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Final Technical Report

NASA Cooperative Agreement NCC2-650

"SYNTHESIS AND DEVELOPMENT OF POROUS POLYMERIC COLUMN PACKING AND MICROCHIP DETECTORS FOR GC ANALYSIS OF EXTRATERRESTRIAL ATMOSPHERES"

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Thomas C. Shen
Principal Investigator

Submitted by:
SETI Institute
2035 Landings Drive
Mountain View, CA 94043

(650) 961-6633

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This report summarizes the last nine years research accomplishments under Cooperative Agreement NCC-2650 between NASA, Ames Research Center and SETI Institute. Four Major research tasks are conducted:

1. Gas chromatography column development,
2. Pyrosensor devilment,
3. Micro-machining gas chromatography instrument development,
4. Amino acid analysis and high molecular weight polyamino acid synthesis under prebiotic conditions. The following describes these results.

I. Gas Chromatography Column Development

There are two major objectives in this task. The first is to develop and produce advanced columns and column packing materials having high reproducibility and high performance for flight GC instrument applications. The second objective is to investigate novel column geometries, i.e., Porous Layer Open Tube (PLOT), hollow fiber, micropacked columns, that are more appropriate for flight than those currently available. In addition, the factors affecting separation such as surface area, pore size, and solubility of the polymer surface, will be characterized in order to improve the GC separation. The ultimate goal of this task is to maximize column resolving power while minimizing the weight of the column components, that is, to separate more gases with shorter columns and/or fewer columns while reducing the amount of He required (lower carrier gas flow rates) and reducing the power requirements (lower operating temperatures).

Much progress has been made in this task. A porous silicone polymer column was developed which could separate a wider range of gases than either the nonpolar or polar columns described above. Also, bonded stainless steel PLOT columns with high separation efficiencies and low flow rate (~3 cc/min) requirements, have been developed by in-situ polymerization. In addition, initial results have demonstrated that the preparation of micro-packed columns is feasible. These developments will be described in more detail in the following subsections.

A. Silicone polymer stationary phases

Columns packed with liquid phases on solid supports provide good separation of polar as well as nonpolar compounds. However, the liquid phase bleeds (outgasses) excessively from these columns, making them unsuitable for use with such highly sensitive detectors such as the Metastable Ionization Detector (MID). As an alternative to this type of column, solid porous silicone polymers were synthesized and used to separate polar compounds, such as amines and alcohols, as well as nonpolar compounds, such as alkanes, alkenes, and alkynes.

The solid porous silicone polymers are synthesized by a condensation polymerization reaction. In general, the polymerization by trichlorosilane condensation produces low or noncross-linking polymers which are usually soluble in organic solvents. In order to make highly cross-linked polymers, vinyl groups were included by means of a free radical polymerization reaction. The condensation polymerization process and free radical polymerization of vinyltriethoxysilane and octadecyltrichlorosilane formed highly cross-linked polymers not soluble in most solvents. Several polymerizations with various mole ratios of vinyltriethoxysilane and octadecyltrichlorosilane were carried out. The copolymer product obtained with a 2/1 mole ratio provided the best balance of polar

and non-polar groups. This polymer provided good separation and peak symmetry for many polar and nonpolar compounds as illustrated in Figures 1a-e.

B. Porous layer open tubular (PLOT) columns

1.Dynamic Coating Method

a. Divinyl Benzene Polymer

Porous Layer Open Tubular (PLOT) columns have advantages over packed or wall-coated gas chromatography columns such as lower flow rates, lower operating temperatures, and less column bleeding. An important advantage of the PLOT column over a packed column is that much lower sample concentrations (at the parts per billion level) and lower sample sizes can be analyzed.

Divinyl benzene (DVB) PLOT column for the separation of the light gases and PLOT columns are made by static coating procedures, dynamic coating procedures, or a combination of the two. In general, the first step is the polymerization of monomers; the polymers are then sieved to select the proper mesh size for coating the columns. The coating methods are complicated and require special expertise and unique facilities. These difficulties make the manufacturing process costly which has limited the use of PLOT columns. The method developed by us combines the polymerization and the column coating into one step. This in-situ polymerization results in a straight-forward preparation of a PLOT metal tube column. The in-situ polymerization procedure developed by us involves placing the divinylbenzene monomer and solvent in a coiled metal tube, capping the tube ends and placing the coiled tubing in an oven equipped with a mechanical rotation rod. The polymerization process was carried out at 80°C while the column was being rotated.

An important aspect of this research was finding a solvent system that provided suspension polymerization of the monomer and prevented the resultant polymer from swelling, which tended to form column plugs. Only with methanol did the polymerization and wall coating occur in a way such that the excess dilutents were easily eluted from the column, leaving the polymer coated on the inside of the tube. Also, we found that slower rotation speeds were more effective for uniform coating of the tube; higher rotation rates led to column plugging.

The DVB PLOT columns, prepared by in-situ polymerization, efficiently separated the light gases. As illustrated in Figure 2, as the divinylbenzene concentration increases, the separation efficiency also increases. At a divinylbenzene concentration of 25%, the separation efficiency of the PLOT column is almost as good as that of a packed column. Four columns were prepared and tested for reproducibility. For N2O, the resulting capacity factors are 34.3, 35.6, 34.8, and 34.7, with the number of plates at 4096, 4065, 4081, and 4088, respectively. Columns as long as 15 ft. have been prepared by this method. This technique is very reproducible and some flexibility in the concentration of the polymerizable monomer in the starting mixture is allowed.

Although many factors affect the outcome of polymerization such as monomers, initiator, solvents, temperature and the forth. In our previous studies, it is believed that either heptane or heptane/MTBE (methyl tert-butyl ether) gives best products. We tried hexadecane later on because of concerns about the possible explosive nature of the solvents (bp around 80 ^{o}C) at higher temperature (90-95 ^{o}C) under sealed conditions. But, the result was not particularly impressive. Temperature should be kept at 60-80 ^{o}C and the polymerization should be allowed to proceed for much longer time.

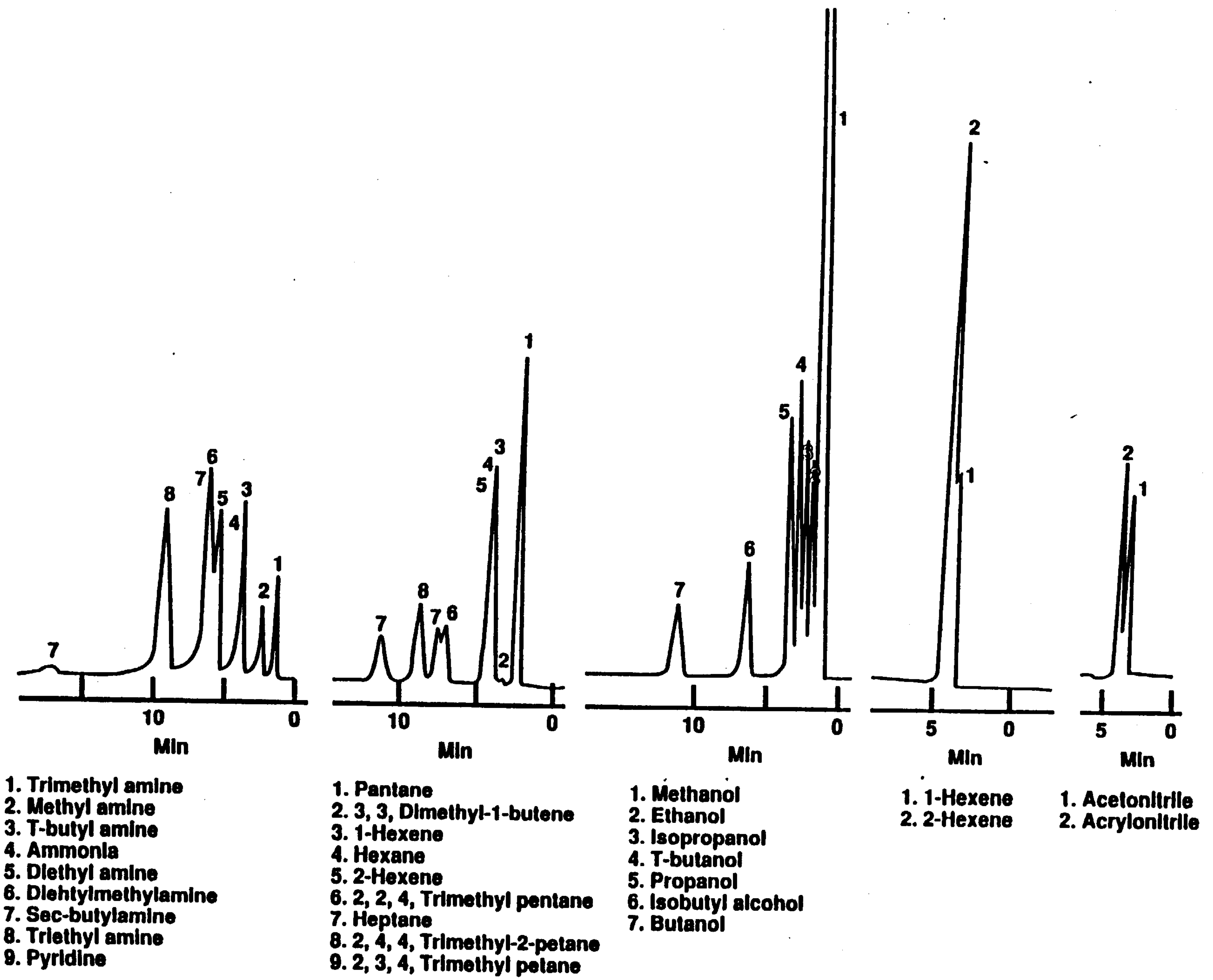


Figure 1. vinyltriethoxylsilane/octadecyltrichlorosilane column (8A), 6 ft SS, 1/16 id, 107 ^{o}C, and 15 ml/min. He

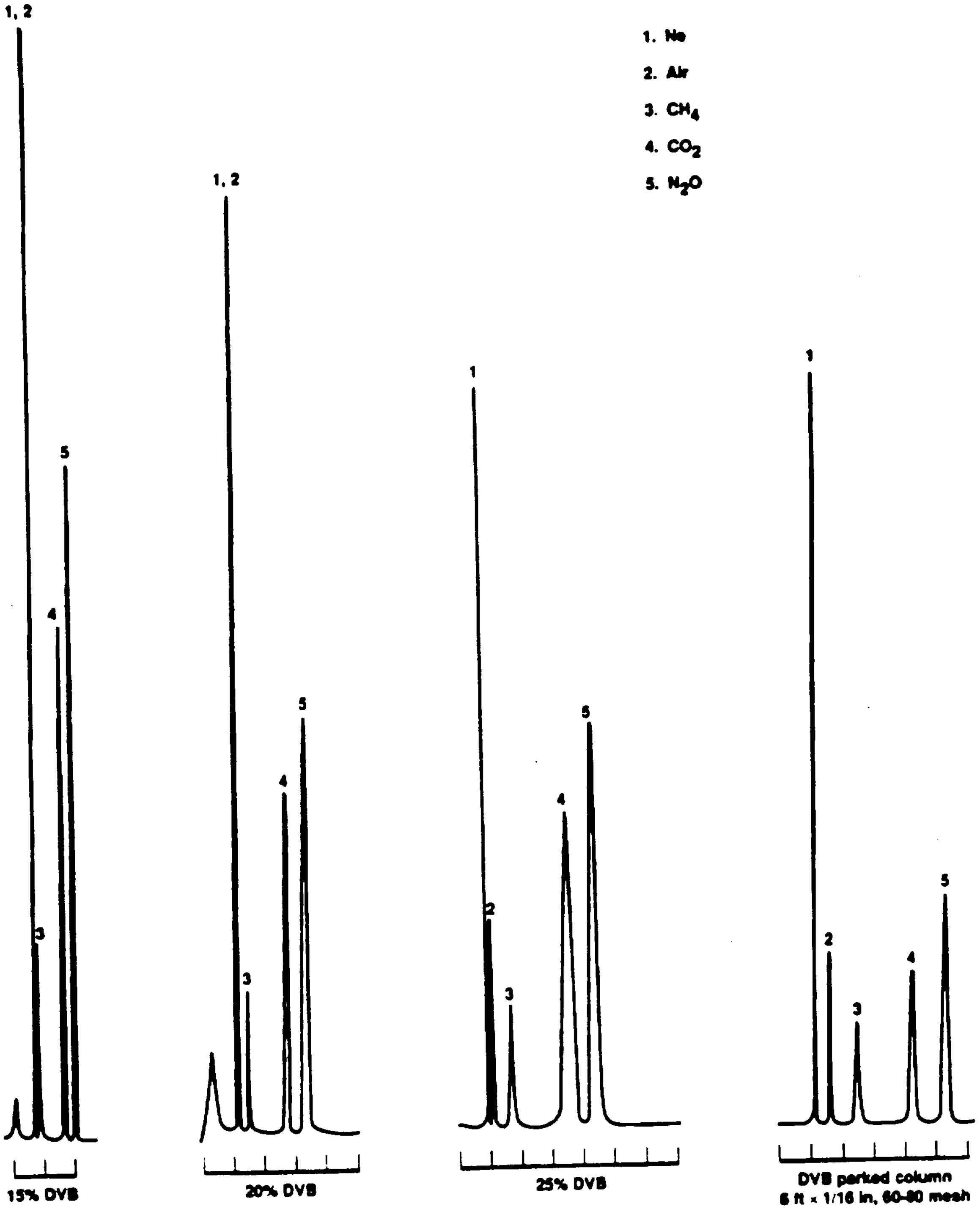


Figure 2. Separation of some light gases using various DVB PLOT columns and a packed column. (all columns operated at 26°C and 4.8 mL/min flow rate)

We have found that the concentration range of DVB performed better between 8% and 12.5%. We would continue working on this matter searching for the most optimum condition. The use of monomer with longer linkage might improve in situ polymerization in some way. Another type of polymerization initiators is also on the list for consideration.

b. DVB copolymer PLOT columns for water and ammonia

Exobiology has been and continues to be a subject of interest to NASA. The examination of extraterrestrial bodies, e.g. planets, moons, comets and planetary dust, for the presence of the compounds and elements necessary for the development of life is therefore an objective of much analytical effort. From our knowledge of life on Earth, we know that the presence of water and ammonia are of critical importance to the development of life. Gas chromatography is a technique which can be used for the analysis of water and ammonia, however, good separation columns are difficult to find. Although several liquid coated columns have been reported for this application, they can not be used in coordination with such highly sensitive detectors as the ion mobility spectrometer(IMS) or metastable ionization detector (MID) because of bleeding problems. For these reasons, NASA-Ames Research Center is involved in low or no bleed column development for gas chromatographic use. Last year, two PLOT columns were developed for water/ammonia separation, but the resolution is not good enough for flight program application.

The copolymer of Divinyl benzene/ Ethylene glycol dimethacrylate (DVB/EGDM), was used in the synthesis of Porapak® N, which has been used to separate water and ammonia. Using in-situ polymerization procedures similar to those described in the last section, DVB/EGDM PLOT columns were prepared. Different ratios of DVB/EGDM were investigated for optimizing the separation of water and ammonia. It was found that a DVB/EGDM of 60/14 by weight in a PLOT column optimally separated water and ammonia (See Figure 3a). Figure 3b illustrates the resulting chromatogram of ammonia, water, and HCN this time on a 60/40 (by weight) DVB/styrene column.

The relative retention (TR H2O/TR NH3) of water/ammonia varies as a function of ethylene glycol dimethacrylate concentration. Therefore, the pore size of the copolymer may be the controlling factor in this separation. To test this hypothesis, DVB/styrene and DBV/ethylenegylcoldimetharylate in-situ polymerization PLOT columns were prepared. The relative retentions of water/ammonia (TR H2O/TR NH3) increased with an increase in the styrene and ethylenegylcoldimetharylate concentration (see Figure 4). PLOT columns prepared from homopolymers of triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,4-butadiol dimethacrylate, and 1,6-hexamethylenediol dimethacrylate were tested. The results demonstrated that the pore size is a function of cross-linking, the higher the cross-linking density, the smaller the pore size and thus, directly affecting the relative retention of water/ammonia.

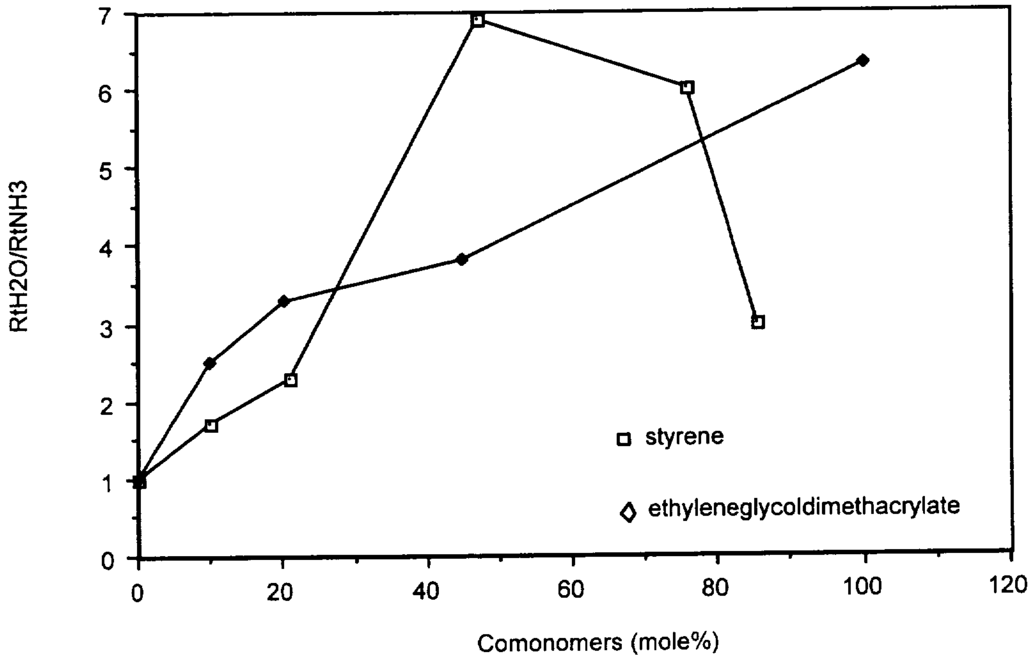


Figure 4a. Effect of mole % of styrene and ethylenegylcoldimetharylate comonomers in DVB copolymer PLOT columns for water/ammonia separation.

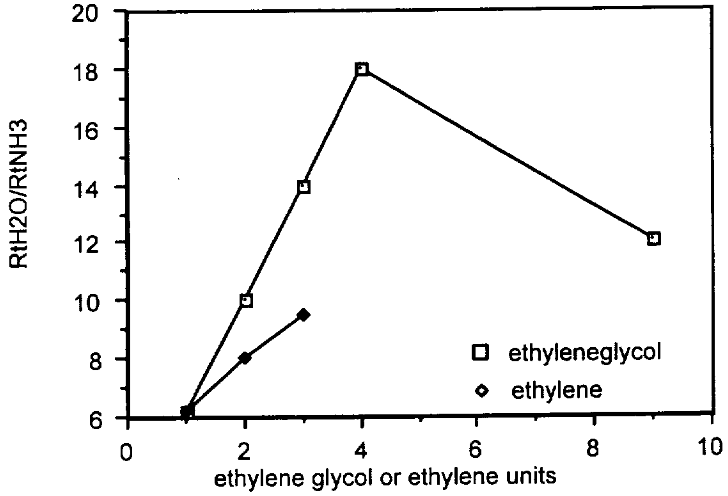


Figure 4b. Effect of chain length between dimetharylate in water/ammonia separation.

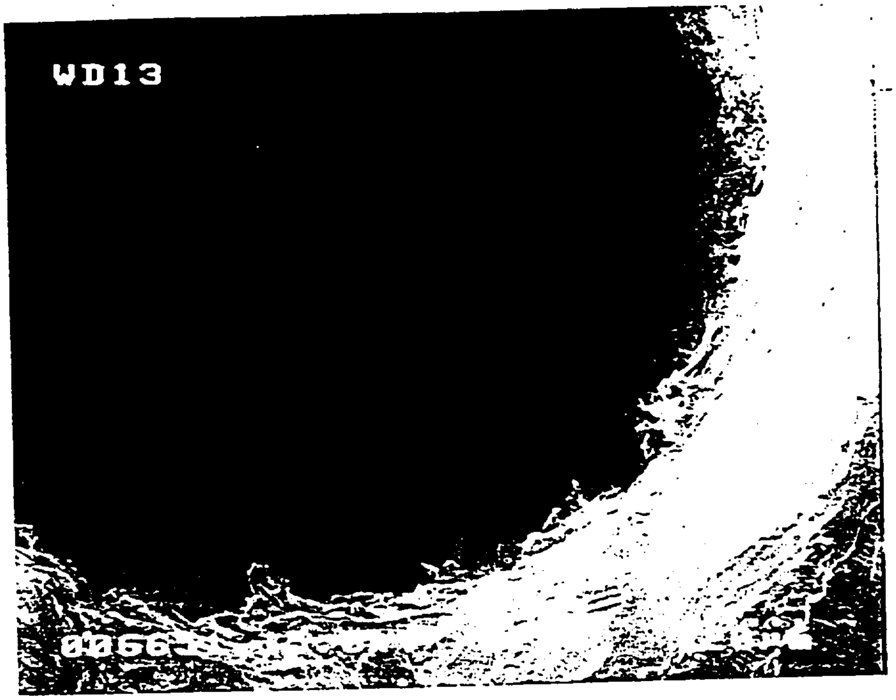


Figure 5A cross section of bonded PLOT column 103-1

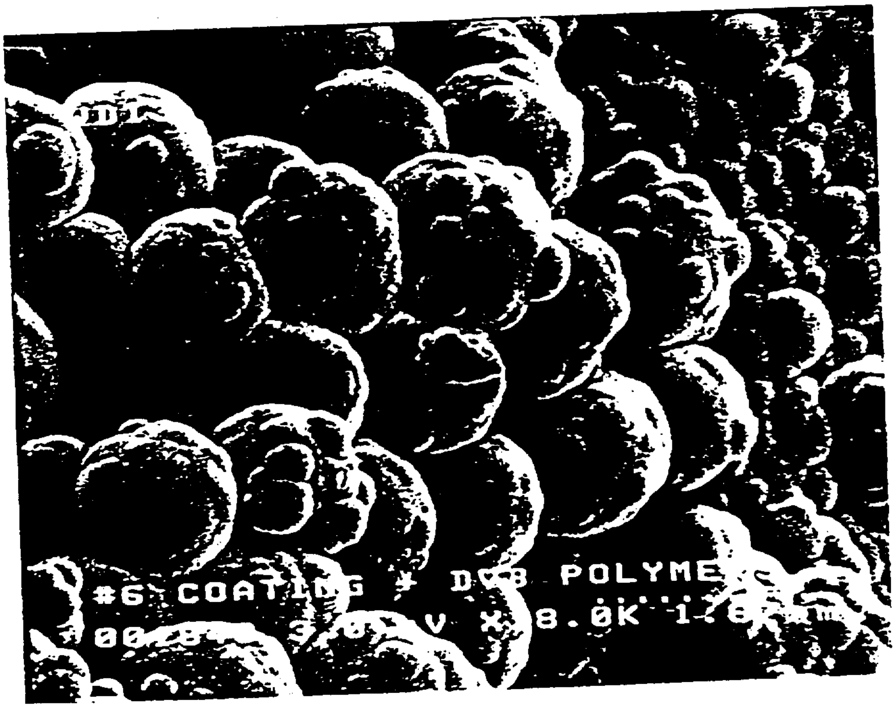


Figure 5B Polymer particles on the surface layer of 5A

2. Silane Modified Bonded stainless steel PLOT columns

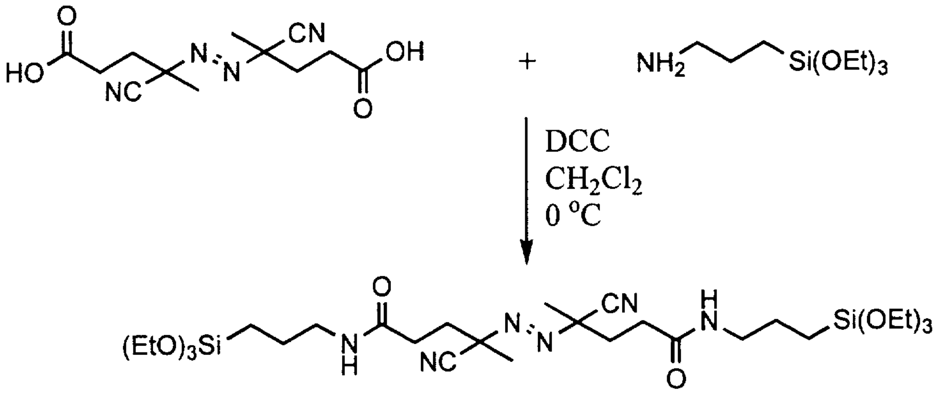
Fused silica tubing has been used for capillary columns for many years due to its inert character. Also, it can be modified. However, due to the brittleness of these columns, they are difficult to connect, can break very easily and are prone to bleeding. For these reasons these type of columns are not suitable for use within a spacecraft type of environment. Inert coated stainless steel capillary columns were studied. A bonded in-situ polymerization PLOT stainless steel column was developed from a coated silicon polymer with a polymerized vinyl group. This type of PLOT column with the adsorbent deposited and bonded on the wall of the column as a thin layer has very high permeability, thus, very long columns can be used, with high separation power. A scanning electromicroscopic (SEM) photograph indicated that the porous polymer particles are bonded on the wall as demonstrated in Figure 5. Initial results show that adequate chromatographic separation could be obtained from this column although not as good as the ones obtained using the other coated PLOT columns discussed previously.

3. Bonded Fused Silica capillary columns

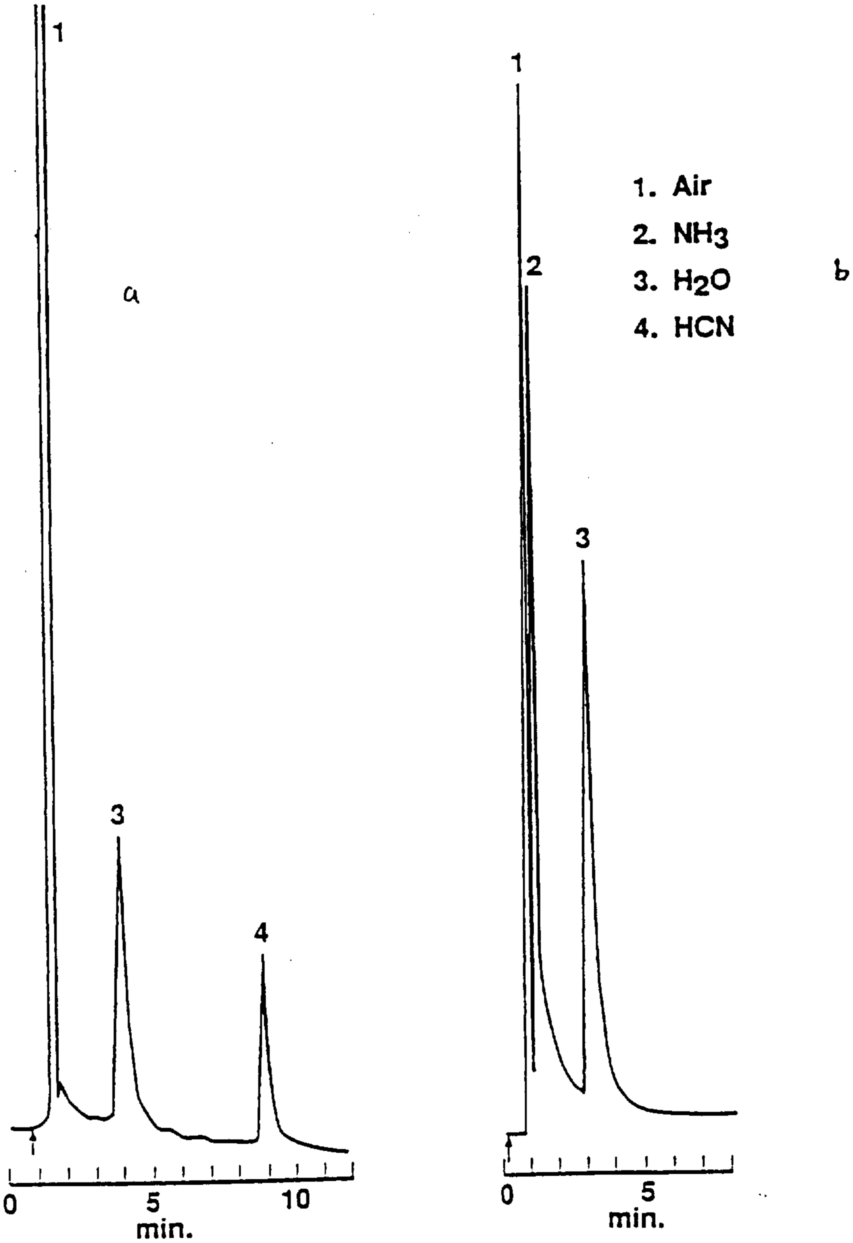
Three approaches were investigated for preparing these columns. 1). modifying fused silica surface with polymerizable monomers, such as trialkoxysilyl methacrylates, 2). modifying fused silica surface with free radical chain transfer agents, such as trialkoxysilyl thiol agents, 3). modifying fused silica surface with initiators, such as azo-trialkoxysilanes.

The first two approaches have proved to be not reasonably reproducible to form bonded porous polymer particles on the silica surface. Due to this observation, we designed and prepared a novel immobilized azo initiator, which would allow us to prepare Bonded Porous Layer Open Tubular (PLOT) DVB-based columns using our innovative *in situ* polymerization. There were several problems we encountered in these studies such as: (1) purity of polymerization initiator azo-silanes; (2) the reproducibility of quality of prepared GC columns; and other minors. We have looked into these individual areas, identified some new potential pitfalls, and made efforts to solve these problems using varied approaches.

In order to attach a polymerization initiator to the surface of the fused silica capillary column, we need to functionalize a commercially available azo polymerization initiator with a trialkoxysilyl group. Two azo silanes were synthesized as follows:



Scheme 1



53-2
Flow rate = 4.0 ml
100° C

53-2
Flow rate = 4.0 ml
100° C

Figure 3. Wtaer/ammonia and water/HCN separation by ethylene glycol dimethacrylate PLOT column

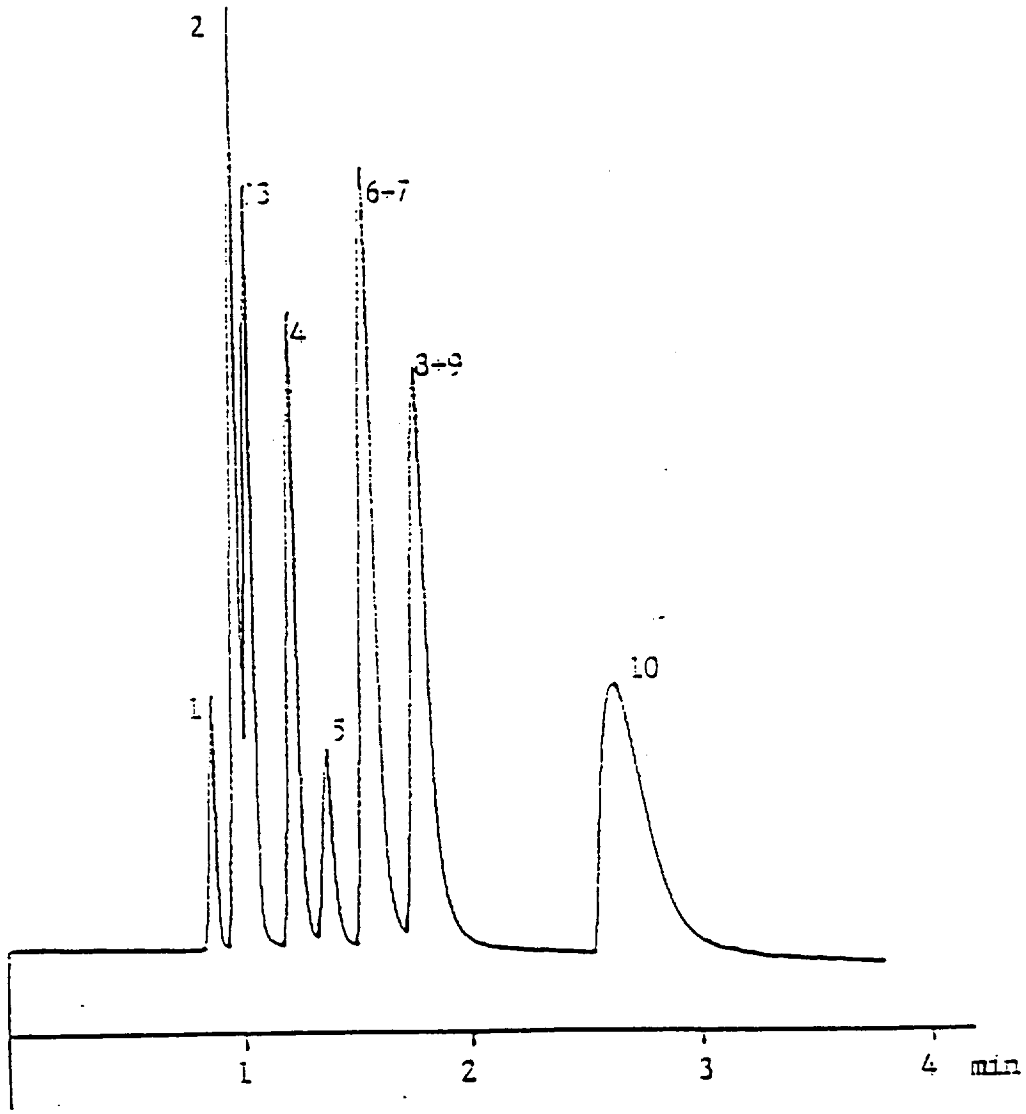


Figure 6 Separation of hydrocarbon mixtures on polymeric octadecyl bonded phase. Conditions: Column length 3.0 m; inlet pressure 40 psi; carrier gas He - 8.5 ml/min; Temperature 50°C; 100 µl injection loop; chart speed 3.0 ml/min. Peak identifications: (1) methane, (2) ethane, (3) ethene, (4) propane, (5) acetylene, (6) propene, (7) propadiene, (8) isobutane, (9) butane, (10) propyne.

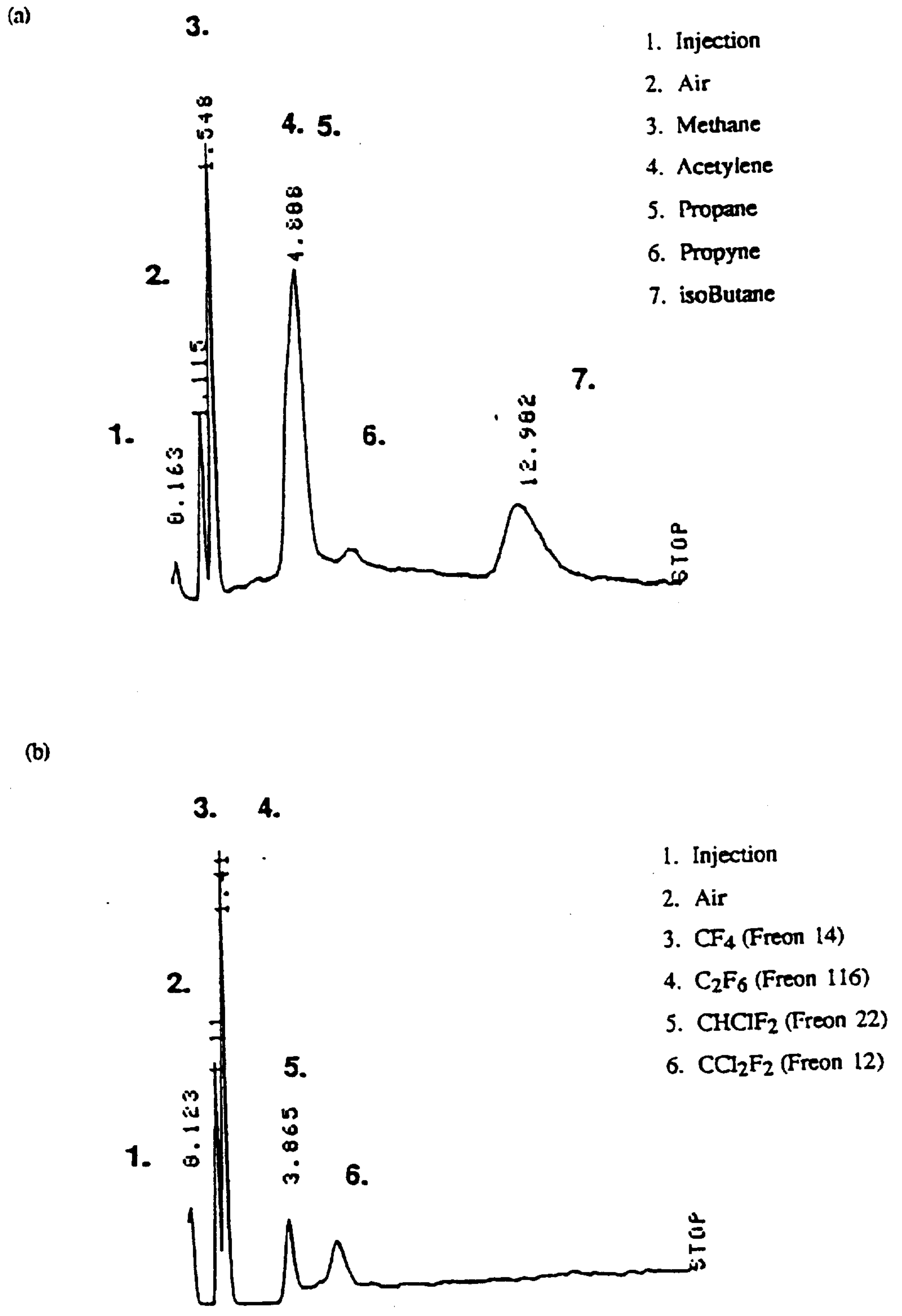
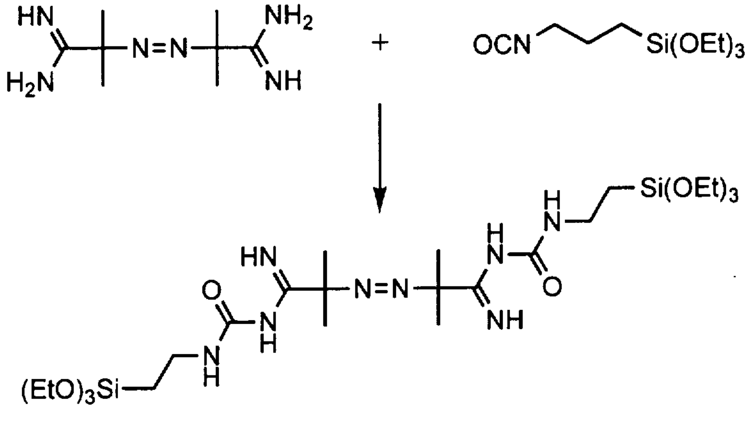


Figure 7 Separation of (a) five hydrocarbons, and (b) four Freons by a divinylbenzene micropacked column. column: 2 ft x .0025" ID SS; packing: divinylbenzene polymers, .042 gm; temperature: 84 °C; flow rate: helium, 1.55 mL/min.; pressure: 41 psi.



Scheme 2

Due to the problems of stability of the initiators the polymerization was not tested. If funding is continued, other approaches will be investigated.

C. Micropacked GC Columns

In general, silica-based columns are subject to hydrolysis when the sample contains water or acid and base compounds. To improve our previously developed silica-based good column, we have designed new silica-based polymers which form from our newly synthesized monomers. The polymerization is not only based on a Si-O-Si bond, but also includes $CH_2=CH-$. Two monomers were synthesized by reacting n-octadecyltrimethoxysilane with allylmagnesium chloride or 4-bromostyrene magnesium. Micropacked GC columns were prepared using stainless steel tubes with an I.D. 1 mm and lengths as small as 2 feet. These micropacked columns contain chemically bonded stationary phases incorporating Si-O-Si bonds and vinyl groups. They may play a key role in future space missions because of the following characteristics: 1) low flow rates, e.g., allowing a direct GC-MS coupling; 2) minimized bleeding of the stationary liquid phase, 3) increased loading capacity, 4) a small value of the C term of the Van Deemter equations, and 5) they are easier to miniaturize.

Three types of octyl- and octadecyl phases were prepared by different approaches: (1) a monomeric phase using excess monofunctional silane, (2) a monomeric phase using di- or trifunctional silane under anhydrous condition, and (3) a polymeric phase using di- or trifunctional silane in the presence of small amounts of water. The columns could be operated at an average flow rate of 10 ml/min without any appreciable pressure drop. A ten-hydrocarbon mixture was separated in approximately 3 minutes (see Figure 6) on the polymeric octadecyl phase compared to 15 min. using Isocyanate phases.

A 2 foot long, stainless steel column was also prepared with a stationary phase consisting of very small polymeric particles (10 to 30 μm). The stationary phase was prepared using a nonsurfactant organosolvent system followed by polymerization of the divinylbenzene in a mixture of heptane and butyl alcohol. This column efficiently operates at flow rates as low as 1.55 ml/min (Figure 7). Initial results show that it can be used to resolve a mixture containing Freons (Figure 7b) more efficiently than the hydrocarbon mixture (Figure 7a).

In conclusion, three types of GC Columns were developed, 1. bonded stainless steel DVBs PLOT columns, 2. micro-packed columns, and 3. bonded silicon PLOT fused-silica columns.

1. Bonded stainless steel DVBs PLOT columns

Three azo-silanes was synthesized for bonding to the stainless steel tube's surface using *in-situ* polymerization of DVBs monomers to form bonded PLOT columns. The results are shown in Fig. 1. Although, the separation of 10 hydrocarbons is not very impressive. The method for making bonded stainless steel Polymeric PLOT column is demonstrated. The major problem is the synthesis and purification of the azo-silane.

2. Micro-packed Columns

In general, silica-based columns are subject to hydrolysis when the sample contains water or acid and base compounds. To improve our previously developed silica-based good column, we have designed new silica-based polymers which form from our newly synthesized monomers. The polymerization is not only based on a Si-O-Si bond, but also includes CH_2=CH-.

3. Bonded Silicon PLOT Fused-silica Columns

As demonstrated in the previous section, a highly efficient bonded PLOT column had been developed. A patent disclosure has been filed with Ames Research Center.

II. Pyrosensor Development

One of the most important facts brought to light by the Viking Mission to Mars was the highly reactive nature of the Martian soil observed during the Viking Biology experiments. Small amounts of oxygen and larger amounts of carbon dioxide gas rapidly evolved from samples when they were exposed to a humid environment (Gas Exchange Experiment, GEX). When nutrients were added to the Martian soil, they were oxidized to carbon dioxide gas (GEX and Labeled Release (LR) Experiments).1 When soil samples were heated at high temperatures (145-165° C), the evolution of carbon dioxide gas was observed (LR); oxygen still came off upon humidification of this sample (GEX). These results, in particular, could be explained by searching for the presence of nonbiological oxidants such as peroxides or superoxides in the soil. For this reason, we have proposed to develop pyrosensors for determination of the possible oxidant in the Martian soil.

If a material has internal electrical symmetry, it is generally neutral and lacks a permanent dipole. If it is asymmetric, e.g., water, it has a permanent electric dipole. Most asymmetric materials in bulk have a zero dipole effect because of a random or self-cancelling arrangement. Some asymmetric materials, however, maintain a net dipole orientation even in bulk. Heating such a material (within limits) does not randomize the dipoles, but instead rotates them in unison and thus produces a polarization. Because this occurs in the absence of an external electric field, it is called a spontaneous polarization. A spontaneous polarization which is induced by heating is called the pyroelectric effect. In a pyroelectric device, a change in temperature creates a change in polarization. A pyroelectric device thus produces current only as it experiences a temperature change. When it is at a constant temperature, no current is produced.

A thin film of a pyroelectric material which has electrodes deposited on both faces is a pyroelectric sensor or pyrosensor. The electrodes gather charge. Because the material is a very good

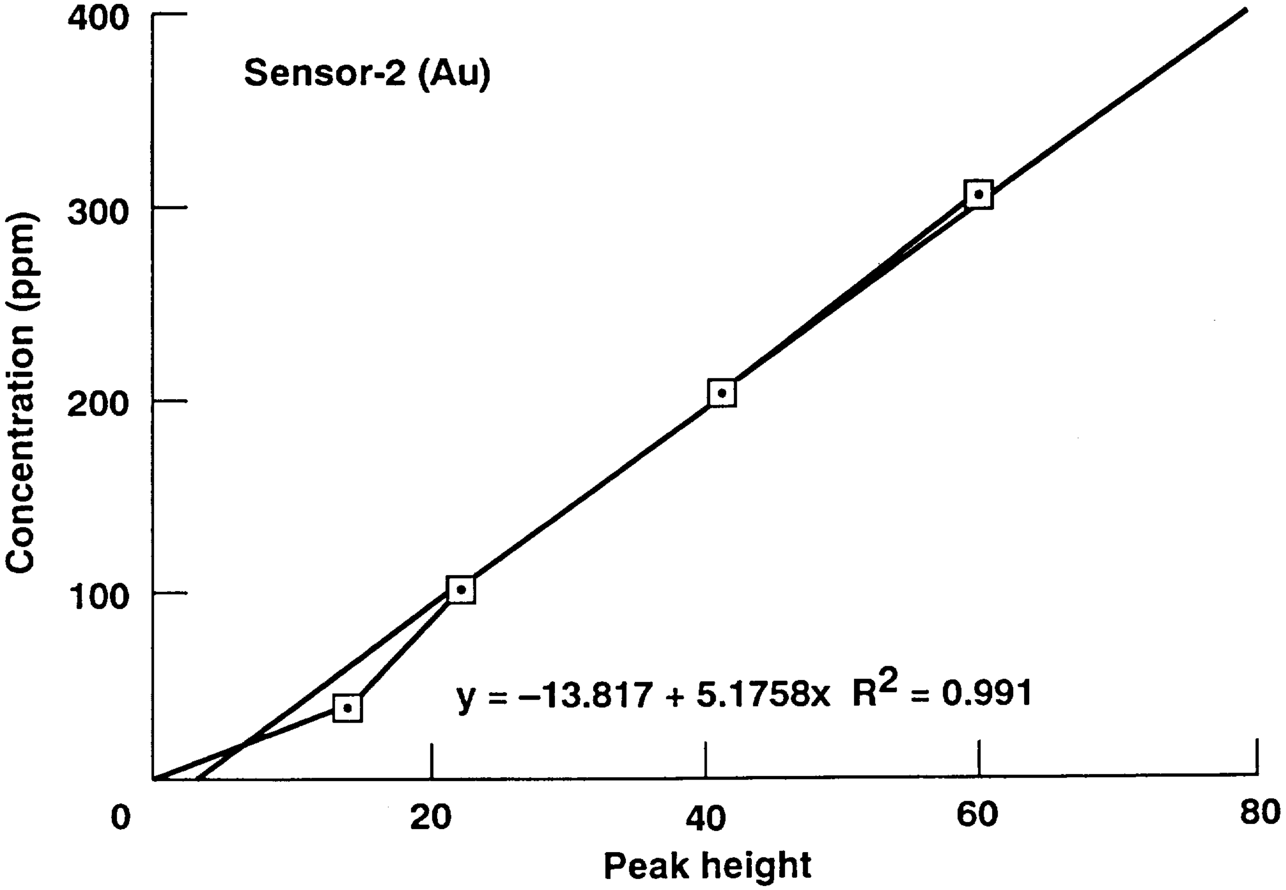


Figure 8. Hydrogen peroxide test (preliminary result)

Figure 9. Sensor design from IBM

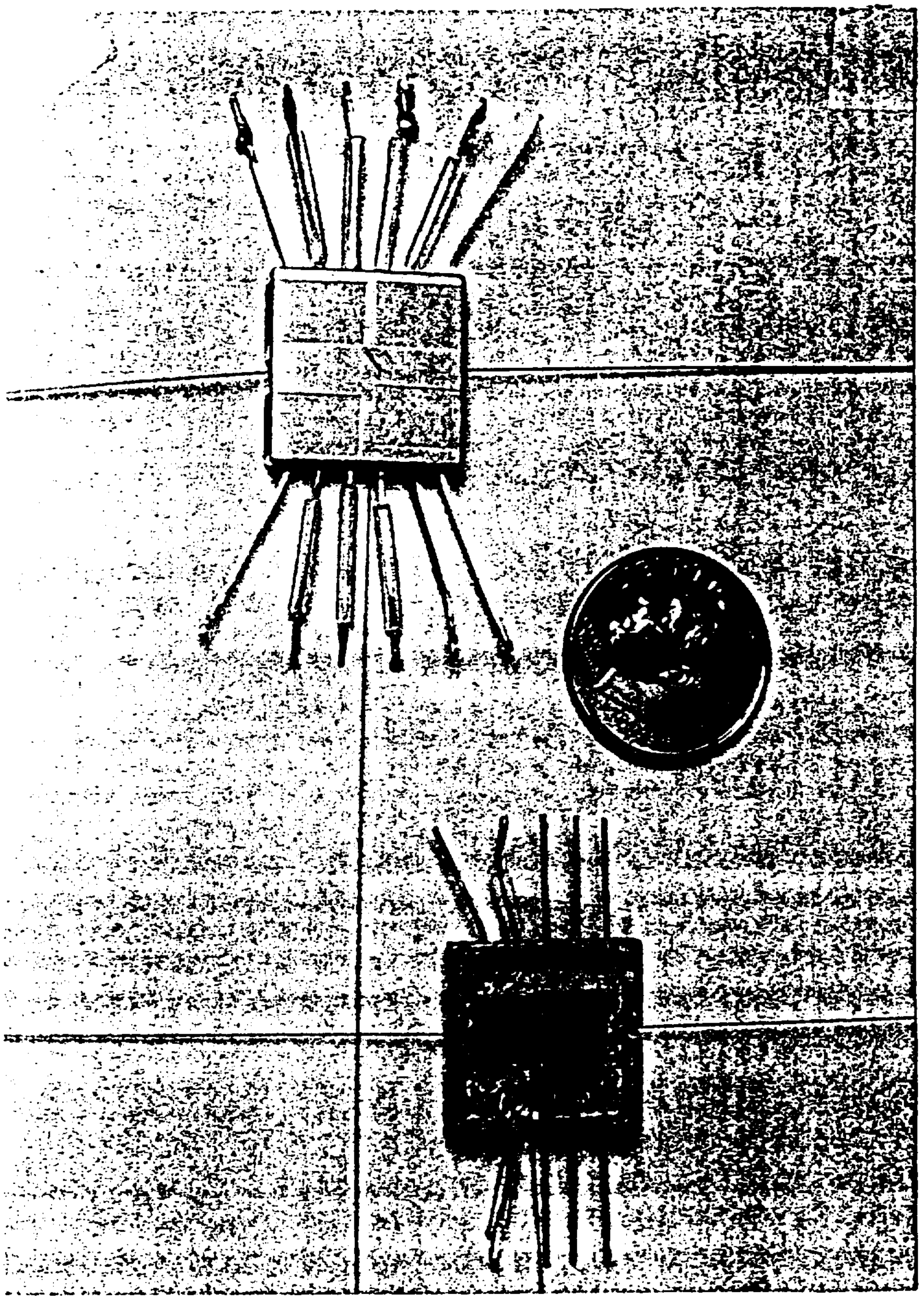


Figure 10. Micro-machined Gas Chromatography System

dielectric the charge is unable to leak through the thin film. In its simplest form, the pyroelectric sensor is both a charge capacitor and a charge generator.

There are two approaches using the pyroelectric principle for determination of chemical compounds in solution. In the first approach, the heat generated by an exothermal or endothermal chemical reaction is sensed by a pyrosensor. This allows for the continuous quantitative detection of some substances. An example of this is: the determination of peroxide concentration using catalysis of enzyme-coated polyvinylidene difluoride (PVDF). PVDF film is commercially available and has outstanding pyroelectric response; a change of one degree Celsius gives an output of about 3V for a typical thickness of 25 μm.

The second approach involves the use of laser light. The sample absorbs energy from the laser and the heat generated travels to the nearby sensor which is not in the path of the laser light. This heat creates an electric signal that is measured and translated into an analytical concentration. Examples are: coccine, B-carotene, MnO4- , Cd and Fe complexes all excited by a laser and analyzed using pyrosensors. This technique also has been applied to measurements of phosphorus (as PO4-3) and nitrogen (as NO3-) concentrations in natural waters. In the case of phosphorus, a detection limit of about 2 ppb was obtained.

We have applied these approaches and constructed our own pyrosensors. The sensor provides a very stable baseline, and demonstrates that hydrogen peroxide concentration can be determined from 40 to 300 ppm with a reasonable calibration curve as shown in Figure 8. In recent collaboration with Dr. H. Coufal, IBM Almaden Research Center, CA., the sensor (Figure 9) was shown to be sensitive to 100 nJ of energy. Using this sensor, hydrogen peroxide concentrations can be detected as low as 1 ppm in a 50 μL sample size with 300 mV signal amplitude. Further application of this technology will be proposed and investigated.

III. Micro-machined GC Instrument Development

The development of gas chromatographic equipment for planetary atmospheric probes and soil, gas or pyrolysis analysis was required for both the Viking mission to Mars and the Pioneer Venus mission. A GC instrument was used for the Pioneer Venus mission. However, future missions such as the Mars Exploration Missions and missions to probe outer planet atmospheres or outer planet moons, will require further reduction in weight, volume, and power requirements for their equipment.

A silicon-micromachined gas chromatography system containing both detector and column integrated into a small piece of silicon have been studied by several researchers. The problem is that no sensitive detector has been designed and tested. Here, we had proposed to use our Meta-stable Ionization Detectors (MIDs) detector principle, and replace the radioactive material with a Glow Discharge method which has not been studied on the silicon micromachined GC system. A very narrow discharge distance can be produced and controlled, a helium ionization detector can be produced, and a highly sensitive analysis can be obtained (sub. ppm can detected) through a micromachined silicon wafer. In addition, a column on a chip using our in-house, newly developed, highly efficient silicon polymer material (U.S. Patented) will be modified and coated to separate most of the chemical components. This small and highly sensitive GC system will be able to meet future missions' requirements. The complete system is shown in Figure 10. Our first step is to design and fabricate the micro machine glow discharge detector to replace the current MID.

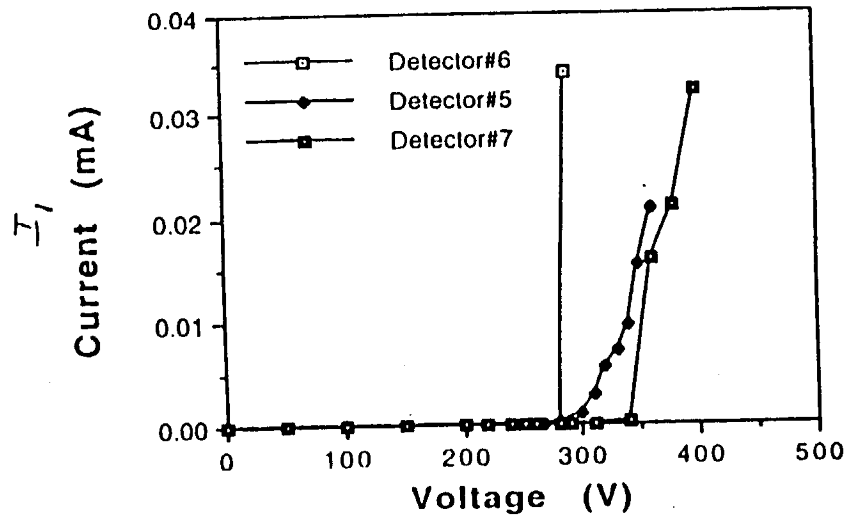


Fig.1 1.Micro-machined glow discharge detector

Discharge Curves

MIDs in general belong to a class of "cold" ionization devices which also includes the Electron Capture Detector (ECD) and Cross Section Detector (CSD). They are all ion chambers with a radioactive source in an electric field. Recently, a glow discharge detector (not micromachined) has been developed with highly sensitive results (ppb). An MID can be made by using a silicon micromachining technique and replacing the radioactive sources with the glow discharge method. This glow discharge MID (GDMID) can be extremely small. The volume of the detector cell is less than 10 pico liter (or $< 10^{-2}$ ul). This will increase the sensitivity of the detector. Furthermore, silicon micromachining allows the GDMID to be batch fabricated with good reproducibility. Recently, four batches of micro-machining detector have been engineered and fabricated. The evaluation of the detector is in process. A glow discharge detector has been successfully miniaturized onto a silicon chip. The gas path in this micro-machined detector was established by using 280 mm OD silica tubing. The difficulty of connecting the tubing to a chip has been overcome by choosing the proper epoxy adhesive.

1. Interface Connection Method

The micro-machining silicon detector is so small that the inlet/outlet holes are difficult to connect with GC tubing. Currently, we are using epoxide adhesive to connect fused silica capillary tubing and the micro-machining detector's inlet and outlet. Preliminary results indicate that this connection is sufficient without displaying any leakage.

2. Testing of Discharge

A glow discharge detector has been successfully miniaturized onto a silicon chip. The gas path in this micro-machined detector was established by using 280 mm OD silica tubing. The difficulty of connecting the tubing to a chip has been overcome by choosing the proper epoxy adhesive. The detector was finally fabricated in a 16x16x2 mm case (see Fig. 11). The discharge current is being tested. Due to the high applied voltage, the silicon chip was breaking down and the charge leaked. The new glass chip design had been completed and fabrication is in progress.

3. Micro-porous silicon surface for discharge

A possible attempt to get light emission out of silicon is to use nanocrystalline structures. By forming a porous silicon film with differently doped wafers and with different anodizing procedures, Richter et al. (IEEE Electron Device Letter, 12, 691, 1991) and Kozlowski et.al. (Sensors and Actuators A 53, 284, 1996) had demonstrated the plasma emission. Our second discharge detector is designed using this principle. Unfortunately, due to technical difficulties, the devices failed to work. New designs with silicon and glass chip have been finished and fabrication is in process.

In conclusion, several micro-machined emission detectors had been fabricated and tested. The results indicate that some problems in fabricating inert and strong bonded electrodes on the silicon surface exist. A Pt electrode will replace the gold electrode, and a 100 micron of silicon oxide will replace the 50 micron currently used in the metal-silicon interface to reduced leakage of electron through the silicon layer.

IV. Development of a Method for the Fast Separating and Detecting of Amino Acids

The development of chromatographic instruments for the analysis of gas, soil, and rock samples is important in supporting scientific investigations on future planetary missions. In the wake of the successful mission of Pathfinder on Mars, interest in finding biological molecules or their prebiotic precursors is again prevailing. In the fundamental classes of biomolecules, L-amino acids are especially outstanding in their distinct chirality as a biosignature for Earth life. Detection of L-amino acids will, therefore, provide a direct evidence for possible extinct and extant life in planetary systems, and may lead to the discovery of potential biodeposit sites for further planetary exploration.

A miniaturized, fully automatic analysis instrument, incorporated with affinity microcolumns which are highly specific for L-amino acids was studied. Affinity microcolumns were prepared using techniques, developed in our laboratory, such as *in situ* polymerization, sol gel process, and molecular imprinting.

During the second half of the 1997-1998 year, we also focused on prepared amino acid-imprinted polymers using several approaches which have practiced in the literature. Several factors were considered to be important in designing and synthesizing molecularly imprinting polymers: 1. the choice of functionalized monomers and cross-linker; 2. the solvent used; 3. the procedure adopted. We have used a variety of monomers and performed polymer synthesis under several different conditions. The results from the experiments performed were less than encouraging, but there is still a lot of room for improvement and modifications. Some affinity experiments of molecularly imprinting polymers are in progress.

V. Publications

1. T. Shen, "Highly Crosslinked Silicon Copolymers for Gas Chromatography Columns", U.S. Patent 5,360,878 (1994).
2. "A New Method for the Preparation of Polymeric Porous Layer Open Tubular Columns for GC Application", by Thomas C. Shen and Mei-Ling Wang, J. Microcolumn Separations, 7(5),471 (1995)
3. "In-situ Polymerization Method to prepare Polymeric Porous Layer Open Tube Columns for GC Application", Thomas C. Shen and Cindy Zhou, Fourth Pacific Polymer Conference, December, 1995, pp140.
4. "Bonded Porous Layer Open Tubular (PLOT) Columns", by T. Shen and Cindy Zhou, *Ames Research and Technology* 1995, pp 140.
5. "A Helium GC/IMS for the Analysis of Extraterrestrial Volatiles in Exobiology Flight Experiments". by D. R. Kojiro, G. C. Carle, D. E. Humphry, M. Shao and N. Takeuchi, Proceedings of the Fourth International Workshop on Ion Mobility Spectrometry, Cambridge, United Kingdom, (1996)
6. "The Mini-CIDEX GC/IMS: Analysis of Cometary Ice and Dust". by D. R. Kojiro, G. C. Carle, D. E. Humphry, M. Shao and N. Takeuchi, Third International Workshop on Ion Mobility Spectrometry, Galveston, Texas, NASA Conference Publication 3301, (1995).
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Patents

Following an invention disclosure and release from SETI Institute, NASA applied for and received U.S. Patent No. 5,360,878, entitled "Highly Crosslinked Silicon Polymers for Gas Chromatography", dated November 1, 1994.

An invention disclosure was made on June 30, 1998 for NASA Case No.: ARC 14278-1NP "Highly Cross-linked Silicon Polymeric Porous Layer Boned Tubular Columns for G C Application". On April 16, 1999, SETI Institute indicated it is not interested in pursuing patent or title rights in that invention.

A New Method for the Preparation of Polymeric Porous Layer Open Tubular Columns for GC Application*

Thomas C. Shen† and Mei-Ling Wang
SETI Institute, NASA Ames Research Center, Moffett Field, California 94035-1000, USA

Abstract. A new method to prepare polymeric PLOT columns by using *in situ* polymerization technology is described. The method involves a straightforward *in situ* polymerization of the monomer. The polymer produced is directly coated on the metal tubing. This eliminates many of the steps needed in conventional polymeric PLOT column preparation. Our method is easy to operate and produces very reproducible columns, as shown previously (T. C. Shen, *J. Chromatogr. Sci.* 30, 239, 1992). The effects of solvents, tubing pretreatments, initiators and reaction temperatures in the preparation of PLOT columns are studied. Several columns have been developed to separate (1) highly polar compounds, such as water and ammonia or water and HCN, and (2) hydrocarbons and inert gases. A recent improvement has allowed us to produce bonded polymeric PLOT columns. These were studied, and the results are included also.

Key words: *porous layer open tubular column, polymeric porous layer capillary column,* in situ *polymerization*

INTRODUCTION

Capillary columns are extensively used in gas chromatographic analytical techniques for the separation and quantitation of gaseous to semi-volatile samples. In general, capillary columns comprise a liquid phase or a porous solid phase. Coating a liquid phase onto the inside of a capillary is relatively easy and routine, but the coating/bonding of a solid porous layer inside the capillary tube can be difficult in terms of reproducibility. Porous layer open tubular (PLOT) columns are currently produced either by static coating, dynamic coating, or by a combination of static and dynamic coating procedures. These procedures are complicated and require special expertise and facilities, since the suspension must be stable throughout the entire coating process, which can take up to days in the case of the static method. Dynamic processes are somewhat quicker and easier, but reproducibility is a major problem [2–8]. In the case of polymeric PLOT columns, the current existing method requires that polymerization of monomers takes place in the first step. The polymer particles that are produced are then sieved and washed to recover the size required for preparing a stable suspension solution. In order to overcome these difficulties, we have developed a novel method to prepare polymeric PLOT columns by *in situ* polymerization [1, 9, 10]. This method combines the polymerization and the coating procedure into one step. Although the method is still under development, some factors affecting column performance have been studied and are presented in this article.

EXPERIMENTAL

Materials. The materials were obtained as previously described [1, 9]. In addition, Sol-Gel A (Membrane & Polymer Technology Inc., San Jose, CA), vinyltrimethoxy silane (VTS) (Aldrich Chemical Co.), 3-methacryloxypropyltrimethoxy silane (MAPTMS) (Union Carbide Co.) were used as received without purification.

Column preparation. Nonbonded PLOT columns: columns were prepared by the *in situ* polymerization method previously described [1,

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†To whom correspondence should be addressed.

Table I. *Solvent effect.*

Solvent	Performance
Isopropanol	Suspension powder blown out
Heptane	Column plug
Methanol	Good column
Methanol/water	Fiber materials blown out
Methanol/heptane	Column plug
Ethyl acetate	Column plug
Butanol	Column semi-plug

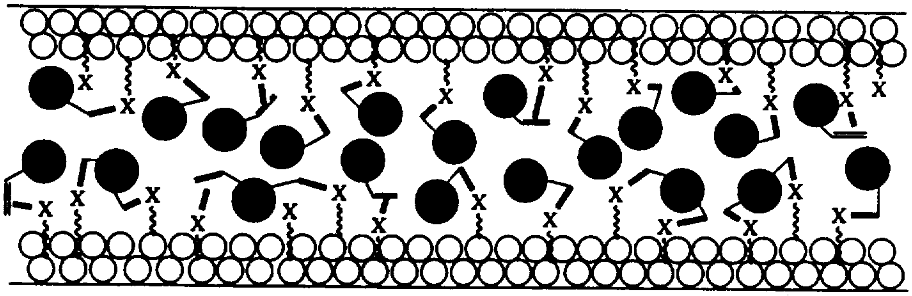
Table II. *Effect of monomer concentration.*

DVB concentration (wt %)	Result
20	Column plug
15	Column plug
12	Good column (operating pressure: 50 psi)
8.1	Good column (operating pressure: 30 psi)

9]. The general procedure for the preparation of bonded PLOT columns involved the following steps: the stainless steel tubing was washed with water, methanol, and acetone and dried with a nitrogen sweep. After oxidation of the tubing at 400°C for 10 min, it was coated with a mixture containing Sol-Gel A (2.08 g), THF (3.00 g), and water (0.20 g). The tubing was then cured with 1% NH_3/H_2O for 30 min and, under He sweep, was heated in a variable temperature heating oven to 150°C at a heating rate of 2°C/min. The tubing was kept at 150°C for 30 min. It was then treated with a solution mixture of MAPTMS (2.27 g), VTS (2.06 g), THF (6.00 g), and water (0.80 g). A water vapor flow was introduced into the tubing for 2 h. Both ends of the tubing were capped. Next, the tubing was heated to 60°C on a rotated cylinder for 4 h. After the coil was cooled to room temperature by He flow, a mixture including divinylbenzene (DVB) (0.07 g), *t*-butanol (0.50 g), heptane (1.50 g), benzoyl peroxide (0.02 g), and methylethylketone (0.20 g) was added to the tubing via a glass funnel. With both ends being capped with stainless-steel endcaps, the tubing was slipped over a hollow metal cylinder which was then fixed to a mechanical rotation rod in an oven. The oven temperature was set at 95°C and the coil was rotated at 15 rpm for 16–18 h. The tubing was cooled to room temperature and both ends were opened. The solvent was purged with nitrogen at a low pressure of 10–20 psi. After the solvent was completely eliminated, the column was conditioned at 150°C for over 12 h.

Gas chromatographic evaluation. The column prepared from the *in situ* polymerization method was installed in a GC that was equipped with a thermal conductivity detector. Helium carrier gas was used to separate the various compounds. Gas samples were injected onto the column using a gas sample valve. Flow rates and operational temperatures are given in the figures.

Scanning electron microscope evaluation. The scanning electron microscope (SEM) pictures (Figure 3) were taken by a Hitachi S-4000 Field Emission Scanning Electron Microscope. The samples were prepared by the following method: a portion of the column (1 in. in length) was cut using a file. The samples were then mounted on a plate. In order to prevent the samples from charging, they were sputtered for 3 min with gold using a Polaron E5100 SEM



X = $H_2C{=}C(CH_3)CO$—, HS—, or others

Figure 1. *Scheme of in-situ polymerization stainless steel bonded PLOT column formation.*

Coating Unit. Finally, the samples were viewed and pictures were taken at 2.0 kV and magnifications of 7.00 and 50.0 K, respectively.

RESULTS AND DISCUSSION

A. Nonbonded PLOT column. The conditions for the polymerization reaction involving divinylbenzene (DVB) are studied in detail in the following.

1. Tubing pretreatment: The inner surface of the stainless steel tube was treated with acid, such as concentrated hydrochloric acid, or with a base, such as 10% NaOH solution. This was followed by washing with distilled water, methanol, acetone, and methylene chloride. Neither the acid nor the base treatments produced good columns; all polymers flowed out without coating. Only when the inner surface was cleaned with a sequence of methanol, acetone, and methylene chloride were good columns with good separation characteristics produced.
2. Solvent selection: The selection of a suitable solvent system is the key to producing good columns. Table I shows several solvents that were tested for the polydivinylbenzene PLOT columns. Only methanol gave good column performance. The reason is not clear at this moment.
3. Effect of DVB concentration: The polymerization concentration also affects the PLOT column formation. Particle size increased with increasing DVB concentration. Big particles will plug the column. As shown in Table II, different concentrations were tested. It was observed that both the 12 and 8.1% DVB columns gave good results.
4. Temperature effect: Three different temperatures were studied. The results (Table III) indicate that higher temperatures produced plugged columns. This may be because at lower temperatures the smaller and less crosslinked particles form at the beginning of the reaction. Small particles will adhere better to the metal tubing and ultimately form better columns. At higher temperature, the particles grow too fast to adhere on the wall [1, 9].

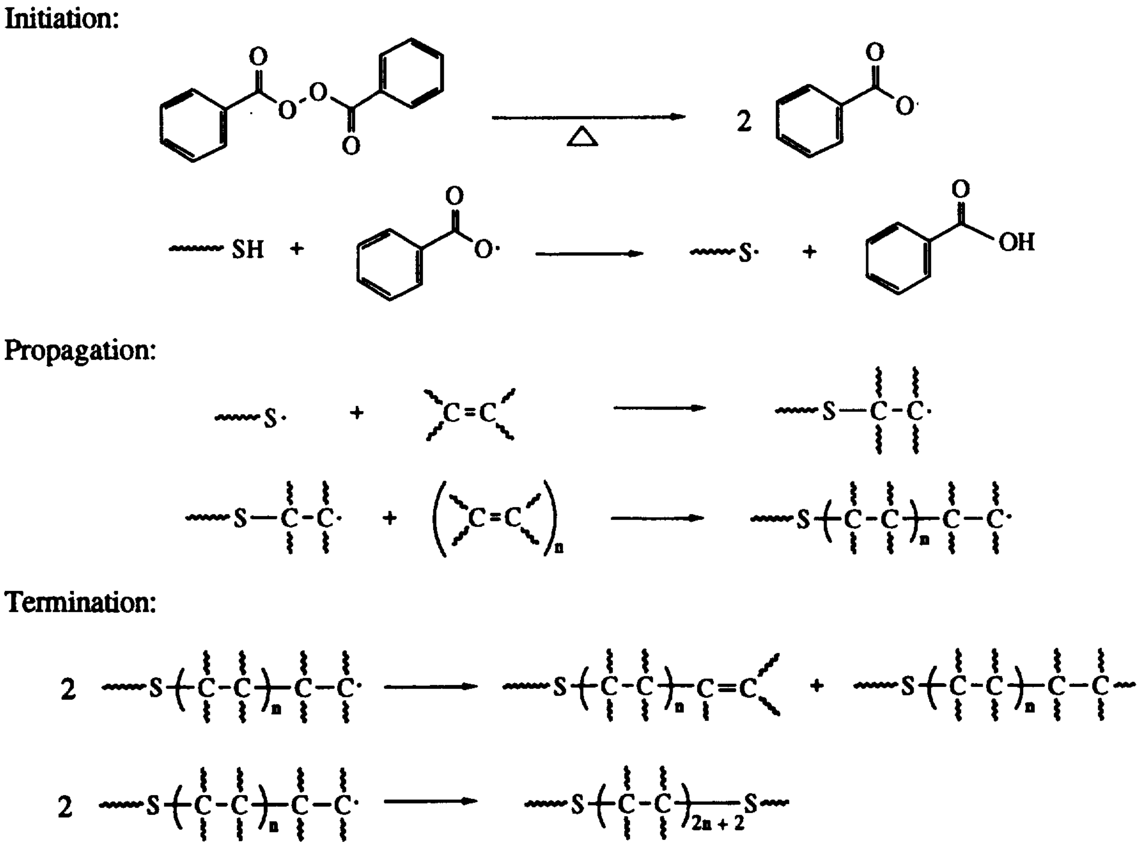


Figure 2. *Scheme of anticipated reaction mechanism when using 3-mercaptopropyltrimethoxy silane as coating reagent.*

Table III. *Temperature effect.*

Temperature (°C)	Performance
75	Good column
85	Column slight plug
95	Column plug

B. Bonded PLOT columns. We have developed high-efficiency PLOT coated columns that would be useful in the gas chromatographic investigations of planetary atmospheres in future space missions. However, when shock or vibration (similar to what occurs during spacecraft launch and travel) is applied, the columns bleed out because the polymeric particles are not bonded onto the stainless steel wall. This problem is also found in commercial PLOT columns. In addition, metal capillary columns have been considered attractive because their coil radii can be made smaller than those of fused silica capillary columns and have high mechanical durability. For these reasons, we investigated bonded stainless steel PLOT columns. Although the procedures for creating metal capillary columns are still under development [11–13], we have developed a polymer precoating that meets the requirement of forming strong bonding to the metal tubing. The bonding mechanism is similar to most Latex coating procedures [14]. This precoating can also be modified with the prepolymer containing a polymerizable functional group X as shown in Figure 1. Currently, two prepolymers containing different polymerizable functional groups are selected for bonding polymeric particles during the *in situ* polymerization step (see Figure 1).

The ideal case is one in which the polymerizable functional groups are initiated by the initiator first and then form polymer particles thereafter (Figure 2). In many cases, however, the initiators are not just initiating polymerizable functional groups but monomers as well. For this reason, some nonbonded polymer particles are formed. This problem can cause the column to plug or to have an insufficient number of bonded particles on the column wall. By careful control of the reaction conditions, we were able to prepare bonded PLOT columns from *in situ* polymerization. Figures 3 and 4 give these results.

Figure 3A demonstrates the polymeric bonding layer on the wall of a stainless steel tube. Figure 3B shows the structure of polymeric particles of the bonded layer. The column withstood our shock and vibration test, as no free particles flowed out. In addition, column performance remained the same as before the test. Figures 4A and 4B demonstrate the separation of fluorohydrocarbons and hydrocarbons using a bonded PLOT column made by the *in situ* polymerization method.

Although the *in situ* polymerization method to prepare nonbonded or bonded polymeric PLOT columns has been developed for the separation of water and ammonia, light gases, hydrocarbons, and fluorohydrocarbons, the

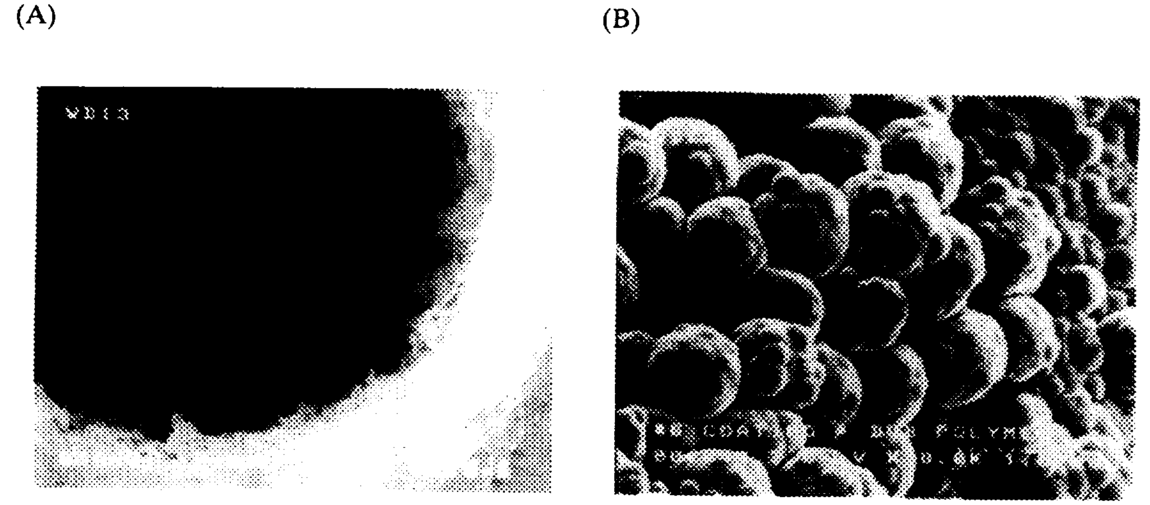


Figure 3. *SEM Photograph of a bonded PLOT column (A) polymeric bonding layer on the wall of a stainless steel tube, (B) structure of polymeric particles of the bonded layer.*

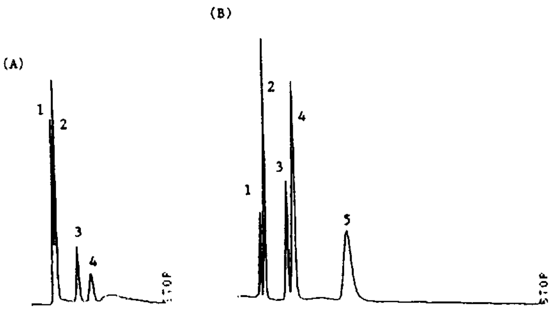


Figure 4. *Gas chromatograms of a PLOT column (12 ft., .042 in. o.d., .02 in. i.d.) operating at 85°C and 1.87 mL / min, with helium as the carrier gas (A) separation of 4 freons: (1) air and CF_4, (2) C_2F_6, (3) CCl_2F_2, (4) $CHClF_2$. (B) separation of 5 hydrocarbons: (1) air and methane, (2) acetylene, (3) propane, (4) propyne, (5) isobutane.*

method is still in its infant stage. Our next step will be the synthesis of a prepolymer containing peroxide or azo-nitrile groups which will initiate polymerization and form bonded polymer particles thereafter.

ACKNOWLEDGMENT

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In-Situ Polymerized PLOT Columns III: Divinylbenzene Copolymers and Dimethacrylate Homopolymers

Thomas C. Shen and Michael M. Fong
SETI Institute, NASA, Ames Research Center, Moffett Field,
California 94035-1000

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Thomas C. Shen* and **Michael M. Fong**
SETI Institute, NASA, Ames Research Center, Moffett Field, California 94035-1000

Abstract

Studies of divinylbenzene copolymers and dimethacrylate homopolymers indicate that the polymer pore size controls the separation of water and ammonia on porous-layer-open-tubular (PLOT) columns. To a lesser degree, the polarity of the polymers also affects the separation of a water–ammonia gas mixture. Our results demonstrate that the pore size can be regulated by controlling the cross-linking density or the chain length between the cross-linking functional groups. An optimum pore size will provide the best separation of water and ammonia.

Introduction

Exobiology has been and continues to be a subject of interest to NASA. From our knowledge of life on Earth, we know that the presence of water and ammonia was of critical importance for chemical evolution and the origin of life. The examination of extraterrestrial bodies (in other words, planets, moons, comets, and planetary dust) for the presence of water, ammonia, and other biogenic compounds and elements is an object of much analytical effort. Gas chromatography (GC) can be used for the analysis of water and amines (1–3); however, columns that produce good separation are difficult to find. Although several liquid-coated columns have been reported (4,5) for this application, they cannot be used in conjunction with highly sensitive detectors such as the ion mobility spectrometer (IMS) or metastable ionization detector (MID) because of bleeding problems associated with these columns (6,7). For these reasons, NASA-Ames Research Center is involved in low or no-bleed column development for GC use.

Current commercial columns separate water–ammonia solutions through temperature programming. In flight missions, an isothermal condition is preferred. Under isothermal conditions, most of the commercial columns either cannot give good separation or have severe tailing problems. Recently, several porous-layer-open-tubular (PLOT) columns were developed and investigated in our laboratory for the separation of water–ammonia solutions (8). We describe the polymer pore size and solubility effects on water–ammonia separation.

Experimental

Materials. Divinylbenzene (DVB) (95% purity) (Dow Chemical; Midland, MO) and ethyleneglycoldimethacrylate (EGDM) (Arco Chemical Co.; Newton Square, PA), diethyleneglycoldimethacrylate (DEGDM), triethyleneglycoldimethacrylate (TEGDM), tetraethyleneglycoldimethacrylate (TTEGDM), polyethyleneglycol (400)dimethacrylate (PEGDM), 1,4-butanediol dimethacrylate (BTDM), 1,6-hexamethylene dimethacrylate (HMDM), pentaerythritol tetramethacrylate (PTMA), and pentaerythritol triacrylate (PTAA) (all from Polysciences, Inc.; Warrington, PA) were passed through a column of Supersorb 22 (Membrane & Polymer Technology; San Jose, CA) to remove the polymerization inhibitor before use. Styrene (Aldrich; Milwaukee, WI) was treated with 1M NaOH solution. The styrene layer was separated and dried with CaO before use. Methanol (J.T. Baker; Phillipsburg, NJ), isopropanol, heptane (Matheson Coleman & Bell; Cincinnati, OH), 2,2'-azobisisobutyronitrile (Polysciences), and methylethylketone (J.T. Baker) were used as received without purification.

Column preparation. Columns were prepared by the in situ polymerization method previously described (8). In each case, a solvent was selected from one of the following to produce the column: methanol, isopropanol, heptane, or mixtures of each.

Gas chromatographic evaluation. The column prepared from the in situ polymerization method was installed in a GC that was equipped with a thermal conductivity detector. Helium carrier gas was used to separate the various compounds. Gas samples were injected onto the column using a gas sample valve. The flow rate and operational temperature are given in the figures.

Scanning electron microscope evaluation. The scanning electron microscope (SEM) pictures (Figure 1) were taken by a Hitachi S-4000 Field Emission Scanning Electron Microscope. The samples were prepared by the following method: A portion of the column (1 in. length) was cut using a file; the samples were mounted on a plate; to prevent the samples from charging, the samples were sputtered for 3 min with gold using a Polaron E5100 SEM Coating Unit; finally, the samples were viewed and pictures were taken at 2.0 kV and magnifications of 7.00 K and 50.0 K, respectively.

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*Author to whom correspondence should be addressed.

Results and Discussion

Column preparation

The PLOT columns prepared by in situ polymerization can be classified into three types:

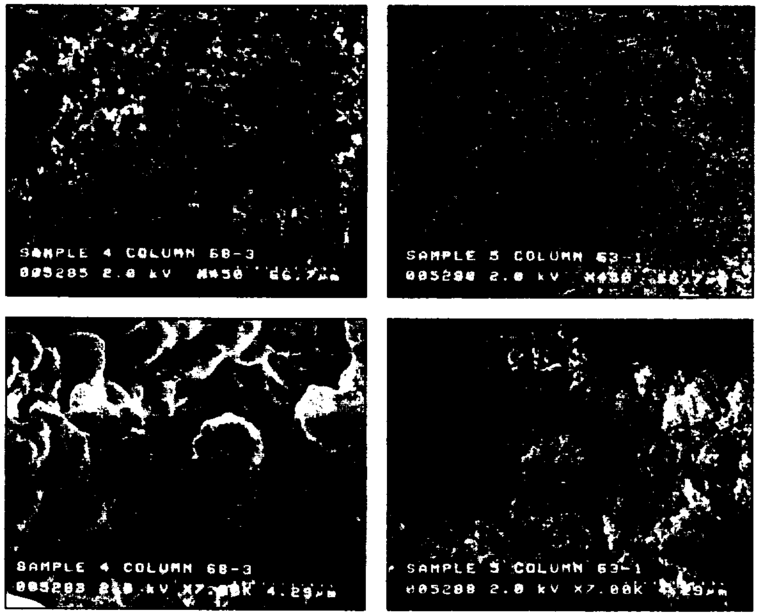
- Columns with very low operational pressure (less than 10 psi at 3–4 mL/min flow rate) that are formed when the particles are small but stable and the coating is uniform
- Columns with medium operational pressure (P) (50>P>10 psi) that are produced by formation of very small and unstable particles that coagulate and form large clusters thereby reducing the column passway
- Columns with high operational pressure (more than 50 psi) that are formed when small particles aggregate and completely block the column in many thin segments.

Figure 1A shows an HMDM PLOT column made using a butanol–hexane solvent system. The formation of properly sized latexes produces a very uniform coating. The operational pressure at a flow rate of 4–6 mL/min is only 10 psi. The column separation efficiency is also very high. Figure 1B shows an HMDM PLOT column produced using a heptane solvent system. Very small particles form at the beginning; later, aggregation occurs, and clusters form. Although it has high porosity, the column is plugged even at pressures over 100 psi. It is clear that selection of a suitable solvent system for polymerization is very important for producing PLOT columns with low operational pressures.

Water and ammonia separation

Porapak N, which is made from DVB–EGDM, has already been shown to separate water and ammonia (9,10). Therefore, different ratios of DVB–EGDM were used to produce in situ polymerized PLOT columns for this separation. The water–ammonia solution relative retention (r_{H_2O}/r_{NH_3}) can be calculated as follows:

$$V_{H_2O}/V_{NH_3} = (r_{H_2O}/r_{NH_3}) = (t_{H_2O} - t_{air})/(t_{NH_3} - t_{air}) \quad \text{Eq 1}$$



A B

Figure 1. Scanning electron microscope photographs of 1,6-hexamethylenedimethacrylate (HMDM) polymer particles coated on the wall of the porous-layer-open-tubular (PLOT) columns prepared from in situ polymerization: A, butanol–hexane solvent system and B, heptane solvent system.

where V_{H_2O} and V_{NH_3} are the specific retention volumes of water and ammonia, and t_{H_2O}, t_{NH_3}, and t_{air} are retention times of water, ammonia, and air, respectively. The water–ammonia relative retention increases with an increase in the concentration of EGDM as shown in Figure 2.

Two factors, pore size and solubility, are important in GC separation, adsorption, and desorption processes (11). Adsorption is related to the solubility factor, which is mainly determined by the ability of the gases to condense as well as the physical interaction of a gas molecule with the polymer matrix. Desorption is primarily determined by the size of a gas molecule as well as factors such as polymer segmental mobility and intersegmental packing density (or pore size).

To determine which factor influences the separation of water and ammonia in DVB–EGDM PLOT columns, we examined the solubility parameter first.

In recent years, gas–liquid chromatography (GLC) has been used to determine thermodynamic parameters for polymer substrates (12–14). Based on inverse chromatography, the solubility parameter can be estimated (15). It is clear that the retention volume of a substrate is related to the polymer-solvent (or Flory-Huggins) interaction parameter (16), *x*, as shown in the following equation:

$$x_{12} = \ln (273.15\ R\ v_{2sp} / Vg\ v_1\ P_1) - (1 - v_1/M_2 V_{2sp}) - (P_1/RT)(B_{11} - v_1) \quad \text{Eq 2}$$

where M_2 is the number average molecular weight of the polymer, v_{2sp} is the specific volume of the polymer at the column temperature (T), Vg is retention volume from GC analysis, v_l is the molar volume of the solvent, P_l is the vapor pressure of the solvent at the column temperature, B_{ll} is the gas-state second virial coefficient of the solvents, and R is the gas constant. Although this equation is only applied at the polymer melt state, the retention volumes should also relate to the interaction between gases and the cross-linking polymer. Based on the interaction parameter (x_{12}), the solubility parameter of the polymer and the solvent can be expressed by the following equation:

$$x_{12} = (v_1/r)(\gamma1 - \gamma2) \quad \text{Eq 3}$$

where γ_1 and γ_2 are the solubility parameters of the polymer and solvent, respectively.

Because the solubility parameters of DVB and EGDM are very close (9.28 and 9.5 [cal/cm^3]$^{1/2}$) as estimated by Fedors' method (17), the solubility parameters of their copolymers should be very close. Therefore, their water–ammonia separation factors should be similar. This is not observed (Figure 2).

In this case, the pore size may be the controlling factor. To test this hypothesis, DVB–styrene in situ polymerized PLOT columns were prepared. The solubility parameter for styrene is 9.3 (cal/cm^3)$^{1/2}$, which is very close to the DVB value. The relative retention of the water–ammonia solution also increases with increasing styrene concentration up to 43% (Figure 2).

To further confirm the pore size effect, PLOT columns prepared from homopolymers of DEGDM, TEGDM, TTEGDM, and PEGDM were tested. The results listed in Table I indicate that an increase in the chain length between the dimethacrylate func-

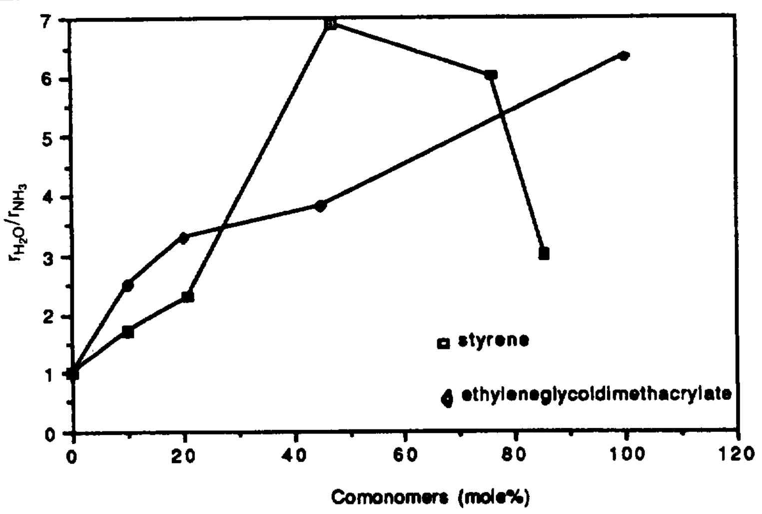


Figure 2. Effect of the mole percent of styrene and EGDM comonomers in divinylbenzene copolymer PLOT columns for water–ammonia solution separation.

Table I. Water–Ammonia Relative Retentions (r_{H_2O}–r_{NH_3})

Column	Polymers*	r_{H_2O}–r_{NH_3}	Operational pressure†	Solvent system
50-1	EGDM	6.2	a	heptane–*t*-butanol–MEK
78-5	DEGDM	10.0	a	MEK–*t*-butanol
71-2	TEGDM	12.8	a	MEK–heptane
78-1	TTEGDM	18.1	b	MEK–*t*-butanol
56-3b	PEGDM	12.0	b	heptane–*t*-butanol–MEK
68-2	BTDM	8.0	a	MEK–methanol
68-3	HMDM	9.5	a	MEK–methanol
62-2	PTAA	1.1	b	heptane–*t*-butanol/MEK
78-2	PTMA	1.2	b	MEK–*t*-butanol
	Porapak N‡	4.7		

* See Appendix for abbreviations.

† Carrier gas pressure applied to obtain flow rate of 4 mL/min. a < 10 psi, 50 psi < b < 10 psi, and c > 50 psi.

‡ Alltech Chromatography, Deerfield, IL.

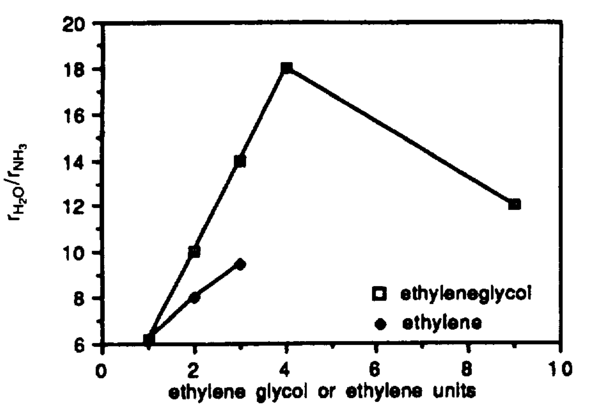


Figure 3. Effect of chain length between two methacryloyl groups in water–ammonia solution separation.

tional groups of the dimethacrylate homopolymer increases the separation between water and ammonia (Figure 3).

It is clear that cross-linking density may control the pore size; the higher the cross-linking density, the smaller the pore size produced. The multifunctional monomers, such as PTAA (which has a trifunctional double bond) or PTMA (which has a tetrafunctional double bond), form higher cross-linked and smaller pore-sized polymers; therefore, water and ammonia are not separated as completely (Table I).

When the styrene concentration is more than 43%, the relative retention of a water–ammonia solution decreases with increasing styrene concentration (Figure 2). A possible explanation for such behavior is that because styrene has nonfunctional double bonds, any increase above a 43% styrene concentration will cause the polymer cross-linking density to decrease, resulting in the pore size becoming over sized and unstable (Figure 4B). This in turn will lead to the pore walls collapsing or entangling to form a smaller pore size. On the other hand, increasing the DEGDM concentration (which has difunctional double bonds) does not reduce cross-linking density; therefore, there is no pore over sizing and no pore collapse. The same phenomena is also observed in PEGDM; when the polyethylene-glycol unit is too large, the pores become over sized (Figure 4C) and collapse. The result of this collapse is that the relative retention of a water–ammonia solution also decreases (Figure 3 and Table I).

One could argue that the improved separation using the ethyleneglycol derivatives may be caused by increased water absorbency as the number of ethyleneglycol units is increased. To test this effect, DEGDM and TEGDM were replaced with BTDM and HMDM. The results indicate that the ethyleneglycol unit gives better separations than the CH_2–CH_2 unit, as shown in Figure 3. This may be caused by the effect of the water soluble ethyleneglycol units.

The chromatograms shown in Figures 5 and 6 demonstrate that water–ammonia is clearly separated within 4 minutes using one of these columns under isothermal conditions and low flow rate. The PLOT column made from DVB and styrene copolymer is capable of separating water–ammonia solutions and water–HCN solutions (Figure 6). Since water, ammonia, and HCN are present in comets that will be studied in future NASA missions, the DVB–styrene copolymer PLOT column was selected for further study.

Conclusion

Several DVB copolymer and dimethacrylate homopolymer PLOT columns were developed and investigated for the separation of water and ammonia.

Microscopic examination of two PLOT columns made from HMDM in different solvent systems revealed that a suitable solvent system is important for proper polymerization. The solvent system must allow the polymers to form into appropriately sized particles that uniformly coat the column wall.

Using an in situ polymerization method, several DVB copolymer and dimethacrylate homopolymer PLOT columns were developed and investigated for the separation of water and ammonia. Based on the following results, we concluded that the pore size of the polymers plays an important role in the separation of water–ammonia solutions:

- An increase of styrene or EGDM contained in the DVB copolymer increases the relative retention time of water and ammonia
- An increase in the chain length between dimethacrylate functional groups of the dimethacrylate homopolymers also increases the separation between water and ammonia

In addition, because ethyleneglycol chains between dimethacrylate functional groups in the dimethacrylate homopolymer (e.g., TEGDM homopolymer) give better separation than ethylene chains between dimethacrylate functional groups in the dimethacrylate homopolymers (e.g., HMDM homopolymer), the polarity of the polymers also affects water and ammonia separation.

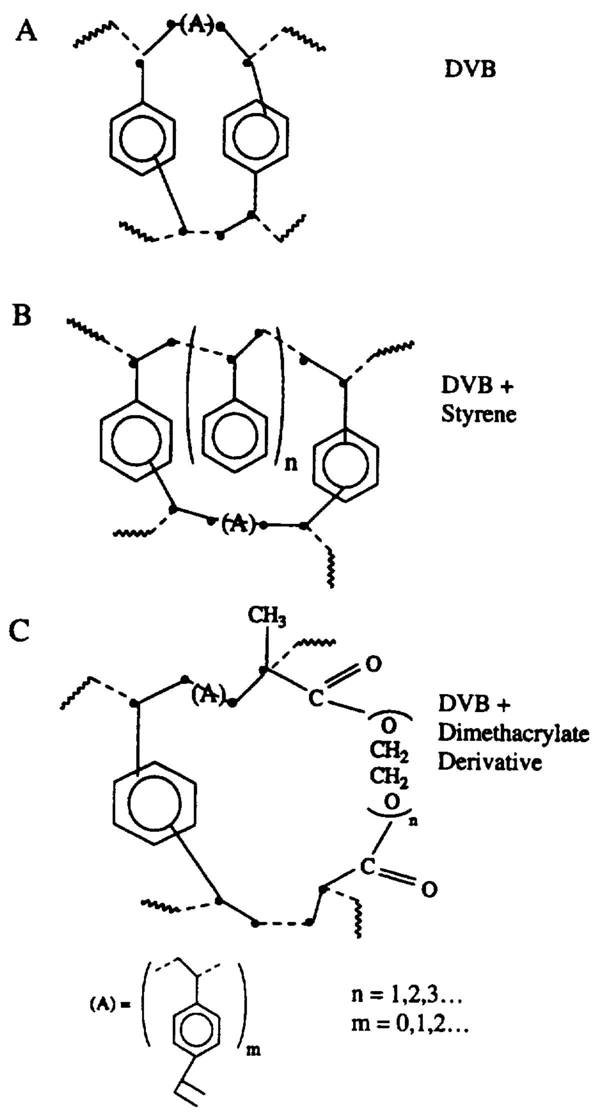


Figure 4. Possible microstructures of the cross-linked polymers.

Acknowledgments

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Appendix

Key to abbreviations

BTDM	1,4-butanediol dimethacrylate
DEGDM	diethyleneglycoldimethacrylate
DVB	divinylbenzene
EGDM	ethyleneglycoldimethacrylate
HMDM	1,6-hexamethylene dimethacrylate
PEGDM	polyethyleneglycol (400)dimethacrylate
PLOT	porous layer open tubular
PTAA	pentaerythritol triacrylate
PTMA	pentaerythritol tetramethacrylate
TEGDM	triethyleneglycoldimethacrylate
TTEGDM	tetraethyleneglycoldimethacrylate

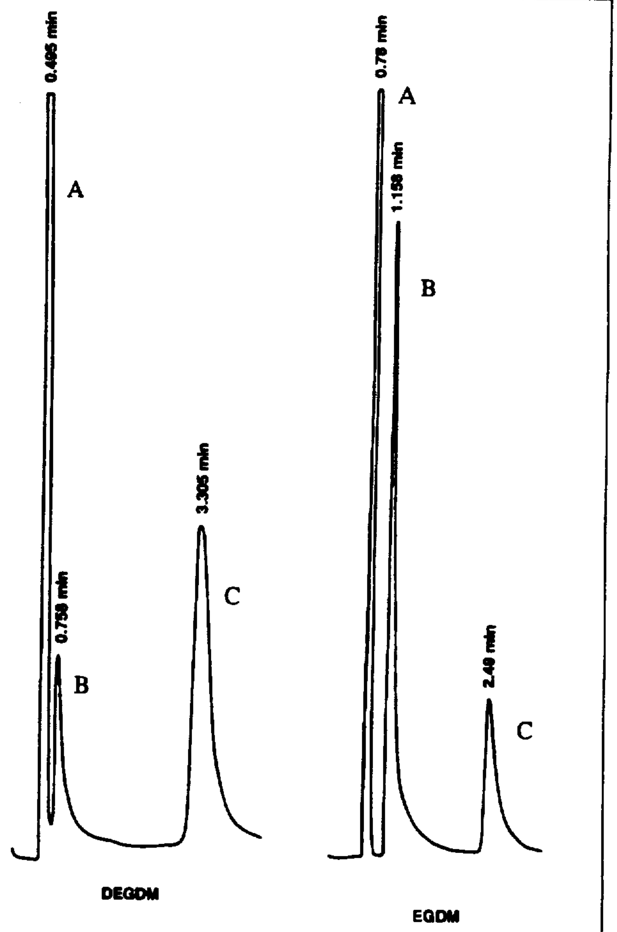

Figure 5. Gas chromatographic separation of water and ammonia using ethyleneglycoldimethacrylate (EGDM) or diethyleneglycoldimethacrylate (DEGDM) PLOT columns (12 ft. × 0.03-in. i.d., stainless steel) operating at 100°C and 4 mL/min, with helium as the carrier gas. Peaks: A, air; B, NH_3; and C, H_2O.

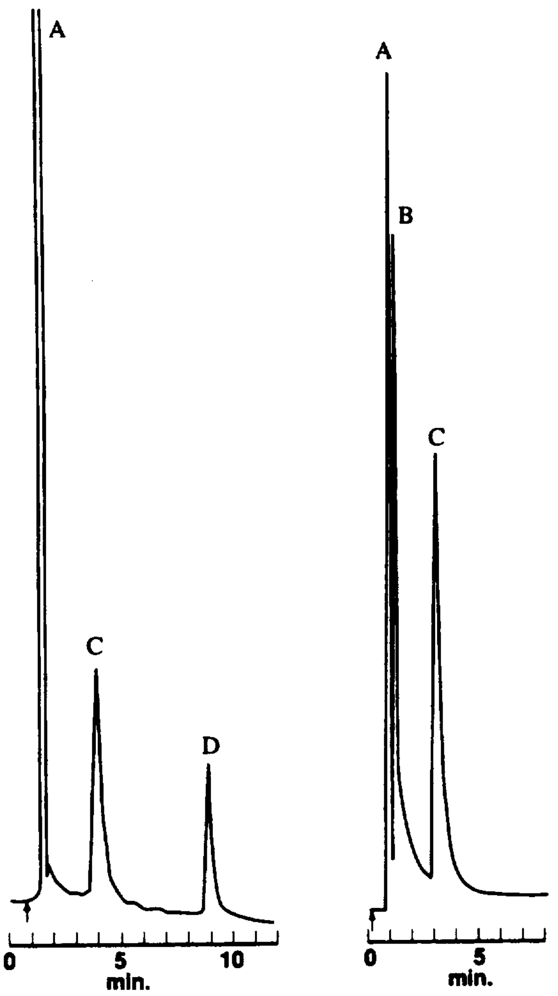

Figure 6. Gas chromatographic separation of water–ammonia and water–HCN solutions using a divinylbenezene–styrene copolymer PLOT column (12 ft × 0.03-in. i.d., stainless steel) operating at 100°C and 4 mL/min, with helium as the carrier gas. Peaks: A, air; B, NH_3; C, H_2O; and D, HCN.

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PROCEEDINGS

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Advanced instrumentation for exobiology

Glenn C. Carle [1], Daniel R. Kojiro [1], Todd B. Sauke [2], Jose R. Valentin [1], Thomas C. Shen [2], and John R. Marshall [2]

1. NASA Ames Research Center, MS 239-12, Moffett Field, CA 94035
2. SETI Institute, 2035 Landings Drive, Mountain View, CA 94043

ABSTRACT

Advanced microdevices for the exploration of the solar system have become increasingly important in the current environment of fiscal constraints and payload size limitations. The Discovery-class missions being proposed for future exploration, while being clearly responsive to this environment, will require highly miniaturized and efficient instruments based on these advanced devices. Several instrument concept developments are continuing at Ames Research Center in support of specific exobiology science goals in future solar system studies on candidate Discovery and other missions. Developments include highly miniaturized metastable ionization detectors for gas chromatography that weigh as little as 1-2 grams with sensitivities of 10^{-14} mol/second and an advanced ion mobility spectrometer that has near-universal sensitivity and weighs as little as 200 grams. New chemical sensors based on solid-state pyroelectric devices are being studied and developed that weigh a few milligrams and, for example, have a sensitivity of 0.1 ppm for H_2O_2. Advanced X-ray diffraction and fluorescence instruments for crystallographic and geochemical measurements on unprepared soil and rock samples are under test. A stable isotope laser diode spectrometer for determination of $^{12}C/^{13}C$ and $^{18}O/^{16}O$ isotope ratios on Mars at fractional percent accuracies has been breadboarded. Finally, advanced computational methods are being applied to new instrument concepts allowing new, less complex, and thus, smaller instruments.

Key Words: gas chromatography, exobiology, ion mobility spectrometry, microdevices, isotopic analysis, x-ray analysis, pyrosensors, multiplex chromatography

1. INTRODUCTION

Several advanced, miniaturized, analytical devices are currently being developed at NASA Ames Research Center (Solar System Exploration Branch) for the purpose of conducting exobiological research in the solar system. The acquisition of exobiological data from interplanetary dust, comets, asteroids, planetary surfaces, planetary rings, and planetary atmospheres will address scientific questions about the origin and distribution of biogenic elements and compounds. It will also address questions about the potential for life to have evolved in the solar system beyond our own planetary confines, and the cosmic and planetary settings in which life, its chemical precursors, or fossil remains could survive.

Given the number of scientific questions raised by exobiology, the diversity of information that can be collected, the diversity of the environments from which the data may be gathered, and the range of operational constraints imposed by planetary missions, it is appropriate to engage in the development of a diverse and flexible suite of instruments, instrument sensors, and analytical techniques. The range of sensor instrumentation allows us to investigate volatile gaseous species, the isotopic ratios of elements within some of these gases, and the elemental and mineralogical composition of solid phases in the dusts and rocks of planetary environments.

To accommodate the rigors of the flight environment, advanced instrument and instrument sensor concepts require that attention be given to miniaturization, ruggedization, efficiency of power consumption, efficient thermal management, and so forth. In addition to addressing these flight-related engineering aspects, the development of breadboard concepts at Ames continues to emphasize the improvement of instrument detection limits, detection ranges, and the precision, accuracy, and reliability of measurements. Commensurate research includes the development of data analysis techniques and scientific and experimental protocols to optimize data acquisition during flight operations, as well as to improve the fidelity of the data.

2. GAS CHROMATOGRAPHIC DETECTORS

To facilitate exobiology research in the extraterrestrial environment, improved methods and highly sensitive instrumentation must be developed for in situ chemical analyses of the volatile chemical species that occur in the atmospheres and surfaces of various bodies within the solar system. The development of new or improvement of existing sensitive, miniaturized detectors, with both selective and universal response, for gas chromatography (GC) is a fundamental part of improving and designing this type of future flight instrumentation.

The focus of our research into GC detectors has been the Metastable Ionization Detector (MID). When used with highly purified helium, the MID provides universal sample detection with part per billion (ppb) sensitivity. Commercial MIDs, commonly referred to as Helium Ionization Detectors, can have internal volumes over 300 µl and can respond to sample concentrations over only two to three orders of magnitude. In contrast, the Voltage Modulator for MIDs developed at Ames[1] adjusts the applied voltage to the MID and allows it to operate over a concentration range of over 10^6. The flight prototype MID developed from this research and currently used in our laboratory is shown in Fig. 1. This Miniature Triaxial design Metastable Ionization Detector (mini-MID),[2] has an internal volume of 180 µl and is the GC detector in an advanced and streamlined version of the Cometary Ice and Dust Experiment, (mini-CIDEX), of the Cometary Coma Chemical Composition (C4) Mission, a proposed Discovery-class Mission. Our research into smaller detectors has produced Microvolume MIDs (µMIDs) having internal volumes of 12 µl with still smaller ones being investigated. Although not currently part of a proposed flight instrument, the µMID has the same sensitivity as the mini-MID while using flow rates below 2 ml/min, and is compatible with the Voltage Modulator.

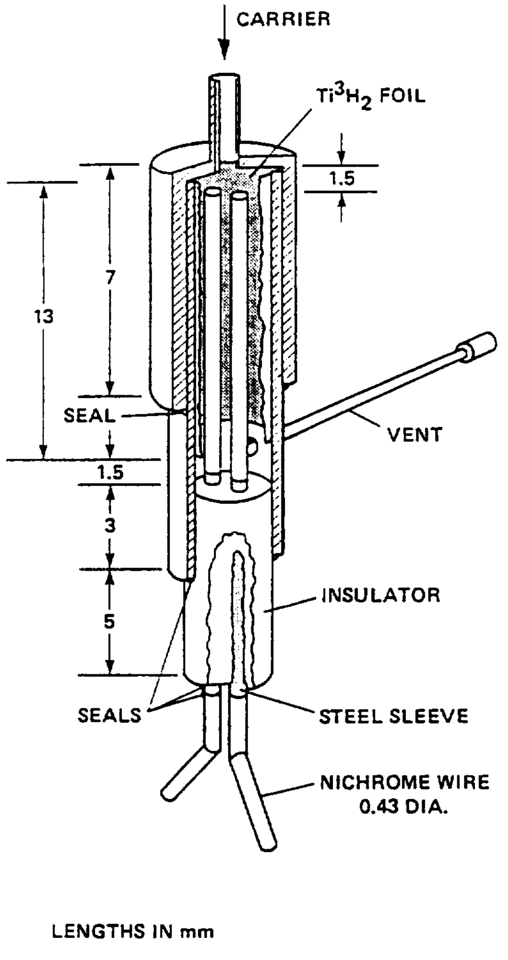

Fig. 1. Triaxial Mini Metastable Ionization Detector.

These detectors, although tiny, highly sensitive, with wide response range and universal response, do not provide any sample identification information other than the GC retention time. The complex mixtures that may be encountered by exobiology flight experiments can place a heavy burden on the chromatographic column(s) to provide resolution of all species present. A GC detector providing sample identification independent of GC retention time identification can reduce the number of columns required for a given analysis as well as increase the analytical capability of the instrument.

To fulfill this sample identification role, the Ion Mobility Spectrometer (IMS) is being developed for use as a flight instrument. The IMS is an ion reaction chamber coupled with an ion drift tube, all operated at or near a pressure of one atmosphere. Reactant ions, produced by the action of a radioactive source on the carrier gas, ionize sample molecules in the reaction region. Both reactant ions and any resultant product ions are admitted into a drift region through an ion gate. An electric field moves the ions through the drift region against the flow of a drift gas. The ions, separated by differences in structure and charge distribution, are detected at the end of the drift tube by a collecting electrode. The resultant ion intensities versus drift time data, the IMS spectra, are used to identify the sample. Fig. 2 shows an analysis of a mixture of ten hydrocarbons at concentrations in the low ppm range using the mini-CIDEX breadboard GC. The chromatogram in the center is the mini-MID response. Each GC peak is further identified by the IMS spectra shown in the surrounding boxes. This flight prototype IMS uses very high purity dry helium and employs a reaction region / drift tube that is 2 x 10 cm. Because conventional IMS systems use air or nitrogen drift gas, a helium-based IMS was a necessary development to enable compatibility with the GC columns and MIDs that use helium. The dry helium also allows detection of many molecules not previously detected by conventional IMS.[3]

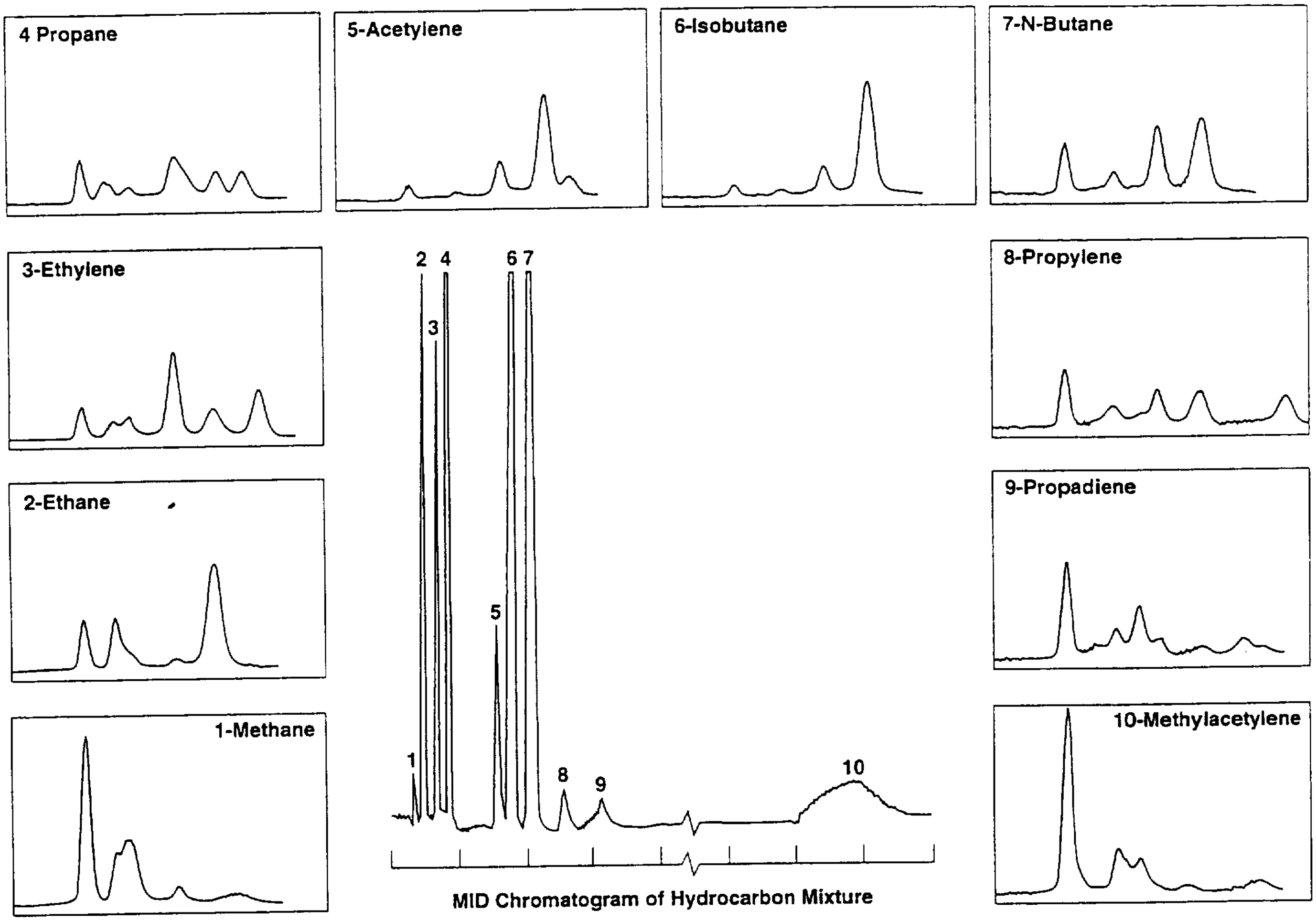

Fig. 2. Mini-CIDEX GC-IMS analysis of a 10-hydrocarbon mixture.

3. PYROSENSORS

Chemistry experiments aboard the Viking mission to Mars suggested that there may be oxidizing agents in the surface sediments of the planet. Such oxidants would be hostile to the preservation of organic matter and would thus inhibit the ability of primitive life to survive at the surface. Also, they would be detrimental to the preservation of the chemical signatures of extinct biota. Innovative solid-state sensors are being developed for a Mars flight instrument that would enable the detection of hydrogen peroxide -- a candidate oxidant species. The detectors are based on the following principles. If a material has internal electrical symmetry, it is generally neutral and lacks a permanent dipole. If it is asymmetric, e.g., water, it has a permanent electric dipole. Most asymmetric materials in bulk have a zero dipole effect because of a random or self-cancelling arrangement. Some asymmetric materials, however, maintain a net dipole orientation even in bulk. Heating such a material (within limits) does not randomize the dipoles, but instead rotates them in unison and thus produces a polarization.[4,5,6] Because this occurs in the absence of an external electric field, it is called a spontaneous polarization. A spontaneous polarization which is induced by heating is called the pyroelectric effect. In a pyroelectric device, a change in temperature creates a change in polarization. A pyroelectric device thus produces current only as it experiences a temperature change. When it is at a constant temperature, no current is produced.

A thin film of a pyroelectric material which has electrodes deposited on both faces is a pyroelectric sensor or pyrosensor. The electrodes gather charge, and because the material is a very good dielectric, the charge is unable to leak through the thin film. In its simplest form, the pyroelectric sensor is both a charge capacitor and a charge generator. There are two approaches using the pyroelectric principle for determination of chemical compounds in solution. In the first approach, the heat generated by an exothermal or endothermal chemical reaction is sensed by a pyrosensor. This allows for the continuous quantitative detection of some substances.[7,8] An example of this is the determination of peroxide concentration using catalysis of enzyme-coated polyvinylidene difluoride (PVDF).[9] PVDF film is commercially available and has outstanding pyroelectric response; a change of one degree Celsius gives an output of about 3V for a typical thickness of 25 µm.[10]

The second approach involves the use of laser light. The sample absorbs energy from the laser and the heat generated travels to the nearby sensor which is not in the path of the laser light. This heat creates an electric signal that is translated into an analytical concentration. This technique has been demonstrated for coccine, ß-carotene, MnO_4^-, Cd and Fe complexes which have all been excited by a laser and analyzed using pyrosensors.[11] This technique also has been applied to measurements of phosphorus (as PO_4^{-3}) and nitrogen (as NO_3^-) concentrations in natural waters. In the case of phosphorus, a detection limit of about 2 ppb was obtained.[12]

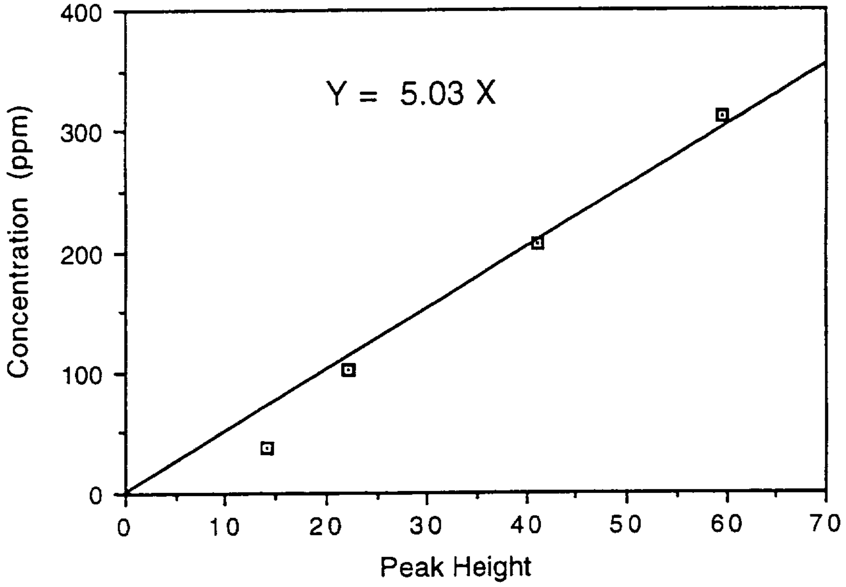

Fig. 3. Detection of hydrogen peroxide with the pyrosensor.

We have applied these approaches and design to construct our own pyrosensors.[13] The sensor provides a very stable baseline, and demonstrates that hydrogen peroxide concentration can be determined from 40 to 300 ppm with a reasonable calibration curve, as shown in Fig. 3. In recent collaboration with H. Coufal of IBM Almaden Research Center, the sensor was shown to be sensitive to 100 nJ of energy. Using this sensor, hydrogen peroxide concentrations can be detected as low as 1 ppm in a 50 µL sample size with 300 mV signal amplitude (a 30 mV signal can be obtained at 0.1 ppm level).

4. X-RAY INSTRUMENTATION

The X-ray instrument[14,15] under development is being designed primarily for Mars exploration and will provide a general compositional survey of both rock and soil materials at the surface of the planet. The instrument will utilize a Charge Coupled Device (CCD) detector to provide simultaneous X-ray fluorescence (XRF) and X-ray diffraction (XRD) data, thus enabling the acquisition of both geochemical and mineralogical information from the same sample. These data will address exobiology questions regarding the ancient hydrology of the planet through the detection of minerals and elemental abundances associated with evaporating ponded water, volcanologically-associated hydrothermal activity, and aqueous weathering processes.

To accommodate the mass, volume, ruggedness, heat flow, and power consumption constraints imposed by pending Mars missions, the X-ray instrument will utilize highly compact engineering configurations with miniaturized, solid-state components wherever possible. To accommodate the operational constraints of the lander platform (e.g., immobility or limited sample acquisition capability), the X-ray instrument is being designed to conduct analyses without the need to acquire a sample, or make any preparations of the analyzed material whatsoever. Normally, X-ray diffraction instruments require powdered materials for analysis in order to randomize the signal. In contrast, this device will simply be pressed up against a rock surface or pressed into the soil in order to conduct an analysis (taking typically one hour per analysis).

Development efforts have focused on 1) data analysis techniques and software development for acquisition of simultaneous XRF and XRD data from the single CCD detector, 2) innovative design configurations of the X-ray geometry to enable contact or proximal positioning between sample and instrument, 3) defining the analytical methods for extracting diffraction data from non-powdered, solid rock surfaces, and 4) engineering designs to ruggedize and miniaturize the instrument.

In fulfillment of this development effort, we have fabricated (with ARACOR of Sunnyvale, CA) a breadboard instrument[16] with compact sensor design and energy-efficient operational methods that are compatible with the flight environment (Fig. 4). The device is comprised of an iron target X-ray tube, a cadmium-109 isotopic source, and a CCD detector. During operation of the X-ray tube, the diffraction pattern and the fluorescence spectrum of the elements from silicon to chromium are collected simultaneously. The 10 mCi cadmium-109 source produces 22.2 KeV X-ray emission that will excite the K-shell emission of all elements below ruthenium (Z = 44) and the L-shell emissions through uranium (Z = 92). Diffraction data and fluorescence data are separated in the CCD detector by computer interrogation of the pixel array; diffraction events are detected by position for energies equal to the primary radiation, while fluorescence events are identified by their energy level. The X-ray tube has a maximum power rating of 9 W to keep the diffraction measurement under 4.5 hours (duration of a martian night). The output of the tube was filtered with a manganese K-edge filter to create an essentially monochromatic iron X-ray beam for both diffraction and fluorescence.

The CCD and the X-ray tube are configured in a non-scanning powder camera geometry with a radius of 3.8 cm. The CCD has a 512 x 512 array of 27 μm pixels. The CCD in current use does not have sufficient size to cover the desired angular range (corresponding to crystallographic d-spacings from 1.5 to 20 Å), and so the CCD is repositioned manually (a 1024 x 1024 array would suffice and will be incorporated in the near future). Although the breadboard utilizes powdered samples, we have demonstrated with commercial diffractometers that mineral identification can be accomplished on solid, unprepared materials. The breadboard is currently being reconfigured to include this capability.

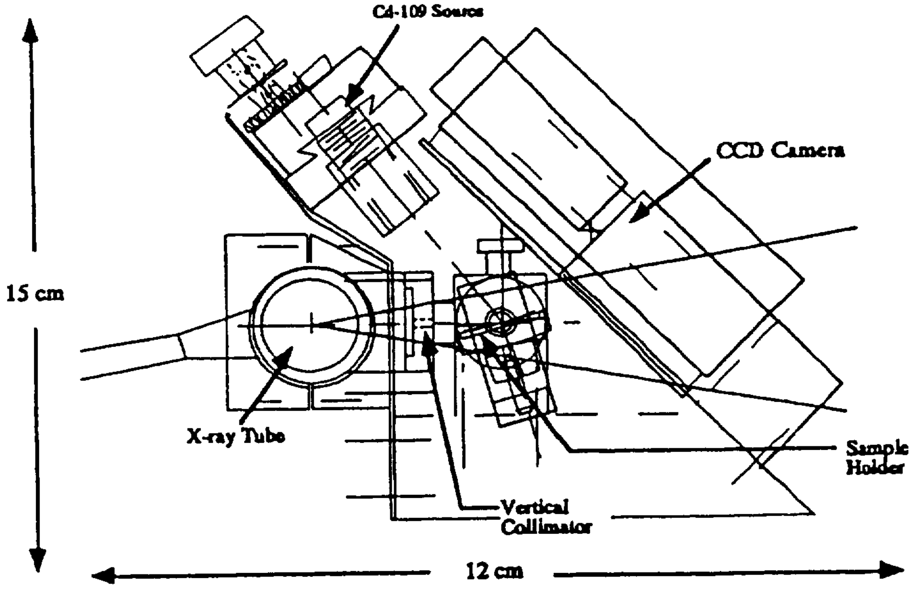

Fig. 4. X-ray instrument breadboard.

5. STABLE ISOTOPE LASER SPECTROMETER

A tunable diode laser spectrometer capable of accurately measuring isotopic ratios in soil samples is also being developed at Ames Research Center. This instrument, the Stable Isotope Laser Spectrometer (SILS),[17,18,19] will be able to measure isotopic ratios of carbon and oxygen in martian soils and rocks without the extensive gas purification procedures required in the conventional mass spectroscopic method. The study of the variations of the isotopic ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ on Earth has provided important information about Earth's biological and geological history. Similarly, the $^{13}C/^{12}C$ ratio may provide clues about an extinct martian biota and its influence on the planet's atmosphere and surface chemistry. The isotopic ratio $^{18}O/^{16}O$ in carbonates on Mars might be able to determine the temperature at which the carbonate was formed. This would provide a method of elucidating the thermal history of the planet's surface, a very important factor in assessing the ability of Mars to engender and support life. The SILS instrument, when on the surface of Mars, possibly in a robotic rover vehicle, will have the capability to perform step-wise pyrolysis of rock and soil samples retrieved from the planet's surface and accurately analyze the resulting carbon dioxide gas for its carbon and oxygen isotopic composition.

In order to assure meaningful and useful isotopic data, such measurements on Mars should be made to an accuracy of 0.1% or better. The differences in abundance for the isotopes of carbon (and oxygen) are large, resulting in significant differences in the absorbance of the various isotopic spectral bands. This absorption mismatch makes accurate measurement of the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios difficult. To overcome this difficulty, Wall, et al.[20] proposed to make absorption measurements of individual rotational lines in a spectral region where the ν_3 rovibrational bands of the isotopes overlap, and certain closely spaced isotopic absorption lines have approximately equal absorbance, thus minimizing measurement errors. A set of overlapping bands containing a group of isotopic spectral lines from $^{12}C^{16}O^{16}O$, $^{12}C^{18}O^{16}O$, and $^{13}C^{16}O^{16}O$ can be used for measuring ratios of both oxygen and carbon isotopes (Fig. 5). Other lines are visible in this region, including one from $^{12}C^{17}O^{16}O$ which, although separated from the $^{12}C^{16}O^{16}O$ line by only 0.02 cm^{-1}, is readily resolved because the laser linewidth is more than two orders of magnitude narrower than the gas absorption line.

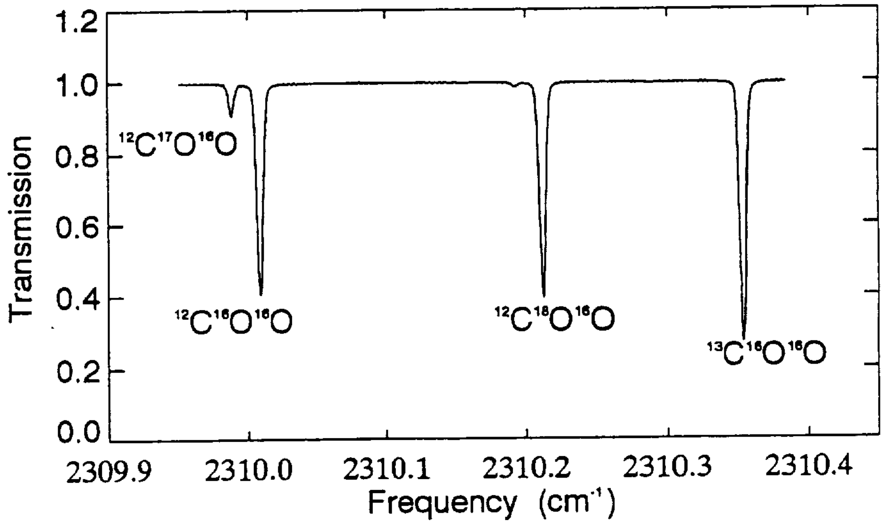

Fig. 5. Transmittance spectrum of CO_2 in the 2310 cm^{-1} region of the ν_3 vibrational bands showing absorption lines for various isotopic species.

The latest version of SILS is a four-beam, table-top instrument allowing simultaneous measurement of a sample of unknown isotopic composition, a known reference, measurement of the laser output, and a germanium etalon for frequency calibration and linearization. The light source is a buried heterostructure-type tunable diode laser fabricated using the molecular beam epitaxy (MBE) technique and composition-tuned to operate in the 2280 to 2380 cm^{-1} spectral region. Although the present laser operates continuous-wave at temperatures only up to 120 K, commercially available lasers[21] now operate at temperatures higher than 200 K, close to the average martian surface temperature. The instrument has not yet been miniaturized, but developments have been made with anticipation of eventual miniaturization; the laser light source and the detectors are lightweight, rugged, low power, solid-state devices which inherently lend themselves to instrument miniaturization. The pyrolysis oven and gas handling systems are similar to those developed for other space flight missions. Thus a miniature, reliable, lightweight instrument can be assembled and flown to accurately measure isotopic ratios on Mars. Isotopic ratio measurements for both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ have been made to a precision and accuracy of 0.1% and 0.2% respectively, values sufficiently small to provide important information for exobiologists, geologists, and planetary scientists.

6. DATA ANALYSIS TECHNIQUES

Concurrent with our instrument and sensor work, signal processing techniques are being developed to increase the amount of information obtained by analytical instrumentation onboard spacecraft under the time and data-rate restrictions imposed by missions. Development of these techniques goes hand in hand with the hardware development described in this paper. For example, techniques such as Fourier-transform analysis have been used to recover the chromatograms generated from Multiplex Gas Chromatography (MGC). Such computations allow the utilization of MGC to monitor changes in the composition of a sample while it is being acquired. The data analysis techniques developed have improved the dynamic range of MGC. One of the techniques being investigated at present utilizes the maximum entropy method; in this technique a model chromatogram of a given sample is computer-generated to create a "template." This template is compared with the actual GC output and the statistical significance of the approximated template is determined. This procedure is repeated with other templates until the one with the highest statistical confidence is produced. Such data analysis techniques and refinements will add a significant measure of analytical power and confidence to data returned from space-flight instruments.

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In-situ Polymerization PLOT Columns I: Divinylbenzene

T.C. Shen
SETI Institute, MS-239-12, Ames Research Center, Moffett Field, California 94035

Abstract

A novel method for preparation of porous-layer open-tubular (PLOT) columns is described. The method involves a simple and reproducible, straight-forward in-situ polymerization of monomer directly on the metal tube.

Introduction

In this paper, I describe a novel method for preparation of a porous-layer open-tubular (PLOT) column. This method uses straight-forward in-situ polymerization of monomer during the coating of the inside of the metal column. It is simple, reproducible, efficient, and eliminates many of the steps needed for conventional PLOT column preparation.

PLOT columns offer many advantages compared to packed or wall-coated gas chromatography columns (1–5). At this time, all PLOT columns are made either by static coating procedures (1,6,9), by dynamic coating procedures (1,10–12), or by a combination of static and dynamic coating procedures (13). In general, existing methods require that polymerization of monomers takes place in the first step. Polymers are then sieved to recover the size required for packing in columns. These methods are complicated and require special expertise and facilities. These difficulties and the resulting high cost have limited the application of PLOT columns. The method described in this paper accomplishes the polymerization and the coating of the column surface in the same step. The in-situ polymerization procedure allows for straight-forward preparation of a PLOT column in metal tubing. The important requirement in this technique is finding a suitable solvent system that provides suspension polymerization of the monomers and does not swell the polymers to any extent. The primary objective of this publication is to demonstrate a new method for preparing polymeric PLOT columns.

Experimental

Materials. 304 stainless-steel thin-wall tubing was used because of its low cost and the suitability of its surface properties. The tubing dimensions were 0.03-in. i.d. × 12-ft long with a 0.005-in. wall thickness. The tubing was washed with hydrochloric acid (20%), distilled water, methanol, and acetone, and dried with nitrogen sweep.

Chemicals. Divinylbenzene (95%) was obtained from Dow Chemical, azobisisobutylronitrile (AIBN) from PolyScience, methanol from J.T. Baker, and acetone from Aldrich Chemical.

Procedure. A mixture of methanol (3.010 g), divinylbenzene (0.543, 0.760, or 1.02 g), and AIBN (0.034 g) was added into the dried, coiled tubing through a glass funnel. Both ends of the tubing were capped with stainless-steel endcaps. The coil was slipped over a hollow metal cylinder and placed in an oven equipped with a mechanical rotation rod. The reaction temperature was set at 80°C. The coil was rotated at 15 rpm. After 7 h, the coil was cooled to room temperature and both ends were opened. The solvent was expressed with nitrogen at a low pressure of 10–20 psi. After the solvent was completely eliminated, the column was conditioned at 180°C for longer than 12 h.

Gas chromatographic evaluation. The column prepared from the in-situ polymerization method was installed in a gas chromatograph with a thermal conductivity detector (TCD). Helium carrier gas was utilized to demonstrate the separation of the gas mixture containing Ne (5760 ppm), CH_4 (528 ppm), CO_2 (1060 ppm), and N_2O (1580 ppm). The gas mixture was first introduced into a 1-µL loop, and then it was injected onto the column for analysis. The flow rate was 4.8 mL/min, and the operation temperature was 26°C.

Results and Discussion

The PLOT columns prepared from in-situ polymerization give very good separation of light gases, as demonstrated in Figure 1. As the divinylbenzene concentration increases, the separation efficiency also increases. At a divinylbenzene concentration of 25%, the separation efficiency of the PLOT column is almost as good as the packed column. Four columns were prepared and tested for reproducibility. The results are 34.3, 35.6, 34.8, and 34.7 for the capacity factor of N_2O with the respective number of plates at 4096, 4065, 4081, and 4088. The advantage of the PLOT column is that a lower concentration (ppb) and smaller sample can be detected using highly sensitive detectors than with a packed column. This is very important to a space mission.

In the course of this investigation, several solvents other than methanol were tried as diluents, e.g. ethanol, isopropanol, methylethylketone, ethylacetate, tetrahydrofuran, and heptane. In all cases except methanol, the columns became plugged, or the solidified polymer was extruded as solid cylindrical fragments (Figure 2). Only when methanol was used did the polymerization and coating of the wall occur in a way that the excess diluents could be easily expressed from the column, leaving the polymerization products coating the wall of the tube. The speed of the rotation of the cylinder in the oven was also investigated. It was found that the slow rotation was necessary for successful coating as a much higher rotation rate led to column plugging. While columns longer than 12 ft have been successfully made (for example, 15 ft), much longer columns have not been investigated using this technique. This technique has been found to be reproducible, and as indicated in Figure 1, some flexibility in the concentration of the polymerizable monomer in the mixture is allowable. Further investigation using the technique is being carried out with different column materials, i.e., nickel and Teflon® tubing.

Because it is already known that different monomers or monomer mixtures lead to polymers giving a wide variety of compound separations, various polymerizable monomers and monomer mixtures will be investigated using this new technique.

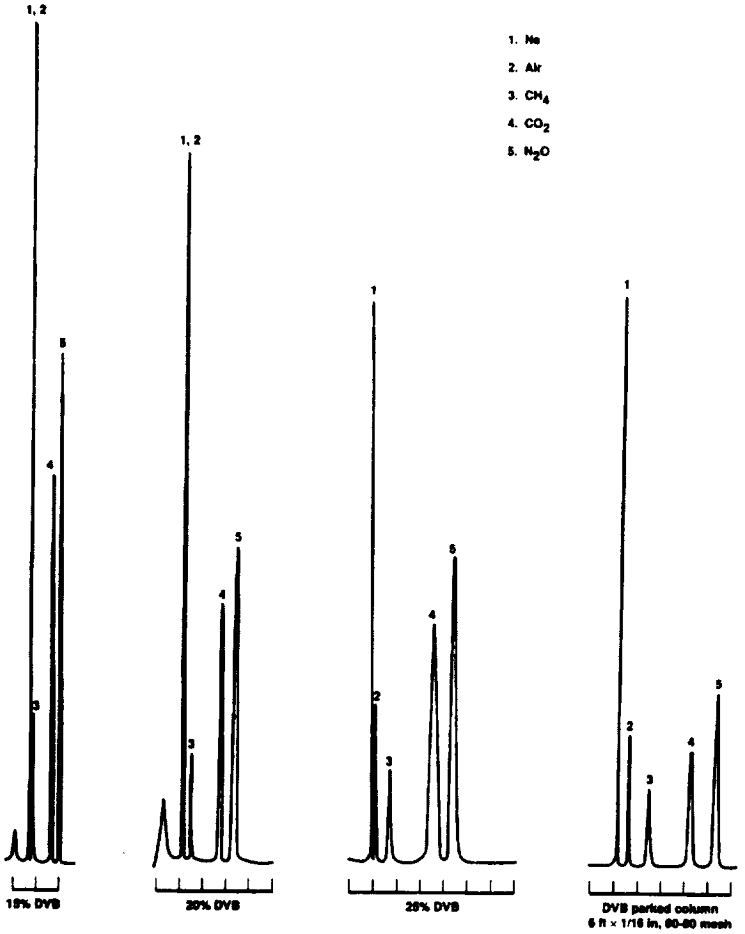

Figure 1. Separation of some light gases using various DVB PLOT columns and a packed column. (all columns operated at 26°C and 4.8 mL/min flow rate)

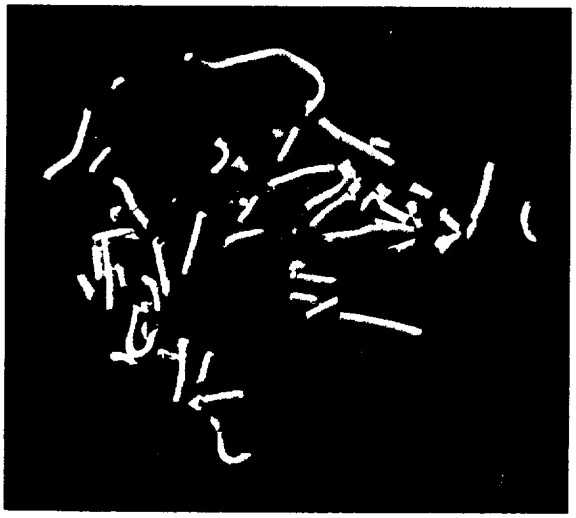

Figure 2. Example of polymerization materials obtained with diluents other than methanol.

Conclusion

A new method to prepare PLOT columns was developed. This method is so simple and reproducible that it may be very useful in preparing other types of PLOT columns.

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