

Monitoring of Trace Constituents in Simulated Manned Spacecraft

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MANY TRACE contaminants will appear in the artificial atmosphere maintained in a manned spacecraft. These contaminants arise principally within three areas: (1) metabolic processes of the inhabitants, (2) simple out-gassing of supplies and materials stored aboard, and (3) secondary out-gassing resulting from physical and chemical changes of the spacecraft contents. A compilation of the literature^{1, 2, 3, 4} indicates that about 400 materials have been reported as occurring in the by-products of man. These materials result from respiration, saliva, urine, feces, and flatus.⁴ Trace contaminants arise from materials stored within the environmental compartment such as the breathing gases, food supplies, and other logistic materials.⁵ The third area for origin of the trace contaminants might be from equipment used in the operation of the environmental system.⁶ Included in this group would be the biomedical and physical testing equipment. Contamination also results from hardware and processes used in recycling and regeneration of solid, liquid and gaseous waste.

The isolation and identification of trace contaminants in sealed environments is important in the study of bioastronautics. Unlike the study of the sealed environments of submarines which the Navy Research Laboratory has had under intensive study since 1956,⁷ the investigation of sealed environments related to bioastronautics often must be accomplished at reduced pressures and in an atmosphere enriched with oxygen. The size of the currently available monitoring equipment precludes its use in space capsules. The atmospheric conditions in the capsule often have a deleterious effect upon the components of the monitoring equipment unless they are specially protected. Studies of the contaminants in the Mercury spacecraft atmosphere have been accomplished in-flight by desorption of the absorbed contaminants from activated carbon filters.⁶ This technique is not the optimum approach due to the possible chemical reactions and interactions of the absorbed material.

The availability of sealed environments of space cabin simulators operating at the specific atmospheric parameters of proposed spacecraft has made possible the establishment of a program to define qualitatively and

quantitatively the nature and source of possible contamination. This approach eliminates the need for desorption of contaminants from carbon filters and permits the development of techniques for collecting and separating microcontaminants. The problems associated with the identification and quantitation by suitable analytical techniques of a wide variety of material further complicate the characterization of the contaminants.

This investigation deals with an approach to these technological problems of collection, isolation, and identification of trace contaminants using the two-man space cabin simulator as a source. Both normal and abnormal atmospheric conditions (i.e., during a fire) have been sampled and the contaminants partially identified.

METHODS

Isolation of Materials:—The value of any atmosphere sampling system is dependent upon its ability to separate the trace constituents in the atmosphere and isolate them free of contamination. A collection system composed of a pumping mechanism and an isolation device was designed for collecting and containing samples for subsequent analysis of trace materials. This system was utilized in an experiment conducted at a total pressure of 258 mm. Hg and an oxygen partial pressure of 242 mm. Hg.

Sampling duration was dependent upon the time that had elapsed during the flight. Initially, before large

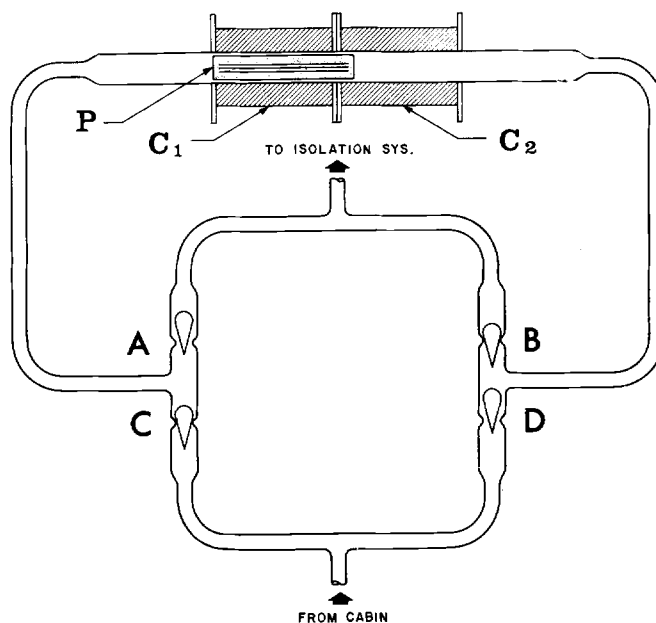


Fig. 1. All glass circulating pump for gases.

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amounts of trace constituents had accumulated, it was necessary to sample for periods of approximately one-half hour. As the flight progressed and contaminants accumulated within the sealed chamber, constantly occurring constituents could be easily recognized and new low-level contaminants appeared. Accordingly, as the flight progressed, collection was reduced to 10- and 15-minute sampling periods, generally at 12-hour intervals.

Pumping System:—In a sealed environmental system, it is necessary to have a non-contaminating system for propelling the gas from the environmental simulator to the trapping system and returning the uncondensed portion to the simulator. A circulating pump similar to that described by Watson,⁸ but made entirely of glass, was constructed to maintain a continuous air circulation of several liters per minute. The pump was constructed in such a manner as to be operable at variable atmospheric pressures. The major atmospheric constituents, oxygen and nitrogen, were recycled to the chamber. The pump, shown diagrammatically in Figure 1, consisted of a cylinder assembly with a piston operating on the horizontal. The pump has only glass surfaces exposed to the circulating atmosphere. The pumping action is achieved by the two solenoids, C_1 and C_2 , the rate dependent upon a fixed pulse frequency. The double action pump draws gas into the valved section and expels it with each pumping action; the glass valves, B and C, operate alternately with valves A and D. The features of the pump are: (1) variable amounts of gas may enter the system; (2) limited temperature variations may be used for extended periods without adverse operation; and (3) the unit is mobile.

Isolation System:—The contamination collection system is shown in Figure 2. As indicated by the modular

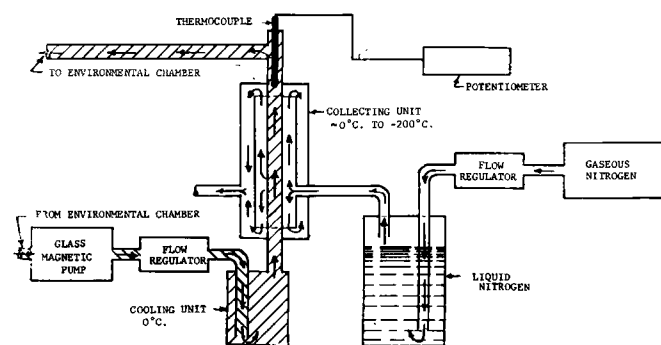


Fig. 2. Isolation system for microconstituents in a sealed atmosphere.

representation, two systems are in concurrent operation; the cooling system and the air flow through the condensation-collection system from the simulator. The latter pathway is indicated by the sectioned area. The condensation system is based upon passing dry nitrogen gas through liquid nitrogen. The rate of flow of the gas functions as a temperature programmer and the cooled nitrogen is allowed to reach preselected temperatures. This allows the sample to pass from -200°C to ambient temperature.

A single isolation chamber is employed in the present system, but with the modular design, it is relatively sim-

ple to incorporate a greater number of units to collect as many fractions as desired. The value of multiple fractions permits the detection of materials which might otherwise be masked. When the collecting unit contains two isolation chambers, the first chamber operates from ambient to approximately -50°C and this fraction contains most water soluble compounds and others of this temperature range. From the preliminary chamber, the vaporous materials pass to another isolation unit which is operable from approximately -50° to -200°C . This effectively traps the materials condensing at lower temperatures. If desired, the temperatures can be further decreased by changing the cryogenic material, but preliminary studies indicate that most of the materials will probably be contained within this range. A valuable modification is the placing of cryosorptive materials directly into the isolating system with a subsequent release of materials from the sorbent and into the assay instrumentation. The sorbents that were evaluated included activated charcoal, Drierite (anhydrous calcium sulphate) and Ascarite (calcium-magnesium silicate coated with sodium hydroxide). Only the latter one revealed additional contaminants.

The isolation procedures are critical since the sought microconstituents occur in minute amounts and extraneous outside materials are several orders of magnitude greater than the chamber contaminants. Furthermore, any method that would cause decomposition, degradation, fragmentation or other alterations would nullify the results. Other systems for isolation of trace contaminants have been employed, but the condensation-collection system has proved the most effective.

The collecting unit is shown in Figure 3. Several different designs and sizes were fabricated by the glass

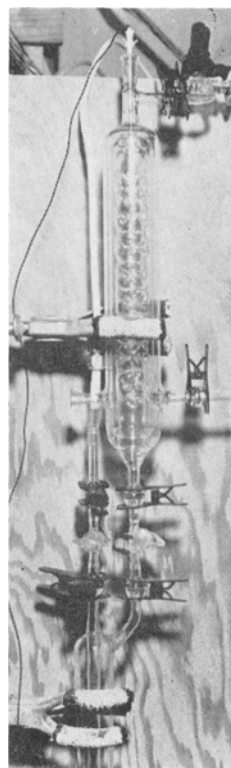


Fig. 3. Collecting unit.

blowing facilities until optimal parameters were achieved. The atmosphere from the simulator passes through the inner part of the condenser which has a large, irregular surface area. Entering through the port on the side of the condenser and circulating in the outer jacket is the chilled gaseous nitrogen. This allows the trace constituents to collect in the lower area which serves as the collecting container. This unit contains glass Raschig and Lessing rings and during the trapping operation is surrounded by a coolant to retain the isolated fraction. It is possible to transfer the entire unit or only the collecting container to suitable analytical instruments. At the top of the condenser is a thermocouple which indicates the temperature of the eluted gas as it leaves the system.

Sample Transfer:—After collection the cryogenic samples were transferred to the gas chromatograph or infrared spectrophotometer for analysis. By non-destructive testing, the same sample can be subjected to multiple analyses. Generally, it was found desirable to collect the sample initially in a variable path, infrared, gas sampling cell and after infrared examination transfer the constituents from this cell directly into the gas chromatograph. The effluents from the chromatograph could be collected *in toto* or as individual constituents since separation was effected on the chromatographic columns. The eluted materials were then contained in gas sampling cells or passed into select solvents for further determinations by standard chemical methods. The last procedure was followed only with the samples that were collected during the fire.

An alternative sampling technique was to pass the heterogeneous material directly into the chromatograph and subsequently collect individual effluents in micro-sampling cells. This was accomplished by measuring the retention times of each component on the chromatographic columns. The components were generally pure and contained only the inert carrier gas. The micro cells were then mounted on the spectrophotometer for infrared analysis. This technique requires, however, considerable deftness and precision.

DETECTION OF TRACE CONSTITUENTS

Gas Chromatography:—The components of the condensate are passed through a column of packing material or a coated capillary column. Due to partition coefficients and/or sorptivity, the components are separated and identified according to their retention time. They then pass to a sensitive detector and subsequently are recorded. The packed columns presently in use contain sorbent materials of silica gel and molecular sieve. The silica gel column is useful for the separation of many of the organic, low molecular weight compounds such as methane, ethane, propane, ethylene and other hydrocarbons up to C₃, in addition to carbon dioxide. The molecular sieve column is presently the most suitable packing material for the separation of the light inorganic gases. Materials which are differentiated by this synthetic zeolite include hydrogen, carbon monoxide, oxygen and nitrogen, all of which occurred in the cabin during normal operation. In addition, the molecular sieve serves as a monitor for the inert gases.

The capillary column was coated with a polyglycol derivative, Ucon LB-550-X. Ucon is a moderately polar, general purpose column which is especially responsive at the temperature that was employed. It detects a variety of materials including hydrocarbons and oxygenated compounds. The columns thus arranged allow for the determination of a wide group of compounds when operated at slightly above ambient temperatures.⁹ Both thermal conductivity (packed columns) and flame ionization (capillary column) detection systems were employed.

Two salient features of gas chromatography include 1) monitoring all of the constituents within a single collected sample and 2) accurate assay with samples having greatly different concentrations. For example, many of the trace constituents were at a level of less than 1 ppm., while the oxygen was maintained at a level of around 94 per cent. With this detection system, gases were monitored which showed a difference of 10⁶ concentration.

Infrared Spectrophotometry:—Gas analyses were routinely conducted with an infrared prism-grating spectrophotometer over the wave number range from 4000 to 400 cm.⁻¹. A variable path cell (10 cm. to 10 m.) was used to compensate for different concentrations of contaminants. Wave numbers from 4000 to 650 cm.⁻¹ were scanned with sodium chloride prisms and those from 650 to 400 cm.⁻¹ by cesium iodide prisms. The upper limit with cesium iodide optics is 200 cm.⁻¹, but in the present investigations was limited to 400 cm.⁻¹ due to the potassium bromide windows in the spectrophotometer.

Samples were introduced into the variable path cell through a gas manifold. In preparing the cell for sample introduction, the system was evacuated to an absolute pressure of less than one millimeter of mercury and the system was then pressurized to ambient pressure with nitrogen or other inactive gases. The cell was again evacuated and the solvent gas was passed over the sample, sweeping the sample into the cell. The pressure was increased with solvent gas to standard atmospheric pressure (760 mm. Hg). Due to the large volume of carbon dioxide and water vapor in the samples, many areas of the spectrum were occluded. To alleviate this condition, studies were conducted on the feasibility of placing selective sorbents upstream of the trapping system. In the present state of the art, however, these sorbents remove a portion of the trace contaminants, or only partially retain the carbon dioxide and/or water vapor.

RESULTS

The glass circulating pump operated effectively in the circulation of the chamber atmosphere. The flow used in this experiment was regulated to one liter per minute. It was noted that friction caused a powdered glass to be formed on the piston. This may be correctable by operation of the piston in the vertical rather than the horizontal position.

The cryogenic collection system effectively removed all components of the chamber atmosphere with condensation temperatures above the operational tempera-

ture of -100°C . These materials were contained within the trap until the analysis operations were accomplished.

The packed columns of the gas chromatograph routinely identified and quantitated the four major gases (oxygen, nitrogen, carbon dioxide and carbon monoxide) present in the space cabin simulator, as shown in Figure 4. Reliable values were obtained by multiplying

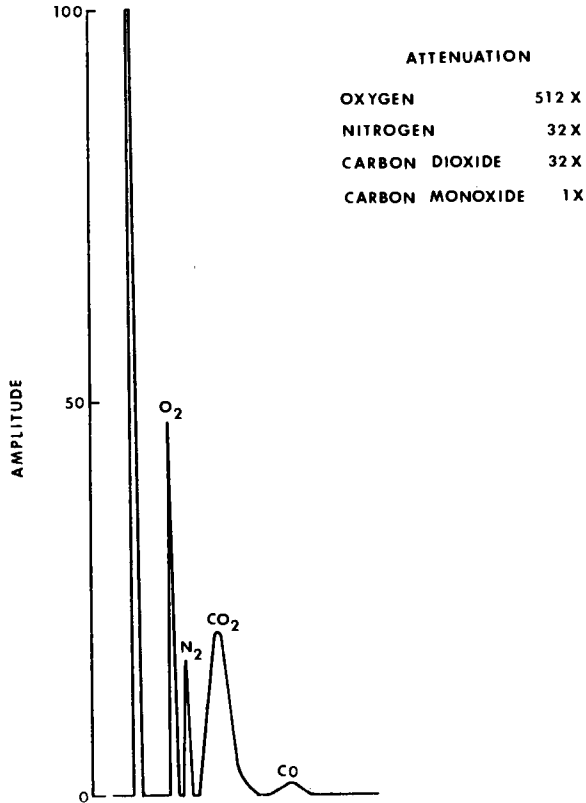


Fig. 4. Chromatogram of cabin air.

the attenuation and peak height. Definitive values were shown on standard curves as previously described.⁹ The results were in agreement with other standard laboratory instruments used in the analysis of these gases. In addition, traces of methane, acetylene and acetone were usually present in variable amounts.

The efficacy of the capillary column is indicated in Figure 5. This chromatogram, obtained from the coated

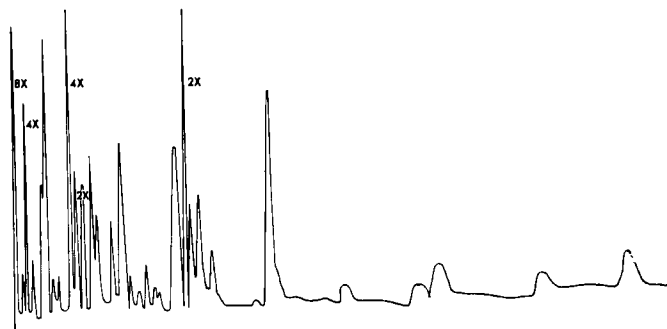


Fig. 5. Chromatogram of space cabin atmosphere during fire.

capillary column of material collected at the onset of the fire in the simulator, indicated 32 discernible peaks.

At the present time, tentative identification has been made of six peaks as shown in Table I. Research is in

TABLE I. RETENTION TIMES OF COMPOUNDS ISOLATED BY GAS CHROMATOGRAPHY FROM A SEALED ATMOSPHERE DURING A FIRE

Retention Time		Compound	Retention Time		Compound
Min.	Sec.		Min.	Sec.	
3	50	Methane	13	15	Ethylene Chloride
4	40		13	45	
4	55		14	50	
5	15	Methanol	15	20	
5	45	Acetaldehyde	16	05	
6	30		16	50	
6	55		19	15	
7	15		20	05	
7	55		21	45	
8	45		26	35	
9	35	Acetone	27	10	
10	15		32	10	
11	10		36	15	
11	55	Propanol	37	40	
12	20		41	20	
12	50		45	05	

Column—150' length—0.010" O.D.
Carrier Gas Flow Rate— ~ 4 ml./min.
Temperature— 40°C .

progress to identify the remaining unknown peaks.

Absorbance maxima were routinely identified with the prism-grating spectrophotometer over a wave number range of from 4000 to 400 cm^{-1} . The quantitative aspects of dispersive infrared were evidenced in monitoring carbon dioxide. This substance was read at the usual wave numbers of 3570 cm^{-1} and 2330 cm^{-1} ; additionally, six other wave numbers $720, 740, 790, 945, 970$ and 2070 cm^{-1} were present at higher concentrations. Careful measurements of the peak magnitudes demonstrated accurate assay at several points. High concentrations of carbon dioxide was evidenced by the appearance of the peaks in the $800\text{--}700\text{ cm}^{-1}$ and 2070 cm^{-1} ranges; during extremely high concentrations the $1000\text{--}900\text{ cm}^{-1}$ peaks were evidenced and were shown as overtones and combination bands. Water appeared in the frequency range from $200\text{--}1300\text{ cm}^{-1}$ with greatest absorption at 1590 cm^{-1} . Ethyl alcohol was evidenced from $1100\text{--}1000\text{ cm}^{-1}$. A hydrocarbon which exhibited stretching bonds was clearly delineated at 2950 cm^{-1} , and acetylene appeared at 728 cm^{-1} . A number of arti-

TABLE II. TENTATIVE IDENTIFICATION OF COMPOUNDS AND CLASSES OF COMPOUNDS ISOLATED FROM A SEALED ATMOSPHERE DURING A FIRE

Compound	
Acetaldehyde	Ethyl chloride
Acetone	Ethylene
Acetylene	Ethylene chloride
Ammonia	Formaldehyde
Benzene	Hydrogen chloride
Carbon dioxide	Methane
Carbon monoxide	Methanol
Ethanol	Methyl chloride
Ethyl ether	Nitrogen dioxide
	Propanol
Class	
Aldehydes	Hydrocarbons
Carbohydrates	Cyanates
	Sulfides

facts were shown in the 1200-1050 cm^{-1} range and an impurity was exhibited in the potassium bromide windows at 1960 cm^{-1} . With Ascarite placed upstream in the collection system, two additional spectra were delineated; carbon monoxide at 2200 cm^{-1} and ethylene at 947 cm^{-1} . Three peaks which appeared to be valid, but which are as yet unidentified occurred at 1090, 1015 and 800 cm^{-1} .

Many materials have yet to be identified even though the routine cabin air samples constitute a relatively clean atmosphere. The problems arising after gross contamination of the atmosphere are much more complex. For example, during sampling of the fire in the space cabin simulator, a sample of the atmospheric gases was obtained. Tentative identifications have been made (Table II) by several chemical and physical methods and 19 compounds and 5 classes of compounds have been noted. Undoubtedly, there were many more present that remain either unidentified or undetected.

SUMMARY

Innovations in instrumentation and cryogenics have been employed in the isolation and detection of microconstituents in a manned spacecraft simulator. Since the isolation of materials is a tedious and time consuming procedure, specialized units were constructed for the collection of the trace constituents and also to occlude extraneous contaminants from entering the system. Gas chromatography was employed for broad spectrum analysis of compounds and sample separation. Infrared spectrophotometry served as a parallel detection system. During normal operation, three to seven constituents consisting of nitrogen, oxygen, carbon dioxide, carbon monoxide, acetylene, acetone, and methane were normally found. A fire in the space cabin resulted

in numerous compounds being liberated, several of which were tentatively identified. Many of these were probably pyrolysis products from the construction components aboard.

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