Reports

Apollo Lunar Module Engine Exhaust Products

Abstract. *Organic combustion products generated by the lunar module descent engine, which burns a 1:1 mixture of unsymmetrical dimethylhydrazine fuel and nitrogen tetroxide oxidizer, have been analyzed. The major gaseous combustion products found were ammonia, water, carbon monoxide, nitrous oxide, oxygen, carbon dioxide, and nitric oxide. The minor products were acetylene, hydrogen cyanide, ethylene, formaldehyde, propadiene, ketene, cyanous acid, hydrazoic acid, various methylamines, acetaldehyde, methyl nitrite, formic acid, nitrous acid, butadiyne, nitrilohydrazines, nitromethane, and nitrosohydrazines with other oxidized derivatives of unsymmetrical dimethylhydrazine and hydrazine. The ion intensities of the various species in all mass spectra were estimated as the following concentrations: the gases* (NH_3, H_2O, CO, NO, O_2, CO_2, *and* NO_2), *87.7 percent; compounds of C, H, and O, 6.0 percent; and compounds of C, H, and N* (*with traces of O*), *5.8 percent.*

The return of lunar samples by the Apollo lunar landing missions offers an opportunity for the study of extraterrestrial material free of the ambiguity surrounding meteorite analysis (*1*) caused by unknown contamination histories. The nature of the Apollo program is such, however, that it will be impossible during early missions to return lunar samples that are completely free of significant amounts of contamination. "Significant" in this case refers to amounts detectable by the most up-to-date analytical techniques. Mass spectrometry and gas chromatographic techniques used in organic geochemical and bioscience investigations are capable of detecting organic compounds in quantities of less than 1 ng (1×10^{-9} g). It is, then, desirable from an organic geochemical point of view to control potential contamination to such a degree that specific lunar samples analyzed for organic content are not contaminated organically in excess of 1 part per billion. This low amount of indigenous organic matter is expected for some types of lunar samples.

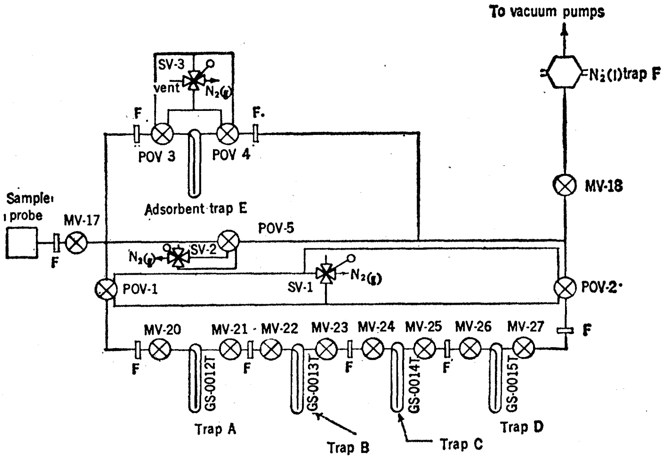
Several potential sources of organic contamination exist throughout the entire lunar sample collection procedure. Initial consideration of these potential contamination sources led to the conclusion that the major and least controllable source of organic contamination, as well as inorganic contamination, would be the lunar module (LM) descent and reaction control system engines. These engines burn a 1:1 (by volume) mixture of fuel, which is 50 percent (by weight) hydrazine and 50 percent (by weight) unsymmetrical dimethylhydrazine (UDMH) (structure I) and nitrogen tetroxide oxidizer (N_2O_4). A theoretical

$$(CH_3)_2N \cdot NH_2$$

I

calculation (*2*) based on thermodynamic properties and assumed surface interaction phenomena yielded curves showing the distribution of the combustion products over the LM landing area. Only inorganic compounds were considered.

Since engine development and performance tests were carried out at the NASA White Sands Test Facility, the engine exhaust gas collection was conducted at this site. The investigation was conducted in two phases. Phase I consisted of building a model rocket engine, housed in a clean vacuum system, and a sample-collection system for trapping exhaust gases and trans-



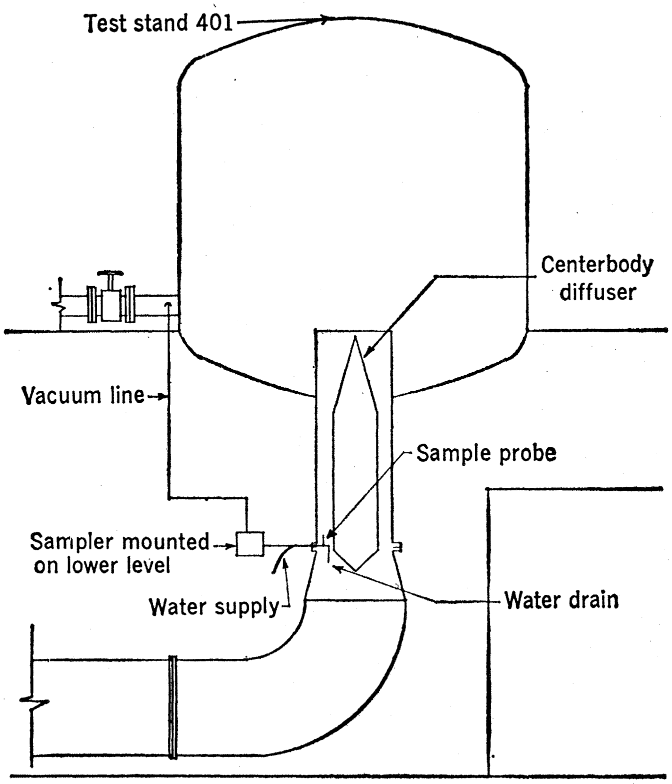


Fig. 1 (above). Gas-collection system. Abbreviations are: *POV*, pneumatically operated valves; *SV*, solenoid valve; *MV*, manual valve; and *F*, flange.

Fig. 2 (right). Phase II test facilities.

Table 1. Trap extract weights obtained from background of the lunar module engine (phase II, series V) and from exhaust after the engine had been fired.

Sample	Extract weight in trap (mg)			
	A	B	C	D
Firing, test 005	132.4	31.3	15.9	7.1
Background, test 006 (100 seconds)	1.3	3.2	2.5	1.8

ferring them to the laboratory for analysis (Fig. 1). The pneumatically operated valves (POV's) (Fig. 1) are controlled so that the center leg POV may be operated independently of the others. The adsorbent trap (trap E) POV's and the temperature-controlled trap (traps A through D) POV's may be operated separately. Trap E was designed to collect material for analysis of rare inorganic gases in an environment similar to lunar surface conditions and was filled with degassed pumice. The sampling system is pumped by untrapped Stokes mechanical pumps. The objectives of this first phase were to demonstrate the feasibility of the sample-collection system and to obtain and analyze samples free from the background contamination expected when gases from the full-size LM engine were collected.

Table 2. Lunar module exhaust products and relative concentrations. The N_2 is present (+) in all the spectra and is due mostly to air in the mass spectrometer, with possible traces from the traps. Not detectable, ND.

Compound*	Molecular weight	Relative concentration			
		Trap A	Trap B	Trap C	Trap D
NH_3	17	100	32	36	3.5
H_2O	18	100	67	100	100
CN	26	0.1	0.1	ND	ND
$HC \equiv CH$		0.1	0.3	1.0	1.5
HCN	27	4.0	0.7	0.6	0.4
$CH_2 = CH_2$	28	0.1	0.5	1.0	1.6
CO		5.0	12	14	15
N_2		+	+	+	+
CHO	29	0.4	2.4	2.0	16
NO	30	85	100	30	17
$CH_2 = O$		0.3	0.6	0.4	3.0
CH_3NH_2	31	ND	0.8	<0.1	ND
CH_3OH	32	<0.1	0.5	2.4	23
O_2		5.0	8.0	8.0	7.0
C_3H_2	38	<0.1	0.3	0.2	0.8
C_3H_3	39	2.0	1.0	1.0	5.0
C_2HN		ND	0.8	<0.1	ND
C_3H_4	40	0.1	0.4	0.1	1.2
C_2H_3N	41	ND	0.6	0.5	0.5
$CH_2C = O$	42	0.2	0.2	0.1	0.5
CNO		0.5	1.5	0.3	0.4
$CH_2 = N = CH_2$		0.1	1.3	1.2	0.6
HCNO	43	3.5	7.2	3.0	1.0
$CH_3 - N = CH_2$		ND	0.6	1.0	0.4
HN_3		ND	1.7	1.2	2.2
CH_3CO^+		0.6	1.6	0.8	3.0
CO_2	44	20	70	20	30
CH_2NO		3.0	<0.1	0.6	1.0
CH_3CHO		<0.1	0.2	ND	0.3
CH_3NO	45	1.0	0.2	ND	0.4
$CH_3 - NH - CH_3$		ND	1.2	3.0	<0.1
NO_2	46	80	35	12	3.0
HCOOH		0.2	<0.1	ND	ND
HNO_2	47	1.5	1.0	0.3	ND
C_4H_2	50	0.5	0.3	0.2	1.0
C_4H_4	52	0.3	0.3	<0.1	1.5
$HN = N - CN$	55	ND	0.4	0.2	1.0
$CH_3 - N_3$	57	ND	0.1	0.2	0.8
CH_3COCH_3	58	<0.1	ND	ND	ND
$(CH_3)_3N$	59	ND	0.6	0.4	<0.1
$HN = N - NO$	60	0.1	ND	0.5	0.6
CH_3COOH		0.1	ND	0.5	0.6
$CH_3NH - N = 0$		2.2	<0.1	ND	0.2
CH_3NO_2	61	ND	ND	ND	0.5
$H_2N - NH - NO$		ND	ND	ND	0.7
$CH_3 - N = N - CN$	69	ND	0.1	<0.1	ND
$CH_3N = N - CH = NH$	71	ND	0.1	0.2	0.7
$CH_3N = N - NO$	73	ND	ND	ND	0.4
$(CH_3)_2N - N = O$	74	ND	9.5	1.4	0.6
$CH_3NH - NH - NO$	75	ND	ND	ND	0.6
C_6H_4	76	0.3	0.4	ND	ND
$C_3H_5N_3$	83	ND	0.3	<0.1	0.1
$C_2H_5N = N - NO$	87	ND	ND	ND	0.2

* Detected as positively charged ionic species in the high-resolution mass spectral data.

Experience gained in sample-collection system preparation and collection during phase I served as a basis for modifying equipment and procedures in phase II of the investigation. Figure 2 shows a simplified version of the test stand 401 installation with the sampling system position designated. A full-size LM engine is mounted in the vacuum chamber above the center body diffuser. The sample probe is approximately 1.3 cm in diameter and penetrates the center body diffuser section of the steam-ejection system through a tap at the flange joint above the water ejection point. The steam-ejection system serves as a very high capacity pump to remove the engine exhaust gases. The sample probe opening is in the middle of the exhaust gas-flow path in the center body diffuser and is water-cooled for a line distance of approximately 20 cm inside the center body diffuser. This same water is used to cool the exhaust gases near the bottom of the center body diffuser. The primary objective of phase II was to obtain samples of the full-size LM engine exhaust products and analyze them for organic content. Only the results from the most recent and also most successful run (tests 005 and 006) will be discussed (*3*).

All traps for tests 005 and 006 were filled with glass beads and maintained at the temperature of liquid nitrogen.

Only the LM descent engine exhaust products were examined. It was assumed that the exhaust products from the reaction control system engines would be the same as in the case of the LM engine, because the same fuel and oxidizer are used.

The volatile gases in the trap series were analyzed by high-resolution mass spectrometry, with a mass spectrometer (G.E.C.-A.E.I. MS-902) attached online to a computer (Scientific Data Systems Sigma 7) (*4*). In a composite plot of some of the data (Fig. 3), the three major peaks were as follows: the mass to charge ratio (m/e) was 28, showing N_2 and CO; m/e 32, showing O_2; and m/e 44, showing CO_2. The minor components were acetylene, $HC \equiv CH$; hydrogen cyanide, HCN; formaldehyde, HCHO; nitrous oxide, NO; propadiene, $CH_2 = C = CH_2$; cyanous acid, HCNO;

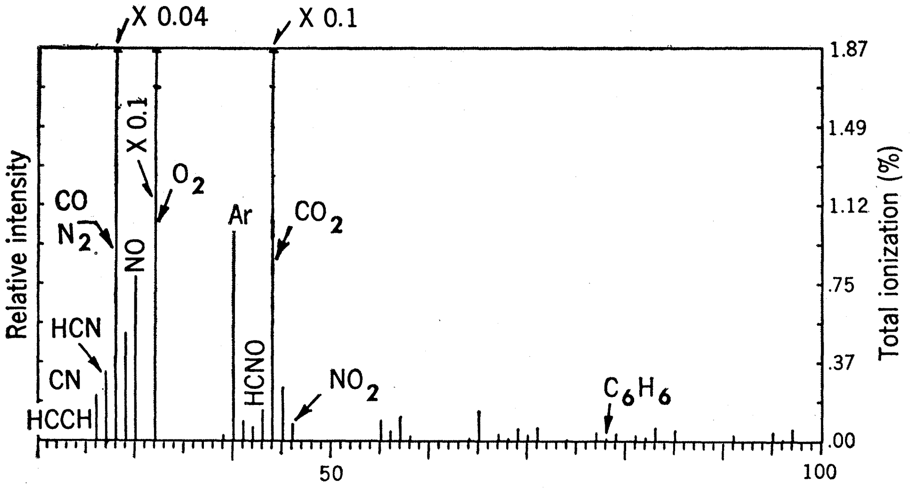


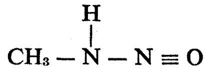
Fig. 3. Composite mass spectrum of trap A volatiles.

nitric oxide, NO_2; and formic acid, HCOOH. Hydrocarbon contamination background is shown in peaks in the *m*/*e* range 55 to 71.

The background extracted from the traps of test 006 with a mixture of benzene and methanol (3:1) (same conditions as during test except that the LM engine was not fired) was low (Table 1). The gas chromatographic traces and the high-resolution mass spectral data indicated Octoil and minor amounts of hydrocarbons.

The traps were extracted with a mixture of benzene and methanol (3:1) and the extract weights are listed in Table 1. An infrared spectrum was determined on the neat extract of trap A (Fig. 4) and indicated bands fitting -OH, -NH, -CH, -CO, $CO_3^{=}$, NH_4^+, and NO_3^-. This extract had a *p*H of 3.0. Gas chromatography showed no peaks attributable to any exhaust products, because they are mostly polar in nature; there were no peaks of background components detectable.

Series of high-resolution mass spectra were determined by multiple scanning of each extract, with the mass spectrometer setup cited (*4*). This permits an evaluation of relative volatility of the mixture components and a rough estimate of their respective concentrations. The exhaust products and their respective approximate relative concentrations in this extract series are listed in Table 2. A series of plots of the pertinent data from high-resolution mass spectral data for trap A is shown in Fig. 5 (scan No. 2) and in Fig. 6 (scan No. 6). The masses are plotted in methylene units (*5*). There are 14 units between each principal division. The number of hydrogen atoms of an unsaturated or cyclic ion is obtained simply by subtracting the number of units (hydrogens) from the $2n + 1$ hydrogens of the respective saturated principal divisions, C_nH_{2n+1}. This trap has the largest amount of exhaust products (see Table 1) of the sampling series. The major constituent of the extract is water (ratio of C to H plotted against O, Figs. 5 and 6); NO, CO, and CO_2 also comprise a substantial amount of this mixture. In the early scans, only limited nitrogenous compounds are found as low amounts of HCN, NO, HCNO, CNO, CH_2NO, and CH_3NO (see plotting of C/H against N and C/H against NO, Fig. 5) with some residual benzene. Residual methanol is found (C/H plotted against O, Fig. 5), as well as a trace of acetaldehyde. The later scans show that substantial quantities of salts are decomposed (pyrolized). Compounds such as CO, CO_2, NH_3, NO, NO_2, HNO_2, and HNO_3 (Fig. 6) can be ascribed to decomposition of the fuel, especially since NH_3 is absent in the early scans. The group of peaks on the plot of C/H against NO of Fig. 6 are CNO, HCNO, CH_2NO, and CH_3NO, definite exhaust products. The peak with the composition CH_4N_2O (plot of C/H against N_2O, Fig. 6) is a partial oxidation product of the UDMH fuel and can be assigned as structure II. In the plots of C/H against O_2, C/H against O, and C/H



$$CH_3-\overset{\displaystyle H}{\overset{|}{N}}-N\equiv O$$

II

of Fig. 6, minor products such as formaldehyde, acetaldehyde, formic acid, acetylene, ethylene, propadiene (struc-

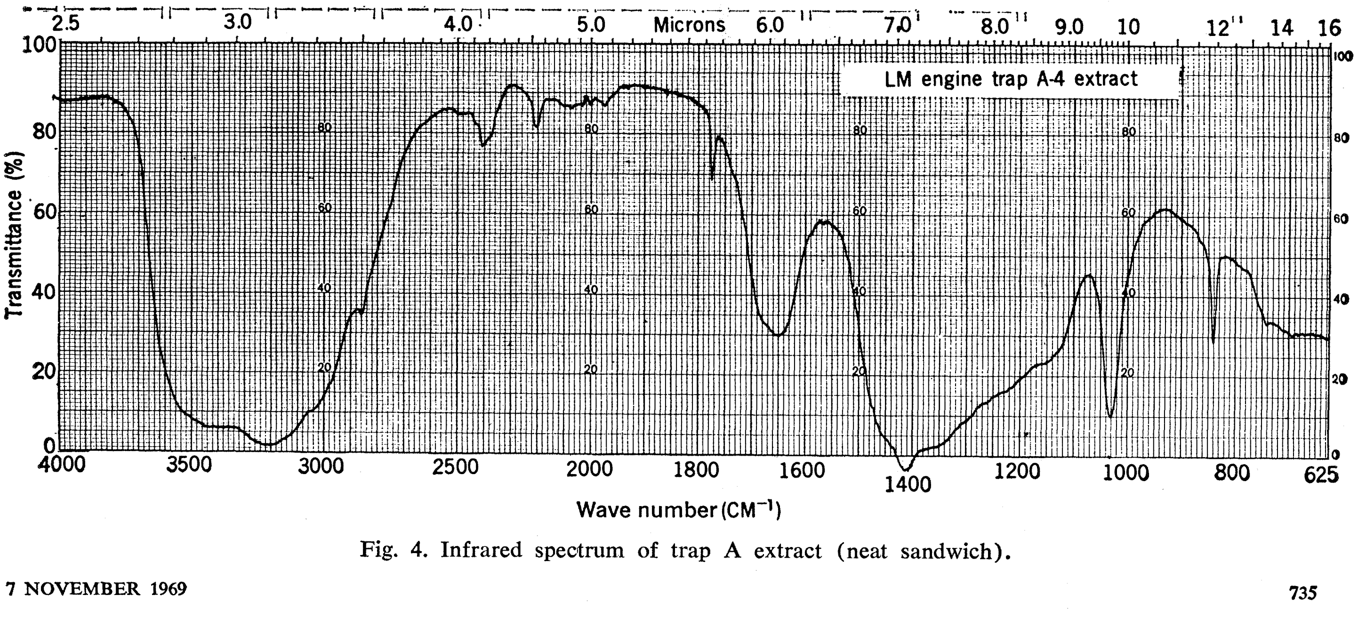


Fig. 4. Infrared spectrum of trap A extract (neat sandwich).

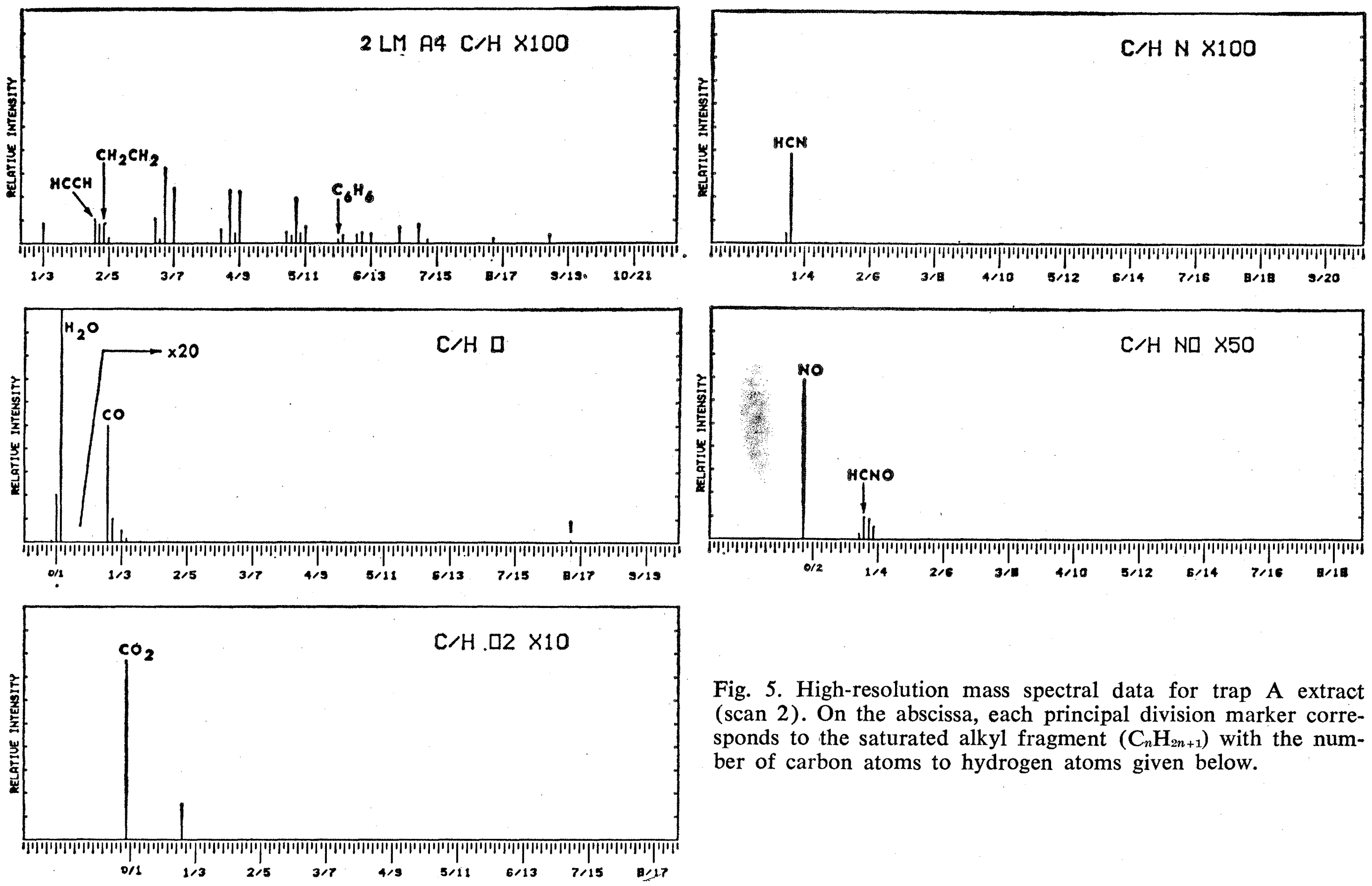


Fig. 5. High-resolution mass spectral data for trap A extract (scan 2). On the abscissa, each principal division marker corresponds to the saturated alkyl fragment (C_nH_{2n+1}) with the number of carbon atoms to hydrogen atoms given below.

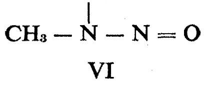
ture III), butadiyne (structure IV), and 3-hexen-1,5-diyne (structure V) are found.

$$CH_2 = C = CH_2 \qquad HC \equiv C - C \equiv CH$$
III IV

$$HC \equiv C - CH = CH - C \equiv CH$$
V

The latter hydrocarbons can be thought of as polymerization products of acetylene and they are absent in the background spectra consisting of substantial quantities of hydrocarbons.

In the trap B extract, the concentration of volatile compounds (H_2O, NH_3, NO, CO, and so forth) is lower than in the previous sample. Since this extract weighs significantly less (see Table 1), the hydrocarbon background appears in greater intensity. The other compounds found in the trap A extract are also present in this sample, but at lower concentrations (see Table 2). The high-resolution mass spectra show a peak at composition $C_2H_6N_2O$. This is an oxidation product of UDMH and can be assigned as structure VI.



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{N} - N = O$$

VI

A homologous series of azides, such as hydrazoic acid, methyl azide, ethyl azide (or structure VII),

$$CH_3 - N = N - CH = NH$$
VII

and nitrilohydrazines with structures (for example, VIII and IX) of composition $C_nH_{2n-1}N_3$ for $n = 0$ to 5 are also present (Table 2).

$$HN = N - C \equiv N$$
VIII

$$CH_3 - N = N - C \equiv N$$
IX

The extract from trap C is composed of the same compounds as those in traps A and B (Table 2). Nitromethane, CH_3NO_2, is detectable in some scans. The volatile products are present in about the same concentrations, as is the case for trap B.

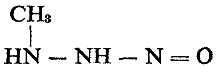
The compounds found in the trap D extract mixture are essentially the same as those in the other traps except that they appear in somewhat lower concentrations (Table 2). A new series of oxidation products is evident in this sample. A group of peaks in the plot of C/H against N_3O (Fig. 7), with the compositions $C_nH_{2n+1}N_3O$ for $n = 0$ to 2 and $C_nH_{2n+3}N_3O$ for $n = 0$ and 1, are found. Structures such as X and XI can be assigned to the former series, and structures XII and XIII

$$H - N = N - N = O$$
X

$$CH_3 - N = N - N = O$$
XI

to the latter series:

$$H_2N - NH - N = O$$
XII



$$\overset{\overset{\displaystyle CH_3}{|}}{HN} - NH - N = O$$

XIII

It should be noted that no UDMH, methylhydrazine, or hydrazine was found in the mass spectra of any trap extract.

With the LM descent engine firing at 100 percent thrust, the total mass flow rate is 928.7 kg/min. The cross section of the center body diffuser is 2.0×10^4 cm^2. If the mass flow rate is equal across the opening of the sampling probe, the mass flow rate per unit of time per area would be

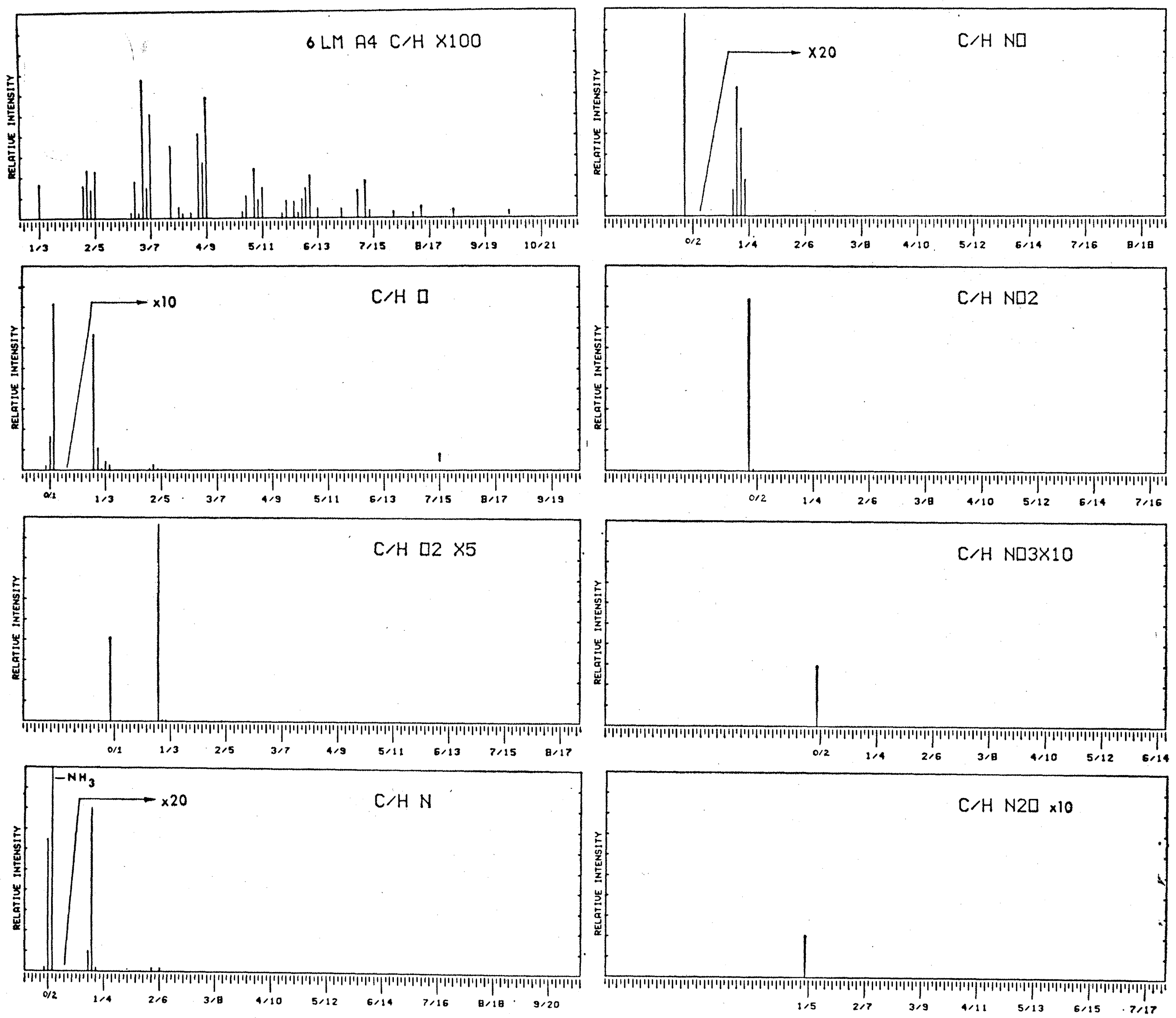


Fig. 6. High-resolution mass spectral data for trap A extract (scan 6). The measurement is similar to that in Fig. 5.

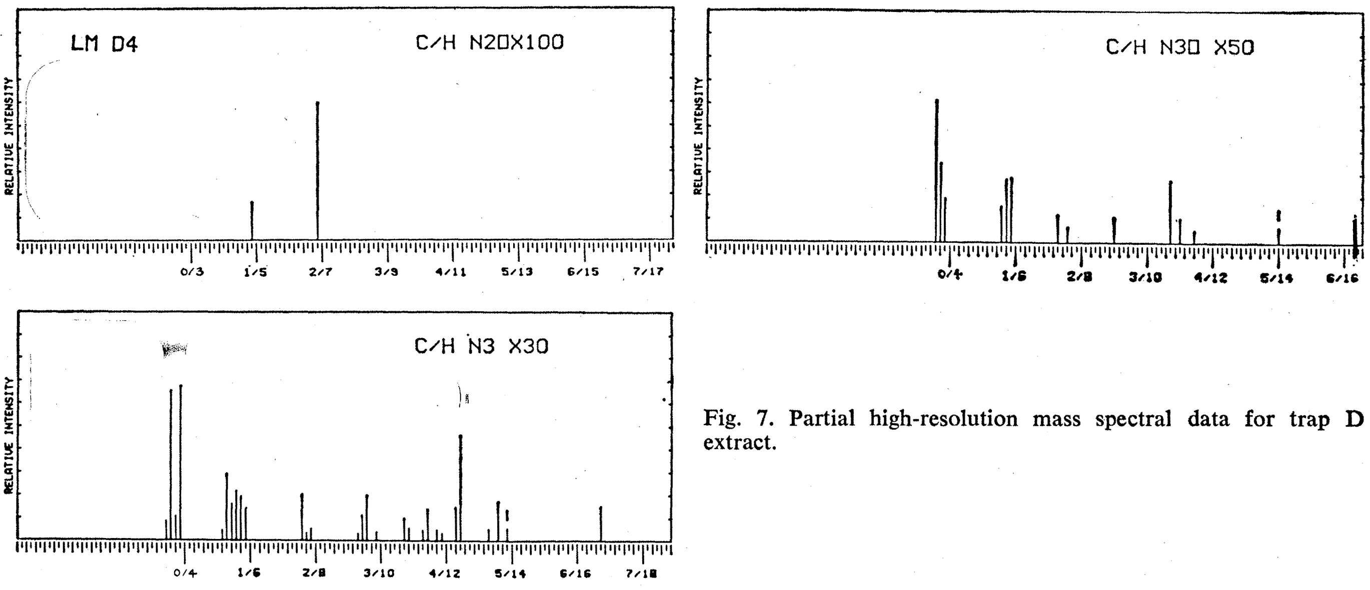


Fig. 7. Partial high-resolution mass spectral data for trap D extract.

0.7721 g sec^{-1} cm^{-2}. The opening of the exhaust gas sampler probe is 1.29 cm^2 in area, giving a mass flow rate of 1.09 g/sec. Assuming all exhaust products impinging upon the open area are pulled into the sampling system, a total of 81.8 g should be collected in all four traps (A, B, C, and D) for the 150-second firing (test 005) less the background (test 006). The actual amount extracted with a mixture of benzene and methanol was 0.178 g. Several factors could lead to this large difference between theoretical and actual yields, including (i) trapping efficiencies, (ii) solubility of trapped species in the benzene and methanol mixture, and (iii) reduced flow due to more complex flow dynamics than assumed. The experiment was not originally designed to obtain quantitative data on the organic products, but an estimate of organic material produced can be made assuming the trapping efficiency is 100 percent for the organic components of the exhaust gases. If the ion intensities of various species in all the spectra taken (some of which are listed in Table 2) are summed, the gases NH_3, H_2O, CO, NO, O_2, and NO_2 account for 87.7 percent (*6*) of the total exhaust product extract; the compounds containing only C, H, and O amount to 6.0 percent (*6*); and the components consisting of C, H, and N (with traces of O) amount to 5.8 percent (*6*). The latter two compound groups can be considered the organic exhaust products, and they amount to 11.8 percent of the extract.

In conclusion, virtually all LM engine exhaust products are of low molecular weight, the most being free and combined gases. The organic products are somewhat minor in concentration and quite varied in composition (see Table 2). Of particular interest are the following compounds: acetylene, hydrogen cyanide, ethylene, formaldehyde, propadiene, ketene, cyanous acid, hydrazoic acid, various methylamines, acetaldehyde, methyl nitrite, formic acid, nitrous acid, butadiyne, various hydrazines, nitromethane, and some nitrosohydrazines with traces of other oxidation derivatives of UDMH and hydrazine.

B. R. SIMONEIT, A. L. BURLINGAME
Space Sciences Laboratory, University of California, Berkeley 94720
D. A. FLORY
NASA-Manned Spacecraft Center, Houston, Texas 77058
I. D. SMITH
NASA-White Sands Test Facility, Las Cruces, New Mexico

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3. For a detailed description of the procedures, see D. A. Flory, B. R. Simoneit, A. L. Burlingame, I. D. Smith, *NASA Technical Report*, in press.
4. A. L. Burlingame, in *Advances in Mass Spectrometry*, E. Kendrick, Ed. (Institute of Petroleum, London, 1968), vol. 4, p. 15.
5. A. L. Burlingame and D. H. Smith, *Tetrahedron* **24**, 5759 (1968).
6. These estimated percentages were calculated on the assumption that the sensitivities were inversely proportional to the molecular weight within each homologous series and also directly proportional to the number of π-electrons in each structure.
7. We thank Mrs. E. Scott for technical assistance and NASA for financial support.

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Superpressure Balloon Flights in the Tropical Stratosphere

Abstract. *Seven balloons were launched successfully from Ascension Island in January 1969. The balloons, flown at altitudes of 20 and 24 kilometers, will make possible a detailed analysis of the stratospheric circulation near the equator and will hopefully lead to an understanding of the quasi-biennial stratospheric oscillation in the tropics.*

In March 1966 flights of superpressure balloons (nonextensible balloons that are not vented and float at a predetermined altitude characterized by constant density) were begun from Christchurch, New Zealand (*1*). Since that time 200 flights have been made in a joint New Zealand–U.S. program. The longest flight thus far is 441 days at an altitude of 16 km (100 mb). The average duration for stratospheric flights in the last year has exceeded 6 months. The balloons fly stably at their design altitude, never deviating by more than 30 m from a surface of altitude characterized by constant density. Thus far the balloons have been located by telemetry of the elevation angle of the sun (*2*). In 1970 a much more precise location system, which uses the Nimbus D satellite, is planned. The Nimbus D program is intended to demonstrate the feasibility of the location of balloon vehicles by satellite. Included in plans for the future is the intention to fly several thousand balloons at a number of altitudes in both hemispheres with a satellite being used to locate the balloons and to transmit to the ground.

In this first test program to demonstrate the capability of balloon tracking with the Nimbus D satellite, a meaningful research objective was desired. The decision was made to use this program to study the quasi-biennial wind oscillation, with the use of balloons flown from a launch site near the equator. The oscillation, which has yet to be adequately explained, is a major feature of the circulation of the tropical stratosphere (*3*). During the course of a cycle the wind direction near the equator reverses from east to west, and the speed at some levels changes by as much as 50 m/sec. Ascension Island, situated 8° south of the equator in the mid-Atlantic, was chosen as the launch site since the island provides excellent logistic support with its radar stations and satellite communications links.

Three groups of launches were planned to test launch techniques and the performance of balloon vehicles. The location system to be used on these flights consists of a sun-angle sensor which varies the period of repetition of a letter of the Morse code that identifies the balloon. Cooperative tracking stations include Ascension Island, Boulder, Buenos Aires, Christchurch, Honolulu, Huancayo, Manila, Point Reyes, California, Mauritius Island, Pretoria, Santiago, and Jerusalem. Although this crude system positions a balloon only once daily with an accuracy of no better than 100 km, it is nevertheless adequate for delineating the large-scale features of the stratospheric circulation.

The first series of flights was conducted in May–June 1968. The problem of launching the large (11 m in diameter) delicate balloons from an island where the winds are always in excess of 5 m/sec and usually in excess of 7 m/sec was solved by the use of a launch wagon which carried the balloon down the runway until its speed equalled the wind speed whereupon the balloon was launched at a relative wind speed of zero without damage. The first series of flights was handicapped by an excessive ascent rate near float altitude which caused balloon damage. The longest flight achieved on this first series was 10 days.

In the second series, conducted in January 1969, the excessive ascent rate was reduced by the inclusion of a ballast of Freon-11 in a black plastic container. A period of 6 hours was required to evaporate all the Freon and permit