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CONCENTRATION AND ANALYSIS OF ORGANIC VOLATILES IN SKYLAB 4

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SUMMARY

The volatile components in the cabin atmosphere of Skylab 4 at various times during the mission were concentrated and analysed. More than 300 compounds could be detected by high-resolution gas chromatography with differences in concentration of as much as six orders of magnitude. 107 substances were identified by mass spectrometry, covering a molecular-weight range of approximately 60 to more than 500. The concentrations of 80 compounds were determined for three samples taken on days 11, 47 and 77 of the mission. The composition of the volatiles in the spacecraft's atmosphere differs significantly from other environments. A wide variety of various silicon compounds, mostly methylated siloxanes of molecular weight up to 584, was detected. Fluorocarbons (Freons) were also present.

INTRODUCTION

Some of the factors which determine the efficiency of a well trained group of astronauts in a closed space capsule are related to the integrity of their breathing atmosphere. Relatively little is known about the synergistic effects of a number of volatile substances which have been detected in space capsules although the toxicity of most individual chemicals which have been detected in man's environment has been determined.

The isolation and identification of contaminants in closed environments is, therefore, of great importance to both the well being of the individuals involved as well as to their ability to perform in an optimal manner under situations of extreme stress. Only after the appropriate analytical techniques have been developed which are either suitable for in-flight measurement of post-flight analysis appropriate steps

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can be taken to optimise the design of necessary atmospheric purification equipment and to determine the production rates of volatiles which can interfere with the performance of a flight crew.

From an analytical point of view, information is needed on: (a) the presence of any toxic materials at concentration levels which could interfere with flight performance of the crew and (b) changes in the contamination profile during the mission.

A wide variety of substances can be found in air, ranging from gases such as methane, ethane, ethylene, etc., to high-molecular-weight compounds which are solids at room temperature, such as polynuclear and heterocyclic aromatic hydrocarbons. In addition to these organic substances, particulate matter is often found in close association to industrial air pollution, consisting mostly of inorganic material. Different analytical techniques are required for the analysis of the various classes of substances, since no single technique can handle the entire spectrum. Only "volatiles" shall be considered here. The term "volatile" does not describe a group of substances having common chemical properties but rather regards these in terms of analysis. In this text, the term refers to compounds which have sufficient vapor pressure at moderate temperatures (approx. 200°) to be transferred into the gas phase and subsequently be analyzed with gas-phase techniques. Although this definition does include gases and other substances of low molecular weight, only compounds being less volatile than acetone will be considered here.

The introduction of gas chromatography–mass spectrometry (GC–MS) has provided an extremely powerful tool, especially suitable for trace analysis of organic substances.

Owing to the relatively low concentration of volatile material in air, concentration methods must be applied during the sampling step. Besides fixed gases, water constitutes the major component of air. This can lead to considerable difficulties in both sampling and analysis. If a sample of 100 l is required for detection of traces down to the 0.01-ppb[*] level, the sample will contain *ca.* 1 g of water if collected at 50% relative humidity and 25°. The organic materials to be analyzed, however, are present at a concentration level of seven to ten orders of magnitude lower. These facts have hindered the development of successful analytical techniques and only recently have methods been developed which can effectively cope with these problems.

A number of synthetic polymers[1,2] and surface-modified adsorbents[3] have been introduced recently, which are hydrophobic in nature and can, therefore, be used for concentration of volatiles from air samples. One of these adsorbents, a porous polymer of 2,6-diphenyl-*p*-phenylene oxide (Tenax GC), is noticeable for its temperature stability[4], and will allow successful collection and desorption of substances up to a molecular weight of several hundreds. Tenax GC has been used for trace analysis of biologically important volatiles[5–7] and air pollutants[8] for about two years and compares very favorably to other common adsorbents of both natural and synthetic origin, and its general application to other problems is presently underway.

Compactness is one of the most important features of a sampling system to be employed in a spacecraft. Such a system must be rugged and simple requiring only minimum attention by the crew. Desirable features of an air sampling system can be summarized as follows:

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[*] Throughout this article the American billion (10^9) is meant.

(a) Efficient concentration of volatile from a large air sample with no interference from moisture;

(b) Complete collection in the volatile range considered and quantitative regeneration;

(c) Storage capability for later analysis or potential for a simple automated procedure on board;

(d) Short sampling interval to follow rapid compositional changes.

The information expected determines the most suitable method for particular analytical needs. The use of a solid adsorbent appears to be most appropriate from both economical and technical points of view, considering present sampling technology. Such a system would easily lend itself to automation.

EXPERIMENTAL

Sampling system

Fig. 1 illustrates the sampler and Fig. 2 demonstrates the disassembled AVC (Atmospheric Volatiles Concentrator) showing the tubes containing the adsorbent. The metallic parts of the device —body, caps and jets— were made of aluminum.
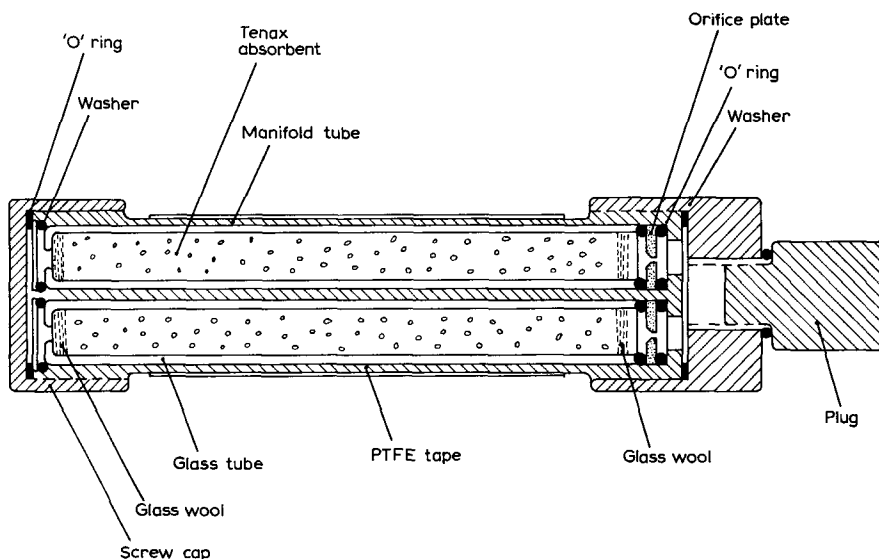

Fig. 1. AVC, drawing.

Other materials used were machined from PTFE and viton, and acted as seals. The sample tubes were made of Pyrex glass and resembled the ones previously described for headspace and air pollution analysis[4,8]. Although the tubes were relatively short, 50 mm × 10 mm O.D., they contained a large amount of the adsorbent, 4.5 ml per tube, to assure maximum retention of substances with a low capacity for this material.
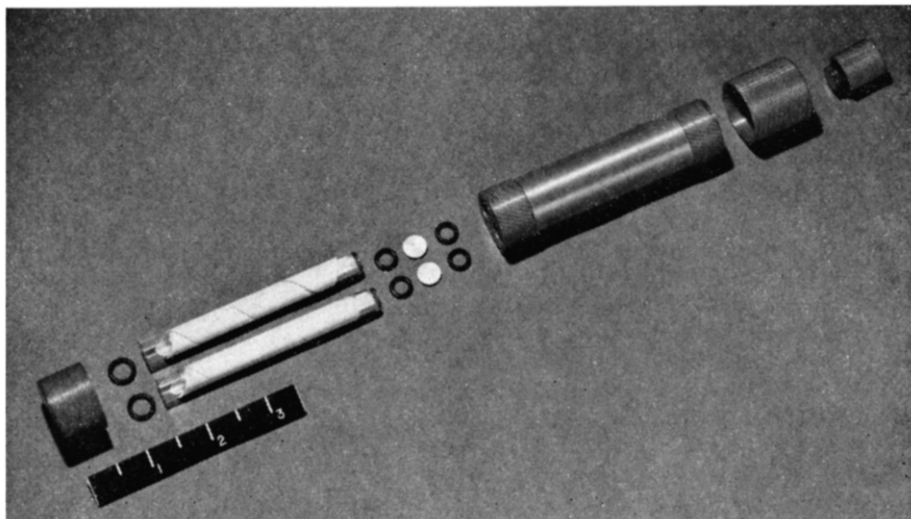
Fig. 2. AVC, disassembled, with Tenax tubes.

Since resistance to shock and vibration was of prime consideration in the design, special care was taken to assure the survival of the tubes under harsh conditions. A single layer of PTFE tape provided the insulation of the tubes from the wall, and three viton washers were installed for each tube to serve both as seals and elastic buffers. A groove was provided for the washer at the air inlet which kept tension on the tube and thus allowed a tight seal for the tube with the jet orifice plate and the main body.

A pressure drop of 5 p.s.i. between the pressure of the cabin atmosphere and the natural vacuum of the space caused air to flow through the system at a rate which was determined only by the size of the orifice in front of each tube. Variations in the particle size and density of the adsorbent, therefore, were of no significance to the measurements.

The AVC was designed and built in the laboratories of the Johnson Space Center in Houston, Texas, U.S.A. The glass tubes were made by Toe Pre Scientific Glassblowing (Houston, Texas, U.S.A.). Tenax GC, 60–80 mesh, and silanized glass wool were purchased from Applied Science Labs. (State College, Pa., U.S.A.).

Air samples were taken from laboratories and other enclosed environments and tested by GC under conditions resembling space flight. Fig. 3 shows the arrangement of the test system. Air flowed through a calibrated flow meter (Model C-1812-SA-G; Fischer and Porter, Warminister, Pa., U.S.A.) at atmospheric pressure. A micro metering valve (Type SS-22RS4; Whitey, Oakland, Calif., U.S.A.) was used before the air entered the loaded AVC. A vacuum pump (diapump pressure/vacuum, Air Control, Norristown, Pa., U.S.A.) served as the vacuum source. The pressure behind the metering valve was kept at 5 p.s.i. by controlling the air intake into the system. A calibrated pressure gauge (Model No. FA-160; Wallace and Tiernan) was used to monitor the inlet pressure into the AVC and the pressure in front of the AVC.

To establish the proper sample size, a series of jet orifices of sizes ranging from

0.002 in. to 0.006 in. were tested. Since it was possible to sample over a period of about 15 h, an orifice opening of 0.005 in. was chosen, resulting in a flow-rate of 115 ml/min. Several different tubes and orifices were used to check the reproducibility of flow-rates and variations were found to be less than 5%.
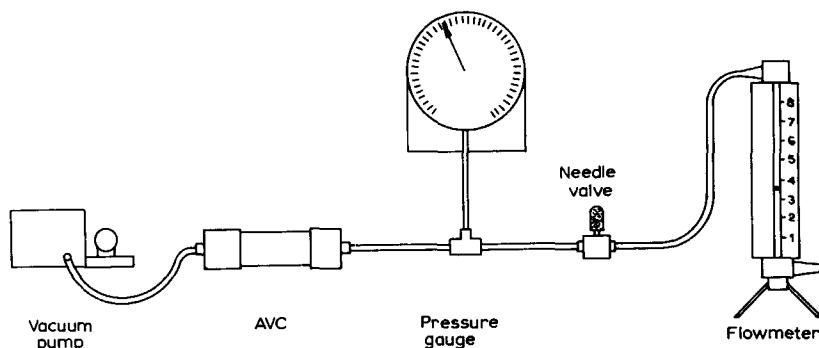

Fig. 3. Experimental arrangement for measurement of flow-rates under reduced pressure.

Air samples taken from a laboratory showed a consistent pattern, which was also observed previously with a different sampling system using the same adsorbent. To check for artefacts due to background contamination, an AVC was stored for a period of 90 days, after a sample had been taken. No significant differences, however, were found in the profiles between the stored sample and another one which was taken at the same day. Prolonged storage of a conditioned Tenax tube in the AVC, up to a period of several weeks, did not produce any artefacts. All parts of the sampler underwent rigorous cleaning procedures before final assembly. Metal parts were washed with a series of solvents —chloroform, benzene, acetone, methanol, water (all spectrograde)— and dried in an oven at 180° for 2 h. Washers and seals were rinsed with acetone, methanol and water and dried in a stream of dry nitrogen. After filling, all tubes were conditioned for 60 min at 340° in a stream of dry nitrogen (zero grade; IWECO, Houston, Texas, U.S.A.).

Analytical techniques

A Shimadzu GC 5AP$_5$ instrument (Aminco, Silver Spring, Md., U.S.A.), equipped with flame ionization detector, was used for the GC analysis. High-resolution open-tubular nickel columns were exclusively used[9]. Fig. 4 is a schematic diagram of the system, which in addition was interfaced with an integrator (Model 480; Varian Aerograph, Palo Alto, Calif., U.S.A.) for calibration and quantitative determinations. Samples were handled according to a procedure previously described[4], which involves heat desorption, sample transfer with a purge gas into a cryogenically cooled trap and temperature-programmed GC. Conditions of analysis are summarized in Table I.

A Varian MAT GC–MS combination (Model CH5; Varian MAT, Bremen, G.F.R.) served to identify the substances and to verify the information obtained by GC. The instrument had a direct interface (heated platinum capillary 0.01 in. I.D.) and employed a highly efficient oil diffusion pump at the ion source housing (600 l/sec). The pump was cooled with liquid nitrogen. Instrumental conditions are sum-
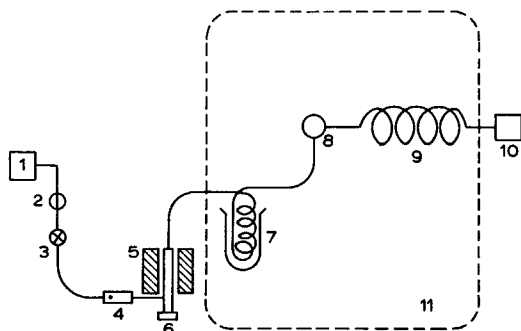
Fig. 4. GC system for Tenax procedure. 1 = Tank; 2 = pressure regulator; 3 = toggle switch; 4 = rotameter; 5 = injector block; 6 = modified injector port; 7 = precolumn (liquid nitrogen); 8 = Swagelok union; 9 = separating column; 10 = detector or mass spectrometer; 11 = oven.

marized in Table II. Chromatographic conditions were the same as described for the GC runs.

All mass spectra were recorded by an oscillograph. Interpretation was done by comparison with data published in the literature, by comparison with spectra kept in this laboratory in the form of a library, and by use of reference catalogs[10]. For some of the mass spectra (high-molecular-weight silicones), no reference spectra could be located and structures were derived on the basis of fragmentation patterns observed with compounds of related structure.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

Column	
material and phase	600 ft. × 0.02 in., nickel, Emulphor ON 870
efficiency	185,000 theoretical plates for tetralin at 150°
Trap, material and phase	5 ft. × 0.02 in., nickel, Emulphor ON 870
Detector (flame ionization) temperature,	265°
Sample introduction (Tenax port):	
temperature,	285°
purge gas (helium)	20 ml/min for 15 min
coolant	liquid nitrogen
Carrier gas (helium)	
inlet pressure	25 p.s.i.
flow-rate	6.8 ml/min at room temperature
Temperature program	70° for 15 min, 70–170° at 2°/min

Quantitative determinations

Immediately before and after GC analyses of the three samples, two standards containing substances of known identity and concentration were run on the same system for calibration purposes. The first standard contained substances which can be found in air pollution samples from both industrial and urban environments (toluene, ethylbenzene, xylenes, tetramethylbenzene, benzaldehyde, and acetophenone), whereas the second standard is more representative for compounds which were present in

TABLE II

CONDITIONS FOR MASS SPECTROMETRY

Ion source	
ionizing voltage, eV	70
emission current, μA	100
accelerating voltage, kV	3
Total pressure monitoring source	
ionizing voltage, eV	20
emission current, μA	100
Mass scan	linear, 2 sec/decade
Resolution	
run 1	280
run 2	1200
Temperatures, °C	
ion source	220
capillary interface	200
inlet system	260
Pressure, ion source	6×10^{-5} torr at 8.5 ml/min

the atmosphere of Skylab 4 (2-butanone, 4-methyl-2-pentanone, ethyl acetate, *l*-limonene, 2-octanone, benzonitrile, and butoxyethanol).

For the chromatograpic runs, an accurately determined amount of one of the standards, usually about 1 μl, was injected into a Tenax sample tube and analysis was performed under conditions identical to the AVC runs. To check for possible losses and irreversible adsorption on the Tenax adsorbent or glass tube, a direct injection of a standard was also made through an injection port. Another test was conducted to determine possible losses during sample transfer from the adsorbent into the cryogenically cooled trap. No loss was observed. With the exception of Freons, response factors for the compounds encountered do not differ significantly and are well within the level of accuracy desired. Freons, owing to their high volatility, were not quantitatively retained. Quantities and concentrations were, therefore, directly derived by comparison of peak areas and no further adjustments were made.

RESULTS AND DISCUSSION

In this study, special attention has been focused on compounds which could be considered toxic degradation products of plastic and other materials used for the construction of the space capsule. This is a likely possibility since the spacecraft temporarily was subjected to overheating during an earlier portion of its flight.

A summary of the organic volatiles collected in the spacecraft on day 331 (November 27, 1973), day 002 (January 2, 1974) and day 032 (February 1, 1974) is given in Table III. These days correspond to the 11th, 47th, and 77th days of the mission. Fig. 5 demonstrates the complexity of such a sample and the numbers directly refer to Table III. Duration of sampling was close to 15 h for each sample. This is equivalent to a volume of 57 l of air at atmospheric pressure. The mass of air passed through each tube, therefore, was approximately 68 g. Concentrations expressed in Table III are calculated from these data.

TABLE III

VOLATILES IN THE ATMOSPHERE OF SKYLAB 4

Peak No.	Identification of peaks	331		002		032	
		% of sample*	Concentration (ppb)	% of sample	Concentration (ppb)	% of sample	Concentration (ppb)
1	Difluorodichloromethane	0.13	40	0.23	60	0.70	190
2	Freon 112	20.8	5900	33.3	8700	30.6	8400
	Freon 113						
3	Siloxane, normal, $n=2$	0.28	80	0.03	7	0.35	100
4	Cyclohexane	0.10	28	0.05	13	0.15	41
5	n-Heptane + monofluorodichloromethane	0.34	97	0.13	34	0.28	77
6	Acetone	27.8	7900	27.3	7100	10.0	2800
7	C_8-Alkane	0.04	11	0.03	8	0.08	22
8	C_8-Alkane	0.06	17	0.05	13	0.10	28
9	Heptene	0.02	6	0.01	3	0.03	8
10	Heptene	0.31	88	0.20	52	0.42	116
11	n-Octane + heptene	0.10	28	0.15	39	0.10	28
12	Ethyl acetate	1.60	454	1.50	390	0.80	221
13	2-Butanone	5.30	1505	4.70	1222	2.41	665
14	Siloxane, normal, $n=3$	0.37	105	0.45	117	0.50	138
15	Propanol + Freon ($C_2Cl_4F_2$ tent.)	2.51	713	4.40	1144	3.10	856
16	Siloxane, cyclic, $n=3$	0.22	63	0.10	26	—	—
17	Benzene + diacetyl	0.41	116	0.27	70	0.14	38
18	C_9-Alkane	0.08	23	0.05	13	0.07	19
19	4-Methyl-2-pentanone + siloxane, cyclic, $n=4$	7.01	1990	6.52	1625	3.61	996
20	Trimethylsilanol (tent.)	—	—	0.36	94	0.55	152
21	Dichloroethane	1.6	454	0.86	224	0.77	213
22	Toluene + tetrachloroethylene	5.91	1678	4.0	1040	6.22	1717
23	C_{10}-Alkane + siloxane, normal, $n=4$	0.15	43	0.20	50	0.55	152
24	C_{10}-Alkane	0.07	20	0.18	47	0.15	41
25	C_{10}-Alkane	0.02	6	0.03	8	0.03	8
26	n-Decane	0.67	190	0.36	94	0.46	127
27	4-Methyl-4-penten-2-one	0.62	176	0.36	94	0.45	124

		0.07	20	0.09	23	0.10	28
28	C_{11}-Alkane						
29	Ethylbenzene + siloxane, normal, mol. wt. 384 + siloxane, mol. wt. 370	0.41	116	0.20	52	0.28	77
30	p-Xylene	0.46	131	0.59	153	0.64	177
31	m-Xylene	0.95	272	0.63	164	0.60	166
32	Siloxane, normal, $n=5$ + C_{12}-alkane	0.24	68	0.12	31	0.16	44
33	C_{12}-Alkane	0.07	20	0.02	52	0.04	11
34	Silicone compound, mol. wt. 341	0.02	43	0.01	26	0.01	3
35	Aliphatic alcohol + C_{12}-alkane	0.52	148	0.26	68	0.23	64
36	o-Xylene	0.52	148	0.26	68	0.23	64
37	C_3-Benzene	0.01	2	0.02	5	0.02	5
38	Siloxane, normal, $n=5$	0.06	17	0.05	13	0.06	17
39	C_{12}-Alkane + silicon compound, mol. wt. 278	0.19	54	0.12	31	0.22	61
40	Siloxane, mol. wt. 415 + styrene	0.11	31	0.06	16	0.07	19
41	C_3-Benzene	0.15	43	0.11	29	0.13	36
42	C_{12}-Alkane	0.08	23	0.04	10	0.11	30
43	A hydroxyketone (tent.)	2.05	582	1.34	348	1.20	331
44	Limonene	0.96	273	0.61	159	0.50	138
45	Nonene	0.36	102	1.12	291	0.13	36
46	Siloxane, cyclic, $n=6$	0.28	80	0.47	122	0.57	157
47	2-Octanone	0.09	26	0.16	42	0.29	80
48	C_5-Benzene silicon compound, mol. wt. 285	0.04	11	0.05	13	0.05	14
49	Methylstyrene + n-dodecane	0.09	26	0.14	10	0.02	5
50	Siloxane, normal, $n=6$	0.12	34	0.08	21	0.12	33
51	C_3-Benzene	0.07	20	0.05	13	0.08	22
52	C_4-Benzene	0.12	34	0.05	13	0.18	50
53	C_4-Benzene	0.07	20	0.04	10	0.06	17
54	Butoxyethanol	—		—		15.6	4300
55	Silicon compound, mol. wt. 504	0.04	11	0.06	16	0.08	22
56	C_4-Benzene	0.04	11	0.05	13	0.05	14
57	C_4-Benzene	0.01	3	0.02	5	0.04	11
58	Dichlorobenzene	0.09	26	0.05	13	0.09	25
59	C_5-Benzene	0.09	26	0.05	13	0.09	25

TABLE III (continued)

Peak No.	Identification of peaks	331		002		032	
		% of sample*	Concentration (ppb)	% of sample	Concentration (ppb)	% of sample	Concentration (ppb)
60	Siloxane, cyclic, $n=7$	0.63	179	0.38	99	0.27	75
61	C_5-Benzene + C_{13}-alkane	0.07	19.9	0.04	10.4	0.07	19.3
62	C_4-Benzene + C_5-benzene + siloxane, mol. wt. 518	0.23	65	0.34	88	0.30	83
63	Silicon compound, mol. wt. 541	0.22	63	0.12	31	0.27	75
64	Benzaldehyde	0.40	114	0.24	62	0.37	102
65	C_4-Benzene + C_5-benzene + silicon compound, mol. wt. 320	0.06	17	0.05	13	0.02	5
66	C_5-Benzene + C_{12}-alkene + silicon compound, mol. wt. 584	0.15	43	0.12	31	0.17	47
67	C_4-Benzene + C_{12}-alkene	0.09	26	0.15	39	0.04	11
68	C_2-Styrene + C_4-benzene	0.16	45	0.13	34	0.27	75
69	Benzonitrile	0.16	45	0.15	39	0.15	41
70	C_5-Benzene	0.16	45	0.09	23	0.17	47
71	C_5-Benzene + C_{14}-alkane	0.09	26	0.04	10	0.09	25
72	C_5-Benzene	0.11	31	0.08	21	0.10	3
73	Acetophenone	0.6	170	0.05	13	0.10	3
74	Silicon compound, mol. wt. 358	0.21	60	0.08	21	0.28	77
75	Dimethyldihydroindane (tent.)	0.20	57	0.15	39	0.16	44
76	C_{15}-Alkane	0.04	11	0.03	8	0.05	14
77	C_5-Benzene	0.08	23	0.09	23	0.13	35
78	Naphthalene	0.04	11	0.03	8	0.07	19
79	Methylnaphthalene	0.32	91	0.23	60	0.41	113
80	Methylnaphthalene	0.17	48	0.11	29	0.12	33
81	C_{17}-Alkane	0.16	45	0.13	34	0.17	47

* Refers only to material adsorbed on Tenax. Values are too low for substances eluting before benzene (peak No. 17).
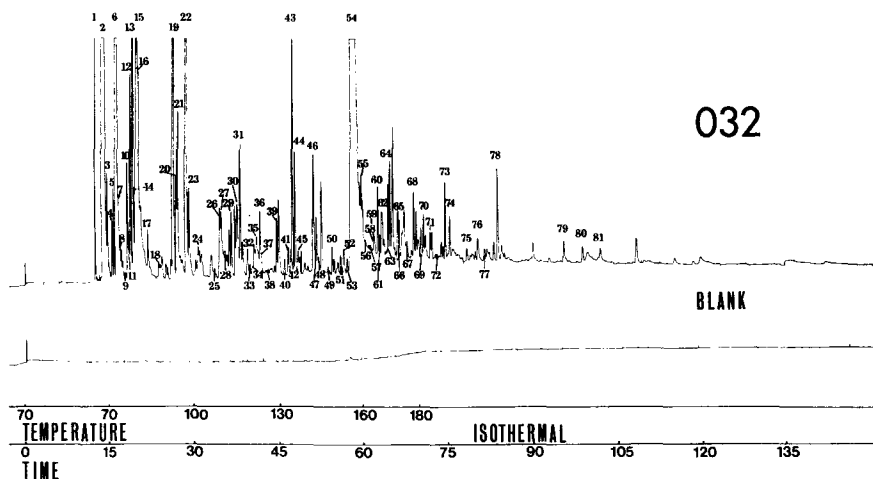
Fig. 5. Profile of volatiles on day 77 of the Skylab mission (sample 032). Instrumental conditions, see Table I. Numbers refer to Table III.

It is not possible to express the concentration of the total volatiles at this point, owing to incomplete adsorption of substances being more volatile than approximately the volatility of benzene. Within this limitation, concentrations of 28.4, 26.0 and 27.6 ppm have been determined for the volatiles on days 11, 47, and 77 of the mission. It should be noted that the total amount of volatile material actually present was higher, but no estimate can be made here.

Fig. 6 compares the GC profiles of all three AVC samples. It can be seen that these profiles are reasonably consistent from sample to sample with only minor differences in the concentrations of some of their components. One major difference can be observed in sample 032, where a compound which is totally absent in the first two samples appeared at a high concentration. This substance was identified as butoxyethanol and could be traced as the major ingredient of a fire extinguisher obviously used that day.

Air samples taken from both urban and industrial environments show a characteristic pattern which is relatively constant in composition regardless of sample site and conditions. Although these samples can vary in total concentration by as much as $1\frac{1}{2}$ orders of magnitude, depending on factors such as sample location, density of nearby traffic and weather conditions, two classes of substances make up as much as 95% of the total sample in the volatility range considered. Alkanes are predominant at the low-molecular-weight end of the spectrum whereas substituted aromatics are highly concentrated towards the end of the chromatogram. Only traces of other substances such as olefins and chlorinated hydrocarbons can be found. The atmosphere of Skylab, however, contained only a relatively small amount of hydrocarbons, approximately 10% of the total sample. Several classes of substances can be distinguished, notably ketones, chlorinated hydrocarbons, and Freons, and a few alcohols, aldehydes, and olefins. A unique characteristic of these samples is the presence of several types of siloxanes, normal and/or branched as well as cyclic systems. These compounds are
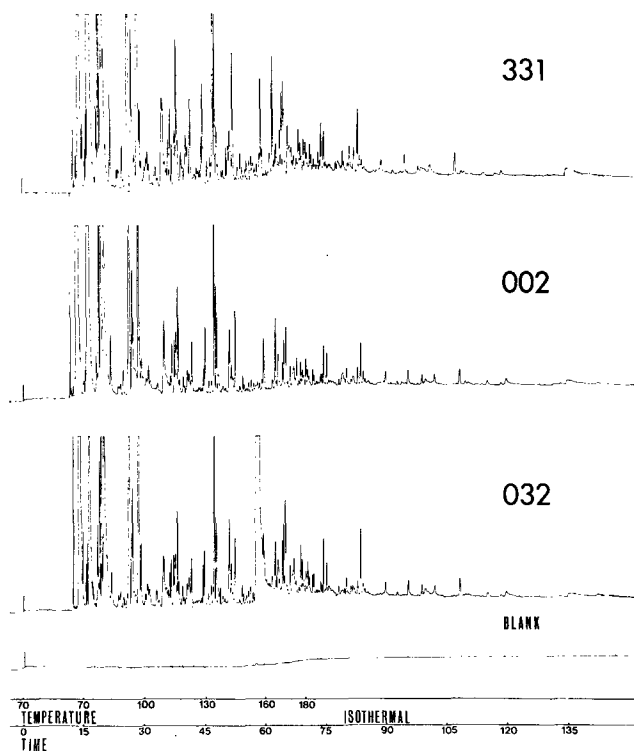
Fig. 6. Comparison of AVC profiles from the 11th, 47th, and 77th days of the mission (samples 331, 002, and 032, respectively). Conditions as in Fig. 5.

all of relatively high molecular weight, between 200 and 500+ mass units and are clearly distinguishable by mass spectrometry.

Coolanol 15, a mixture of orthosilicate esters, which was reported leaking out of the spacecraft's system was originally suspected to be the source of these silicon compounds. This, however, proved to be an incorrect assumption. A careful study was undertaken and retention behavior and mass spectral data of the Coolanol 15 sample were compared with data for the silicon compounds collected from the atmosphere of Skylab. Unfortunately, no siloxane standards were available, however, the chemical nature of the silicon substances can be considered as established. Major fragment ions can be predicted by applying principles of cleavage patterns observed with related structures.

The molecular ion cannot be observed directly by electron impact mass spectrometry. The highest-molecular-weight ion which can be detected is 15 atomic mass units below the molecular ion, corresponding to the loss of a methyl group. Table IV gives a survey of the most important ion fragments of the major siloxanes observed in the three Skylab samples. Data for some isomers from the Coolanol sample are included in the same table for comparison.

A prominent ion of non-cyclic siloxanes, often the base peak of the mass spectrum, is a fragment with a mass number of 73, corresponding to the cleavage of a trimethylsilane group from the ends of an open structure. This type of cleavage is not
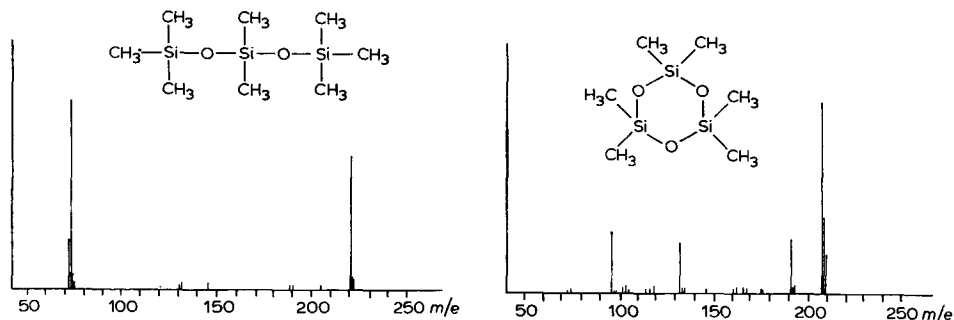
Fig. 7. Mass spectra of three-membered siloxanes, straight-chain *vs.* cyclic structure (peaks No. 14 and No. 16 of Fig. 5).

possible for a cyclic structure, therefore, a fragment of 73 being absent. Substituted cyclic siloxanes, however, also split off a fragment of mass 73. Fig. 7 shows representative mass spectra of both types of siloxanes. Although there are a large number of possible structures fitting the mass spectrometric patterns, little more than one dozen different molecules could actually be observed at significant concentration levels. It is conceivable that these substances have similar chemical and physiological properties and no attempt towards further elucidation of these structures was therefore made.

Depending on the concentration level of the substances, an impressive number appear in the volatility range considered here. About 320 individual components can be visually distinguished in the gas chromatograms. Rejecting substances at levels of less than 0.007 % in sample 331 leaves about 140 volatile substances. The compounds identified and summarized in Table III represent the following percentages of the total matter of each sample, collected by the adsorbent: sample 331, 89%; sample 002, 95%; sample 032, 88%. Volatiles eluting after benzene (Fig. 5, peak 17) are essentially quantitatively retained, but there are a few known exceptions, *i.e.*, acetophenone and benzaldehyde.

The concentration of organic volatiles in the atmosphere of the spacecraft is a measure of the effectiveness of the air purification system of the space capsule. Since other mechanisms for reduction or removal of volatile material, such as photooxidation, are not available under such circumstances, a steady-state concentration is built up. This constitutes a balance between the production of volatiles from sources such as man and equipment on one side, and the rate of disappearance as dictated by both the speed of the atmospheric circulation cycle and the system's capacity on the other.

TABLE IV

SURVEY OF MASS FRAGMENTATION PATTERNS FOR SILICON-CONTAINING COMPOUNDS[*]

The values for base peaks are underlined.

Substance	Ret. time[**] (sec)	Mass range					
		0–100	100–200	200–300	300–400	400–500	500–600
Siloxane, normal, $n=2$	864	73	<u>147</u>				
Siloxane normal, $n=3$	1150	73		221			
Siloxane, cyclic, $n=3$	1197			<u>207</u>			
Siloxane, cyclic, $n=4$	1557			<u>281</u>			
Siloxane, normal, $n=4$	1727	73		<u>207</u>, 295	369[***]		
Siloxane, normal, $n=5$	2173	<u>73</u>		267, 281	355		
Siloxane, cyclic, $n=5$	2341	<u>73</u>		207, <u>281</u>	<u>341</u>		
Unknown	2392			207, <u>249</u>, 263	<u>369</u>		
Siloxane normal, $n=5$	2581	73	147	207			
Unknown	2654		165	263, 277			
Unknown	2736	73		<u>221</u>, 281	327		
Unknown	3040	73		277	325, <u>341</u>	<u>415</u>	
Unknown	3126			281		429	
Siloxane, normal, $n=6$	3238	<u>73</u>	147	291	355	443, 475	
Unknown	3553		179	<u>207</u>, 281		424[***], 489[***]	
Siloxane, cyclic, $n=7$	3728	<u>73</u>	147	249	327, 341	415	503
Unknown	3855	73	169			462	<u>526</u>
Unknown	3910		179				
Unknown	3006				305		
Unknown	4495	73			327, <u>343</u>	462	<u>526</u>, 569
Coolanol 15[§]							
$SiO_4(i\text{-}C_3H_7)_4$	2204	<u>79</u>	121, 165	207, 249			
$SiO_4(i\text{-}C_4H_9)_3(n\text{-}C_4H_9)$	2667	79	121, 165, 179	207, <u>249</u>, 263			
$Si_2O_7(i\text{-}C_3H_7)_8$	3681		<u>157</u>, 199	241	368		
$Si_2O_7(i\text{-}C_3H_7)_5(n\text{-}C_4H_9)$	4187		<u>157</u>, 199	241	368, 383		

[*] For ions with estimated intensities of 20 % or more, relative to base peak.

[**] Uncorrected, for conditions see text.

[***] Less than 2 %.

[§] Some representative substances from 11-component mixture.

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