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SUMMARY

A gas chromatograph (GC)/mass spectrometer (MS) system that allows the speciation of unburnt hydrocarbons in the combustor exhaust has been developed at the NASA Lewis Research Center. Combustion gas samples are withdrawn through a water-cooled sampling probe which, when not in use, is protected from contamination by a high-pressure nitrogen purge. The sample line and its connecting lines, filters, and valves are all ultraclean and are heated to avoid condensation. The system has resolution to the parts-per-billion (ppb) level.

INTRODUCTION

The presence of unburnt hydrocarbons (UHC) in combustor exhaust is a significant concern to the atmospheric community. Presently, the total UHC are measured via the flame ionization method which reports the total number of unburnt carbon atoms but gives no detailed information about the hydrocarbon compound types present. Atmospheric modelers are more interested in the speciation of the hydrocarbons than in the total number of carbon atoms present. An experimental program was initiated utilizing a GC/MS system to identify the carbon molecules in the flow field.

The two components of the system are a gas chromatograph and a mass spectrometer that is used as a detector for the GC. The GC separates the test sample by means of column material, carrier gas flow rate, and column temperature. The MS identifies and measures the concentration of each separated species by employing one of two operating modes: (1) scanning all ions in a specified mass/charge range and (2) selected ion monitoring (SIM) to only look at specific ions. The scan mode would be required for identification purposes whereas the SIM mode yields a much stronger signal because it only looks at a limited number of specified ions.

APPARATUS

Room

The GC/MS system is installed adjacent to the combustor test cell in a room constructed specifically for the instruments. The room has its own air conditioner and filtered air system to eliminate dust from a working area nearby. Liquid nitrogen is used to cool the gas chromatograph oven to the required subambient temperature but because of safety concerns, the room must be vented (about 1 m³/min) when occupied. Exhaust gases from the GC/MS are vented through the system to the outside.

Sample Lines

The approximately 4.5-m stainless steel sample line for the flame tube rig is silica lined. To minimize contamination, the line was purged with nitrogen gas for 1 hr after it was installed. Because some of the lining that flaked off during construction was not completely removed, even with the 1-hr nitrogen purge, an in-line filter was installed to protect the valves and GC/MS. All the valves and connectors used were ultraclean. The approximately 10-m sample line for the combustor sector rig was ultraclean stainless steel tubing, which avoided the flaking problem. Both lines shared the same nitrogen purge line, filters, and exhaust lines. The lines for the standard gas sampling were ultraclean stainless steel tubing approximately 3 m long.

To eliminate condensation of the combustion gas in the sample line, both lines were heated to about 120 °C with steam tracing wrap; the valves, filters, and connecting lines to the GC were electrically heated. The temperature of the gas sample entering the sample loop was about 116 °C.

Sample Probe

Combustion gas samples were withdrawn from the experimental combustion flame tube rig through a water-cooled sampling probe that had three sample ports spaced over the inserted portion. An air-driven cylinder inserted the probe into the combustion zone when the gas stream was sampled and withdrew it when the test was over. The sample probe for the combustor sector rig was fixed in position and was water cooled. A high-pressure nitrogen purge protected the probe from contamination whenever it was not used for sampling. The nitrogen pressure was always 2 to 3×10^5 Pa above the combustion chamber pressure and was on even during the long warmup process to protect the probe from contamination resulting from poor combustion conditions. The retractable probe is preferred to better prevent contamination.

Gas Chromatograph

The gas chromatograph (Hewlett Packard model 5890) is equipped with automatic oven temperature programming, has an oven temperature profile of -80 to 450 °C and is capable of multilinear temperature programming with up to 3 ramps. The subambient temperature is obtained by setting up a liquid nitrogen pumping system that includes a 25-liter liquid nitrogen dewar and a pressurized nitrogen gas line to force the liquid into the GC. However, the maximum temperature is limited because parts in the GC valve system will be damaged if the oven temperature rises above 200 °C for a long period. The first stage is set to -30 °C so that all condensables are in the column entrance.

Several modifications to the GC were necessary before testing began. The standard sample loop that comes with the GC has a 0.25-cc capacity. After a series of tests, it was decided that a sample loop capacity of 10 cc was needed to provide the sensitivity required. Because the sensitivity is also effected by the helium carrier gas flow rate, it was lowered to approximately 3 cc/min to reach ideal conditions. To achieve this low rate of flow, the original flow restrictor was replaced. Another consideration was the suitability of the column that came with the system. The original column was not suitable for the task because it did not appropriately separate the hydrocarbons. Therefore, for the analysis of gases with a starting temperature in the subambient range, a 25-m-long plot column (PoraPLOT Q) with a 0.32-mm inside diameter and a 10-mm film thickness was chosen. The time required to put all of a sample into the column is about 3.5 min.

Mass Spectrometer

The mass spectrometer has long been recognized as an excellent detector for a gas chromatograph. The spectral data it produces provides the qualitative information lacking in other GC detectors. The unit used in the present work (Hewlett Packard model 5989) has a quadrupole mass filter with a high-energy dynode detector to improve the sensitivity. It operates in either the scan mode or the selected ion monitoring (SIM) mode. The scan mode scans the whole spectrum within a range of mass units and can be used to identify molecules by comparing the spectrum of the unknown molecule with the established mass spectra library, which contains approximately 138 000 entries. The SIM mode is much more sensitive (by approx. a factor of 10^3) because it only looks at a number of limited specified

ions instead of at the whole mass range. However, the SIM mode does not allow one to identify the molecule by its spectrum alone; identification is accomplished by establishing a data base from a series of calibration runs that utilize standard gas mixtures having concentrations in the desired parts-per-million (ppm) or parts-per-billion (ppb) ranges.

Computer

Both GC and MS are connected to a 486 PC. The software provides the controls for setting up all the parameters for the GC (oven temperature program, interface temperature, and pressure) and for the MS (operation mode, mode parameters, quadrupole parameters). The data set is stored directly on the hard disk. The software also provides the postanalysis tools.

Standard Gas Mixtures

Each set of standard gases has two cylinders that contain identical gas mixtures with different concentrations: one is approximately 15 ppm and the other, approximately 50 ppb. The three sets of standard gases have the following compositions: 14 hydrocarbons having 1 to 6 carbon atoms; 13 hydrocarbons having 7 to 9 carbon atoms; and 4 aldehydes having 2 to 5 carbon atoms. In addition, one smaller cylinder contains seven saturated straight-chain hydrocarbons having one to seven carbon atoms with concentrations of approximately 10 ppb.

It is necessary to emphasize that these sets only represent a fraction of the possible saturated and unsaturated hydrocarbon compounds. The research discussed in this report is considered preliminary, and a complete calibration work (with a complete set of standard gases) is not in the current plans.

EXPERIMENTAL PROCEDURE

Calibration Process

The gas line and the sample loop are flushed with the three sets of standard gases for 6 min before the sample is taken. In the case of the 10-ppb standard gases where the gas sample line is much shorter (approx. 0.3 m), a regulator is used to fill and flush six times before the sample is taken.

The ppm mixture of each set of the standard calibration gases was run in the scan mode to identify the molecules and their retention times. The ppb mixture was then run in the SIM mode. Because of the excellent agreement in the retention times of the two, the retention time was used to identify the molecule.

Sample Process

When the combustion operation conditions are satisfactory for taking the gas sample, permission is given. The sample probe for the combustor flame tube rig is inserted in the flow field (the probe for the sector rig is fixed and stays in the flow). The nitrogen purge is turned off and a venting valve opened. The gas sample line that connects the probe and the sample loop is then flushed with the combustion gas sample for 8 to 9 min. The probe for the combustor flame tube rig is then withdrawn from the flow. The purging nitrogen is turned on and the permission removed. The gas sample trapped in the loop is vented for about 3 min before the analysis is initiated to keep it at atmospheric pressure.

RESULTS AND DISCUSSION

Standard Gas Mixtures

Figures 1 and 2 show the spectrograms of the 14- and 13-hydrocarbon standard gas mixtures containing 1 to 6 and 7 to 9 carbon atoms, respectively, with a concentration of approximately 15 ppm run in the mass spectrometer scan mode. Figure 3 presents spectrograms for aldehydes with the same level of concentration. In this mode of operation, each species was identified as it escaped from the column. As seen from the figures, the temperature schedule did not completely separate all the species from each other. After evaluating the length of time for each run and the limited temperature steps available, the present method and results were considered acceptable.

Figures 4 and 5 present the spectrograms of the same standard gas mixtures but at lower concentrations, approximately 50 ppb. Figure 6 is the spectrogram of saturated straight-chain seven-hydrocarbon standard gas mixtures having seven to nine carbon atoms with concentrations of approximately 10 ppb. These spectrograms were obtained with the mass spectrometer using the SIM mode in which three or four ions were selected for each carbon group. These ions were selected after comparing the primary ions of each hydrocarbon type: straight chains, branched chains, unsaturated, and aldehydes. Each type has to be represented in the ions selected, as can be seen by the present selection which produced a good signal for each species in the standard mixture. Because the standard gas mixtures containing ppb aldehydes had a short lifetime (approx. 2 months), no usable data base was generated. The problem is being investigated by the company that provided the mixtures. Reactions between the aldehydes and the unprotected cylinder wall are the suspected cause.

Gas Samples from the Combustor Sector Rig

Table I lists three sets of data obtained from the combustor sector rig. Note that all the species are categorized as different carbon groups and several are identified. Concentrations were calculated on the basis of the calibration work done on the standard gas mixtures (table II). Figure 7 shows one chromatogram from the three sets. Several ppb of C_4H_8 (2-methyl-1-propene or 1-butene) and a few ppb of C_5H_{12} (2,2-dimethyl-propane) were identified in all three cases. Several ppb of C_6H_{12} (1-hexene) and C_6H_{14} (hexane) were identified in some cases. Several ppb of some unidentified C_4 , C_5 , and C_6 and approximately 50 ppb of an unidentified C_7 compound were also observed in some cases. Aldehydes including C_2H_4O (ethanal), C_3H_6O (propanal), C_4H_8O (butanal), and $C_5H_{10}O$ (pentanal) were observed in almost all three cases. Unfortunately, because of the problem of the standard gas mixtures containing ppb aldehydes, the concentrations of the aldehydes could not be determined.

Discussion

Species with concentrations less than 1 ppm could not be detected with the GC/MS and the operating instructions supplied by the manufacturer. The following changes greatly improved the sensitivity of the instrument and allowed the measurement of concentrations as low as 10 ppb: (1) the sample loop was changed from 0.25 to 10 cc, the largest size recommended by the manufacturer; (2) the carrier gas flow rate was reduced to 3 cc/min by replacing the flow restrictor (10 to 200 cc/min) with one having a range of 1 to 20 cc/min; (3) the mass spectrometer was manually tuned to be specifically sensitive to the mass range of interest.

In split-mode operation, only a fraction of the gas sample goes to the mass spectrometer for analysis. This fraction is an inverse function of the carrier gas flow rate. The lower the flow rate, the more the gas sample available for analysis. A flow rate of 3 cc/min was near the lower limit of operation. At this flow rate, about one-quarter (2.5 cc) of the gas sample is analyzed by the mass spectrometer; however, the time required to completely flush the sample loop is about 3.5 min. Thus, a subambient temperature was required for trapping most of the larger molecules at the entrance of the column. An initial oven temperature of $-30\text{ }^\circ\text{C}$ for 3.75 min was perfect for this purpose.

Comparing the chromatograms of the same gas mixture pairs with different concentration levels revealed that the retention time remained consistent for the ppm and the ppb standard gases. This assures that identification of species by the retention time is applicable but with the limitation that the species only be identified if they are contained in the standard gases.

Note that the ratios of the areas under each peak in SIM and scan modes are different. The reason is that the ions selected have different degrees of contribution for each species. Only the abundance obtained in the SIM mode operation is used to calculate the concentration of the unknown species because that is the operation mode for taking the exhaust samples.

The species and retention times are recorded in table II along with the abundance per unit concentration. Although all the species have about the same concentration, the area under each peak within each carbon group is quite different, suggesting that good measurements of the concentration can only be obtained if the standard gas contains the species being measured. However, by closely examining the spectrum, a neighboring compound can be chosen to provide a relatively good estimation of the concentration of the unknown species (which can only be identified as a species containing a certain number of carbons).

A problem still under investigation is the peak that appears around the 14-min retention time. In all the runs under scan mode, this peak could be identified as water. But in the SIM mode, in which the possible ions for the water molecule were not selected, the peak still appeared. We believe that nitrogen dioxide and possibly other nitrogen compounds are being carried through the column by the water. More work would be required to better determine the identities of those species.

CONCLUSION

In this preliminary research, hydrocarbons were categorized by carbon groups with some additional detailed identification. For those identified species, concentrations could be calculated within a factor of 2. For the remaining categorized species, their concentrations were estimated within an order of magnitude. A complete identification of all the possible hydrocarbon species requires detailed calibration work with a complete set of standard gases, which is beyond the scope of the current investigation. The problem of the missing standard gases with the ppb-level aldehydes may be solved if new standard gases can be obtained. The mysterious 14-min peak may require much more work to identify the unknown species.

FUTURE WORK

A set of standard gases containing benzene and toluene has been acquired recently because they are possible combustion products. Formaldehyde is also generally believed to be one of the combustion products. However, only one cylinder of standard gas containing formaldehyde has been acquired since it is only available at concentrations of 10 ppm or higher. Calibrations will be performed. New samples from the same combustor rig will be taken and analyzed to investigate the existence of these species.

Sulfur emissions also concern the atmospheric community. Sulfur dioxide (SO_2) can usually be measured by an SO_2 analyzer or can be calculated from the sulfur content of the fuel. The more serious concern is that SO_3 may be present in some significant portion of the sulfur compounds. The sulfuric acid (H_2SO_4) that will be formed may coat particulates and affect heterogeneous chemistry. The possibility of using GC/MS to obtain direct measurement of SO_x is under investigation.

TABLE I.—COMBUSTOR EXHAUST GASES

Species	Sample 1		Sample 2		Sample 3	
	Retention time, min	Concentration, ppb	Retention time, min	Concentration, ppb	Retention time, min	Concentration, ppb
H ₂ O + ^a NO ₂	14.145 14.637 14.756 14.950 -----	(b)	14.190 14.309 14.428 14.503 14.935	(b)	14.024 14.322 14.591 14.889 -----	(b)
C ₂ H ₄ O Ethanal	16.757	—	16.696	—	16.680	—
C ₄ (a)	17.160	3.0	-----	—	17.112	0.5
C ₄ H ₈ 2-methyl-1-propene (1-butene)	17.562	4.5	17.516	6.4	17.530	1.0
C ₄ (a)	-----	—	17.819	—	-----	—
C ₃ H ₆ O Propanal	19.001	—	18.961	—	18.979	—
C ₅ H ₁₂ 2,2-dimethyl-propane	19.112	2.6	19.073	1.3	19.090	1.4
C ₄ H ₈ O Butanal	22.510	—	22.442	—	22.464	—
C ₆ (a)	22.639	5.0	22.593	1.8	22.615	—
C ₆ H ₁₂ 1-hexene	-----	—	24.231	.4	24.231	7.4
C ₆ H ₁₄ Hexane	24.945	4.0	-----	—	-----	—
C ₅ H ₁₀ O Pentanal	28.281	—	28.273	—	-----	—
C ₇ (a)	28.335	50.0	28.380	55.0	-----	—

^aIt cannot be definitely identified as NO₂, but our best estimate is that it is.

^bAt this time, the concentration cannot be calculated.

TABLE II.—CONCENTRATION AND RETENTION TIMES OF STANDARD GAS MIXTURES

Sample	Species		Retention time, min		Abundance, ppb	
			Mean	CV%	Mean	CV%
1	C ₂ H ₄	Ethene	12.030	0.070	3 961	2.163
2	C ₂ H ₆	Ethane	13.152	.063	5 316	6.228
(a)	H ₂ O +	Water	14.652	0.193	(b)	(b)
3	C ₃ H ₆	1-propene	15.768	0.036	8 901	1.850
4	C ₃ H ₈	Propane	15.934	.044	6 704	4.563
5	C ₂ H ₄ O	Ethanal	16.762	0.039	(b)	(b)
6	C ₄ H ₁₀	2-methyl-propane	17.425	.047	17 507	1.808
7	C ₄ H ₈	2-methyl-propene	17.571	.047	11 537	1.915
8	C ₄ H ₈	1-butene	-----	-----	-----	-----
9	C ₄ H ₁₀	Butane	17.819	.057	17 202	4.810
10	C ₃ H ₆ O	Propanal	18.977	0.011	(b)	(b)
11	C ₅ H ₁₂	2,2-dimethyl-propane	19.058	.049	26 603	1.844
12	C ₅ H ₁₀	3-methyl-1-butene	19.631	.059	6 941	2.613
13	C ₅ H ₁₀	2-methyl-butene	20.209	.065	18 041	2.527
14	C ₅ H ₁₀	1-pentene	-----	-----	-----	-----
15	C ₅ H ₁₂	Pentane	20.725	.076	17 291	5.333
16	C ₄ H ₈ O	Butanal	22.512	0.051	(b)	(b)
17	C ₆ H ₁₄	2,2-dimethyl-butane	23.184	.060	16 978	2.257
18	C ₆ H ₁₂	4-methyl-1-pentene	23.456	.062	15 236	3.125
19	C ₆ H ₁₂	2,3-dimethyl-1-butene	-----	-----	-----	-----
20	C ₆ H ₁₄	2-methyl-pentane	23.991	.061	21 409	2.008
21	C ₆ H ₁₂	1-hexene	24.329	.064	21 502	4.094
22	C ₆ H ₁₄	Hexane	24.864	.073	22 259	4.678
23	C ₅ H ₁₀ O	Pentanal	28.187	0.092	(b)	(b)
24	C ₇ H ₁₆	2,4-dimethyl-pentane	28.587	.009	32 968	4.747
25	C ₇ H ₁₄	2,3-dimethyl-1-pentene	29.338	.010	8 843	9.026
26	C ₇ H ₁₄	4-methyl-1-hexene	29.897	.012	29 985	5.505
27	C ₇ H ₁₆	2-methyl-hexane	30.328	.011	30 778	4.096
28	C ₇ H ₁₄	1-heptene	31.136	.011	28 195	5.825
29	C ₇ H ₁₆	Heptane	32.186	.105	29 365	4.278
30	C ₈ H ₁₈	2,5-dimethyl-hexane	39.323	0.030	27 505	4.603
31	C ₈ H ₁₈	2-methyl-heptane	42.734	.021	29 931	5.227
32	C ₈ H ₁₆	2-methyl-1-heptene	43.480	.030	2 436	11.174
33	C ₈ H ₁₆	1-octene	44.496	.022	53 451	14.171
34	C ₈ H ₁₈	Octane	46.483	.024	36 295	6.890
35	C ₉ H ₁₈	2-methyl-1-octene	69.815	0.035	2 863	20.980
36	C ₉ H ₁₈	1-nonene	71.689	.174	36 764	25.597
37	C ₉ H ₂₀	Nonane	76.235	.035	46 224	19.659

^aAn unidentified species was carried out by the water.

^bAt this time, the concentration cannot be calculated.

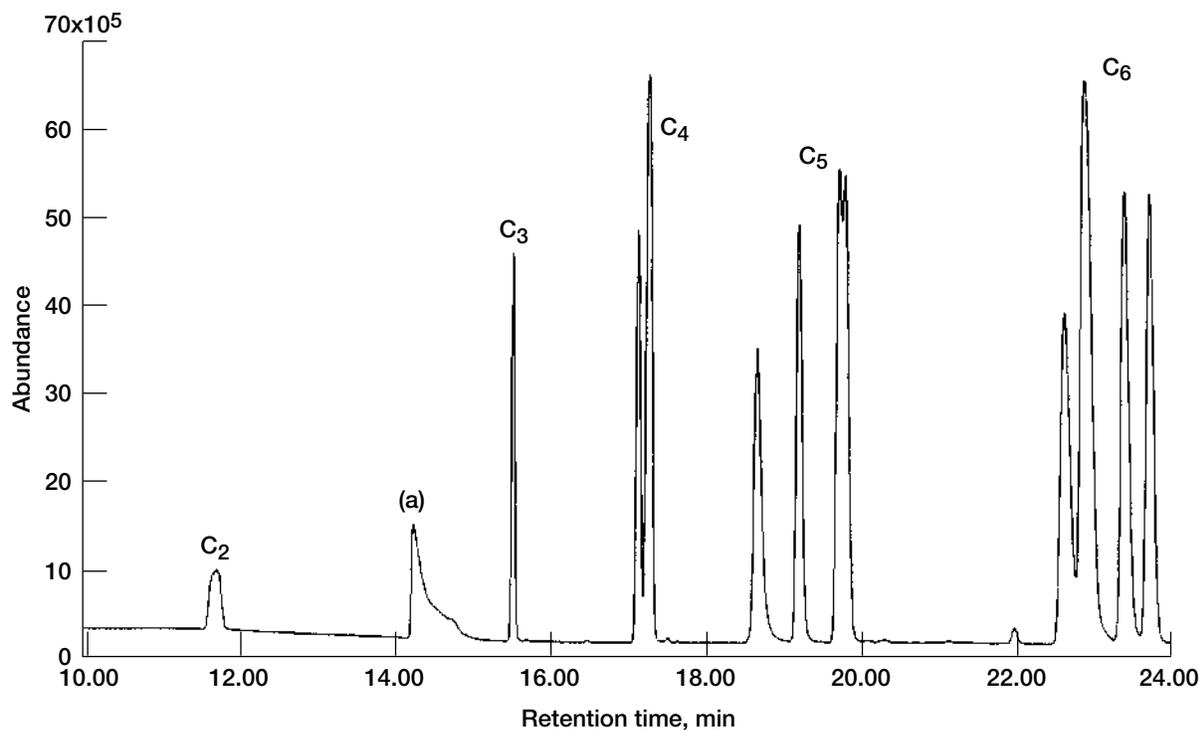


Figure 1.—Spectrogram of 14-hydrocarbon standard gas mixture containing 1 to 6 carbon atoms with approximately 15-ppm concentration. ^aAn unidentified species was carried out by the water.

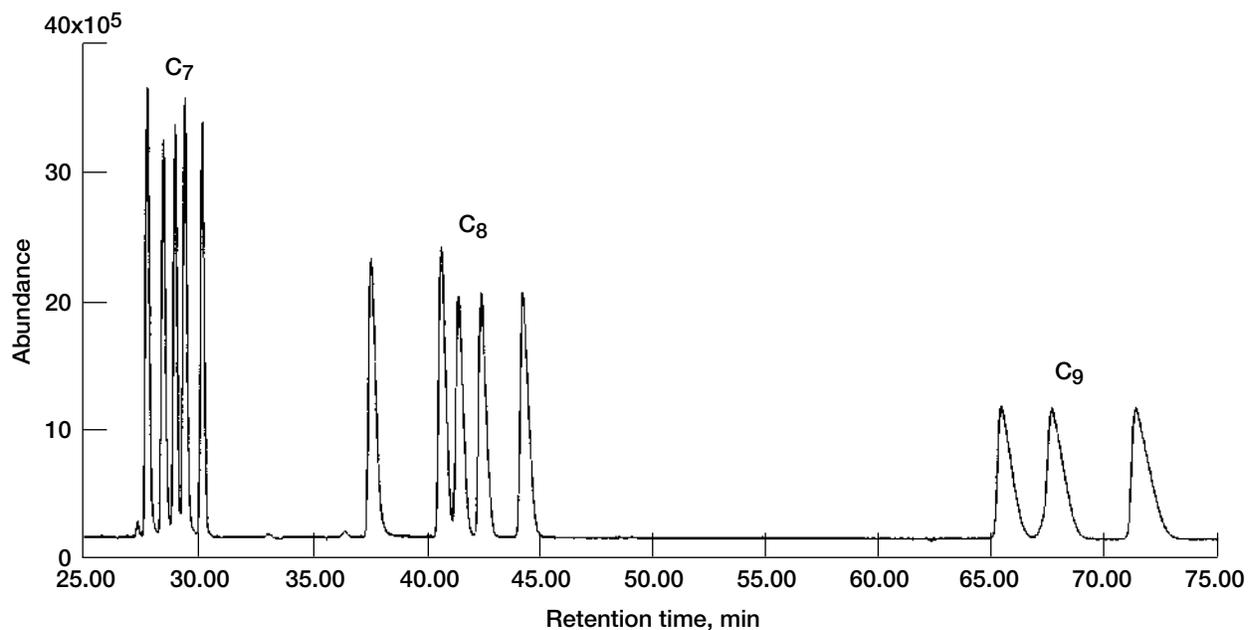


Figure 2.—Spectrogram of 13-hydrocarbon standard gas mixture containing 7 to 9 carbon atoms with approximately 15-ppm concentration.

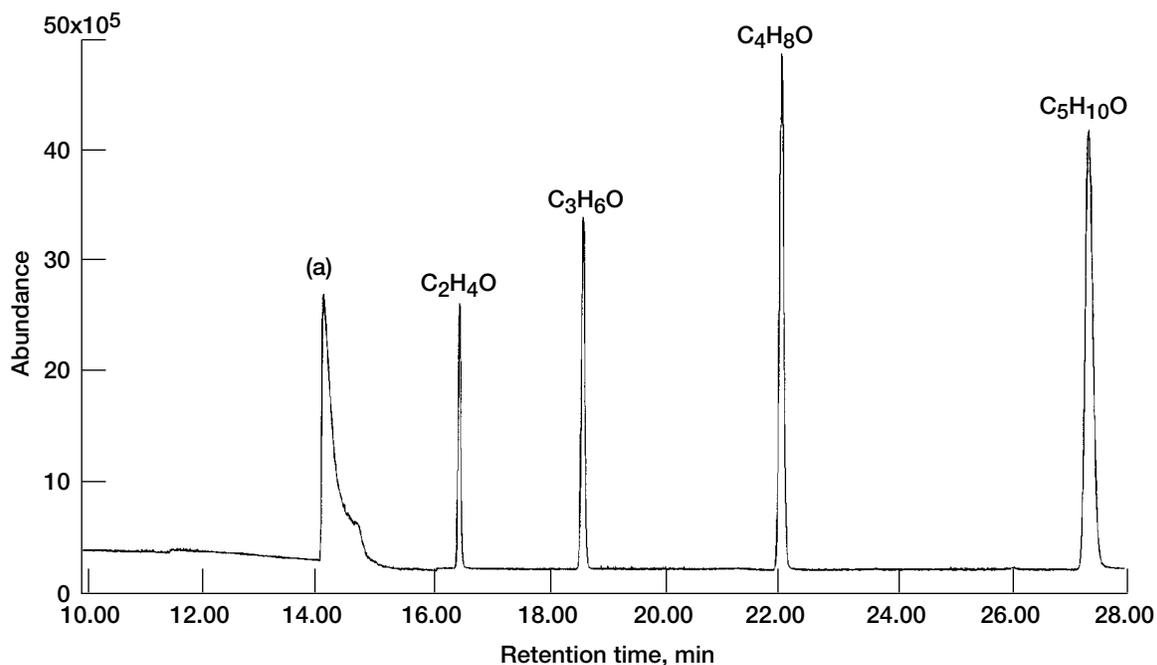


Figure 3.—Spectrogram of 4-aldehyde standard gas mixture containing 2 to 5 carbon atoms with approximately 15-ppm concentration. ^aAn unidentified species was carried out by the water.

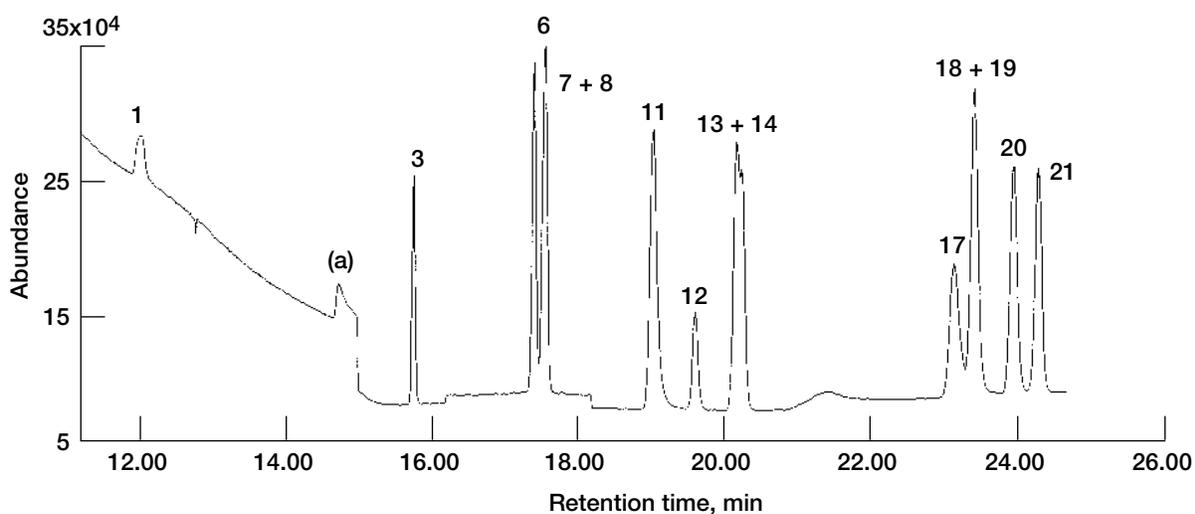


Figure 4.—Spectrogram of unsaturated 14-hydrocarbon standard gas mixture containing 1 to 6 carbon atoms with approximately 50-ppb concentration. ^aAn unidentified species was carried out by the water.

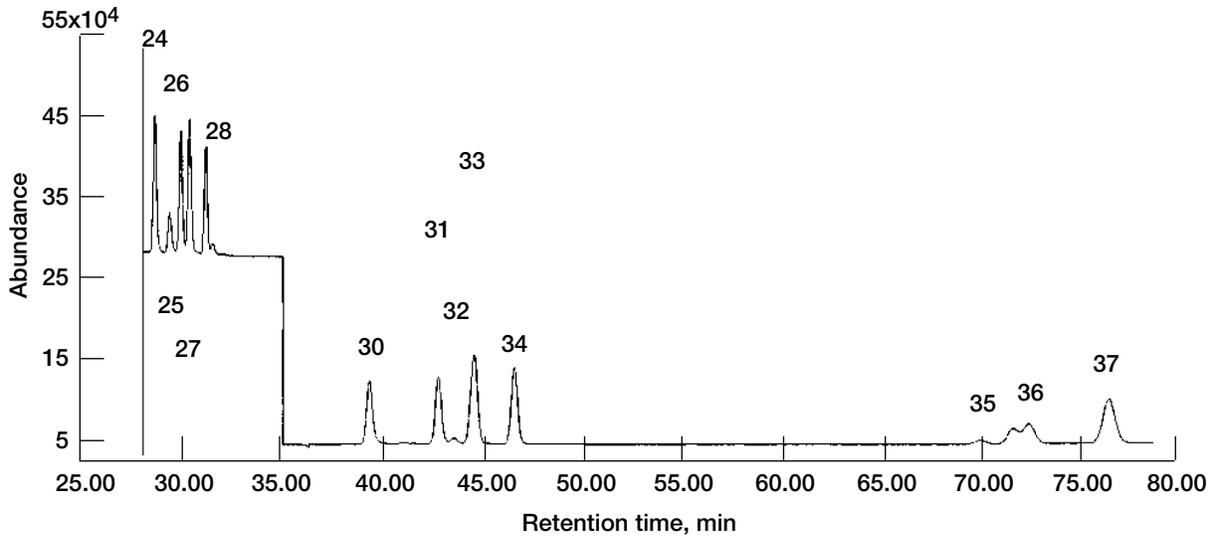


Figure 5.—Spectrogram of 13-hydrocarbon standard gas mixture containing 7 to 9 carbon atoms with approximately 50-ppb concentration.

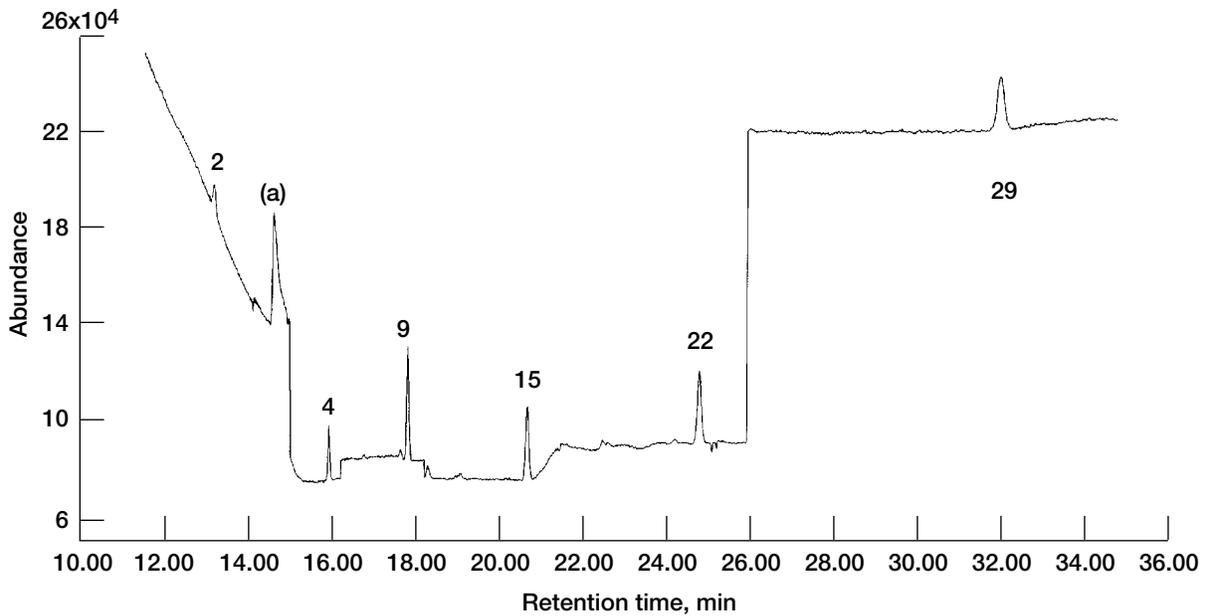


Figure 6.—Spectrogram of 7-saturated straight-chain 6-hydrocarbon standard gas mixture containing 1 to 7 carbon atoms with approximately 10-ppb concentration. ^aAn unidentified species was carried out by the water.

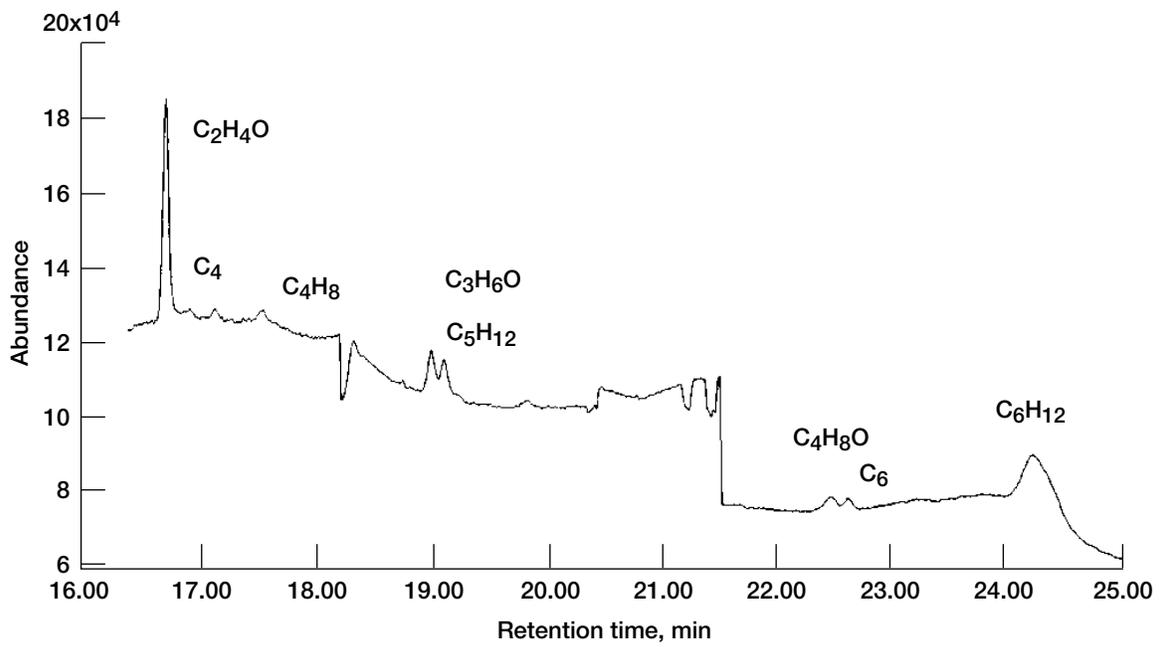


Figure 7.—Spectrogram of typical gas sample from combustor sector rig.

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