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TRACE ORGANIC IMPURITIES IN GASEOUS HELIUM

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16. Abstract

A program to determine trace organic impurities present in helium has been initiated. The impurities were concentrated in a cryogenic trap to permit detection and identification by a Gas Chromatographic-Mass Spectrometric (GC-MS) technique. Gaseous helium (GHe) exhibited 63 GC flame ionization response peaks which are illustrated. Relative GC peak heights and identifications of 25 major impurities by their mass spectra are given. As an aid to further investigation, identities are proposed for 16 other components, and their mass spectra are given.

It is felt that further investigation of gaseous helium is not necessary at this time. The technique and information gained in this study will be used as a basis for the investigation of oxygen and nitrogen.

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INTRODUCTION

Routine analyses per Marshall Space Flight Center (MSFC) Specifications (Ref 1) are performed on facility gases at Kennedy Space Center (KSC). One analysis, the total hydrocarbon limit, is somewhat misleading in that the procedure used does not exclude other classes of organic compounds which may be present. The specification of total hydrocarbons is more accurately a measure of total organic compounds.

In the past, the chemical and biological activity of low-concentration impurities has been deemed acceptable over short periods of time even though their identities have been unknown. With the advent of extended time in flight, the following question arises: Will these low-level impurities be a source of biological disturbance and hardware malfunction, or can it be assumed, as in the past, that they will be acceptable and pose no problems?

The answer to this question can not be determined without a knowledge of what makes up these trace impurities in the gas systems at KSC. The work described in this report was performed in an attempt to answer this question.

ANALYTICAL PROCEDURE

Cryogenic Trapping - Condensation

The gases under investigation were trapped with the liquid nitrogen (LN_2) system shown in Figure 1. The system is similar to that used for trace gas analyses of Apollo Spacecraft 101, 103 and LEM-3 atmospheres (Ref 3 and 4). Helium was allowed to flow through the trapping system at atmospheric pressure because of its low boiling point. Oxygen and nitrogen samples will require the use of a diaphragm pump to maintain a vacuum suitable for the prevention of condensation.

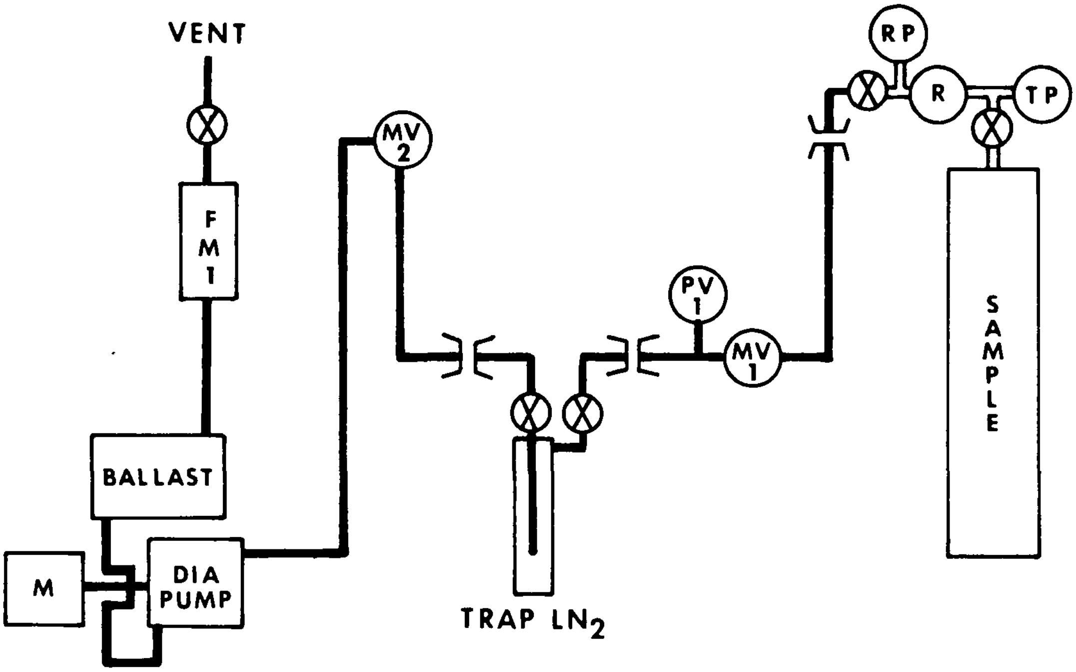
Two different traps were tried: a 3.048-meter (10-foot) coil of 0.0063-meter (1/4-inch) stainless steel tubing, and the 75-cubic centimeter (cc) Hoke bottle shown in Figure 1. It was found that both the coil and 75 cc trap clogged with ice if the inlet was on the down pipe valve, but connected in the way shown (inlet on side port), no clogging was encountered.

Since the identities of the trace components were unknown, and only qualitative analyses were being made, extensive trapping efficiencies were not carried out. To test efficiency and optimum flow rates, two traps were fitted to the system in series and three trappings of GHe were made at flow rates of 400, 600, and 800 cc/min. The trapping time for each was 6 hours. The six samples were then analyzed chromatographically. Comparison of the chromatographic peak heights of the first trap in series (75 cc trap) to the second trap (3.048-meter (10-foot) coil) indicated that at the optimum flow rate of 600 cc/min, the trapping efficiency was greater than 50 percent in the single 75 cc trap. Care must be taken in interpreting the relative flame response peak heights, because without 100-percent trapping efficiency, the risk of selective loss of low-boiling material exists.

Gas Chromatographic Conditions

Two types of columns were tried: Polyphenolether and XE-60, both on Chromosorb G. The XE-60 proved to be the most favorable for separation and for prevention of high column bleed to the mass spectrometer. Its versatility had been established during spacecraft toxicology investigations (Ref 3 and 4).

A matched set of 0.0032-meter (1/8-inch) by 7.010-meter (23-foot) stainless steel columns were packed with a 5.75 percent XE-60 on 80 to 100 mesh Chromosorb G. They were conditioned at 170°C for 24 hours, then installed on a Hewlett-Packard F&M Scientific Model 5750 gas chromatograph. A variety of temperature programs and flow rates were tried, using a standard gas with 12 components present in trace levels. The best separation and peak shapes were obtained at a carrier (He) flow of 35 cc/min and temperature program of 4°/min to 170°C, where it was held for 20 minutes. The program was started 8 minutes after injection, which permitted the lighter low boilers to clear the column before programming began.



Legend:

SAMPLE	Standard K-bottle
TP	Tank total pressure
R	Regulator
RP	Regulated pressure (20 psig)
MV1	Whitey 0.0063-meter (1/4-inch) micrometer valve
MV2	Whitey 0.0063-meter (1/4-inch) micrometer valve
DIA PUMP	Two-stage diaphragm pump
PV1	Pressure vacuum gauge
M	1/3-hp electric motor
BALLAST	500 cc Hoke bottle
FM1	Rota-ball flowmeter

Figure 1. Liquid Nitrogen System Used to Trap Gaseous Helium to Determine Trace Organic Impurities

The carrier effluent was split three ways: 20 percent to the flame ionization detector, 1 percent to the Nickel 63 electron capture detector, and 79 percent to the mass spectrometer. The temperature of the detectors was maintained at 200°C.

These conditions gave good separation, low bleed rate to mass spectrometer, high sensitivity, wide range, and electron capture indications of halogenated organic compounds.

Mass Spectrometric Conditions

A Model 21-104 Consolidated Electrodynamics Corporation (CEC) mass spectrometer was used in combination with the F&M gas chromatograph (GC). The Biemann separator and effluent inlet line from the GC was maintained at 200°C. Since the Model 21-104 total ion current detector can not be used in a scanning mode of operation, fast magnetic scans were made for all observed GC flame response peaks. To ensure high sensitivity, the anode current, ionizing voltage, and accelerating voltage were maintained at 40 μa, 70 ev, and 2,000 v, respectively. The detection of ions was accomplished with the electron multiplier operating at maximum output, 180 v/stage.

Magnet current was set at 14 amps and scanned down, allowing coverage of masses approximately 200 to 12. A chart speed of 4 in./sec permitted accurate counting of all peaks.

The mass spectrometer analyzer pressure, while open to the GC effluent, was maintained at a pressure of 1×10^{-6} Torr.

TEST RESULTS - GASEOUS HELIUM (GHe)

A total of seven cryogenically trapped samples of GHe were obtained from a K-bottle (H-97206). Total hydrocarbon analysis was performed by the Propellants System Components Laboratory (PSCL) at KSC and found to be less than 1 ppm.

The first six trapped samples represented the impurities in 216 liters of GHe. They were used for testing the cryogenic trapping apparatus, determining the best GC-MS operating parameters and adding confidence in the reproducibility of the chromatograms. The seventh trapped sample was used for the analyses given in this report. It represents a total flow of 5,000 liters GHe at 600 cc/min through the cryogenic trap. Qualitatively, chromatograms of all seven samples were identical with the exception of slight variation of retention times.

An additional aid to mass spectrometric identification was obtained from a gas chromatographic, GHe carrier moisture trap (molecular sieve, type 5A) that had been in use for over a year. It was plumbed into the foreline of the cryogenic trap (between the

K-bottle and MV1, Figure 1). A laboratory heating tape was used to raise the temperature of the filter to 200°C, and a flow of 600 cc/min was provided by the K-bottle. The ensuing effluent was cryogenically trapped for 4 hours and analyzed.

The analysis showed an impurity concentration of three to five times that of the 5,000-liter trapped sample. Unfortunately, catalytic reaction from heating the filter could cause degradation of impurities or interaction between impurities. Therefore, this method could not be used as an end in itself. It was, however, used as an aid in the mass spectral interpretation wherever GC retention time and low-intensity mass spectra matched that of the 5,000-liter trapped sample. An additional 20 GC peaks were observed with the filter sample, all of which were of lower intensity than the GC peaks obtained from the 5,000-liter trapped sample. These could be due to degradation or interaction, but could also be additional impurities in the GHe of insufficient concentration for detection. At any rate, this report deals only with those impurities found in the 5,000-liter trapped sample. The gas chromatogram of the sample is given in Figure 2. Sixty-three impurities were found (numbered ① to (63)).

Figure 3 shows the relative peak heights of all gas chromatographic peaks. They are broken down into three classifications.

Identified (Table 1, Appendix): There were 25 peaks in which a sufficient quantity of GC effluent reached the mass spectrometer to give representative mass spectra (Ref 5, 6, and 7), and for which boiling point and molecular weight data fit chromatographic retention times.

Possible Identifications (Table 2, Appendix): There were 16 chromatographic peaks which did not give sufficient effluent for a representative mass spectrum or were not sufficiently separated by the gas chromatograph for a reasonable match to standard mass spectra, even though five to ten mass/charge peaks appeared above background.

Unidentified (Table 3, Appendix): Twenty-two peaks gave insufficient effluent for identification. Less than five mass/charge peaks appeared above background, none of which were of sufficient intensity for identification.

DISCUSSION

The results of the Grade A helium investigation were very encouraging from the standpoint of developing successful procedural methods for collection and analysis of impurities in the part-per-billion range.

Possible sources of error can be categorized as statistical, concentrational, and analytical. Statistically, the single analysis of a 5,000-liter trapped sample can not be generalized to indicate that these impurities are present in all Grade A gaseous helium. The repeatable chromatograms obtained from the single K-bottle indicate these impurities were present in the helium under investigation.

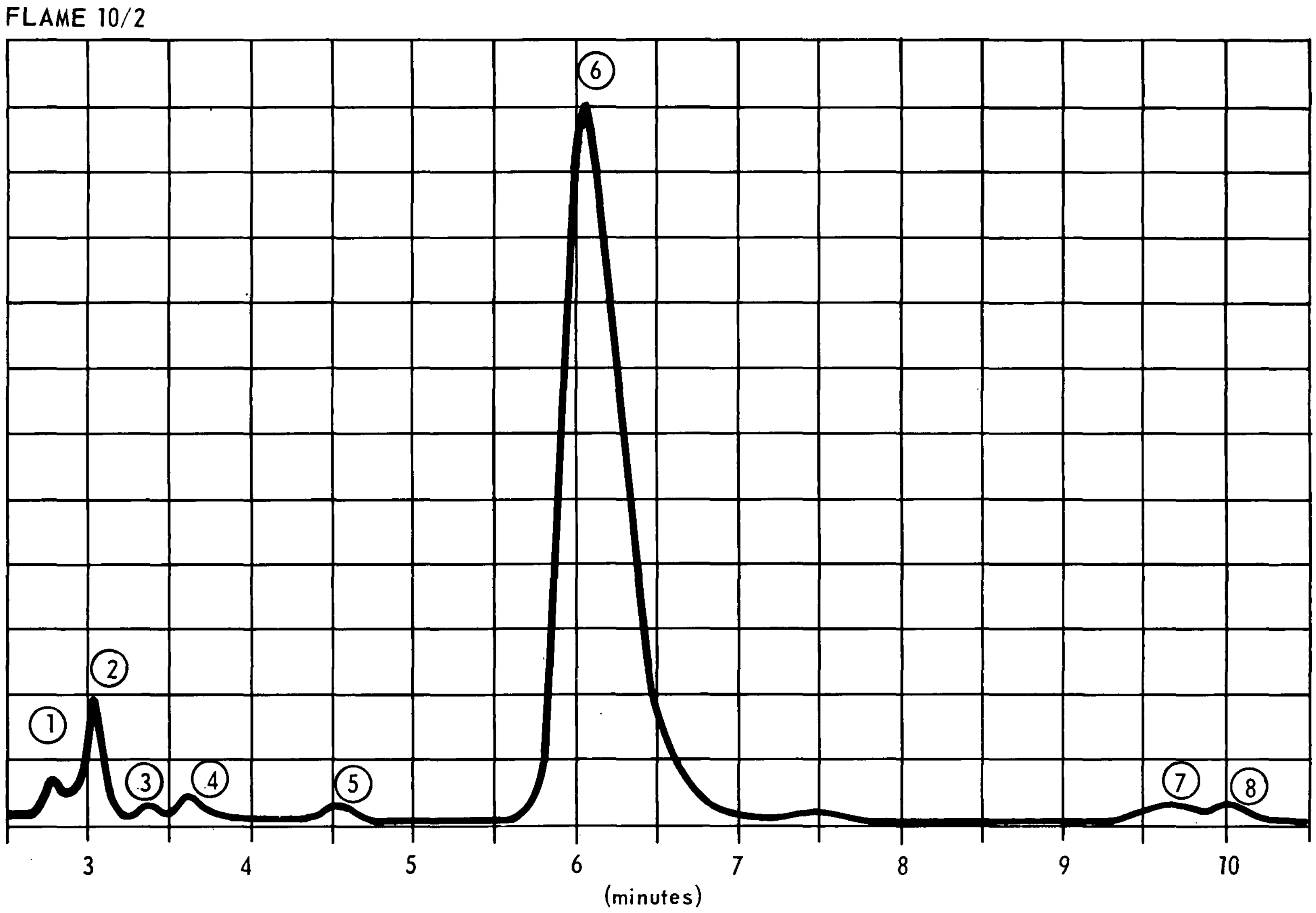


Figure 2. Gas Chromatogram of the 5,000-Liter Trapped Sample (Sheet 1 of 4)

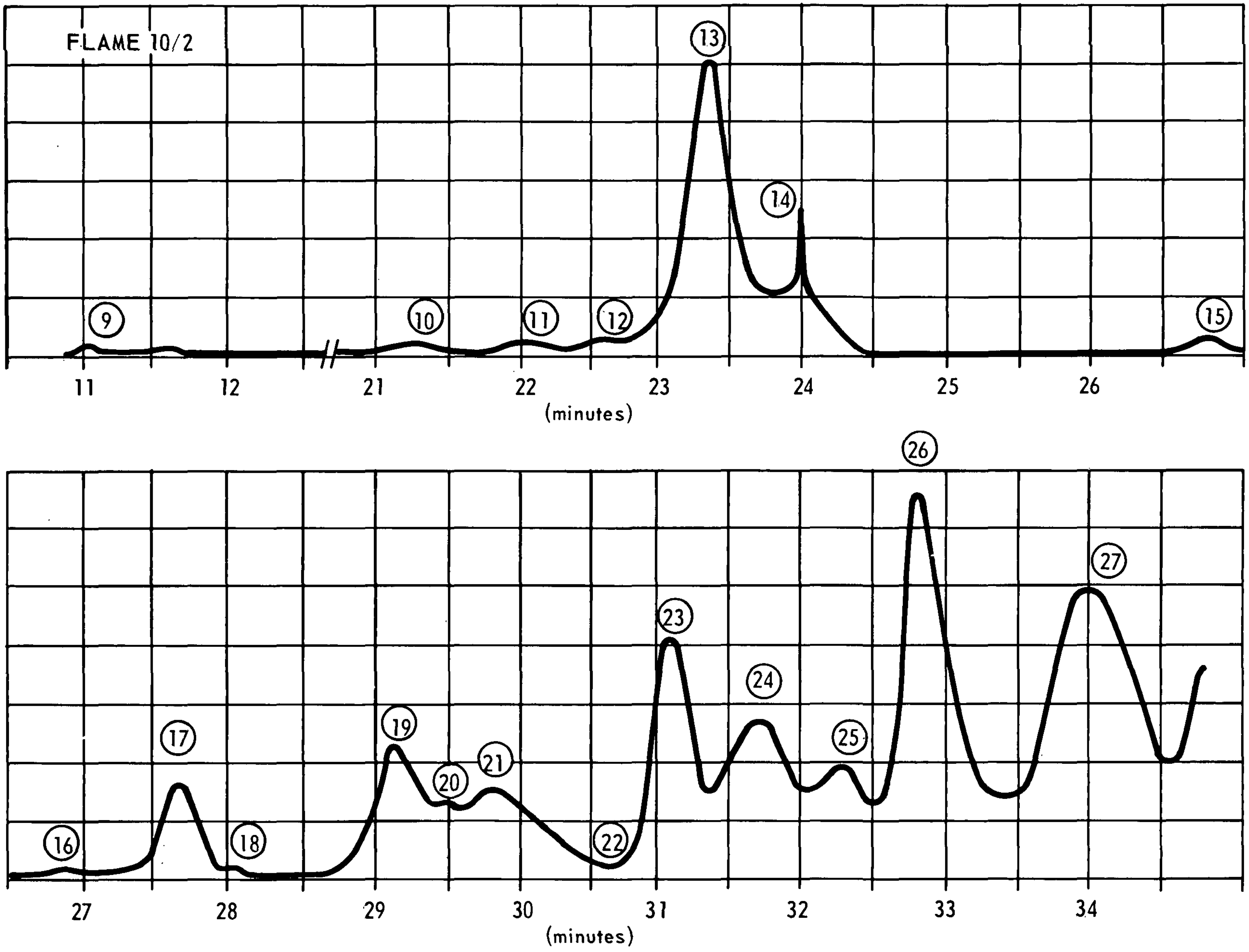


Figure 2. Gas Chromatogram of the 5,000-Liter Trapped Sample (Sheet 2 of 4)

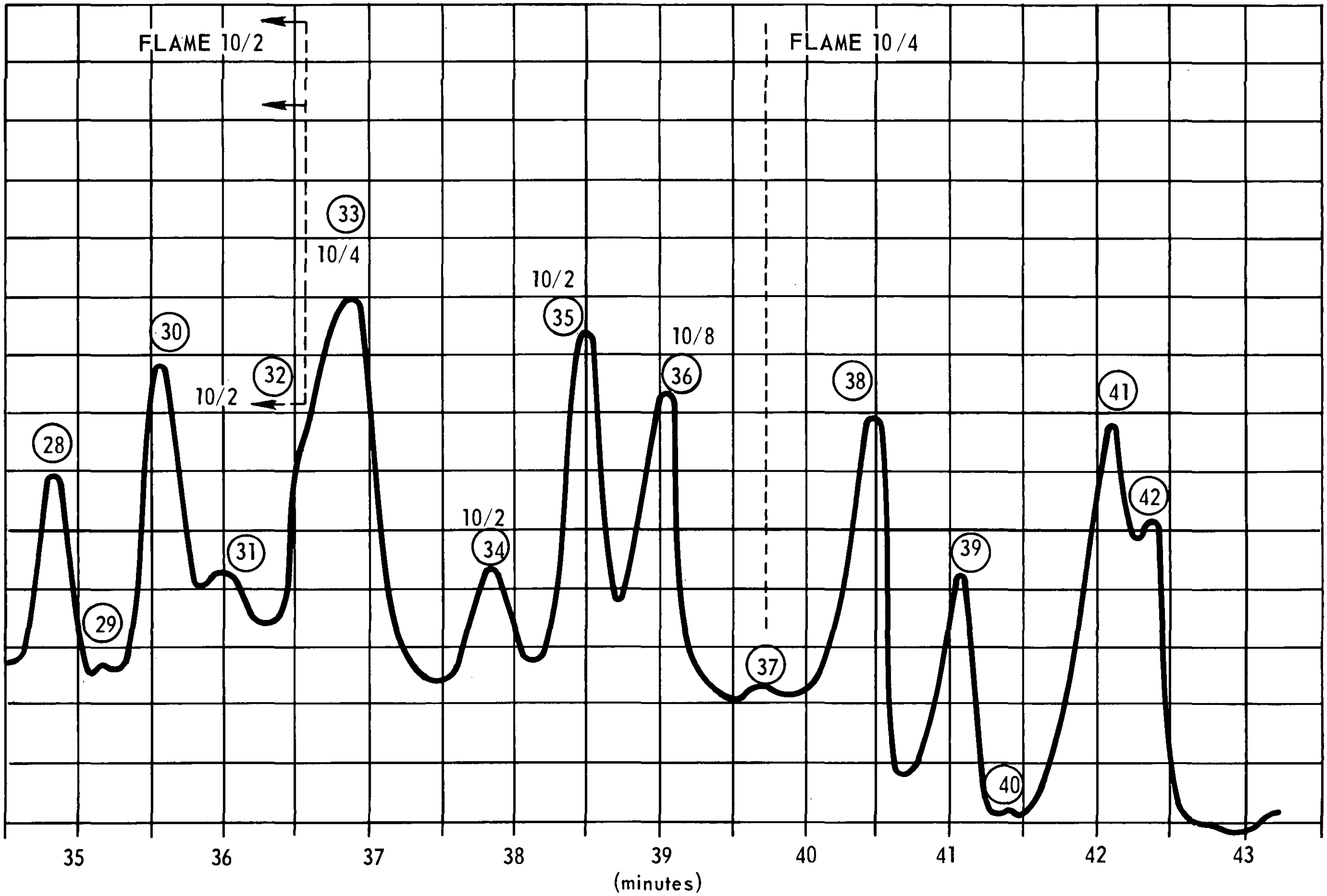


Figure 2. Gas Chromatogram of the 5,000-Liter Trapped Sample (Sheet 3 of 4)

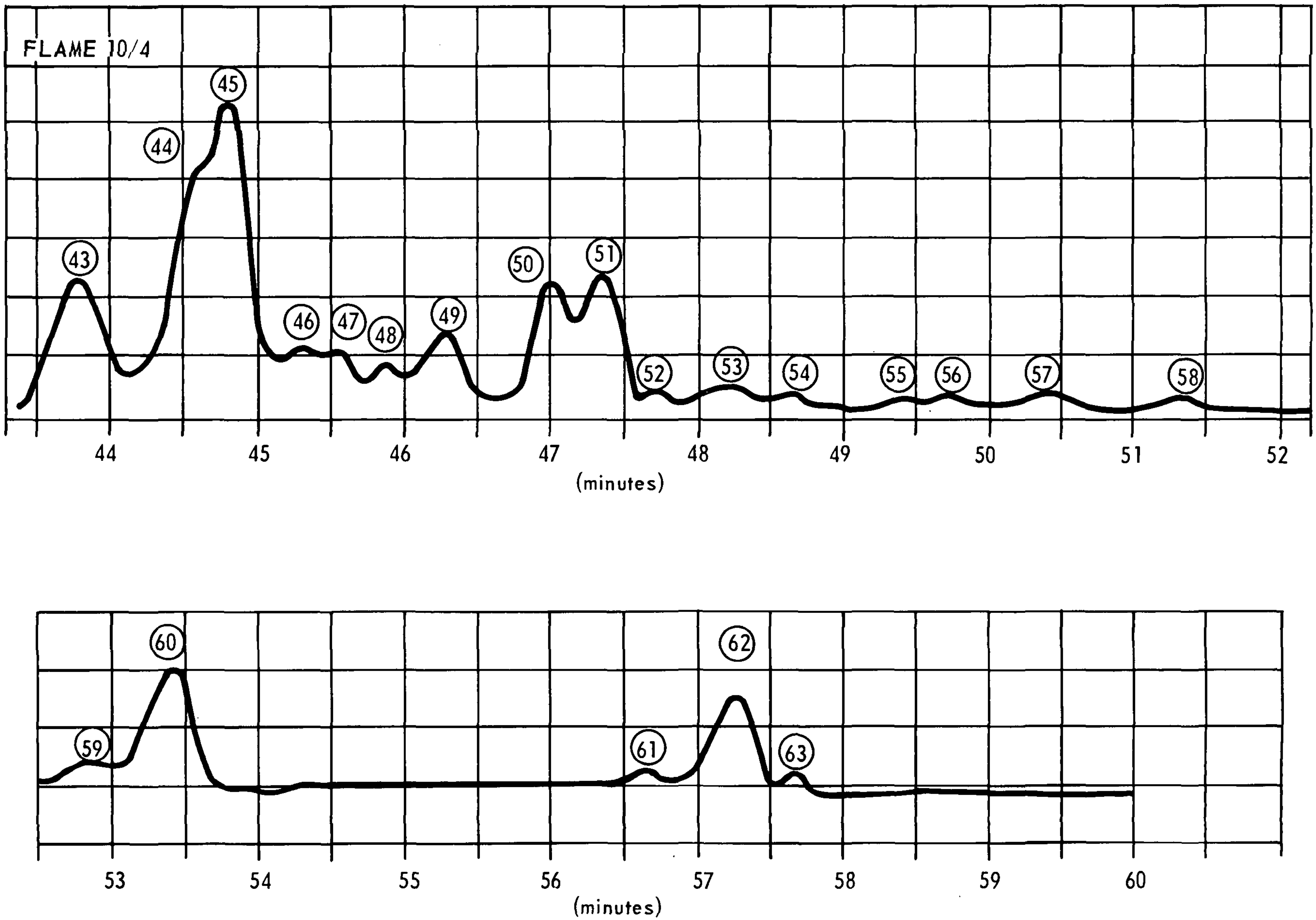


Figure 2. Gas Chromatogram of the 5,000-Liter Trapped Sample (Sheet 4 of 4)

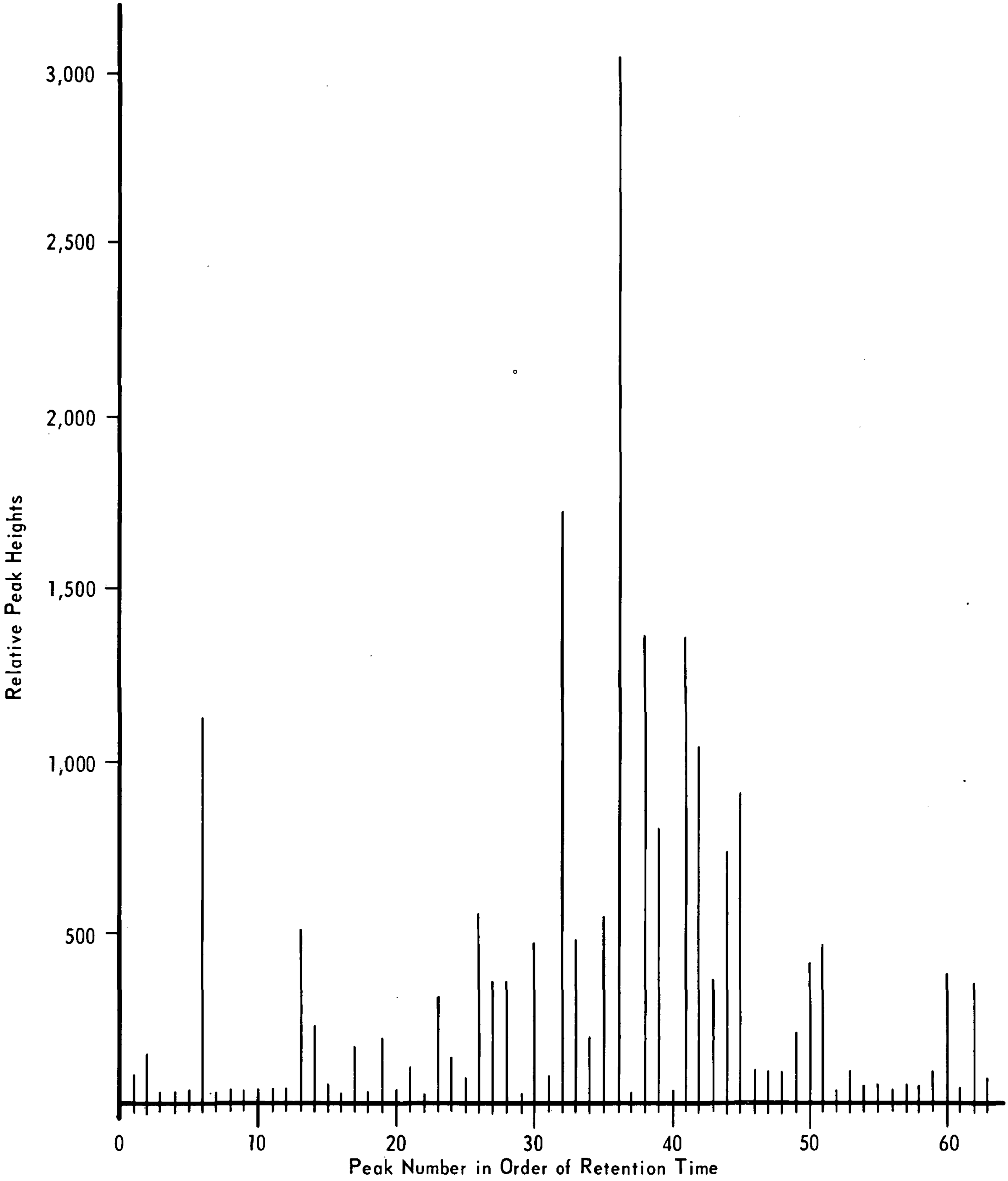


Figure 3. Relative Peak Heights of Gas Chromatographic Peaks

Cryogenic trapping of gases can give erroneous results if trapping efficiencies are not known. Low boiling impurities may not be trapped, and those which are trapped may not be representative of the actual quantities present. This source of error could be eliminated by the construction of a multi-purpose trapping system. Standardization of such a system with low-concentration mixed gas standards would also permit quantification of the results. Those components which would not be cryogenically trapped (i.e., hydrogen, nitrogen, oxygen, argon, carbon dioxide, and methane) require direct gas analysis which, at KSC, is performed by the PSCL on all facility gases.

Analytical problems involved in trace gas analysis are for the most part in quantification. Relative peak-height quantification can not be construed as being accurate without extensive individual sensitivity runs. This task requires that known volume standards that contain the impurities found in the gas under investigation be chromatographed and accurately measured. Qualitative errors could occur if the impurity had little or no flame or electron capture ionization response. This problem could be eliminated if the impurity of interest were specified and a separate analytical procedure used for its detection.

For the purpose of this investigation, the XE-60 column was chosen because it separated the greatest number of impurities.

The analytical information obtained in this study indicates that the "total hydrocarbon as methane" analysis is, on the whole, a valid procedure. All impurities found, with the exception of acetone, were hydrocarbons. Those containing chlorine, and to some extent those which are unsaturated, are undesirable in both manned and unmanned systems (Ref 3, 4, 9, and 10). At the present time, helium is not used in the Spacecraft Life Support System but is often employed in leak-testing large closed systems. The possibility of contamination under these conditions exists but is very remote, expecially at the low concentrations found.

CONCLUSIONS

It is felt that further investigation of gaseous helium is not necessary at this time. The technique and information gained in this study will be used as a basis for the investigation of oxygen and nitrogen which are vital to the Life Support Systems at KSC.

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APPENDIX

Table 1. Identified Components

Peak No.	MS-GC Identifications	Molecular Weight	Boiling Pt (Ref 5)	Relative GC Peak Height
1	Xenon	131.3	-108.1	60
3	2-Methylpropene	56.1	- 6.9	20
5	cis-Dimethylcyclopropane	70.1	37.0	30
6	1,1,2-Trichloro-1,2,2,-trifluoroethane	187.4	47.6	30
7	cis-Dichloroethylene	96.9	60.3	20
8	1,1,2-Trimethylcyclopropane	84.1	-	30
13	Trichloroethylene	131.4	87.2	500
17	Toluene	92.1	110.6	160
25	p-Xylene	106.2	138.4	60
26	m-Xylene	106.2	139.1	540
27	2,2,4-Trimethylheptane	142.0	147.7	340
28	o-Xylene	106.2	144.4	340
32	m-Ethyltoluene	120.2	161.3	1720
33	p-Ethyltoluene	120.2	162.0	480
35	o-Ethyltoluene	120.2	165.2	520
36	m-Diethylbenzene	134.2	181.1	3120
38	o-Diethylbenzene	134.2	183.5	1360
39	p-Diethylbenzene	134.2	183.8	800
42	3,5-Dimethylethylbenzene	134.2	183.8	1040
43	2,5-Dimethylethylbenzene	134.2	186.9	360
44	2,4-Dimethylethylbenzene	134.2	188.4	720
45	3,4-Dimethylethylbenzene	134.2	189.8	900
60	Naphthalene	128.2	218.0	400
62	β-Methylnaphthalene	142.2	241.1	350
63	α-Methylnaphthalene	142.2	244.8	50

Table 2. Possible Component Identifications

Peak No.	MS-GC Identifications	Molecular Weight	Boiling Pt °C (Ref 8)	Relative GC Peak Height
2	1-Chloro-1,2,2-trifluoroethylene	118.5	17	140
10	Acetone	58.1	56.2	10
15	2,5-Dimethyl-2,4-hexadiene	110.2	134.0	40
19	4-n-Propylheptane	142.3	162.0	180
23	3,3-Dimethylpentane	100.2	86.1	300
30	3-Methylhexane	100.2	92.0	460
34	C_4-Chlorinated Hydrocarbon	-	-	160
41	Dihydroindene	118.2	177.0	1360
49	2-Methyl-2,3-dihydroindene	132.2	187.0	200
50	1,2,4,5-Tetramethylbenzene	134.2	196.0	400
51	1-Methyl-2,3-dihydroindene	132.2	188.9	440
52	1,2,3,5-Tetramethylbenzene	134.2	197.9	20
53	1,2,3,4-Tetrahydronaphthalene	134.2	205.0	80
57	6-Methyl-1,2,3,4-Tetrahydronaphthalene	146.2	229.0	40
58	2,6-Dimethyl-1,2,3,4-Tetrahydronaphthalene	160.2	238.0	40
59	A Chloroprene dimer	176.0	-	80

Table 3. Unidentified Components

Peak No.	Mass Spectra Above Background	Relative Flame Ionization Peak Height
4	m/e 30	40
9	m/e 67	20
11	m/e 81-96-67-61	25
12	m/e 78-69-83	10
14	Spike	160
16	m/e 43-32-41-44	20
18	-	10
20	-	20
21	m/e 82-67-109-124	100
22	-	10
24	m/e 56-57-97-81 (97-99 1 Cl)	120
29	-	10
31	m/e 97-96-104-154	60
37	m/e 135-43-149-93	10
40	-	10
46	-	80
47	m/e 139-149	80
48	-	80
54	-	40
55	-	40
56	-	20
61	-	40

Note: m/e = mass/charge

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