



Apr 5th, 8:00 AM

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# ACCELERATED PROCEDURE FOR DETERMINATION OF GAS-OFF PRODUCTS FROM SPACE CABIN MATERIALS

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## Summary

A fast and accurate method for the empirical evaluation of the degassing characteristics of materials and supplies carried aboard a space capsule is described. The proposed procedure utilizes 72-liter flasks as reaction chambers. Materials to be tested were introduced into one group of flasks for a period of 30 to 60 days. The flasks were maintained under temperature, pressure, and lighting conditions expected to prevail within the spacecraft. Parallel experiments were conducted over a 24-hour period at a flask temperature of 120°F obtained by irradiation of the flask with mercury vapor lamps. At regular, predetermined intervals the flask atmospheres were tested for outgassed contaminants by gas chromatography in conjunction with infrared spectroscopy. Several examples of test results are presented. They indicate that different temperatures did not affect the reaction mechanism involved in the outgassing processes. The type of products which had outgassed remained the same; and, as expected, only the quantity of released products was higher at higher temperatures.

## Introduction

Air pollution inside a spacecraft is, in many respects, comparable to smog condition in urban atmospheres. All of the components required for the build-up of synthetic smog are present in the spacecraft. Occupants, materials, and supplies carried aboard the spacecraft are continuously releasing trace amounts of contaminants. Irradiation by normal or by extraneous light sources penetrating into the space cabin will form potentially toxic reaction products. Since the mechanisms of photo-chemical smog formation are similar, both aloft and on the ground, it is safe to assume that the physiological effects experienced on days of intense smog episodes will be duplicated in the space cabin. In view of the harmful effects of these trace contaminants on the crew members, their effective control is imperative.

## Comparison Studies

### Possible Approaches

The use of air purifiers to remove contaminants from any random selection of candidate materials could create an impossible hardware design situation or an impossible power-weight-volume requirement. However, screening of the materials by test and provision of contaminant control devices, such as a toxin burner and filters, can provide an efficient combination, as evidenced by the Douglas space cabin simulator test program.

The selection of most materials on the basis of their outgassing properties allowed a degree of control of the ultimate composition of the space cabin air. Materials with high outgassing properties were excluded and replaced with alternate materials better suited for use in a space cabin. This approach was followed by the performance of extensive tests on most materials used in the Douglas space cabin simulator life-support test program. The information derived from this toxicology program allowed the selection of materials used within the space cabin compartment prior to the now-completed 30-day life-support system tests. These tests were conducted with a crew of four men.

### Outgassing at Ambient Temperature

The method ordinarily used in testing the outgassing properties of materials involves the use of 72-liter Pyrex flasks as reaction chambers. A wide-mouthed, 72-liter flask, as shown in Figure 1, is equipped with a tightly fitting stainless steel lid with several inlet tubes. These tubes are either connected to air purification systems or gas-handling systems, or they are capped with serum stoppers for injection of small volumes and withdrawal of samples from the flasks. Test samples of known weight and surface area are suspended from the center of the flask. The flask atmosphere may be readily adapted for a variety of gas systems, as well as for a variety of conditions of illumination and temperature.

The flexibility of this technique therefore permits the incorporation of any changes of physical requirements in this testing set-up, whenever the physical parameters for the operational spacecraft are changed. In most instances, the outgassing experiments have been conducted at room temperature, with samples withdrawn from the flasks after 30, 60, and 90 days for analysis.

It is desirable to evaluate candidate materials under the same conditions as those to which the crew members will be exposed. However, the conduct of all experiments under "realistic conditions" may at times lead to difficulties which could be hard to overcome. Some of these difficulties are as follows:

1. At ambient temperature the amounts of contaminants released, even after long curing times, are frequently too minute to be recognized by extremely sensitive detection devices. Yet, because it is exactly the presence of these compounds in the space cabin which may produce deleterious effects on the occupants of the spacecraft, their identification is imperative.
2. The large number of materials to be tested and the time schedules to be met make delays of 30 to 90 days impracticable. This was especially true in the case of the manned space simulator program recently completed by Douglas, where frequently a rapid selection between alternate materials had to be made.
3. Furthermore, extended time delays before actual analyses can be performed necessitate the storage of large numbers of reaction flasks. This alone is space and time consuming. Also, whenever replicate measurements are required, such as in doubtful cases or after sample losses, further delays are caused.

### Outgassing at Elevated Temperature

The question arose whether meaningful and reliable data could be obtained in shorter time periods, without sacrificing accuracy for speed. All past and present

experience in which several hundred flask experiments have been involved<sup>1</sup> indicate that this is indeed possible. The alternate approach consists of conducting all outgassing experiments at a temperature of 120°F with an exposure time of 24 hours. Materials to be tested are introduced into 72-liter flasks and irradiated by four mercury vapor lamps (Figure 2). With the use of ventilating fans, the temperature within the flask can be kept within a rather narrow range.

### Previous Comparison Study

Studies of the effects of different temperatures on the formation of those compounds which cause eye irritation were carried out by air pollution agencies<sup>2</sup>. The results of one study are demonstrated in Figure 3. The ordinate represents the hydrocarbon concentration present in the reaction flask, and the abscissa indicates the length of time, in seconds, until the eye compounds formed in the flask produce eye irritation. The shorter time interval before eye irritation is noticeable is due, of course, to formation of a higher concentration of eye irritants, regardless of their molecular structure. The quantities of material which cause eye irritation are considerably higher at the elevated temperature than at ambient conditions. However, it is evident from the parallelism of the statistically computed regression lines that the reaction mechanism is identical for both temperatures. It is interesting to note that the regression lines remain parallel for hydrocarbon concentrations in the 1 to 10 parts per million range, and may be extrapolated in either direction, without significant change in slope. The complete identity of the reaction mechanism which was first observed in air pollution studies provided the first indication that the use of elevated temperatures was technically correct and reasonable.

### Comparison of Three Paints and Two Moccasins

The first outgassing experiments were carried out with three different paints intended to be applied on all inner-wall surface areas of the space-cabin simulator. The three paints were polyvinyl acetate paint, epoxy-paint, and a water-based methacrylate paint.

Rectangular metal strips whose surfaces had been sandblasted were first treated with a primer, and then evenly sprayed with the respective paints to a thickness of 3 mills. A 72-hour drying period was allowed before the painted strips were introduced into the reaction flasks. Pressure within the flasks was adjusted to one-half of an atmosphere, which was composed of 50% oxygen and 50% nitrogen. While one flask was maintained at ambient temperature, another flask which had been identically charged was exposed to 120°F for 2 days. Later experiments showed that the irradiation time could be reduced to 1 day without affecting the results. Samples were then withdrawn from the flask atmosphere by the syringe and needle method for gas chromatographic analysis. This was satisfactory for most of the samples from the irradiated flasks; however, at ambient temperature the condensation of a sample volume of several liters was required.

For highest sensitivity, a Perkin-Elmer Model 800 gas chromatograph equipped with a flame-ionization detector has been used. In early tests, one Apiezon L column was used. In more recent tests, a second column containing Carbowax 1540 as a stationary phase is being used for the determination of retention ratios of compounds expected to be present in the flask atmosphere. In most instances the use of 1-milliliter samples has been sufficient to obtain well-defined chromatographic peaks.



Figures 4, 5, and 6 show the results obtained with the three paints at two temperatures. The upper section of the graphs represents chromatograms of irradiated samples; these can be compared with the chromatograms run under ambient conditions, which are shown on the lower section of the graph. Although certain differences in detail are noticeable on close inspection, it is evident that a good overall similarity between these graphs does exist. Most of the major peaks noticeable at elevated temperature appear to be present at ambient conditions. This applies especially for the epoxy and polyvinylacetate paints. In the case of the methacrylate paint, a good similarity exists in the peaks eluted during the first 8 minutes. However, two major peaks which appear at the elution times of 19.2 and 22.4 minutes in the irradiated sample are absent at ambient conditions. Since larger volume samples had to be applied with the use of water-based paint, the possibility exists that these peaks would have appeared if a sample of larger volume had been introduced. A slight indication of a peak in the vicinity of 19 minutes becomes apparent with the use of a sample from a 10-liter condensate.

Further comparisons of temperature effects on outgassing properties were carried out with two pairs of moccasins, one pair with rubber soles and one pair with leather soles. The results of these experiments, shown in Figures 7 and 8, also indicate the similarity of most of the outgassing components at ambient and at slightly elevated temperatures.

Figure 9 shows a combination of the gas chromatograms of all three paints. On the basis of the total amount of outgassing materials, it is evident that the volumes from methacrylate paint are substantially less than the volumes outgassed by the other two. These differences are even more apparent when consideration is given to the five-milliliter sample size. The use of a one-milliliter sample would have produced peaks not much higher than the baseline.

Figure 10 compares the gas chromatograms of the two moccasins. The amount of outgassed materials from the leather-soled moccasin appears to be substantially lower than the amount from the rubber-soled moccasin. This comparison warranted the selection of the leather-soled moccasin for use in the space cabin simulator.

Infrared absorption spectra carried out with flask atmospheres from two paints at two temperatures also show the existence of major quantitative differences of outgassed materials. Table I gives the optical densities measured at three specific wavelengths for polyvinyl acetate and methacrylate paints. It is apparent that the relative concentrations of hydrocarbons, carbonyl linkages, and organic esters are considerably lower for methacrylate paints than for polyvinyl acetate; this, of course, is in good agreement with the quantitative gas chromatographic values, and justifies the selection of methacrylate paint as interior coating for the space cabin simulator.

The identification of several chromatographic peaks has been tentatively based on retention ratios obtained with one column material, namely, Apiezon L. The retention times of many of the compounds used in the calibration of the gas chromatograph are consistent with the peaks observed in the outgassed materials. However, more definitive peak assignments will be possible by the determination of a second set of retention ratios, using, as previously mentioned, Carbowax 1540 as the column material; this work is now in progress. As the identities of individual peaks become more reliably established, it will be possible to select candidate materials on the basis of the toxicities of the identified compounds, provided, of course, that agreement between the various government hygienists and

public health agencies can be reached regarding threshold limit values for continuous exposures.

The good agreement between chromatograms produced with off-gassing samples at ambient and at slightly elevated temperatures remains valid for a narrow temperature range. When the flask temperature is increased beyond 120°F, as it is in air pollution studies, the results are different. A temperature of 194°F resulted in chromatograms and infrared spectra which had no resemblance to those obtained at ambient conditions. As an example, in studies conducted at Douglas, carbon monoxide was found to form at high temperatures by decomposition of organic compounds, while very little, or none at all was detected at ambient temperature. On the other hand, the toxicologically important ozone is formed and persists only at ambient temperature, but decomposes readily at high temperature. It is therefore important to emphasize that the good similarity observed within narrow temperature ranges can not be extrapolated over other ranges without prior investigation.

### Space Cabin Simulator

Because of stringent schedule requirements for the space cabin simulator program, the accelerated procedure described in this paper was used in the rapid evaluation of "Micarta," a phenol-formaldehyde resin used as a sound dampener, and a glasswool insulation material. Sizeable quantities of both are used inside the space cabin. When it was found that "Micarta" released copious amounts of formaldehyde which could accumulate in the space cabin to more than 2 parts per million, it was replaced with sheets of aluminum. Glasswool insulation material, although flash-fired by the manufacturer at 700°F, showed the release of considerable amounts of contaminants. Asbestos ribbon was then considered as a possible alternate, but upon testing, it showed an even higher outgassing potential than glasswool. At present, a search for a more suitable insulation material is being made.

During the normal operation of the space cabin simulator, concentrations of oxygen, carbon monoxide, carbon dioxide, hydrocarbons, and relative humidity were routinely recorded. Daily samples were collected for chemical and gas chromatographic determinations. They indicated the presence of methane, acetone, isopropanol, and 2-ethylbutanol, in addition to several not definitely identified peaks. The 2-ethylbutanol was formed upon hydrolysis of Coolanol, which was used as refrigerant. It was interesting to note that the presence of high levels of this compound could be associated with a loss of Coolanol in the refrigeration system. In most instances, higher carbon monoxide values were noticeable at the same time. Formation of both contaminants could be traced to the absorption of the escaping refrigerant by the glasswool fibers of the insulating material. The high temperature of the Coolanol lines caused the formation of hydrolysis and degradation products. The repair of the Coolanol leak resulted in the return of both the 2-ethylbutanol and the carbon monoxide to normal levels. It is also interesting to note that after the curing of the methacrylate paint, no significant outgassing of space cabin samples could be observed during the 12-day checkout and the 30-day manned space cabin simulator tests.

### Conclusions

1. Comparisons were made of the effects of temperature on the outgassing properties of materials and supplies. It was found that the use of 120°F in this study produced results which are closely comparable with those observed at ambient temperature.

2. The types of compounds released at the two temperatures are closely related. However, the quantities of outgassed products are higher at higher temperatures.

3. This method is both practical and technically sound. It provides a convenient means to evaluate a large number of candidate materials in a relatively short time, without sacrificing accuracy for speed.

4. The similarity of outgassing results reported in this paper has been observed over a narrow temperature range and can not be extended over other temperature ranges without prior investigation.

#### References

1. Mader, Paul P., J. Gliksman, Marcel G. Eye, and L. A. Chambers, "Photochemical Formation of Air Contaminants from Automobile Exhaust Vapors," *Industrial and Engineering Chemistry*, 50, 8, 1173-1174 (1958).
2. Air Pollution Control District, County of Los Angeles Technical Progress Report, "The Chemistry of Urban Atmospheres," Volume III, December 1962.

# IRRADIATION FLASKS MAINTAINED AT AMBIENT TEMPERATURES

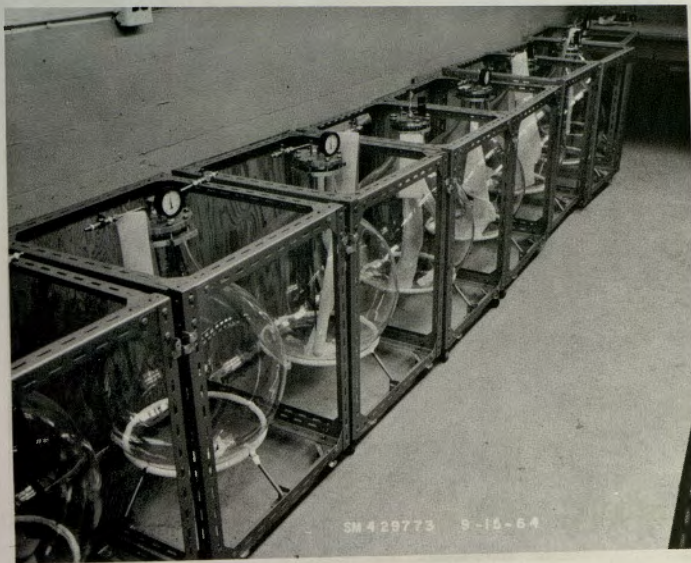


FIGURE 1



# IRRADIATION FLASK EQUIPPED WITH 4 MERCURY VAPOR LAMPS

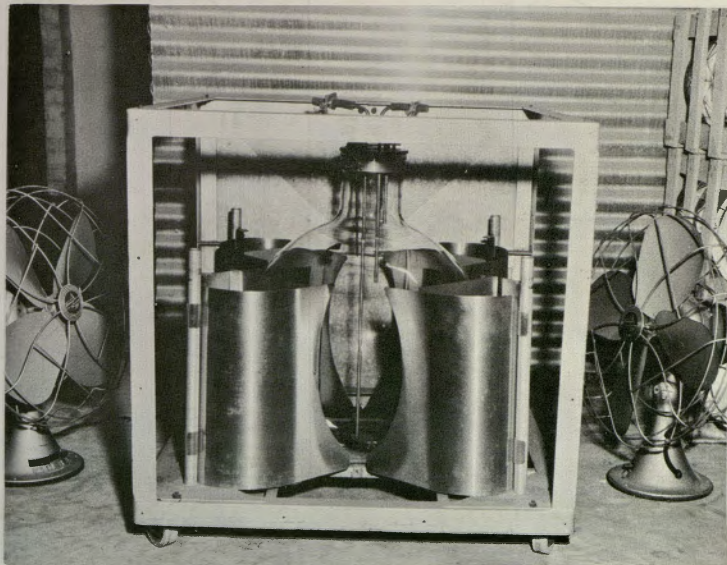


FIGURE 2

# EFFECTS OF 2 TEMPERATURES ON THE FORMATION OF EYE IRRITANTS

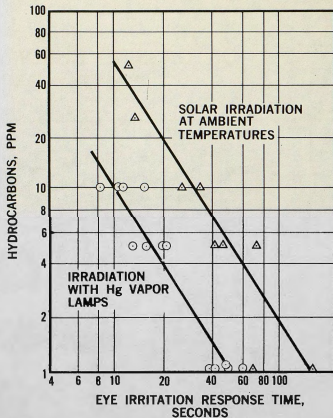


FIGURE 3

# OUTGASSING CHROMATOGRAM OF POLYVINYL ACETATE PAINT

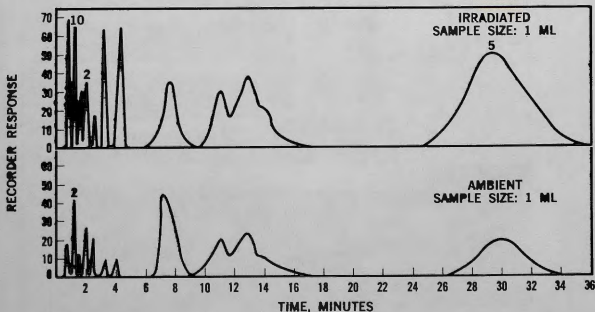


FIGURE 4

# OUTGASSING CHROMATOGRAM OF EPOXY PAINT

M-23991

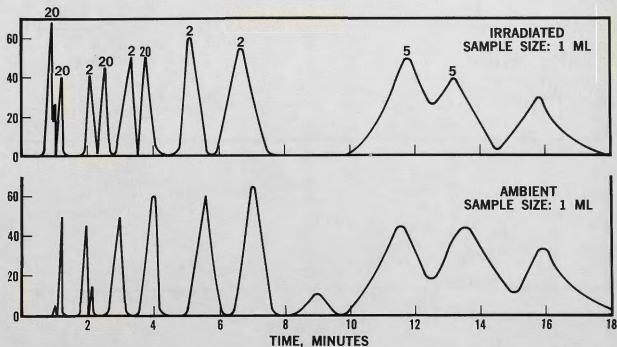


FIGURE 5

# OUTGASSING CHROMATOGRAM OF ACRYLIC ESTER PAINT

M-23990A

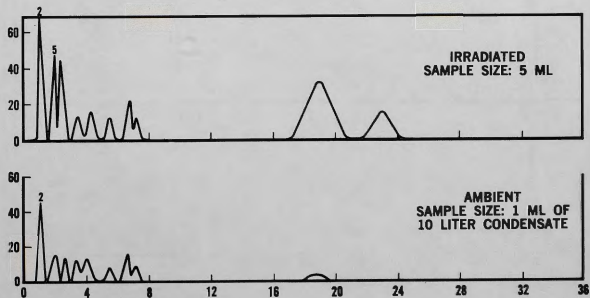


FIGURE 6

## OUTGASSING CHROMATOGRAM OF RUBBER-SOLED MOCASSIN

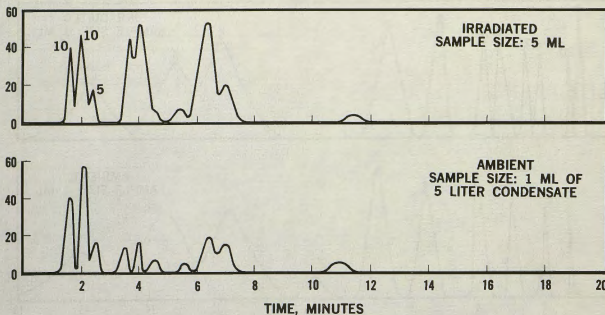


FIGURE 7

## OUTGASSING CHROMATOGRAM OF LEATHER-SOLED MOCASSIN

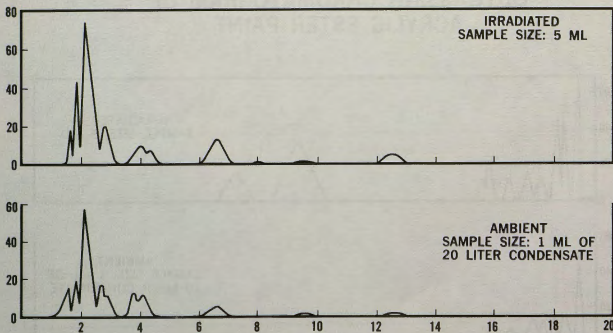


FIGURE 8

M-23985A

### OUTGASSING CHROMATOGRAMS OF 3 PAINTS (IRRADIATED)

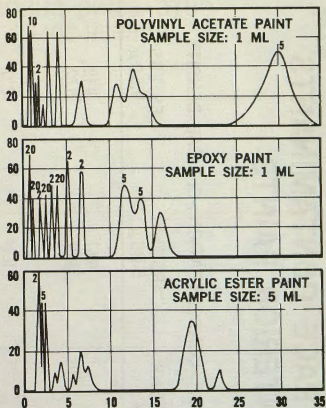


FIGURE 9

M-23987

### OUTGASSING CHROMATOGRAM OF TWO MOCCASINS (IRRADIATED)

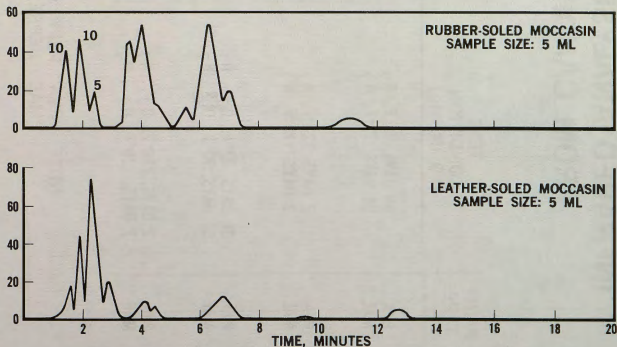


FIGURE 10



TABLE I

M-23983

# INFRARED ANALYSES OF TRACE CONTAMINANTS FROM CANDIDATE INTERIOR PAINTS

PAINT TYPE	TEST CONDITION (15 IN. Hg)	RELATIVE CONCENTRATION: OPTICAL DENSITY		
		HYDROCARBONS 3.45 $\mu$	CARBONYL 5.85 $\mu$	ESTERS 9.50 $\mu$
PVA	30 DAYS, 72°F., N <sub>2</sub>	0.93	0.57	0.19
MAE	30 DAYS, 72°F., N <sub>2</sub>	0.04	0.02	0.02
PVA	2 DAYS, 120°F., N <sub>2</sub>	0.26	0.64	0.32
MAE	2 DAYS, 120°F., N <sub>2</sub>	0.06	0.03	0.02
PVA	30 DAYS, 72°F., O <sub>2</sub> , N <sub>2</sub>	0.17	0.41	0.05
MAE	30 DAYS, 72°F., O <sub>2</sub> , N <sub>2</sub>	0.03	0.02	0.01
PVA	2 DAYS, 120°F., O <sub>2</sub> , N <sub>2</sub>	0.85	0.94	0.22
MAE	2 DAYS, 120°F., O <sub>2</sub> , N <sub>2</sub>	0.25	0.20	0.03

NOTE: "PVA" REPRESENTS "POLYVINYL ACETATE" PAINT  
"MAE" REPRESENTS "METHACRYLATE ESTER" PAINT