Development and Characterization of Gas Chromatographic Columns for the Analysis of Prebiological Molecules in Titan’s Atmosphere

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Parametric studies were conducted to design, develop, and integrate three gas chromatographic columns with a miniaturized mass spectrometer to be part of the Cassini—Huygens mission for studying the atmosphere of Saturn’s moon Titan. Separation and identification of low-molecular-weight hydrocarbons and nitriles (important prebiological molecules) were carried out on dimethylpolysiloxyane (DMPs) and 14% cyanopropylphenyl—86% dimethylpolysiloxyane (CPPS—DMPs) column stationary phases. These phases were deposited as thin films on the inner surface of fused silica coated steel capillary columns. The interaction of hydrocarbons and nitriles with these phases was studied under various column inlet pressure and carrier gas flow conditions. The selectivity for nitriles was enhanced by using the CPPS—DMPs phase. On this phase, the modeling number (log M) values varied linearly with the column temperature. Pronounced differences were observed in the order of elution for C2 hydrocarbons between CPPS—DMPs and DMPs phases. On CPPS—DMPs phase, the retention time decreased as 1,3-butadiene > 1-butene > n-butane, whereas on DMPs phase the order was n-butane > 1,3-butadiene > 1-butene. With the exception of certain temperature intervals, the retention times of C2 hydrocarbons predicted by the thermodynamic retention index model were comparable to experimentally determined values. Experimental and modeled retention times for benzene, toluene, and xylene, and nitriles also exhibited good agreement. Resolution of C2 hydrocarbons on low-temperature glassy carbon phase was demonstrated for the first time by our GC/MS studies. Trace quantities of carbon monoxide and methane present in a large volume of N2 were separated by porous carbon phase, micropacked in steel capillary columns. The selected three GC columns can provide in situ separation of various gas components expected to be present in Titan’s atmosphere.

Prebiotic chemistry may be defined as the subdiscipline studying the origin and evolution of organic compounds that lead to the formation of living organisms. Several possible pathways have been proposed for the synthesis of prebiotic molecules during the formation of Earth.¹ In particular, hydrogen cyanide and formaldehyde were identified as the key prebiotic intermediate compounds in planetary environments responsible for the formation of biomolecules: enzymes/proteins, phospholipids, and nucleic acids.²

Among the array of planets and their satellites in the solar system, the present environmental conditions on Titan (satellite of Saturn) appear to resemble Earth’s palaeoatmosphere (prior to 2.5 GA on geological time scale, 1 GA is equal to 10⁹ years). It is presumed that chemical sensing of Titan’s atmosphere can provide a better understanding of the origin and evolution of prebiological molecules on Earth. Certain environmental differences exist between Titan and Earth. The surface pressure on Titan is 1.5 times higher than on Earth and the temperature on Titan is only 95 K. Titan’s atmosphere is a unique natural laboratory where organic synthesis and chemical evolution can be studied on a planetary scale. The ability to conduct in situ compositional analysis of the planetary atmosphere will be of considerable importance for our understanding of exobiology and the origin of life.³

Earlier missions of the Voyager space probe have confirmed the predominance of nitrogen in the atmosphere of Titan. The infrared spectrometer (IRIS) experiment onboard the Voyager remotely sensed the presence of a suite of hydrocarbons, CH₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₂, and nitriles, HCN, C₂N₂, and HC₅N.⁴ Similarly, laboratory simulation of Titan’s atmosphere has demonstrated the formation of hydrocarbons and nitriles, including 1,2-propadiene, 1-buten-3-yne, acetonitrile, 2-propenenitrile, and propanenitrile.⁵ Observational and theoretical models also indicate that photolysis of methane in the stratosphere is the fundamental driving force for the formation of higher molecular weight hydrocarbons and aerosols.⁶

In an attempt to explore planetary atmospheres, NASA in collaboration with the European Space Agency (ESA) and the

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Italian Space agency (ASI) launched the Cassini–Huygens mission on October 15, 1997, to explore the planet Saturn and its largest moon Titan. The Cassini orbiter spacecraft comprised 12 different scientific instruments intended to study the Saturnian system, including the rings, the atmosphere, and its various satellites.7 Attached to the Cassini orbiter was the Huygens probe that consisted of six instruments capable of providing in situ physical, chemical, and compositional analysis of Titan’s atmosphere. The probe will remain dormant throughout the 6.7-year interplanetary cruise and its main mission phase will occur during its 3 h parachute descent through Titan’s atmosphere in the year 2004.

The six instruments on the Huygens probe include the descent imager/spectral radiometer intended to take images and make spectral measurements covering a wide spectral range. The atmosphere instrument was designed to make measurements of physical and electrical properties of the atmosphere, and the Doppler wind instrument would enable the determination of the wind velocity on Titan. The surface science sensors were developed to characterize the physical properties of Titan’s surface while the gas chromatograph/mass spectrometer (GC/MS) would provide analysis of various atmospheric constituents. The aerosol collector pyrolyzer combined with the GC/MS would enable the characterization of Titan aerosols.8

The atmospheric samples collected from the stratosphere of Titan would be introduced into the mass spectrometer system directly by means of pressure-reducing devices; however, the grab samples obtained from the lower part of the atmosphere will be analyzed by the GC/MS system.9 The aerosols of the atmosphere will be pyrolyzed by the aerosol collector/pyrolyzer (ACP) prior to the MS and the GC/MS analysis.10 Since compounds with varying degree of dipole moment (polar and nonpolar compounds) may occur on Titan significantly diluted in nitrogen, the GC subsystem was designed to contain three columns with distinct stationary phases capable of resolving gaseous hydrocarbons, nitriles, carbon monoxide, and inert gases.11

Previous studies on GC columns for space applications were carried out on a molecular sieved porous layer open tubular column (PLOT).12 Although chromatographic resolution of certain representative organic compounds were possible, these types of columns were prone to mechanical disintegration during vibration testing.13 To overcome this problem, wall-coated open tubular (WCOT) columns were recommended with the stationary phases capable of resolving gaseous hydrocarbons, nitriles, carbon monoxide, and inert gases.14

Capillary column. Commercial WCOT fused silica columns with methyl silicone stationary phase were used for laboratory analysis of lower molecular weight hydrocarbons and nitriles.14

In contrast to Earth-based stable laboratory environments, space instruments are subjected to extreme vibration and shocks, requiring the wall of the capillary column to be sturdy and shockproof. Since no commercial columns were suitable for this project, there was a need for developing specialized columns capable of separating prebiotic molecules under space probe conditions. Earlier metal columns were reported to suffer from adsorption problems.15 More recent developments in column technology provided a means of depositing a few micrometers of liquid stationary phase on a fused silica surface, contained in deactivated stainless steel tubing. These types of metal capillary columns were comparable in chromatographic performance to conventional fused silica capillary columns.16 Concurrent to these findings, we focused our attention to the design and development of metal capillary columns for space science applications.

Laboratory studies were carried out to develop gas chromatographic columns in conjunction with optimum operating conditions defined for the miniaturized GC/MS instrument.9 The conditions of limited time (~13 min for analysis per sample), temperature (isothermal mode between 30 and 40 °C for all samples and 60 °C for the aerosol sample), and gas flow rate (1–2 mL/min) during the space probe experiment precluded the use of a single GC column for separating multicomponent gas mixtures. In this paper, we demonstrate the application of three novel GC columns designed for separation of hydrocarbons and nitriles, the C1, hydrocarbons, CO, and CH4, respectively, from a large volume of N2. Also, to understand the molecular interaction on polysiloxane liquid stationary phases, a method for indexing hydrocarbons and nitriles was studied.

### EXPERIMENTAL SECTION

In contrast to previous column studies, column development work in our laboratory was subject to constraints imposed by the engineering requirements of the mission (as stated above). Combined gas chromatographic and mass spectrometric analysis of multicomponent gaseous mixtures was carried out followed by a critical evaluation of the effect of instrumental parameters (analysis time, temperature, and carrier gas flow rate) on the separation of the important atmospheric components of Titan.

**Laboratory GC/MS Experiments.** Compositional similarity between Titan’s atmosphere and laboratory gas mixtures was obtained by diluting 100 ppm of low-molecular-weight hydrocarbons, nitriles, and inert gases (argon, krypton, neon) in 99% of nitrogen (gas mixtures were prepared by Matheson Gas products, Seacaucus, NJ). Both carbon monoxide and carbon dioxide were included in the multicomponent mixture of 1-propane, n-propane, n-butane, n-pentane, 1,3-butadiene, cis-2-butene, trans-2-butene, isobutene, and 1-butene (each component was in the range of 100 ppm balanced with nitrogen). The 2-methylpropane, 2-methylbutane, 2-methylpentane, 3-methyl-1-butene, and 2,2-dimethylpro-

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(10) Israel, G. In Aerosol collector pyrolyzer (ACP) for the Huygen’s probe, European Space Agency (ESA)-SP-1177, 1997; pp 59–84.
pane, benzene (B), toluene (T), and xylene (X), commonly referred to as the "BTX" compounds, and the three nitriles acetonitrile, 2-propenenitrile, and propanenitrile were also diluted and premixed with nitrogen. These sample gas mixtures were introduced into the GC, through a gas mixing system (GMS, shown in Figure 1). The GMS was coupled to a Siemens GC (SiCHROMAT 2, ES Industries, Marlton, NJ) and an ion trap detector (ITD, Finnigan MAT, San Jose, CA). A series of digital flowmeters (Matheson flowmeter 8143, Matheson Instruments, Montgomeryville, PA) were used to monitor the flow rate of gas mixtures. Sample injection into the GC column was carried out by a 10-port rotary valve and electrically actuated in two positions: (A) load and (B) inject. During the load position, sample loop was continuously purged with sample, while in the inject mode, the fixed loop volume was introduced in the column by an external activating switch. In most of the cases, a fixed sample loop volume of 10 μL was utilized. However, to estimate column capacity and sample loading effect, the sample loop volume was systematically increased from 2 to 50 μL in certain experiments. High-purity helium gas (Air Products and Chemical Inc., Allentown, PA) was used as the carrier gas, purified by a gas purification trap (Supelco Inc., Bellefonte, PA). The experimental configuration in the laboratory provided a means for rapid on-line comparisons of differences in carrier gas type (helium versus hydrogen) on the resolution of the components.

The GC/MS interface consisted of deactivated silicosteel tubing (Restek Inc., Bellefonte, PA), 1 m in length and 0.28 mm in internal diameter, that was used in place of the open split interface configuration of standard GC–ITD system (Finnigan Inc.). This interface modification resulted in obtaining similarity in configuration between the laboratory GC/MS and the design of the miniaturized GC/MS instrument. A four-port column switching valve (Valco Instruments Inc., Houston, TX) was used to connect the analytical GC column to the GC/MS interface tubing. The valve had a fixed internal loop volume of 0.5 μL, with two-way position that provided easy isolation of the mass spectrometer from the GC subsystem (see Figure 1). It also allowed for convenient replacement of the analytical column without periodic venting of the mass spectrometer to the atmosphere.

The ion trap was operated in the electron impact (EI) ionization mode. The ions produced were trapped within the electrostatic field resulting from the ion trap electrodes. Ejection of the ions from the ion trap occurred during the mass-selective instability mode of operation. The ITD system was controlled by a Gateway 2000 4DX-33V computer running a customized version of the Trap Master software (Finnigan Inc.). It provided the capability to scan the mass range of the analytes between 10 and 150 amu. The scan rate was 2 s/scan in the full-scan mode that was varied to 0.25 s/scan during the experiments with the narrow-bore columns. The automatic gain control (AGC) of the ITD software increased the sensitivity for lower concentration analytes that were present in nitrogen gas as main component. Mass calibration was carried out with perfluorotributylamine (PFTBA) calibration compound. The retention time of individual components with characteristic fragmentation pattern was compared to the known reference spectra in the NIST library of mass spectra (NIST library, 54k version, Finnigan Inc.). Both the total ion

Figure 1. Schematic representation of a gas mixing system (GMS) interfaced with a laboratory GC/MS system, used for studying the interaction of gases with different gas chromatographic columns and stationary phases. Key: CG (carrier gas), CL (gas chromatographic column), FM (flowmeter), GMS (gas mixing system), IV (10-port rotary valve), ITD (ion trap detector), MV (metering valve), Mx1 (aliphatic hydrocarbon mixture balanced in nitrogen), Mx2 (methyl substituted hydrocarbons and BTX compounds in nitrogen), Mx3 (nitrile mixture in nitrogen), Mx4 (100 ppm CO in 99% nitrogen), OV (oven), P (pressure transducer), PR (pressure regulator), SWI (switching valve), QMS (quadrupole mass spectrometer), RS (flow restrictor), V (valve), and VP (vacuum pump).
current and selected single-ion chromatograms were used for the identification of individual components.

**GC Columns and Methods for Stationary-Phase Characterization.** At first, we identified several gas chromatographic stationary phases suitable for the analysis of hydrocarbons and nitriles. In particular, we focused our attention on two polysiloxane phases, namely, 100%dimethyl polysiloxane (DMPS) and 14% cyanopropylphenyl–86%dimethyl polysiloxane (CPPS–DMPS). These phases were synthesized and immobilized on silicosteel open tubular columns (Restek Inc.).

The initial experiments involved the study of columns with dimensions of 25 and 30 m in length and 0.32 and 0.28 mm in internal diameter, coated with 7.0 and 5.5 μm of DMPS and CPPS–DMPS phases, respectively. The second series of experiments was carried out with shorter columns (10 m), that had internal diameters of 0.18 and 0.15 mm, respectively. These narrow-bore columns were custom-made and had thinner coatings of the stationary phase (1–3 μm). The overall effective number of plates for these short columns was in the range of 10 000.

Several isothermal experiments for temperatures ranging from 30 to 100 °C, and for temperature program rates of 5, 10, and 15 °C/min, were used to study the effect of column parameters on the separation of components.

The retention time of the components is influenced by the chemical composition of the stationary phase, temperature, GC column length, internal diameter, carrier gas type, and flow rate.20 Therefore, in order to compare and contrast the interaction of the separation of components.

The phase ratio (β) is defined by the ratios of the volume of the mobile (gas) and stationary (liquid) phases and can be calculated by the dimensions of the column:

\[
\beta = \left( r_c - d_i \right)^2 / 2r_c d_i
\]

where \( r_c \) is the inner radius of the column and \( d_i \) is the liquid-phase film thickness. For thin films the expression is reduced to

\[
\beta = \gamma / d_i
\]

The thermodynamic values were transformed to modeling number (log \( M \)) values. The empirical basis of modeling number has been discussed by Mowery.21 Briefly stating,

\[
\log M = b_2 - aT
\]

where \( M = \log K \), \( b_2 \) is the intercept, \( a \) is the slope of the line, and \( T \) is the temperature (in celsius). This method provides a convenient means of indexing and characterizing organic compounds on different stationary phases.

An alternate approach was also adopted by calculating the change in the entropy, \( \Delta S \), and enthalpy, \( \Delta H \), values of the molecules, partitioning between gas and liquid stationary phases.22 The thermodynamic retention index (TRI) model (ProEZGC software, Analytical Innovation Inc.) relates the capacity factor to entropy, enthalpy, and temperature \( T \) by the following expression:

\[
\ln k = -\frac{\Delta H}{R T} + \frac{\Delta S}{R} - \ln \beta
\]

This model also provided a rapid means for computer simulation of various column configurations under several analytical conditions, enabling generation of databases that can be used for detailed column analysis.

**RESULTS AND DISCUSSION**

Separation of Hydrocarbons and Nitriles. The first set of experiments was carried out on long (25 and 30 m) columns to obtain a reference GC/MS spectrum of the gaseous components of interest. Higher column inlet pressure (1.2 bar) and helium flow rate (1 mL/min) were applied during these experiments. The sample injection pressure was maintained at 1.5 bar. Figure 2a is a reconstructed ion chromatogram (RIC) of 2-methylpropane, 2-methylbutane, 2-methylpentane, 3-methyl-1-butene, and 2,2-dimethylpropene resolved on the DMPS phase. The bottom plot of the spectrum represents the total ion current (TIC), which is equivalent to a GC profile. The monitoring of selected ions as shown in Figure 2a provided a means for resolving 2-methylbutane and 2,2-dimethylpropene, which appeared to be coeluted on the TIC profile. Under identical experimental conditions, separation of BTX compounds were also observed (see Figure 2a). In Figure 2b, the selected ions reveal the resolution of 1-propane, n-propane, n-butane, n-pentane, 1,3-butadiene, cis-2-butene, and trans-2-butene. However, chromatographic separation of isobutene from 1-butene was not evident on the DMPS column. The electron ionization spectrum of both these molecules was similar and selected ions could not be used to differentiate the two components. Isothermal analysis of BTX compounds required higher column temperatures (100 °C). However, at such temperature settings, coelution of lower molecular weight hydrocarbons (C₁–C₄) occurred. Conversely, at isothermal temperatures of 30–50 °C, the retentivity of the BTX compounds on polysiloxane phase was significantly increased. Therefore, the reduction in analysis time of BTX compounds required column temperature programming.

To satisfy the experimental constraints, the design of chromatographic columns compatible with the space flight instrument specifications was achieved by optimizing following column parameters: length, film thickness, and internal diameter of the column. Short narrow-bore steel capillary columns (10 m) with

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internal diameters (2r) of 0.18 and 0.15 mm were developed. Reduction in column diameter minimized the volume of both the stationary and the mobile phases and provided a distinct advantage for interfacing columns directly with the mass spectrometer. Also, the retention time of the BTX compounds could be reduced without using higher temperatures. Increased column selectivity toward nitriles was achieved by changing the phase chemistry from DMPS to CPPS—DMPS.

The second set of experiments was carried out with the newly developed narrow-bore columns (L = 10 m, 2r = 0.15 mm, d = 0.6 μm CPPS—DMPS), to resolve the components discussed above. Our studies indicated that even under stringent conditions (column inlet pressure, 0.5 bar absolute, flow rate 0.1 mL/min) all of the methyl-substituted hydrocarbons and the BTX compounds could be identified. Lowering the temperature to 30 °C, increased the retention time of methyl-substituted hydrocarbons from 2 to 4 min and improved the resolution of C1–C4 hydrocarbons. The three nitriles, acetonitrile, 2-propenenitrile, and propanenitrile, were identified within a 10-min time interval at an isothermal temperature of 50 °C.

It is evident from these experiments, that column dimensions, film thickness, and analysis temperature can be tuned to obtain desired separation results for a wide range of column inlet pressure and gas flow conditions.

Separation of C2 Hydrocarbons. Chromatographic separation and quantitative analysis of ethane, ethylene, and acetylene (C2 hydrocarbons) is an important objective for understanding the photochemical process of Titan’s atmosphere. Resolution of C2 hydrocarbons on polysiloxane stationary phase requires cryofocusing and/or subambient cooling of the column. These methods are difficult to implement for the space probe experiment because of limited analysis time and power. We observed that, at 30 °C, the C2 hydrocarbons on a CPPS—DMPS phase elute in the proximity of the unresolved peak corresponding to N2, CH4, and CO, and the response was sensitive to changes in experimental conditions.

In addition to the polymeric liquid phase, the utility of several micropacked columns with solid phases, such as styrene—divinylbenzene (Haysep A, Hayes Separation Inc., Bandera, TX) and Carboxen (Carboxen 1000, Supelco Inc.), was examined. These experiments typically required higher column inlet pressures (>1.5 bar) and gas flow rates (2–5 mL/min). The Haysep A-type column required an isothermal temperature of 70 °C and a time interval of 16 min to resolve the C2 hydrocarbons. When the temperature was lowered to 50 °C, the analysis time increased to 20 min. The study revealed that at lower temperatures, peak width of the eluants increased from 0.5 to about 2–3 min. Resolution of C2 hydrocarbons diminished significantly when the column inlet pressure and flow through the column were lowered. As pointed out previously, elevated GC column temperatures and high carrier gas flow rates are some of the limiting factors for integrating this type of column with a miniaturized GC/MS instrument.

To circumvent the above limitations, the application of low-temperature glassy carbon (LTGC) stationary phase for gas chromatographic analysis was explored in our laboratory. In particular, we focused on the separation of C2 hydrocarbons by this phase. The LTGC stationary phase was formed by controlled heating of diethynyl and ethynyl aromatic oligomers deposited as a liquid film on the inner wall of deactivated metal capillary column. Certain applications for high-performance liquid chromatography and supercritical fluid chromatography were shown previously.23 The GC columns were prepared on pretreated steel tubing (L = 14 m, 2r = 0.18 mm) that were doubly coated (d = 0.6 μm film thickness) with 5 mg/mL glassy carbon precursor, dissolved in methylene chloride.24 In Figure 3, we demonstrate the separation of ethane from ethylene and acetylene by the LTGC column at an isothermal temperature of 30 °C. Separation of ethylene and acetylene was also possible when column lengths were increased to about 30 m. The nitrogen saturation resulted in band spreading of m/z 28, observed even during monitoring of the ion current at m/z 27 and 29. Under identical conditions

(24) Albau, D., Ohio State University, personal communication, 1996.
(30 °C), ion monitoring of m/z 41 enabled the identification of 1-propene within 29 min (see Figure 3). Increasing the temperature to 50 °C with all other column conditions remaining the same, the retention time of 1-propene was reduced to 12 min and resolution 1-propene from propane was also possible by monitoring the ion m/z 29. At higher temperature (50 °C), the peak width of 1-propene was reduced to 3 min and the separation of ethane from ethylene and acetylene could be maintained.

Separation of Nitrogen, Methane, and Carbon Monoxide. Chromatographic identification of primary gases such as N\textsubscript{2}, CO, CH\textsubscript{4}, and noble gases (He, Ne, Ar, Kr) is important for understanding the origin and evolution of Titan's atmosphere. The resolution of N\textsubscript{2} and CO is possible under controlled laboratory conditions on a Molsieve PLOT (Chrompak Inc., Middleburg, The Netherlands) column. However, the mechanical weakness of the PLOT columns limits their application for space deployed instruments.\textsuperscript{25} GC/MS analysis of these components by micropacked capillary columns (L = 1 m, r\textsubscript{c} = 0.75 mm, Restek Inc. Bellefonte, PA) packed with molecular sieves (5, 6, and 10 Å) provided resolution of CO from N\textsubscript{2}. The separation of CH\textsubscript{4} from N\textsubscript{2} was observed to be sensitive to column inlet pressure (i.e., when the inlet pressure was lowered from 1.5 to 0.5 bar) and flow rate conditions (reducing the flow from 3 to 0.5 mL/min). In addition to these limitations, the hydrophilic character of molecular sieves (zeolites) required higher column conditioning temperature (>200 °C) prior to analysis.

In our search for stationary-phase longevity and tolerance to variability during space probe experiments, we studied the application of particulate porous carbon packing (Carboxen-1000, Supelco Inc.). This Carboxen phase was micropacked into stainless steel tubing (L = 1 m, r\textsubscript{c} = 0.75 mm, Restek Inc.) and was customized for our application by placing a metal frit inside the outlet end of the column. Figure 4a shows the separation of 100 ppm CO from 99% N\textsubscript{2} gas mixture on the micropacked column that was interfaced directly to the mass spectrometer. Analysis was carried out at 30 °C, and the carrier gas flow rate of helium was in the vicinity of 2.4 mL/min. Lowering the gas flow rate to approximately 0.7 mL/min did not alter the resolution. Even at a flow rate of 0.3 mL/min, the characteristic ions for N\textsubscript{2} (m/z 28), CO\textsuperscript{13} (m/z 12) in CO, and CH\textsubscript{4} (m/z 16) were clearly resolved (Figure 4b). On the basis of study of several Carboxen micropacked columns under varied experimental conditions (column inlet pressure ranging from 0.5 to 1.5 bar and flow rates from 0.5 to 2 mL/min), it became evident that resolution of key components on Carboxen-phase column (L = 2 m, r\textsubscript{c} = 0.75 mm) was less likely to be affected by changes in pressure drop between column inlet and outlet ends, carrier gas type, and flow rate.

Indexing of Hydrocarbons and Nitriles on DMPS and CPPS–DMPS Phase. During the space probe experiment, the temperature of the column containing the CPPS–DMPS phase will be increased from 40 to 60 °C for the analysis of the aerosol pyrolysates. Maintaining an exact column temperature during the experiment may not be possible; therefore, a method for predicting retention times of components based on measured column temperatures was studied. This method also provides a means for indexing hydrocarbon isomers that are not differentiated by mass analysis (EI mode). For this purpose, reliable log M values were calculated based on retention time measurements.

To index hydrocarbons and nitriles with the two liquid stationary phases (DMPS, CPPS–DMPS), modeling number equations were determined for temperature intervals over 30–100 °C. The modeling number (log M) provides a measure of molecular interaction between the mobile (gas) and the stationary

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**Figure 3.** Isothermal analysis (30 °C) of C\textsubscript{2} hydrocarbons on low-temperature glassy carbon phase: nitrogen, CO, and methane (17), ethylene and acetylene (18), ethane (19), and 1-propene (9).

**Figure 4.** (a) Isothermal analysis (30 °C) of 100 ppm CO in 99% N\textsubscript{2} gas mixture on a micropacked column with Carboxen phase. CO\textsuperscript{13} from CO (20) and nitrogen (21). (b) Analysis of 100 ppm CO and CH\textsubscript{4} in N\textsubscript{2} at 30 °C on the same column under reduced column inlet pressure and carrier gas flow rate (0.5 mL/min) conditions: methane (22).

with change in temperature. 21 The DMPS phase was used as a (liquid) phases and has been shown to exhibit a linear relationship between 40 and 50 °C on the DMPS—DM PS phase, and cis-2-butene were lower on the CPPS—DM PS phase when compared with DM PS. A significant (10%) divergence was observed in the log M values at 50–55 and 60–65 °C for trans-2-butene and cis-2-butene, respectively.

On DM PS, 2-methylpropane, 2-methylbutane, and 2-methylpentane exhibited a linear decrease in log M values when the temperature was increased from 30 to 70 °C. Acetonitrile on DM PS exhibited two linear regions (30–40 and 45–60 °C) with a slope change between 40 and 45 °C. At 70 °C, the relative retention time of acetonitrile on DM PS was significantly reduced, resulting in a sharp change in the slope of the log M—temperature relationship. Under identical temperature, the nitrile log M values were higher on CPPS—DM PS than on the DM PS phase (Table 1). The presence of cyanopropylphenyl groups in the CPPS—DM PS phase accounted for the noted increase in the log M values, as well as a broad range in linear relationship between log M and temperature.

The validity of the modeling number approach was demonstrated by comparing the experimental values used to generate the log M expression with the values predicted by the log M equations. The small relative error values indicate that the log M values vary linearly with change in temperature and are independent of the enthalpy of the molecule. However, in certain temperature intervals (especially for the C4 hydrocarbons), a significant change in the enthalpy of the solute molecule interacting with the liquid stationary phase may account for the observed linear discontinuities.

To understand the behavior of thermodynamic parameters (enthalpy and entropy) during the interaction of analytes on different stationary phases, we applied the TRI model. The model also provided a rapid means for predicting the retention times based on the calculated change in entropy and enthalpy of the molecules, interacting with the liquid stationary phase.

The thermodynamic retention indexes were calculated on the DM PS stationary phase with known column dimensions (L = 30 m, 2r = 0.28 mm, d = 5.5 μm) for the C4 and C5 hydrocarbons. Experimental retention times and the modeled values for column dimension (L = 25 m, 2r = 0.32 mm, d = 7.0 μm) on DM PS stationary phase were determined at five temperatures (30, 40, 50, 60, and 70 °C, respectively). Table 2A shows a comparison of the modeled and experimentally determined retention times for C4 and C5 hydrocarbons on the DM PS phase. The increase in the percent deviation (4–19%) with increasing temperature may be related to the observed slope changes in the log M—temperature relationship (as discussed in the previous section). The TRI model assumes a linear relationship between the capacity factor and inverse of column temperature; however, in the case of nonlinearity, the differences between model predictions and experimental results become significant. On the CPPS—DM PS phase, the modeled retention time of the C6 hydrocarbons at an isothermal temperature of 50 °C (Table 2B) shows 3–10%
deviation from the experimental values. The deviations between modeled and experimental results are significantly lower on CPPS–DMPS than on the DMPS phase (12–13% deviation), at 50 °C (Table 1A). Only slight improvements were observed between modeled data and experimental results for trans-2-butene and 1,3-butadiene when the number of input temperature values in the model was increased from two (b) to six (a) (Table 2B).

Upon comparison with DMPS, the percent deviation between modeled and experimental results was less on the CPPS–DMPS phase for the C4 hydrocarbons. The TRI for the BTX components were obtained on a DMPS phase, linearity between the capacity factor and the inverse of temperature may not exist over the entire temperature interval. It may be concluded that, within the limits of certain temperature intervals (especially in case of C4 hydrocarbons shown in Table 1), the TRI approach may be useful for modeling retention times for our column geometry, film thickness, and experimental conditions.

**CONCLUSIONS**

The analysis of Titan's atmosphere would require three GC columns. Each of the three columns selected comprise stationary phases that were targeted for a specific group of compounds. Separation of hydrocarbons (C3–C4) and nitriles was achieved by the CPPS–DMPS phase column. A lower isothermal temperature of 40 °C is suitable for analysis of atmospheric samples. Higher isothermal temperatures (60 °C) were needed to analyze the BTX compounds, which may be likely products of Titan aerosol pyrolysis. Indexing of hydrocarbons and nitriles on CPPS–DMPS provides a method for predicting the retention times of components at several different temperatures. Separation and detection of trace quantities of CO (10–100 ppm) from a large volume of
nitrogen gas will be possible by porous carbon micropacked column mass spectrometry. The LTGC column enables the determination of the ratio of ethane to ethylene and acetylene from various altitudes of Titan’s atmosphere. This ratio can provide valuable information about the origin, the vertical mixing of hydrocarbons, and the dynamics of Titan’s atmosphere. An increase in the ratio of ethane to ethylene and acetylene with a decrease in altitude (toward the surface) may indicate the likelihood of ethane condensation on the surface. Our investigation also revealed that minor changes in experimental conditions do not affect the separation of components studied on the selected columns. Therefore, variability in the space flight environment during the descent of the Huygens probe in the Titan’s atmosphere is not likely to influence the results of the in situ GC/MS experiments.

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