH_3CH_2CH(CH_3)_2$	U	28	72	NP
	69	n-Pentane	$CH_3(CH_2)_3CH_3$	S	36	72	NP
	68	Propane	$CH_3CH_2CH_3$	S	-42	44	NP
	72	Propylene	$CH_3CH{=}CH_2$	S	-47	42	NP

*Sax, N. L. (Dangerous Properties of Industrial Materials (1963)),
Classifications: U = Unknown, S = Slight, M = Moderate, H = High
Note: Numbers are parts per million.

Table 11. List of Trace Material Characteristics (Continued)

TYPE	NASA ITEM NO.	COMPOUND	FORMULA	TOXICITY*	T 760mm (°C)	MOLECULAR WEIGHT	POLARITY
CARBON-HALOGEN	18	Chloroacetone	$CH_2ClC(CH_3)O$	M	121	93	P
	20	n-Chloropropane	$CH_3CH_2CH_2Cl$	M	47	79	P
	32	Ethylene dichloride	CH_2ClCH_2Cl	50	84	99	P
	37	Freon 11	CCl_3F	1000	25	137	NP
	38	Freon 12	CCl_2F_2	1000	-29	121	NP
	39	Freon 22	$CHClF_2$	U	-41	86	P
	40	Freon 23	CHF_3	M	-82	70	P
	41	Freon 114	$CClF_2CClF_2$	1000	4	171	(NP)
	42	Freon 114 unsym	CCl_2FCF_3	1000	-2	171	NP
	43	Freon 125	CHF_2CF_3	U	(-70)	120	NP
	55	Methylene chloride	CH_2Cl_2	500	40	85	P
	57	Methyl chloroform	CH_3CCl_3	500	74	133	P
	76	Tetrachloroethylene	$CCl_2=CCl_2$	100	121	166	NP
	77	Tetrafluoroethylene	$CF_2=CF_2$	U	-78	100	NP
	79	Trichloroethylene	$CHCl=CCl_2$	100	87	131	P
	82	Vinyl chloride	$CH_2=CHCl$	500	-14	62	P
	83	Vinylidene chloride	$CH_2=CCl_2$	U	32	97	P
CARBON-OXYGEN	1	Acetaldehyde	CH_3CHO	200	21	44	P
	2	Acetone	$CH_3C(CH_3)O$	1000	56	58	P
	4	Allyl alcohol	$CH_2=CHCH_2OH$	5	97	58	P
	6	iso-Amyl alcohol	$CH_3CH(CH_3)CH_2CH_2OH$	20	132	88	P
	54	iso-Butyl alcohol	$CH_3CH(CH_3)CH_2OH$	H	108	74	P
	12	n-Butyraldehyde	$CH_3(CH_2)_2CHO$	M	76	72	P
	13	Butyric acid	$CH_3(CH_2)_2COOH$	S	164	88	P
	15	Carbon monoxide	CO	100	-192	28	NP
	16	Caprylic acid	$CH_3(CH_2)_6COOH$	U	238	142	P
	30	Ethyl acetate	$CH_3CH_2OC(CH_3)O$	400	77	88	P
	31	Ethyl alcohol	CH_3CH_2OH	1000	79	46	P
	44	Formaldehyde	CH_2O	5	21	30	P
	56	Methyl alcohol	CH_3OH	200	65	32	P
	58	Methyl ethyl ketone	$CH_3CH_2C(CH_3)O$	200	80	72	P
	59	Methyl isopropyl ketone	$CH_3CH(CH_3)C(CH_3)O$	U	95	86	P
	53	iso-Propyl alcohol	$(CH_3)_2CHOH$	400	82	60	P
	71	n-Propyl acetate	$CH_3CH_2CH_2OC(CH_3)O$	200	102	102	P

*Sax, N. L. (Dangerous Properties of Industrial Materials (1963)), Classifications: U = Unknown, S = Slight, M = Moderate, H = High
Note; Numbers are parts per million.

Table 11. List of Trace Material Characteristics (Continued)

TYPE	NASA ITEM NO.	COMPOUND	FORMULA	TOXICITY*	T 760mm (°C)	MOLECULAR WEIGHT	POLARITY
ACYCLIC-MISC	14	Carbon disulfide	CS_2	200	46	76	NP
	23	Cyanamide	H_2NCN	U	140 19mm	42	P
	27	unsym-Dimethylhydrazine	$NH_2N(CH_3)_2$	0.5	(62)	60	P
	35	Ethyl mercaptan	CH_3CH_2SH	250	35	62	P
	36	Ethyl sulfide	$CH_3CH_2SCH_2CH_3$	U	92	90	P
	62	Methyl mercaptan	CH_3SH	50	6	48	P
	63	Monomethylhydrazine	CH_3NHNH_2	1	(87)	46	P
	73	Propyl mercaptan	$CH_3CH_2CH_2SH$	U	68	76	P
CARBOCYCLIC	7	Benzene	$CH{=}CHCH{=}CHCH{=}CH$	25	80	78	NP
	19	Chlorobenzene	$CH{=}CHCH{=}CHCH{=}CCl$	75	132	113	P
	21	Cyclohexane	$CH_2(CH_2)_4CH_2$	400	81	84	NP
	22	Cyclohexanol	$CH_2(CH_2)_4CHOH$	50	161	100	P
	24	1, 1-Dimethylcyclohexane	$CH_2(CH_2)_4C(CH_3)_2$	U	120	112	NP
	25	trans-1, 2-Dimethylcyclohexane	$CH_3CH(CH_2)_4CCH_3$	U	123	112	NP
	34	trans-1, 3-Methylethylcyclohexane	$CH_3CH_2CH(CH_2)_3CH(CH_3)CH_2$	U	(154)	126	NP
	67	Phenol	$CH{=}CHCH{=}CHCH{=}COH$	5	182	94	P
	78	Toluene	$CH{=}CHCH{=}CHCH{=}CCH_3$	200	111	92	NP
	81	1, 1, 3 - Trimethylcyclohexane	$CH(CH_2)_2CH(CH_3)CH_2C(CH_3)_2$	U	136	126	NP
	84	m-Xylene	$CH{=}CHCH{=}C(CH_3)CH{=}CCH_3$	200	139	106	NP
	85	o-Xylene	$CH{=}CHCH{=}CHC(CH_3)CCH_3$	200	144	106	NP
	86	p-Xylene	$CH{=}CHC(CH_3){=}CHCH{=}CCH_3$	200	138	106	NP
HETERO-CYCLIC	28/29	1, 4-Dioxane	$OCH_2CH_2OCH_2CH_2$	100	101	88	NP
	46	Hexamethylcyclotrisiloxane	$Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2O$	U	134	210	(NP)
	52	Indole	$NHCH{=}CHC{=}CCH{=}CHCH{=}CH$	U	253	117	P
	74	Skatole	$NHCH{=}C(CH_3)C{=}CCH{=}CHCH{=}CH$	U	266	131	P

*Sax, N. L. (Dangerous Properties of Industrial Materials (1963), Classifications: U = Unknown, S = Slight, M = Moderate, H = High
Note: Numbers are parts per million.

of the pulsed leaks. The pulsed leaks nominally deliver one micro-mole per pulse when set at the proper pulse dwell and inlet pressure. Each delivery channel is provided with an infinitely variable control of pulsing frequency from 1 to 10,000 pulses per hour in four ranges and of pulse dwell from 25 to 250 milliseconds.

Introduction rate accuracy of the control unit is as follows:

Introduction Rate (moles hour^{-1})	Accuracy (percent)
1 to 10 x 10^{-6}	±10
1 to 10 x 10^{-5}	±10
1 to 10 x 10^{-4}	±10
1 to 10 x 10^{-3}	± 5

CONSOLE

The control unit console is approximately 93 inches long, 50 inches high (exclusive of casters) and 30 inches deep. It is of steel frame and panel construction and is mounted on locable casters. Color is NASA blue with instrument panels of metallic gray and black markings. The interior of the cosole is accessible through lockable doors at the sides, ends, and top.

A 17 by 90-inch instrument panel, inclined from vertical for ease of viewing and operation, extends the entire length of the unit at above-waist height. Three pull-out writing surfaces are located under this panel. The panel itself includes individual control stations for the 10 delivery channels and a master control station. The controls and displays are listed in Table 12. Details of the control panel are shown in Figures 9 and 10. Temperature of the liquid channels may be adjusted by means of the two panels inside the access door at the end of the console. These can be seen in Figure 11.

Table 12. Instrument Panel Controls and Displays

Location	Item	Description or Number (See Figure 9)
Main Control	Switches (on-off):	
	- Main Power, Vacuum Guage	A-1
	- Ventilation Blower	A-2
	- Manifold Pump	A-3
	- Vacuum Pump	A-4
	- Temperature Indicators	A-46
	- Pulse Generators	A-5
	- Manifold Heaters	A-63
	- Cooling Blower	A-62
	Circuit Breakers:	
	- Main Power	CB-1
	- Ventilation Blower	CB-2
	- Vacuum Pump	CB-4
	- Manifold Pump	CB-3
	- Temperature Indicators	CB-9
	- Pulse Generators, AC	CB-5
	- Manifold Heater	CB-10
	- Solenoid Valves (Vacuum)	CB-7
	- Solenoid Valves (Nitrogen)	CB-8
	- Pulse Generators, DC	CB-6
	Delivery Manifold Pressure Gauge	0-15 PSIA
	Temperature Indicator	100°C to 300°C (M-2)
	- Point Select Switch	4-Points
	- Set-Point Read Switch	
	- "On-Off" Indicator Light	
	Temperature Indicator	-10°C to 130°C (M-3)
	Same as M-2 except 6-Point	
Channel 1 (Benzene)	Pulse Generator	
	- On-Off Switch	
	- Frequency Adjustment	Coarse
	- Frequency Adjustment	Fine
	- Dwell Adjustment	25-250 m seconds
	- Output Monitor	Indicator Light
	- Output Monitor	Test Plug Receptical (2)
	Delivery Pressure Gauge	0-30 PSIA
	Switches:	
	- Nitrogen (Purge)	A-26
	- Vacuum (Purge)	A-16
	- Trim (Pressure)	A-47
	- Heater	A-36
Channel 2 (n-Propyl Acetate)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 1)
	Switches:	
	- Nitrogen	A-27
	- Vacuum	A-17
	- Trim	A-48
	- Heater	A-37

Table 12. Instrument Panel Controls and Displays (Continued)

Location	Item	Description or Number (See Figure 9)
Channel 3 (Isopropyl Alcohol)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 1)
	Switches:	
	- Nitrogen	A-28
	- Vacuum	A-18
	- Trim	A-49
	- Heater	A-38
Channel 4 (Acetone)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 1)
	Switches:	
	- Nitrogen	A-29
	- Vacuum	A-19
	- Trim	A-50
	- Heater	A-39
Channel 5 (Freon-114)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	0-45 PSIA
	- Nitrogen	A-30
	- Vacuum	A-20
	- Trim	A-51
	- Heater	A-40
Channel 6 (Hydrogen)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 5)
	Switches:	
	- Nitrogen	A-31
	- Vacuum	A-21
	- Trim	A-52
	- Spare	---
Channel 7 (Carbon Monoxide)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 5)
	Switches:	
	- Nitrogen	A-32
	- Vacuum	A-22
	- Trim	A-53
	- Spare	---
Channel 8 (Methane)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 5)
	Switches:	
	- Nitrogen	A-33
	- Vacuum	A-23
	- Trim	A-54
	- Spare	---
Channel 9 (Hydrogen Sulfide)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 5)
	Switches:	
	- Nitrogen	A-34
	- Vacuum	A-24
	- Trim	A-55
	- Spare	---
Channel 10 (Ammonia)	Pulse Generator	(Same as Channel 1)
	Delivery Pressure Gauge	(Same as Channel 5)
	Switches:	
	- Nitrogen	A-35
	- Vacuum	A-25
	- Trim	A-56
	- Spare	---

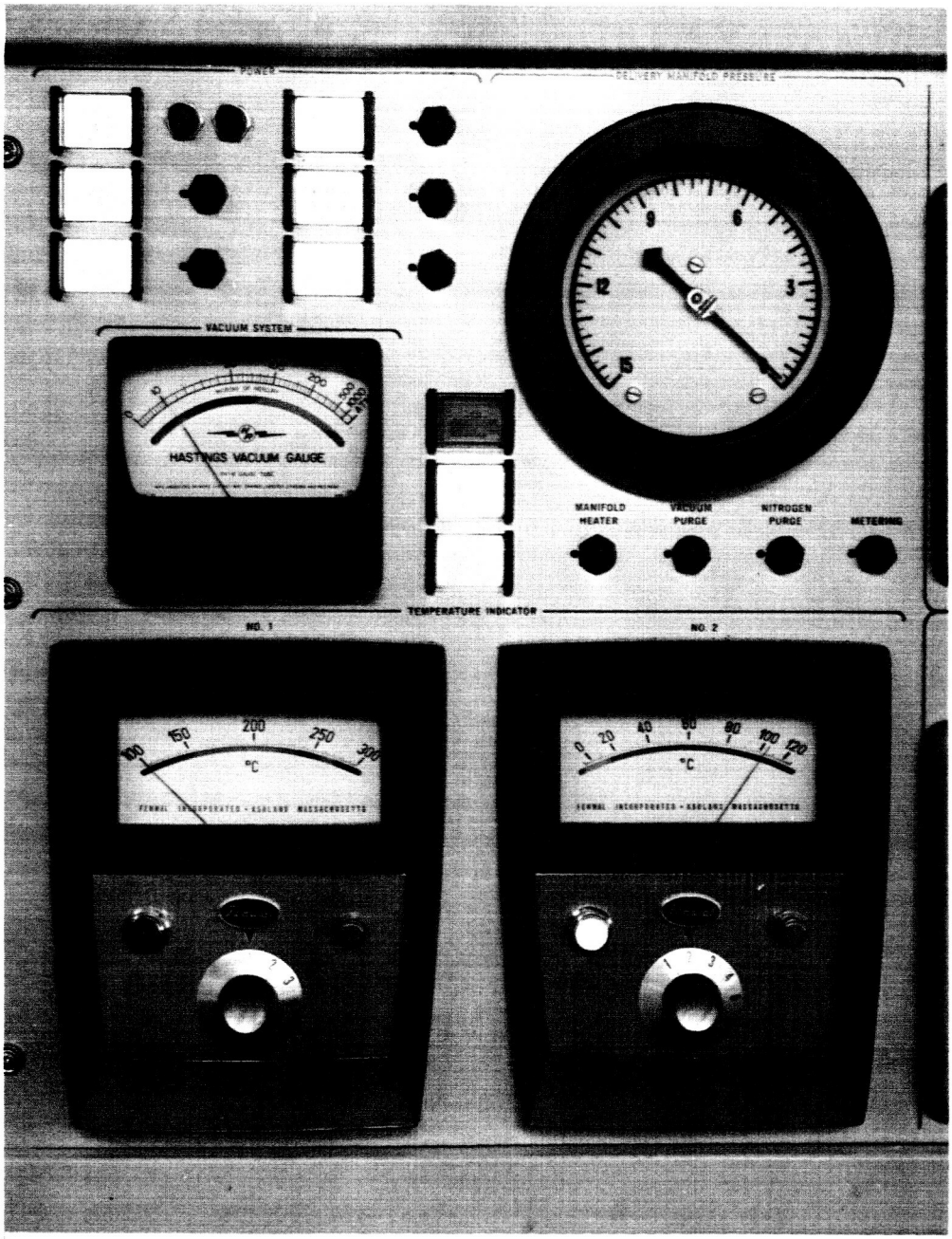


Figure 9. Detail of Main Controls

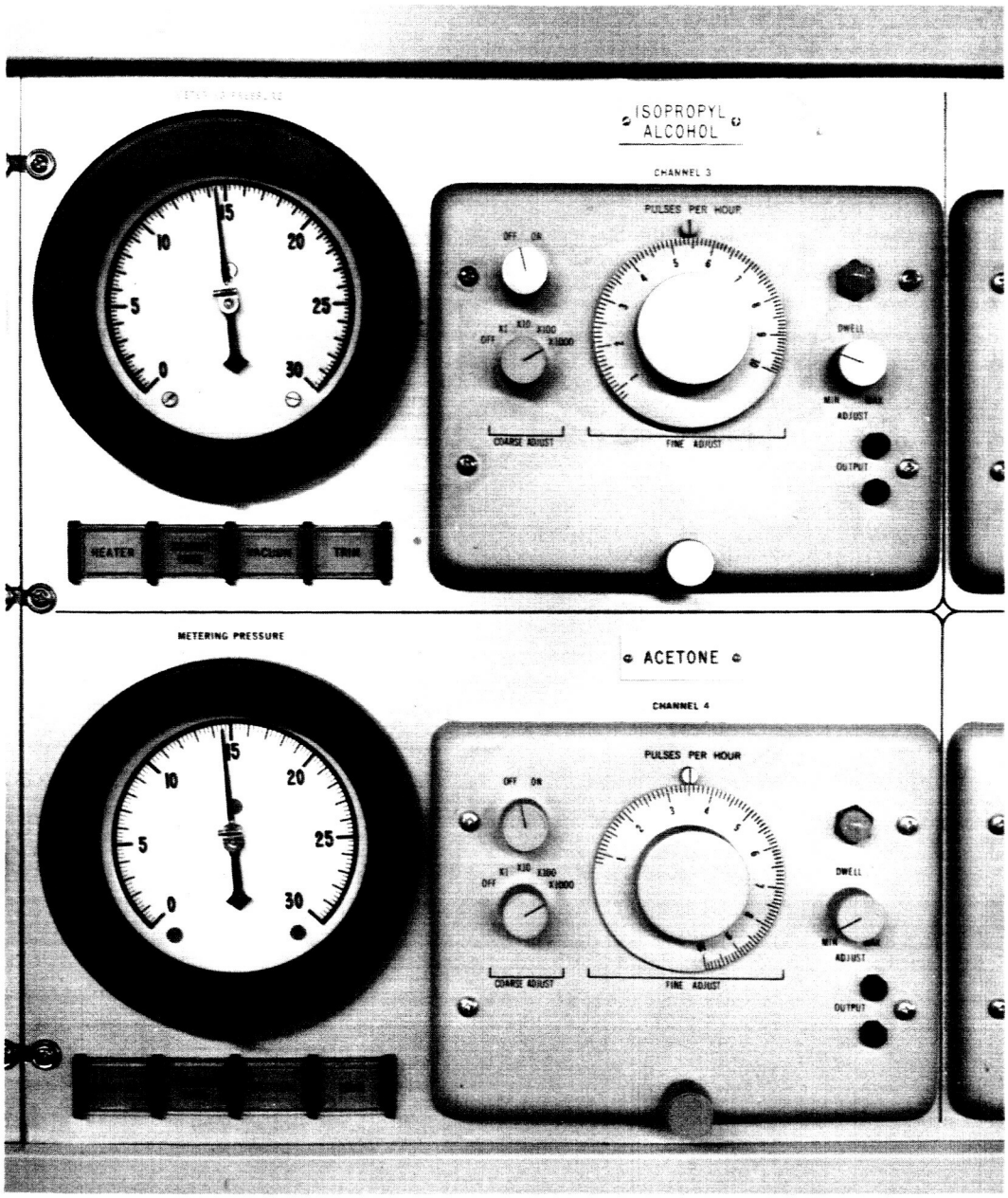


Figure10 Detail of Typical Individual Channel Controls

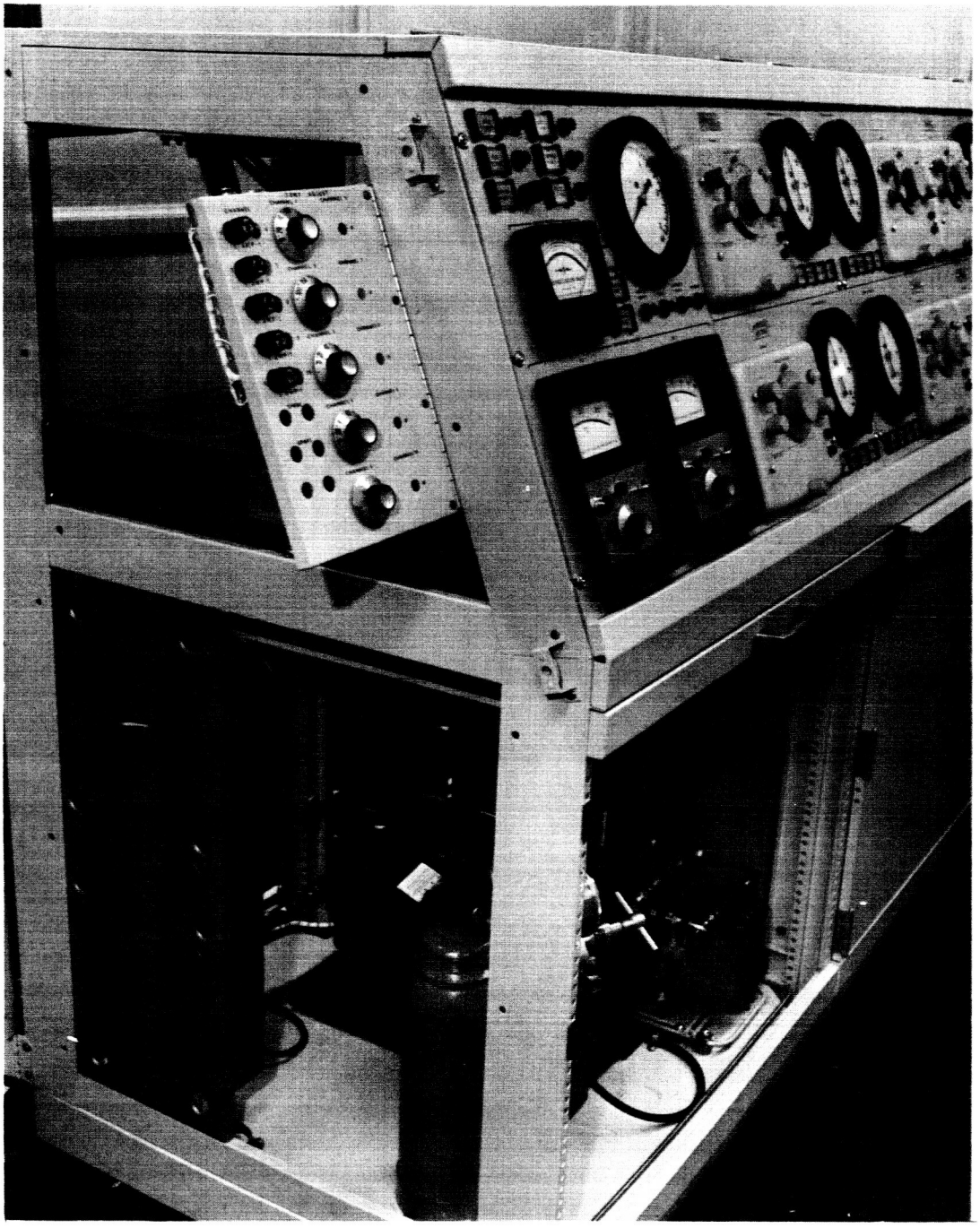


Figure 11. Service Compartment Showing Temperature Control Panels, Nitrogen Purge Storage, Manifold and Vacuum Pumps, One of the Ventilating Blowers, and Shutoff Valves

Two-thirds of the lower part of the console is occupied by the material storage enclosure. The remaining third is a service compartment containing the delivery manifold pump, vacuum pump, dry-nitrogen supply, and the two ventilating blowers, as shown in Figure 11. The service connections to the control unit are available at the rear of the service compartment and include two delivery manifold connections and shut-off valves, one gas analysis connection and shut-off valve, and one four-pin electrical power connection. The ac-dc power supply and temperature controllers are located at the rear of the instrument panel in the service compartment, as shown by Figure 12.

The trace materials are stored in a sealed sheet-steel enclosure approximately 20 x 24-1/8 x 62-1/8 inches (approximately 17-cubic-foot volume). This enclosure is mounted in turn in the lower part of the control unit console as shown in Figure 13. Two doors on either side of the enclosure, together with adjacent outer doors in the console, give access to the stored materials. The enclosure provides space for 20 liquid and gas storage cylinders, although only ten are presently installed.

The enclosure is ventilated by a 200-cfm centrifugal blower. The blower motor is the shaded-pole type and, therefore, does not create a sparking hazard if flammable materials are leaking. Another blower (shaded-pole motor) of 137-cfm capacity is provided for cooling specific locations within the enclosure by blowing room air to the location. The use of higher temperature delivery channels could require such cooling for the pulsed leak solenoids.

A component list for the control unit is given in Table 13.

FLOW SYSTEM

The Trace Gas Simulator flow system is shown schematically in Figure 14. Gas flow to and from the test chamber circulates through a delivery manifold where

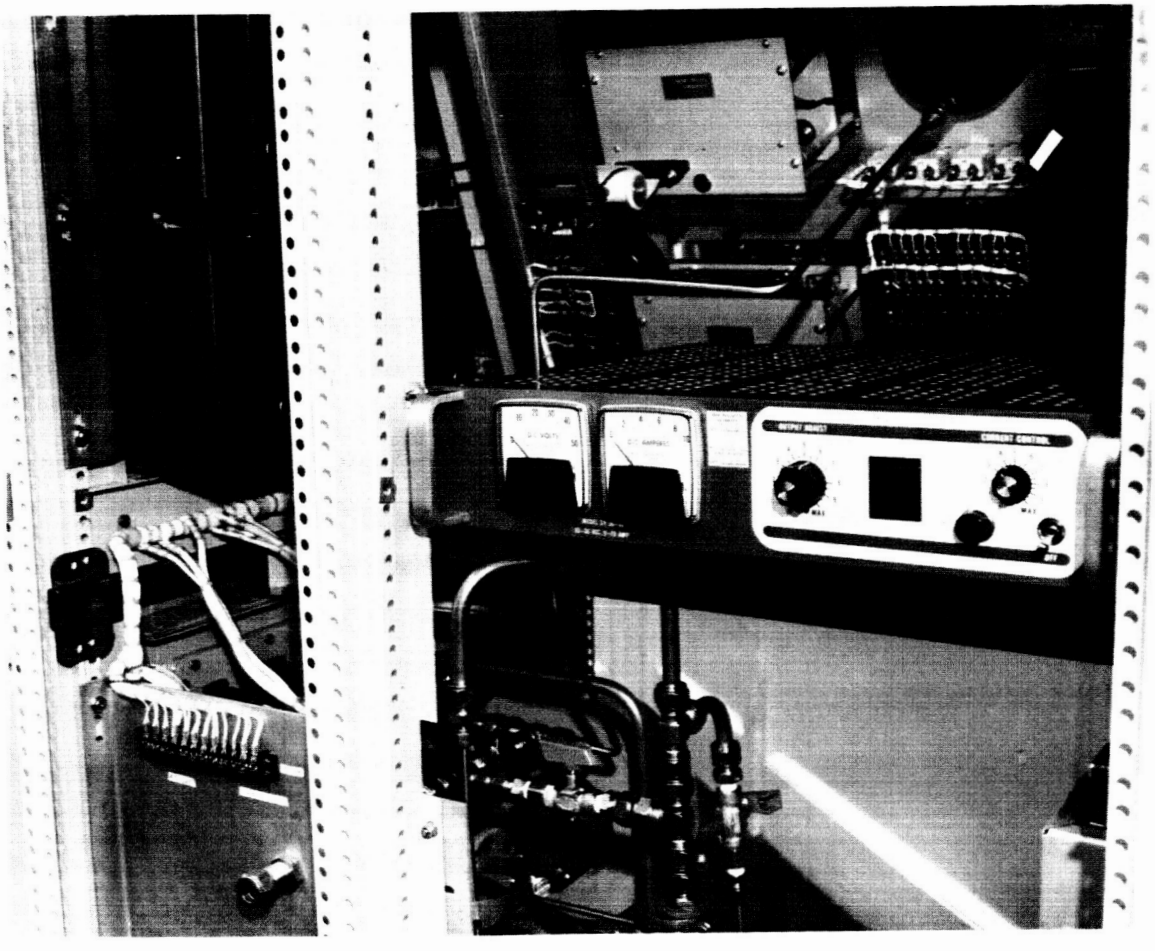


Figure12. Service Compartment - Rear View

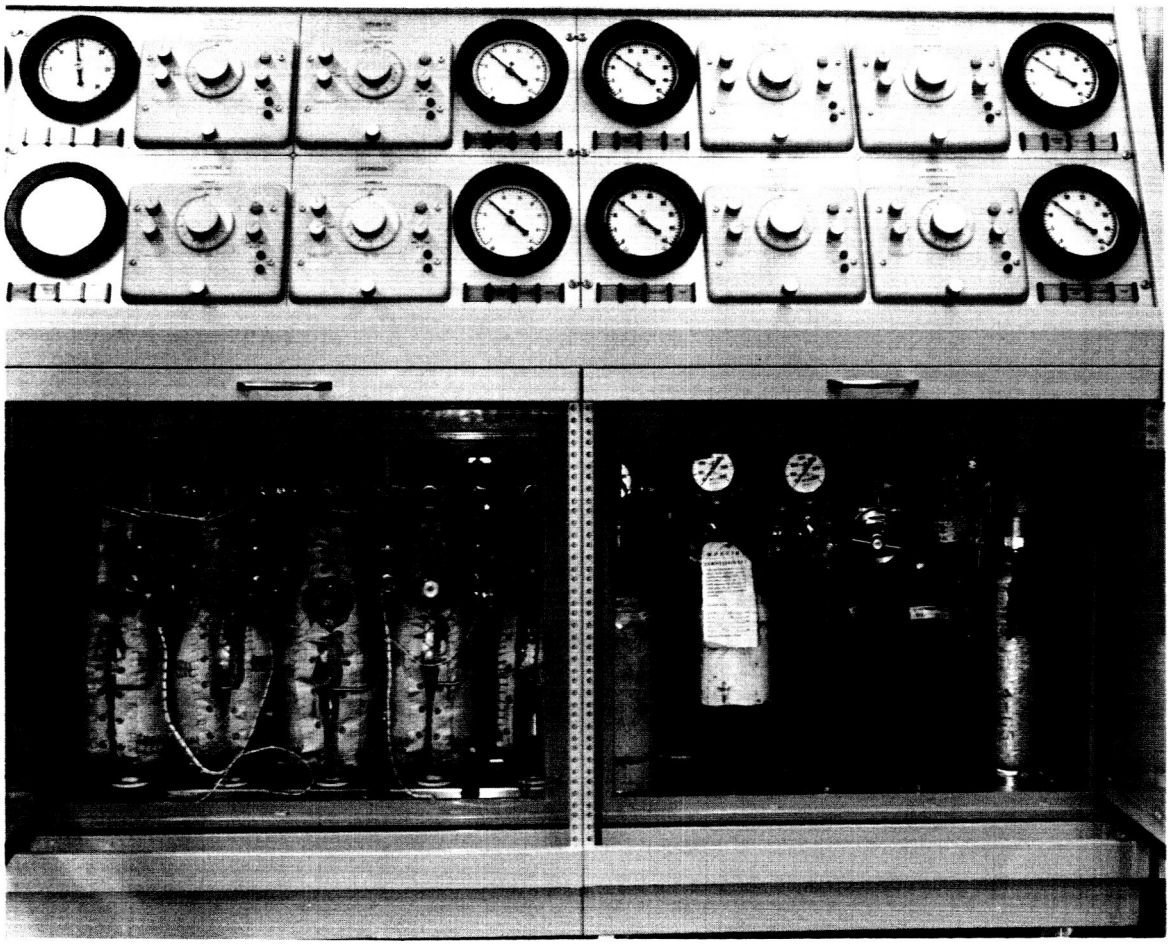


Figure13. Storage Enclosure with Front Access Doors Open

Table 13. Trace Material Control Unit Components

Component	Quantity	Model	Manufacturer	Honeywell No.
Blower, Cooling	1	2C647	Dayton Electric	SK 87901
Blower, Ventilating	1	INB424	McLean Engineering	SK 87589
Controller, Temperature -10°C to 130°C	4	53602-1	Fenwal, Inc.	SK 87574-1
Controller, Temperature 100°C to 300°C	1	53602-1	Fenwal, Inc.	SK 87564-2
Cylinder, Ammonia No. 4	1	---	Matheson Co., Inc.	SK 87564
Cylinder, Carbon Monoxide No. 4	1	---	Matheson Co., Inc.	SK 87566
Cylinder, Hydrogen No. 4	1	---	Matheson Co., Inc.	SK 87568
Cylinder, Hydrogen Sulfide No. 4	1	---	Matheson Co., Inc.	SK 87563
Cylinder, Liquid 1-liter	5	803	Matheson Co., Inc.	SK 87570
Cylinder, Methane No. 4	1	---	Matheson Co., Inc.	SK 87565
Cylinder, Nitrogen No. 4	1	---	Matheson Co., Inc.	SK 87569
Disc, Assembly	6	1/2-305A	Fike Metal Products	SK 87586-1
Disc, Rupture 100 psi	6	---	Fike Metal Products	SK 87585-1
Gauge, Pressure 0-15 psia	1	Series 1833 with Customer Modified Dial	U. S. Gauge	SK 87577-4
Gauge, Pressure 0-30 psia	4		U. S. Gauge	SK 87577-2
Gauge, Pressure 0-45 psia			U. S. Gauge	SK 87577-2
Gauge, Vacuum	1	VT-6	Hastings-Raylist, Inc.	SK 87578-1
Heater, Manifold 1/2-inch - 25 watts per foot	3	Special	Glas-Col Apparatus Co.	---
Heater, Mantle	5	Special	Glas-Col Apparatus Co.	SK 87588
Indicator, Temperature -10°C to 130°C	1	58004-12	Fenwall, Inc.	SK 87572-1
Indicator, Temperature 100°C to 300°C	1	58004-14	Fenwall, Inc.	SK 87572-2
Probe, Temperature -10°C to 13-°C	4	74502-103	Fenwall, Inc.	SK87575-1
Pulse Generator	10	No. 10 (Modified)	Wavetek	
Pulsed Leak	10	SK 87835	Honeywell, Inc.	SK 87835
Pump, Delivery Manifold	1	G-3	Air Control, Inc.	SK 87576
Pump, Vacuum Manifold	1	1400B	W.M. Welch Scientific Co.	SK 87573
Regulator	3	19	Matheson Co., Inc.	SK 87558
Regulator	1	19	Matheson Co., Inc.	SK 87559
Regulator	2	15BB	Matheson Co., Inc.	SK 87560
Valve, Liquid Cylinder	5	939SS	Matheson Co., Inc.	SK 87561
Valve, Shut-off	7	30201-6	Hoke, Inc.	SK 87587
Valve, Solenoid	20	590D340HTM	Hoke, Inc.	SK 87571

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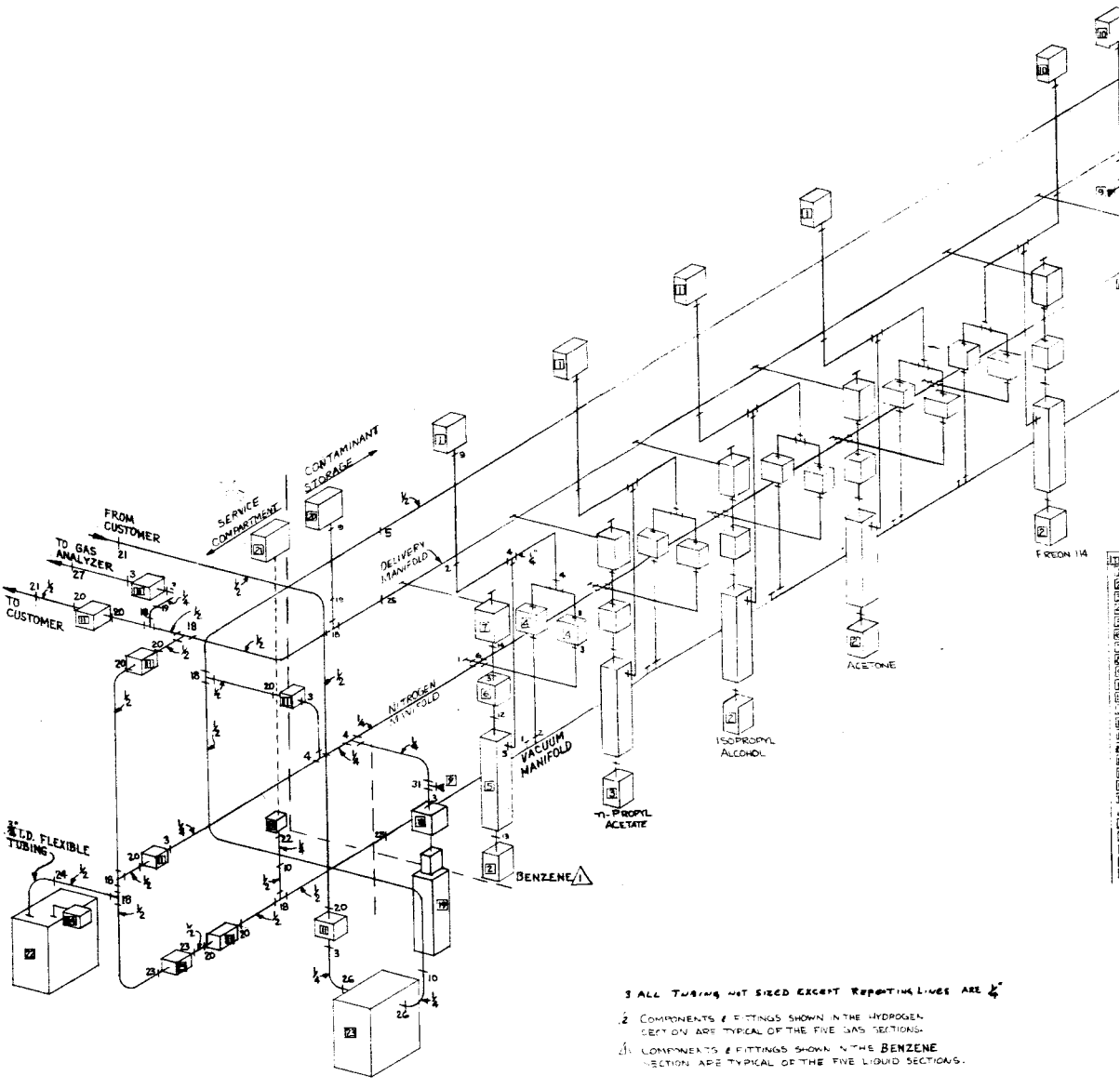
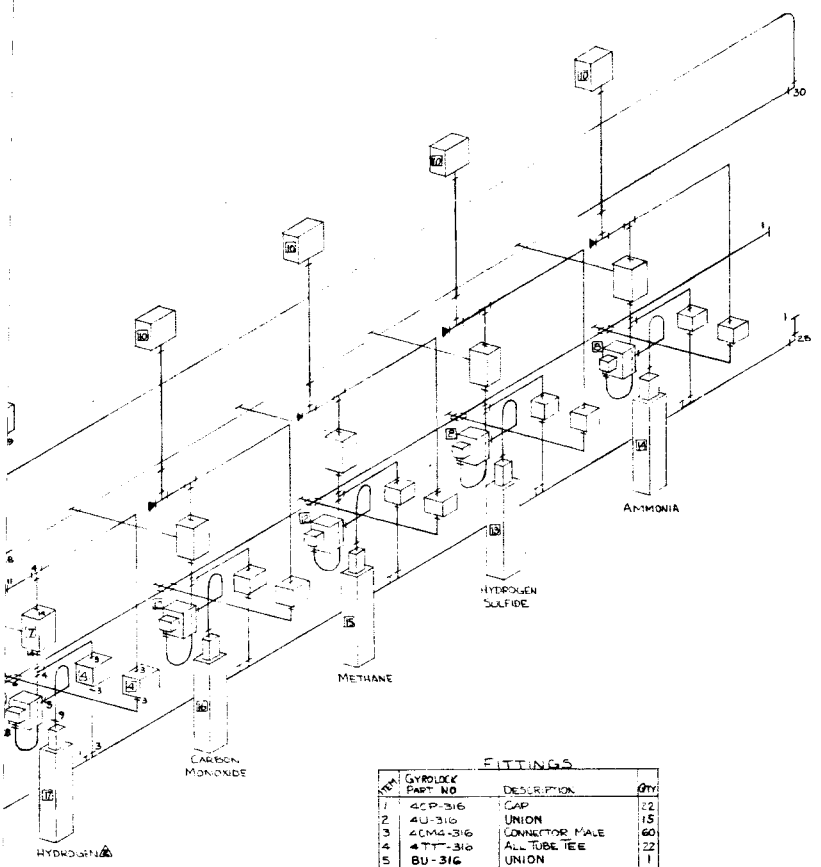


Figure 14 Flow System S



FITTINGS

ITEM	GYROLOCK PART NO	DESCRIPTION	QTY
1	4CP-316	CAP	22
2	4U-316	UNION	15
3	4CM4-316	CONNECTOR MALE	60
4	4TTT-316	ALL TUBE TEE	22
5	BU-316	UNION	1
6	4C-316	TUBE CROSS	10
7			
8			
9	4CF4-316	CONNECTOR FEMALE	18
10	BRU4-316	REDUCING UNION	6
11	4TFT4-316	TEE	5
12		ADAPTER MALE	5
13		ADAPTER FEMALE	5
14		FLARE FITTING FEMALE	20
15		TANK COUPLING	5
16	4P6-316	REDUCER	14
17	12RUB-316	REDUCING UNION	2
18	8TTT-316	ALL TUBE TEE	7
19	4R6-316	REDUCER	2
20	8CM6-316	CONNECTOR MALE	9
21	8BU-316	BULKHEAD UNION	2
22	4CF2-316	CONNECTOR FEMALE	1
23	8CF4-316	CONNECTOR FEMALE	2
24	BR12-316	REDUCER	2
25	8CM12-316	CONNECTOR MALE	2
26	4CM2-316	CONNECTOR MALE	2
27	4BU-316	BULKHEAD UNION	1
28	4LM4-316	ELBOW MALE	5
29			
30	BLMG-316	ELBOW, MALE	1
31	4TTF4-316	TEE	1

COMPONENTS

ITEM	PART NO	DESCRIPTION	QTY
	SKB7577-1	GAUGE	4
	SKB7575-1	PROBE (-10°C TO 130°C)	4
	SKB7575-2	PROBE (100°C TO 300°C)	1
	SKB7571-1	VALVE SOLENOID	20
	SKB7570-1	CYLINDER LIQUID	5
	SKB7562-1	VALVE SHUT OFF	5
	SKB7[illegible]-1	PULSE LEAK	10
	SKB7560-1	REG LOW PRESSURE	2
	SKB7586-1	SCREW DISC ASSY	6
	SKB7577-2	GAUGE	6
	SKB758[illegible]	VALVE	7
	SKB7558-1	REG HIGH PRESSURE	3
	SKB7563-1	GAS & CYLINDER	1
	SKB7564-1	GAS & CYLINDER	1
	SKB7565-1	GAS & CYLINDER	1
	SKB7566-1	GAS & CYLINDER	1
	SKB7568-1	GAS & CYLINDER	1
	SKB7559-1	REG HIGH PRESSURE	1
	SKB7569-1	GAS & CYLINDER	1
	SKB7577-4	GAUGE	1
	SKB7578-1	VAC GAUGE THERMOCOUPLE	1
	SKB7573-1	PUMP VAC - 2 STAGE	1
	SKB7576-1	PUMP VAC PRES	1
		EXHAUST FILTER (PART OF 32)	1
	SK	INTAKE FILTER	1

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trace materials are added through action of ten delivery channels. Flow through the manifold is induced by a diaphragm pump of vacuum quality as to tightness and material properties. Manifold flow is approximately 21 liters per minute at atmospheric pressure (15 liters per minute at 1/3 atmosphere), providing high dilution of the added trace materials. Since this flow rate gives dilutions of the individually delivered materials from about 1.3×10^3 to 1.3×10^7 (at 1/3 atmosphere manifold pressure), their partial pressures are extremely low, and their dew points are much lower than the manifold gas stream temperature.

Materials are delivered to the "pulsed leak" metering valve at a pressure above the critical pressure ratio so that pulsed leak calibration is independent of fluctuations in manifold pressure. Supply pressure of the liquid-phase materials is controlled by keeping their storage temperature constant, while regulators control the supply pressure of the gas-phase materials.

Materials are delivered by the pulsed leaks which in turn are operated by the digital control circuits. Pulsing rates are from one to 10,000 per hour, and delivery (moles per hour) is proportional to the pulsing rate.

Delivery lines and manifold can be purged using purge valves connecting the unit's vacuum and dry nitrogen sources. The delivery manifold is equipped with heating tapes and thermal insulation to facilitate purging by heating. Heat is maintained at approximately 200°F by thermostat control.

Delivery Manifold

The delivery manifold contains the gas stream flow into which the trace materials are introduced. The manifold is made of stainless steel tubing 0.875-inch O.D. x 0.635-inch I.D. at the pulsed leaks and 0.500-inch O.D. x 0.375-inch I.D. elsewhere. The manifold provides mountings for 20 pulsed

leaks, with ten leaks presently installed and the remainder of the connections blanked off for future use. The manifold also contains the diaphragm pump, shut-off valves at inlet and outlet, a valved connection for gas analysis equipment, and fittings for connecting the control unit to a test chamber. The latter are for a one-half-inch O.D. tube equipped with precision-ground and formed ferrules which provide vacuum-quality seals. The connection for gas analysis equipment is for a one-fourth-inch O.D. tube but is otherwise similar to the test chamber connections. The manifold is equipped with 25-watt-per-foot heating tapes overlayed with one-half-inch thick type-475 Johns-Manville microfoil tape. Two double-element tapes are placed oppositely on the manifold tubing in three separate circuits, each under the control of bimetal thermostats located on the manifold in three places. The three circuits operate on 115-volt a-c power from a common heater switch located on the instrument panel.

Delivery Manifold Pump -- The delivery manifold pump is a diaphragm type with wetted parts of stainess steel and Teflon (diaphragm and valves). The pump operates at 1750 strokes per minute and has a mechanical displacement of about one cubic foot per minute. Air flow through the pump operating at the low head required to overcome pressure drops in the manifold is about 21 liters per minute at atmospheric pressure and 15 liters per minute at one-third atmosphere. This latter flow rate gives dilutions of the individually delivered materials from about 1.3×10^{3} to 1.3×10^{7}. Data for the delivery manifold pump are given in Table 14.

Shut-Off Valves -- The delivery manifold inlet and outlet can be closed off by manually-operated shut-off valves. Wetted surfaces of these valves are of stainless steel with Teflon seals. A micro-finished ball with one-fourth-inch diametral hole provides quarter-turn on-off operation at low torque. Leak rate does not exceed 10^{-8} std cc of air per second. A similar valve is used in the connection provided for gas analysis.

Table 14. Delivery Manifold Pump Data

Item	Design Data
Input Voltage	105 to 125 volts, 60-cycles
Allowable Voltage Variation	90 to 130 volts
Power	190 watts at 115 volts
Current	2.6 amperes at 115 volts
Power Rating	one-eighth hp, drip-proof, split-phase induction motor
Speed	1750 rpm
Airflow	21 liters per minute at one atmosphere outlet and inlet 15 liters per minute at one-third atmosphere outlet and inlet
Ambient Temperature Rating	-20°F to 120°F
Materials	Wetted pump components: 316 stainless steel
Connections	one-eighth-inch NPT

Pulsed Leaks

The control unit contains ten pulsed leaks which provide digital metering of the trace materials to the delivery manifold. The pulsed leaks are mounted directly to the manifold to minimize possibilities for condensation before the delivered material is swept into the manifold flow stream. The pulsed leaks used for liquid-phase materials are insulated and heated by the mantle which also surrouds the liquid storage cylinder and intervening delivery line. Sufficient heat is applied by the mantle to prevent condensation in the passages of the pulsed leak.

The pulsed leak (Figure 15)is a solenoid-operated miniature poppet valve with wetted parts constructed of chemically inert materials -- stainless steel, teflon, and sapphire. The solenoid operates under the control of the pulsed generators at a prescribed frequency and dwell. The solenoid armature lifts the valve poppet, allowing gas to flow through an orifice. In the unenergized position, a spring diaphragm holds the poppet tightly on the seat to effect closure. The orifice is a 0.002-inch-diameter hole in a sapphire disc. The face of the disc is the valve seat. The single moving part is the diaphragm-armature-poppet assembly which is secured to the body of the device at the perimeter of the diaphragm. The integrity of this mounting arrangement provides positive closure and consistency of flow per pulse. Sonic velocity is obtained through the orifice by operating the leak above critical pressure ratio*; in this way the effects of downstream pressure fluctuations on calibration are minimized. The design features of the pulsed leak are summarized in Table 15.

Table 15. Pulsed Leak Design Data

Item	Design Data
Voltage Rating	24 volts dc
Power Rating	10 watts
Flow Range	0 to 10^{-2} gram-moles per hour, minimum
Pulse Rate	5 per second at 200 millisecond dwell, maximum
Inlet Pressure	4 atmospheres, maximum
Temperature Rating	260°F vapor temperature
Leakage	Environment: 10^{-8} std cc air per second Seat: 10^{-7} std cc air per second
Endurance	10^{7} cycles, minimum
Dimension, including connections	3 x 2 x 3-1/4 inches
Weight	1.3 lbs
Inlet Filter	Stainless steel mesh - 2 microns
Materials	All wetted surfaces of stainless steel, teflon, or sapphire
Connections	Electrical: Mates with Amphenol 10SL-45 Gas Flow: one-fourth-inch tubing

* Defined as: $\frac{Pin}{Pout} = \left(\frac{2}{K+1}\right)^{\frac{K}{K-1}}$ where K is the ratio of specific heats of the gas.

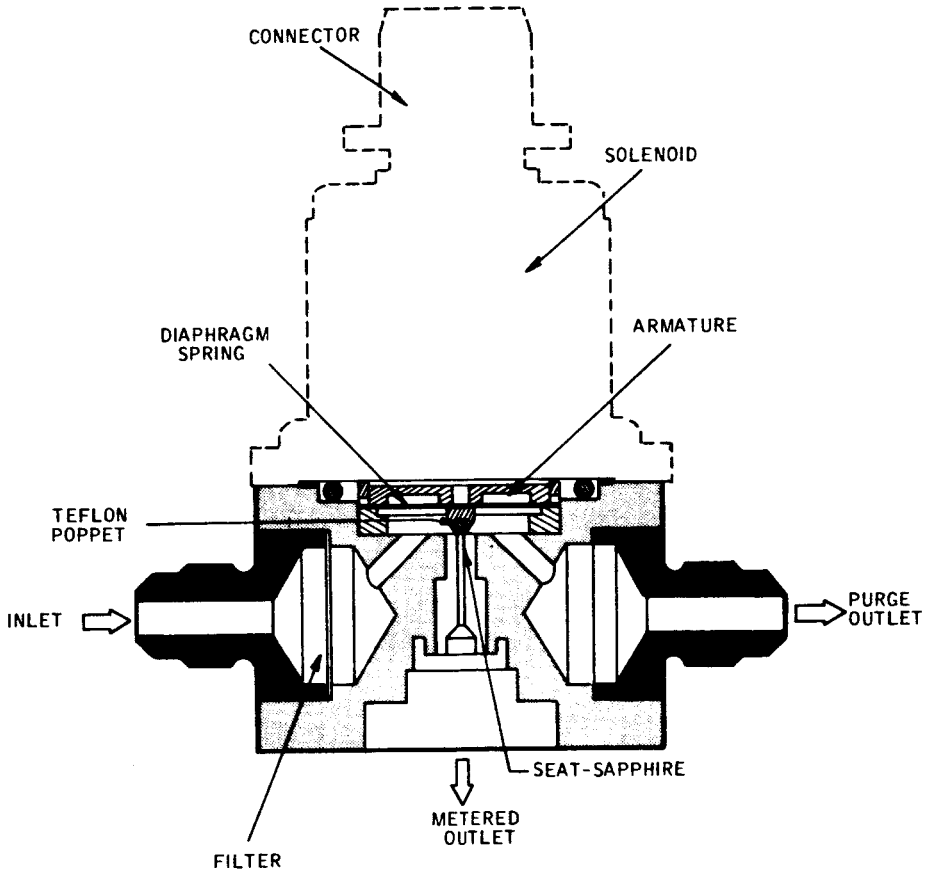


Figure 15 Pulsed Leak - Section View

Vacuum Manifold

The vacuum manifold is provided for the following purposes:

- For purging the various delivery channels of undelivered trace materials and nitrogen
- For purging the delivery manifold
- For bleeding off gases resulting from delivery pressure trimming in the event of marginal regulation by the pressure regulators at near-zero flow.

The vacuum manifold contains 10 solenoid valves connecting to the 10 delivery channels; three manually-operated valves each connecting to the delivery manifold, the vacuum pump, and a thermocouple vacuum gauge. Exhaust from the manifold is pumped by the vacuum pump to ambient through molecular and particulate traps. The manifold is fabricated of 3/4-inch stainless steel tubing with 1/2-inch and 1/4-inch connections to its components. It is leak tight to 1×10^{-9} std cc air per second.

Solenoid Valves -- The vacuum manifold is connected to each of the 10 delivery channels by solenoid valves which are operated by either of two push-button switches at the individual control stations on the instrument panel. These two switches are the "Vacuum" (Purge) and delivery pressure "Trim". The latter of these is used momentarily as a trim on the pulsed leak inlet pressure if needed.

These solenoid valves are constructed of stainless steel and use a teflon valve disc and body gasket. They are two-way, normally-closed valves, operating with 24-volts dc and rated for continuous operation. The valve orifice is 1/16-inch diameter. When closed, the valve leak rate is less than 10^{-7} cc std air per second.

Manually-Operated Valves -- These valves, connecting to the delivery manifold, nitrogen manifold, and vacuum pump are similar to the manually-operated shut-off valves previously described.

Vacuum Pump -- The vacuum pump used in the vacuum manifold is rated at 21 liters free air per minute and draws a vacuum to 0.1 micron. The vacuum pump may be equipped with a molecular trap at its inlet, and it contains a particulate trap at its outlet.

Thermocouple Vacuum Gauge -- The thermocouple vacuum gauge in the vacuum manifold reads out at the instrument panel of the circuit unit on a meter-movement scale having a 0 to 1000 micron range.

Nitrogen Manifold

The nitrogen manifold connects a pressure-regulated source of dry nitrogen for purging the 10 delivery channels, the delivery manifold, and the vacuum manifold. Dry nitrogen purging may be used together with vacuum purging and line heating to assure decontamination of delivery channels and delivery manifold when changing test materials.

The nitrogen manifold is fabricated from 1/4-inch stainless steel tubing. Connections to the delivery channels are each by solenoid valves and to the delivery and vacuum manifolds each by a manually-operated shut-off valve. The source of the dry nitrogen (99.7 percent purity) is a No. 4 cylinder whose outlet pressure is regulated to about 4-psig.

Delivery Channels

Liquids -- Each liquid delivery channel contains:

- 1-liter stainless steel storage cylinder and shut-off valve (manual)
- Replenishment valve and fittings
- Connections to vacuum and nitrogen manifolds
- Pulsed leak
- Heating mantle
- Temperature probe
- 0-30 psia pressure gauges (channels 1, 2, 3, and 4)
- 0-45 psia pressure gauges (channel 5)

These items have been described in other parts of this document. The pressure gauges, located on the instrument panel of the control unit, have 4 1/4-inch dial faces and are accurate to 1/2 of 1 percent of full scale.

Liquid materials are delivered to the delivery manifold in the vapor phase by the operation of the pulsed leaks.

Gases -- Each gas delivery channel contains:

- No. 4 storage cylinder and shut-off valve (manual)
- Pressure regulator
- Pressure-relief rupture disc

- Connections to vacuum and nitrogen manifolds
- Pulsed leak
- Pressure gauges, similar to liquid channels except the range if 0-45 psia

Gas materials are delivered to the delivery manifold through pressure regulators and the pulsed leaks. Data on the pressure regulators is given in Table 16.

Table 16. Pressure Regulator Data

Item	Corrosive Service	Non-Corrosive Service
Material	Ammonia Hydrogen Sulfide	Carbon Monoxide Hydrogen Methane
Delivery Rate	0 to 0.1 gram per hour	
Compatibility	Suitable for use with applicable trace materials vacuum purging, and 5 psig dry nitrogen purging.	
Leakage:		
Environment	Less than 10^{-6} std cc air per second	
Lock-up	Less than 10^{-7} std cc air per second	
Delivery Pressure Range	5-50 psig	
Regulation Accuracy	±1/2 psi over delivery pressure range	
Connections	1/4-inch NPT	
Filter	25-micron built-in (sintered metal)	

Pressure relief rupture discs are installed on the gas-phase delivery channels 6 through 10. These are set to burst if the delivery pressure to the pulsed leak should inadvertently reach 100 psi ± 5 percent. The burst disc is teflon-coated aluminum and the body is of stainless steel.

MATERIAL STORAGE AND DELIVERY

The control unit contains sufficient storage capacity so that channels can deliver continuously for at least 14 days at maximum delivery (3.36 gram moles). Table 17 shows the storage capacity of the 10 channels relative to the maximum 14-day consumption.

Storage capacity is predicated on maximum delivery rates over at least a two-week period. Stored quantity is indicated by storage pressure for gas-phase materials and by operating log records for liquid-phase materials.

The material storage enclosure is ventilated by a blower exhausting to the atmosphere. This ventilation prevents toxic or flammable concentrations from occurring in the enclosure in the event of material leakage within the unit and also removes waste heat from the heating mantles.

The control unit design is such as to accommodate any of the compounds listed in Table 11. Compounds whose vapor pressures are less than one atmosphere at room temperature are stored at an elevated temperature in liquid form and delivered as a vapor to the pulsed leaks at the corresponding vapor pressure. Compounds whose vapor pressures are greater than atmosphere at room temperature are delivered to the pulsed leaks through pressure regulators. The pulsed leaks are normally closed, but open for a brief interval when pulsed with a d-c voltage. At each pulse, 1×10^{-6} gram mole of the compound is metered. The metered quantity is proportional to pulse frequency.

Gas-Phase Materials

Trace materials having relatively high vapor pressures are stored and delivered through pressure regulators from No. 4 commercial gas cylinders having appropriate

Table 17 Relation of Trace Material Storage Capacity to Maximum Consumption

Trace Material	Weight of 3.36 Gram moles		Volume (ml) 3.36 gram-moles (liquid at 20 °C)	No. 4 Cylinder		Storage Margin	
	Grams	Lbs.		Pressure (psig)	Capacity (lbs)	One-liter Cylinder	No. 4 Cylinder
Liquids							
Acetone	195	0.43	246			4 X	
Benzene	262	0.58	298			3.4X	
Freon-114	575	1.27	399 (30°C)			2.5X	
Isopropyl Alcohol	202	0.45	255			3.9X	
n-Propyl Acetate	343	0.76	387			2.6X	
Gases							
Ammonia	57	0.13		114	2		15 X
Carbon Monoxide	94	0.21		1500	0.65		3.1X
Hydrogen	7	0.015		2000	0.05		3.3X
Hydrogen Sulfide	114	0.25		250	3		12 X
Methane	54	0.12		2000	0.54		4.5X

color marking and Compressed Gas Association (CGA) connection number. Data pertinent to ordering and use is given in Table 18.

Liquid-Phase Materials

Trace materials having relatively low vapor pressures are stored and delivered from one-liter stainless steel cylinders having an ICC pressure rating of 450 psig. These materials are in the liquid phase in the cylinders and are temperature controlled to provide saturated or slightly superheated vapor to the pulsed leaks. Data pertinent to the delivery of these materials is given in Table 19.

ELECTRICAL CONTROL

Electrical Distribution System

A schematic diagram of the electrical distribution system is shown in Figure 16. Electrical service to the control unit is three-wire, 230-volt single-phase, alternating current with a four-pin service connection. All circuits within the unit operate with 110-volts ac from the two legs of the three-wire supply. A simplified block diagram of the wiring system is shown in Figure 17.

The unit contains 10 circuit breakers which are operated manually with push-buttons and which are thermally (bi-metal) open upon overload. Individual components are energized with push-button switches equipped with pilot lights. A listing of circuit breakers and switch functions is given in Tables 20 and 21, respectively.

Table 18 Gas Data and Storage Conditions

Gas	Grade	Molecular Weight	Minimum Purity (percent)	Cylinder Pressure (psig)	Approximate Cylinder Contents (lbs)	Delivery Pressure Range (psig)	Cylinder Size and Color	CGA Connec-tion	Honeywell Gas and Cylinder Drawing No.	Honeywell Regulator Drawing No.
Ammonia	Anhydrous	17	99.99	114	2	5-50	No. 4 Black	240	SK 87564	SK 87560
Carbon Monoxide	Chemical Purity	28	99.5	1500	1/2	5-50	No. 4 Blue-White-Red	350	SK 87566	SK 87558
Hydrogen	Prepurified	2	99.95	2000	0.05	5-50	No. 4 Gray-Yellow	350	SK 87568	SK 87558
Hydrogen Sulfide	Chemical Purity	34	99.5	252	3	5-50	No. 4 Blue-Gray	330	SK 87563	SK 87560
Methane	Chemical Purity	16	99.0	2000	1/2	5-50	No. 4 Blue-Green-Red	350	SK 87565	SK 87558
Nitrogen (Purge)	Extra Dry	28	99.7	2000	1	5-50	No. 4 Red-Pink	580	SK 87569	SK 87559

*Data Source: Matheson 1963 Catalog for Compressed Gases and Fluid Controls

Table 19. Liquid-Phase Materials Data

Vapor	Molecular Weight	Temperature/Vapor Pressure					
		1 Atm.		1-1/2 Atm.		2 Atm.	
		°F	°C	°F	°C	°F	°C
Acetone	58	135	57	158	70	174	79
Benzene	78	176	80	201	94	219	104
Freon-114*	171	38	3.5	57	14	73	23
Isopropyl Alcohol	50	181	83	205	96	214	101
n-Propyl Acetate	102	216	102	240	116	260	127

*Because of the relatively high vapor pressure of Freon-114, it is delivered at room temperature or slightly elevated temperature. Some vapor pressures listed in the Matheson Gas Data Book for Freon-114 are:

Temperature		Pressure	
°F	°C	mm Hg Abs.	Atm.
70	21	1400	1.84
80	27	1680	2.21
90	32	2020	2.66
100	38	2380	3.13

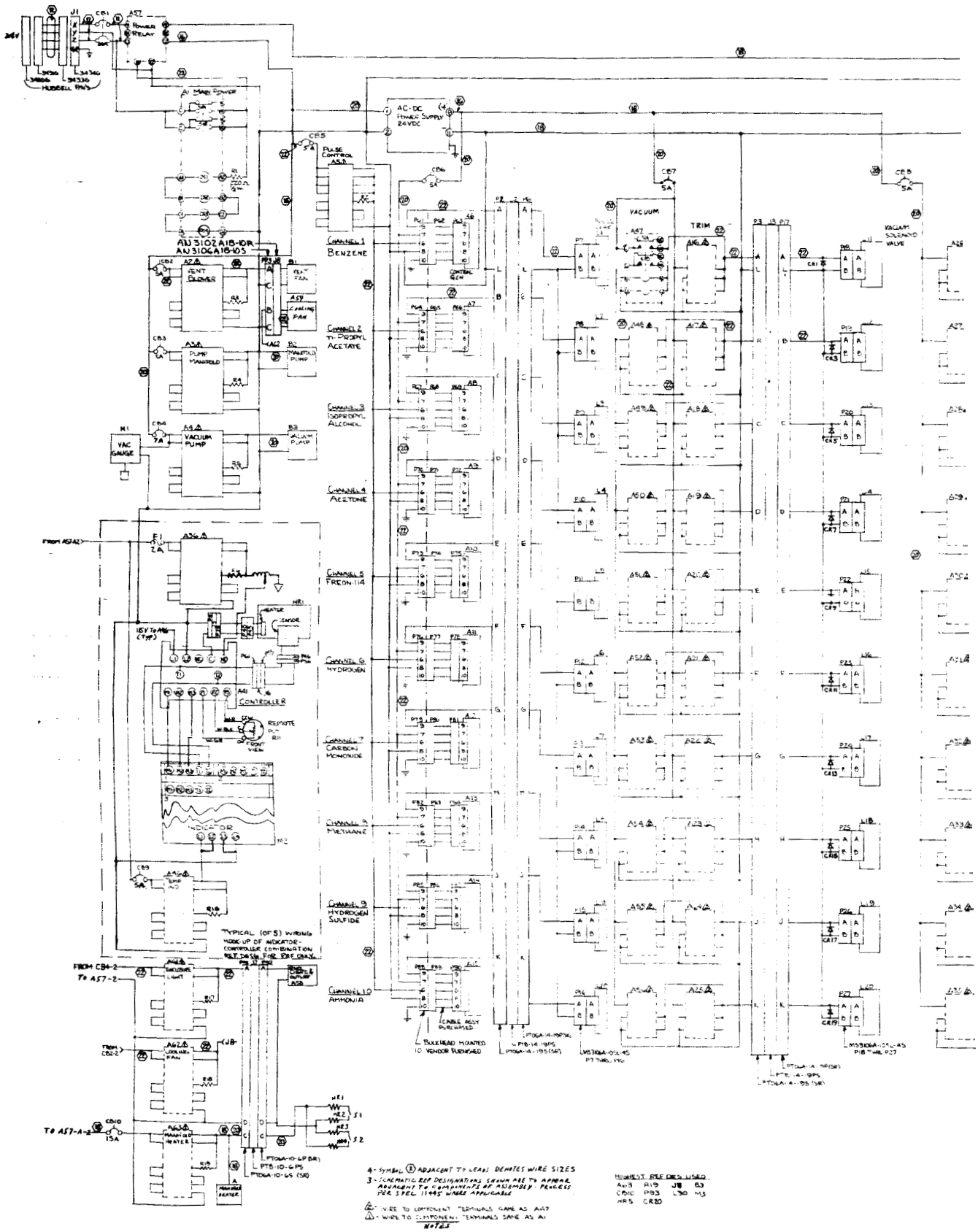
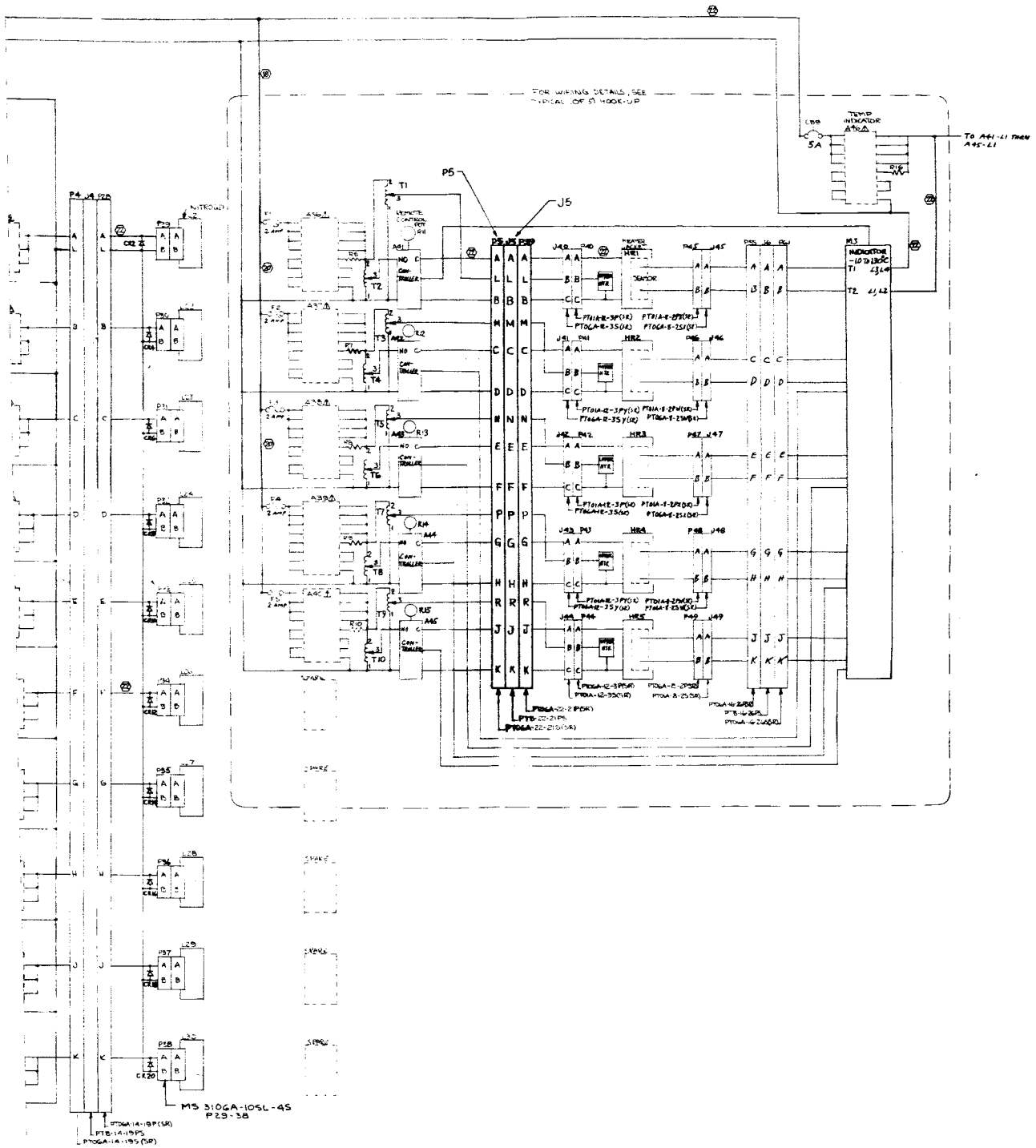


Figure 16 Electrical Distrib



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ution System Schematic

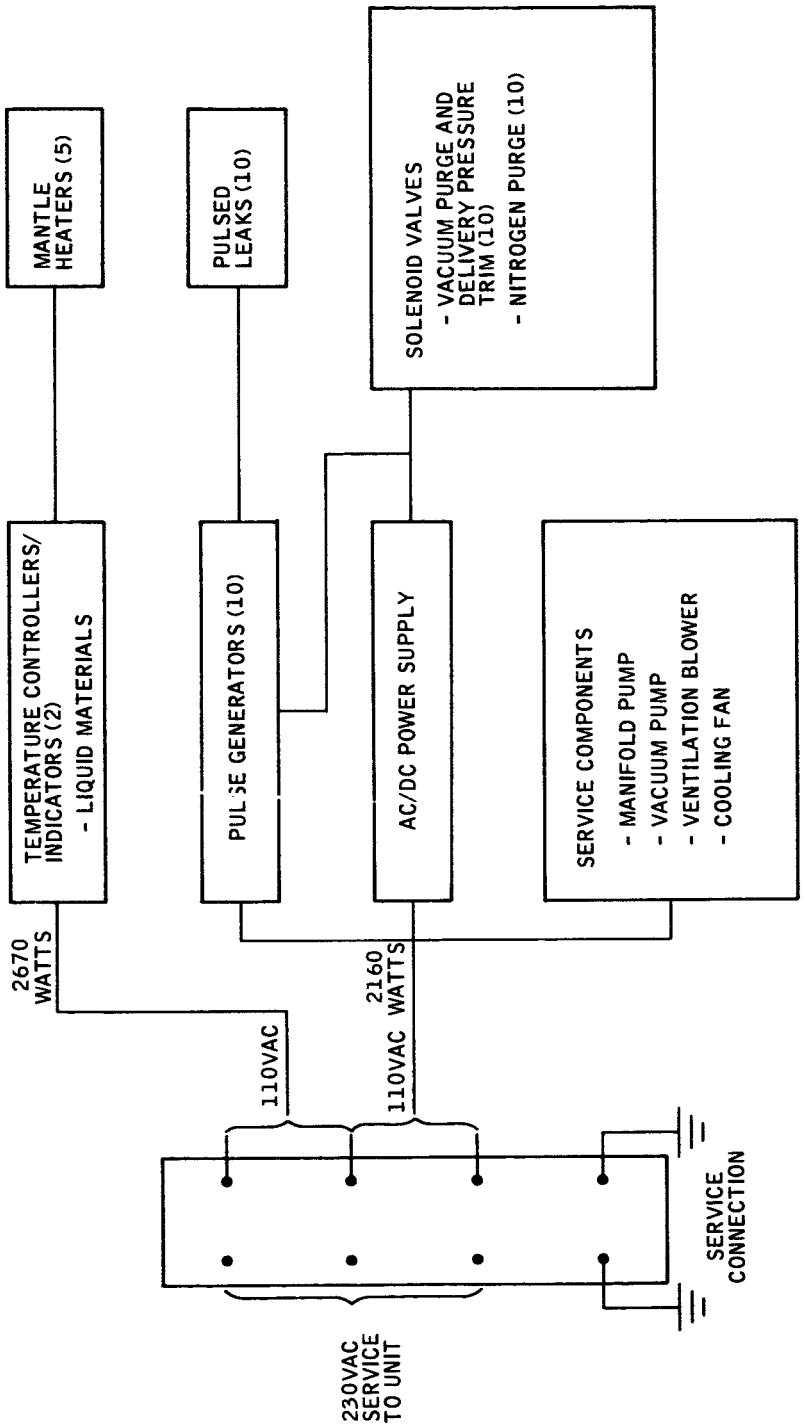


Figure 17. Electrical Distribution System Block Diagram

Table 20. Control Unit Circuit Breaker Functions and Fuse Ratings

Circuit Breaker Number*	Function	Fuse Rating** (amperes)
CB-1	Main Power	30
CB-2	Ventilation Blower	5
CB-3	Manifold Pump	5
CB-4	Vacuum Pump	7
CB-5	Pulse Generators, ac (10)	5
CB-6	Pulse Generators, dc (10)	5
CB-7	Solenoid Valves, Vacuum Purge and Delivery Pressure Trim (10)	5
CB-8	Solenoid Valves, Nitrogen Purge (10)	5
CB-9	Temperature Indicators (2)	5
CB-10	Manifold Heater	15

*See Figure 16

**In addition to the circuit breaker fuses each of the heating mantle temperature control circuits contains a 2-ampere fuse (F1 - F5).

Table 21. Control Unit Switch Functions

Switch Identification*	Function
A-1	Main Power, Vacuum Gauge
A-2	Ventilation Blower
A-3	Manifold Pump
A-4	Vacuum Pump
A-5	Pulse Generators, ac (10)
A-6 through A-15	Individual Pulse Generators, ac and dc
A-16 through A-25	Solenoid Valves, Delivery Pressure Trim
A-26 through A-35	Solenoid Valves, Nitrogen Purge
A-36 through A-40	Temperature Controllers and Mantle Heaters
A-41 through A-45	Temperature Control Set-Point Adjust
A-46	Temperature Indicators (2)
A-47 through A-56	Solenoid Valves, Vacuum Purge
A-57	Main Power Relay
A-59	Cooling Fan
A-62	Cooling Fan
A-63	Manifold Heater

*See Figure 16

Pulse Generators

The control unit contains 10 solid-state pulse generators which operate the pulsed leaks at the prescribed frequency and pulse width (dwell) to obtain required trace material delivery. The pulse generator has manual coarse and fine adjustments to provide a range of pulse rates from 1 to 10,000 per hour (see Figure 10). A manually-set dwell adjustment permits the pulse duration to be changed from 25 to 250 milliseconds. The pulse output itself is a square-wave voltage of 24-volts amplitude. Coincident with the pulse delivery, a panel light glows as a visual indicator. Panel-mounted test jacks provide for electrical signalling of pulse delivery. A block diagram of the pulse generator is shown in Figure 18. The circuit modifications made to the unit are shown in Figures 19 and 20.

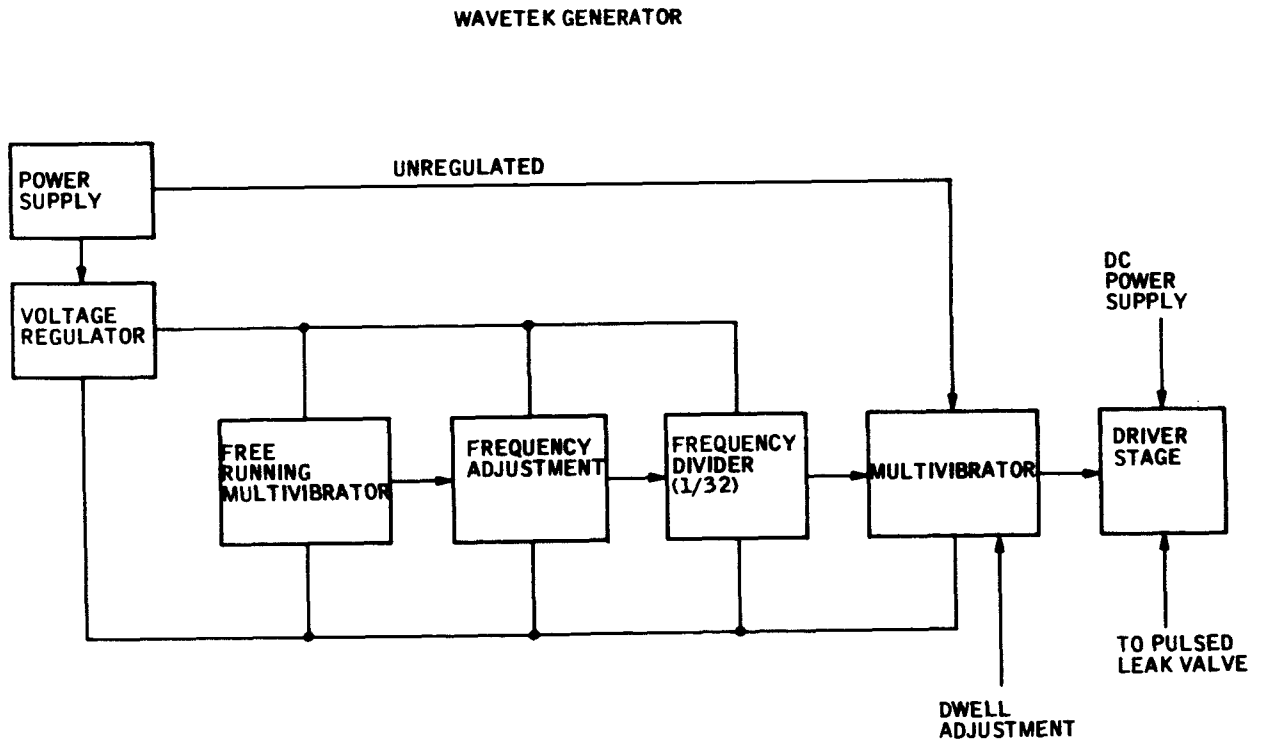


Figure 18. Pulse Generator Block Diagram

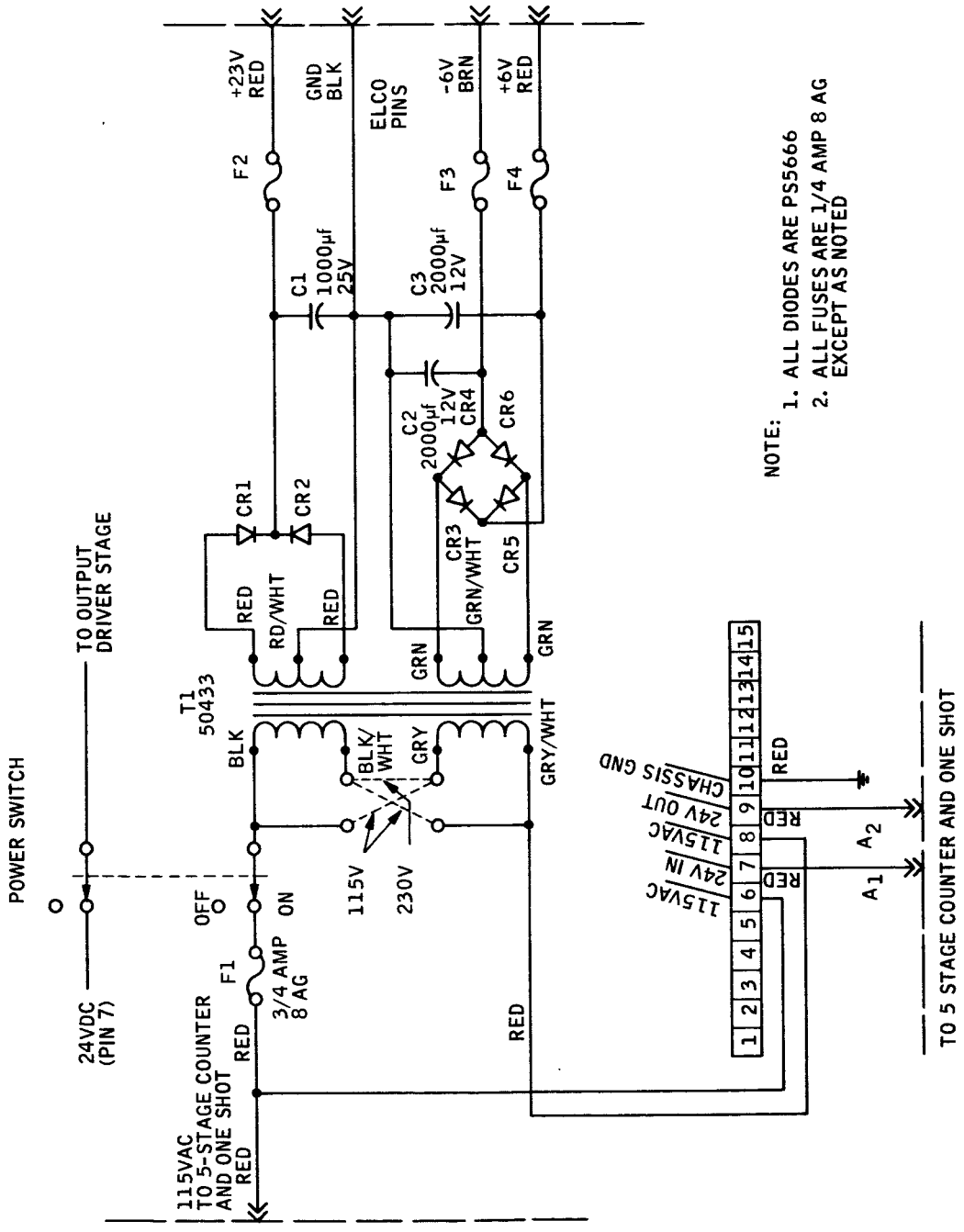


Figure 19. Wavetek Schematic - Power Supply

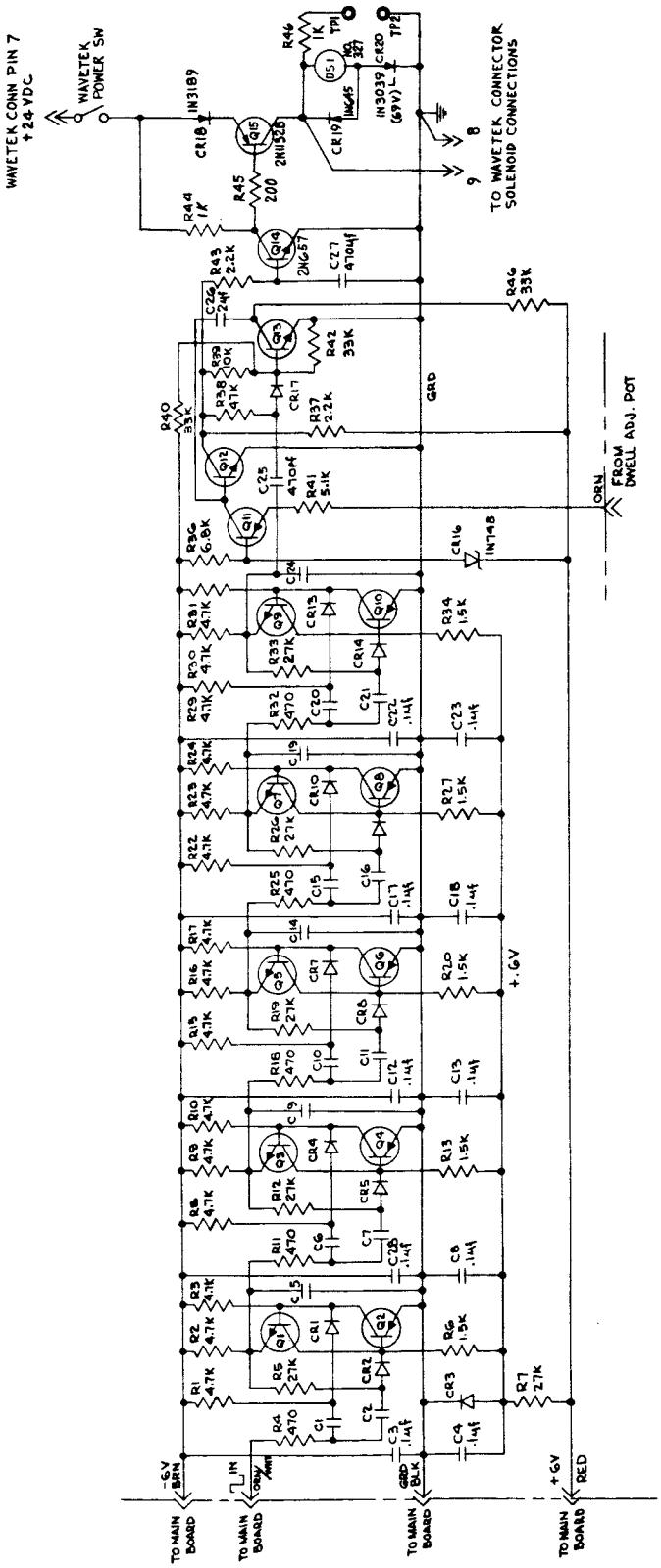


Figure 20. Wavetek Schematic - Counter/Driver Stages

The pulse generator contains square-wave oscillator circuitry with a five-position (off, X1, X10, X100, X1000) frequency range switch. The oscillator frequency corresponding to a frequency dial (fine) setting of "10" and a multiplier switch (coarse) setting of "X1000" is 88.89 cps (or 32,000 cph). This frequency becomes 0.008889 cps with a fine setting of "1" and a coarse setting of "1". The fine setting dial has coarse graduations from one through 10, each with 10 intermediate fine graduations. The coarse and fine controls provide 10,000 discrete dial markings and infinitely variable frequency adjustment.

The oscillator feeds into a five-stage binary counter, each stage of which successively divides the input frequency by two. The output frequency of the counter is then 1/2 x 1/2 x 1/2 x 1/2 x 1/2 / 1/32 of the oscillator frequency, ranging from 1 to 10,000 pulses per hour.

The output of the binary counter feeds into flip-flop amplifying circuits which in turn operate a 24-volt transistor driver. This driver then operates the solenoid of the pulsed leak causing it to pulse at the prescribed frequency. Pulse duration is dependent upon the rate of operation of the flip-flop circuit and is governed by the variable resistance of the dwell adjust potentiometer.

AC-DC Power Supply

The control unit contains an ac-dc power supply for operating the pulsed leaks and the solenoid valves for vacuum and nitrogen purging. Data for the power supply are given in Table 22.

Table 22. AC-DC Power Supply Data

Item	Design Data
Input Voltage	105 to 125 volts, single phase
Input Frequency	55 to 65 cycles per second
Output Voltage (coarse and fine adjust	10 to 36 volts, dc
Output Current Rating	0 to 10 amperes
Static Regulation	±0.01 percent from no load to half
Load	±0.01 percent from no load to half load and half load to full load
Line	±0.01 percent with ±10 percent input line change
Ripple	1 millivolt rms, maximum
Transient Response	50 microseconds for no load to full load stepping
Overload Protection	Variable current limiting from 5 to 105 percent of rating by front panel adjustment
Meters (front panel)	Voltmeter accurate within 2 percent full scale Ammeter accurate within 2 percent full scale

TEMPERATURE CONTROL

The inlet pressure of each liquid-phase pulsed leak is maintained at a fixed level between 1 and 1 1/2 atmospheres* by controlling the temperature of the 1-liter storage cylinder. A heating mantle envelopes the cylinder, connection

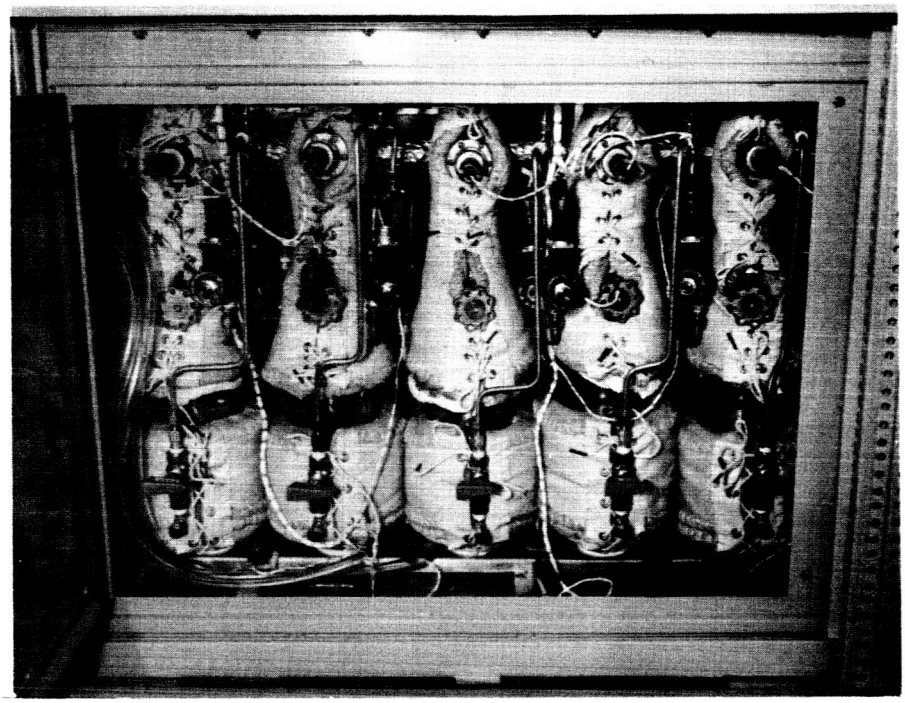
* Except for Freon-114 which is controlled at ambient temperature.

to the pulsed leak, and the pulsed leak, as shown in Figure 21. This mantle contains two heating elements mounted in fiber glass insulation. One heating element surrounds the lower half of the storage cylinder and is cycled by a temperature controller. The upper element surrounds the pulsed leak and its connection to the cylinder. It is continuously energized when the delivery channel is in operation by a variable transformer adjusted permanently to provide a heating level some degrees higher than that of the control point of the lower element (see Figure 11).

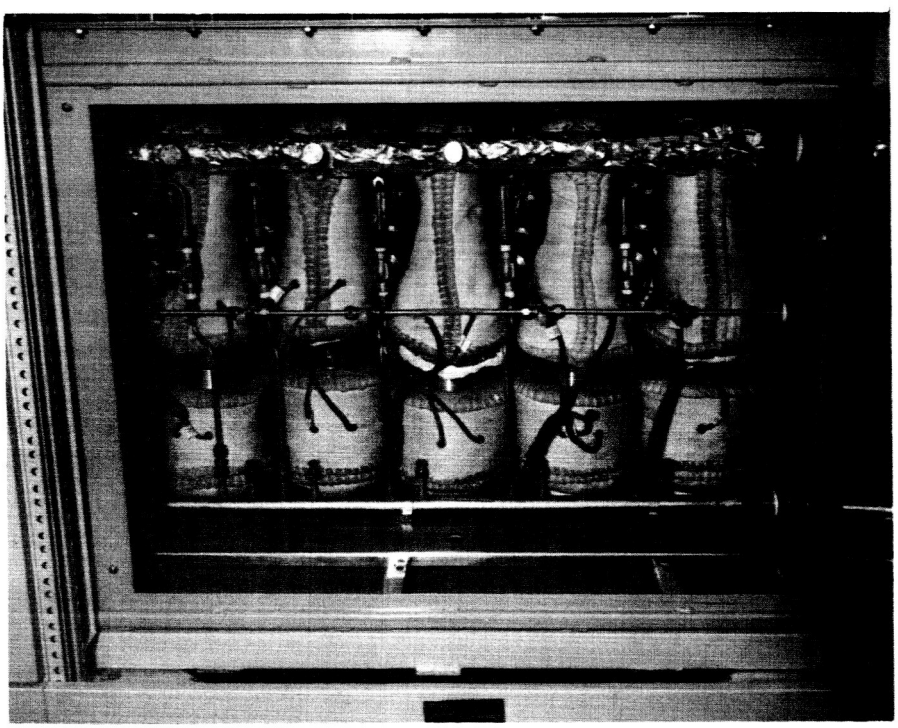
The temperature control scheme uses two multi-point indicators and five controllers. The multi-point indicators together can monitor up to 10 stations and have five additional controllers should greater capacity desired of the control unit in the future. The six-point indicator covers a range of -10°C to 130°C and monitors channels 1, 2, 3, 4, and 5. The four-point indicator covers a range of 100°C to 300°C and may be used at temperatures higher than 130°C (see Figure 9).

The temperature of the stored liquids is sensed by matched thermistor probes enclosed in a stainless-steel well installed in the lower part of each storage cylinder. Each thermistor operates both controller and indicator circuits. Each of the controllers may be set to control over a range corresponding to those of the indicators by adjusting their remotely located potentiometers. The five potentiometers are located on a hinged panel located to the left of the temperature indicator positions on the instrument panel, as shown in Figure 11. The selector switch dials on the temperature indicator identify the point being monitored. A pilot light indicates if the indicator is powered. The actual temperature of the liquid being monitored is normally shown by the indicator meter, but when the push button to the right of the selector is pressed, the meter shows the set point temperature. The meter reading should always be used in setting the control point rather than the coarse indication of the remote potentiometer scale.

Indicator and controller data are given in Table 23.



Front View



Rear View

Figure 21. Heating Mantles on Liquid Channels

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Table 23. Temperature Indicator and Controller Data

Item	Design Data
Indicators	
Temperature Range	10°C to 130°C and 100°C to 300°C
Input Voltage	115 volts ac, single-phase, ±10% Connections are to terminals L1 and L2 (common) and L3 and L4 (common)
Input Frequency	50-60 cps
Temperature Ranges	-10°C to 130°C 100°C to 300°C
Accuracy	Average error ±0.7% of scale range
Ambient Temperature Range	0° to 125°F
Power	10 watts, maximum
Controls	Selector switch: six-point and four-point Set point temperature: Push Button
Controllers	
Input Voltage	115 volts ac, single-phase, ±10%
Input Frequency	50-60 cps
Power	10 watts maximum (exclusive of external load)
Ambient Temperature Range	0°F to 125°F
Control Mode	Proportional
Contract Arrangement	SPDT
Control Contact Rating	10A-115 volts, ac resistive
Differential (mid-range)	~0.5°F at nominal line voltage and ambient temperature
Set-Point Stability (mid-range)	0.2°F at ambient temperature
Temperature Adjustment	Remote potentiometer

SECTION VI
TESTS AND CALIBRATION

INTRODUCTION

A series of tests were conducted to determine operating characteristics and performance capabilities of the Trace Gas Simulator. The tests are first described, and the results presented in the subsequent sections.

The primary test was a 72-hour run during which the pulsing rates of three channels (benzene, n-propyl acetate and acetone) were changed periodically. The delivery per pulse of each channel was determined before and after the 72-hour test by the pressure rise technique. The gas stream was monitored by gas chromatographic analysis.

Several additional tests were subsequently performed. Initially, it had been intended to run two 72-hour tests: the first to check out the test system and the second to check out the Trace Gas Simulator. As time requirements prevented a prior test system check-out, however, a 4-hour test was run to check the test system. Troubles with the n-propyl acetate channel in the 4-hour test led to a series of extended pressure rise tests.

The pressure rise technique to determine channel delivery per pulse involves the use of the volume of the delivery manifold of the Simulator. The determination of this volume is given in the final portion (Miscellaneous Measurements) of this section.

The calibration of the chromatograph for the three materials delivered in the 72-hour test is also given in the final portion.

72-HOUR TEST DESCRIPTION

Apparatus

The test system is shown in Figure 22. It consists of two sections: the flow section, and the analysis section.

- Flow section. The gas stream from the Simulator passes through the 6-liter bottle, two cold traps, reheater bath and flow meter and back to the Simulator. Thermocouples were used to measure the gas stream temperatures downstream of the traps and the reheater. The pressure was monitored upstream of the flowmeter. (The delivery manifold pressure gauge on the Simulator was also observed.) The first cold trap was a 15-inch length of 3/8" copper tubing; the second cold trap was a large glass cold-finger condenser. The reheater was a 36-inch length of 1/4-inch copper tubing in a water bath.
- Analysis section. The gas stream was periodically sampled downstream of the 6-liter bottle, raised to slightly above ambient pressure by an external diaphragm pump, and returned to the flow section upstream of the 6-liter bottle. An analysis was run every 30 minutes.

Start-Up Procedure

The heaters of the three channels were turned on. Then the deliveries of the channels were checked via the pressure rise technique after the channels reached operating pressures. The dwells were adjusted to attain the desired delivery. A mathematical error resulted in adjusting dwells to give 0.73 micromoles per pulse rather than 1 micromole per pulse as intended. The manifold was isolated from the flow section of the test apparatus by closing the inlet and outlet valves

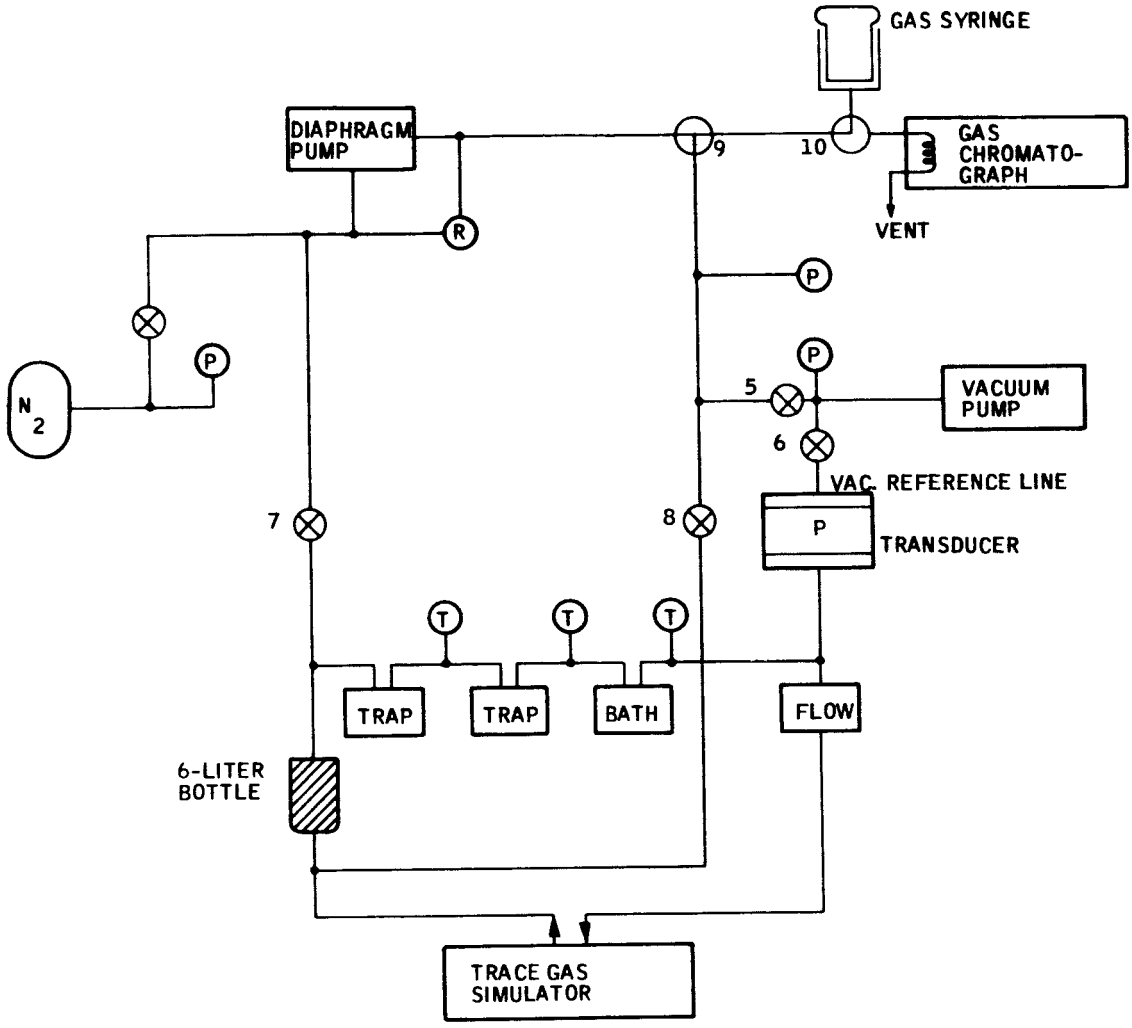


Figure 22. Flow System - Analysis System

on the Simulator. The pressure rise was measured with a manometer connected to the gas sampler of the Simulator.

The flow and analysis sections, including the delivery manifold of the Simulator, were vacuum purged three times, adding 5 psia of nitrogen between purges. Finally, the pressure in the flow and analysis sections was established at 5 psia with nitrogen.

Programmed Delivery

For the first part of the 72-hour test, each of the three channels was pulsed separately. The delivered materials were not trapped, so delivery rates were low enough to avoid condensation in the system.

After separate operation of the three channels, the cold traps were immersed in alcohol-dry ice baths. Larger pulsing rates were used and the channels were operated concurrently. The pulsing rate program is given in Table 24.

The gas stream was analyzed every thirty minutes, each analysis removing about two percent of the flow stream. When the delivery manifold pressure decreased to 4 psia, nitrogen was added to return the manifold pressure to 5 psia.

The flow section was isolated from the analysis section, except during analysis, by closing valves 7 and 8 (see Figure22).

Analysis Procedure (Refer to Figure 22)

Valve 10 was turned to connect the gas syringe to the analysis section; valves 7 and 8 were opened. The external diaphragm pump was turned on to circulate the flow stream through the analysis section. After two minutes, valve 8 was closed. The external pump subsequently increased the pressure between the pump and valve 8

Table 24. 72-Hour Test Program

Time	Benzene	Pulses Per Hour		Remarks (See Below)
		n-Propyl Acetate	Acetone	
12/5/65 1400	0	6	0	
1916		24		
2016		60		
2046		120		
2100	6			
2101		0		
12/6/65 0030	0		30	
0200		120	0	
0300	6		12	(1)
1000				(2)
1530	30			
1830	90	360	36	
12/9/65 1000			0	
1300	0			
1400	360	0	360	
1500	0	600	0	
1600	120		60	
1700	0	120	0	
1800	60		30	
1900	90	240	40	
2000	120	60		
2100	150	30	50	
2200	180	15	60	
2300	210		50	
2400	240		40	
12/8/65 0100	60		6	
0430	120	30	12	
0900	6	6	45	
1230			90	
1300			180	(3)
1500	0	0	0	

(1) Trapping begun with alcohol-dry-ice.

(2) Wavetek pulsing unit on Channel 2 (n-propyl acetate) replaced.

(3) Trapping with liquid nitrogen.

above ambient, raising the plunger in the gas syringe. (The regulator across the external pump was set to limit this pressure to 5 psi above ambient). When the plunger had risen to 60 cc, valve 10 was turned to vent the syringe to ambient through the gas injector of the chromatograph.

Valve 8 was opened and the external pump was turned off. When the syringe plunger reached 20 cc, so that about 30 cc of sample had purged the gas injector lines, a 1 cc sample was injected into the chromatograph. Valve 10 was turned to isolate the syringe, and valves 7 and 8 were closed.

Trapping Procedure

Alcohol-dry ice baths were used for trapping during most of the test run. These were later replaced with liquid nitrogen baths.

At the end of the test, the two traps were isolated by clamps on the tubing that connects the traps to the flow system. The nitrogen (gas) supply was replaced with helium, and the reheater coil was replaced with a third, small, weighted glass trap. Except for the first and second traps, the flow system was evacuated and backfilled with helium. Liquid nitrogen was added to the third trap. The first and second traps were then opened to the system, and pressure in the system increased to above-ambient with helium. The flow system was opened at the inlet to the Simulator venting helium to ambient, and the liquid nitrogen was removed from the first and second traps. The flow of helium transferred the trapped material to the third trap. The amount of material trapped was determined by weighing, while the relative proportions were determined by gas chromatography.

ADDITIONAL TESTS

Four-Hour Test

The first of the additional tests was a four-hour test, run at high pulse rates.

It was intended to check-out the trapping method. An unexpected indication of trouble resulted with the n-propyl acetate channel. The trouble was subsequently attributed to a fault in the hand shut-off valve of the n-propyl acetate supply.

The flow system for the four-hour test was the same as the flow section used in the 72-hour test given in Figure 22, except that both traps were glass and the second trap was weighed before the test.

The deliveries of the three channels were determined by the pressure rise technique - before and after the test. The recovered material was weighed, then analyzed with a gas chromatograph.

Extended Pressure-Rise Measurements

The usual pressure-rise measurement involved a delivery of 300 pulses at a rate of 3600 pulses per hour. Because of the "low" recovery in the four-hour test, and because of varying delivery of the n-propyl acetate channel as shown by five minute measurements, a series of extended pressure-rise measurements were run. The pulse rate was the usual rate, but the time of the run was increased to fifteen minutes and the pressure rise noted each 100 seconds. These tests were run on the benzene, n-propyl acetate, iso-propyl alcohol and acetone channels. The dwell setting for n-propyl acetate was reduced to prevent saturation of the delivery manifold during the test.

TEST RESULTS

72-Hour Test

Monitoring Analyses -- The n-propyl acetate concentrations from the monitoring analyses are shown in Figure 23. The concentration varies as expected with only one region of odd behavior. At 9:50 A.M. (12/6/65), the time between pulses for channel 2 as indicated by the light on the pulsing unit was observed to be much greater than the programmed thirty seconds (120 pulses per hour).

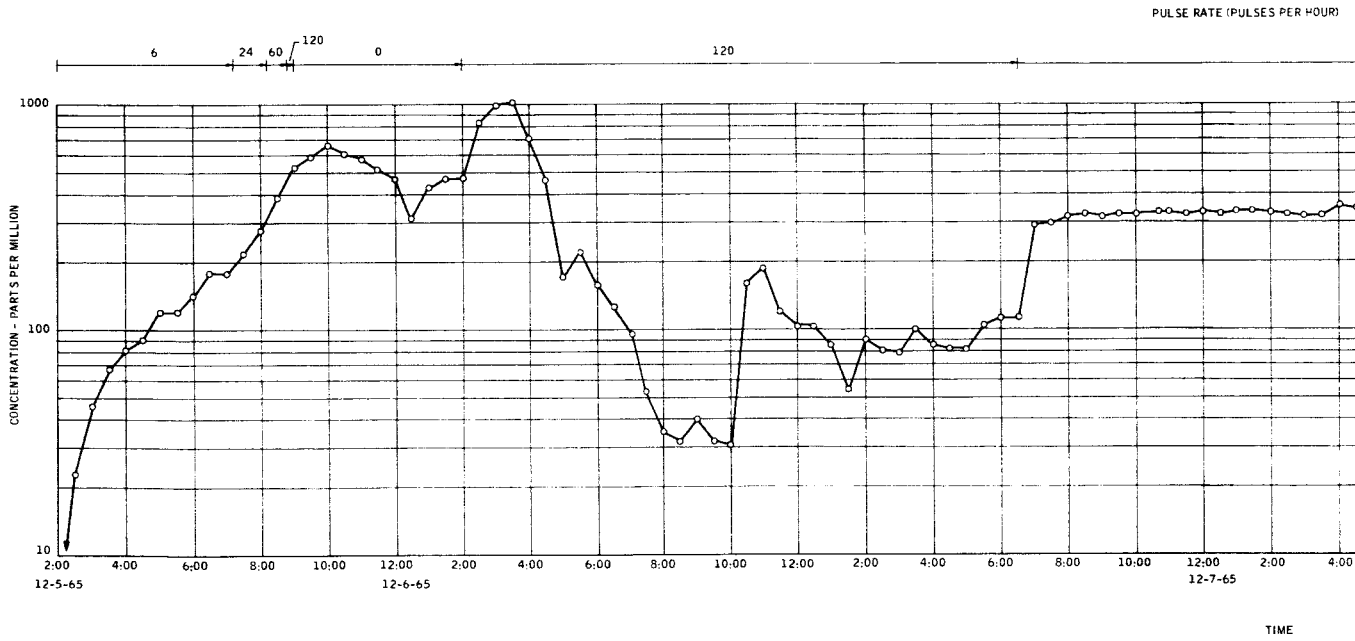
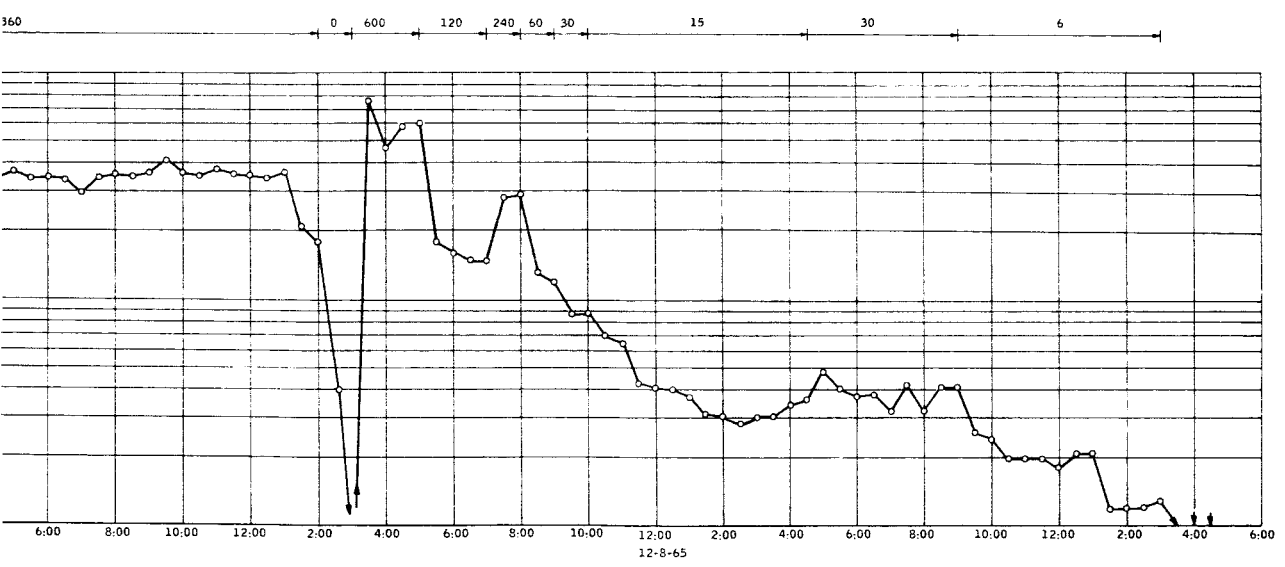


Figure 23. Monitor
n-Propy



ing Gas Analyses
l Acetate

This behavior was not apparent from the monitoring analyses since the decline in concentration from 3:30 A.M. (12/6/65) was attributed to the trapping begun at 3:00 A.M. The pulsing unit was replaced at 10:00 A.M. The subsequent increase in concentration indicates that the original pulsing unit was pulsing at an estimated 15 pulses per hour from 7:00 A.M. to 10:00 A.M.

Recovered Material -- The weight of the recovered material and the expected weight are given in Table 25. The sampling loss was calculated as follows: Each sample removed about 60 cc of the gas mixture at about STP, so that each sample removed 0.0027 total moles. The removal of each component is then given by:

$$\text{Loss in } \mu \text{ moles} = \Sigma\,(0.0027)\,(\text{concentration in ppm}).$$

The mole ratio of the recovered material was determined by gas chromatographic analysis. The chromatograph was calibrated with a standard solution prepared with the expected mole ratios.

The delivery of the n-propyl acetate channel was measured to be 0.73 μ mole per pulse at a dwell of 126 milliseconds before and after the 72-hour test. Subsequently, it was found that this "low" delivery (since a dwell of 126 milliseconds should deliver 1 μ mole per pulse) was due to a constriction in the hand shut-off valve of the n-propyl acetate supply. The data in Table 25 agrees with a delivery of 0.73 μ mole per pulse during the test.

In Table 25 the total number of pulses for n-propyl acetate is based on a pulse rate of 15 pulses per hour from 7:00 A.M. to 10:00 A.M. on December 6 rather than the programmed rate of 150 pulses per hour given in Table 24.

The agreement between expected and found values given in Table 25 is considered satisfactory.

Table 25. 72-Hour Test Material Balance

Material	Benzene	n-Propyl Acetate	Acetone
Dwell (m. sec)	68	126	60
Delivery (μ moles/pulse)	0.73	0.73	0.72
Total Pulses	4167	10837 (1)	2156
Total Moles	3.04×10^{-3}	7.94×10^{-3}	1.57×10^{-3}
Total Weight (grams)	0.235	0.804	0.091
Sampling Loss (grams)	0.005	0.010	0.014
Net Weight Expected (grams)	0.230	0.794 1.101	0.077
Recovered (grams)		1.115	
Mole Ratio Expected (2)	1.00	2.63	.44
Mole Ratio Found (2)	1.00	2.7	.52

Note:
(1) Pulse rate taken to be 15 pulses per hour from 7:00 A.M. to 10:00 A.M. on December 6.
(2) Mole ratio relative to benzene.

Four-Hour Test

The test conditions and results for the four-hour test are given in Table 26. The data shows adequate delivery for the benzene and acetone channels and insufficient delivery for the n-propyl acetate channel.

The average delivery for the n-propyl acetate channel, based on the gas chromatograph analysis, was about 0.08 micromoles per pulse. The information obtained later, (discussed under the extended pressure rise measurements), verifies this low delivery. Thus, the four-hour test adequately checkedout the trapping method and analysis used in the 72-hour test.

Extended Pressure Rise Measurements

Figures 24 and 25 contain the data for extended pressure rise measurements. The curves for benzene, iso-propyl alcohol and acetone in Figure 24 show constant delivery with time. The n-propyl acetate curves 1, 2, and 3 of Figure 25 are sequential runs between which the manifold pressure was reduced to 10 microns of mercury. These curves show a steady decrease in the delivery with time.

A fifteen minute run, made after the channel had remained overnight at operating temperature gave data closely matching curve 1. This gave reason to suspect that the supply to the pulsed leak was faulty. The hand shut-off valve on the n-propyl acetate was removed. Inspection revealed that this valve did not open properly. The valve was therefore replaced.

The satisfactory delivery of n-propyl acetate afterwards is shown by curve 4 of Figure 25. Curve 4 is the average of three fifteen minute tests. The delivery of curve 4 was 0.67 μ moles per pulse with a dwell of 83 milliseconds.

Table 26. Four-Hour Test

Material	Benzene	n-Propyl Acetate	Acetone
Dwell (m. sec)	72	112	65
Delivery (μ moles/pulse)	0.80	(0.73) (1)	0.73
Pulse Rate Program	3600 per hour for 2.58 hours 1000 per hour for 1.50 hours		
Total Pulses	10,788 Each Channel		
Total Moles	8.30×10^{-3}	(7.87×10^{-3}) (2)	7.87×10^{-3}
Total Weight Expected (grams)	0.648	(0.08) (3) 1.185 (3)	0.457
Recovered		1.116	
Mole Ratio Expected (3)	1.00	0.91	0.91
Mole Ratio Found (3)	1.00	0.1	0.85

Note: (1) Delivery of n-propyl acetate at a dwell of 112 milliseconds was found to be 0.73 μ moles per pulse before the test and 0.46 μ moles per pulse three hours after the test.

(2) Delivery of 7.87×10^{-3} moles of n-propyl acetate obviously not attained.

(3) Based on the mole ratio of the recovered material, about 0.08 grams of n-propyl acetate were delivered, for an expected total weight of about 1.18 grams.

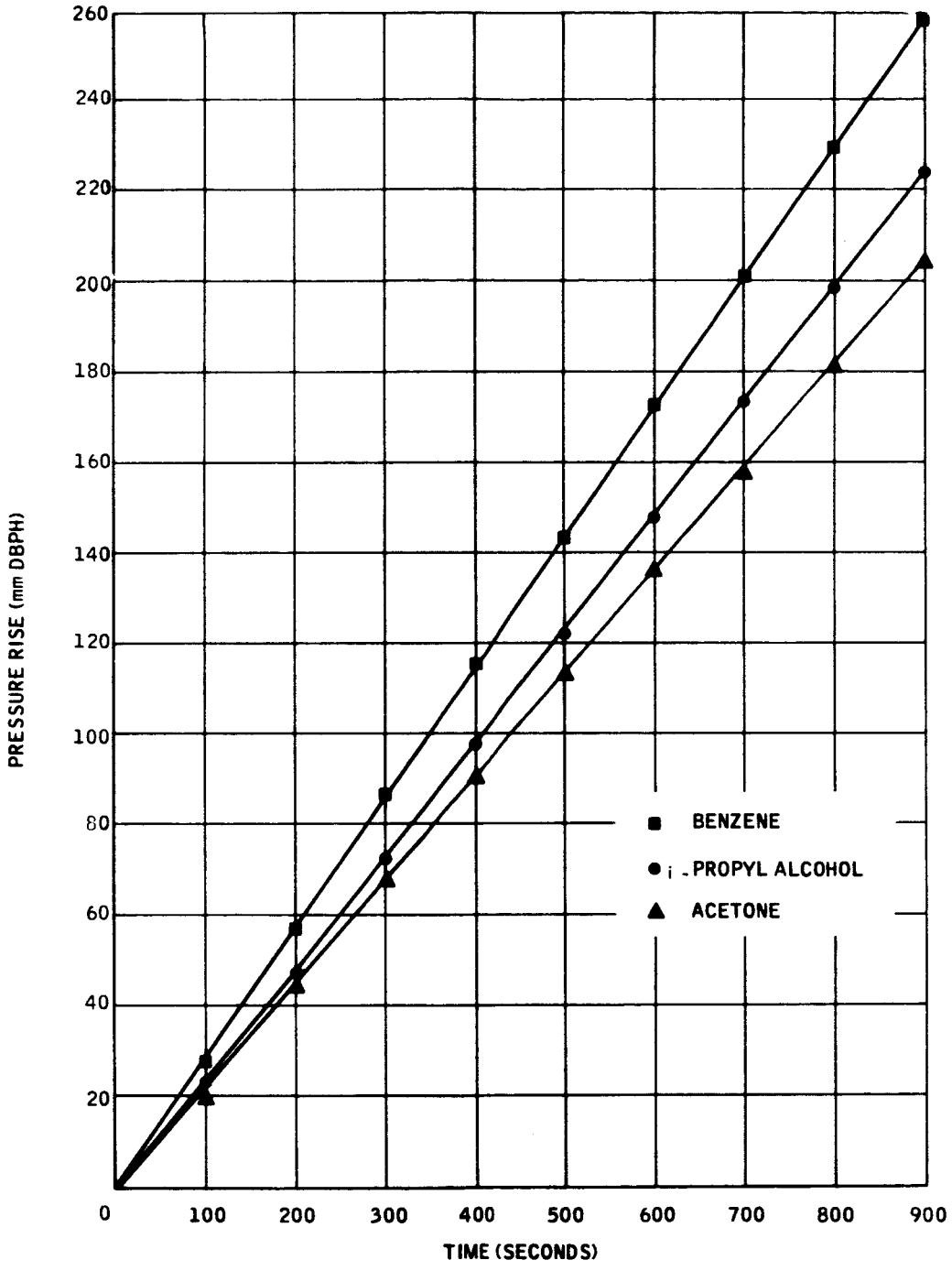


Figure 24. Extended Pressure Rise Tests Benzene, i-Propyl Alcohol and Acetone

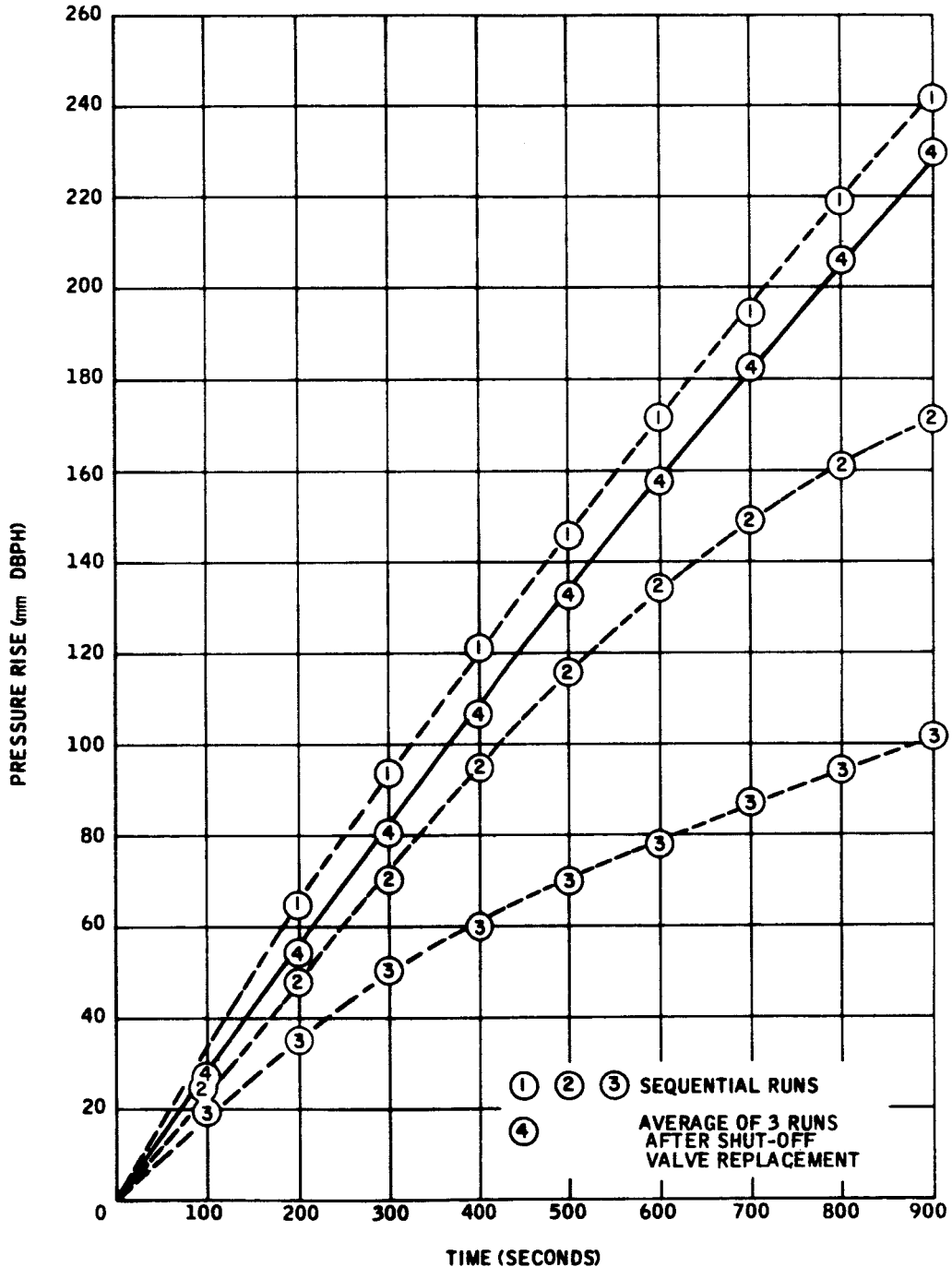


Figure 25. Extended Pressure Rise Tests n-Propyl Acetate

The faulty valve is considered responsible for the low delivery during the four-hour test, and for the different deliveries as measured before and after the four-hour test.

MISCELLANEOUS MEASUREMENTS

Delivery Manifold Volume

Before the delivery manifold could be used in the pressure rise measurements, it was necessary to know the volume of the manifold. To determine this value, a known volume was connected to the delivery manifold. An initial pressure was established in either the known volume or the manifold volume and the other volume evacuated. The final pressure of the two volumes, connected by opening the manifold inlet valve, was then measured. The manifold volume was found with the following equations:

$$P_v V_m + P_i V_k = P_f (V_m + V_k)$$

and

$$P_i V_m + P_v V_k = P_f (V_m + V_k)$$

where P_i, P_f were the initial and final pressures respectively ($P_v = O$), V_m and V_k were the manifold volume and the known volume respectively. Nitrogen was used as the gas, and P_i was about 760 millimeters of mercury. The manifold volume was found to be 600 cubic centimeters.

Gas Chromatograph Analysis

The gas chromatograph employed in the analysis was a Jarrell-Ash Model 27-705. An argon diode was used for the detector with argon as the flow gas.

Gas Analysis -- The calibration system is represented in Figure 26. The gas syringe was connected to the flask, the flask evacuated, and known quantities (microliter) of a standard solution (e.g., benzene diluted with n-butyl acetate) injected into the flask through the septum. Nitrogen was added until the plunger of the gas syringe raised to 100 cc. The plunger was depressed to O and the gas mixture stirred four minutes. The plunger was released and when it had risen to 100 cc, the three-way valve was turned to vent the gas in the syringe through the gas injector of the chromatograph. A 1-cc gas sample was injected when the plunger fell to the 20-cc mark. The calibration curves are shown in Figure 27.

Liquid Analysis -- The gas injector on the chromatograph was replaced by a liquid injector. Preliminary calibration was done by injecting microliter quantities of standard solutions (e.g., benzene diluted with n-butyl acetate). For the final analysis, a standard solution was prepared containing benzene, n-propyl acetate and acetone in the mole ratios as delivered by the Simulator (based on the total number of pulses for each material).

The separation column was a 10-foot length of 1/4 inch stainless steel tubing containing 10 percent Carbowax 4000 on firebrick. Column temperature was 70°C. The carrier was argon at a flow of 60 cc/minute. Upstream column pressure was 14.5 psi.

The injector system was heated to 130°C. A splitter ratio of 80:1 prevented overloading the detector by venting most of the column effluent directly into the room.

CALIBRATION

The procedure used to determine delivery accuracy was the pressure rise heat. In this procedure, the trace material was pulsed into an evacuated known volume and the pressure rise noted as a function of upstream delivery pressure, and pulse duration and frequency. Pressure rise determinations were initially made

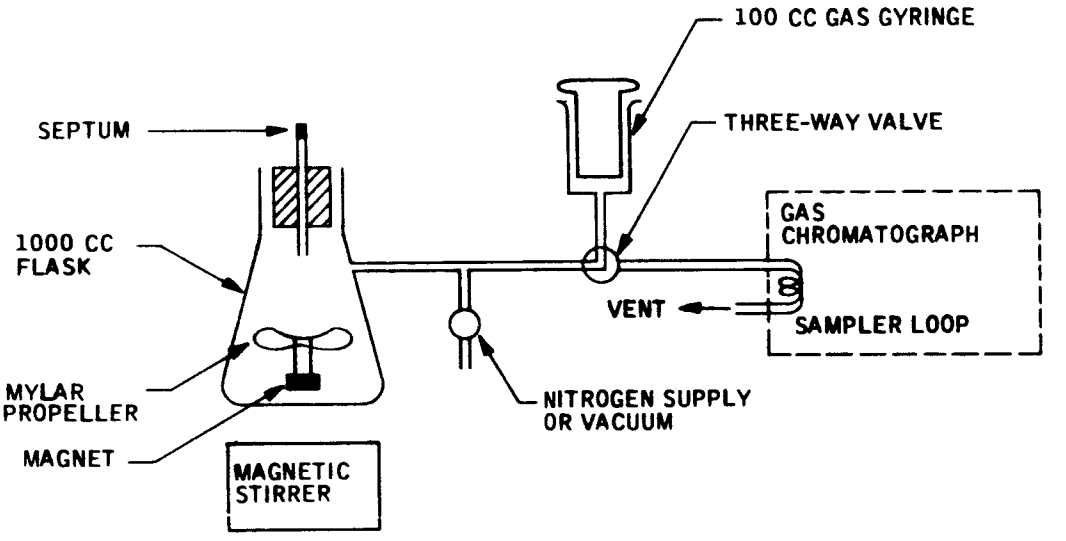


Figure 26. Calibration System

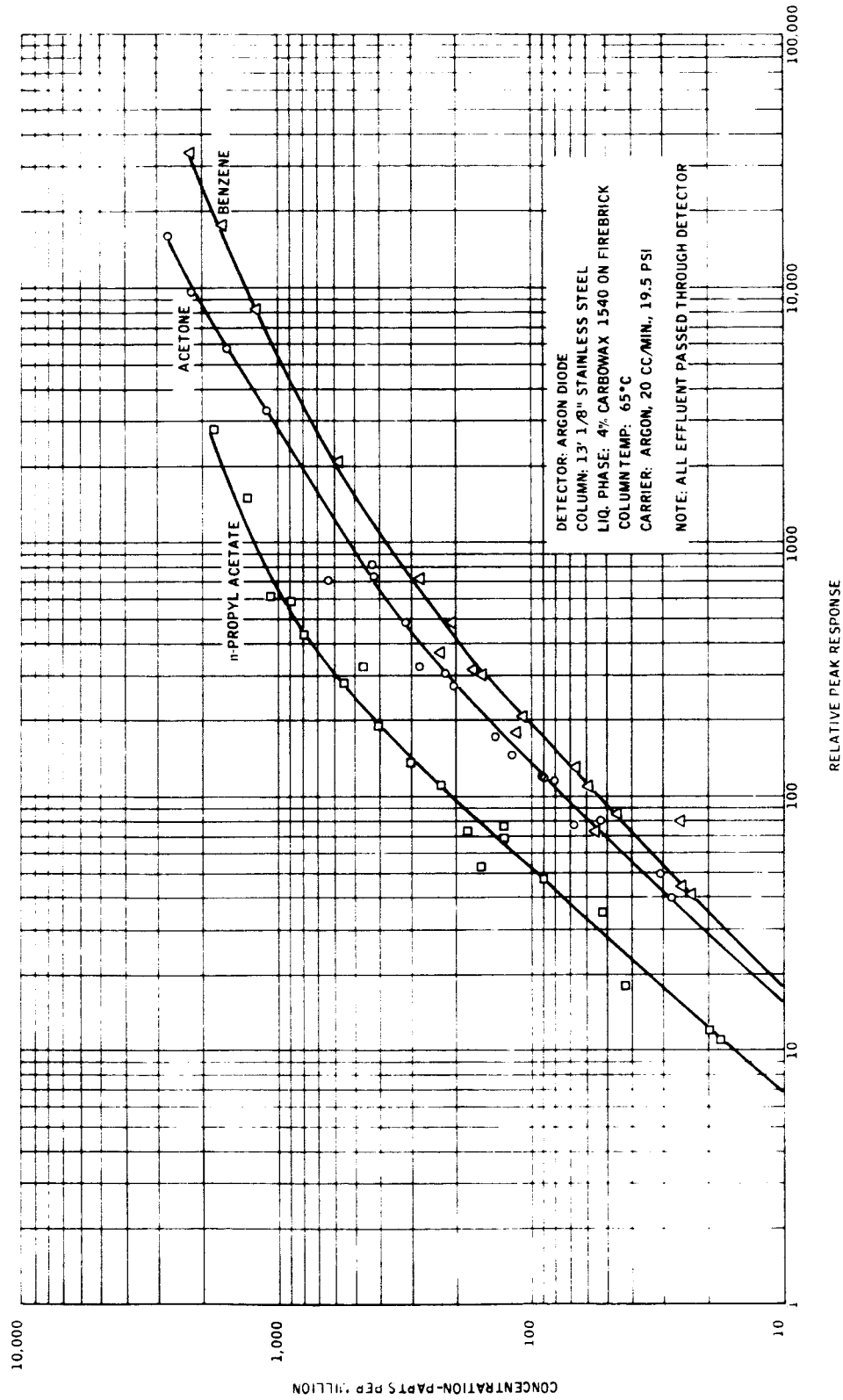


Figure 27. Gas Analysis Calibration

using bench apparatus; later however, determinations were made on the Trace Gas Simulator directly by using the delivery manifold as the known volume.

The tests showed that channel calibration is dependent on:

- Electrical characteristics of the Pulse Controller output circuitry
- Electro-magnetic and mechanical characteristics of the pulse leak valve, such as solenoid inductance, magnetic force and armature spring reaction, armature travel and valve orifice diameter

Other considerations affecting readings are ambient conditions and delivery manifold temperature.

Inasmuch as valves and pulse controllers were modified appreciably, subsequent to completion of the preliminary bench calibrations of the individual channel components, the data were no longer strictly applicable. Calibration information is based on tests conducted on the completed unit. The results of these pressure rise tests are shown on the accompanying graphs, which contain data obtained during the test programs in Minneapolis, as well as those obtained in the demonstration tests at the Manned Spacecraft Center, NASA, Houston.

The ten graphs that follow, Figures 28 - 37, show the amount of material delivered per pulse (corrected to 14.7 psi channel pressure, except 29.4 psi for Freon-114) as a function of the pulse dwell setting for each channel. In total, the results show generally consistent, linear characteristics. The data points represent tests conducted over a period of several months while final design refinements and modifications were being incorporated in the key components (the pulse controllers and metering valves).

The straight lines fitted to the points reflect the best estimate based on judgement and observed characteristics. It should be noted that the lines may intercept

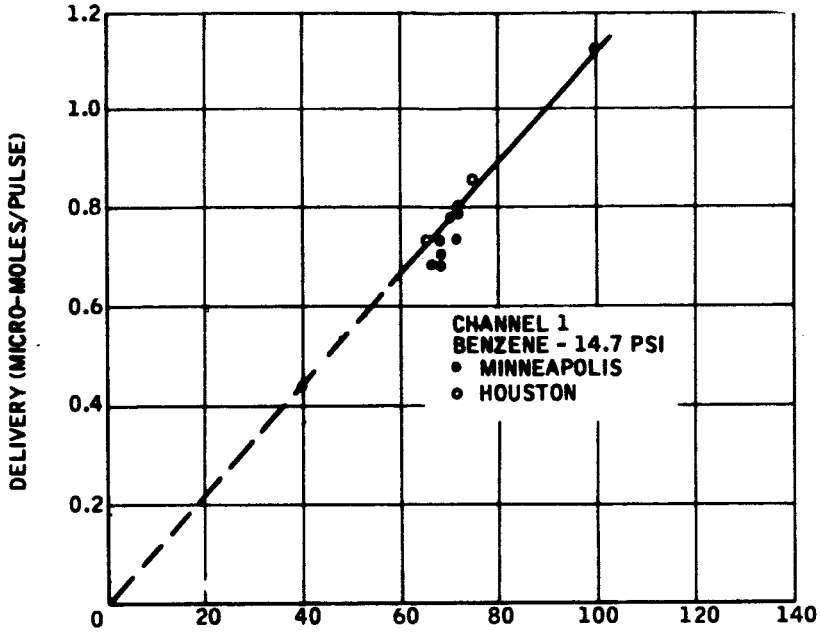


Figure 28. Channel 1

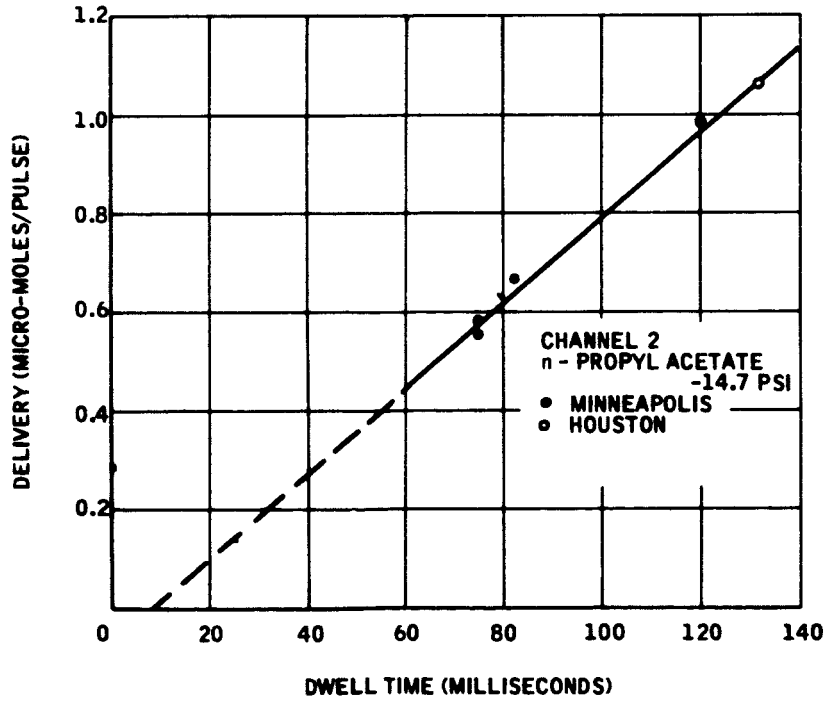


Figure 29. Channel 2

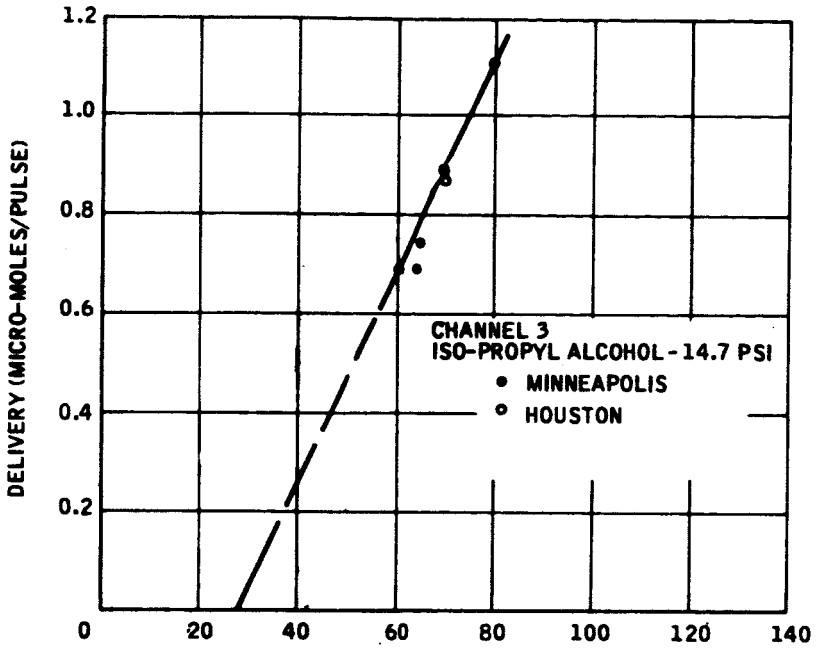


Figure 30. Channel 3

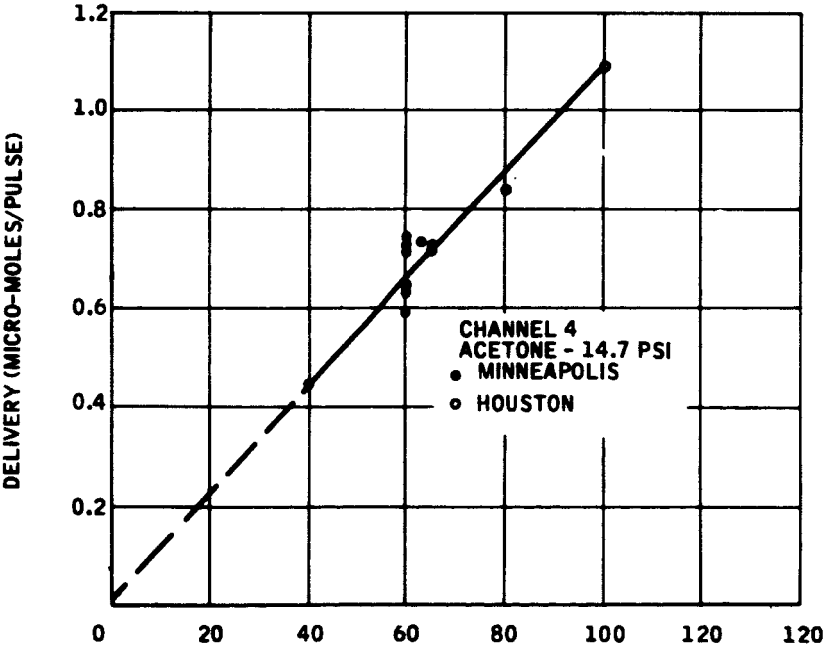


Figure 31. Channel 4

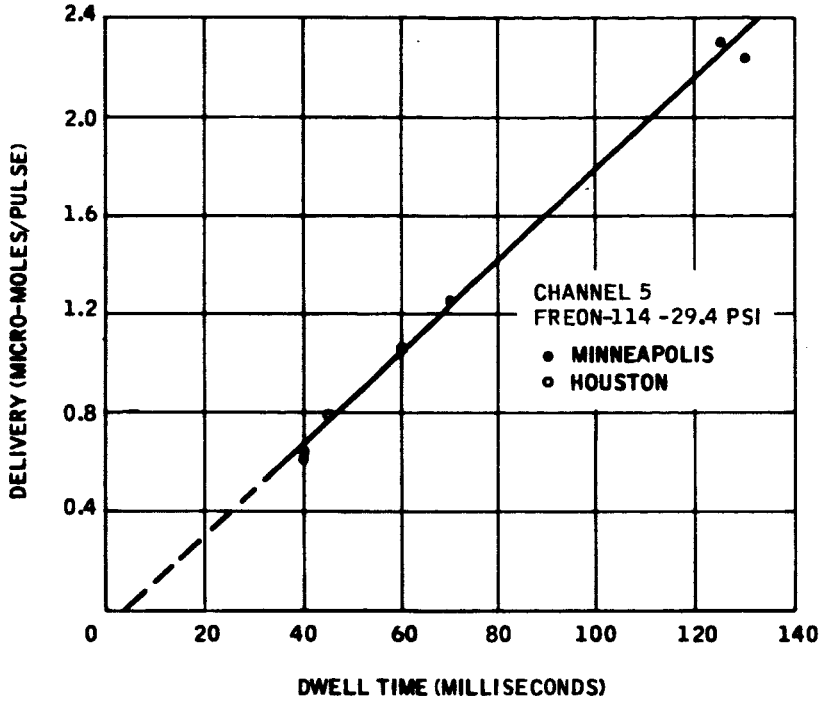


Figure 32. Channel 5

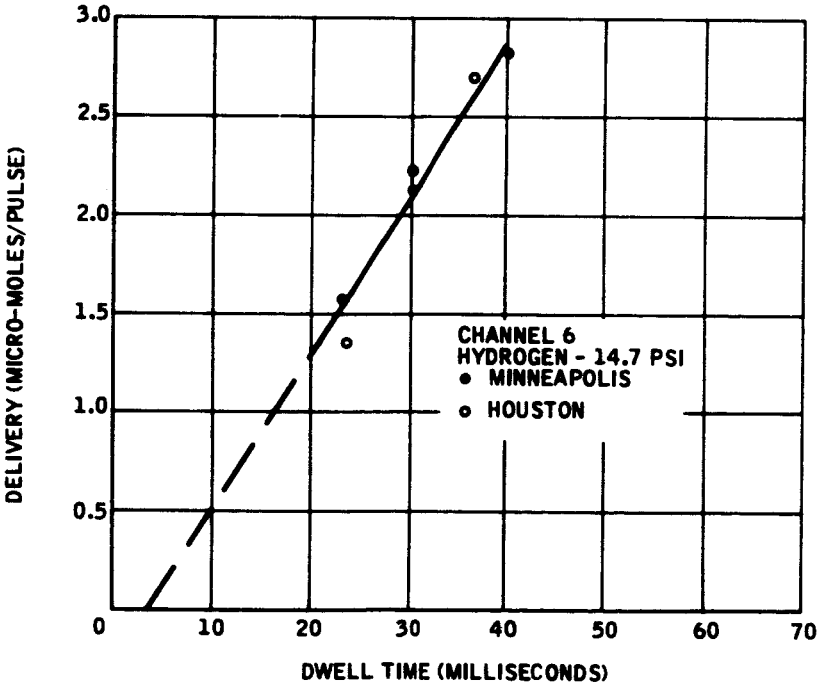


Figure 33. Channel 6

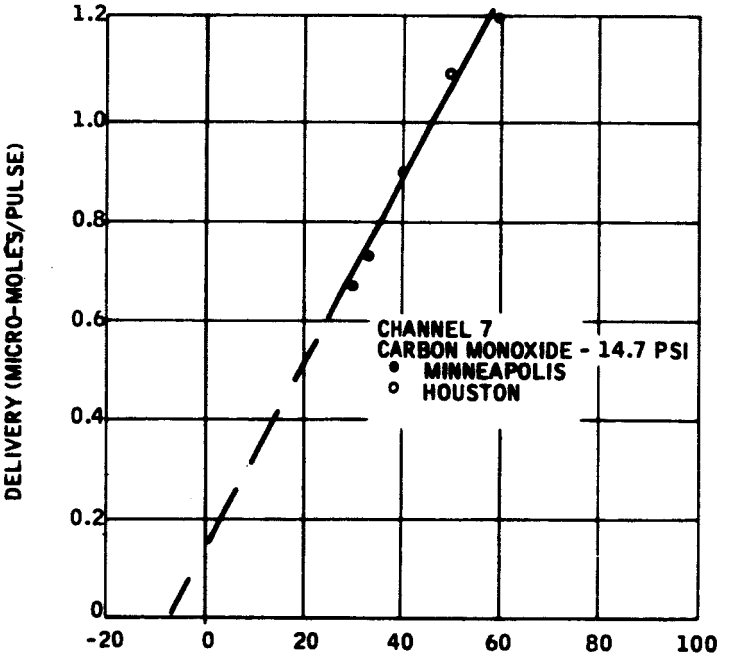


Figure 34. Channel 7

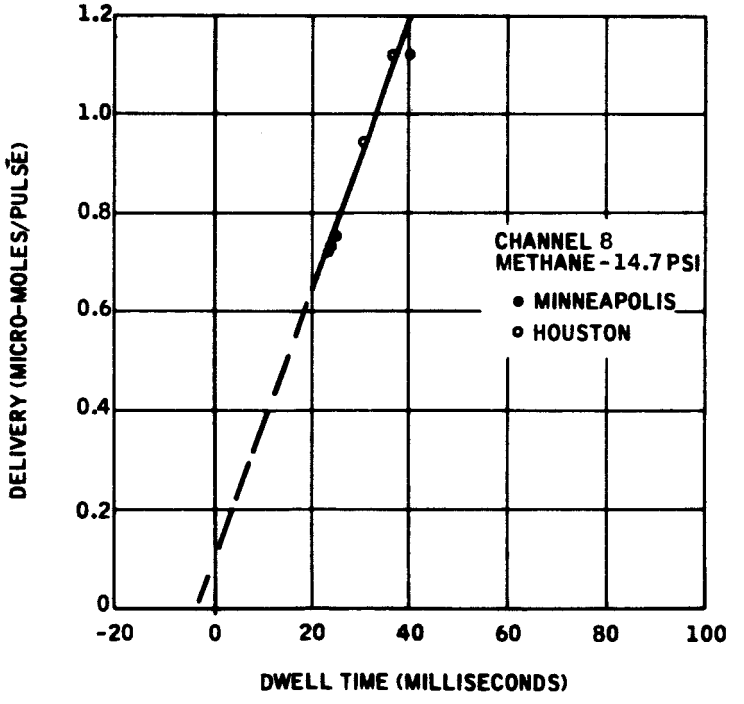


Figure 35. Channel 8

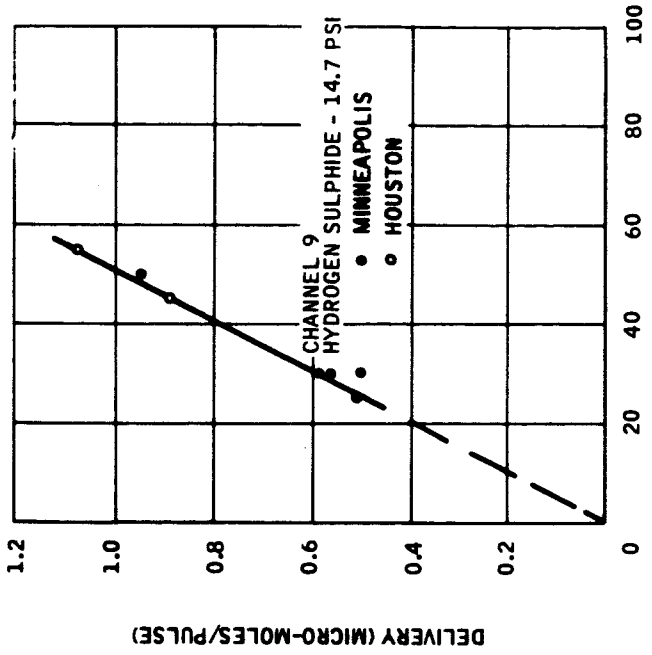


Figure 36. Channel 9

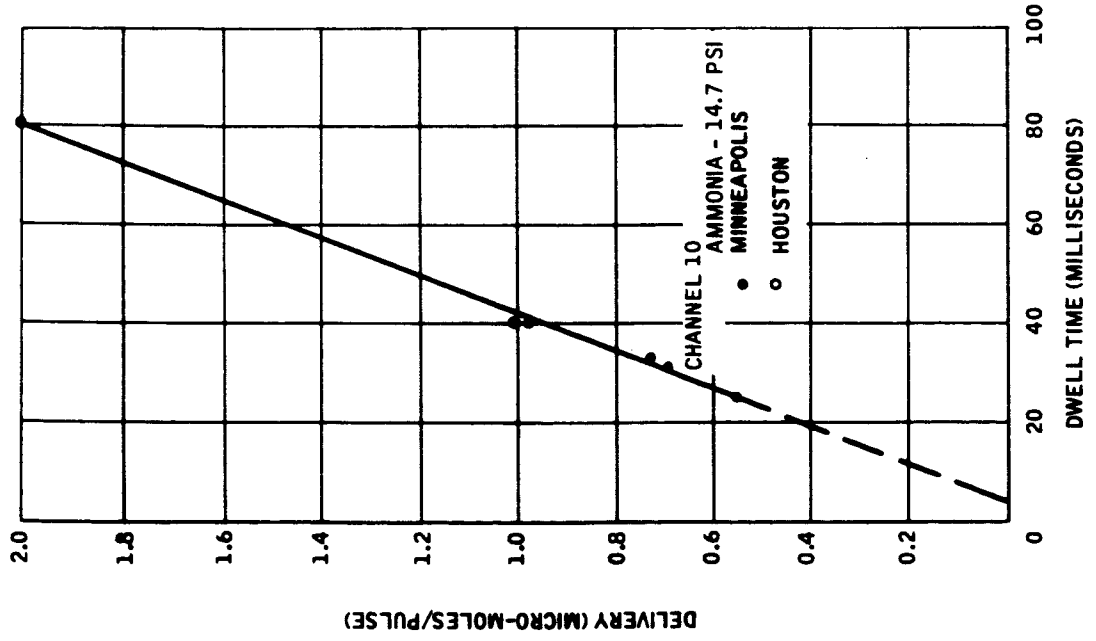


Figure 37. Channel 10

the abscissa at either a positive or negative dwell valve. This increment represents a time offset that reflects the combined operating characteristic of the specified pulse controller and pulse leak valve. The valve used for the time "t" in the delivery calculation should be corrected by this amount.

The data presented for iso-propyl alcohol shows an unusually large value for the abscissa intercept, depending on the interpretation and weighting given to the data points. Although tests showed the unit to be functioning properly insufficient data is available to establish the delivery characteristic conclusively and the characteristics shown for iso-propyl alcohol should be used primarily for reference, and actual delivery be verified by additional pressure rise tests as needed.

The delivery equation $D = 0.02\ P\ d^2\ t\ M^{-1/2}$ (previously presented in Section IV) shows how the delivery is related to pressure (P), valve open time (t), orifice diameter (d) and molecular weight (M). The bench tests on each channel, while not strictly applicable to the final delivery system, confirmed this equation. It was noted that the orifice diameters, nominally 2.4 mils, ranged from 2.3 to 2.55 mils. This was determined by measuring the amount of nitrogen delivered when the pulse leaks were held open continuously (rather than pulsed). For convenience, the delivery can be estimated using an orifice diameter of 2.4 mils so that the equation becomes:

$$D = (.1152)\ PtM^{-1/2}$$

This equation can be used to estimate the pressure and valve open time needed to deliver any material.

The equation is not needed for materials for which data as given in Figures 28 - 37 are available. In this case, the necessary dwell is the dwell corresponding to a correlated delivery, found by multiplying the desired delivery in micro-moles per pulse by the ratio of the pressure given in the appropriate figure to the available pressure.

For example, for a delivery of 1 micromole of Freon-114 at 33 psi, the corrected delivery is $1 \times \frac{29.4}{33}$ or 0.89 micromoles per pulse. From Figure 32, the necessary dwell is 52 milliseconds. In other words, a dwell of 52 milliseconds which would deliver 0.89 micromoles per pulse when the pressure is 29.4 psi, would deliver 1 micromole when the pressure is 33 psi.

For accurate delivery of materials not presently used in the Simulator, data similar to that given in Figures 28 - 37 should be obtained with pressure rise measurements.

SECTION VII
RESULTS AND RECOMMENDATIONS

The Simulator development program culminated in the fabrication and checkout of the Trace Gas Simulator described in Section V. The digital metering technique underlying the design of the unit has been demonstrated as being capable of providing accurate and controlled delivery of trace contaminants over the entire range of delivery rates desired. Construction of the unit permits flexible operation with all but the highest boiling materials listed in Table 6 (those in excess of 238°C).

The tests and results described in Section VI demonstrate the capability of the simulator to meet all the technical requirements specified in the contract document, and recapitulated in Section III of this Report.

Immediate applications of the Trace Gas Simulator are recommended in the area of Chamber Studies and for the evaluation of Atmospheric Purification Devices.

Chamber studies would be designed and conducted to study the effects of various contaminant concentrations, total dosage, and rate and duration of exposure on suitable test subjects. With proper selection and programming of contaminant introduction, characteristics of human occupancy or equipment outgassing may be simulated. The Simulator offers a capability of accurately controlled introduction of contaminants into a test chamber that should enhance the validity of such experiments relative to previous work in the same field.

With respect to atmospheric purification devices, the Trace Gas Simulator can be utilized to determine the contaminant removal capability of various atmospheric control and removal systems. Controlled amounts of material may be introduced into the device being evaluated, and the output analyzed to determine

removal or conversion effectiveness. Alternately, the Simulator can be used to introduce contaminants into a chamber equipped with atmospheric purification devices. The chamber atmosphere would then be analyzed to determine the effectiveness of the devices.

The Simulator can also be utilized to prepare gaseous mixtures of known concentrations for general laboratory use. Such mixtures are required in gas chromatography and for evaluation and calibration of various gas and vapor detectors, for example.

The analysis under Task B* of the contract was undertaken with the object of arriving at trace material generation rates based on available information. It was apparent that data are lacking for complete and accurate development of generation rates, and for the making of meaningful toxicity predictions. Recommendations for additional work to gather the required data on generation rates, presented in the Task B Final Report, are summarized below. The three major alternatives which may be considered are:

1. Analysis of the accumulation of gaseous contaminants in a space capsule carried through a simulation of actual use.
2. Development of understanding based on mathematical and experimental analyses of the actual processes contributing to gaseous contamination occurring in each component material.
3. Development of empirical data on gaseous output from each component material.

The first alternative can most easily be accomplished. But it will provide the basic data least capable of permitting prediction of effects when alterations are made in material components or operating conditions. The second alternative is the most desirable; it may however, prove to be overwhelming in magnitude of effort required. The third alternative would not provide for as great extrapolation as the second, but it can be more readily accomplished.

*See Appendix for list of References.

In addition, further work is suggested with respect to contaminants arising from biological sources. Specific steps are:

1. A literature search in depth for additional information on the identity and generation rates of volatile materials from biological sources. Particularly helpful in sharpening and evaluating the estimates would be interviews with investigators who are actively concerning themselves with questions such as the identity of the components of sweat, the effect of bacterial action on sweat, and the identity of flatus components.

2. An experimental study of expired air to identify and measure normal trace contaminants. Because of the large volume of respiratory air, the presence of very small amounts of foreign chemical species could make a large contribution to the contamination of the space capsule atmosphere. Very little evidence of systematic investigation of this source was evident from exploration of the literature. Such studies would seem to merit high priority.

3. A study to identify and measure the unidentified components of flatus. Dr. Murphy of the United States Department of Agriculture had estimated that as much as one percent of flatus components remain unidentified. This could be an important source of contamination and is deserving of continued research emphasis.

4. A study of apocrine sweat. Research on sweat constituents has given little attention to apocrine sweat. Systematic studies of its constitution are needed.

These comments relate to the identification and quantification of those materials which might predictably appear as contaminants of the space capsule atmosphere.

The assessment of their significance in terms of effects on man represents an area where very little meaningful work is available. This is expecially true when one considers possible additive and synergistic effects, and possible effects on human behavior and efficiency. Studies are needed pertaining to the effects of combinations of the significant contaminants on behavior as well as upon the usual indicators of toxicity. The initial experiments should be in animals with final confirmation of safety in man.

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APPENDIX

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