Gas Separations: A Comparison of GasPro™ and Aluminum Oxide PLOT Columns for the Separation of Highly Volatile Compounds

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Gases and highly volatile compounds (such as the light hydrocarbons) are most frequently analyzed by gas-solid chromatography (GSC). Recently, the first new concept in GSC stationary phases in nearly two decades was introduced. It separates a wide variety of inorganic and organic gases and volatile compounds. A comparison is made between the conventional doped aluminum oxide capillary column and the GasPro porous layer open tubular column. Both effectively separate light hydrocarbon mixtures; however, there are selectivity differences between these two columns. Several examples are given. The GasPro column is not adversely affected by H_2O, CO_2 *or sulfur gases. It also appears to be more inert than aluminum oxide columns since it does not cause the decomposition of most reactive analytes.*

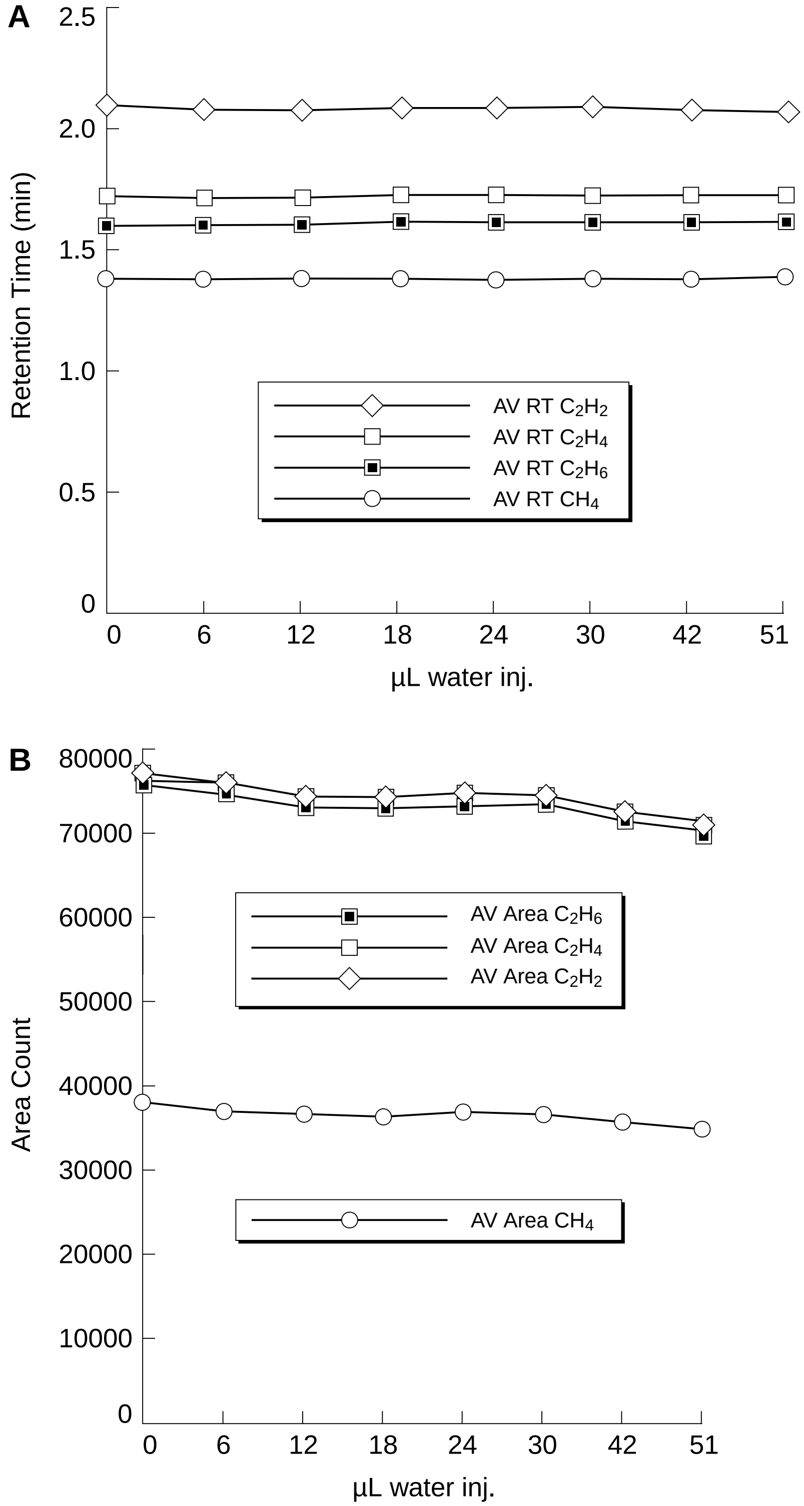
Capillary gas chromatography (GC) is one of the most important, efficient and sensitive analytical techniques available for the analysis of volatile compounds. GC separations can be classified according to the state of the stationary phase used. Gas-liquid chromatography (GLC) has a liquid stationary phase film either coated or bonded to a support. The analyte is partitioned between the gas mobile phase and the liquid stationary phase. Unfortunately, gases and many other highly volatile, nonpolar compounds do not associate appreciably with most liquid stationary phases. Therefore, these analytes tend to elute rapidly with little or no retention. The only GLC columns that separate light hydrocarbons, for example, are very long (often > 100 m) and/or have thick stationary phase films. Gases and highly volatile compounds tend to be retained (adsorbed) to a greater extent on active solid surfaces. Hence, gas-solid chromatography (GSC) uses specific solid stationary phases to retain and separate analytes that are not appreciably retained with GLC columns. Conversely, compounds of moderate to low volatility, that are nicely separated with GLC, tend to be very highly or irreversibly retained and display inefficient separations with GSC. Also, solid stationary phases can sometimes cause catalytic decomposition or react with more labile or sensitive analytes. GSC stationary phases have been reviewed recently (1-3).

The nature and availability of solid stationary phases for GSC separations hasn't changed much until recently. Aluminum oxide-based columns (usually deactivated with various salts to increase efficiency and reduce tailing) were most frequently used for the separation of light hydrocarbons (1-3). Molecular sieves were used mainly to separate argon, oxygen, nitrogen and carbon monoxide (4,5). Porous polymer-based columns were also available for the separation of some light hydrocarbons, polar solutes and some solvents (6). Contaminants such as H_2O and CO_2 strongly adsorb to the first two types of GSC stationary phases and can interfere with, or alter the separation of other gases and volatile analytes (1-5).

Recently, we developed a broadly applicable GSC capillary stationary phase that utilizes a novel porous layer deposition system (1,7,8). The original impetus for developing this stationary phase was the need for a widely useful PLOT column which could be used for the direct injection of real world samples, such as automobile ex-

F1

Effect of injected water on the (A) retention and (B) peak areas of methane, ethane, ethylene and acetylene on a 30 m x 0.32 mm (ID) GasPro GSC column. The carrier gas was N_2 at 40 cm/sec, a split ratio of 1:34, oven temperature was 85 °C, isothermal.



haust (7), halocarbon mixtures (8), propellants and so forth. Consequently, the solid adsorbent could not excessively retain or be adversely affected by water vapor, carbon dioxide or sulfur gases. Also, it should not catalytically decompose or otherwise react with labile compounds. Finally, the selectivity should be equivalent to or better than existing GSC stationary phases. In this work we compare the GasPro™ PLOT column with the well-known aluminum oxide PLOT column using a variety of light hydrocarbons and gases.

Experimental

Instrumentation

A Hewlett-Packard (Avondale, PA, USA) 5890 Series II gas chromatograph equipped with a split/splitless injection port and flame ionization and thermal conductivity detectors was utilized in this study. The injector and detector ports were set at 200 °C. The oven temperature program is given in the caption of each figure. Data collection was accomplished with a Hewlett-Packard 3396B Series II integrator. Helium was used as the carrier gas for all separations unless noted otherwise in the individual figures. The flow rates and split ratios were 1.5 mL/min and 1:80, respectively, unless noted otherwise in the figures. Flame ionization detection (FID) was used unless otherwise noted in the individual figure captions. Hamilton gas tight syringes were used for all injections.

Chemicals and Columns

All hydrocarbons and halocarbons reported in this work were obtained from Aldrich Chemical Company, (Milwaukee, WI, USA). Inorganic gases were obtained from Scotts Specialty Gases (Plumsteadville, PA, USA). The columns used were the GasPro GSC Capillary (PLOT) Column (either 15 m x 0.32 mm, ID or 30 m x 0.32 mm, ID) from Advanced Separation Technologies (Whippany, NJ, USA) and the Aluminum Oxide·KCl PLOT column (50 m x 0.53 mm) from Chrompak (Raritan, NJ, USA). The natural gas sample was obtained from Columbia Gas Distribution Company (Columbus, OH, USA).

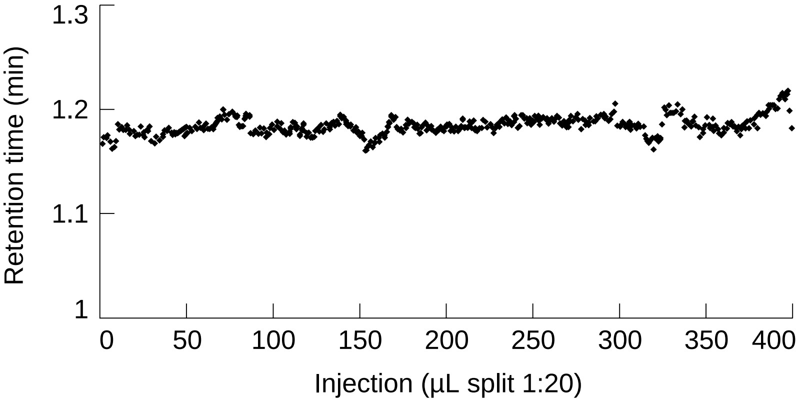
Results and Discussion

Effect of H_2O and CO_2

Water vapor and carbon dioxide are ubiquitous in nature. It is well-known that both water and carbon dioxide interact strongly with aluminum oxide PLOT col-

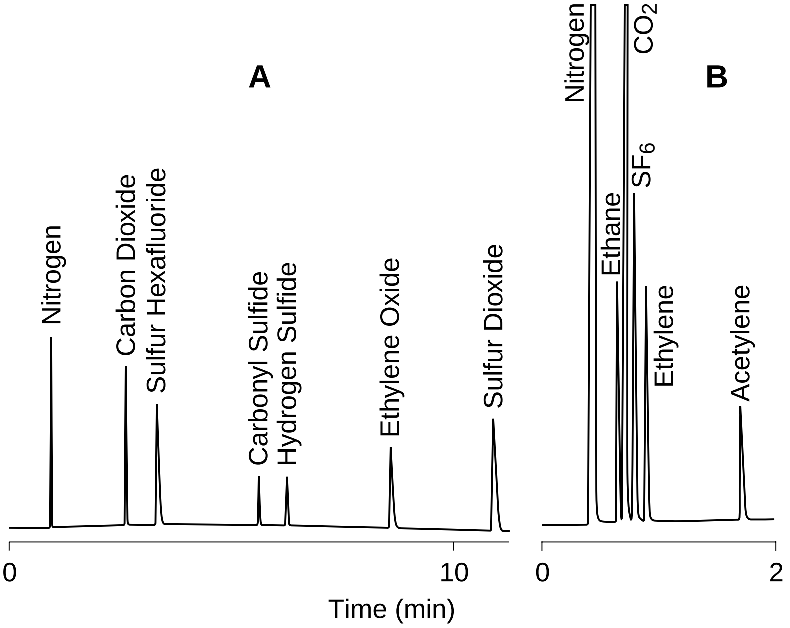
F2

A plot of the retention time of acetone vs. the number of injections of a 100 ppm acetone in water solution on a 5 m x 0.32 mm (ID) GasPro GSC column. The carrier gas was He and the split ratio was 1:20.



F3

(A) GSC separation of carbon dioxide and ethylene oxide from several sulfur gases on a 15 m x 0.32 mm (ID) GasPro GSC Column. The carrier gas was He at 30 cm/sec. The oven temperature was held at 25 °C for 3 min and then ramped at 10 °C/min. TCD detection was used. (B) GSC separation of carbon dioxide and sulfur hexafluoride from ethane, ethylene, acetylene and nitrogen on the same GasPro column. This was an isothermal separation (30 °C) with TCD.



T1

Hydrocarbon elution order comparison on PLOT columns: GasPro GSC, styrene-Al_2O_3/KCl and divinyl benzene (least retained to most retained).

GasPro GSC	Al_2O_3/KCl	SDVB
methane	methane	methane
ethane	ethane	ethylene
ethylene	ethylene	acetylene
acetylene	propane	ethane
propane	propylene	propylene
propylene	acetylene	propane
isobutane	isobutane	propyne
butane	butane	isobutane

umns thereby altering the retention, selectivity, efficiency and peak areas of other analytes (1-3). When using GSC columns that are sensitive to or affected by these compounds, special pre-separations must be done to exclude them from the sample. It would be beneficial to be able to directly inject samples onto a GSC column without having to remove or to take into account for the effects of H_2O and CO_2 on the separation. At times it is also useful to quantitate H_2O and CO_2 in mixtures of other gases or light hydrocarbons.

F1 (previous page) shows the affect of repetitive injections of water on the retention and peak areas of methane, ethane, ethylene and acetylene separated on a 30 m GasPro PLOT column. The slight point to point variations in peak areas are a result of typical experimental errors associated with manual injections. ***F2*** shows the results of a more extensive test in which 400 successive 1 µl aliquots of 100 ppm aqueous acetone samples were injected on a short 5 m GasPro column. It appears that even the repeated direct injection of water does not affect the column and does not significantly affect the separation of other volatile analytes. This confirms a previous report where it was observed that the water vapor in automobile exhaust did not appear to interfere with the separation and quantitation of the other exhaust compounds (7).

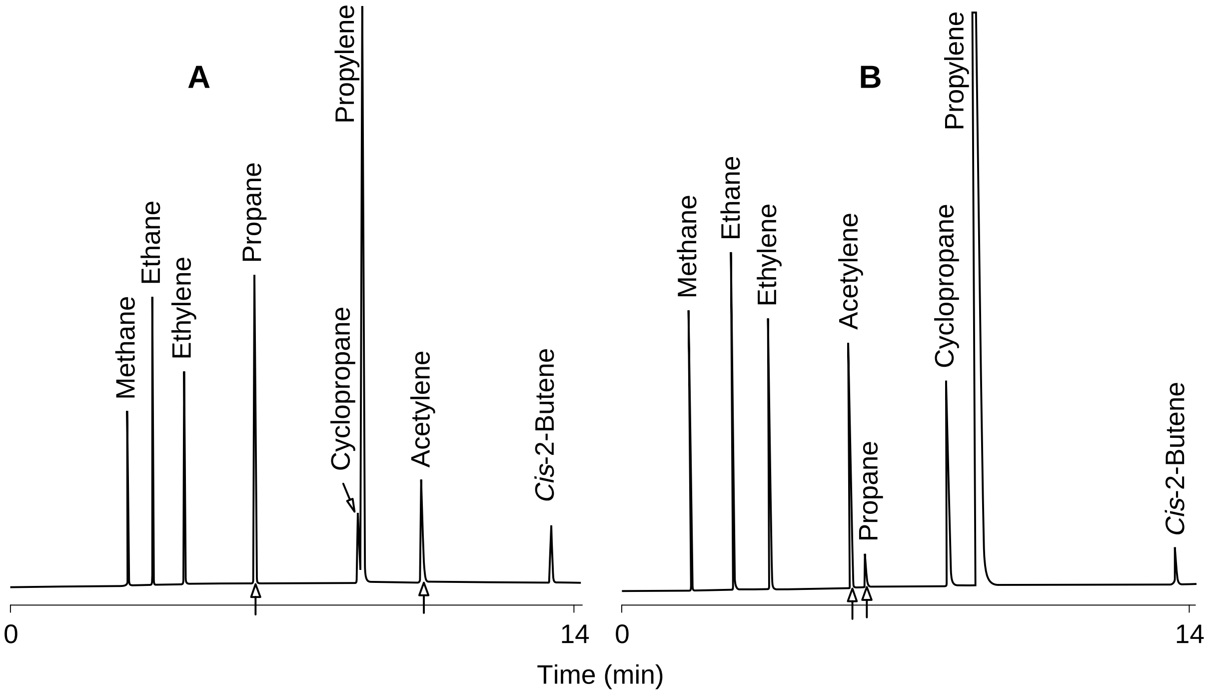
Unlike aluminum oxide and some other highly active GSC stationary phases, carbon dioxide is not strongly or irreversibly adsorbed on the GasPro PLOT Column. In fact, it tends to elute at relatively low temperatures as a sharp peak with little tailing. This is shown in ***F3A*** where CO_2 and ethylene oxide are separated from several sulfur containing gases and in ***F3B*** where CO_2 is separated from hydrocarbon gases and sulfur hexafluoride. Also, note that this is one of the few GSC columns that effectively separates all manners of sulfur gases.

Selectivity

The doped aluminum oxide PLOT column is widely used for the separation of light hydrocarbons. The selectivity of the GasPro and aluminum oxide columns is somewhat different for these compounds. This can be seen in ***T1***, which gives the relative retention order of some of the light hydrocarbons. The main difference is in the

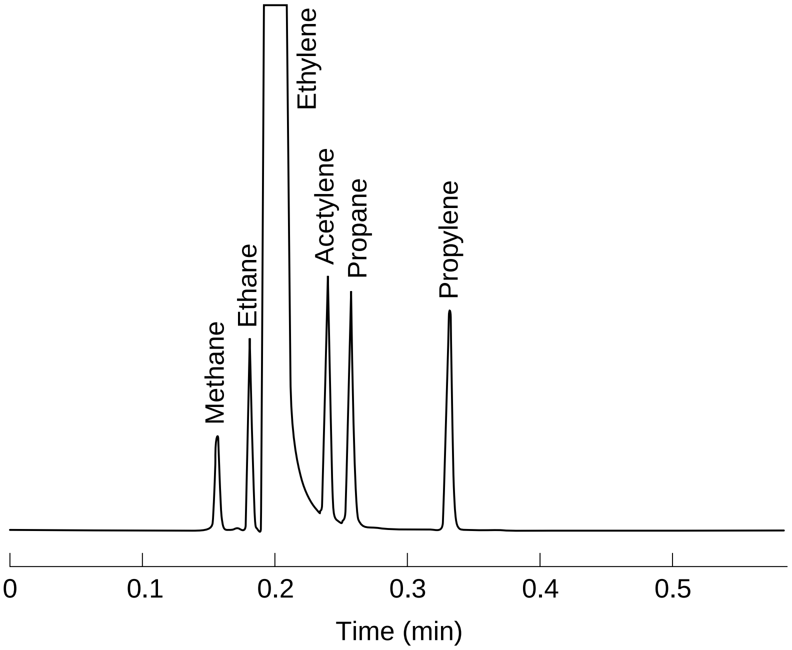
F4

A comparison of the selectivity on (A) 50 m aluminum oxide, vs. (B) 30 m GasPro GSC columns for the separation of propylene from its associated hydrocarbon impurities. In both cases, nitrogen was the carrier gas at 29 cm/sec. The temperature program was 40 °C for 3 min for Al_2O_3 (and 2 min for GasPro) followed by an increase of 10 °C/min and then held at 200 °C.



F5

Fast GSC separation of ethylene from its associated hydrocarbon impurities on a 5 m x 0.32 mm ID GasPro column.



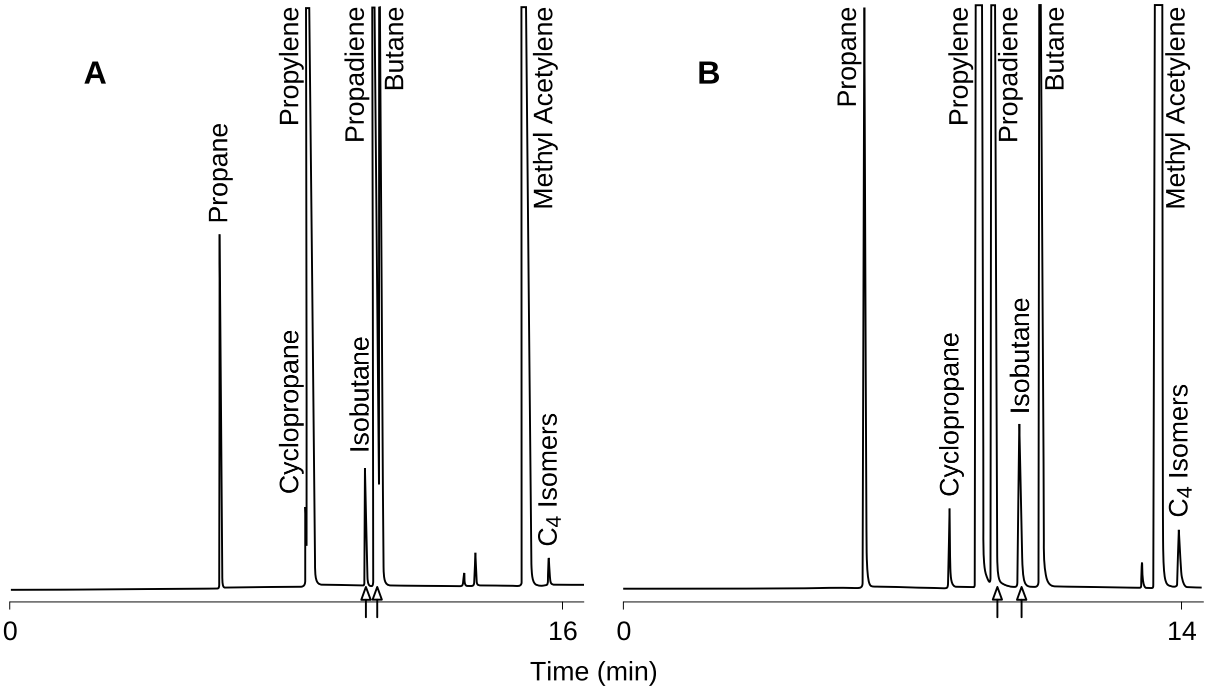
retention of alkynes compared to other hydrocarbons. Unsaturated compounds in general and alkynes in particular are more strongly adsorbed on aluminum oxide stationary phases. Hence, acetylene elutes just before butane on the aluminum oxide PLOT column. However, all C_2 hydrocarbons (including acetylene) elute before any of the C_3 hydrocarbons on the GasPro PLOT column.

When analyzing complex multicomponent mixtures, there are usually overlapping peaks. This can be a problem if the analyte of interest is one of the overlapped peaks. Having another column of different selectivity frequently allows one to isolate the peak of interest. An interesting example of this is shown in ***F4***. Propylene starting material, used in the manufacture of the polymer polypropylene, contains several hydrocarbon impurities. The type and concentrations of these unwanted hydrocarbons can affect the polymerization process, and therefore the polymer product. Consequently, the composition of the starting material must be known and controlled. ***F4A*** shows the separation of propylene, plus the associated hydrocarbon impurities, on a doped aluminum oxide PLOT column. ***F4B*** shows the separation of the same mixture on a shorter GasPro column. Note that on the aluminum oxide column, propylene and cyclopropane are overlapped. However, they are more than adequately resolved on the GasPro column. Also, note the aforementioned relative position change of acetylene in the two chromatograms. ***F5*** shows an analogous separation of hydrocarbon impurities in synthetic ethylene (which is used in the production of polyethylene). By using a short column and higher flow rates, the entire analysis can be completed in approximately 20 seconds.

Another example of hydrocarbon selectivity differences between the GasPro and aluminum oxide PLOT columns is shown in the analysis of MAPP gas (***F6***). MAPP

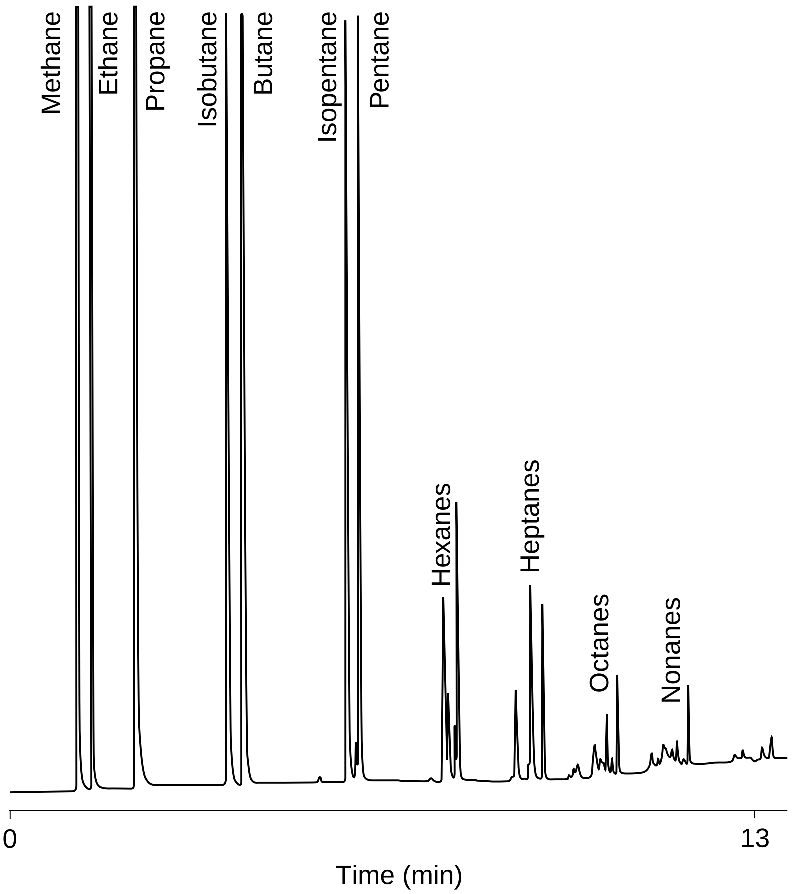
F6

A comparison of the separation of MAPP gas on (A) a 50 m aluminum oxide vs. (B) a 30 m GasPro GSC column. Note the selectivity differences and the overlapping peaks in chromatogram A. In both cases, nitrogen was the carrier gas at 29 cm/sec. The oven temperature was held at 40 °C for 2 min on GasPro (and 3 min on Al_2O_3) and then increased at 10 °C/min until 200 °C.



F7

GSC separation showing the composition of a sample of natural gas from the Columbia Gas District Co., Columbus, Ohio. The separation was done on a 30 m x 0.32 mm (ID) GasPro column with helium carrier gas at 42 cm/sec and a split ratio of 1:20. The oven temperature was held at 75 °C for 2 min and then increased at 20 °C/min until 260 °C.



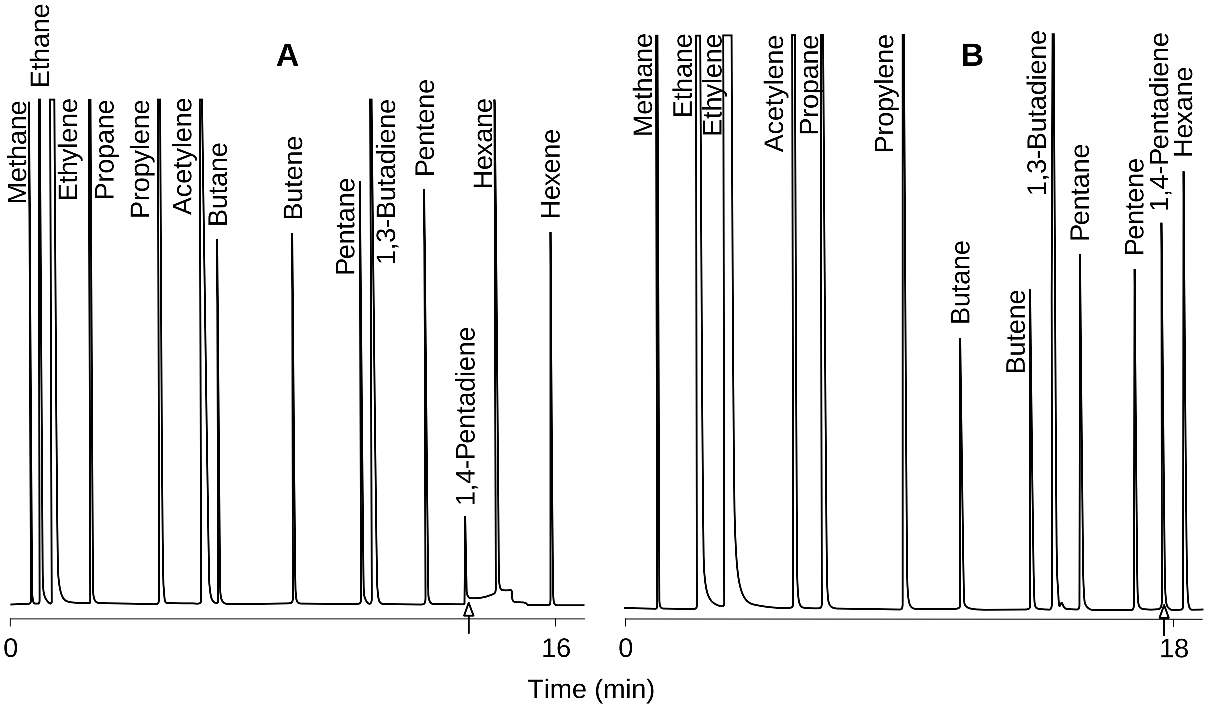
gas is used in high temperature torches because it burns at a higher temperature than propane. MAPP gas (an acronym that stands for: methylacetylene, propylene, propadiene) is a mixture of 56% liquid petroleum gas and 44% methyl acetylene. Note that in the ***F6A*** chromatogram (aluminum oxide column) isobutane elutes prior to the overlapping peaks of propadiene and butane. However, in ***F6B*** (GasPro column) the propadiene and butane peaks are well-resolved with isobutane eluting between the two. ***F7*** shows the composition of a natural gas sample from Columbia Gas as determined on a 30 m GasPro PLOT column.

Decomposition of Analytes

Highly active, strongly adsorbing stationary phases are often needed in order to retain and separate gases, as well as highly volatile, nonpolar compounds. However, at the temperatures used in GSC, these stationary phases can also react with or cause the decomposition of labile or somewhat reactive compounds. ***F8*** illustrates one such case. The compound 1,4-pentadiene is a component of “Crack” gas. When the components of “Crack” gas are separated on an aluminum oxide PLOT column, 1,4-pentadiene catalytically decomposes (***F8A***). Consequently, it cannot be accurately quantitated, and also can interfere with the quantitation of other components (e.g., hexane). However, decomposition of

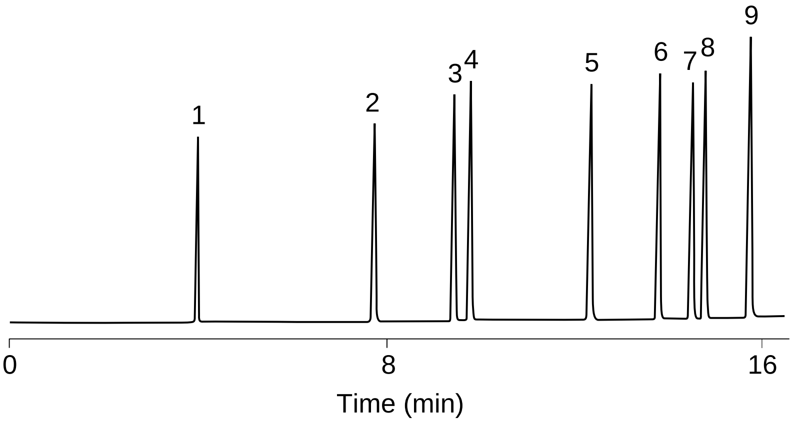
F8

A comparison of the separation of “Crack” gas on (A) 50 m aluminum oxide, vs. (B) a 30 m GasPro thick film column. Note the relatively small peak height and tailing of the 1,4-pentadiene peak that only occurs in chromatogram A. This is due to the decomposition of this component on the Al_2O_3 stationary phase. In both chromatograms He was used as the carrier gas at 15 psi. The oven temperature was held at 40 °C for 2 min and then increased at 10 °C/min to 200 °C.



F9

GSC separation of some hydrogen substituted halocarbons:
1. CHF_2Cl (bp=-40.7),
2. $CHFCl_2$ (bp=8.9),
3. CH_3I (bp=42-3),
4. CH_2Cl_2 (bp=40),
5. $CHCl_3$ (bp=61),
6. CH_3CH_2I (bp=70),
7. CH_2Br_2 (bp=96-8),
8. $CHCl_2$ (bp=87),
9. $CHClBr_2$ (bp=119-20), on a 30 m x 0.32 mm ID GasPro column. No dehydrohalogenation occurs during the separation. The temperature program was: 130 °C isothermal for 4 min, then increased at 10 °C/min to 225 °C.



this compound does not occur on the GasPro PLOT column (***F8B***) making quantitation possible. Note that when identical samples are injected, the relative peak size of 1,4-pentadiene in ***F8B*** is greater and there is no peak distortion or tailing.

Reaction and decomposition of certain halocarbon compounds also are known to take place on aluminum oxide columns (9,10). Halocarbons are widely used as refrigerants, propellants, inhalants, asthma remedies and anesthetics. The use of most of these chlorofluorocarbons (CFCs) is being restricted because of their potential damage to the Earth’s ozone layer. CFC replacement compounds contain additional hydrogen substituents. These replacement CFCs are often referred to using the acronym: HCFC (for hydrochlorofluorocarbons). HCFCs are less inert than CFCs and currently are thought to be less of a hazard to the ozone layer. Because of their greater reactivity, the HCFCs and HFCs undergo dehydrohalogenation reactions on aluminum oxide PLOT columns (9,10). Therefore, they cannot be quantitated accurately. Fortunately, the GasPro PLOT column is much more inert and effectively resolves the “replacement” CFCs without inducing dehydrohalogenation (see ***F9***). Indeed, a previous report showed that standard curves for HCFCs were linear for more than three orders of magnitude of concentration (8).

Conclusion

Acknowledgement

The GasPro™ PLOT column is the first completely new concept in GSC stationary phases in over 15 years. It has wider selectivity than any other existing PLOT column. Its selectivity is also unique when compared to aluminum oxide and porous polymer PLOT columns. Neither water, carbon dioxide nor sulfur gases irreversibly bind to, or otherwise affect the column or other analytes being separated on it. Although the GasPro column strongly retains a variety of gases and volatile compounds, it is relatively inert compared to aluminum oxide-based PLOT columns. Hence, compounds that undergo reactions or catalylic decompositions on Al_2O_3 are easily resolved and quantitated on the GasPro™ PLOT column.

Support of this work by the Environmental Protection Agency

(No. R823360-01-0) is gratefully acknowledged.

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