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# Multi-Stage Cryogenic Trapping System

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A portable, easily operated, multi-stage cryogenic trapping system contained in a box 86 x 66 x 61 centimeters has been developed. Liquid nitrogen, gaseous nitrogen, ice, dry ice and 110 volt 60 cycle power required for operation of the system are available to most military installations.

Ice formation in the  $-78^{\circ}\text{C}$  trapping cylinder entrance tube and liquid oxygen formation in the  $-175^{\circ}\text{C}$  trapping cylinder were eliminated in the design of the system. Catalytic conversion of trapped materials was minimized by use of stainless steel and Teflon. Operation of the system was simplified by inclusion of a liquid nitrogen level-controller.

Partial separation of compounds was accomplished by operating the trapping cylinders of the system at three different temperatures. Several compounds are listed according to the temperature at which they are expected to be concentrated in significant quantities. The system is efficient for concentration of micro and macro contaminants in an atmosphere. The concentration of a contaminant in a sample area may be estimated from the total trapping time, the flow through the system during trapping and the concentration of the contaminant in the trapping cylinders.

**T**HE DETERMINATION of trace contaminants in a spacecraft, an aircraft or the ambient atmosphere can be divided into several discrete problem areas: sample collection, sample concentration, separation of the individual contaminants, identification and quantitation.

Techniques that have been used for sample collection, sample concentration and separation of the individual contaminants include gas pressurization in steel bottles,<sup>2</sup> activated carbon bed sampling<sup>2,3,4</sup> and cryogenic trapping.<sup>5</sup> Each of these methods has its disadvantages. Gas pressurization in the steel cylinders does not concentrate the sample appreciably. Carbon bed sampling, while it effectively concentrates the sample, requires additional operations to separate the contaminants from the carbon. In carbon bed sampling catalytic reaction may cause degradation of a contaminant or interaction between contaminants. One cryogenic system<sup>6</sup> that has been used effectively to concentrate samples is constructed of delicate material and requires that the sample be maintained at the temperature at which it was taken, or that the sample be transferred to another container for shipment or storage.

One approach which does not have the disadvantages of other techniques is multi-stage cryogenic trapping. This technique permits greater concentration than the pressurization approach, separates the contaminants according to their vapor pressures and degradation is minimized due to the relatively low temperatures involved. This paper will describe the design and evaluation

of such a system and discuss the potential uses of this device.

## METHOD

The air stream from which the contaminants are to be removed and concentrated is passed through sample cylinders maintained at three different temperatures. The trapping system uses an ice bath at  $0^{\circ}\text{C}$ , a pulverized dry ice bath at  $-78^{\circ}\text{C}$  and a liquid nitrogen bath regulated to  $-175^{\circ}\text{C}$  to fractionate the contaminants in the air stream. Materials which are not concentrated are oxygen, nitrogen and compounds which have sufficient vapor pressure at  $-175^{\circ}\text{C}$  to pass through the system.

The air stream, consisting of atmospheric gas, first enters a flow meter (Figure 1) and then passes to the first trapping cylinder, which is maintained at a temperature of  $0^{\circ}\text{C}$  with ice water. The gas, having passed through the ice bath trapping cylinder, flows through a heated inlet into the trapping cylinder, maintained at  $-78^{\circ}\text{C}$  with pulverized dry ice. The pulverized dry ice requires occasional tamping to ensure contact with the wall of the trapping cylinder. The gas then passes to a trapping cylinder maintained at  $-175^{\circ}\text{C}$  where many of the materials not previously removed from the gas stream are condensed. The remaining gas is conducted to the vacuum inlet of a circulating pump and exhausted by the pump into the atmosphere or into a closed ecological system.

The trapping cylinders (Figure 2) are stainless steel with an internal volume of 150 cc. The cylinders are fitted with Swagelock connections, modified pipe fittings and needle valves. Teflon and stainless steel are used throughout the system to minimize catalytic conversions and contamination of samples. A thermocouple is mounted through a tapped port in the bottom of the cylinder. Temperatures are monitored with copper-constantan thermocouples on a pyrometer calibrated in degrees centigrade.

In the  $-78^{\circ}\text{C}$  trapping cylinder there is a rapid ice formation in the inlet tube. This formation, due to the

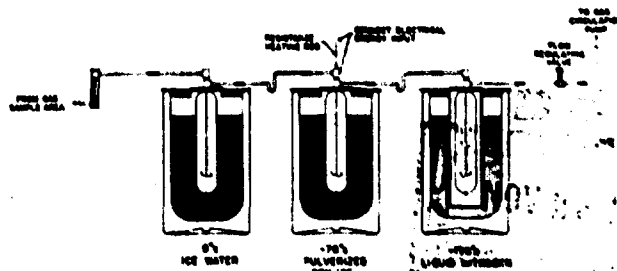


Fig. 1. Diagrammatic flow representation, multi-stage cryogenic trapping system.

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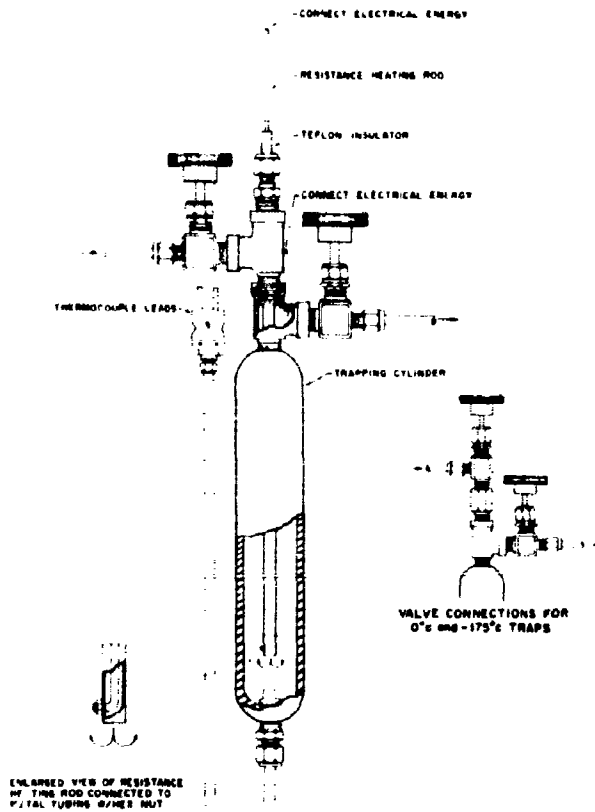


Fig. 2. Trapping cylinders, multi-stage cryogenic trapping system.

temperature gradient along (or down) the entrance tube, is prevented by heating the entrance tube. The heater consists of a 1/16-inch stainless steel rod inserted through a Teflon insulated Swagelock fitting at the top of the cylinder. It is positioned in the center of the entrance tube and projects to the bottom where it is bent at a 90° angle. The rod is threaded and secured to the wall of the entrance tube with a nut. This connection serves as the electrical contact between the cylinder and the rod. Electrical energy from a variable transformer is applied across the primary of a filament transformer, the secondary of which is connected to the rod and cylinder wall. Sufficient energy is applied to the heater to prevent the formation of ice in the tube without affecting the operational temperature of the trap.

The final trapping cylinder is controlled at a temperature of -175°C in order to prevent the formation and entrapment of liquid oxygen (-183°C at standard pressure). The presence of liquid oxygen in the trap would present an explosive hazard for personnel handling the cylinders, and it would make available a supply of oxygen for degradation of the original contaminants and the formation of new compounds.

This cylinder is positioned with two glass-phenolic rings in a well which is surrounded by liquid nitrogen (Figure 3). A flow of dry warm nitrogen from the bottom of the well controls the temperature of the trapping cylinder. The flow of gaseous nitrogen is regulated with a micrometer needle valve. One of the glass-phenolic rings covers the top of the well to maintain a positive pressure of gaseous nitrogen and prevent back

diffusion of atmospheric air and liquid oxygen formation.

The well is positioned by a fitted lid for the Dewar flask. The lid also contains a vent, a well for the liquid nitrogen level sensor and the liquid nitrogen filling device.

A liquid nitrogen level control device was developed to simplify the operation of the system (Figure 4). The level controller uses a thermister as a sensor so that a change in resistance of the thermister, in or out of liquid nitrogen, results in a change in current. The change in current operates a control meter which actuates a solenoid operated liquid nitrogen transfer valve.

The trapping system was designed for use in studies of trace contaminants in simulated space cabin atmospheres but may be used in any situation where there is a desire to concentrate atmospheric contaminants for identification and quantitation. The unit is portable and easily operated, making air contaminant studies feasible in locations which do not have facilities for analysis of complex chemical mixtures. The multi-stage cryogenic trapping system (Figure 5) is put into operation by connecting liquid nitrogen and gaseous nitrogen to their respective inputs and providing 110 volt 60 cycle power. The liquid nitrogen controller is activated and the -175°C trap Dewar filled, ice water is placed in the 0°C trap Dewar and pulverized dry ice in the -78°C trap Dewar. Gaseous nitrogen flow is adjusted to achieve the desired temperature in the liquid nitrogen trap well. The system is contained in

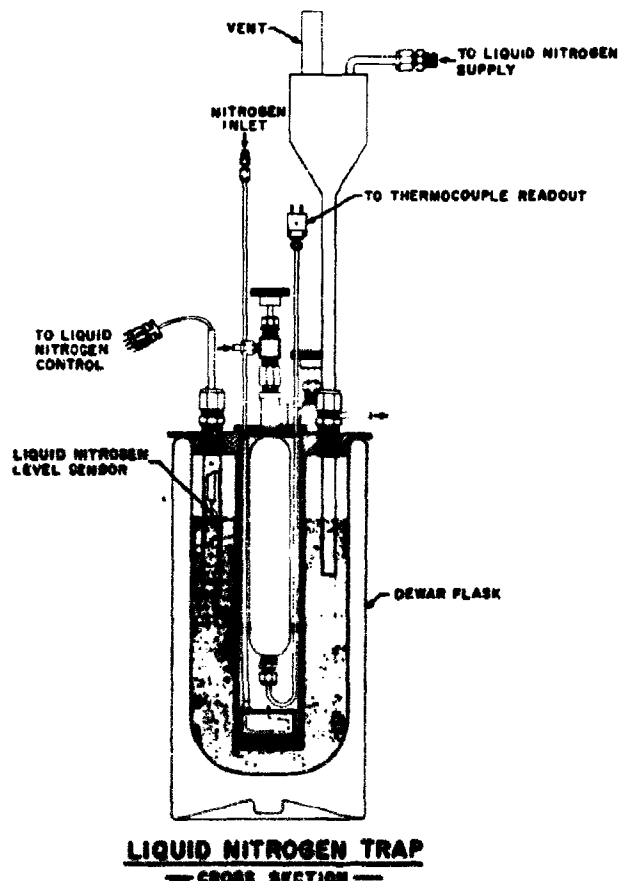


Fig. 3. Liquid nitrogen trap, multi-stage cryogenic trapping system.

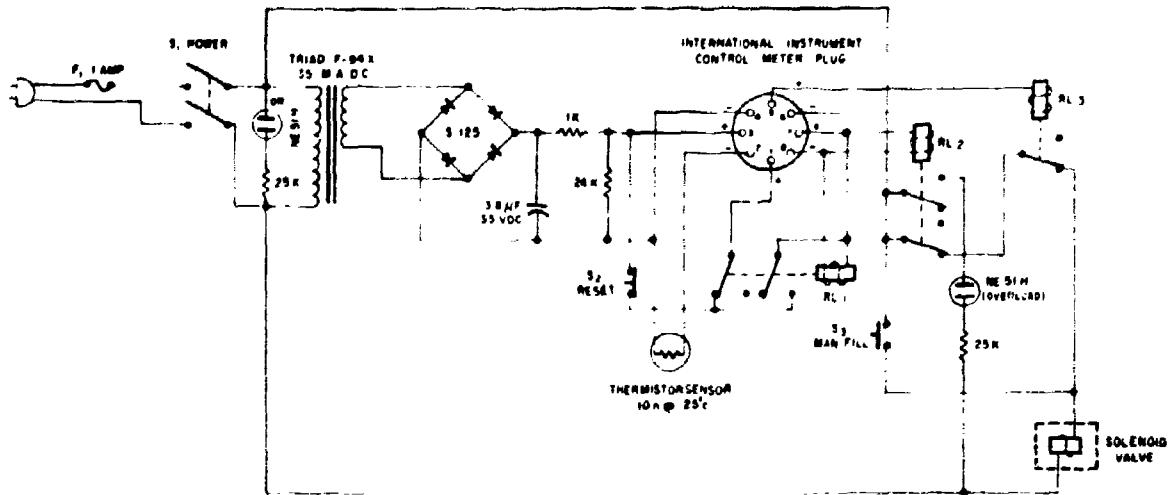


Fig. 4. Schematic of liquid nitrogen level controller.

a box 86 x 66 x 61 centimeters. The unit requires 25 liters of liquid nitrogen, 11.3 kilograms dry ice, 11.3 kilograms ice and 1.41 standard cubic meters of gaseous nitrogen for six hours' operation. The need for a gaseous nitrogen source may be eliminated by heating the boil-off of liquid nitrogen to provide the required dry warm nitrogen for the control of the trapping cylinder temperature.

Preliminary evaluation of the multi-stage cryogenic trapping system was made using a 255-liter chamber. The chamber was evacuated and 5 microliters of acetone added. The chamber was pressurized to 760 millimeters of Hg with nitrogen. The amount of acetone in the chamber was determined by extraction of a sample into a 10-meter multi-path infra red cell, and quantitated by infra red absorbance (Figure 6).

The trapping system was attached to the chamber and operated for six hours. The flow through the system was indicated by a variable-area flow meter. At the end of the trapping period the amount of acetone in the chamber and the trapping cylinders was determined by infra red absorbance.

RESULTS AND DISCUSSION

Information gained during the preliminary tests of the system (Table I) indicate that a useful tool for the study of trace contaminants was developed. Initial chamber, final chamber and the -175°C trapping cylinder contents and concentrations were determined by infra red absorbance and are reported in milligrams or parts per million.

The amount of acetone in the chamber at any time t can be expressed by the 1st order reaction equation:

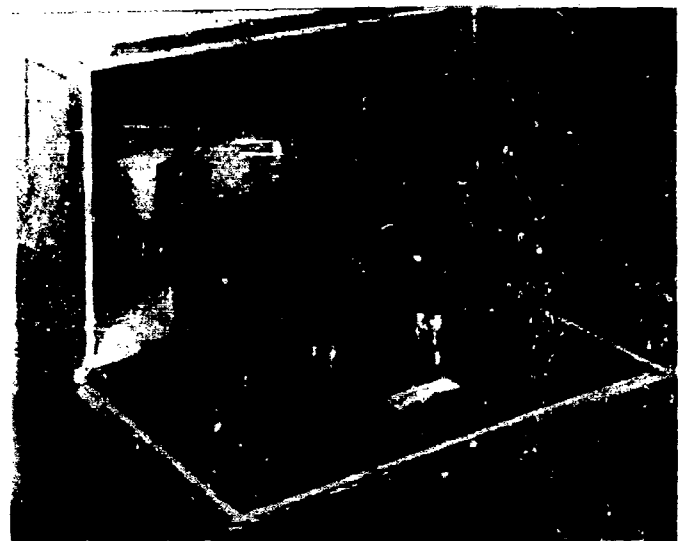


Fig. 5. Portable multi-stage cryogenic trapping system.

$$C_t = C_0 e^{-kt} \tag{equation 1}$$

where

C<sub>t</sub> = amount of acetone in the chamber at time t in minutes.

C<sub>0</sub> = initial amount of acetone in the chamber.

k = a constant.

e = 2.71828.

t = trapping time in minutes.

Assuming complete removal of acetone from the gas passing through the trapping system, a theoretical value for k in equation 1 was determined. The amount of acetone removed in successive one minute increments was summated for a period of ten minutes. The resultant was subtracted from the initial amount of acetone

TABLE I. RESULTS OF PRELIMINARY EVALUATION: EFFICIENCY AND RECOVERY

Run	Flow		Amount of Acetone in Chamber (mg.)		Amount of Acetone in 175°C Trapping Cylinder (mg.)			Per cent Recovery $\frac{F}{D-E}$	Per cent Efficiency $\frac{F}{G}$
	A	B	C	D	E	F	G		
1	300	360	4.072	2.610	1.50	1.762	1.491	102.6	86.1
2	300	360	4.210	3.117	1.07	1.457	1.088	97.9	75.4
3	300	360	4.210	2.900	1.19	1.457	1.510	90.8	61.7

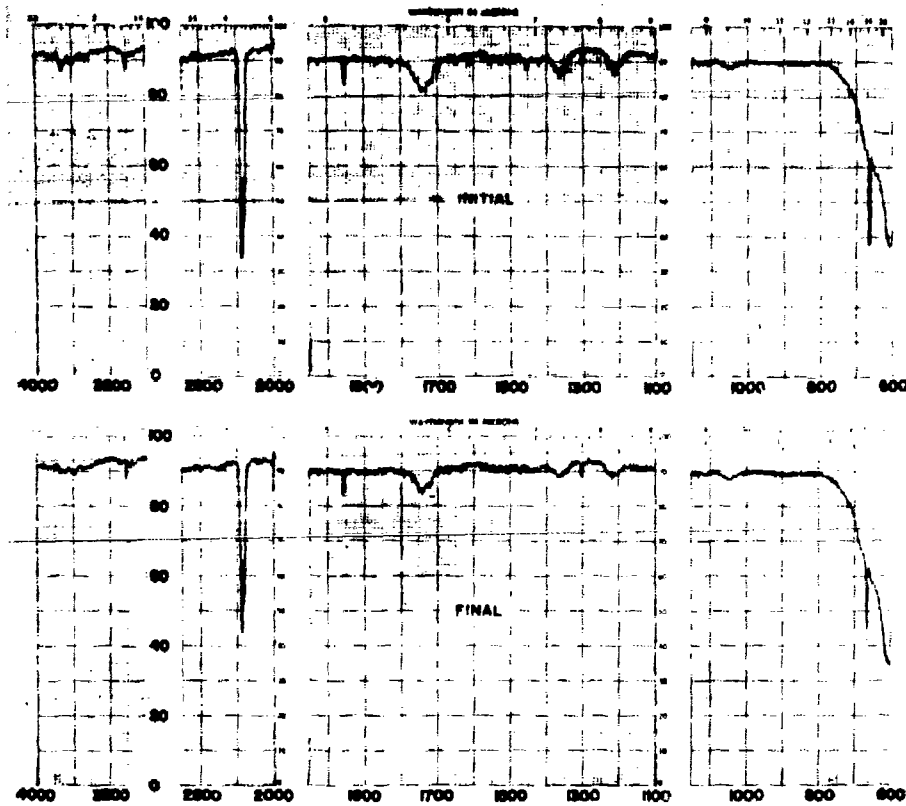


Fig. 6. Typical initial and final infrared scans.

to obtain the amount of acetone in the chamber after ten minutes. The initial amount of acetone in the chamber ( $C_0$ ), the final amount of acetone in the chamber ( $C_t$ ) and the time ( $t=10$  minutes) were substituted in equation 1 to obtain  $k$ .

To predict the amount of acetone in the chamber after a trapping period of 360 minutes the initial amount ( $C_0$ ), the trapping time ( $t=360$  minutes) and the theoretical value for  $k$  were substituted in equation 1.

The predicted amount of acetone in the  $-175^\circ\text{C}$  trapping cylinder was determined by subtraction of the predicted final amount of acetone ( $C_t$ ) from the initial amount of acetone ( $C_0$ ) in the chamber.

The multi-stage cryogenic trapping system efficiency was determined using equation 2.

$$\text{Per cent efficiency} = \frac{\text{amount of acetone in } -175^\circ\text{C trapping cylinder}}{\text{predicted amount of acetone in } -175^\circ\text{C trapping cylinder}} \times 100 \quad (\text{equation 2})$$

The values obtained for the efficiency of the system were 73.4, 81.7, and 88.1 per cent (Table I). A varia-

tion of plus or minus 10 per cent in flow gives values of 76.2 or 89.8 per cent for the 81.7 per cent value. Greater accuracy in the control of flow and the incorporation of a mass flow meter will decrease the variation in values obtained. The change in amount of acetone from the initial to final chamber values and the amount of acetone in the  $-175^\circ\text{C}$  trapping cylinder were used to determine the recovery of the system. The indicated recovery of the system was 102.6, 97.9 and 90.8 per cent.

The results indicate that the average concentration in the chamber can be directly estimated. The amount of acetone present in the  $-175^\circ\text{C}$  trapping cylinder, the flow rate of the sample gas through the system and the total trapping time were used to calculate the average acetone concentration in the chamber during the trapping period. This is compared in Table II with the result determined by averaging the initial and final concentrations of the chamber.

Water vapor is concentrated in the  $0^\circ\text{C}$  and the  $-78^\circ\text{C}$  trapping cylinders (Figure 7). This aids in analysis by minimizing the interference of water absorption bands in the  $-175^\circ\text{C}$  trapping cylinder sample.

TABLE II. RESULTS OF PRELIMINARY EVALUATION: CONCENTRATION

Run A	Flow cc/min B	Time min C	Chamber Concentration (ppm)			$-175^\circ\text{C}$ Trapping Cylinder Concentration (ppm) F	Estimated Chamber Concentration (ppm) G	Sample Concentration 2F D+E
			Initial D	Final E	Average $\frac{D+E}{2}$			
1	300	360	6.65	4.25	5.45	4164	4.56	764.04
2	300	360	6.88	5.08	5.98	2970	4.12	496.66
3	300	360	6.88	4.75	5.80	3304	4.58	589.16

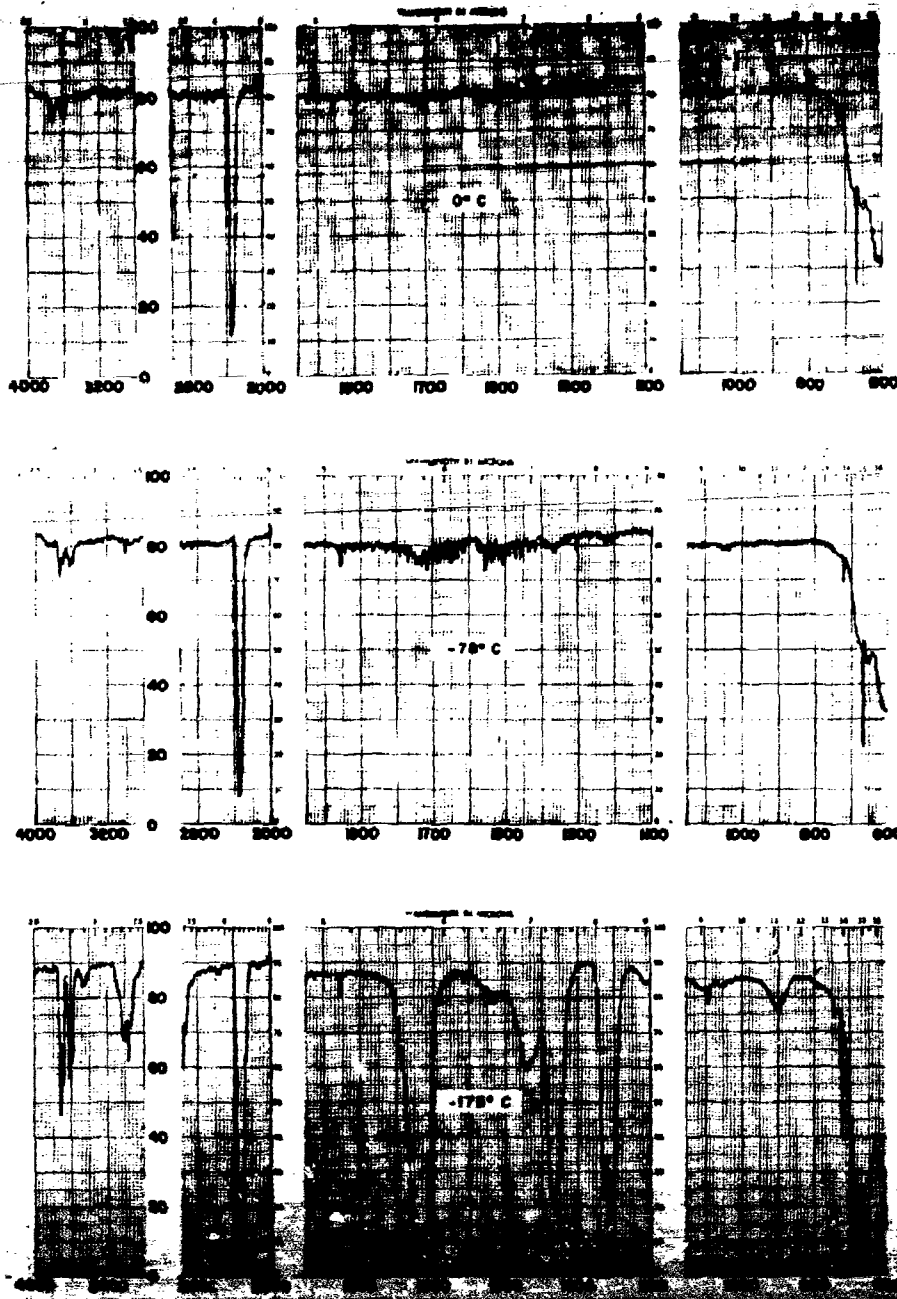


Fig. 7. Typical 0°C, -78°C and -175°C trapping cylinder infra red scans.

Acetone is present in all three traps but concentration occurs in the -175°C trapping cylinder.

The acetone concentration was several hundred times greater in the -175°C trapping cylinder than in the chamber after trapping. This degree of concentration aids identification of materials present in trace amounts.

The multi-stage cryogenic trapping system will concentrate a compound if the vapor pressure at the trap temperature is less than its partial pressure in the sample stream. Partial separation of compounds occurs due to the different operational temperatures of the three traps. This separation simplifies identification and quantitation.

After liquification and/or solidification there is no significant loss from a trap by transfer of particulate material in the form of fog or snow. This is minimized by the construction of the trapping cylinders.

TABLE III. DISTRIBUTION OF COMPOUNDS BY TRAPPING CYLINDER TEMPERATURE

Multi-Stage Cryogenic Trapping Cylinder			Untrapped
0°C	-78°C	-175°C	
Water (L)	Water (S) Freon-12 (L) Benzene (S) Toluene (S)	Acetone (S) Hydrogen Sulfide (S) Nitrous Oxide (S) Sulfur Dioxide (S)	Methane Nitrogen Oxygen Hydrogen
Ethylene glycol (L)	Ethylene glycol (S) Diethyl ether (L) Trimethyl amine (L) Monoethyl amine (L)	Trimethyl Amine (S) Monoethyl Amine (S) Freon-12 (S) Freon-13 (L) Methyl mercaptan (S) Carbon Dioxide (S) Ammonia (S) Methanol (S) Carbon tetrachloride (S)	

(L) = Liquid  
(S) = Solid

Table III depicts the distribution of several compounds as a function of the temperature at which they are expected to be concentrated in significant quantities. Substances are identified in each column according to the state in which they exist at that temperature, either as a liquid(L) or as a solid(S). Any material existing as a solid at a given temperature will not be found concentrated in a succeeding trapping cylinder.

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