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EVALUATION OF DESORBATES FROM A REGENERATIVE CO_2 REMOVAL SYSTEM USED IN A 60-DAY MANNED TEST

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Prepared Under Contract No. NASw-1539

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Office of Advanced Research and Technology
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Advance Biotechnology and Power Department
McDonnell Douglas Astronautics Company — Western Division
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FOREWORD

The work described herein was conducted for Walton L. Jones, M.D., Director of Biotechnology and Human Research Division, J.N. Pecoraro, and A.L. Ingelfinger of the Office of Advanced Research and Technology, Headquarters, the National Aeronautics and Space Administration, Washington, D.C., under the direction of Mr. Rex B. Martin, NASA Langley Research Center. The work was performed by the Advance Biotechnology and Power Department of the McDonnell Douglas Astronautics Company--Western Division, Santa Monica, California, under NASA Contract No. NASw-1539.

Those who contributed to this report are as follows:

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ABSTRACT

Desorbates from silica gel and molecular sieve beds used as a part of a regenerative CO_2 removal unit in a life support system during a 60-day manned test were identified and quantified. The capacities of these two sorbers to adsorb and accumulate trace contaminants from the cabin atmosphere were compared. Material desorbed from activated charcoal of the toxin control subsystem was subjected to qualitative analysis. The results indicated that a significant amount of organic compounds was released from the silica gel and molecular sieve beds during the regenerative cycle. The daily reduction in organic contaminant level in the simulator (4, 100-ft^3 volume) amounted to approximately 7.7 parts per million (ppm).

The operation of the water recovery system inside the Space Station Simulator (SSS) inadvertently led to the formation of sizable quantities of ammonia because of incomplete pretreatment of urine. It was effectively adsorbed by the silica gel sorbent beds. The ammonia was generated at a rate equivalent to 32.0 ppm per day and was disposed of in the condensed water after regeneration. The silica gel unit helped remove the ammonia from the cabin at a faster rate than the water recovery post-treatment system could accomplish alone. However, with the processing of the silica gel water condensates eventually all of the ammonia would have been removed by the ion exchange resin in the post-treatment system.

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Section 1

INTRODUCTION AND SUMMARY

During the 60-day manned operation of the Space Station Simulator (SSS) under Contract NASw-1612, reported in Reference 1, three types of sorbent beds were used: silica gel, molecular sieve, and activated charcoal. The first two sorbents were used in the regenerative CO_2 removal subsystem, the latter formed a part of a catalytic burner, manufactured by Mine Safety Appliances Corporation. It had been previously established that silica gel and molecular sieve beds used in the regenerative adsorption of water and carbon dioxide were also capable of accumulating sizable quantities of organic and inorganic compounds present in trace concentrations in manned space station compartments.

The question arose whether any replacement of the present regenerative molecular sieve/silica gel CO_2 concentrator system concepts for long-duration mission spacecraft by more advanced techniques such as solid amines or carbonation cells would affect trace contaminant control within the cabin atmosphere. The principal objective of this program was to evaluate the regenerative silica gel and molecular sieve systems to remove and control contaminants. Qualitative testing of activated charcoal, which comprised a part of the catalytic burner trace contaminants control unit, also was included in the program to provide an indication of all species of contaminants present in the atmosphere. The types of organic compounds desorbed from all three sorbents were qualitatively identified. Quantitative measurements were carried out on gases desorbed from silica gel and molecular sieve sorbents by the use of gas chromatographic, mass spectrometric, and wet chemical procedures. Determinations of concentrations are reported as explained in the Appendix.

To accomplish the objectives of this program, the following tasks were carried out: calibration of gas chromatographs for organic compounds, determination of optimum desorption conditions, establishment of baseline data from unused adsorbent, identification and quantitative estimation of desorbed compounds from the sorbents in CO_2 removal unit, and qualitative identification of compounds desorbed from the activated charcoal bed in the toxin burner unit. The results of this study are summarized as follows:

1. Qualitative analyses of the desorbates from all three sorbent beds led to the identification of over 40 specific organic and several inorganic compounds that were removed and controlled by the life support system. In addition to the analyses conducted by the McDonnell Douglas Astronautics Company, a number of separate specimens were independently evaluated by the NASA Langley Research Center by microwave spectroscopy.

2. Quantitative analyses of desorbates from silica gel and molecular sieve sorbents indicated that the use of these two beds led to a daily reduction in organic contaminants of 4.2 ppm and 3.5 ppm respectively. The combined reduction of the organic contaminant level by about 7.7 ppm daily represents an important contribution to the purity of the space station atmosphere.

   The Davison Chemical Division of W.R. Grace and Company provided quantitative analyses for the silica gel and molecular sieve materials confirming independently the above results (Reference 2).

3. Analyses of desorbed gases from silica gel and molecular sieve showed the presence of ammonia equivalent to a concentration of 1.0 ppm and 0.06 ppm respectively in the cabin (volume 4, 100 ft^3). Although the alert level concentration for this contaminant is 50 ppm at standard conditions, the occupants of the space station detected its presence by odor at 5 to 8 ppm. It is of special significance to note that the quantity of ammonia desorbed from silica gel sorbent could have produced 32.0 ppm daily, if the entire amount of this contaminant had been dispersed into the cabin and no ion exchange resin column had been included within the water recovery post-treatment system.

4. The desorbed gases from the silica gel and molecular sieve beds also showed the presence of oxides of nitrogen equivalent to a concentration of about 0.01 ppm in the cabin. However, atmospheric samples taken during a 60-day manned run showed concentrations of oxides of nitrogen ranging from 0.1 to 0.7 ppm. The presence of oxides of nitrogen was probably caused by the catalytic oxidation of ammonia that passed through the toxin burner.

Test procedures, results, and supporting data are presented in the sections entitled as follows:

- Life Support System Description
- Test Conditions and Procedures
- Test Results
- Conclusions

Section 2

LIFE SUPPORT SYSTEM DESCRIPTION

Trace contaminants were adsorbed by the solid sorbent beds which formed a part of Space Station Simulator (SSS) life support subsystem. A brief description of the subsystem involved and their principles of operation follow.

2.1 CARBON DIOXIDE CONCENTRATOR

The molecular sieve and silica gel sorbents used in this project were obtained from the sorbent beds of the regenerable CO_2 concentrator, shown schematically in Figure 1. The concentrator included two molecular sieve beds for the removal of carbon dioxide. However, since molecular sieve beds would preferentially adsorb any traces of atmospheric moisture, thus reducing their CO_2 adsorption capacity, two silica gel beds were provided in the system to remove the moisture content of the circulated atmosphere. These beds were arranged so that one pair of sorbent beds adsorbed and accumulated water and carbon dioxide during a 45-minute cycle, while the other pair released the previously loaded gases thereby regenerating the sorbent beds. The desorbed CO_2 was then transferred, under pressure, to an accumulator for processing in the Sabatier oxygen recovery subsystem. At the end of each 45 minutes, a cycle timer operated sequencing valves to switch the adsorbing and desorbing beds. The silica gel and molecular sieve sorbents evaluated in this study were taken from a desorbed set and an undesorbed set of beds. A photograph of the carbon dioxide concentrator is shown in Figure 2.

2.2 ACTIVATED CHARCOAL

The activated charcoal samples used in this project were taken from the activated charcoal bed that formed a part of the toxin control subsystem.

A catalytic burner, particulate filter, heat exchanger, and the 5-pound charcoal sorbent bed were the major components of the toxin control subsystem shown in Figure 3. The simulator atmosphere was drawn into this unit. Approximately 100 cfm was passed through the charcoal bed and then returned to the cabin. A small fraction of the atmospheric gas (0.7 cfm) was diverted to the toxin burner. This unit was designed to oxidize carbon monoxide and organic contaminants in the simulator atmosphere to more innocuous compounds.

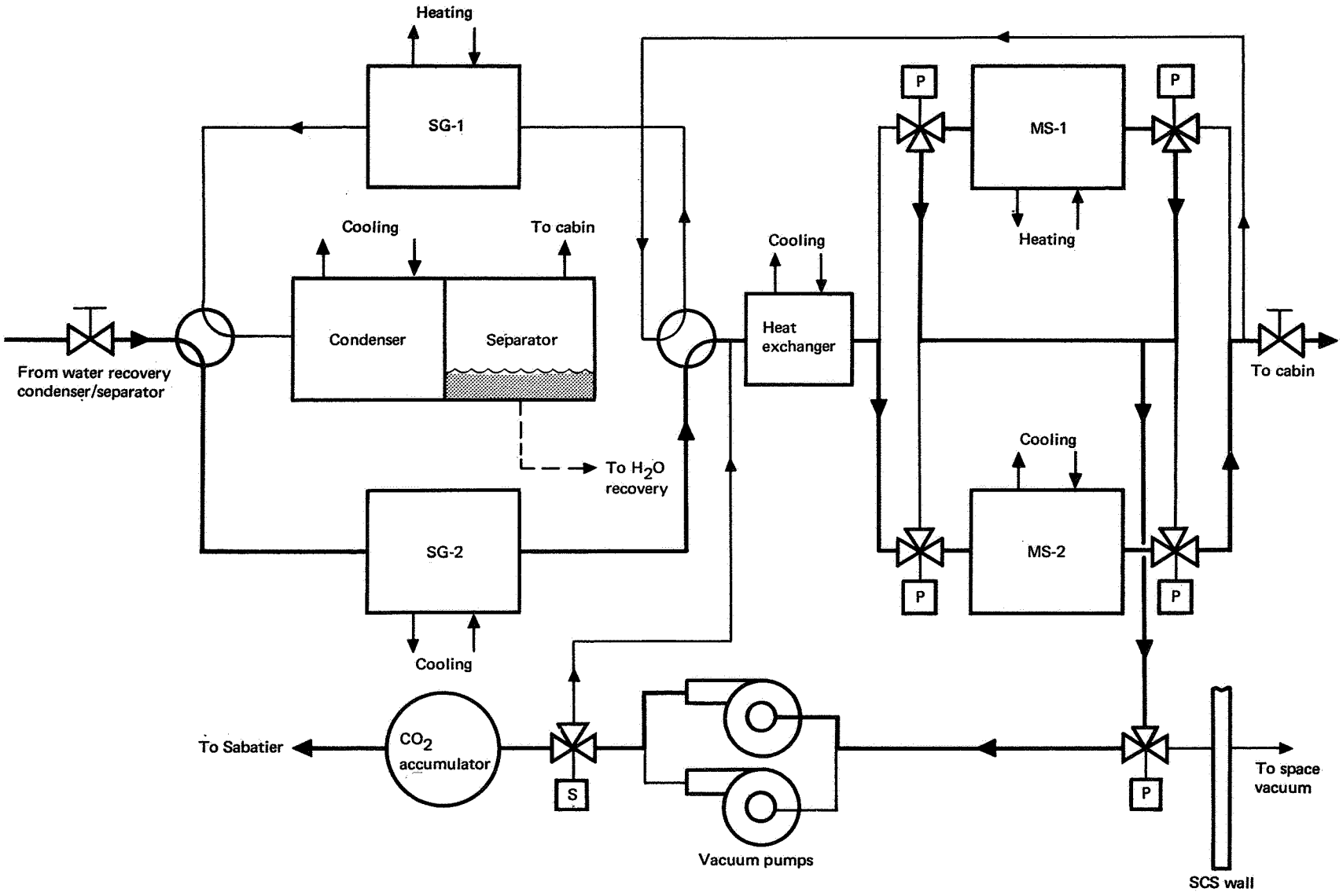

Figure 1. CO_2 Concentrator Unit

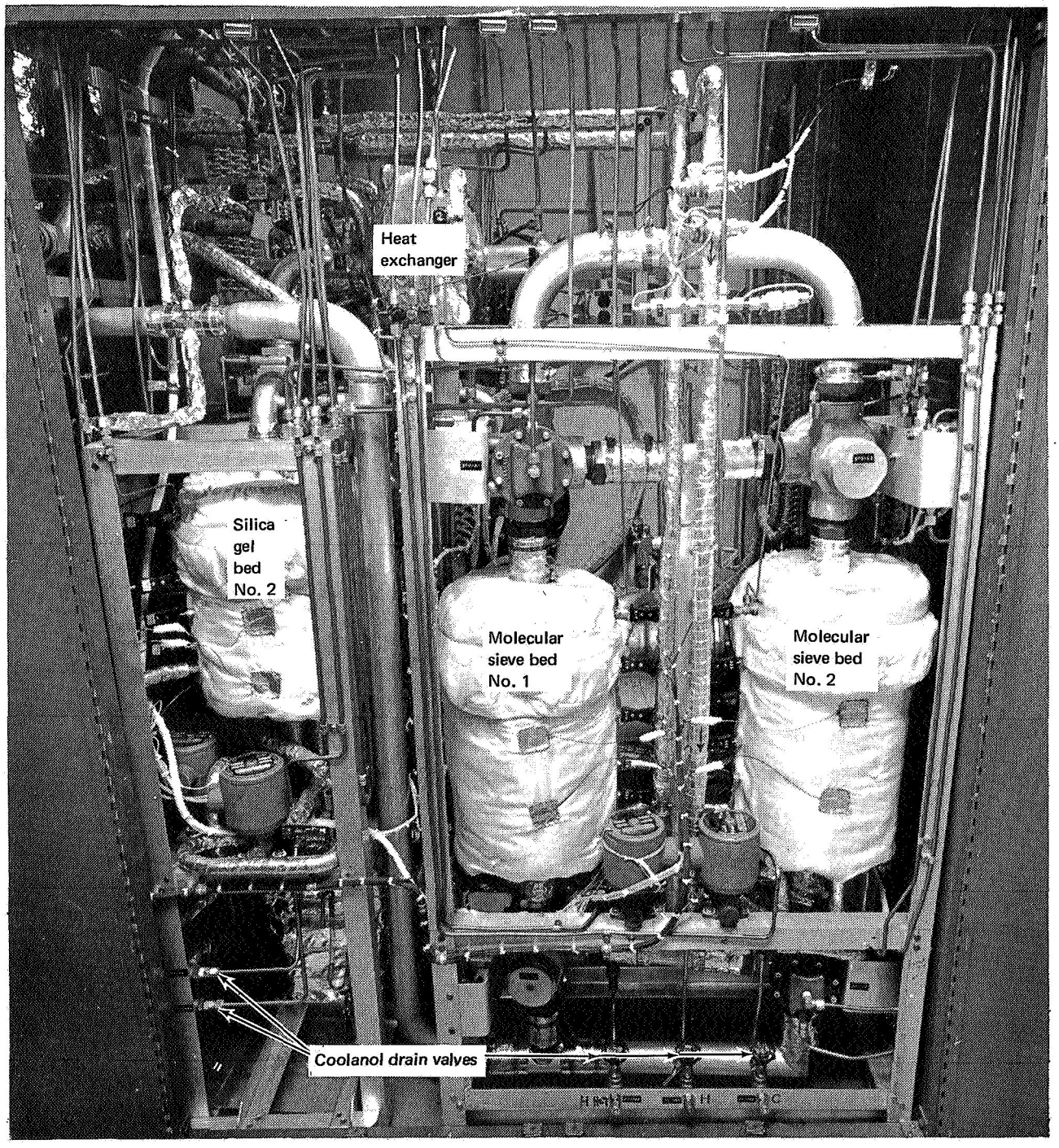

Figure 2. Front View of the CO_2 Concentrator Subsystem Toxin Control Subsystem

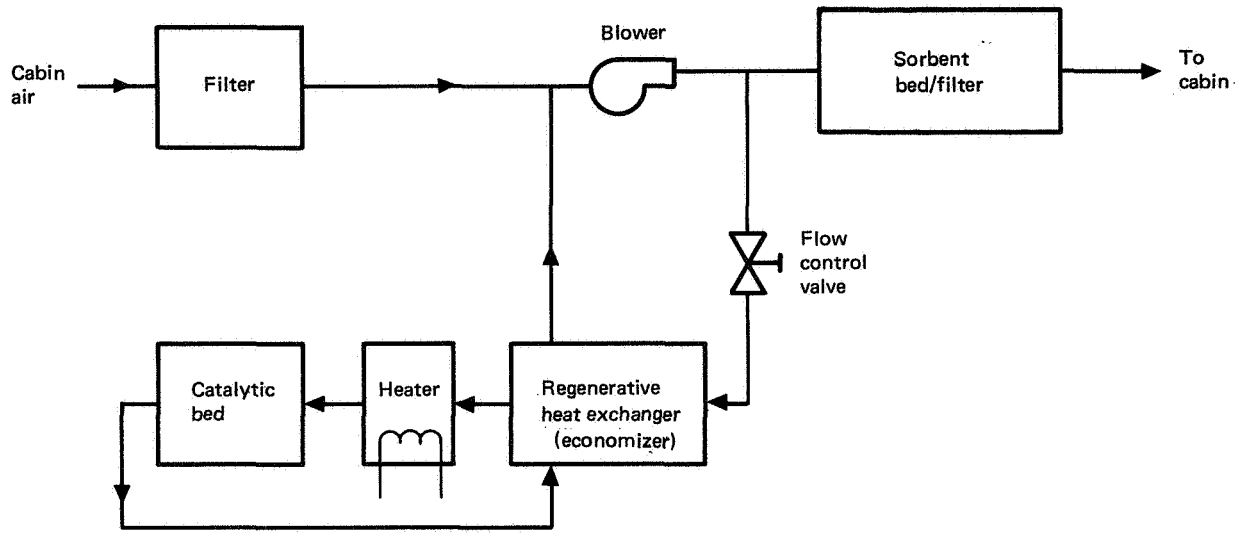

Figure 3. Toxin Control Subsystem

In addition to the activated charcoal bed in the toxin control subsystem, trace contaminants and odor control was also provided by the large charcoal filter in the potable water recovery subsystem. It is important to note that both charcoal beds were in uninterrupted operation during the entire 60-day test.

Section 3

TEST CONDITIONS AND PROCEDURES

3.1 CALIBRATION OF GAS CHROMATOGRAPHS

The materials desorbed from each of the three types of sorbents were first identified by gas chromatography and then confirmed by mass spectral analyses.

Two Perkin-Elmer gas chromatographs, Model 800, were used. Each instrument was equipped with 12-foot dual columns and dual flame ionization detectors. The columns of one instrument were packed with didecylphthalate (DDP) on Chromosorb W, 80-100 mesh, the columns of the second instrument contained Carbowax (CW) 1500 on Chromosorb W. Helium was the carrier gas in both instruments. A flow rate of about 30 ml/min was maintained. Gas samples of known composition were then introduced into each of the two gas chromatographs, while the column temperature was maintained at 100 °C. Thus, two elution times were obtained, one with each instrument. Two additional elution times were obtained for the same compound when the column temperatures were lowered to 50 °C. A total of 90 organic compounds were calibrated. They were selected on the basis of materials identified in the space station atmosphere by MDAC-WD and other workers in this field. These calibrations had to be repeatedly checked and brought up to date. They were then used to identify unknown samples by matching the exhibited elution times with the tabulated data. Whenever all four elution times from a sample matched all four elution times of the calibrated material, the identification of the samples was assumed to be positive.

At times, preliminary identifications had to be based on three elution peaks if the fourth one was covered by an interfering major peak from another substance. In these instances, it was possible to confirm the identification by mass spectrographic analyses.

3.2 OPTIMUM DESORPTION CONDITIONS

A procedure for the optimum desorption of contaminants from silica gel (SG) and molecular sieve (MS) was first established. The apparatus used for the desorption of the sorbents is shown in Figure 4. A known amount of SG or MS was placed into a 500-ml Erlenmeyer flask. By means of a heating mantle, the temperature of the material inside the flask was raised to 75 °C, 125 °C, 175 °C, and 250 °C during successive test runs. During the heating process, the pressure inside the flask was maintained below 4 mm Hg. The desorbed gases were carried by a very low helium flow to a

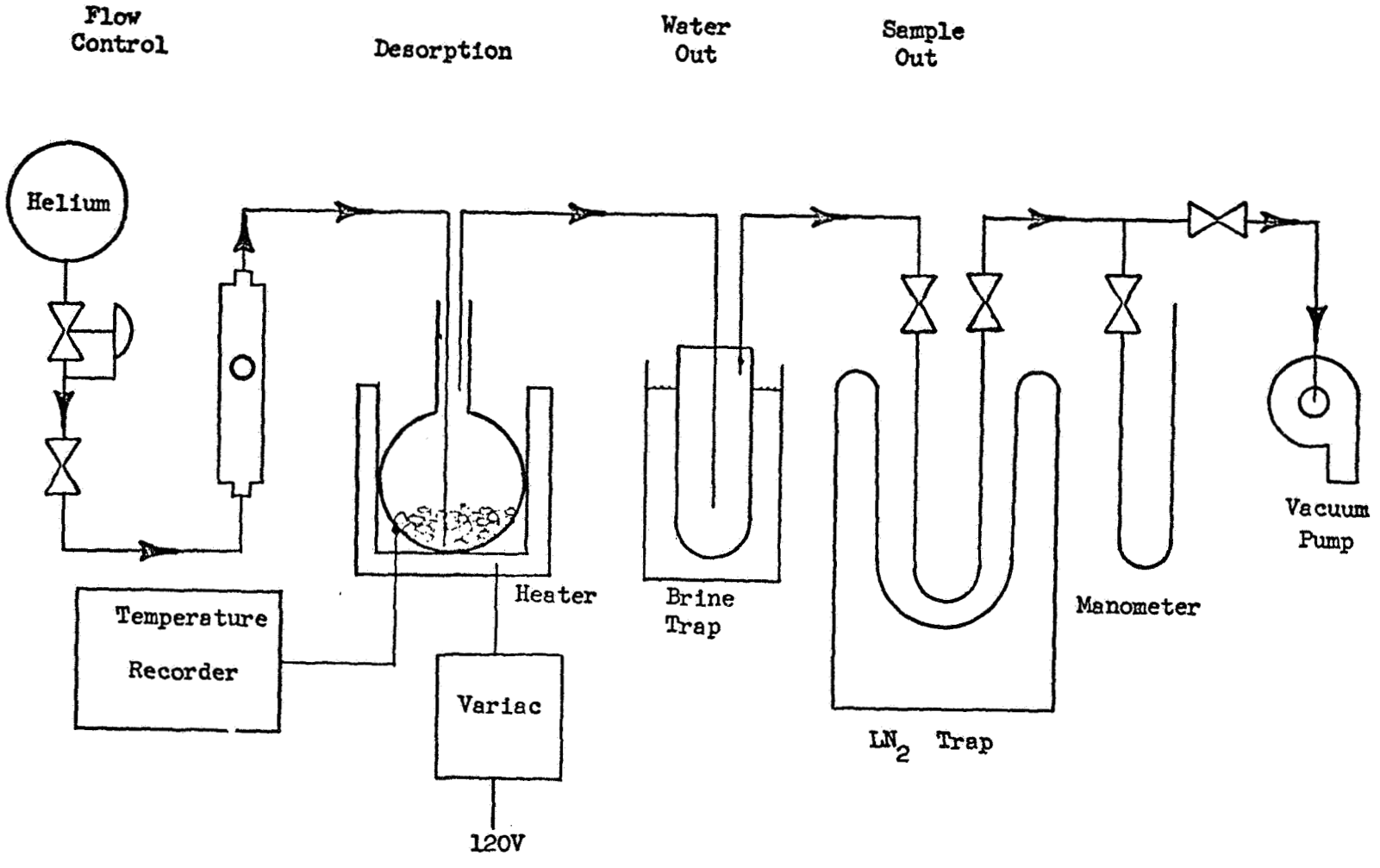

Figure 4. Desorption Apparatus

brine trap (-20 °C) where most of the water was condensed. The desorbed gases were then swept into a U-shaped stainless steel trap immersed in liquid nitrogen. Samples of 5 ml from this trap were then introduced into the two gas chromatographs and the peak heights obtained at the four different temperature were compared.

Measurements were made of the quantities of organics released at each of the four temperatures for each kilogram of sorbents.

Results in Table 1 and Figure 5 indicate that a desorption temperature of 175 °C was close to optimum since the largest quantities of materials were found to desorb in this range.

To determine the optimum sampling time, one sample of each sorbent was desorbed in 40-minute time intervals. The amount of toluene eluted during each sampling period was determined. Toluene was selected because it was desorbed from each sorbent and exhibited a prominant peak in all chromatograms. Results in Table 2 indicate that molecular sieve and silica gel readily released the toluene during the first 40 minutes of desorption. After that time, the amounts of toluene desorbed decreased rapidly. A sampling time of 40 minutes at a temperature of 175 °C was then established as optimum conditions for desorbing organic compounds from molecular sieve and silica gel beds.

Table 1

EFFECT OF TEMPERATURE ON QUANTITIES OF ORGANICS RECOVERED FROM SORBENTS

(Sample Size: 1 gram)

	Quantities of Organics Desorbed (mg/m^3)	
Desorption Temperature	Molecular Sieve	Silica Gel
75 °C	0.23	0.27
125 °C	0.25	0.27
175 °C	4.40	7.19
250 °C	2.38	2.50

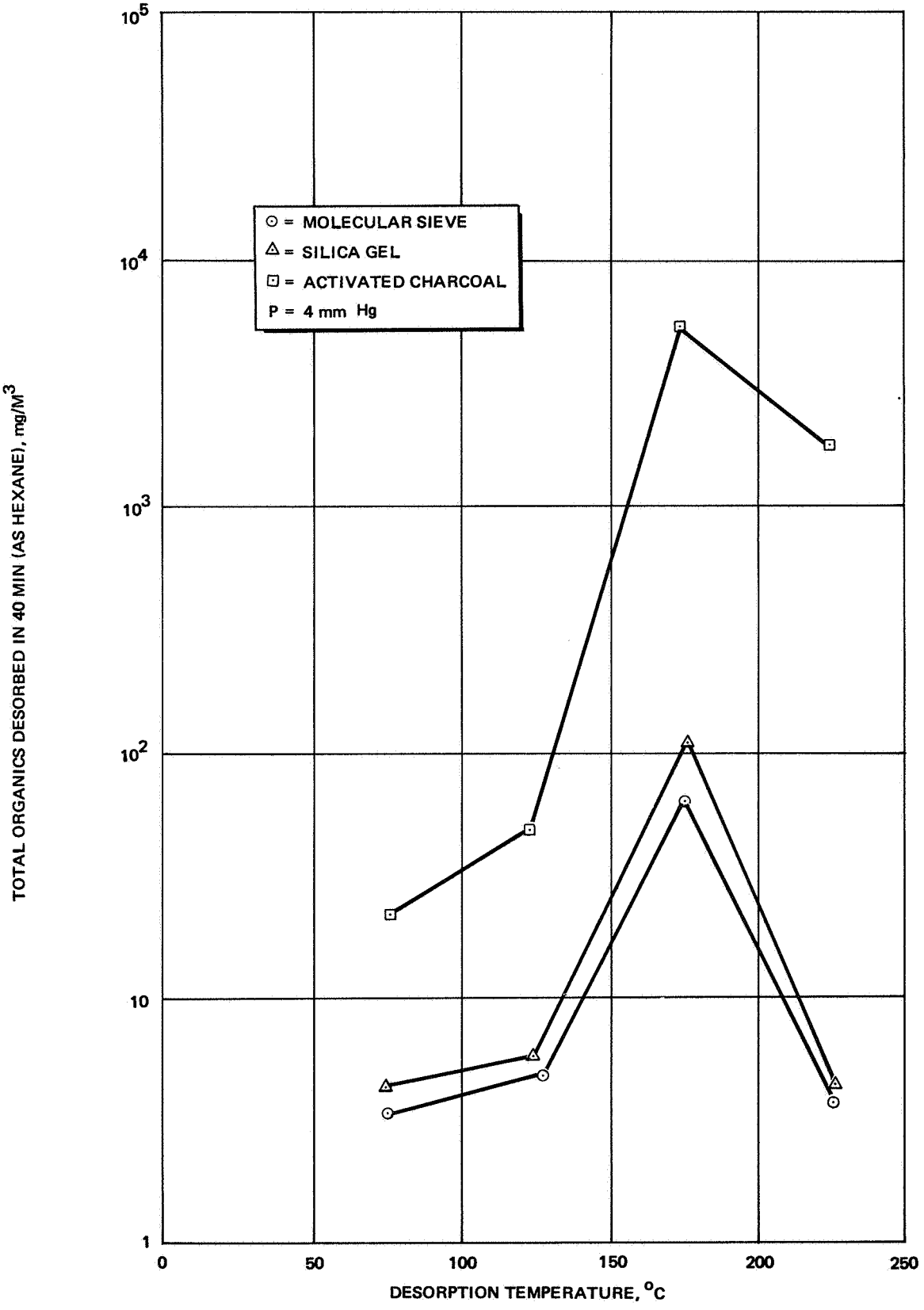

Figure 5. Effect of Temperature on Quantity of Organics Desorbed from Three Different Sorbents

Table 2

EFFECT OF SAMPLING TIME ON QUANTITIES OF TOLUENE DESORBED FROM THREE SORBENTS

(Sample Size: 1 gram)

Sampling Time	Quantities of Toluene Desorbed (mg/m^3) Molecular Sieve	Silica Gel
First 40 min	10.78	12.21
Second 40 min	0.41	0.99
Third 40 min	0.54	1.72
Fourth 40 min	---	0.12
Fifth 40 min	0.13	0.33
Sixth 40 min	---	0.06

3.3 CHROMATOGRAPHIC BASELINE DETERMINATION

Baseline data were established by placing unused silica gel, molecular sieve, and activated charcoal into the desorption apparatus and applying the desorption procedure previously described. Care was taken to get the SG and MS specimens from the botton of their containers, preferably from areas that had not been in contact with laboratory air. The same procedure was followed with activated charcoal. The desorbed gases were again condensed in a liquid nitrogen trap and analyzed by gas chromatography. The chromatograms showed the presence of two to three compounds; however, the quantity represented by these low peaks was insignificant compared with the peaks obtained from a used sorbent.

Section 4

TEST RESULTS

4.1 IDENTIFICATION OF DESORBED COMPOUNDS

Desorption of organic materials from the three sorbents was carried out according to the procedures derived in Section 3. Assignment of individual peaks to specific compounds was based on calibrated elution times as described previously. Agreement of four elution times was considered sufficient for positive identification. In most instances, mass spectrographic analyses provided final confirmation of gas chromatographic identification. These mass spectral analyses also revealed the presence of 2-methylpentene-1 and Freon TF, for which the gas chromatographs had not been calibrated. The presence of Freon TF was attributed to the fact that it had been used to clean components for the Space Station Simulator (SSS). A list of identified contaminants which were desorbed from the three sorbents that were on line at the end of the 60-day run is shown in Table 3.

Parallel samples of molecular sieve and silica gel sorbents were submitted to NASA-LRC for analysis by microwave spectroscopy. In addition to ammonia, methanol, and ethanol identified in molecular sieve and silica gel samples, the presence of acetonitrile was also established in both sorbents. Additional compounds not yet definitely identified were methanethial, 1, 2 chloropropane, and carbonyl sulfide.

4.2 QUANTITATIVE DETERMINATION OF DESORBED COMPOUNDS

After identification of gas chromatographic peaks and confirmation by mass spectroscopy, it was important to determine concentration levels of individual contaminants as well as total organics driven from the sorbents. This involved the quantitative calibration of one chromatograph with the organic compounds of interest. Known quantities of specific materials were introduced into the 5-ml sample loop of the gas chromatograph and the peak heights produced with different concentrations were determined. This provided a measure of the concentration of the specific compounds in terms of parts per million by volume or in weight of the sample contained in the 5-ml sample loop. Table 4 shows the peak heights, in recorder divisions, produced by each of 13 individual compounds, based on 1 ppm of each compound. Total organics were later estimated by using average values of peak heights and molecular weights, which are included in Table 4.

Table 3

IDENTIFICATION OF CONTAMINANTS DESORBED FROM THREE SORBENTS (page 1 of 2)

(175 °C and 4 mm Hg)

Sorbent Contaminants	Silica Gel	Molecular Sieve	Activated Charcoal
Acetaldehyde	X	X	X
Acetone	X	X	X
Acetylene	X	X	X
Acrolein	-	X	X
Benzene	X	X	X
Isobutane	X	X	X
Tertiary butyl alcohol	X	-	-
Secondary butyl alcohol	X	-	X
Chloroform	-	X	X
Dichloromethane	X	-	X
2, 2 dimethyl butane	X	X	-
Ethyl alcohol	X, Y	X, Y	X
2-ethyl butanol	X	-	-
Ethyl benzene	X	X	X
Ethylene dichloride	X	X	X
Formaldehyde	-	X	-
Hexane	X	X	X
Cyclohexane	X	X	X
Cyclohexanone	-	X	X
Heptane	-	-	X
Methyl alcohol	X, Y	X, Y	-
Methyl ethyl ketone	X	X	X
Methyl isobutyl ketone	X	X	X
3-methyl pentane	X	-	X
2-methyl furan			X
Octenes, 1, 2	X	X	X
Pentane	X	-	X
3-pentanone	X	-	X

Table 3 (page 2 of 2)

Sorbent Contaminants	Silica Gel	Molecular Sieve	Activated Charcoal
Isoamyl alcohol	X	X	X
Propane	X	X	X
Propionaldehyde	-	X	X
Isopropyl acetate	X	-	-
Isopropyl alcohol	X	-	X
1, 1, 1-trichloroethane	X	X	X
Trichloroethylene	X	-	X
Toluene	X	X	X
Isovaleraldehyde	X	X	-
O-xylene	-	X	-
P-xylene	X	X	X
Freon TF	nc	nc	nc
Hexene-1	X	X	X
2-methyl pentene-1	nc	nc	nc
Acetonitrile	Y	Y	
Ammonia	Y	Y	

Legend:

X Identified by gas chromatograph

- Not found

nc Identified by mass spectrometer

Y Identified by microwave spectroscopy by the NASA Langley Research Center

Table 4

MOLECULAR WEIGHTS AND PEAK HEIGHTS PER PPM FOR 13 INDIVIDUAL ORGANIC COMPOUNDS

Organic Compounds	Molecular Weight	Recorder Divisions per ppm
Acetone	58.08	15.0
Benzene	78.11	77.4
Carbon tetrachloride	153.84	5.2
Chloroform	119.39	7.7
1, 2-dichloroethane	98.97	17.6
Dichloromethane	84.91	13.4
Hexane	86.17	67.0
Isobutane	58.12	86.4
Methyl ethyl ketone	72.10	23.6
1, 1, 1-trichloroethane	133.42	19.8
Trichloroethylene	131.40	16.3
Toluene	92.13	32.0
P-xylene	106.16	27.7
Average	97.90	31.4

4.3 QUANTITATIVE ANALYSIS OF INDIVIDUAL COMPOUNDS

Although a large number of saturated and unsaturated hydrocarbons were identified in the gases desorbed from the various sorbents, it was decided to emphasize chlorinated and oxygenated compounds for calibration and quantitative estimation. This was based on the higher toxicity of these compounds in relation to hydrocarbons and on the fact that they may be readily converted into highly toxic products by oxidative processes.

The quantitative results obtained with the 13 compounds, which were individually studied, are shown in Table 5. In columns 1 and 2, the results are expressed in milligrams of specific contaminant per kilogram of each sorbent. Columns 3 and 4 show weight of contaminants for the total amount of sorbents actually used inside the SSS during each regeneration cycle. In columns 5 and 6 the contaminant concentrations from the silica gel and molecular sieve were converted into parts per million, based on an atmospheric gas volume of 600 ft^3. This volume actually passed through these two sorbents during every 45-minute adsorption cycle. The concentration found in the beds represent contaminants removed during this time. Following each adsorption cycle, these beds were thermally desorbed during a 45-minute period. The freshly regenerated silica gel and molecular sieve beds did not show these contaminants.

The contaminants found in these beds were, therefore, collected during the last adsorption cycle at the end of the test. The activated charcoal bed, by contrast, had remained inside the SSS during the entire 60-day run without desorption. During this time, a gas volume of about 8,640,000 ft^3 had passed through it. This charcoal material from the toxin burner was used for qualitative identification only.

Two chromatographic peaks assigned in Table 5 to acetone and dichloromethane also include methyl alcohol, ethyl alcohol, formaldehyde, and propionaldehyde. They could not be separated without resorting to different columns, different column temperatures, and additional calibrations. Because the overall concentrations of the latter contaminants were very low, compared with their MAC's, the additional effort did not seem warranted.

The last line of this table shows the totals of the individual organic compounds; they will be compared with the data obtained from total organics.

4.4 ANALYSIS OF TOTAL ORGANICS

The results obtained from the total organics driven off the silica gel and molecular sieve sorbents are shown in Table 6. The data of this table were based on averages of the 13 individual contaminants in Table 6. Column 1 gives the milligrams of contaminants for each kilogram of sorbent. The fact that different quantities of each sorbent were used was taken into consideration in Column 2. The weight of desorbed contaminants was then converted in Column 3 into parts per million by volume, based on a gas flow volume of 600 ft^3 at 7.0 psia. The 600-ft^3 air volume which passed

Table 5

QUANTITATIVE ANALYSIS OF INDIVIDUAL CONTAMINANTS FROM TWO SORBENTS

Column	1	2	3	4	5	6
	mg/kg(1)		mg/total sorbents(2)		ppm/600 ft^3 air	
Organic Contaminant	45-Min Molecular Sieve	45-Min Silica Gel	12-lb Molecular Sieve	9-lb Silica Gel	600 ft^3/45 min Molecular Sieve	600 ft^3/45 min Silica Gel
Acetone	1.87	2.75	10.2	11.3	0.256	0.283
Benzene	0.009	0.045	0.048	0.183	0.00089	0.00341
Carbon tetrachloride	--	1.49	--	6.1	--	0.0575
Chloroform	0.135	--	0.735	--	0.00895	--
1,2-dichloroethane	0.228	0.164	1.24	0.669	0.0182	0.00987
Dichloromethane	3.87	4.57	21.1	18.7	0.362	0.320
Hexane	0.615	0.913	3.36	3.73	0.0565	0.063
Isobutane	0.438	1.38	2.39	5.64	0.0598	0.141
Methyl ethyl ketone	0.111	0.071	0.605	0.29	0.0121	0.00587
Toluene	0.418	1.31	2.28	5.37	0.0359	0.0849
1,1,1-trichloroethane	0.235	0.336	1.28	1.38	0.0140	0.0150
Trichloroethylene	--	0.500	--	2.04	--	0.0226
O-Xylene	0.237	0.274	1.29	1.12	0.0177	0.0153
Totals	8.166	13.803	44.528	56.522	0.84204	1.02145

(1) mg of contaminants per kg of each sorbent

(2) Total sorbents consisted of: 12-lb molecular sieve and 9-lb silica gel.

Table 6

TOTAL ORGANICS DESORBED FROM TWO SORBENTS

	1	2	3	4
Sorbent	mg/kg of Sorbent	mg/Total Sorbent[1] per 45 min.	ppm Organics, Removed from 600 ft^3 of SSS Air	ppm Organics Removed from 4, 100-ft^3 Cabin
Molecular Sieve	10.9 (45 min)	59.1	0.87	0.13
Silica Gel	13.5 (45 min)	55.1	0.81	0.11

(1) Total sorbents: 12-lb molecular sieve
9-lb silica gel

every 45 minutes through the silica gel and molecular sieve beds led to an accumulation of 55.1 and 59.1 mg of total organics, respectively. An amount corresponding to 0.81 and 0.87 ppm was, therefore, removed from the 600-ft^3 atmospheric gas volume. Based on the SSS volume of 4, 100 ft^3, the organic contaminants collected by the two sorbents were 0.11 and 0.13 ppm. Therefore, approximately 0.245 ppm of total organics were removed every 45 minutes or about 7.7 ppm every 24 hours.

Most of the organic material collected in the molecular sieve bed was desorbed together with the carbon dioxide to a holding tank used with the oxygen recovery unit. After undergoing Sabatier reaction this was ultimately vented with the methane gas byproducts.

With regard to organic compounds recovered from the silica gel beds, a distinction has to be made between the water-soluble and water-insoluble organics. The organic compounds which were water soluble remained in the water condensate and thereby contributed to the purification of the cabin atmosphere, while the water-insoluble compounds were returned to the SSS atmosphere during the regeneration process. This removal of water-soluble compounds effectively reduced the level of organic pollution inside the SSS, as indicated by Table 6.

It may be of interest to note that the high chemical oxygen demand (COD) content of silica gel water condensates observed during the 60-day run (Reference 1) is in good agreement with the total organics recovered from the silica gel beds. It is of further interest that analyses of water formed during the Sabatier reaction showed a high degree of purity. This is evidenced by the low COD values, low ammonia contents, and low specific conductivities. These test results indicated that organic and inorganic air contaminants, desorbed from the molecular sieve sorbent had been vented overboard together with the methane byproduct.

Total organics desorbed by silica gel and molecular sieve beds when expanded into 600 ft^3 result in a calculated concentration of approximately 2.0 ppm. This is in agreement with the hydrocarbon values of 1 to 5 ppm recorded by the infrared analyzer during the 60-day run. The "totals" for 13 individual organic compounds shown in Table 5 also agree closely with the total organics of Table 6.

4.5 INORGANIC COMPOUNDS

The desorbed gases from the silica gel and molecular sieve sorbents were also tested by wet chemical procedures for the presence of ammonia, oxides of nitrogen, and sulfur dioxide. The results are shown in Table 7. They are expressed in milligrams of contaminants per kilogram of each sorbent, and in parts per million, based on a simulator volume of 4,100 ft^3. Again, the data obtained with the two sorbents are based on a sorption cycle of 45 minutes during which 600 ft^3 of SSS atmosphere had passed through the sorbents. The test data obtained with the silica gel and molecular sieve sorbents showed the presence of ammonia in samples using a 45-minute adsorption cycle. When scaled to a simulator volume of 4,100 ft^3, the ammonia removed was equivalent to a decrease of 1.0 and 0.06 ppm, respectively. The freshly regenerated silica gel bed had a residual ammonia concentration of 0.244 ppm. Although the alert level concentration for this contaminant is 100 ppm at operating conditions, the occupants of the SSS detected its presence by odor at 5 to 8 ppm. It is of special significance to note that the quantity of ammonia desorbed from the silica gel sorbent could have produced 32 ppm daily, if the entire amount of this contaminant had been dispersed into the cabin, and if no ion exchange column was included in the multifiltration water recovery system.

Table 7

INORGANIC CONTAMINANTS REMOVED BY SORBENTS

Inorganic Contaminants	Silica Gel (1)		Molecular Sieve (1)	
	mg/kg(2)	ppm(3)	mg/kg(2)	ppm(3)
Ammonia	17.20	1.0	0.789	0.06
Nitrogen oxides	0.464	0.01	0.321	0.01
Sulfur dioxide	0	0	0.033	0.001

(1) Based on 45-minute sorption cycle

(2) Milligrams of contaminant per kilogram of sorbent

(3) Decrease in contaminant level effected in the cabin atmosphere.

The source of ammonia was the water recovery subsystem which was placed together with the other equipment inside the SSS. This system processed urine is an open-loop wick evaporator and was found to have applied insufficient pretreatment fluid to the urine to prevent ammonia formation. This problem has been solved for future tests by a redesign of the pretreatment system. However, it is evident that the silica gel sorbent provides an excellent means for increasing the rate of ammonia removal in the event of any malfunction of the water recovery pretreatment system or other system that results inadvertently in the generation of ammonia provided that the desorbed ammonia is not returned to the cabin upon regeneration.

During most of the 60-day manned test described in Reference 1 silica gel condensate was not processed through the multifiltration water recovery for reuse. The metabolic waste water output of all four crew members was processed in the water regeneration system. However, since only two of the four crew members consumed the reclaimed water, while the other two, constituting a control group, drank distilled water, an oversupply of reclaimed water was generated. Therefore the need of processing the silica gel condensate was obviated. If the silica gel condensate were processed as would be required in a spacecraft where all water must be recovered, the ion exchange column would have removed the ammonia from the processed water. A spacecraft design must consider the tradeoffs and associated penalties between processing the silica gel condensate with dissolved ammonia and the expendable ion exchange resin columns.

The presence of oxides of nitrogen in the desorbed gases may have been caused by the catalytic oxidation of ammonia that passed through the toxin burner. The equivalent cabin concentration of oxides of nitrogen removed by the sorbent was less than 0.02 ppm for both silica gel and molecular sieve. Analyses of atmospheric samples taken during a 60-day manned run showed concentrations of oxides of nitrogen ranging from 0.1 to 0.7 ppm as shown in Table 8. This range was well below the alert level of 5 ppm at standard conditions. The redesign of the urine pretreatment system will eliminate the generation of nitrogen oxides from an ammonia source in future tests. However, the silica gel and molecular sieve removed only small amounts of nitrogen oxides. A method to reduce the generation of nitrogen oxides, particularly in an atmosphere contaminated by ammonia, consists in cycling the toxin burner on and off. This will minimize the quantity of ammonia passed through the toxin burner. The 60-day manned test indicated that the toxin burner used with the simulator could be shut off for 6 to 7 days at a time before the carbon monoxide level was sufficiently high to resume its operation.

Table 8

ATMOSPHERIC CONTAMINANTS IN SPACE CABIN SIMULATOR

Contaminant	Method of Analysis	Accuracy	Alert* Level (7 psia)	Test Results	
				Normal	Maximum
CO (ppm)	MSA, Lira Infrared Analyzer	±2.0	100.0	17.0	35.0
CO_2 (mm Hg)	MSA, Lira Infrared Analyzer	±2.0	12.0	4.0	7.25
Hydrocarbons (ppm)	MSA, Lira Infrared Analyzer	±2.0	400.0	5.0	35.0
NH_3 (ppm)	Nesslerization	±1.0	100.0	6.3	17.4
Aldehydes (ppm)	Absorption in Bisulfite Sln.	±0.05	20.0	0.34	0.89
SO_2 (ppm)	Sod. Tetrachloromercurate-p-rosaniline	±0.25	10.0	0.05	0.2
H_2 (ppm)	Ed. Sulfate-amine Sulfuric Acid	±1.0	20.0	0.11	0.7
$(NO)_x$ (ppm NO_2)	Saltzman Reaction	±0.1	10.0	0.11	0.7
O_3 (ppm)	Alkaline Iodide Method	±0.2	0.2	0.0	0.0
Chlorine (ppm)	O-Tolidine Reaction	±0.04	2.0	0.0	0.0
Cyanides (ppm)	Palladium Chelate Reaction	±1.0	20.0	0.0	0.0
Phosgene (ppm)	Test Paper Treated with Indicator	±0.2	2.0	0.0	0.0
Ethanol (ppm)	Gas Chromatography, Flame Detector Carbowax Column	±0.2	200.0	3.5	8.0
Toluene (ppm)	Gas Chromatography, Flame Detector Carbowax Column	±0.2	10.0	0.15	0.5
2-ethyl butanol (ppm)	Gas Chromatography, Flame Detector Carbowax Column	±0.2	40.0	1.2	3.5

*Alert level is based on compressing the gas sample from 7 psia to standard pressure before analyzing.

Section 5

CONCLUSIONS

Qualitative analyses of desorbates from three sorbent beds, silica gel, molecular sieve, and activated charcoal led to the identification of approximately 40 specific organic compounds present in the SSS. Identifications were carried out by gas chromatography in conjunction with mass spectrometric procedures and wet chemical methods.

Quantitative analyses carried out to determine the total amounts of organic compounds driven from the sorbents indicated that the use of molecular sieve and silica gel beds led to a daily reduction in the cabin of 4.2 ppm and 3.5 ppm, respectively. The combined reduction of the organic contaminant level by 7.7 ppm daily represented an important contribution in reducing the cabin contaminant level.

The silica gel and molecular sieve sorbents showed the quantity of ammonia in desorption samples which would have resulted in an increase of 0.06 to 1.0 ppm in the simulator volume of 4,100 ft^3. Although the alert level concentration for this contaminant is 100 ppm at a pressure of 7 psia (see Table 8), the occupants of the SSS detected its presence by odor at 5 to 8 ppm. It is of special significance to note that the quantity of ammonia desorbed from the silica gel sorbent could have produced 32 ppm daily, if the entire amount of this contaminant had been dispersed into the cabin, and no ion exchange resin column had been included within the water recovery post-treatment system.

The source of ammonia was the water recovery subsystem which was placed together with the other equipment inside the SSS. This system processed urine in an open-loop wick evaporator and was found to have applied insufficient pretreatment fluid to the urine to prevent ammonia formation. This problem has been solved for future tests by a redesign of the pretreatment system. However, it is evident that the silica gel bed provides an excellent means for increasing the rate of removal of ammonia in the event of any malfunction of the water recovery pretreatment system, provided the desorbed water with ammonia is not returned to the cabin.

The presence of oxides of nitrogen in the desorbed gases may have been due to the catalytic oxidation of ammonia that passed through the toxin burner. The concentration of oxides of nitrogen removed by the sorbent was less than 0.02 ppm for both silica gel and molecular sieve. Analyses of atmospheric samples taken during a 60-day manned run showed concentrations of oxides of nitrogen ranging from 0.1 to 0.7 ppm. This range was well below the

alert level of 10 ppm. The redesign of the urine pretreatment system will eliminate the generation of nitrogen oxides from an ammonia source in future tests. However, the silica gel and molecular sieve removed only small amounts of nitrogen oxides. A method to minimize the generation of nitrogen oxides, particularly in an atmosphere contaminated by ammonia, consists in cycling the toxin burner, based on a preset allowable carbon monoxide level. The 60-day manned test indicated that the toxin burner used with the simulator could be shut off for 6 to 7 days at a time before the carbon monoxide level was sufficiently high to require operation again.

REFERENCES

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2. NASA Letter, from C. H. Nelson to P. P. Mader, June 9, 1969.

3. Bonura, M.S., et al., Engineering Criteria for Spacecraft Cabin Atmosphere Selection. NASA Report No. CR 891, prepared under Contract No. NASw-1371, Douglas Aircraft Company, Santa Monica, California, September 1967.

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Appendix

DEFINITION OF CONCENTRATION TERMINOLOGY

The expression of trace contaminant concentration requires precise definition to avoid confusion, especially when significant variations in pressure levels are involved. It is generally agreed by toxicologists that the significant variable involved is the partial pressure of the trace contaminant under consideration. On this basis, a subcommittee of the National Academy of Science has recommended that the conventional terminology be the unit of millimoles per 25 m^3. In this report, this is utilized by defining a concentration as follows:

$$\text{parts per million by vol at STP} = \frac{\text{millimoles}}{\text{cubic meters/25 liters}}$$

in which the molar volume of 24.5 cubic meters is used since most concentration measurements were made at approximately 70 °F. This definition is equivalent to the following:

$$\text{ppm} = \text{ml/m}^3$$

As an example of the application of this terminology, it is shown in Table 6 that 59.1 mg of total organic constituents were removed from the cabin by the molecular sieve bed during a 45-minute adsorption cycle. This was removed from a volume of atmosphere which passed through the bed during this time of 600 actual ft^3 (16.9 m^3). Since the atmospheric pressure was 7.0 psia, this was equivalent to 285 scf (8.06 m^3). From Table 4, the average molecular weight of the trace contaminants is shown to be 97.9.

The average change in concentration in trace contaminants in the atmosphere passing through the bed can therefore be expressed as:

$$\Delta\text{ppm} = \frac{59.1 \times 10^{-3}\ \text{gm/45 min}}{97.9\ \text{gm/mole}} \times \frac{24.5\ \text{l/mol}}{16.9\ \text{m}^3\text{/45 min}} \times 10^3\ \frac{\text{millimole}}{\text{mole}} = 0.91$$

The atmosphere samples at the entrance and exit of the beds were compressed to atmospheric pressure for analysis and measurement. Thus the measured density was increased proportional to the compression ratio. This is equivalent to a calculation on the basis of the standard volume of gas flow through the bed, as follows:

$$\Delta\text{ppm} = \frac{59.1 \times 10^{-3}}{97.9} \times \frac{24.5}{8.06} \times 10^3 = 1.83$$

This represents a concentration that is measured after compressing a sample to standard pressure, and is not the concentration that actually existed inside the chamber.

The equivalent reduction in the cabin contaminant concentration at each cycle of adsorption (45 minutes) can be calculated by substituting the actual chamber volume (116 m^3) or the CO_2 concentrator process flow during a 45-minute period.

$$\Delta ppm = \frac{59.1 \times 10^{-3}}{97.9} \times \frac{24.5}{116} \times 10^3 = 0.127$$

This latter number represents an average reduction in contaminant level due to the removal of contaminants by the molecular sieve bed.