Guidelines for the Selection of PLOT Columns for Petrochemical / Chemical Applications

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ABSTRACT

Carbons, porous polymers, and other adsorbents have been used for decades for Gas-Solid Chromatographic separations. The choice of adsorbent properties (physical characteristics and surface chemistry) depends on the properties of the analytes to be separated. The evolution of GSC to incorporate these adsorbents into Porous Layer Open Tubular columns (PLOT columns) with relatively small diameters has considerably improved resolution for key analytes requiring GSC for effective chromatographic separations.

Fused silica PLOT columns have been coated with carbon molecular sieves, zeolite molecular sieves, porous polymers, and activated alumina adsorbents. Each of these adsorbents offers a unique selectivity for the separation of petrochemical and chemical samples. We will demonstrate the selectivity of the various PLOT columns with a variety of petrochemical samples and provide guidelines for the appropriate PLOT column selection based on the sample type.

INTRODUCTION

Carbons, porous polymers, and other adsorbents have been used for decades for gas-solid chromatographic separations (GSC separations). The choice of adsorbent properties (physical characteristics and surface chemistry) depends on the properties of the analytes to be separated. The evolution of GSC to incorporate these adsorbents into porous layer open tubular columns (PLOT columns) with relatively small diameters has considerably improved resolution for key analytes requiring GSC for effective chromatographic separation.

A family of PLOT columns has been prepared and evaluated on the basis of the characteristics of the adsorbents and of the analytes of interest for this study. Both fused silica and stainless steel tubing have been used in preparing columns coated with carbon molecular sieve, zeolite molecular sieve, porous polymers, and activated alumina adsorbents.

ADSORBENT CHARACTERIZATION

Adsorbents can be characterized according to size, shape, porosity, surface area and surface chemistry. Table 1 summarizes important physical characteristics of the adsorbents used to prepare the PLOT columns evaluated in this study.

Table 1

PLOT COLUMN ADSORBENTS

Adsorbent Description	Surface Area	Particle Shape	Particle Size	Adsorbates
Carboxen-1010	800m^2/g	Spherical	2- 3µM	Permanent gases/light hydrocarbons
Carboxen-1006	725m^2/g	Spherical	2- 3µM	Permanent gases/light hydrocarbons
Supel-Q porous polymer	700m^2/g	Spherical	2- 3µM	C1 to C12 hydrocarbons
Zeolite molecular sieve	500m^2/g	Granular	1-10µM	Volatile to semivolatile gases
Activated alumina	250-350m^2/g	Granular	1-10µM	Permanent gases

The choice of which adsorbent/PLOT column to use depends entirely on the analytes to be separated and quantified. In general, the smaller (i.e., molecular size, molecular area, vapor pressure) the analyte, the stronger the adsorbent must be for effective separation and chromatographic distillation. Strength of adsorbent is typically characterized by surface area, where the larger the surface area the stronger the adsorbent. However, this general concept is misleading, and more recent characterizations suggest that above a surface area value of approximately 1000m^2/g, the adsorbent strength begins to decrease as the micropore diameter increases. The reason for this is that BET (Brunauer, Emmett and Teller) surface area measurements[1] are typically performed using a porosimeter instrument with nitrogen (or argon, or krypton) as the probe/test molecule, and pores possessing diameters below approximately 20Å become filled with nitrogen. Therefore, the surface area measurement/value of any microporous region is not actually the surface area value, but instead the micropore volume. Therefore, surface area values provided for porous solids possessing multiple pores are actually macropore (> 500Å) and mesopore (20-500Å) surface area values plus the micropore pore volume. What is more important to measure is the micropore diameter, or micropore diameter range, to determine adsorbent strength when deciding to use adsorbents possessing micropores. This measurement is typically accomplished using porosimetry software programs [i.e., t-plot measurements and/or density functional theory (DFT) plots]. Typically, any porous solid possessing a surface area value above approximately 250m^2/g possesses some microporosity. Therefore, if larger molecules (i.e., C4-type molecules or larger) are the chosen analytes, then mesoporous and macroporous adsorbents are effective for proper separation and chromatographic distillation. Also, the surface chemistry of the adsorbents/analytes must always be considered when selecting the proper PLOT column.

The following descriptions of the PLOT columns have been ranked according to adsorbent pore strength (i.e., strongest to weakest). Surface chemistry will be discussed for each of the adsorbents.

COLUMN PREPARATION

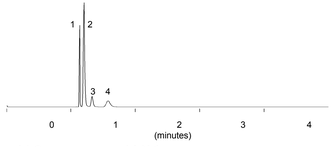
Preparation of the PLOT columns, using the various adsorbents, incorporates a proprietary patented adhesive technology through which the adsorbent particles are immobilized, or cemented, to the wall of the capillary column, whether the surface is fused silica or metal. The adhesive also bonds the particles to one another; therefore there is no loss of particles during routine analyses or rapid temperature programming. A significant feature of the adhesive is its high temperature limit, greater than 360°C, which makes the operating temperature limit of the column a function of the particles used, not a function of the adhesive.

Column preparation also is optimized to ensure that the adhesive does not interfere with the pores in the particles. This, in turn, ensures that analyte molecules are transferred, unrestricted, to the internal micropores in the particles, and that there is no adverse effect on the external-working surface in activated alumina columns.

Mol sieve 5 Å

The mol sieve 5Å PLOT column possesses a granular zeolite (aluminosilicate) which possesses the strongest adsorption strength (for the PLOTs discussed here), and therefore is typically used for the separation of permanent gases (see Chromatogram 1, below). This PLOT is effective for the separation of oxygen, nitrogen, hydrogen, carbon monoxide and methane. The separation of oxygen and argon can be accomplished if a thick film (i.e., ≥ 50 µM) PLOT column is used. Since the surface chemistry of this mol sieve (aluminosilicate) is hydrophilic, the presence of water and/or carbon dioxide will strongly adsorb to the inner pore walls, and begin to reduce the pore capacity of the PLOT column resulting in a decrease in analyte retention. If water, carbon dioxide and/or other larger molecules are introduced into the PLOT column, then removal of these pore/surface contaminants must be routinely performed by thermal conditioning of the columns at temperatures between 280°C and 320°C for extended times. Note the surface area of this porous solid is relatively small compared to the carbons and porous polymer. This comparison will be discussed below.

Chromatogram 1 : Illustrates the separation strength of the 5Å zeolite molecular Sieve
: 65°C isothermal; He flow = 10.0mL/min, TCD



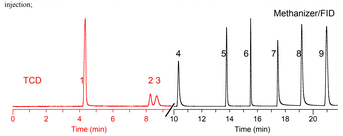
peak 1. Oxygen
peak 2. Nitrogen
peak 3. Methane
peak 4. Carbon monoxide

Carboxen-1010

Carboxen ™-1010 is a synthetic, spherical carbon molecular sieve (2-3 µM particle diameter) with a monoporous, microporous 7Å pore structure. The 2Å increase in pore diameter and the increased number of pores are both responsible for the surface area increase from the zeolite mol sieve 5Å to the 7Å carbon molecular sieve. A small amount of mesopores, present at the particle surface allow for improved access of the analytes to the microporous region where the actual separation work is performed. Also, the 7Å pores allow for effective separation of oxygen and nitrogen as well as larger molecular sized analytes up to propane. For this reason, the working range of this carbon molecular sieve is significantly greater than the zeolite mol sieve 5Å. Since the surface of the carbon sieve is hydrophobic, the strong adsorption of water, present with the zeolite, is not a factor with the Carboxen-1010. Therefore, no retention time shifts occur, and no thermal conditioning is necessary for this column. Chromatograms 2-4 illustrate the performance of this sieve.

Chromatogram 2: Transformer Gas Analysis for ASTM Method D3612-96

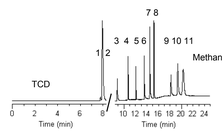
GC oven conditions: 35°C (7.5 minutes) to 250°C at 24°C/minute; Argon flow = 3.0 mL/min.; direct valve injection;



peak 1. Hydrogen (500ppm)
peak 2. Oxygen (500ppm)
peak 3. Nitrogen (500ppm)
peak 4. Carbon monoxide (500ppm)
peak 5. Methane (500ppm)
peak 6. Carbon dioxide (500ppm)
peak 7. Acetylene (500ppm)
peak 8. Ethylene (500ppm)
peak 9. Ethane (500ppm)

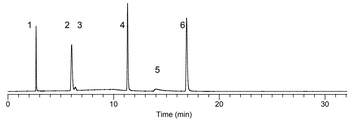
Chromatogram 3: Transformer Gas Analysis for ASTM Method D3612-96 (Expanded)

GC oven conditions: 35°C (7.5 minutes) to 250°C at 24°C/minute; He flow = 3.0 mL/min to 10 mL/min. at 225°C; direct valve injection



Peak Identification
1. Oxygen
2. Nitrogen
3. Carbon monoxide
4. Methane
5. Carbon dioxide
6. Acetylene
7. Ethylene
8. Ethane
9. Methyl acetylene
10. Propylene
11. Propane

Chromatogram 4 : Chromatographic separation of Noble gases
: GC oven temperature: 35°C (6 minutes) to 225°C at 24°C/min; TCD

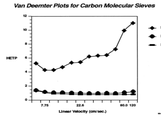


peak 1. Neon (10ppm)
peak 2. Argon (10ppm)
peak 3. Nitrogen (impurity)
peak 4. Krypton (10ppm)
peak 5. Water (impurity)
peak 6. Xenon (10ppm)

Carboxen-1006

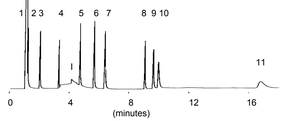
Carboxen ™-1006 is a synthetic, spherical carbon molecular sieve (2-3µM particle diameter) with a multiporous pore structure. The presence of large macropores and mesopores allow for effective access of the 7Å micropores for fast kinetics applications. The van Deemter plots for spherical carbons with varying pore structures is illustrated below in Figure 1.

Figure 1
Van Deemter plot comparisons for microporous, meso-/microporous and macro-/meso-/microporous spherical carbon molecular sieves



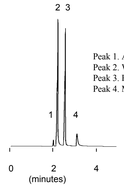
This plot illustrates the efficiency of a multiporous carbon throughout a wide velocity range. Since the velocity of an analyte does not change from the interstitial space to a macropore, maximum pore access is achieved with the Carboxen-1006. Also, since the analyte velocity in a micropore is reduced by a factor of 100-1000 cm/second relative to the interstitial space[2], poor efficiency/capacity can occur without the presence of these pores which transport the analytes from the interstitial space to the working pores. In combination, the large microporous region and large surface area, 725 square meters per gram, ensure effective separations of permanent gases and light hydrocarbons (oxygen and nitrogen are not resolved at ambient temperature). Chromatograms 5 and 6 illustrate the performance of this sieve.

Chromatogram 5 : Permanent gases, C2, to C4 hydrocarbons
: 35°C (1 min) to 250°C at 24°C/min; He, flow:10mL/min, TCD



peak 1. Nitrogen (bulk)
peak 2. Carbon monoxide (215ng on column)
peak 3. Methane (430ng on column)
peak 4. Carbon dioxide (215ng on column)
peak I. Water impurity
peak 5. Acetylene (430ng on column)
peak 6. Ethylene (430ng on column)
peak 7. Ethane (430ng on column)
peak 8. Methylacetylene (215ng on column)
peak 9. Propylene (215ng on column)
peak 10. Propane (215ng on column)
peak 11. n-Butane (215ng on column)

Chromatogram 6 : Formalin solution (0.5µL); the inert surface properties of the Carboxen-1006 allow for the analyses of polar analytes such as water and formaldehyde
: 200°C isothermal; flow: 3.0mL/min, TCD

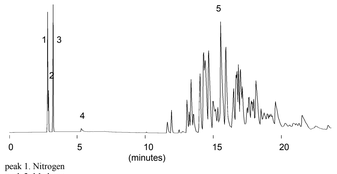


Peak 1. Air
Peak 2. Water
Peak 3. Formaldehyde (~38%)
Peak 4. Methanol (~15%)

Supel-Q

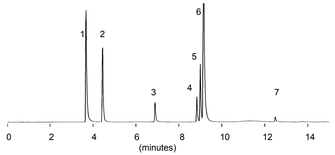
Supel Q porous polymer is a spherical, porous divinylbenzene polymer similar to Porapak Q, but synthesized in a 2-3 µM range effective for PLOT column preparation. The polymer possesses a multiporous pore structure, with the microporous region containing pores with diameters at 15-20Å. These pores are much larger and subsequently significantly weaker than the Carboxen-1006, for example, and therefore the range of analyte size is shifted to the volatile and semi-volatile range of analytes. These larger micropores, are also readily accessed by the mesopores and macropores (e.g., similar to the Carboxen-1006), therefore similar kinetics are obtained with the Supel-Q. Also, the amount of micropores present is sufficient (i.e., 700m^2/g) to resolve carbon dioxide and C1 – C4 hydrocarbons as well as semi-volatile analytes above ambient temperatures. Chromatograms 7 - 9 illustrate the performance of this Supel-Q PLOT column.

Chromatogram 7 : Small molecules in jet fuel; the inert surface of the Supel-Q polymer and microporosity allows for the analyses of light gases, water and high molecular weight analytes such as jet fuel
: 35°C (3 minutes) to 250°C at 16°C/min; He, flow: 3.0mL/min, TCD



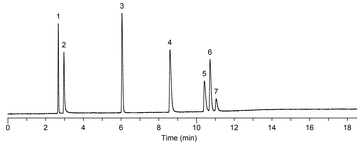
peak 1. Nitrogen
peak 2. Methane
peak 3. Carbon dioxide
peak 4. Water
peak 5. Jet fuel

Chromatogram 8 : Light, polar molecules such as the sulfurs are effectively analyzed with the inert surface of the Supel-Q polymer
: 50°C (1 minute) to 250°C at 10°C/min; He, flow: 3.0mL/min, FPD



peak 1. Hydrogen sulfide (1 ppm)
peak 2. Carbonyl sulfide (1 ppm)
peak 3. Methyl mercaptan (1 ppm)
peak 4. Dimethyl sulfide (1 ppm)
peak 5. Ethyl mercaptan (1 ppm)
peak 6. Carbon disulfide (1 ppm)
peak 7. Sulfur dioxide (5 ppm)

Chromatogram 9 : Volatile and semi-volatile solvents are effectively analyzed with the Supel-Q PLOT, when a TCD is used then the presence of water in the solvent(s) can be analyzed as well.
: 100°C (1 minute) to 200°C at 8°C/min, He, flow: 3.0mL/min, TCD, 10.0µL headspace analysis



peak 1. Air
peak 2. Water
peak 3. Dichloromethane
peak 4. Chloroform
peak 5. Benzene
peak 6. 1,4-Dioxane
peak 7. Trichloroethylene

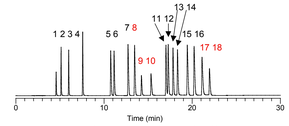
Activated alumina

Activated alumina PLOT columns are prepared using submicron, granular activated alumina (aluminum oxide) particles possessing a significant amount of mesopores. The use of sodium sulfate or potassium chloride as a desiccant and deactivating agent ensures that the activity of the alumina surface is effective in eluting (distilling) the unsaturated hydrocarbons after the saturated hydrocarbons. A small amount of micropores allows for the separation of methane from the C2 hydrocarbons, however surface chemistry plays the most significant role for these PLOT columns. The polarity of the aluminum oxide provides a unique selectivity, eluting/distilling small, unsaturated hydrocarbons after larger (or similar molecular sized) saturated hydrocarbons. This elution pattern is augmented with the alumina sulfate PLOT column, where acetylene elutes after n-butane, and methyl acetylene elutes after n-pentane and 1,3-butadiene.

Use of the alumina chloride still provides these unsaturated/saturated elution profiles, but to a reduced degree. For example, acetylene elutes after propane and propylene, but before n-butane (n-butane/acetylene is reversed for the alumina sulfate PLOT). The alumina chloride PLOTs can also be used for the analyses of Freons®. Examples of these elution patterns, the differences between the sulfate and chloride and the Freon analyses are illustrated in chromatograms 10-15.

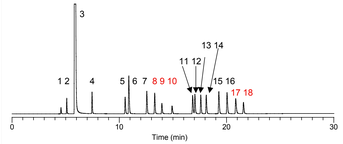
Chromatogram 10 : illustrates the alumina sulfate PLOT analysis of 18 component hydrocarbon mix / 10µL valve injection (direct; no split)
: baseline resolution obtained for 18 C1-C5 hydrocarbons using the 50 meter x 0.53mm ID alumina sulfate column, eluting acetylene after n-butane (reversed for the chloride chemistry), and eluting methyl acetylene after 1,3-butadiene (reversed for the chloride chemistry).

GC oven conditions : 35°C (2.5 minutes) to 150°C at 5°/minute, flow: 3.0mL/minute,

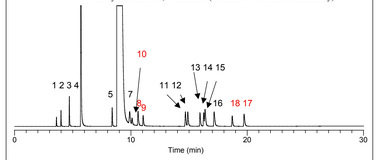


Chromatograms 10, 11 (sulfate) and 12 (chloride) peak identification
1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Cyclopropane
6. Propylene
7. Isobutane
8. n-Butane
9. Propadiene
10. Acetylene
11. trans-2-Butene
12. 1-Butene
13. Isobutylene
14. Cis-2-Butene
15. Isopentane
16. N-Pentane
17. 1,3-Butadiene
18. Methyl acetylene

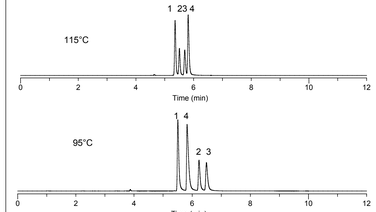
Chromatogram 11: illustrates the analysis of trace impurities in ethylene, using the same chromatographic parameters as those in Chromatogram 1 (peak identifications are also the same).



Chromatogram 12: illustrates the analysis of trace impurities in ethylene using the 50 meter x 0.53mm ID chloride column; the same chromatographic parameters as those in Chromatograms 10 and 11 (peak identifications are listed above, except elution of acetylene before n-butane (reversed for the sulfate chemistry), and eluting methyl acetylene before 1,3-butadiene (reversed for the sulfate chemistry).



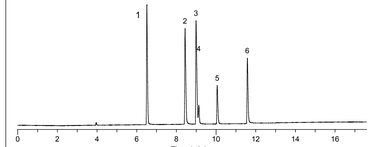
Chromatograms 13 and 14 : illustrate the analyses of mineral oil impurities using both the 50 meter x 0.53mm ID alumina sulfate and 50 meter x 0.53mm ID alumina chloride columns. These 2 chromatograms exemplify the chemistry/elution differences between the two alumina chemistries.



Peak Identification
1. 1-Butene (50ng on column)
2. Isobutylene (25ng on column)
3. Cis-2-Butene (25ng on column)
4. Neopentane (50ng on column)

Chromatogram 15 : illustrate the analysis of FREONS® using the alumina chloride PLOT column. The polarity/selectivity of the alumina chloride PLOT column allows for the separation of the F-114 and the F-114a impurity as well.

GC oven conditions: 35°C (1.0 minute) to 180°C at 12°C/minute; flow = 3.0mL/minute helium; 1.0µL syringe injection; FID



peak 1. Freon 12
peak 2. Freon 22
peak 3. Freon 114
peak 4. Freon 114a
peak 5. Freon 11
peak 6. Freon 21

CONCLUSION

Carbons, porous polymers, and other adsorbents have been used for gas-solid chromatographic separations for decades. The evolution of GSC to include these adsorbents into PLOT columns has considerably improved resolution for key analytes requiring GSC for effective chromatographic separation. Optimizing chromatographic separation is dependent on proper column selection and column preparation (i.e., use of high temperature adhesives and optimized column coating processes). Selecting the correct PLOT column requires an understanding of the properties of both the column adsorbent and the analytes of interest. Adsorbents can be characterized according to size, shape, porosity, surface chemistry and surface area. Porosity, surface area and surface chemistry of the adsorbent, as well as the shape, size and chemistry of the analytes are the key factors determining whether analytes will be resolved on the various PLOT columns.

REFERENCES

1. Webb, P.A., and Orr, C., *Analytical Methods in Fine Particle Technology*. Micromeritics, Norcross, GA, 1997. Reference not available from Supelco.
2. Conder, J.R. and C.L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, New York, 1979. Reference not available from Supelco.