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AN ANALYTICAL GAS CHROMATOGRAPH FOR PRODUCTS OF ISOTHERMALLY DEGRADED POLYMERS

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ADMINISTRATIVE INFORMATION

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SUMMARY OF REPORT

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USNRDL-TR-68-41 dated 5 February 1968

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The Problem

Cellulosic materials constitute the greater portion of combustible items found in homes. For more effective prediction, control or prevention of dwelling fires, it is essential to determine the types and time-resolved amounts of volatile products formed during thermal degradation of these materials. The commercially available gas chromatographic units were not suitable for simultaneous analysis of fixed gases and organic compounds, nor were they capable of frequent, intermittent sampling over extended periods of pyrolysis. The aim of this work was to utilize an improved pyrolysis chamber coupled to a modified, commercially available gas chromatography unit in an arrangement which meets the above requirements.

The Findings

A temperature control and valving system for sample separation and concentration was designed and constructed to couple the pyrolysis chamber to a Beckman Instruments Company Model GC-4 Gas Chromatograph which was modified to accept and analyze simultaneous, parallel inputs of organic compounds and fixed gases. This compact, and completely integrated system has proven satisfactory when applied to the analyses of the degradation products of white α-cellulose.

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ABSTRACT

A Beckman Instruments Company Model GC-4 Gas Chromatograph was modified to simultaneously analyze parallel inputs of organic compounds and fixed gases originating as the degradation products of isothermally pyrolyzed α-cellulose. The pyrolysis chamber and a complex gas-handling system for separating and concentrating the pyrolyzates were attached directly to the GC-4 cabinet, and a complete system of temperature control zones was established. A detailed description of the arrangement and operation of (1) an isothermal pyrolysis chamber for sample generation, (2) a temperature control and valving system for sample separation and concentration, and (3) a parallel liquid partition and solid adsorption gas chromatography system for sample analysis is presented. The technique is applied to trial analysis of the degradation products of white α-cellulose pyrolyzed isothermally for 10 minutes in a nitrogen-fluidized sand bath at 360°C.

SUMMARY

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A temperature control and valving system for sample separation and concentration was designed and constructed to couple the pyrolysis chamber to a Beckman Instruments Company Model GC-4 Gas Chromatograph which was modified to accept and analyze simultaneous, parallel inputs of organic compounds and fixed gases. This compact, and completely integrated system has proven satisfactory when applied to the analysis of the degradation products of white α-cellulose.

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1. INTRODUCTION

The scope of work unit 2531C as given in contract No. 65-200(75) is as follows:

"This work unit is in support of civil defense work in limitation and control of fires. The objective of the work unit is to bring about increased understanding of the fundamental aspects of fire while providing an improved data base for use in applied research. The overall approach is to undertake experimental and theoretical investigations of fire phenomena which are of a fundamental nature and, at the same time, be directed to contributing to the solution of the civil defense fire problem. More specifically, the research will use the following two related approaches:

"1. Investigation of the basic physical and chemical mechanisms of suppression by solid, liquid or gaseous suppressants, of fires in wood, fabrics and other critical urban fuels.

"2. Investigation of the basic physical and chemical mechanism of the effect of trace additives in causing prevention, retardation or suppression of fires in wood, fabrics and other critical urban fuels."

The work described in this report is the required preliminary phase of investigations following the second approach to the fundamental aspects of fire. In the past, the pyrolysis and gas chromatographic procedures have generally followed two basic methods: (1) those using flash-filament pyrolysis, where the carrier stream is used to transport the pyrolyzate directly to the column; and (2) heating the sample in a separate enclosure, trapping off the gases, and admitting the degradation products to the chromatograph after a given interval. Although each method has certain advantages, neither method can be applied to intermittent sampling of the degradation products over an extended period of pyrolysis.

Recent work at NRDL[1] on isothermal degradation of untreated cellulose between 275 and 350°C revealed that there are three distinct stages of pyrolysis; a brief initial period of rapid volatilization (measured in terms of weight loss) and decomposition (measured in terms of monomer units loss); a region in which both the volatilization and decomposition are of zero order; and a region in which the volatilization follows a first order rate, leaving a char deposit which does not undergo further pyrolysis.

In addition to the weight and monomer units loss, information concerning the types and relative amounts of volatile products formed during each of the three distinct stages of pyrolysis of untreated and fire retardant treated cellulose is needed for both the prediction and control of fire spread.

Chromatographic analysis measurements of the degradation products during the course of pyrolysis (as a function of time) involves intermittent sampling of the volatile products. These products are a mixture of organic compounds and fixed gases (CO_2, CO, and low molecular weight hydrocarbons) which are not amenable to efficient quantitative analysis in a single chromatographic column; consequently, it is desirable to separate the fixed gases from the organic compounds prior to chromatographic analysis. The separated components are then introduced into parallel columns, each of which is packed with the material most capable of resolving the respective compounds or gases of each component. Since commercial chromatographs do not provide the sample handling features required for product separation and intermittent, parallel analysis, the aim of this work was to develop such a system and, as a further refinement, provide for coupling it to the inlet of a time-of-flight mass spectrometer.

The following is a detailed description of the arrangement and operation of (1) the sample generation system, (2) the temperature control and valving system for sample separation and concentration, and (3) the parallel liquid partition and solid adsorption gas chromatography system for sample analysis.

2. GENERAL CONFIGURATION

As the basic building block of this system, NRDL procured a Model GC-4 Gas Chromatograph[2] with the following component modules and accessories:

1. Two temperature control modules.[3]
2. One voltage control module.[4]
3. Two thermal conductivity detectors and power supplies.[5]
4. One sampling and two switching valves.[6]
5. Two flow control modules.[7]
6. Three direct injection inlets.

In addition, these Aerograph components were procured:

1. Model 600D Oven.[8]
2. Model 328 Isothermal Temperature Controller.[9]

Figures 1 through 5 show the installation of these components and the location of the pyrolysis chamber and new valve compartment outside the left end of the GC-4 cabinet. This arrangement provided a left-to-right sample flow pattern from the pyrolysis chamber, through the valve compartment and GC-4. When the system is later coupled through a helium separator to a time-of-flight mass spectrometer, these units will be located to the right of the GC-4. This arrangement also provided an unobstructed area for installation of sample separation traps and volumetric loops below the valve compartment where they, and their elevator-mounted heat-control units, are readily accessible for executing the rapid temperature changes necessitated by diffusion transfer techniques for gas handling.

The helium and nitrogen supply tanks, and the vacuum pump are located behind the right side of the GC-4. The recorders are also located behind the GC-4, but to the left where they may be observed by the operator. Electrical and compressed air service are located behind the recorder rack.

3. SAMPLE GENERATION

Figures 4 and 6 show the equipment developed to generate gaseous degradation products of isothermally pyrolyzed α-cellulose. This system is a refinement of a previous NRDL development.[1] The heating agent is a fluidized bed of sand and glass beads heated and levitated by a stream of hot, oxygen-free nitrogen gas, boiled off liquid nitrogen in a heat exchanger. The stream pressure is regulated to 18-20 psi, after which the stream is passed through a flow meter, a 300°C pre-heater, and the main N_2 heater (a pyrex helix within the isothermal oven) and enters the flow-distribution plenum which constitutes the lower portion of the pyrolysis chamber. The last turn of this helix contains a 100 watt tungsten filament (trimmer heater) which gives the nitrogen a final temperature adjustment before it enters the plenum.

The main N_2 heater helix and pyrolysis chamber are located in a flow of hot air circulated by a ducted fan located in an Aerograph Model 600-D Isothermal Oven controlled by an Aerograph Model 328 Temperature Programmer. The sand bath is heated both by the hot air in the oven and by the hot nitrogen which flows up from the plenum through a fritted pyrex disk to fluidize the bath. A partial layer of 0.10 inch diameter pyrex beads in the bottom of the bath minimizes the formation of unequal flow-rate channels in the sand. Specimens of α-cellulose that have been dried and weighed are transported to the loading chamber in closed weighing bottles. When the bottle is in position, cool nitrogen gas is admitted through valve V-29 to purge all moisture from the chamber before the bottle is opened. When the specimen is in the manipulator, the chamber seal and basket assembly is quickly raised, the specimen is placed in the basket which is immediately immersed in the fluidized sand bath. This action re-seals the pyrolysis chamber loading port and initiates pyrolysis of the specimen.

Gaseous degradation products carried out of the chamber by the flowing nitrogen pass through the aliquot chamber where, during actual sampling (i.e., V-6, Fig. 7, open), entrained sand and tar droplets are removed by a 200-mesh stainless steel screen before the sample is drawn into the valve chamber for separation into organic compound and fixed gas components. When valve V-6 is closed the gas/products mixture emanating from the pyrolysis chamber is vented directly to the atmosphere through the aliquot chamber. This method of taking aliquots which constitute less than 100% of a moving gas stream, avoids flow-rate fluctuations which would affect conditions in the pyrolysis chamber.

Except for periods of specimen insertion or residue removal, the temperature of the pyrolysis chamber is constantly monitored by a 1 MV full-scale Brown Recorder (No. 3) attached to a chromel/alumel thermocouple located in the center of the specimen basket. This recorder may also be used to provide a signal for controlling the trimmer heater. All parts of the sample handling system, including the aliquot chamber and valve compartment inlet (VCI) are maintained at a temperature well above the condensation point of any gaseous organic compounds generated in the pyrolysis chamber.

4. VALVE COMPARTMENT AND ELEVATOR SECTION

Figures 1, 2, and 3 show the new valve compartment and its associated elevator section for inerchanging the heating and cooling units used to control the temperature of the traps (T-1 and T-2, Fig. 7) and loops (OC and FG L-2, called OC Loop and FG Loop in Fig. 7 - see also Table II) which project below the valve compartment. This compartment (see Fig. 7) houses valves V-1 (sampling), V-2 and 3 (switching), V-4, 5 and 6 (3-way selectors), and V-12 and 13 (safety). Located externally are valves V-7 and 8 (loop pump), V-9 (foreline), V-10 (trap pump), V-11 (crossfeed), V-28 (He purge), gauges G-2 and G-3 (loop pressure), and valve actuators VA-1, 2 and 3. The valve compartment is constructed of 1/4 inch aluminum plate and is supported by side-mounted brackets to permit access to front, rear, top and bottom.

Only the handles of valves V-4, 5 and 6 need be removed prior to removal of the top plate, and disconnection of the traps and loops permits removal of the bottom plate. The heating element and thermocouple supplied with the original valve compartment were attached to the bottom (after providing suitable holes in the heater for lines to the trap and loop connection), and the entire assembly was encased with 3/4 inch thick Johns-Manville MARANITE insulation and sheathed in 0.025" aluminum. Figure 8 details the heated stems used to connect the traps and loops to the valve compartment. These stems minimize the length of the temperature gradient along the sample path between the heated valve compartment and the low temperatures prevailing at times in the traps and loops.

In Fig. 7, the general arrangement of the valve compartment and its related support systems is shown schematically. Gas flow and direction of flow is indicated by arrows in which six different numerals (in Figs. 7 through 12) are used to indicate the content of each section of the system. Opposed arrows indicate static conditions. Figure 7 also indicates the particular valve settings and flow conditions required for the PUMP-I mode, the first of two preliminary steps needed to ready the system for acceptance of a sample. PUMP-1 and PUMP-II modes are identical with the exception of temperature changes of the traps and loops. (See below.) Changes of these temperatures are accomplished by immersing the traps and loops (Figs. 1 and 3) in either a heated or chilled bath. These baths (Table I) are supported on turntables mounted on elevators. The two turntables on the front elevator serve the traps and the two on the rear elevator serve the loops. The turntables on each elevator are interconnected by a chain and sprocket linkage which causes them to turn in unison and to detent simultaneously. Each of the four turntables carries both a heated and a chilled bath. The elevators are moved by crank-operated winches and the turntables are rotated by hand. Raising the front elevator causes both traps to be simultaneously immersed in either the heated or chilled bath, and similar operation of the rear elevator does the same for the loops. This method of very rapidly heating or cooling the thin-walled stainless steel tubes of the traps and loops produces the square wave type temperature profile required to move discrete sample quantities through the system at a relatively high repetition rate. Table I contains additional data on these temperature control baths. PUMP-I is essentially a bake-out mode with all traps and loops immersed in heated baths. For PUMP-II, the turntables are reversed to chill the traps and loops preparatory to trapping. It will be noted in Fig. 7 that provision is made at V-6 for injection of calibration samples through injection port IP-1 which uses hot nitrogen gas from the pyrolysis chamber to volatilize and entrain liquid samples. There are two other injection ports: IP-2 is located at the inlet end of the liquid partition column (LPC), and IP-3 is located at the inlet end of the solid adsorption column (SAC).

5. SAMPLE SEPARATION AND CONCENTRATION PROCEDURE

Twenty-four sequential steps are required to move an aliquot of gas/products mixture from the pyrolysis chamber to the chromatographic columns of the GC-4. These steps are grouped in four specific stages of operation:

A. TRAPPING:
Separation into organic compounds and fixed gases.

B. TRANSFERRING:
Moving components into volumetric loops.

C. MEASURING:
Determining pressure at known temperature and volume.

D. SWEEPING:
Moving the concentrated components to the GC-4.

A. Trapping Stage (Fig. 9)

The mixture of nitrogen carrier gas and pyrolysis products drawn from the aliquot chamber is separated into organic compounds and fixed gases by 2-stage traps; trap T-1 - half filled with Chromosorb-20 for the organic components and trap T-2 half filled with silica gel for the fixed gases. The gas/products mixture enters the valve compartment at V-6, pass through ports 1-3 of V-1 and into the -78°C Chromosorb of T-1. The unadsorbed fixed gases emerge from T-1 and continue by way of V-5 into the -198°C silica gel of T-2. Any part of the original aliquot not retained in T-2 continues via ports 4-2 of V-1 through V-11 to the vacuum system. Assuming that the system is in PUMP-II Mode, the operational steps for trapping are:

1.	V-6 - SET TO PC (*)	To establish N_2 carrier flow to pump.
2.	V-5 TRAP	To put T-1 and T-2 in series.
3.	V-1 TRAP	To route flow through traps.
4.	INSERT SPECIMEN (**)	In pyrolysis chamber.
5.	HOLD	Hold time dependent on nature of run.
6.	V-6 OFF	To terminate sample input.
7.	V-5 PUMP	To reconnect traps to vacuum in parallel.
8.	HOLD 1 MIN	To pump off unadsorbed carrier gas.

(*) SET to IP for samples injected at IP-1

(**) INJECT at IP-1 for standardizing

B. Transfer Stage (Fig. 10)

The aliquot is now separated into organic compounds (in T-1) and fixed gases (in T-2), and most of the unadsorbed carrier has been pumped off. Each component must now be diffusion-transferred into volumetric loops to determine its pressure at a known temperature and volume. This is done by heating the trapped products in a vacuum while the traps are connected to loops immersed in liquid nitrogen. The cryo-pumping action of the loops coupled with the rapid expansion occurring in the traps causes the major portion of each component to move into its loop. This action is easily observed by noting the sudden rise in pressure indicated by gauges G-2 and G-3. When the needles stop, equilibrium has been reached and the loops are isolated. Operational steps are:

Valve Settings and Time/Temp.	Purpose
1. V-5 OFF	To isolate traps from vacuum.
2. V-7 and 8 - CLOSED	To isolate loops from vacuum.
3. V-1 PUMP	To interconnect traps and loops.
4. TRAP TEMP - HOT	To expand trapped products.
5. HOLD	Hold until gauge needles stop.

C. Measuring Stage (Fig. 11)

The two portions of the system which may be defined as V-2 - OCL - V-2 and V-3 - FGL - V-3; have a measured volume of 5cc. When V-2 and V-3 are in PUMP position, the pressures in these two portions of the system may be read on gauges G-2 and G-3, respectively. If loops OCL and FGL are raised to the same temperature during each run, the quantitative values obtained through pressure readings may be directly correlated. The operational procedure for expansion and quantitative determination of the sample sizes is as follows:

Valve Settings and Time/Temp.	Purpose
1. V-4 OFF	To isolate traps from loops.
2. LOOP TEMP - HOT	To return loop contents to gaseous state and establish known temperature.
3. HOLD	Hold until gauge needles stop. (*)

(*) If pressures exceed 40 psi (indicating too large an aliquot), valves V-12 and 13 will open to protect downstream system from overpressure effects.

D. Sweep Stage (Fig. 12)

If separate recorders are used for the outputs of the LP and SA detectors, analysis of the samples may be accomplished simultaneously. If only one recorder is used, either sample may be held in its loop while the content of the other loop is being analyzed. (See Fig. 15.) Operational steps for the sweep stage and for recycling the system are as follows:

Valve Settings and Time/Temp.	Purpose
1. V-2 and 3 SWEEP	To insert loops in helium carrier flow.
2. HOLD 30 SECONDS	To sweep loops at 10cc/min He flow rate.
3. V-7 and 8 OPEN	To connect loops to vacuum in parallel.
4. V-4 PUMP	To interconnect traps and loops.
5. V-7 and 8 OPEN	To return loops to Pump-I mode.
6. HOLD 5 MIN.	To effect Pump-I "Bake-out".
7. TRAP and LOOP TEMP	Cold.
8. HOLD 5 MIN.	To effect Pump-II "Pump-down".

6. GAS CHROMATOGRAPHY, TEST AND CALIBRATION PROCEDURE

The system and operational procedures described above were applied to the analysis of the thermal degradation products of white α-cellulose specimens ranging from 0.2 to 2.5 grams in weight. These specimens were pyrolyzed at 360°C for 10 minutes and the non-tarry pyrolyzates of each specimen were collected in the 2-stage, pre-chilled traps (Table II).

A. Liquid Partition

The gaseous organic compounds were swept at 60 ml/min from L-1 into the liquid partition column (LPC) which was held at 90°C for 3 minutes, then raised, first to 150°C for 2 minutes and, finally to 220°C for the remainder of the analysis. The degradation products rendered 20 peaks - 18 of which were identified by comparison with retention times of known compounds. Final identification is currently being made with the use of a time-of-flight mass-spectrometer, and will be the subject of a separate report.

The efficiency of the sample separation and concentration system was tested by cryo-trapping degradation products directly from the pyrolysis chamber and then injecting them at IP-2 (at the inlet end of LPC). Twenty-one peaks were obtained - the additional one being an unresolved peak of the fixed gases.

B. Solid Adsorption

A 6-1/2 ft, 1/4 inch diameter, solid adsorption column packed with 80-100 mesh silica gel and programmed at 20°C/min from -10°C to 100°C was used to successfully resolve methane, ethane, carbon dioxide, carbon monoxide, and nitrogen. However, to increase the relative retention time of the lighter gases and improve the resolution of the system, the silica gel was replaced first with 8 feet, and later with 12 feet, of pre-conditioned POROPAK-Q (Table II).

This column was operated at room temperature and showed greatly improved resolution of the lighter gases and less tailing of the peaks of the heavier gases. The degradation products rendered 4 peaks, all of which have been identified by comparison with the retention times of known gases. Again, the efficiency of the sample separation and concentration system was tested, insofar as fixed gases were concerned by cryo-trapping degradation products directly from the pyrolysis chamber and then injecting them at IP-3 (at the inlet end of SAC). One particular advantage to the use of POROPAK-Q is its ability to operate without temperature programming, however, this mode of operation does indicate a probable requirement for frequent reconditioning.

7. ELECTRICAL SYSTEM

The necessity for maintaining precise temperature control in all portions of the system requires a multiplicity of heaters and heater controls. Figure 13 indicates the heaters controlled by the main power switch (S-101) and monitored by the temperature and voltage meters connected to the read-out selector switch (S-107). Although not normally activated, the SA column heater is available for reconditioning or programming of the column. Figure 14 indicates the circuits controlled by the auxiliary power switch (S-201), two of which are also monitored through S-107. One of these, for the helium drier (HeD) is used (only when the detectors are not in use) to regenerate the silica gel in a section of the helium supply line.

The T-1 and L-1 temperature control bath heaters are used to heat the fluidizing air of the sand baths, but may be replaced with immersion type heaters in Dewar-contained baths of suitable perfluorochemicals. The rest of the circuits in Fig. 14 relate to the pyrolysis system.

8. RECORDING SYSTEM

Figure 15 shows the provision made for selecting any one of six inputs to a single recorder, or for selecting paired inputs to two recorders through selector switch S-108 and appropriate jumpers.

9. COMPRESSED AIR SYSTEM

Figure 16 shows the control and distribution system for the 30 psi compressed air required to operate the actuators of valves V-1, 2 and 3, and to fluidize the hot sand baths for trap T-1 and loop L-1. Although not shown, this system should include air-actuated switches in heater circuits of these two baths.

10. CONCLUSIONS AND RECOMMENDATIONS

The equipment and techniques described above have proven quite satisfactory in their present application to the analysis of the degradation products of α-cellulose over extended periods of pyrolysis. However, to improve the analysis of short period aliquots, the following changes are suggested:

1. Install a large orifice, two-way valve at an enlarged (100cc) aliquot chamber to permit isolation and evacuation of this chamber while bypassing the gas/products mixture to the atmosphere. Turning this valve from BYPASS to SAMPLE for 10 seconds would permit a 10 cc/sec flow to fill the aliquot chamber with the gas/products mixture. This aliquot could then be drawn off and analyzed in the usual manner.

2. Use large sample loops, particularly for fixed gases, to improve the quantitative analysis of those yielding only traces.

With the present system, the time required to trap and transfer an aliquot and to recycle the traps through both PUMP modes cannot be reduced to less than five minutes. If it is desired to take samples at shorter intervals, it is quite feasible to install two or more parallel trapping systems operated in sequence and connected through suitable selector valves to the same aliquot chamber and loop system.

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8. Aerograph Instruction, "Model 600-D Gas Chromatograph," Wilkens Instrument and Research, Inc., Walnut Creek, California, 1965.

9. Aerograph Instruction, "Model 328 Isothermal Temperature Controller," Wilkens Instrument and Research, Inc., Walnut Creek, California, 1965.

TABLE I - TEMPERATURE CONTROL BATHS

	Item	Identification	Content	Size	Temperature
ORGANIC COMPOUNDS	Bath	AC	Acetone & Dry Ice (*)	2-liter	-78°C
	Bath	HS	Fluidized Hot Sand	2-liter	220°C
	Bath	LN	Liquid Nitrogen	2-liter	-198°C
FIXED GASES	Bath	LN (2 each)	Liquid Nitrogen	2-liter	-198°C
	Bath	HW (2 each)	Hot Water	2-liter	100°C
SOLID ADSORPTION	Bath	CW(**)	Cold Water	5-liter	Ambient

(*) See Recommendations
(**) To provide isothermal environment for solid adsorption column

TABLE II - TRAPS, LOOPS, AND COLUMNS

	Item	Identification		Content	Size	Temperature Range	
		No.	Code			Low	High
ORGANIC COMPOUNDS	Trap	T-1	OCT	Chromosorb-20	1/4" dia. x 4'	-78°C	220°C
	Loop	OC	OCL	Void	5 cc	-178°C	220°C
	Column	C-1	LPC	Carbowax-20M on Chromosorb T-40-60	1/4" dia. x 6'	25°C	230°C
FIXED GASES	Trap	T-2	FGT	Silica gel	1/4" dia. x 4'	-198°C	100°C
	Loop	FG	FGL	Void	5 cc	-198°C	100°C
	Column	C-2	SAC	Poropak-Q	1/4" dia. x 12'	Ambient	

TABLE III - FUSE SIZE, SERVICE, AND LOCATION

Switch		Fuse No.	Amps.	Code	Service	Fuse Location
Primary	Secondary					
S-101	S-105	F-101	2	VCO	Valve Comp.Outlet Heater	Fuse Panel
		F-102	2	VCI	Valve Comp.Inlet Heater	Fuse Panel
	S-106	F-103	2	SAC	Solid Adsorb.Col. Heater	Fuse Panel
		F-104	2	HePH	Helium Preheater	Fuse Panel
		F-105	2	SV	Solenoid-Operated Valves	Fuse Panel
		F-106	2	M-1	LPC Blower Motor M-1	Fuse Panel
		F-107	2	M-2	AC-DC PS Blower Motor M-2	Fuse Panel
		F-108	1	PS	AC-DC Power Supply	Fuse Panel
	S-120	F-109	1	OCD	GP Detector Power Supply	Fuse Panel
				VC	Valve Compartment Heater	Fuse Panel
	S-130	F-110	8	FGDI	FG Detector Inlet Heater	Fuse Panel
	S-121	F-111	1	OCD	OC Detector Power Supply	Fuse Panel
	S-104	F-115	2	LPCI	LP Column Inlet Heater	Fuse Panel
		F-116	2	OCDI	OC Detector Inlet Heater	Fuse Panel
	S-102	F-117	8	LPC	LP Column Heater	LPC SCR
	S-103	F-118	8	DC	Detector Compart. Heater	DC SCR
S-201	S-202	F-202	8	HeD	Helium Drier	VT 10
	S-203	F-203	8	N_2PH	Nitrogen Preheater	VT 11
	S-204	F-204	2.5	PCT	Pyrolysis Chamb.Trim Htr.	PC Panel
	S-205	F-205	6.25	M-3	PC Fan Motor M-3	Oven Rear
		F-206A	5	PCO	PC Oven Heater	Programmer
	S-206	F-206B	1	PCP	PC Oven Temp. Programmer	Rear
	S-207	F-207	8	OCT	OC Trap Heater	VT 14
	S-208	F-208	8	OCL	OC Loop Heater	VT 15

Fig. 1. Beckman GC-4 Gas Chromatograph modified for isothermal pyrolysis studies.

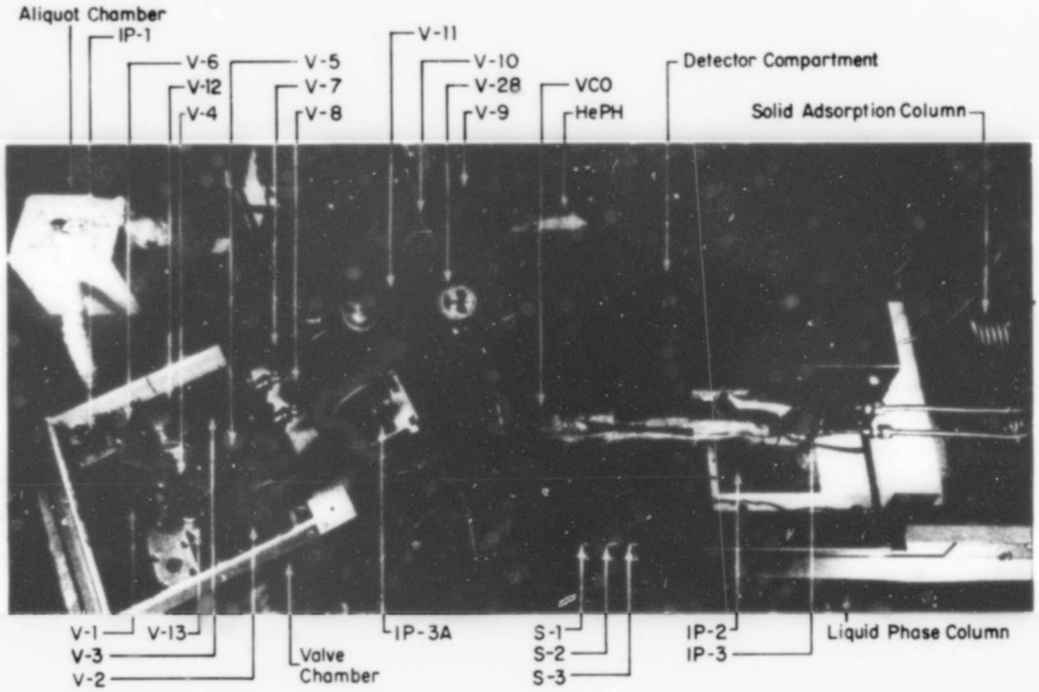


Fig. 2. General arrangement of valve chamber, chromatographic columns and detectors.

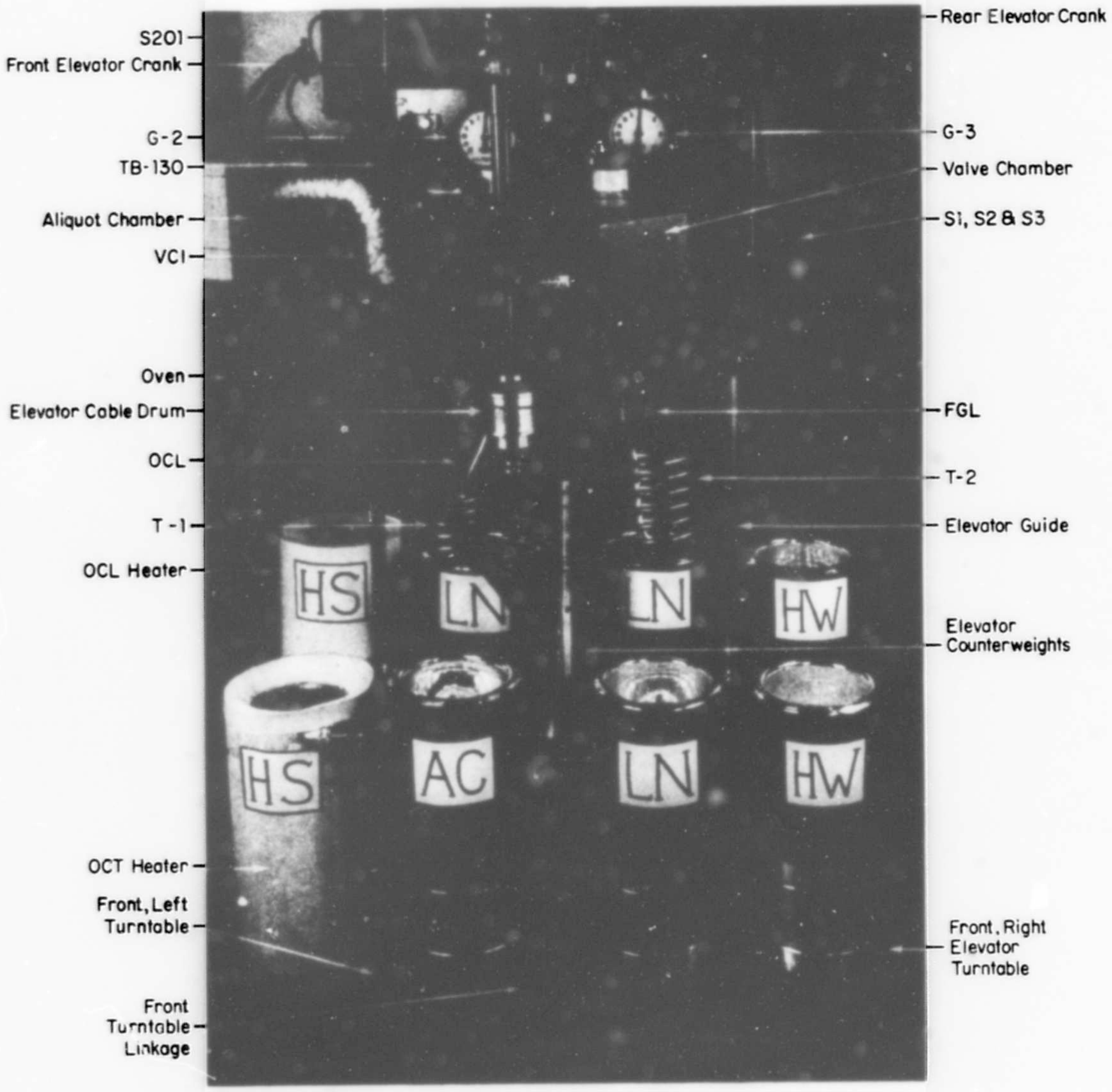


Fig. 3. Trap and loop temperature control baths and elevators.

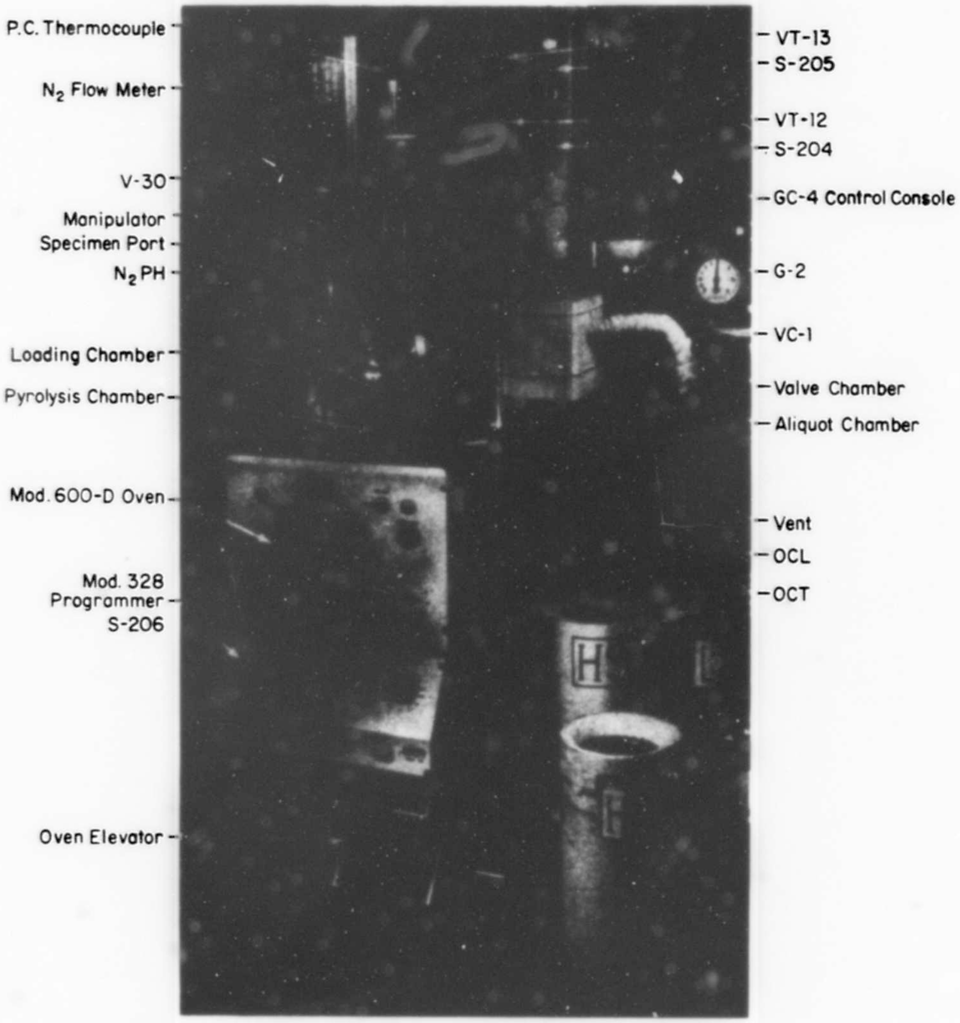


Fig. 4. Isothermal pyrolysis chamber and accessories.

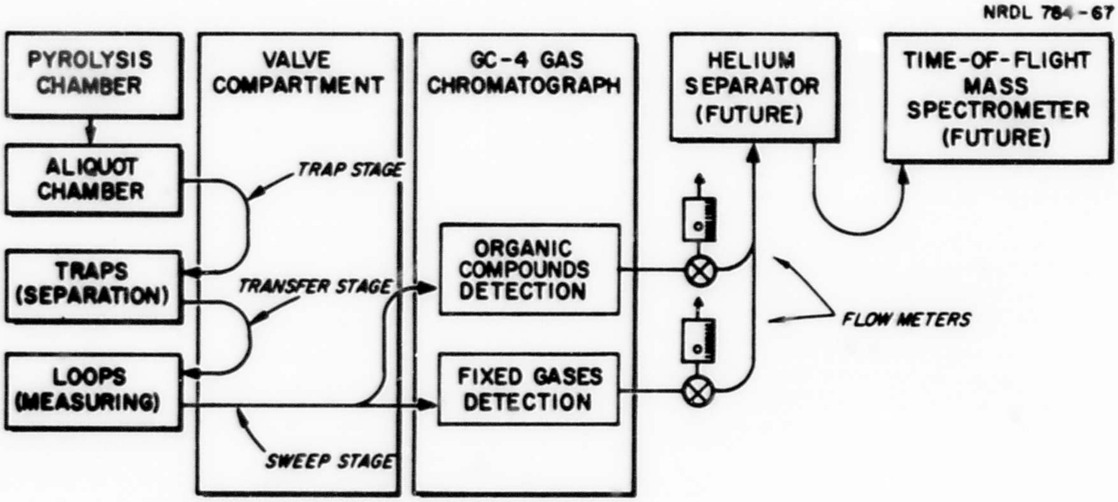


Fig. 5. Basic flow diagram of ultimate system for 2-stage separation, parallel gas chromatographic detection and single channel mass spectroanalysis.

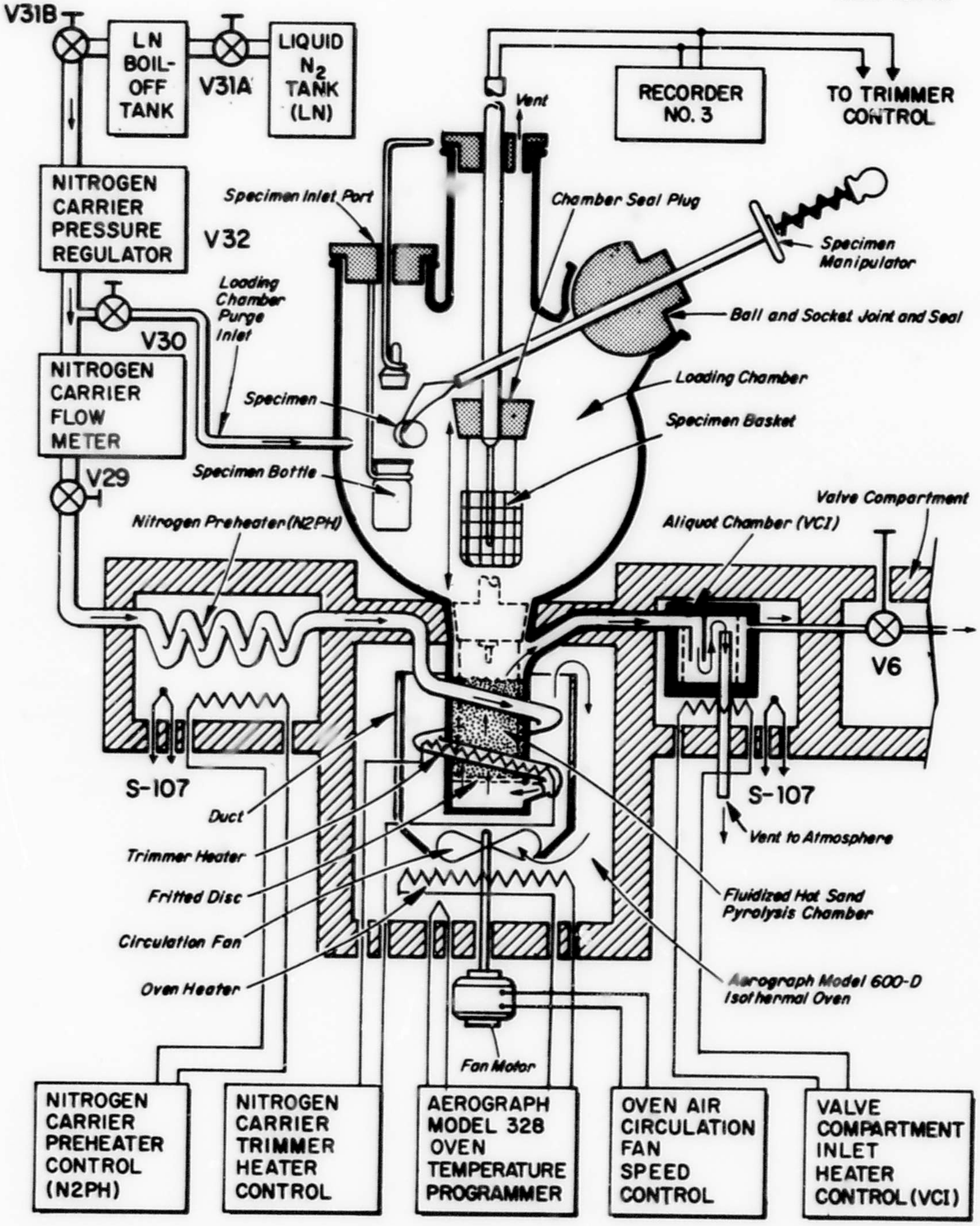


Fig. 6. Fluidized hot sand bath pyrolysis chamber and system.

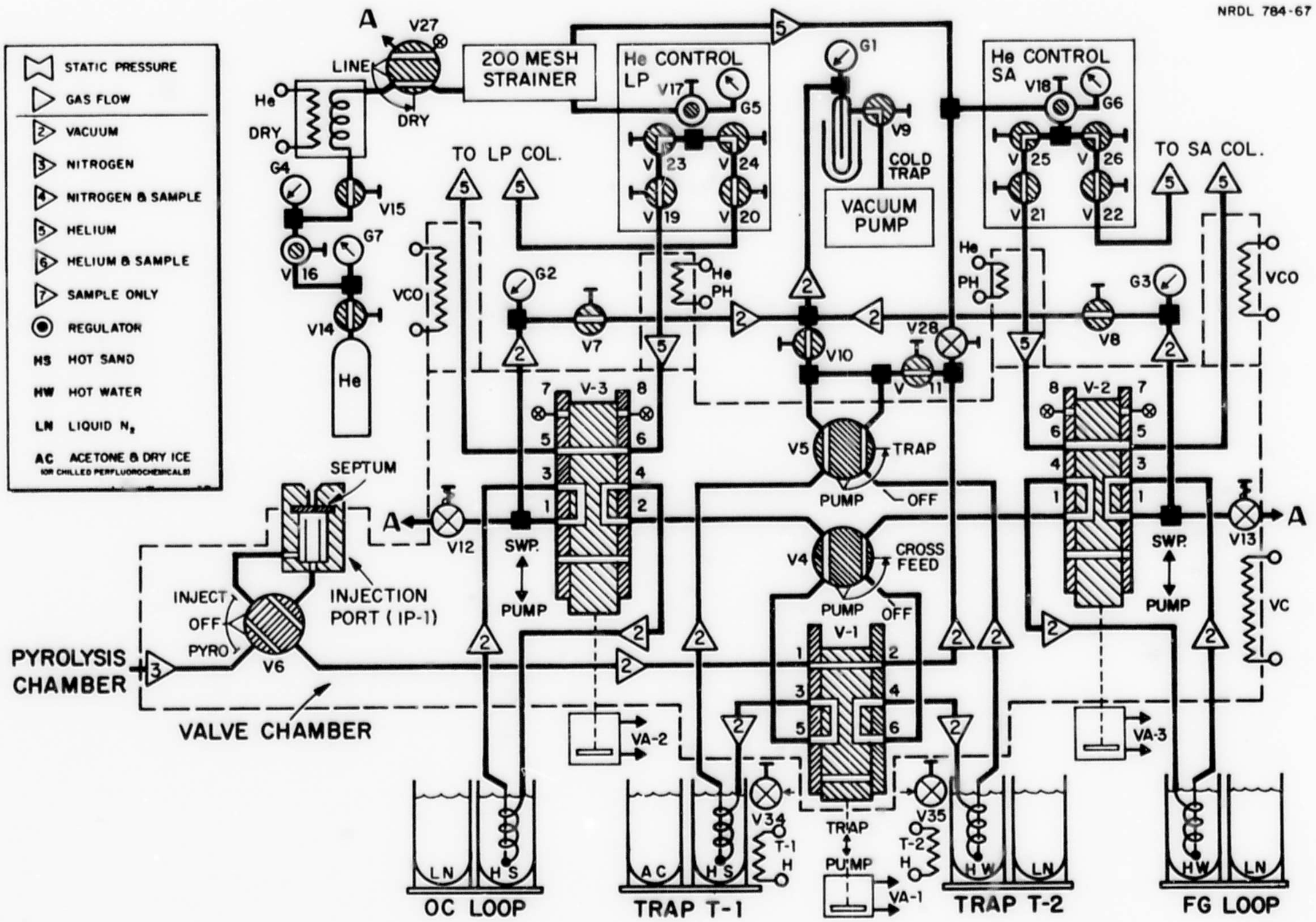


Fig. 7. General arrangement of valve chamber set for PUMP-I operational mode.

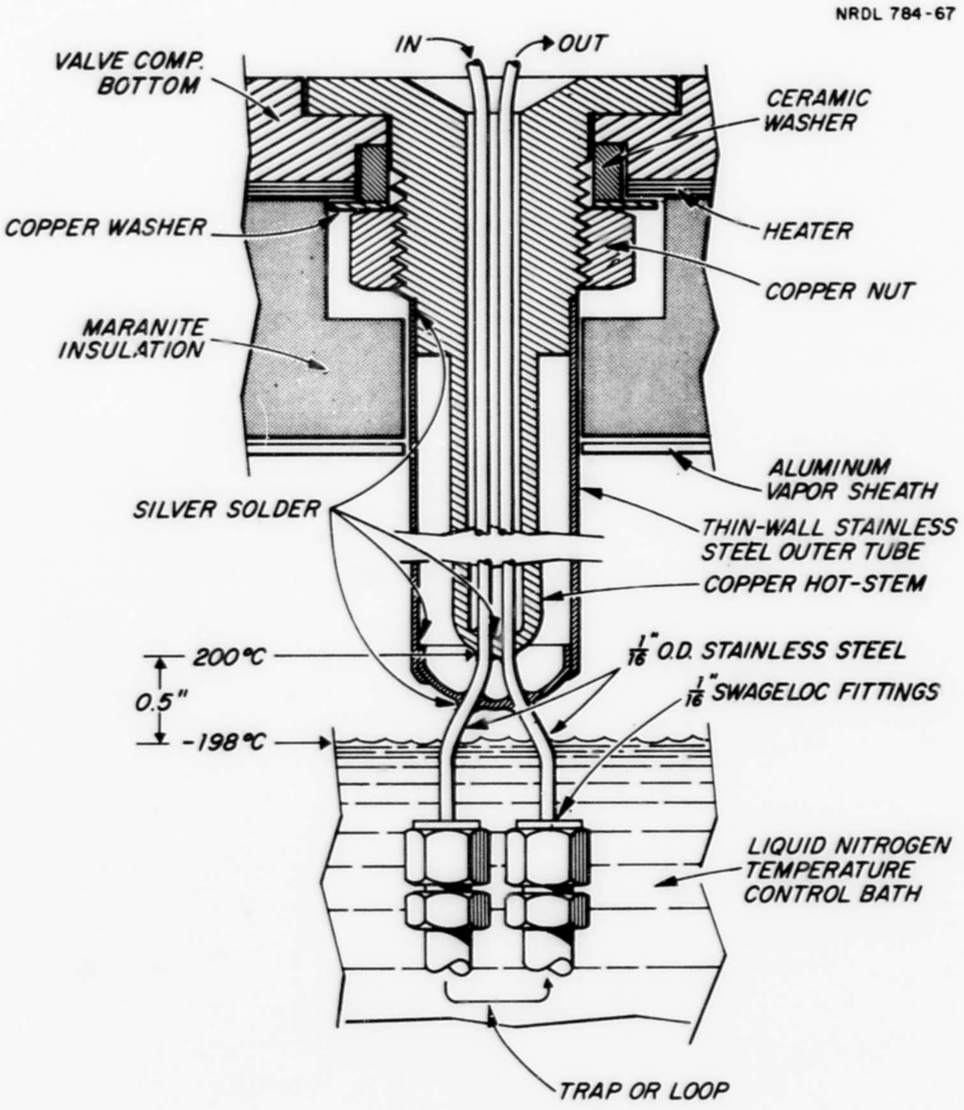


Fig. 8. Detail of typical trap or loop hot-stem.

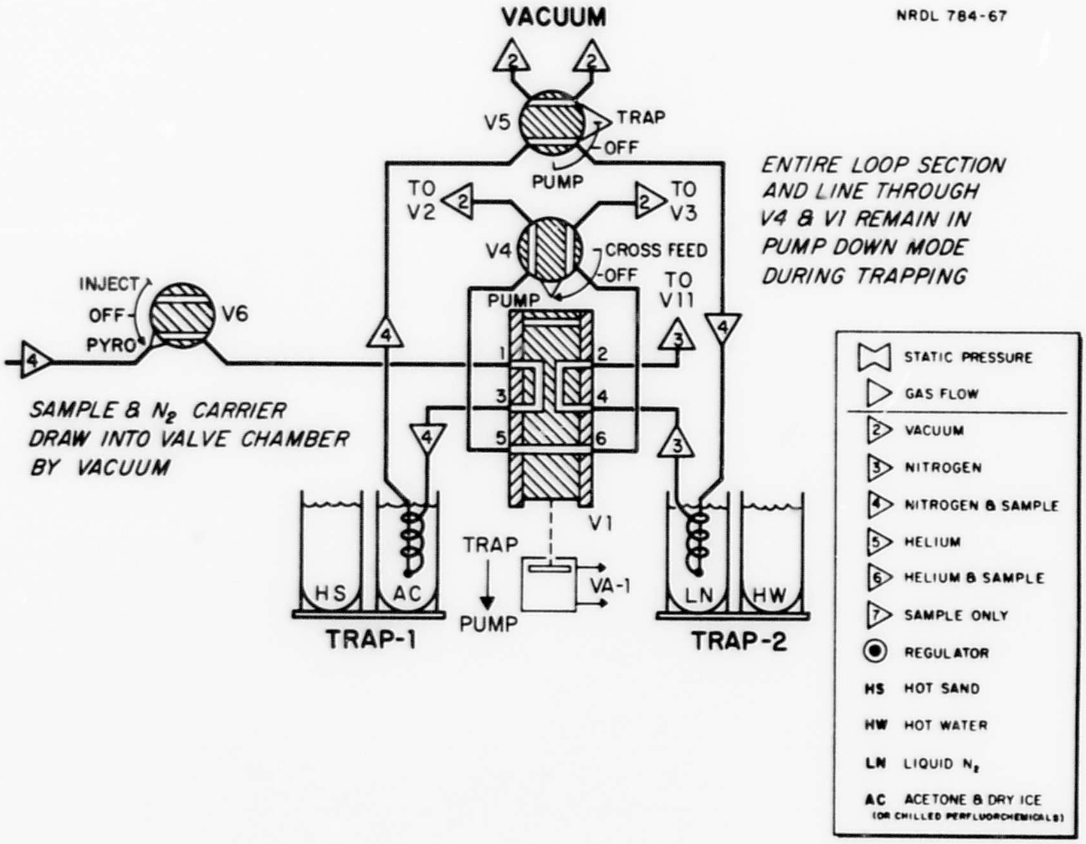


Fig. 9. Valve chamber settings for TRAP mode.

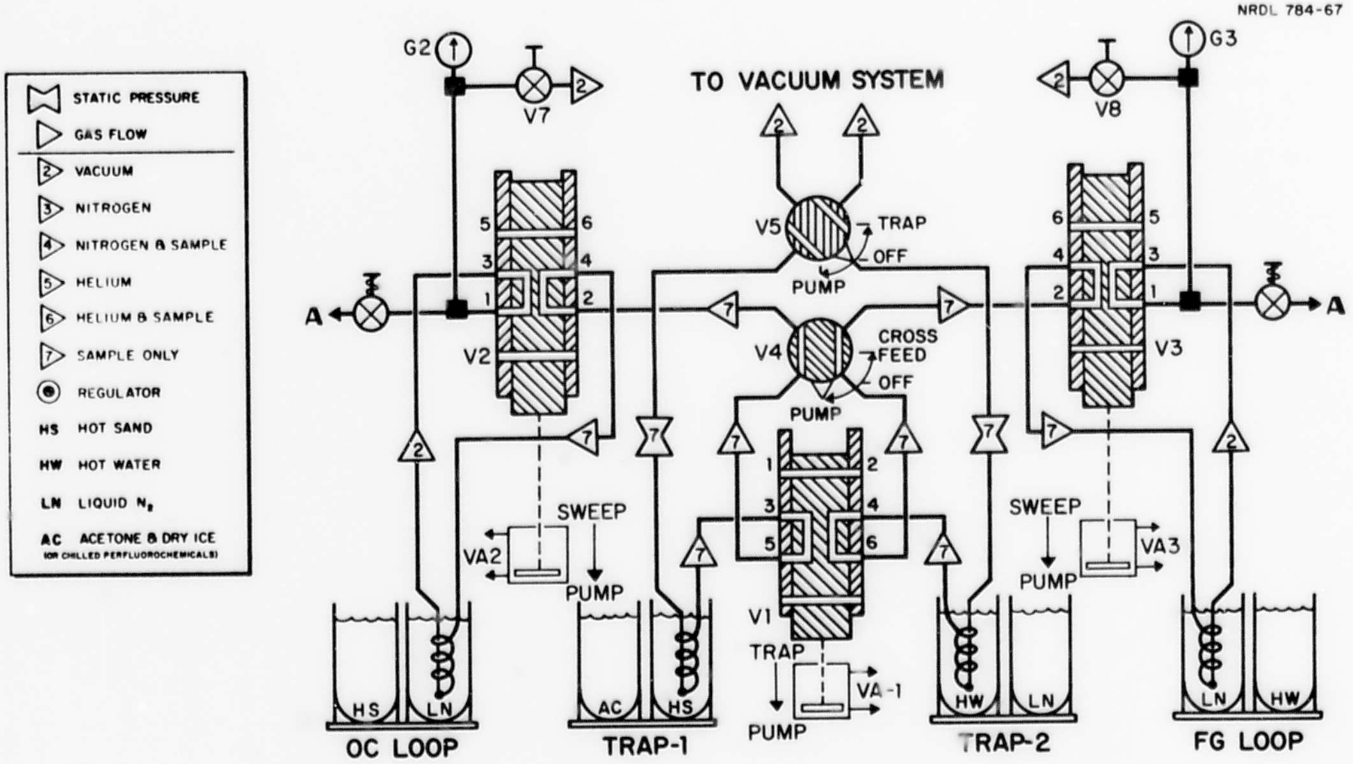


Fig. 10. Valve chamber settings for TRANSFER mode.

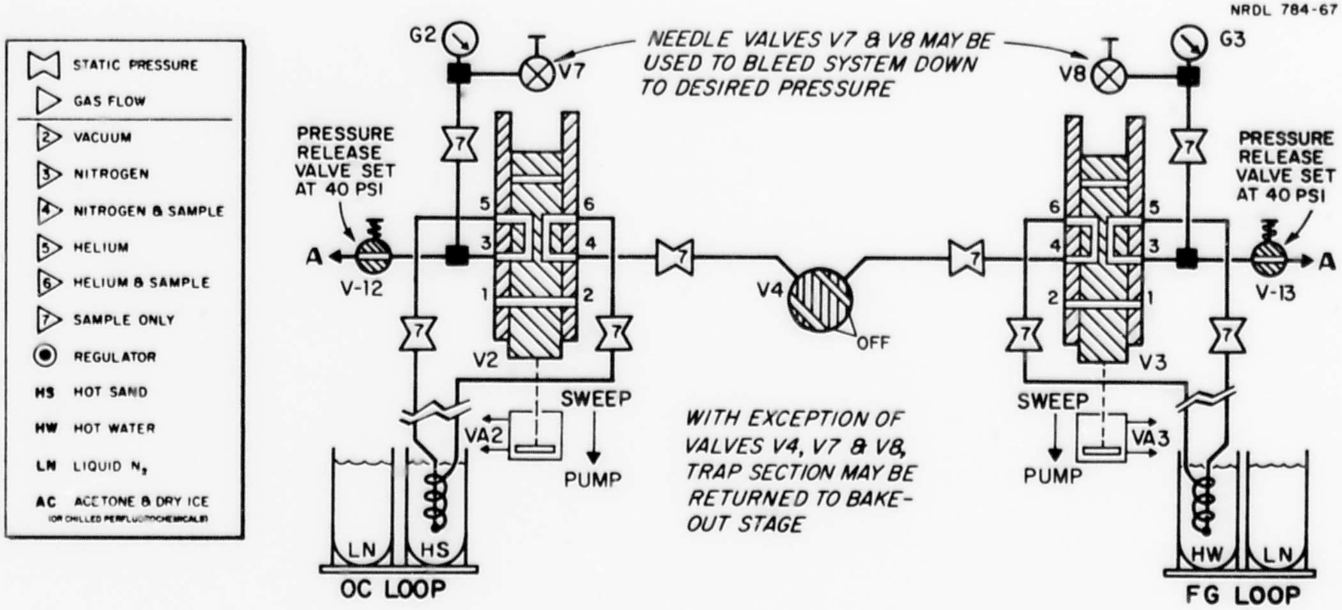


Fig. 11. Valve chamber settings for MEASURING mode.

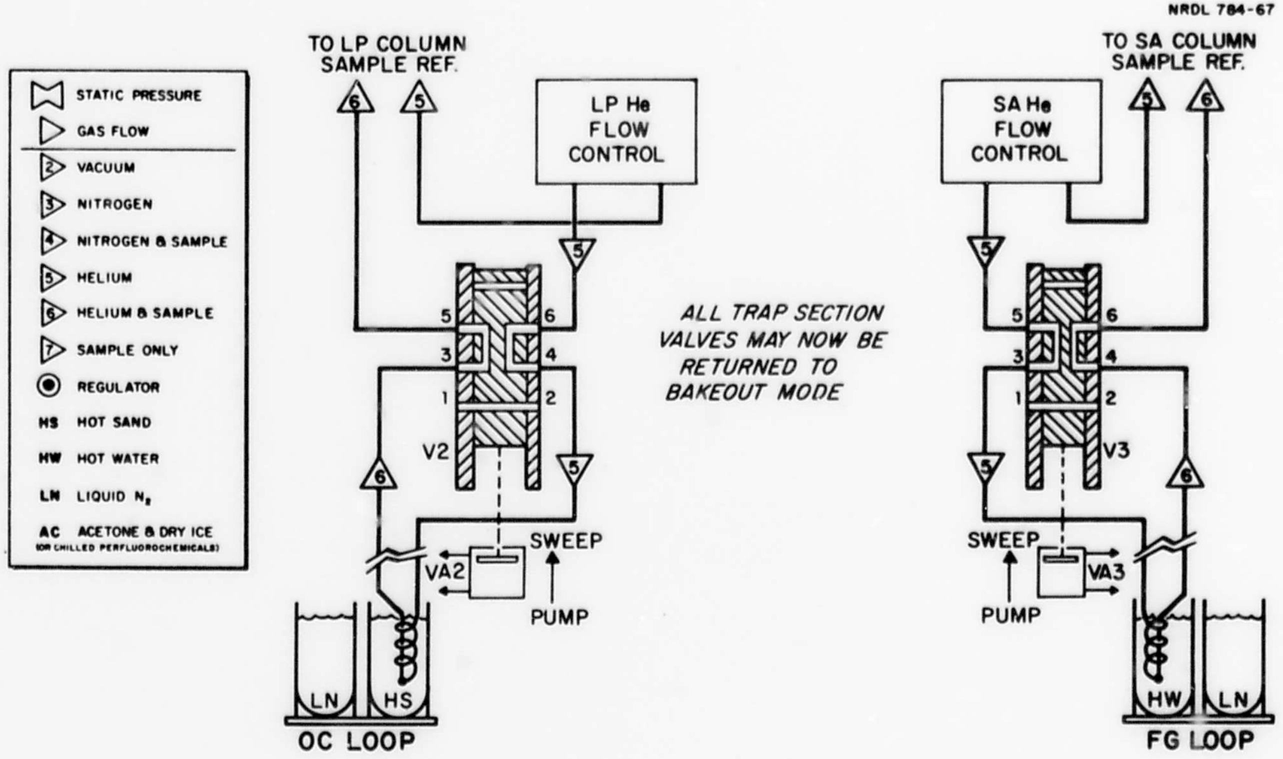


Fig. 12. Valve chamber settings for SWEEP mode.

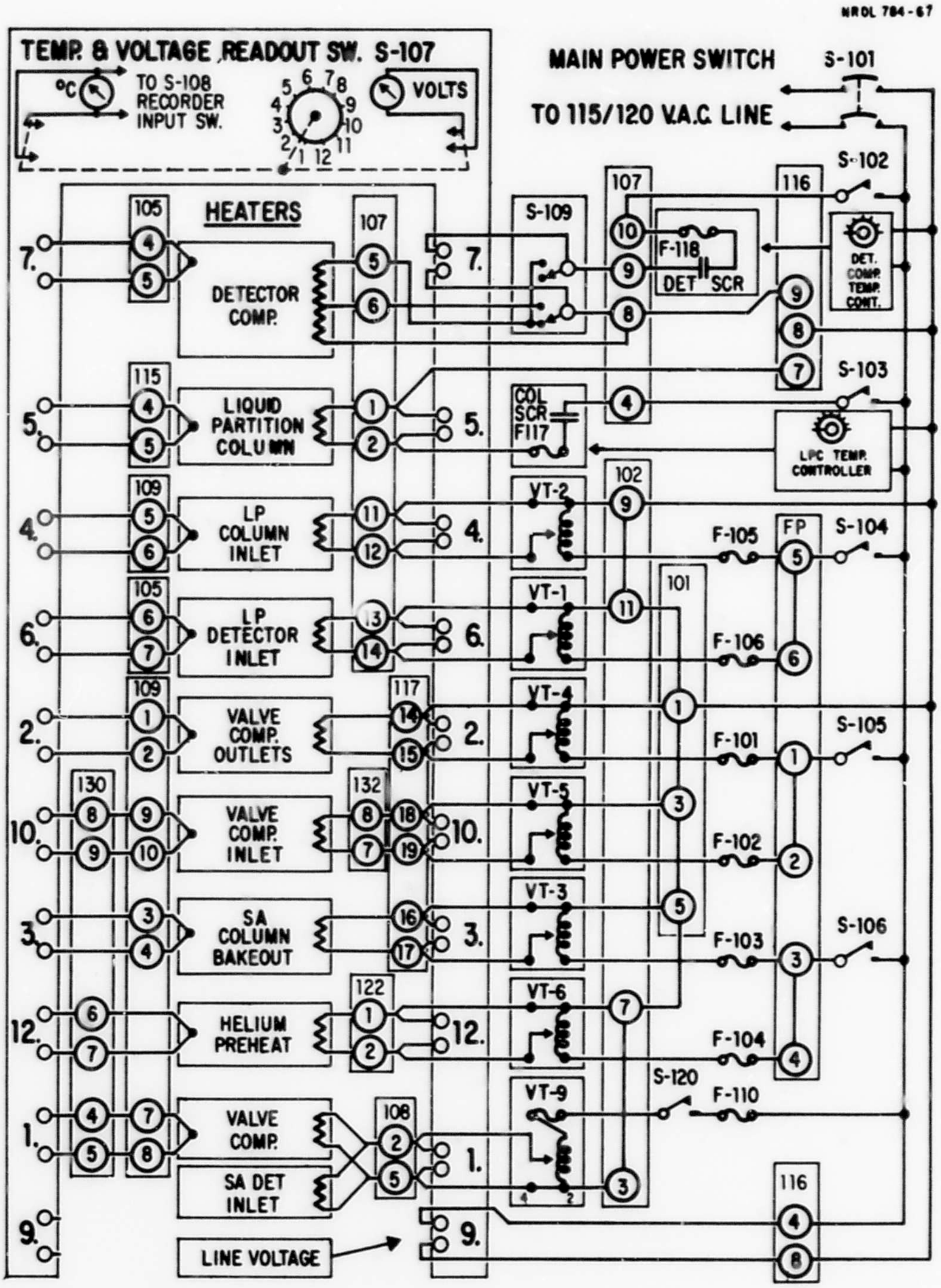


Fig. 13. Main power and temperature read-out switch circuits.

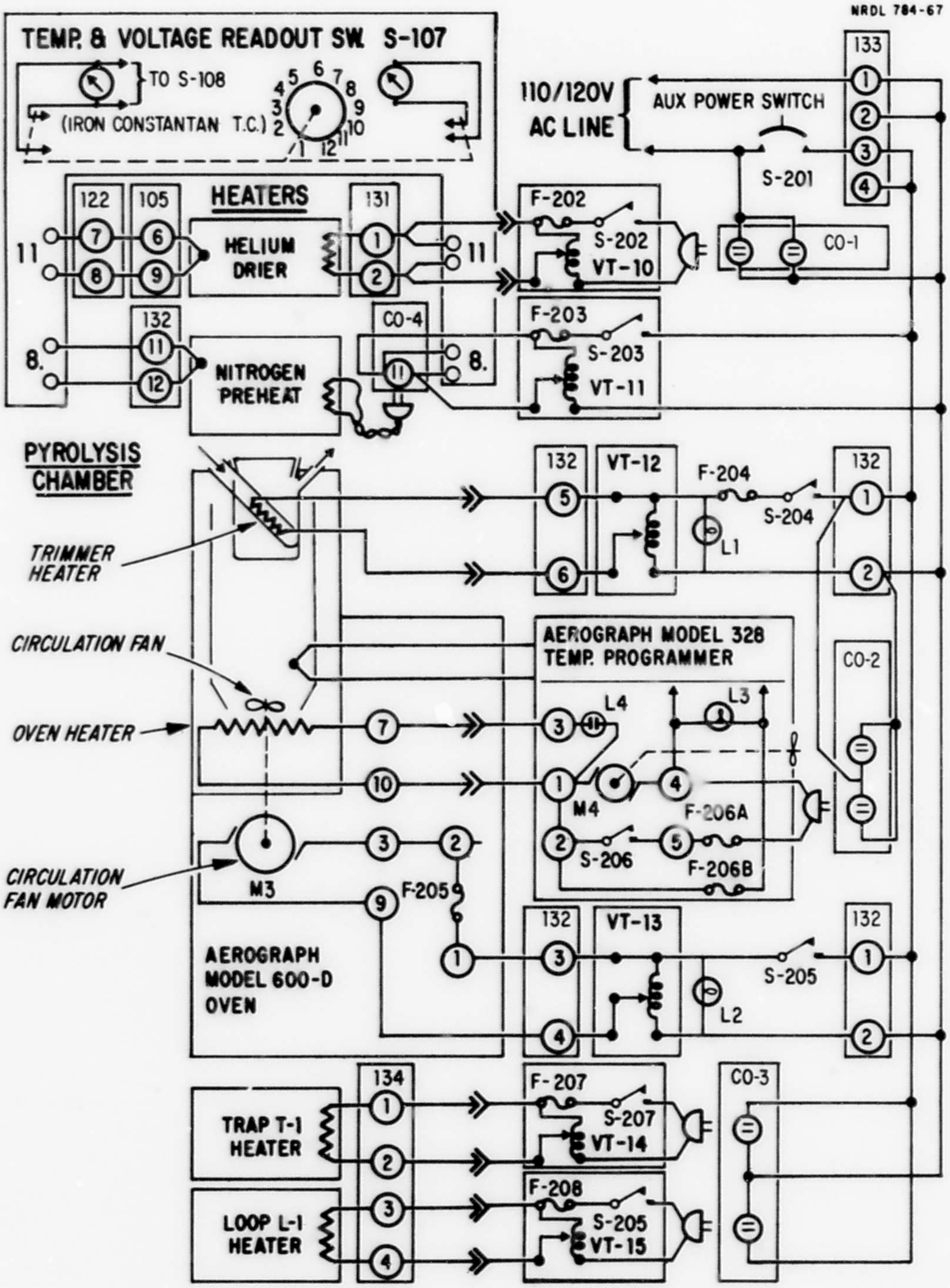
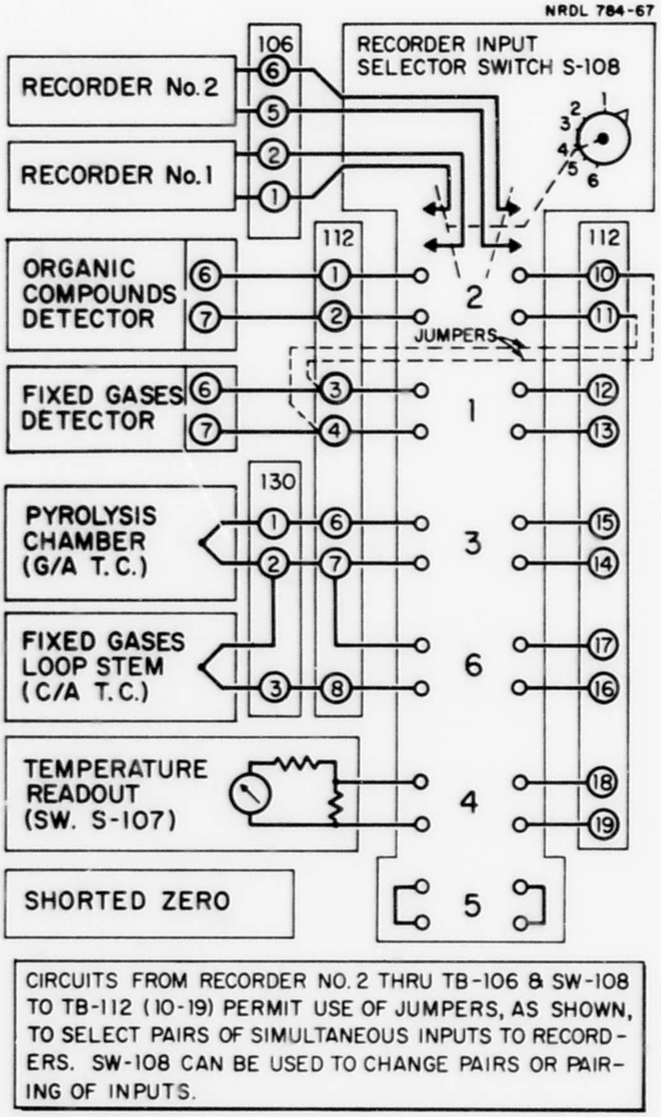


Fig. 14. Auxiliary power, pyrolysis system and temperature control bath circuits.



CIRCUITS FROM RECORDER NO. 2 THRU TB-106 & SW-108 TO TB-112 (10-19) PERMIT USE OF JUMPERS, AS SHOWN, TO SELECT PAIRS OF SIMULTANEOUS INPUTS TO RECORDERS. SW-108 CAN BE USED TO CHANGE PAIRS OR PAIRING OF INPUTS.

Fig. 15. Recorder input selector circuits.

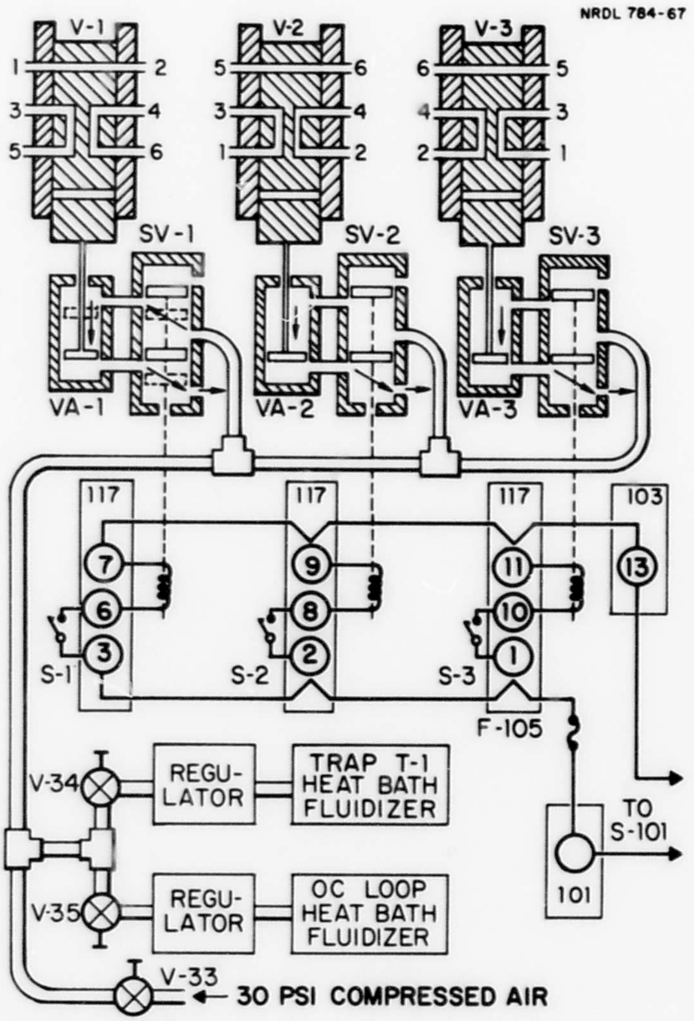


Fig. 16. Compressed air system and control circuits.

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13. ABSTRACT

A Beckman Instruments Company Model GC-4 Gas Chromatograph was modified to simultaneously analyze parallel inputs of organic compounds and fixed gases originating as the degradation products of isothermally pyrolyzed α-cellulose. The pyrolysis chamber and a complex gas-handling system for separating and concentrating the pyrolyzates were attached directly to the GC-4 cabinet, and a complete system of temperature control zones was established. A detailed description of the arrangement and operation of (1) an isothermal pyrolysis chamber for sample generation, (2) a temperature control and valving system for sample separation and concentration, and (3) a parallel liquid partition and solid adsorption gas chromatography system for sample analysis is presented. The technique is applied to trial analysis of the degradation products of white α-cellulose pyrolyzed isothermally for 10 minutes in a nitrogen-fluidized sand bath at 360°C.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gas chromatography						
Isothermal						
Degradation of polymers						
Polymers						
Cellulose						