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THE DEVELOPMENT OF AN AIRBORNE SYSTEM FOR THE SAMPLING OF ATMOSPHERIC ORGANICS

JUNE 1, 1971

BY:

R. L. CHUAN

Final Report, Contract No. NAS2-5421,
NASA Ames Research Laboratory

SYSTEMS DIVISION
ATLANTIC RESEARCH
A Division of The Susquehanna Corporation
Costa Mesa, California

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SECTION 1.0

INTRODUCTION

The development program described in this report is the second phase of a three-phase program designed by the National Aeronautics and Space Administration to help evaluate the concept that airborne atmospheric probes can be useful tools for observing and classifying planetary biological activity. In particular the program seeks to examine the uniqueness of pairing the flora of a biologically homogeneous region with the set of concentrations of organic chemicals found in the surrounding atmosphere when other parameters are fixed. If such relationships exist, they could yield significant information in the search for flora on other planets by looking for similarities to terrestrial forms.

The first phase, conducted by Stanford Research Institute and reported in Reference 1, demonstrated, in a prototype laboratory system, the basic validity of the theory. The second phase, reported herein, is to develop a properly engineering system that can be installed in an aircraft for flight sampling operations.

To this end the Systems Division of Atlantic Research has carried out a program to design, construct, laboratory-test, install and flight-test an airborne system for collecting, concentrating, and storing atmospheric organic chemicals. The program also included land based chromatographic analyses of the samples collected. These analyses together with all standard calibration mixtures used in the program were made by the staff of the California Statewide Air Pollution Research Center, located at the University of California at Riverside. The system, designated a "Flight Instrument for Airborne Collection of Atmospheric Organic Chemicals", has been produced and tested in accordance with the requirements stipulated in NASA Specification No. A-15136 and features automatic sequencing of certain critical functions to assure the safe and effective operation in flight by a single operator.

Central to the design and operation of the Atlantic Research sampling system is a variable temperature cryogenic dewar in which liquid nitrogen can be pressurized to maintain collection trap temperature at any selected value between 78° K and 100° K so that condensation of atmospheric oxygen can be avoided without the usual practice of using liquid argon. The operation of this device, called the Automatic Cryo-Trap, is automatic, thus freeing the operator from having to fill and empty an open dewar. In addition to the Automatic Cryo-Trap, the total sampling system is integrated in such a a way as to provide nearly automated sampling with a minimum of manipulations by a single operator, yet providing him with all necessary monitoring information and manual override capabilities. This makes it possible to operate the system in the confined space of an aircraft cabin, such as that of a Learjet, with ease and efficiency.

Reference 1 - Cavanagh, L. A., "Development of Instrumentation for Airborne Collection of Atmospheric Organic Chemicals," NASA-CR-73253, Sept. 1968, NASA Ames Research Center, Moffett Field, California.

One flight test was conducted with the system installed in a Learjet. Additional flight tests in the Learjet or the larger Convair 990 were not conducted as originally planned due to time and budget constraints. Calibration of the system, using known samples, did not yield satisfactory results, for probable reasons to be discussed. Despite the failure to achieve all calibration and test objectives, the basic effectiveness of the sampler system as an automated aircraft-mounted high altitude air sampler was successfully demonstrated.

This report describes the flight sampling system, its operation and calibration procedures, and results from flight and laboratory measurements. It concludes with recommendations for minor modifications to the system and the calibration procedure which should correct the inadequacies notes in the flight and laboratory tests.

SECTION 2.0

THE FLIGHT SAMPLING SYSTEM

2.1 PRINCIPLES OF OPERATION

The Flight Sampling System is basically a three stage system which uses the phenomena of physical adsorption and solution, phase equilibrium, and the principles of rate processes to: 1) collect, 2) transfer, and 3) store with sufficient concentration and minimum chemical modification those organic compounds which it finds in the gaseous state in its immediate atmosphere.

Flow direction and continuity in the sampling circuit are essentially produced and maintained by using a sorption vacuum pump to establish a "sink" with effectively zero absolute inlet pressure downstream of the final sample concentration point. Rate of flow is controlled solely by the pressure at the point of introduction of gas into the circuit.

Sample collection, or concentration within the sampled atmosphere, is accomplished within specifications using only the pressure difference between the "sink" and the total pressure of the sampled atmosphere relative to the Sampler's inlet to drive the atmosphere through a collector (first-stage trap) which is essentially an adsorption-displacement type gas-chromatographic column. Proper choice of the column packing and operating conditions assures almost 100 percent efficiency in the selective collection of the compounds desired.

At least one liter of atmosphere is passed through the trap where collection is effected by one or more of the mechanisms: physical adsorption, gas-solid phase equilibrium, and physical solution in a non-polar organic solvent. Since the trap has a free volume of approximately five cubic centimeters; the collection also represents a volumetric concentration by at least two hundred.

The second or transfer stage consists of releasing the sample from the collector, displacing it quantitatively from the first stage trap, and recollecting it in a container suitable both for storing and interfacing with gas chromatographs. Release is accomplished by heating the first-stage trap. Displacement and transfer are simultaneously effected by allowing chromatographically pure gaseous nitrogen to flow sequentially through the first and second stage traps - thus sweeping the former clean and allowing recollection in the latter. Collection, in terms of the physical processes involved, is basically the same as that of the first stage. By limiting the void volume of the second stage trap to approximately twenty microliters the process is a further volumetric concentration by a factor of two-hundred fifty.

To maximize the capacity of the two concentration stages and, at the same time minimize the rates of processes which might cause loss in "chemical identity" of the sample the values of pressure, temperature, and their gradients are reduced to levels consistent with the physics and engineering involved.

Storage is accomplished manually by withdrawing the filled second stage trap from its septum-type interface with the sampler, capping it to isolate its contents from the surroundings, and placing it in the proper location in a liquid nitrogen refrigerated cold box. Although storage is limited to about twelve hours per refrigerant charge, an automatic refill feature allows samples to be held for over six days without deterioration of their "chemical identity" when the system is connected to a standard 160 liter liquid nitrogen cylinder.

2.2 DESCRIPTION OF THE SAMPLING SYSTEM

The completed Flight Sampling System is shown in Figure 2-1; its essential features are shown in the schematic in Figure 2-2. It can be seen that functionally it is identical to the laboratory system reported in Reference 1. A detailed description of the system is best accomplished through reference to the flow schematic of Figure 2-2.

The Sampler consists of six subsystems, one of which is the major functioning unit, while the others perform support functions. These are listed below:

(1) Console

(2) Gaseous Nitrogen Supply System

(3) Liquid Nitrogen Supply System

(4) Recorders

(5) Sample Storage System

(6) Inlet-Exhaust Aircraft Interface

These subsystems are identified below and described in terms of their operational functions. Detailed descriptions of the individual components will be found in the Operating Manual of the Sampler.

2.2.1 Console

The console contains all the working components of the sampling system proper, with interface connections to ancillary support systems.

There are two parallel channels in the flow system which receive the incoming sample atmosphere. The α-channel is designed to collect hydrocarbons from C_1 to C_4; and the β-channel collects from C_5 to C_{10} (or higher).

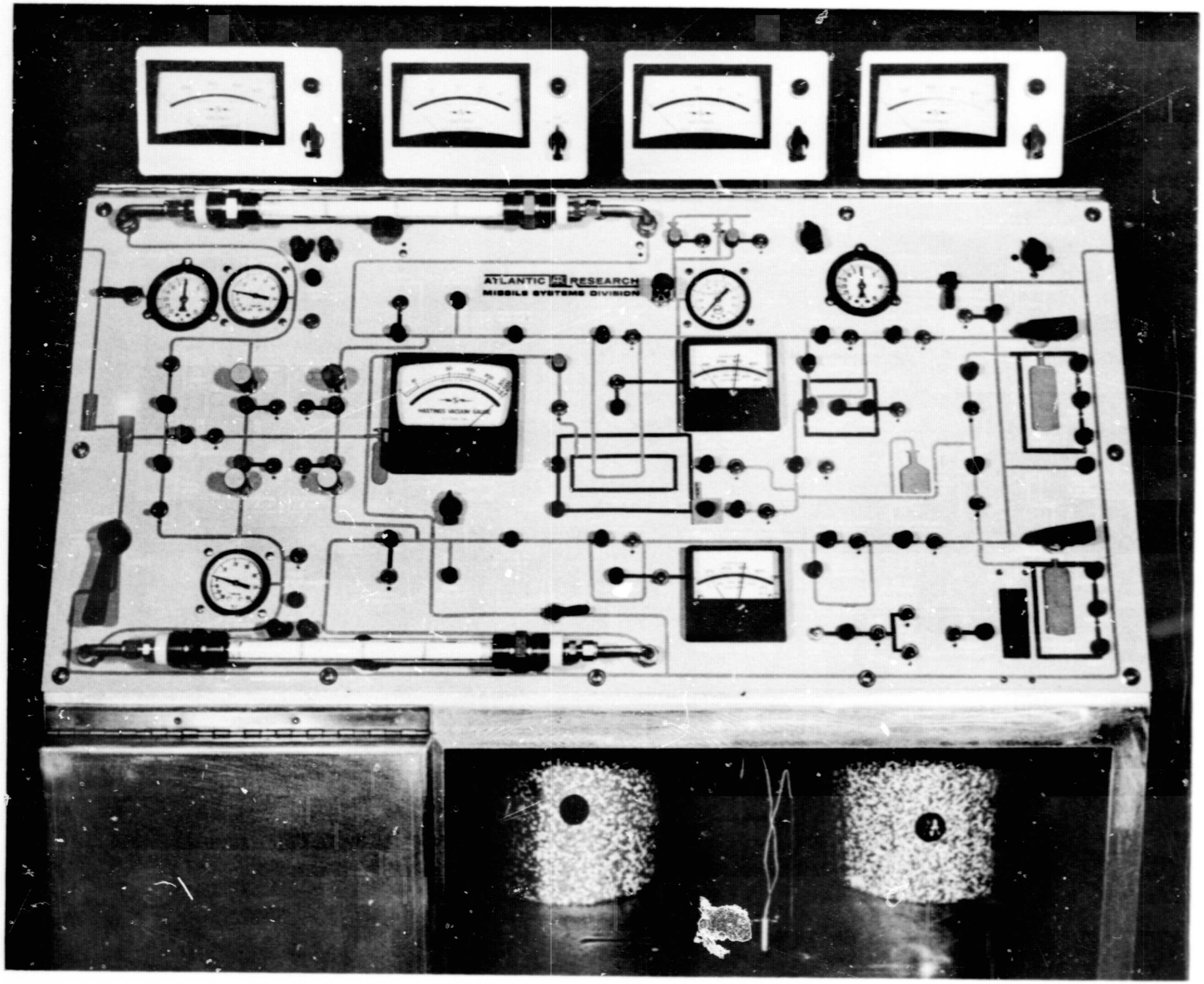
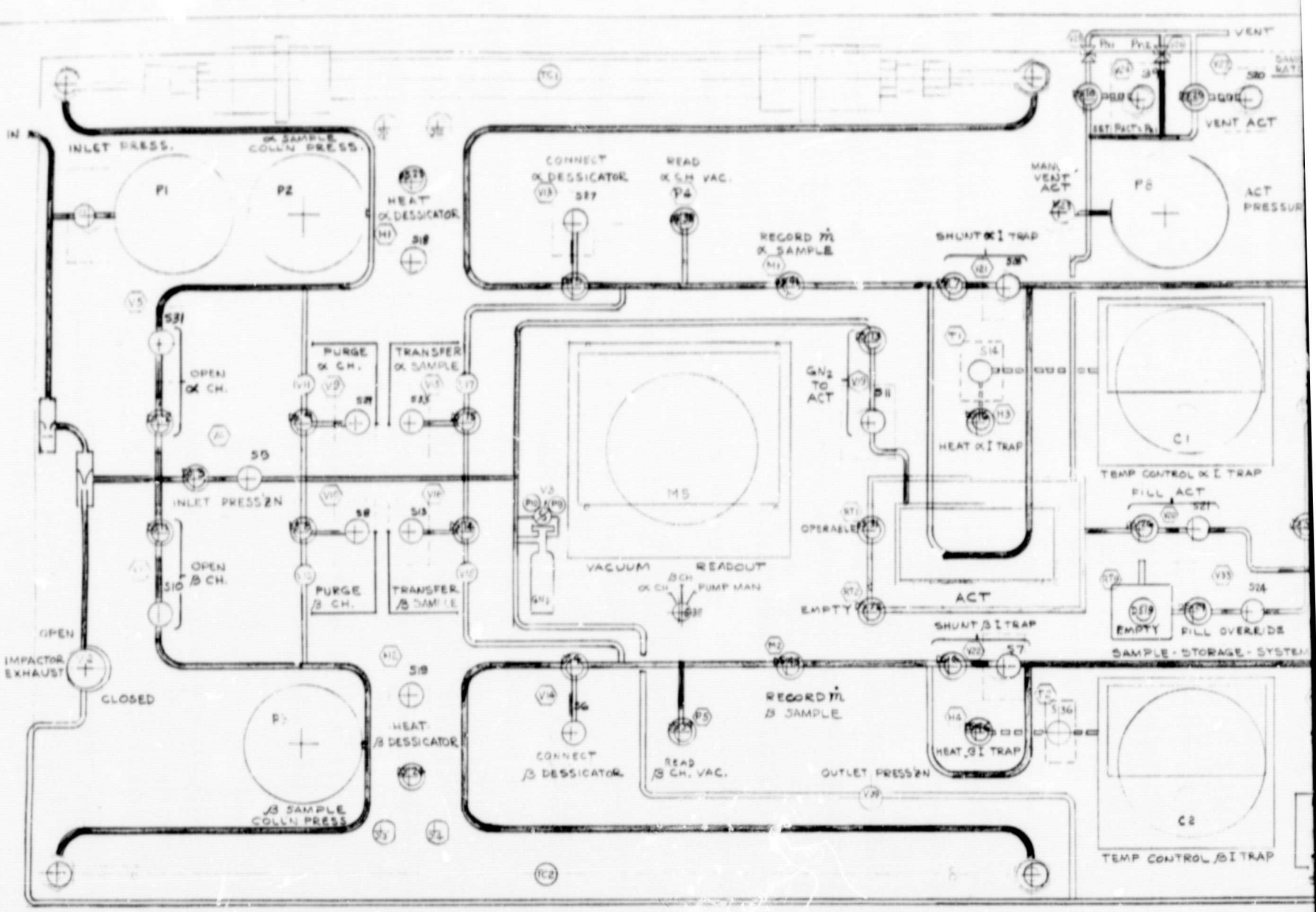
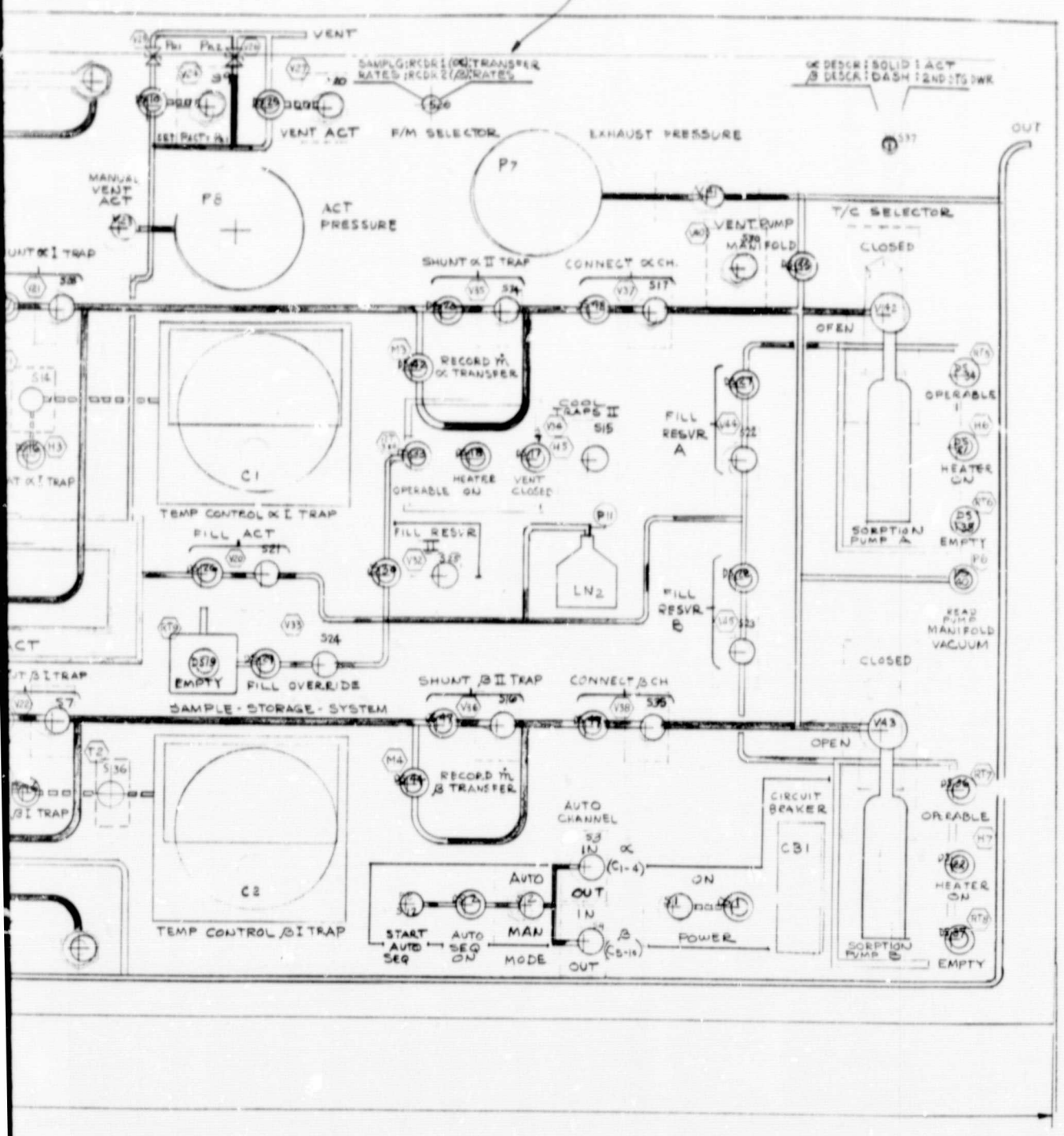


Figure 2-1. Ames Flight Sampler

FOLDOUT FRAME



FOLDOUT FRAME 2



COLOR CODE

SAMPLE ATMOSPHERE FLOW CHANNELS	GREEN
GASEOUS NITROGEN	YELLOW
LIQUID NITROGEN	BLUE
COMPONENTS	BLACK
EXTREMES & CONTROLS	RED

⬡ DENOTES ASSOCIATED COMPONENT

DASH	DASH	DASH	DASH	ITEM NO.	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION	MATERIAL	INITIAL / FINAL COND - HT TR	SPECIFICATION	DATA	ZONE
QTY REQ'D. PER ASSY				PARTS LIST / LIST OF MATERIAL							

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES ON:
ANGLES ± FRACTIONS ± .X DECIMAL ± .XX DECIMAL ± .XXX DECIMAL ±
PROCESS SPECIFICATION CPS 501-601 APPLIES
MATERIAL

DRAWN R.E. Dodd 12 Sept 69
DESIGNED
CHECKED
STRESS
APPROVAL
APPROVAL
PROJ. ENGR. Paul C. Weller

ATLANTIC RESEARCH
MISSILE SYSTEMS DIVISION
COSTA MESA, CALIF.

TITLE: CONTROL PANEL
FLIGHT INSTRUMENT

SIZE J | CODE IDENT NO. 09476 | 03-50013

NEXT ASSY | USED ON
APPLICATION

SCALE FULL | SHEET

Figure 2-2. Flow Schematic

2.2.2 Sample Inlet

These channels receive sample air free of particulate matter from a common inlet-impactor system consisting of a pitot probe located outside the aircraft and a two-stage impactor which removes particulate matter down to 1 micron size. In order to achieve adequate impaction efficiency more flow is maintained through the impactors than is necessary for sampling purpose, the excess air is exhausted outside the aircraft through valve V_2. The inlet pressure is indicated by gauge P_1, connected to the inlet line through valve V_1.

The pitot probe outside the aircraft is sealed with a mylar diaphragm to prevent contaminants from entering prior to collection at altitude. The diaphragm is removed by pressurization with the high pressure gaseous nitrogen supply, through the Inlet Pressurization Valve, V_4.

2.2.3 Dessicator

The particulate-free sample air is divided into the two sampling channels: to α-channel through valve V_5, and to β-channel through valve V_6. The sample air goes through a dessicator, and the inlet pressure to the dessicator is indicated by a pressure gauge - P_2 for α-channel, and P_3 for β-channel. The dessicant used is potassium carbonate, with Drierite as saturation indicator. Sample transmission efficiencies near 100% are obtained by heating the dessicator to between 50° and 60° C. The temperature is monitored by a thermocouple held against the dessicator tubes by a thermally insulating pressure pad - TC1 for α-channel and TC2 for β-channel.

2.2.4 First Stage Collection System

The moisture-free sample air goes into the first stage collection system through trap αI for α-channel and trap βI for β-channel. The pressure into the first stage trap is read by a vacuum gauge, and sampling flow rate is measured with a flowmeter.

Both first stage traps are housed inside the Automatic Cryo-Trap (ACT) which maintains a temperature of 95°K during sample collection by means of pressurized liquid nitrogen in the inner chamber of a two-chamber dewar container. Differential pressure actuated valves in the inner chamber allow liquid nitrogen to flow into or out of the inner chamber. Pressure in the ACT is regulated by a system of preset check valves in the vent line. The liquid in the outer dewar will become pressurized through heating to the pressure set by the check valve, and this increased pressure causes the transfer valves between the outer and inner dewars to open and transfer liquid nitrogen to the inner dewar.

Flow may be shunted past the first stage trap, for purposes of system check-out, through by-pass valves.

At the completion of sample collection in the first stage traps liquid nitrogen is emptied from the inner chamber into the outer chamber of the ACT, by means of pressurization of the inner dewar with gaseous nitrogen. At the same time the pressure in the outer dewar is reduced by the opening of a by-pass valve. With the inner chamber free of liquid nitrogen the first stage trap is heated by current passing through the thin shell of the trap. Temperature control is effected by automatic controller.

There is an emergency manually operated vent valve which is to be used in case of failure of all three of the solenoid actuated valves in the venting circuit.

2.2.5 Sample Transfer and Second Stage Collection

With the first stage trap heated the collected sample is transferred to the second stage trap by means of high purity gaseous nitrogen through a metering system. The high pressure nitrogen gas is fed into the system through a regulator valve and directed to the first stage traps. The sample released from the first stage trap, carried by the transfer flow of gaseous nitrogen, passes through the second stage trap, with metered flow rate.

The second stage traps are housed in the upper section of a two-section dewar, with the lower section acting as the reservoir for liquid nitrogen (Reservoir II). During filling and hold the reservoir is vented to the atmosphere. To cool the second stage traps, liquid nitrogen is transferred to the upper section by pressurizing the lower section. This is effected by closing the vent valve and at the same time turning on a heater.

2.2.6 Vacuum Pumping System

The flow of gas through the sampling system is maintained by a cryo-sorption pumping system consisting of two cryo-sorption pumps A and B, cooled in liquid nitrogen in their respective dewars. The two pumps are connected to a common manifold. Activation of the sorption pumps is accomplished by heating and venting to an external mechanical vacuum pump (not part of the Sampler System).

Filling of the pump dewars with liquid nitrogen is effected through valve V44 for Reservoir A and V45 for Reservoir B, actuated by switches S22 and S23, indicated by lamps DS27 and DS28 respectively. Liquid level in the dewar is sensed by RT5 (operable, lamp DS34) and RT6 (empty, lamp DS35) and A and by RT7 (operable, lamp DS36) and RT8 (empty, lamp DS37), for B.

2.2.7 Purge System

The entire flow system can be purged with high purity gaseous nitrogen, with the purge gas entering upstream of the dessicator inlet, with the flow rate set by metering valves.

2.2.8 Electrical and Control System

The electrical system supplies power to the valve actuating solenoids, the various heaters and liquid level sensors, the temperature controllers, the vacuum gauges and flow meters.

Solenoids:	115 volt A.C.
First Stage Traps:	Low voltage high current from current transformers, controlled by temperature controllers through auto-transformers.
Dessicator Heaters:	Heaters powered by a variable voltage auto-transformer.
Sorption Pump Heaters:	Powered by a variable auto-transformer
Liquid Level Sensors:	26.8 v from a transformer

The entire sampling operation can be controlled manually or automatically through a Program Controller. The programmer is a motor-drive train of cams which actuate relay switches to control the sequencing of various functions. The Mode Switch selects manual or automatic operation. Either of both α and β channels can be placed in auto mode. Auto mode can be overridden any time by switching back to manual, and returned again to auto mode; though the programmer cannot be advanced or retarded during manual override.

2.2.9 Gaseous Nitrogen Supply System

For control and purging purposes high pressure gaseous nitrogen is supplied to the Sampler Console from a high pressure bottle (not supplied as a part of the system) through a two-stage regulator. The regulated reduced pressure gaseous nitrogen enters the console at a manifold marked "Purge GN_2".

2.2.10 Liquid Nitrogen Supply System

Liquid nitrogen for the console and the Sample Storage is supplied from a 50-liter dewar pressurized by heat conduction to a pressure preset by a pressure relief valve. An insulated transfer line takes the liquid nitrogen to the Console, interfacing there with an insulated manifold at the poing marked "LN_2".

A branch transfer line goes to the Sample Storage.

2.2.11 Recorders

Three strip chart recorders are used to record flow rates and temperatures during the sampling operations. A single channel recorder records, when switch to the Console α-channel flow rate for sampling or transfer. Another single channel recorder similarly records flow rate through β-channel. A third dual-channel recorder records thermocouple outputs from the Console.

2.2.12 Sample Storage System

Concentrated samples collected in the second stage traps αII and βII are stored in a dewar with a liquid nitrogen capacity of about 10 liters, sufficient to keep the sample cold for about 12 hours at one filling. An automatic filling system will keep the system filled.

The second stage traps are inserted through slots in a fiberglass float so that they are always immersed in the liquid nitrogen regardless of its level. There are three rows of sample insertion slots, with nine slots in each row, making a total storage capacity of twenty-seven samples.

2.2.13 Inlet-Exhaust Aircraft Interface Assembly

An interface assembly attached to the skin of the aircraft connects the exterior to the interior. There is a forward-facing inlet probe and two rearward-facing exhaust probes. One of the latter is for venting nitrogen gas from vaporized liquid nitrogen from the ACT. The other is for the exhaust of gases from the Sampler Console. Since for flight sampling the sorption vacuum pumps are used for exhausting the sampling channels, the exhaust probe is used only for exhausting the excess flow from the Impactor.

SECTION 3.0

OPERATION OF THE FLIGHT SAMPLER

3.1 PRELIMINARY PREPARATION

3.1.1 Purge Second Stage Traps

A sufficient number of second stage traps should be placed in an oven at 230°C and purged with high purity gaseous nitrogen for at least two hours at a purge flow rate of 30 std mℓ/min through each trap. The purged traps, along with septums and caps should be stored in a clean container.

3.1.2 Cover Aircraft-Mounted Probes

The inlet probe mounted outside the aircraft should be covered with 1/2 mil mylar, by securing the mylar to the probe with a sleeve of 1/2 inch Teflon shrinkfit. The exhaust probe connecting to the vacuum manifold is left uncovered, and connected to an external mechanical vacuum pump.

3.1.3 Purge Sorption Pumps and Sampler

Purge sorption pumps and sampler system with auto-transformer T6 set at 50%, turn on pump heaters H7 and H8 while pumping, through V40, V42 and V43, with a mechanical vacuum pump, for 2-1/2 hours. Simultaneous with this, and using the same mechanical pump, purge the sampler system by flowing 100 std mℓ/min of high purity gaseous nitrogen through each channel. This is accomplished by activating the α- and β-channel purge controls - S29 and V11, S8 and V12. The gaseous nitrogen supply is set at 60 psi. Since the inlet and exhaust probes are sealed, V5 and V6 should be closed. The first stage traps should be heated to 130°C during this purging operation; and the second stage by-pass valves, V35 and V36 should be open. The dessicators should be heated to 60°C. At the end of the purge period close V42 and V43 to isolate the sorption pumps. Check the rubber sleeve valves on the pumps to ensure they are closed.

While still pumping on the sampler system, the metering valves V11 and V12 are to be set for 200 std mℓ/min. Turn off first stage trap heaters. The dessicator heaters are left on if the system is to be used immediately after this preliminary preparation period. Otherwise, turn off dessicator heaters.

Check flow-meters M1 and M2 and recorders to confirm proper operation.

Shut off purge flow. Check system for vacuum integrity by means of vacuum gauges P4, P5 and P6.

Turn off mechanical pump, but leave it connected to the system.

3.1.4 Fill Sample Storage System

Using a ground based liquid nitrogen supply, instead of the 50-liter unit in the aircraft, manually fill the sample storage system.

3.1.5 Cool Sorption Pumps

Allow the sorption pumps to cool down to near room temperature, with the help of a fan if desired, before raising the liquid nitrogen dewars to enclose the pumps. Place the anti-slosh collars over the dewars. Fill manually with liquid nitrogen from ground-based supply. When pumps are cold, check vacuum with V40, V37 and V38 closed, V42 and V43 open, using P6 to read vacuum.

3.1.6 Cool-Down of Automatic Cryotrap

First purge the ACT vent system thoroughly with gaseous nitrogen, while it is at room temperature, to ensure that there be no water present which would clog the system when cold. This is accomplished by supplying gaseous nitrogen through V19.

Fill the ACT with ground-based liquid nitrogen, through the sampler system LN_2 inlet.

3.1.7 Insert Second Stage Traps

Pressurize system, with high purity GN_2 to slightly above ambient pressure about 10 psig on P2 and P3. This is accomplished by closing V5, V6, V37 and V38, opening V35, V36, V13, V14, V9 and V10. V9 and V10 are left on long enough to bring the pressure to 10 psig, then turned off. This pressure is maintained in order to prevent any in-flow of ambient air when the second stage traps are inserted into the septums.

Insert first the upstream end of each second-stage trap, then the downstream end. This ensures positive pressure in the trap while it is being inserted.

Pump the system back down with the mechanical pump through V40. (V42 and V43 are closed.) Check for vacuum integrity.

3.1.8 Set Flow Rate

Set flow rate through second stage traps with V13, V14, V21, V22, V35 and V36 closed, V37 and V38 open, set transfer flow rate, with the "Transfer α Sample" and "Transfer β Sample" controls, to 20 std mℓ /min through each second stage trap. Use mechanical pump.

3.1.9 Disconnect Mechanical Pump

With V40 closed, disconnect mechanical pump from the exhaust probe.

3.1.10 Cover Exhaust Probe

Using same technique as in 1.2 above, cover the second exhaust probe.

3.1.11 Switch to On-Board LN_2

Disconnect the ground-based LN_2 supply, connect the on-board 50-liter dewar to the LN_2 inlet on the sampler console.

This completes the preliminary preparation.

3.2 FLIGHT SAMPLING

3.2.1 Top Off ACT

At 25 minutes before the first sample is taken (T-25) top off the ACT with the on-board LN_2 supply.

3.2.2 Fill Reservoir II

At T-10 fill the second stage trap dewar with LN_2. Turn the toggle of S39 to the up-position.

3.2.3 Verify Dessicant Temperature

If dessicator heaters have been off, turn on. Set temperature at 60°C.

3.2.4 Verify ACT Temperature

The proper operating temperature of the ACT, as marked on the recorder, is -179°C. The corresponding pressure is 56 psi, as read on P8.

3.2.5 Verify Second Stage Dewar Temperature

Referring to the recorder, verify temperature to be -190°C.

3.2.6 Raise Second Stage Trap Temperature

After checking dewar temperature, turn on heater H6 with S43 in the upper section of the dewar to keep the second stage traps near ambient temperature while sampling takes place.

3.2.7 Remove Probe Covers

First remove exhaust cover. Close "Impactor Exhaust" valve V2. Open V41. Open "Outlet Pressurization" valve V39, for a few seconds. The exhaust pressure P7 should rise, to about 10 psi, then drop, indicating removal of cover. Close V39.

With V2 still closed, close V5 and V6. Open V1. Open V4 "Inlet Pressurization" to pressurize inlet. Inlet pressure P1 should rise to about 10 psi, then drop, indicating removal of inlet cover. Close V4.

3.2.8 Purge Inlet Line

Close "Connect α Dessicator" and "Connect β Dessicator" valves, V13 and V14. Open V5 and V6. Open "Purge α Ch" and "Purge β Ch" valves, V9 and V10, to purge inlet line for about 2 minutes. Close V9 and V10, V5 and V6. Open V13 and V14.

3.2.9 Open Impactor Exhaust Valve

Open V2 to establish flow through impactors.

3.2.10 Connect Sorption Pumps

Close "Connect α Ch" and "Connect β Ch" valves, V37 and V38. Open V42 and V43. Confirm vacuum in manifold with "Vacuum Readout" selector switch on "Pump Man".

3.2.11 Verify All Manual Switches are off

3.2.12 Verify Programmer is at Start Position

3.2.13 Place Sampler in "Auto Mode"

3.2.14 Place F/M Selector Switch to "Sample Rate"

3.2.15 Place Thermocouple Selector Switch to Record ACT Temperature

3.2.16 Ready to Sample

Initiate by pressing "Start Auto Seq" switch, S12.

3.2.17 Top Off ACT and Reservoir II

While sampling is under way, top off liquid nitrogen in ACT and Reservoir II.

3.2.18 End of Sampling

Return sampler control to Manual Mode

3.2.19 Second Stage Trap Removal

At the end of the sampling and sample transfer sequence prepare to remove the second stage traps from the console to the sample storage. This must be accomplished rapidly to minimize the chances of sample contamination. First, pressurize the system above ambient, as in Step 2.7. Back off on septum nuts about 1/3 turn to loosen septums. Open lid of sample storage. Remove second stage traps. Cover with caps. Insert in sample storage. Close lid.

3.2.20 Install New Second Stage Traps

Warm up the upper section of the second stage dewar with heater H5, as in Step 2.6 above. Insert second stage traps, upstream end first.

3.2.21 Pump System Down

3.2.22 Ready to Sample Again

Return to Step 11.

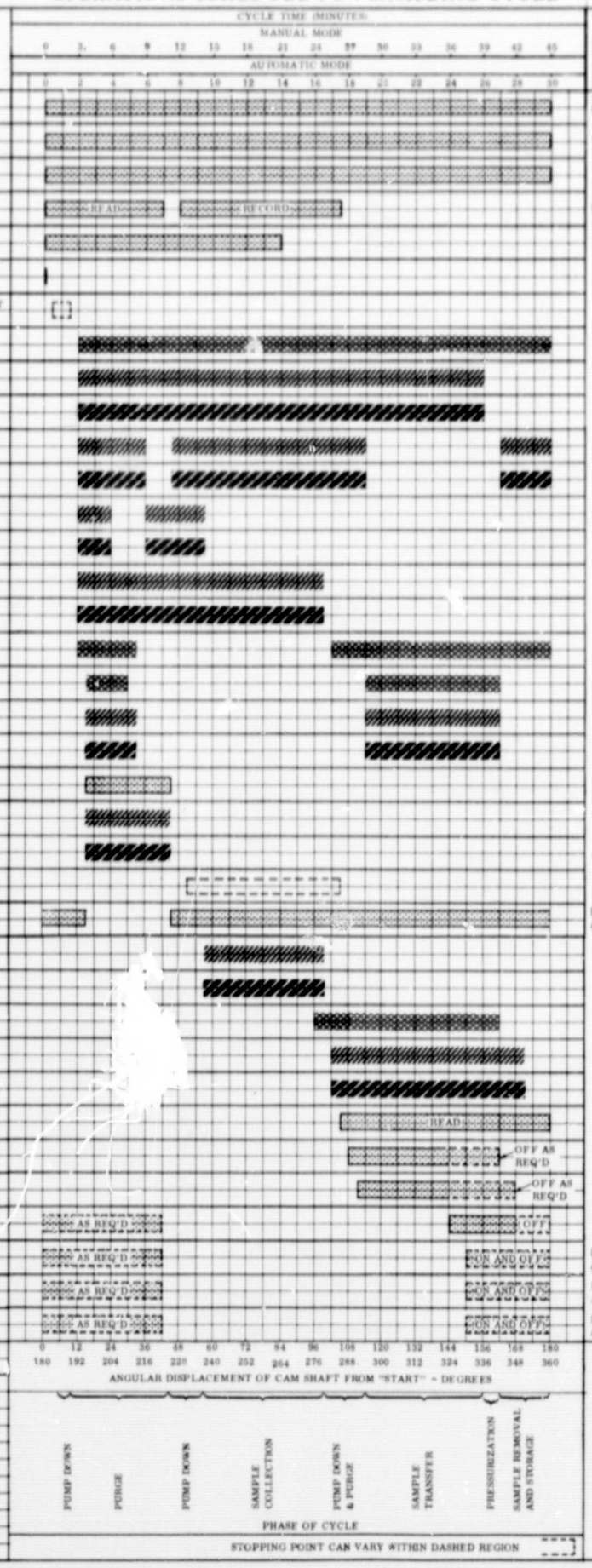
3.3 AUTOMATIC OPERATION

A description of the various sequences of events in the automatic operation of the sampler can be made with the aid of the accompanying table which lists the events commanded by the programmer. See Table 3-1.

Table 3-1. Operations Schedule for Sampling Cycle

OPERATIONS SCHEDULE FOR SAMPLING CYCLE

OPN. NO.	SWITCH NO.	ACTUATED FUNCTION AND/OR (LABEL)	COMMENTS
1	S3	AUTO CH α IN	S3 MUST BE OPEN BEFORE RETURNING TO MANUAL OPERATION
2	S4	AUTO CH β IN	S4 MUST BE OPEN BEFORE RETURNING TO MANUAL OPERATION
3	S2	SELECT AUTO MODE	
4	S26	READ OR RECORD M_α & M_β	MARK END POINTS OF THE SAMPLING PERIOD ON THE GRAPHS
		SAMPLING (F/M SELECTOR)	
5	S43	HEAT α/β II TRAP WELL (HEATERS IN RES'VR II IN)	
6	S12	(START AUTO SEQ)	
7	S5	PURGE IMPACTOR & SAMPLE INLET	
	S2 α&β	(INLET PRESS'ZN)	
8		CONNECT MOTOR OF PROG'MD	
	1 α/β	TIMER TO POWER SUPPLY	
9	S17	CONNECT α CH	
	S14 α		
10	S35	CONNECT β CH	
	S14 β		
11	S34	SHUNT α II TRAP	
	S13 α		
12	S36	SHUNT β II TRAP	
	S13 β		
13	S28	SHUNT α I TRAP	
	S4 α		
14	S7	SHUNT β I TRAP	
	S4 β		
15	S27	CONNECT α DESSICATOR	
	S3 α		
16	S6	CONNECT β DESSICATOR	
	S3 β		
17	S9	SET P_{ACT} = P_{RI}	
	S6 α/β		
18	S11	GN_2 TO ACT	
	S8 α/β		
19	S14	HEAT α I TRAP	
	S11 α		
20	S36	HEAT β I TRAP	
	S11 β		
21	S37	RECORD α & β DESSICATOR	
		TEMPS. (T/C SELECTOR)	
22	S29	PURGE α CH	
	S5 α		
23	S8	PURGE β CH	
	S5 β		
24	S30	VENT PUMP	
	S9 α&β	MANIFOLD	
25	S37	RECORD ACT AND RES'VR II	MARK START POINTS FOR THE CYCLE, SAMPLING PHASE, AND TRANSFER PHASE ON GRAPH
		TEMPS (T/C SELECTOR)	
26	S31	OPEN α CH	
	S7 α		
27	S10	OPEN β CH	
	S7 β		
28	S15	ISOLATES LWR. COMPONENT OF II	
	S12 α&β	(COOL TRAPS II)	
29	S33	TRANSFER α SAMPLE	
	S10 α		
30	S13	TRANSFER β SAMPLE	
	S10 β		
31	S26	READ OR RECORD M_α & M_β	
		TRANSFER (F/M SELECTOR)	
32	S20	VENT ACT	
33	S21	FILL ACT	
34	S25	FILL RES'VR II	
35	S22	FILL RES'VR A	REFILL WITHIN REGIONS INDICATED AND IN SUCH A WAY AS TO AID IN REFILLING RESERVOIR II
36	S23	FILL RES'VR B	REFILL WITHIN REGIONS INDICATED AND IN SUCH A WAY AS TO AID IN REFILLING RESERVOIR II
37	S24	FILL SAMPLE STORAGE SYSTEM BY OVERRIDING	REFILL WITHIN REGIONS INDICATED AND IN SUCH A WAY AS TO AID IN REFILLING RESERVOIR II



CODE:
- MANUAL CONTROL ONLY
- AUTOMATIC CONTROL COMMON TO BOTH CHANNELS
- AUTOMATIC CONTROL α CHANNEL
- AUTOMATIC CONTROL β CHANNEL
- REGION AVAILABLE FOR OPERATION IF REQUIRED
- END POINTS OF REGION FIXED
- STARTING POINT CAN VARY WITHIN DASHED REGION

SECTION 4.0

CALIBRATION OF THE SAMPLER

In the calibration of the sampler system two basic performance parameters are to be established. These are the "Concentration Factor", F_c, and the "Collection Efficiency", E. Known samples prepared by the University of California at Riverside (UCR), and diluted in a traceable precision dilution system at Atlantic Research, are run through the sampler in the standard prescribed procedure as described earlier. The collected samples are then quantitatively analyzed by gaschromatography to yield F_c and E.

For calibration purposes the prepared samples contain the following organics:

(1) n - butane

(2) Benzene

(3) Cyclohexane

(4) Isoprene

(5) β-pinene

The inlet condition to the sampler is equivalent to that for flight at 40,000 ft. altitude at a flight speed of Mach 0.75. This corresponds to an inlet pressure of 204 torr.

4.1 PREPARATION OF TEST SAMPLE

The calibration sample is prepared at UCR, with a total mixture pressure at 760 torr, containing each of the five hydrocarbons listed above at a nominal concentration of 2×10^{-3}, the precise concentration to be determined as the sample is prepared. This is the maximum concentration allowable in the case of β-pinene, to avoid any saturation, since β-pinene has a saturation pressure of about 2.1 torr at 15°C.

The supply sample is then diluted prior to calibration of the sampler in the Atlantic Research Digi-Vac system. This is a calibrated dilution system with fixed (and traceable) dilution ratios (nominally) of 2×10^{-3}, 2×10^{-4}, 2×10^{-5} and 2×10^{-6}. It is described schematically in Figure 4-1. Using the smallest dilution ratio of 2×10^{-6}, the supply sample is transferred into the pre-evacuated (to about 10^{-6} torr) 100-liter Reference Volume of the Digi-Vac. With five transfers the partial pressure of each material in the Reference Volume is $5 \times (2 \times 10^{-6} \times 2 \times 10^{-3}) \times 760 = 1.52 \times 10^{-5}$ torr. This is somewhat less than 2×10^{-5} torr which is 10^{-7} of 204 torr.

The Reference Volume is then back-filled to 204 torr with high purity nitrogen. The diluted sample is then ready for use to calibrate the sampler.

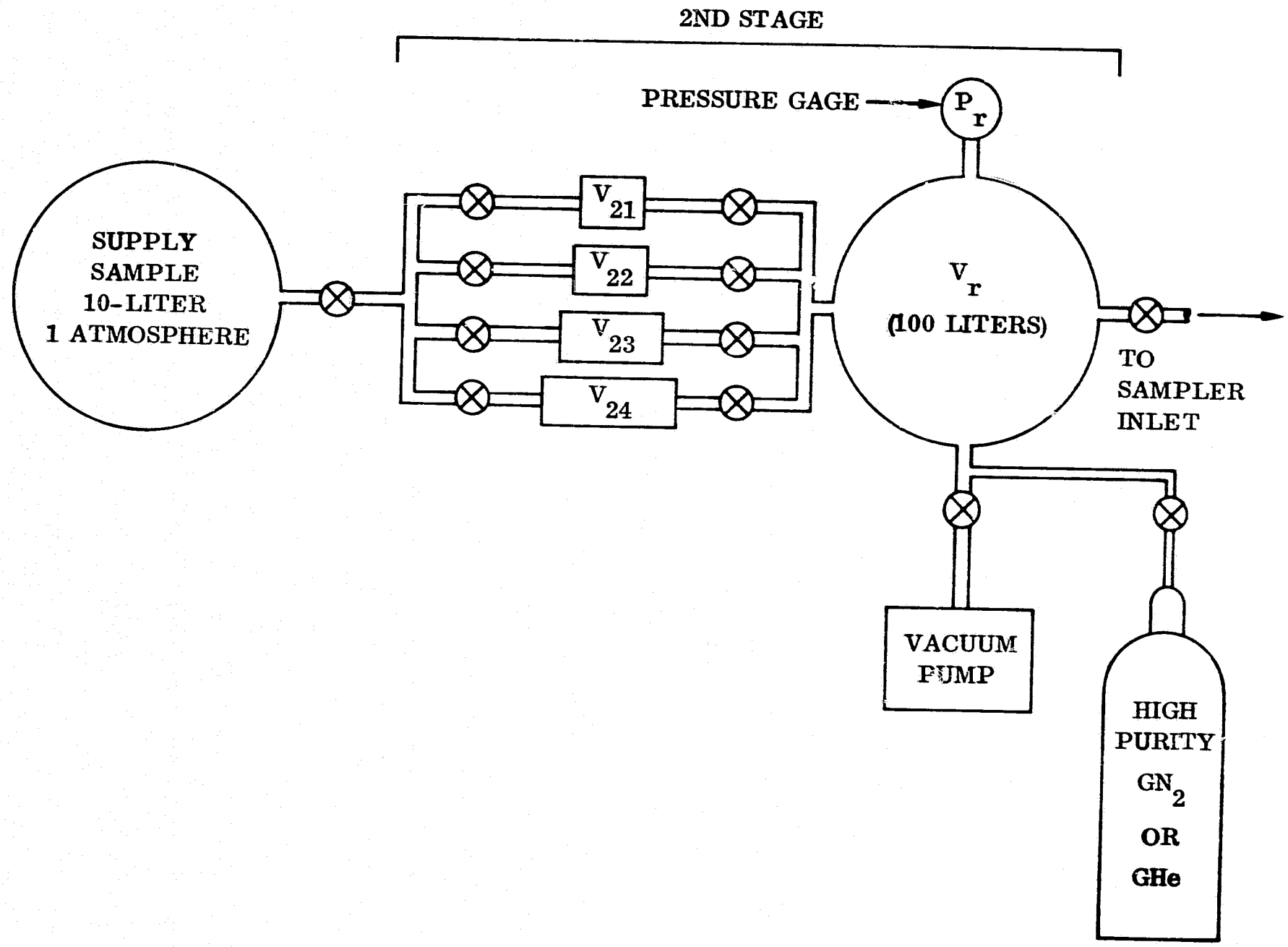


Figure 4-1. Digi-Vac Dilution System

4.2 CONCENTRATION FACTOR CALIBRATION

The concentration factor is defined as

$$F_c = \frac{V_s}{V_2}$$

where V_s is the sampled volume and V_2 is the net volume (exclusive of packing) in the second stage trap. It should be noted that V_2 is a fixed quantity, while V_s depends on the sampling time. The concentration factor thus, in effect, relates to sampling time; and a minimum required concentration factor defines a minimum sampling time at the maximum altitude (or the minimum sampling pressure p_s which, at 40,000 ft. and M = 0.75, is 204 torr).

The sample volume V_s is determined by using the Digi Vac in the following manner. With the inlet of the Flight Sampler connected to the Reference Volume V_R, and the exhaust connected to a vacuum pump, the initial pressure p_{s_i} and final pressure p_{s_f} in the Reference Volume are measured during a sampling run. The mass removed is then $(p_{s_i} - p_{s_f})\, V_R$ and the volume removed at p_{s_i} is thus

$$V_s = \frac{(p_{s_i} - p_{s_f})\, V_R}{p_{s_i}} = \left(1 - \frac{p_{s_f}}{p_{s_i}}\right) V_R$$

The pressure is measured with a precision mercury manometer. Since V_s, by the requirement of NASA, will be about 5 liters at 204 torr (or at least 1 standard liter), p_{s_f}/p_{s_i} is expected to be about 0.95. The accurary of the manometer is expected to be 0.1%, so that the determination of V_s should be good to about 2%.

V_2, the second-stage trap volume is determined in a similar way, by discharging atmosphere pressure nitrogen from the trap into the Digi-Vac Reference Volume and observing the rise in pressure.

$$V_2 = \frac{p_{R_f} - p_{R_i}}{p_{z_i} - p_{2_f}}\, V_R$$

Since p_{R_i}, the initial pressure in the Reference Volume, is less than 10^{-6} torr, and p_{z_f} will be of the order of 10^{-4} torr, the above can be simplified to

$$V_2 = \frac{p_{R_f}}{p_{2_i}}\, V_R$$

The pressure in V_P is measured with a precalibrated vacuum gage (of the ionization type) and will have and accuracy of 5% while p_{2_i} is measured with a mercury manometer with an accuracy of 0.1%. Thus the accuracy in determining V_2 is 5%.

The overall accuracy in determining the Concentration Factor is thus about 5%.

4.3 COLLECTION EFFICIENCY CALIBRATION

The collection efficiency for each of the six organics is defined as the ratio of the mass of each species recovered (as determined at the output of the gaschromatograph) to the mass collected in the sampler.

$$E = \frac{m_2}{m_s}$$

where m_2 is the mass of a species as determined by the area under the curve for the corresponding peak in the G.C. plot, and m_s is the sample mass as determined by the known concentration of the calibration sample, c, and the sampled volume V_s, as previously determined by the method described in paragraph 4.2.

SECTION 5.0

FLIGHT TEST

5.1 FLIGHT SAMPLES

The Sampler was installed in a Learjet and flight-tested on 12 May 1970 over a variety of terrains in order to obtain, hopefully, different samples. The locations where samples were taken are shown in Figure 5-1.

Sample No. 1 was taken at 41,000 ft. over Death Valley, a region devoid of any significant amount of vegetation. Sample No. 2 was taken at 41,000 ft. over the northern Sierra Nevadas bordering California and Nevada, a region heavily wooded with conifers. The third sample was obtained over the San Joaquin Valley, at 41,000 ft. to assess the atmosphere over an extensively cultivated agricultural area. Sample No. 4 was taken over the Pacific Ocean at 41,000 ft. about 50 miles off-shore. Sample No. 5, the last one, was taken while descending over the Los Angeles Basin, although the sampling was conducted at a constant altitude of 9,500 ft. which was considerably above the inversion prevailing on that day. This was done to avoid sampling too much urban air pollutants.

Because of a leak in the α-channel, discovered shortly before the flight, only the β-channel was used. The five samples collected in the β-channel were analyzed by gaschromatography at University of California, Riverside.

No significant quantitative data were obtained because all the chromatographic peaks were very small. Therefore only identification of the peaks could be made, by comparing the elution times of the samples with those of a standard sample. The standard sample contained benzene, toluene, α-pinene and β-pinene. The elution times of this standard sample in two separate runs are shown below.

	Elution Time	
Standard Sample	Run 1	Run 2
Benzene	4' 35"	4' 35"
α -pinene	6' 45"	6' 50"
Toluene	6' 59"	7' 00"
β -pinene	9' 45"	9' 59"

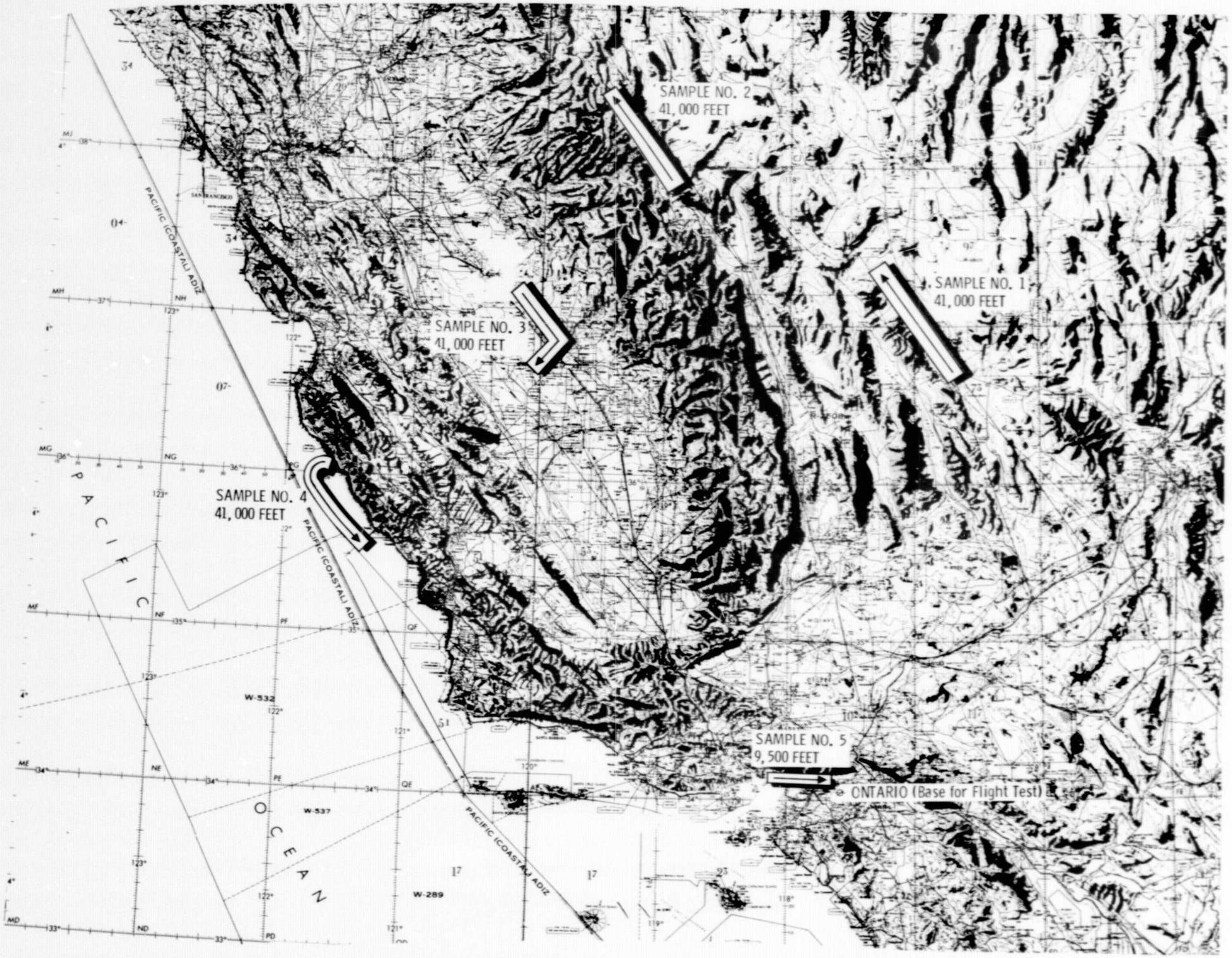


Figure 5-1. Location of Sampling Zones

The discernible peaks from the flight samples and their elution times are listed below. Sample No. 5 was divided, 1/3 and 2/3, into two analysis samples, in anticipation that this might be a large sample, since it was taken at 9,500 ft. over Los Angeles Basin. The precaution turned out to be unwarranted, as the peaks from Sample No. 5 were no higher than those of the other four samples.

Table 5-1. Flight Sample Elution Times

Peak No.	Sample 1	2	3	4	5(1/3)	5(2/3)
1	1' 42"	1' 38"	1' 37"	1' 49"	1' 40"	1' 38"
2	1' 47"	1' 50"	1' 42"	1' 52"	1' 46"	1' 42"
3	1' 58"	1' 55"	1' 48"	1' 59"	1' 52"	1' 48"
4	2' 3"	2' 1"	1' 58"	1' 59"		2' 3"
5	2' 12"	2' 12"	2' 4"	2' 3"		
6	2' 24"	2' 24"	2' 26"			
7	2' 55"	2' 55"	2' 57"	2' 58"	2' 58"	2' 55"
8	3' 29"	3' 28"	3' 32"	3' 36"	3' 30"	3' 28"
9	4' 17"	4' 18"	4' 20"	4' 22"	4' 20"	4' 20"
10	5' 38"	5' 20"	5' 25"	5' 29"		(5' 35"/4' 55")
11	6' 44"	6' 45"	6' 43"	6' 49"	6' 47"	6' 43"
12	9' 45"	9' 43"	9' 44"	9' 49"		9' 45"
12	9' 45"	9' 43"	9' 44"	9' 49"		9' 45"
13		10' 45"	10' 45"	10' 52"		

Upon comparing the flight sample elution times with those of the standard sample it is seen that only two peaks, occurring in all five flight samples, can be correlated with known peaks in the standard sample - and these are Peaks 11 and 12, which match α-pinene and β-pinene. All other peaks could not be identified with any hydrocarbons in the standard sample.

The fact that only α-pinene and β-pinene were found, and that they were found in similar quantities in all the samples, led to considerable discussion by personnel from Atlantic Research, NASA Ames and University of California, Riverside. Two possible explanations were advanced: one that at altitudes above 9,500 ft. the atmosphere over the entire region covered by the flight was uniformly permeated with α-pinene and β-pinene, resulting from extensive mixing; and the other, perhaps more probable, that the sampler itself was somehow contaminated with these two substances. It was therefore decided that a tare calibration would be performed on the β-channel of the sampler exactly as it was at the end of the flight test.

The sampler was accordingly sealed and returned to the laboratory at Atlantic Research, to await the tare calibration. Due to contractual considerations, some seven months elapsed between the flight test and the tare calibration. This, however, did not seem to affect the calibration, as seen from the results discussed below.

5.2 TARE CALIBRATION

High purity gaseous nitrogen was used as the sample gas for the tare calibration of the β-channel. Seven second stage traps were prepared, and of these five were placed in the sampler to collect from the tare calibration, and the other two were used as controls. The gaschromatographic analysis results, furnished by the University of California, Riverside, are tabulated in Table 5-2.

It is seen from the data in Table 5-2, that except for some relatively large unknown peaks in the aromatics in one sample, the samples showed minimal contamination. Sample 19 showed these unknown peaks which were near enough to β-pinene to constitute possibly some interference. All the other samples, however, showed nothing in the way of α-pinene and β-pinene. The large peaks for acetone were expected, because the sample traps were cleaned with acetone. The source of formaldehyde was not known. However, neither of these would interfere with the analysis of the designated hydrocarbons.

The question of the interpretation of the flight sample analysis remains thus largely unresolved. It can be concluded from the tare calibration that the sampler was not contaminated with α-pinene and β-pinene at the time of the flight test. The presence of α-pinene and β-pinene in all five flight samples should be considered real; although an explanation for their almost universal presence remains elusive.

Table 5-2. Concentration in Parts per Billion by Volume

SAMPLE NO. SIZE ml	#17 (0 ml) (3L-2R)	#18 (350 ml) (3L-3R)	#19 (350 ml) (3L-4R)	#20 (0 ml) (4L-0R)	#21 (1500 ml) (4L-1R)	#22 (1000 ml) (4L-2R)	#23 (350 ml) (4L-3R)
Methane							
Ethene	0.8	0.2	2.3	0.8	<0.1	0.1	0.3
Ethane	1.6	0.6	0.6	1.6	<0.1	0.1	0.5
Acetylene		0.2	0.6	<0.1			
Propane	0.8	0.2	0.2	0.8	<0.1	<0.1	0.2
Propene	<0.1	<0.1	0.3		<0.1	<0.1	
Isobutane	<0.1	<0.1	0.5		<0.1	<0.1	<0.1
N-Butane	<0.1	0.5	0.3	<0.1	<0.1	0.2	<0.1
Acetylene		<0.1	0.6				
1-Butene		<0.1	0.2				
Isobutene		1.1	0.1				
Trans-2-Butene							
Isopentane		0.1	0.2				
CIS-2-Butene							
N-Pentane							
3-Methyl Butene-1							
1,3-Butadiene		0.7					
Methyl Acetylene							

Table 5-2. Concentration in Parts per Billion by Volume (Continued)

SAMPLE NO. SIZE ml	#17 (0 ml) (3L-2R)	#18 (350 ml) (3L-3R)	#19 (350 ml) (3L-4R)	#20 (0 ml) (4L-0R)	#21 (1500 ml) (4L-1R)	#22 (1000 ml) (4L-2R)	#23 (350 ml) (4L-3R)
2, 2-Dimethyl Butane							
1-Pentene							
2-Methyl Butene-1							
Trans-2-Pentene							
2, 3-Dimethyl Butane							
2-Methyl Pentane		0.5					
CIS-2-Pentene							
2-Methyl Butene-2							
3-Methyl Pentane		1.6					
Cyclo Pentane							
N-Hexane		1.4					
Cyclo Peniene							
2-Methyl Budadiene		1.3					
Acetaldehyde	4.8	36.2	8.9	8.8	5.5	5.0	10.6
Acetone	46.4	55.0	25.6	44.0	541.0	22.8	14.6
Benzene	0.1	1.1	6.3				
α-Pinene							
Toluene	0.8	1.1	0.7				
β-Pinene			*				

*Unknown — Would interfere with analysis of β-pinene.

Table 5-2. Concentration in Parts per Billion by Volume (Continued)

SAMPLE NO. SIZE ml	#17 (0 ml) (3L-2R)	#18 (350 ml) (3L-3R)	#19 (350 ml) (3L-4R)	#20 (0 ml) (4L-0R	#21 (1500 ml) (4L-1R)	#22 (1000 ml) (4L-2R)	#23 (350 ml) (4L-3R)
Ethylbenzene		0.5	0.7		<0.1	0.2	
p-Xylene		0.7			0.2	0.2	11.0
m-Xylene		0.6			<0.1	0.2	5.5
Cumene							
o-Xylene		0.2					0.9
N-Propylbenzene							
p-Ethyltoluene							
m-ethyltoluene							
o-ethyltcluene							
1,3,5 trimethylbenzene							
Styrene							
1,2,4 trimethylbenzene							
1,2,3 trimethylbenzene							

SECTION 6.0

SAMPLER SYSTEM CALIBRATION

Normally it would be expected that a sampler system such as this would have been calibrated before actual flight operation; but because of scheduling problems it was deemed necessary to flight test the system first, and to calibrate later. Thus the total system calibration was performed after the flight test, and after the tare calibration of the β-channel.

For the system calibration the procedure described in Section 4.0 was used. The test sample was prepared at the University of California, Riverside laboratory. The composition, measured on three successive dates, is shown in Table 6-1.

As noted in Section 4.0, the concentration of β-pinene had to be kept low in order to avoid saturation, because of the fairly low vapor pressure of β-pinene at room temperature. Figure 6-1 shows the vapor pressure of β-pinene from 273°K to 350°K. From this it is seen that at a room temperature of 25°C (298°K) the vapor pressure of β-pinene is 3.9 Torr; and at 20°C it is 2.9 Torr. These values fall within the range found in the sample concentration measured on the three dates. It is apparent that a saturation condition prevailed in the prepared test sample as far as β-pinene was concerned. The fact that the maximum variation in measured concentration of the other compounds was 6%, while with β-pinene it was 58% tends to confirm the saturation conclusion.

The test sample was diluted through the DigiVac system and fed into the sampler system. Eight samples were collected, four in each channel. These collected samples were analyzed by University of California, Riverside, with the results shown in Table 6-2. The first set of values for each sample was from the gaschromatographic analysis, expressed in parts per billion and in nonoliter of vapor. The second set was calculated from the dilution ratio, the test sample concentration and the integrated flow through the collection trap (second stage trap).

The collection efficiency for all compounds is clearly exceedingly low. The highest values shown in Table 6-2 are 8.6×10^{-2}, for n-butane in Sample 2α, and 0.53, for benzene in Sample 2β, all the others being essentially negligible. Their peaks in the chromatograms were barely above the noise level.

Table 6-1. Composition of Test Samples

	2/11/71	2/12/71	2/24/71	Maximum Variation
N-Butane	11,050 ppm 14.5 Torr	10,880 14.3	10,700 14.1	3%
Isoprene	10,150 13.3	10,080 13.2	9,600 12.6	5%
Cyclohexane	9,160 12.0	8,900 11.7	8,920 11.7	3%
Benzene	11,960 15.7	11,220 14.8	11,650 15.3	6%
β-Pinene	2,335 3.1	1,990 2.6	3,090 4.1	58%

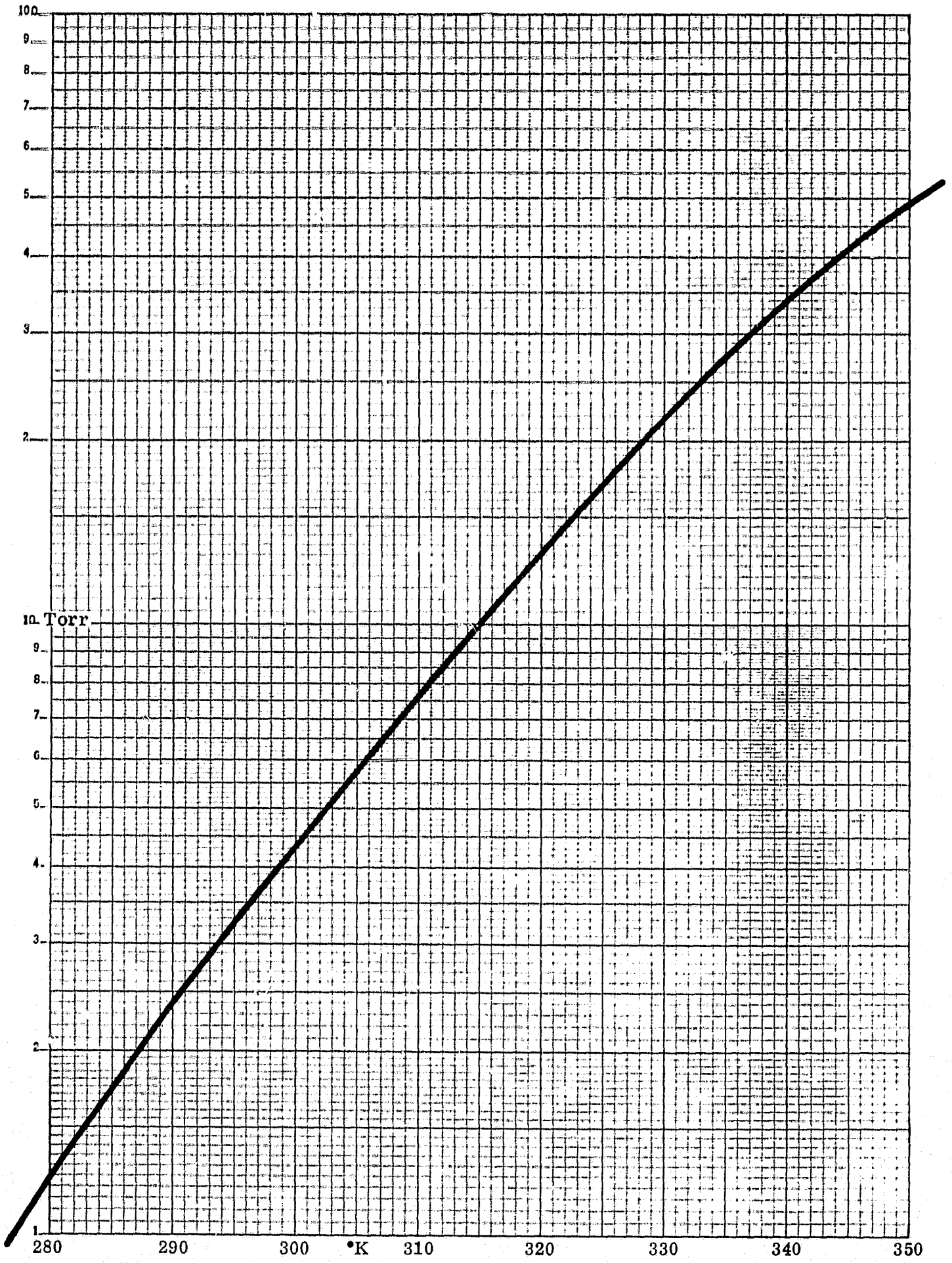


Figure 6-1. Vapor Pressure of β-pinene

Table 6-2. Calibration Results

SAMPLE		N-BUTANE	ISOPRENE	CYCLOHEXANE	BENZENE	β-PINENE
MEAS 1α	ppb	3.4×10^{-1}	---	---	2.5×10^{-1}	1.2×10^{-1}
	nℓ	0.16	<0.2	<0.3	0.12	0.06
THEO	ppb	850	0	0	0	0
	nℓ	620	0	0	0	0
MEAS 1β	ppb	1.3×10^{-2}	---	---	4×10^{-2}	1×10^{-2}
	nℓ	0.08	<0.2	<0.3	0.02	<0.04
THEO	ppb	0	761	710	925	245
	nℓ	0	515	480	625	166
MEAS 2α	ppb	20	3.0	4.7×10^{-1}	42	---
	nℓ	80.6	1.2	1.68	1.7	<0.1
THEO	ppb	166	0	0	0	0
	nℓ	929	0	0	0	0
MEAS 2β	ppb	2.0	---	9.6×10^{-2}	300	---
	nℓ	0.70	<0.2	0.34	334	<0.1
THEO	ppb	0	148	138	182	48
	nℓ	0	517	482	636	168
MEAS 3α	ppb	59	32	220	7.6	---
	nℓ	26.8	14.54	98.4	34.6	<0.1
THEO	ppb	9700	0	0	0	0
	nℓ	7370	0	0	0	0
MEAS 3β	ppb	8.4×10^{-1}	---	9.5	6.0×10^{-1}	6.0×10^{-2}
	nℓ	0.96	<0.2	5.0	1.61	0.16
THEO	ppb	0	8720	8120	10,600	2810
	nℓ	0	5230	4880	6,360	1,687
MEAS 4α	ppb	4.1	3.0	9.4	8.9	---
	nℓ	9.12	6.72	21.0	19.8	<0.1
THEO	ppb	3640	0	0	0	0
	nℓ	8300	0	0	0	0
MEAS 4β	ppb	6.1×10^{-3}	---	3.8×10^{-1}	1.5×10^{-1}	---
	nℓ	0.16	<0.2	1.0	0.4	<0.10
THEO	ppb	0	3260	3040	3960	1050
	nℓ	0	9110	8500	11040	2930

Clearly, the samples were either passed through the sampler without being collected, or were trapped somewhere inside the sampler. The only two non-negligible collections were in Samples 2α and 2β , signifying the second run through the α and β channels of the sampler. This fact plus the fact that these two cases involved the two compounds with the highest vapor pressures among the five in the test sample suggest the following explanation.

The vapors which were released from the heated first stage trap during the sample transfer process were condensed in the line leading out of the first stage trap. As mentioned in the description of the various components of the sampler system, the first stage trap is heated by passing electric current through the thin wall of the trap body. The inlet and outlet lines to the trap are made of thicker wall tubing and therefore do not heat up. In fact, the current to the traps is conducted directly to the thin-wall sections by solid copper conductors. It had been intended that thermal conduction along the lead lines from the first stage traps (inside the emptied inner chamber of the Automatic Cryotrap) to the exterior of the ACT would maintain sufficiently high temperature (near room temperature) to prevent condensation of the sample vapors. In retrospect and on the evidence cited above it would appear that such was not the case. Since there were no thermocouples on the outlets from the first stage traps it is not possible to state with certainty if the explanation postulated above is valid. It will certainly require further testing of the sampler system with adequate additional temperature measurements to resolve the question.

SECTION 7.0

CONCLUSIONS AND RECOMMENDATIONS

It has been found, through laboratory and flight operations, that the Sampler can be operated automatically with proper execution of all the functions designed. It does, however, require an operator with some knowledge of the principles involved and experience with the system to assure adequate monitoring of the sampling operation. This requirement is particularly important because of the limited space aboard an aircraft like the Learjet, and because of the limited time available for sampling in flight. In other words, the operator must be certain that all the preliminary steps prior to sampling are correctly completed, and that all elements of the system are functioning properly, before committing the system to a sampling operation. Monitoring, diagnosis and corrective actions (if necessary) must all be conducted with dispatch in the cramped quarters of an aircraft flying at over 500 mph.

This is not to suggest, however, that the Sampler has not lived up to the expectations of its design. In fact, experience in the laboratory and, more importantly, in flight, has definitely shown that a manually operated sampler with the necessity of filling and emptying dewars with two types of liquid cryogens (nitrogen and argon) could not possibly have performed the desired mission. The sobering fact is that the experience has shown that even an automated system requires more experience and skill than were contemplated originally by the designers of the system.

The problem with the low collection efficiency can be resolved without extensive modification of the first stage trap assembly. It is recommended that the explanation based on recondensation in the first stage trap outlets be confirmed by operating the Automatic Cryotrap with thermocouples attached to the outlets. It will not be necessary to perform an actual sampling operation. All that is required is that ACT cooling and heating sequences be gone through thoroughly in order to assess the temperature problem.

After confirmation of the temperature problem the solution can be effected either by direct electrical heating of the outlets or by attaching heaters to the outlets outside the ACT. Direct heating will mean that instead of feeding current to the traps with separate copper conductors, the current should be fed through the outlet lines themselves. This will require a higher voltage from the high current transformer, since the resistance of the outlet is higher than that of the copper conductor. External indirect heating probably will not be as effective as direct heating. Therefore it is recommended that the solution be sought first through modification of the power supply of the first stage trap heater system to effect direct heating of the outlet lines.