

# A New Bonded Porous Polymer PLOT U Column with Increased Polarity

Zhenghua Ji and Steve Hutt

Agilent Technologies, 2850 Centerville Road, Wilmington, DE 19808

## Abstract

The separation features of a new type of PLOT U column are presented through many applications. This type of PLOT U column is coated with a divinylbenzene–ethylene glycol dimethacrylate copolymer. It has an increased polarity when compared with a conventional PLOT Q type column. The stationary phase of the PLOT U column is truly bonded, thus providing column rinsability and low column bleed.

## Introduction

Porous polymer has been used as an adsorbent for gas solid chromatography for a long time, either in traditional packed column format (1,2) or open tubular capillary column format (PLOT columns) (3–11). One of the features of these PLOT columns is that they can separate a wide range of small molecules from hydrogen to semivolatiles such as decane and inert gas (nitrogen to polar compound-like water) (4). It has been demonstrated that the PLOT columns give out more efficient separations than traditional packed columns (12).

The porous polymers that are used in chromatography are usually made of a divinylbenzene (DVB) polymer (1) or DVB and other monomer copolymers (5–9). These polymers are fine polymeric particles with a size from 10 nm to 100  $\mu\text{m}$  and a pore ranging from 5 to 20  $\text{\AA}$ . They permit small molecules to be strongly absorbed onto its surface by inducing dipole–dipole interaction, thus producing chromatographic separation for these molecules (4).

Commercially available porous polymer PLOT columns are made of PLOT Q-, U-, and S-type polymers characterized by different copolymer structures (5). PLOT Q columns made of DVB polymer are the most popular used because of its

ability to separate  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ , and other polar and active molecules from light hydrocarbons. However, because it lacks sufficient induced dipole–dipole interaction, the separation of polar analytes such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is sometimes inadequate. One of the shortcomings is that the  $\text{H}_2\text{O}$  peak tails. Also,  $\text{CO}_2$  is not sufficiently separated from methane (9).

The PLOT U column generally improves such separations done on PLOT Q columns. PLOT U columns are coated with the

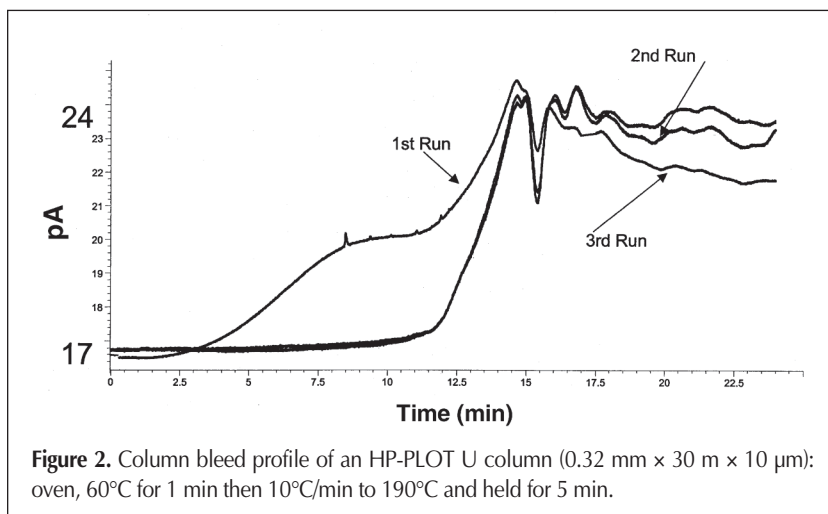
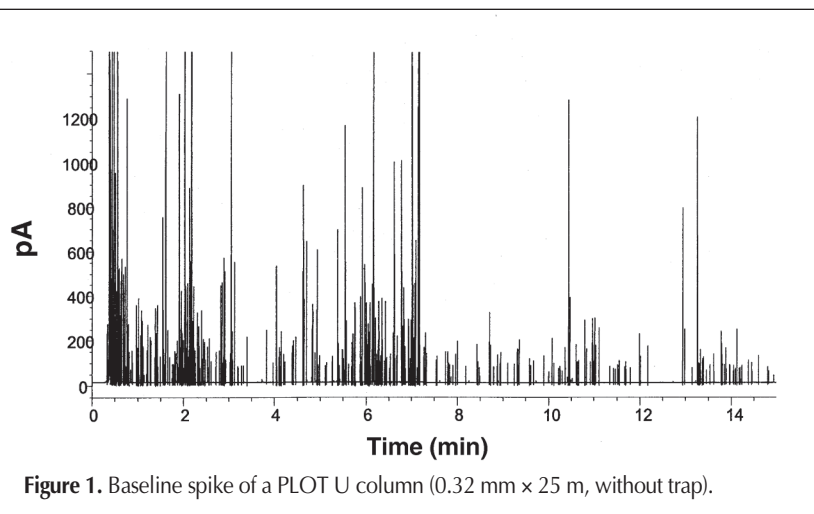
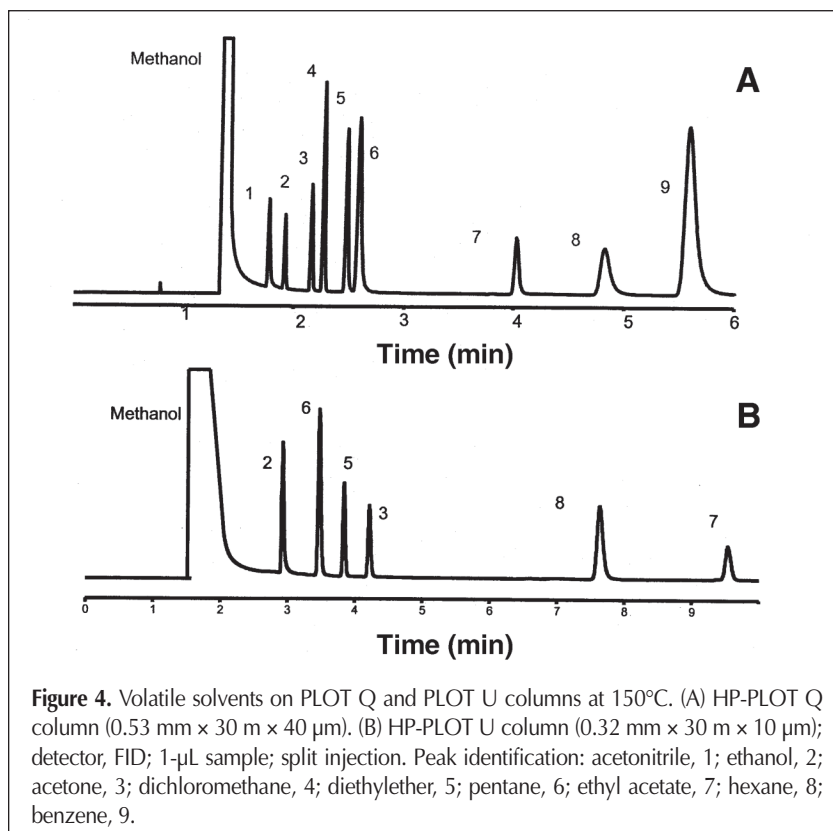
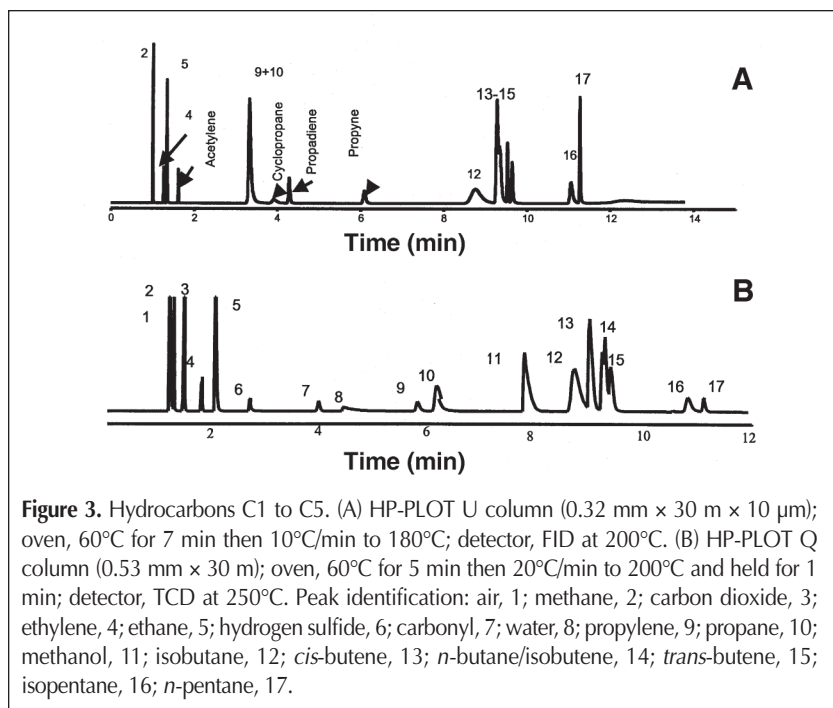


Table I. Retention indices.		
RI	HP-PLOT U column	HP-PLOT Q column
Ethyl acetate at 150°C	630	574
Acetone at 150°C	528	484
Propylene at 60°C	300	291
Acetylene at 60°C	228	172



porous polymer of DVB and ethylene glycol dimethacrylate. Chrompack (Middelburg, The Netherlands) introduced it in 1989 (6). Because of the increased polarity of the acrylate functional group versus the ethyl, PLOT U columns have much more increased polarity over PLOT Q columns, but it is still apolar. As a result, it generates the selective separation of polar compounds such as oxygenates from light hydrocarbons.

In spite of this improvement, PLOT U columns have not gained wide acceptance. One of the reasons is that this type of column has a relatively low upper temperature limit (190°C) compared with 250 to 320°C for PLOT Q-type columns (10,11). As a result, these columns usually exhibit high column bleed. Another reason is that the earlier developed PLOT U columns have a problem with particle immobilization. When the column is used in a gas chromatograph (GC), particles of the coating elute out of the column, which causes baseline spikes as shown in Figure 1. A simple approach for this problem is to use a trap connected at the detector end. The trap is usually a 2-m capillary column coated with a gum stationary phase. It traps the particles coming out of the PLOT columns and prevents them from getting into the detector. However, the particles are still mobile inside the PLOT column, which causes baseline noise. All of these problems result in a less durable column and a lower minimum detection limit.

Therefore, these limitations became the driving forces in the development of the new bonded PLOT U column. This study presents the bonded phase PLOT U column, which focuses on the separation features of this type of PLOT U column through various applications.

## Experimental

### Columns

The bonded-phase HP-PLOT U columns were prepared with a proprietary technique. The porous polymer was made of a DVB and ethylene glycol dimethacrylate copolymer. The coating thickness ranged from 10 to 20 μm, and the column internal diameters were 0.32 mm and 0.53 mm, respectively. The upper temperature limit was 190°C. All columns were rinsed before use with a 2–3-column volume of methylene chloride, followed by gas purging until dry and reconditioning at 190°C for 2–5 h in order to minimize the column bleed.

### GC

HP 6890 GC (Agilent Technologies, Wilmington, DE) equipped with either a flame ionization detector (FID) or a thermal conductivity detector

(TCD) was used. For a gas sample, 6-port gas-sampling valves with a 0.25-mL sample loop size were used. For a liquid sample, a manual injection technique was employed. In all GC runs, hydrogen was used as the carrier gas.

### Sample

Most samples mentioned in this study were not of a standard blend, but instead were in-house blends with water, methanol, air, hydrogen sulfur, and others. The concentration of these samples ranged from 0.1 to 10% unless specified elsewhere.

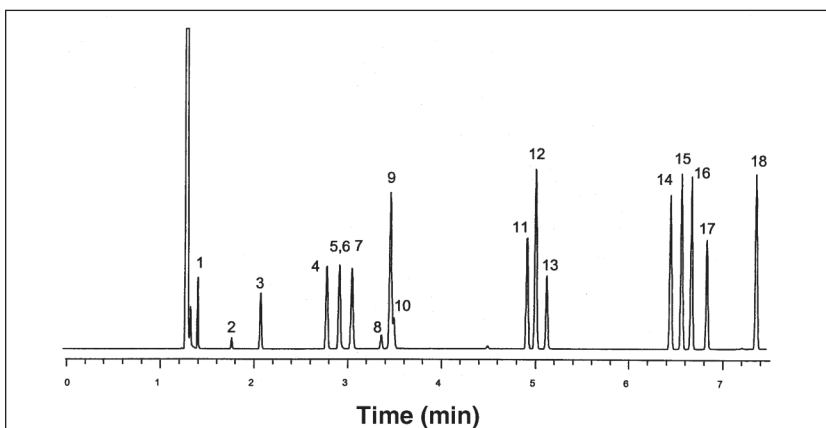
## Results and Discussion

### Column Performance

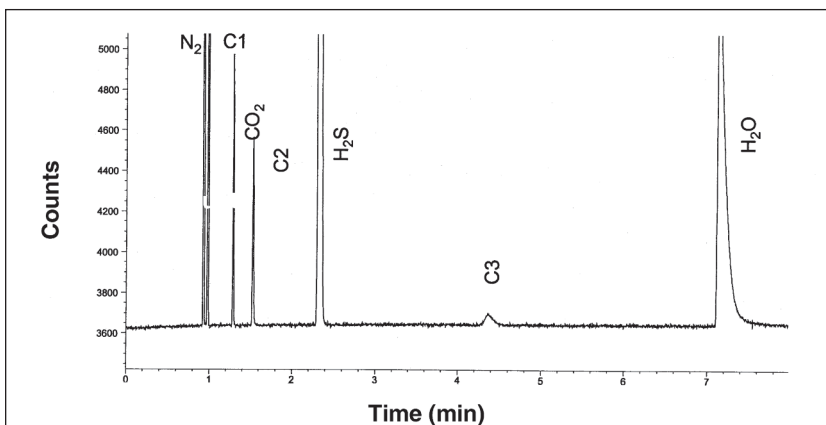
Generally, the HP-PLOT U column exhibited increased polarity and decreased column bleed. Because this type of PLOT U column was truly bonded, the column bleed was expected to be low after rinsing. This is indeed shown in Figure 2, in which a 0.32-mm  $\times$  30-m  $\times$  10- $\mu$ m PLOT U column was used. In this case, this column was installed in a GC, followed with temperature programs at 10°C/min to 190°C for 5 min. The total column bleed measured in picoAmps was less than 7 pA. It was found that the column had increased column bleed to 12 pA with continuous conditioning at 190°C. However, the bleed decreased to 7 pA after over 15 h of conditioning. This explains the distorted baseline shown in Figure 2, which suggests that degradation of the stationary phase occurred slowly. Additionally, Figure 2 shows no baseline spike at the ramping carrier gas pressure because of the continuous flow mode used. This was also true for most chromatograms shown in this study, which illustrated virtually no column particle generation. Both low column bleed and column rinsability expanded the column separation capability. If it were to happen that heavy compounds or contaminants were to get into the column, rinsing would clean up these compounds and restore column performance.

The polarity of the stationary phase of this type of PLOT U column was increased. Table I lists the Kovat retention index (RI) difference between HP-PLOT U and HP-PLOT Q columns.

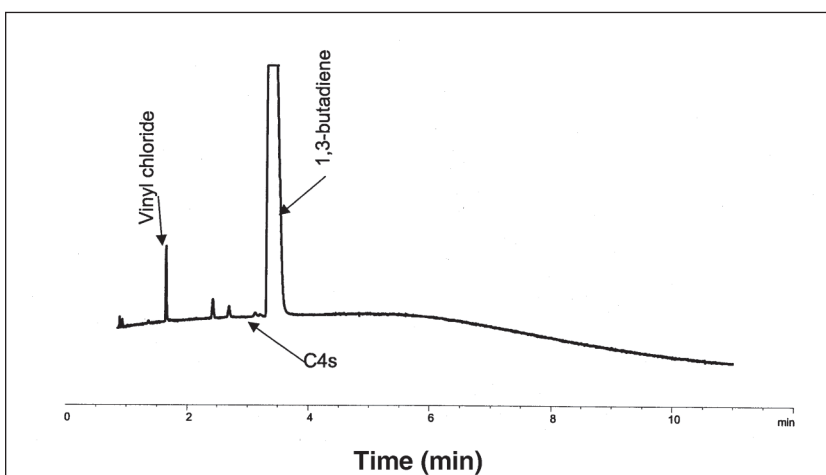
Table I also shows that esters and ketones were retained longer on the PLOT U column than on the PLOT Q column. Similar differences were found for alkynes and alkenes. Furthermore, on the PLOT Q column, water eluted before propylene, and on the PLOT U column, water eluted



**Figure 5.** Common solvents on an HP-Innowax column (0.25 mm  $\times$  30 m  $\times$  0.25  $\mu$ m): oven, 35°C for 2.5 min then 10°C/min to 85°C; detector: FID at 300°C. Peak identification: pentane, 1; methyl formate, 2; acetone, 3; ethyl acetate, 4; methyl ethyl acetate, 5; methanol, 6; 2-methyl-2-propanol, 7; dichloromethane, 8; benzene, 9; ethanol, 10; 2-butanol, 11; toluene, 12; *n*-propanol, 13; ethyl benzene, 14; *p*-xylene, 15; *m*-xylene, 16; 1-butanol, 17; *o*-xylene, 18.



**Figure 6.** Separation of CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>O from light hydrocarbons: HP-PLOT U column (0.32 mm  $\times$  30 m  $\times$  20  $\mu$ m); oven at 75°C; carrier, hydrogen at 5 mL/min; detector, TCD at 200°C; sample, 250- $\mu$ L natural gas blended with water and H<sub>2</sub>S; split ratio, 30:1.



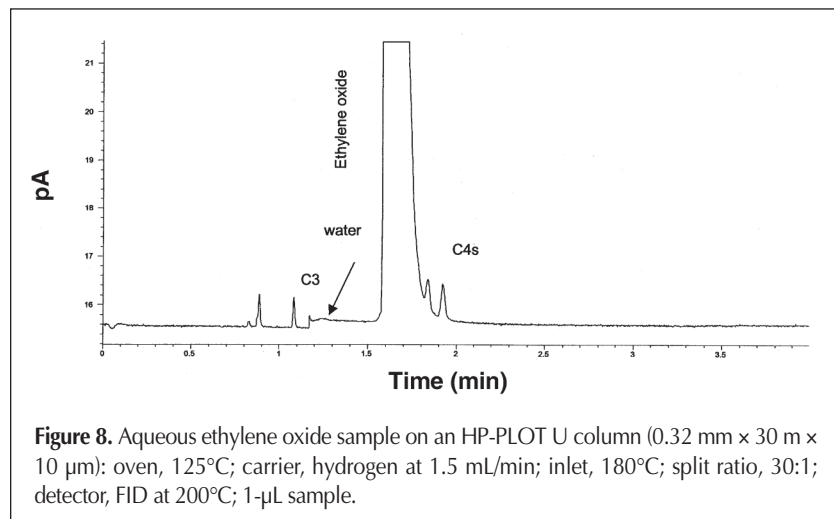
**Figure 7.** Vinyl chloride and 1,3-butadiene on an HP-PLOT U column (0.53 mm  $\times$  30 m  $\times$  20  $\mu$ m): oven, 100°C for 5 min then 10°C/min to 150°C and held for 1 min; carrier, hydrogen at 6 mL/min; inlet, 180°C; split ratio, 25:1; detector, TCD at 200°C; 250- $\mu$ L sample.

after propane-propylene and propyne.

Increased polarity resulted in more retention for carbon dioxide, which also increased its resolution with methane. On an HP-PLOT Q column, the resolution was approximately 7.2 at 60°C, and on an HP-PLOT U column, the resolution was approximately 20 at 75°C.

### Separations

Table II lists several applications generated with PLOT U columns. One of the unique features of the PLOT U column was



**Figure 8.** Aqueous ethylene oxide sample on an HP-PLOT U column (0.32 mm × 30 m × 10 μm): oven, 125°C; carrier, hydrogen at 1.5 mL/min; inlet, 180°C; split ratio, 30:1; detector, FID at 200°C; 1-μL sample.

**Table II. Separations on PLOT U columns.**

Application area	Range*	Comments
Fixed gases	H <sub>2</sub> , He, air (N <sub>2</sub> , O <sub>2</sub> , Ar, CO), CO <sub>2</sub> , H <sub>2</sub> S, COS, N <sub>2</sub> O	complete separation of air under cryogenic condition
Light hydrocarbons	C1–C8 including aromatics	incomplete isomeric separation, broadening branched alkanes
Alcohol†	C1–C6	good isomeric separation, symmetric peak shape
Ether	C1–C3	trace-level water
Amine including ammonia	C1–C6	good ammonia separation from air and water, good column inertness for light primary amines and ammonia
Aldehyde	C1–C4	not inert for formaldehyde
Ketone	C3–C6	separation of trace-level water
Carboxylic acid	C1–C4	separation of formic acid/ acetic acid
Ester	C1–C4	isomeric separation
Halogenated and oxygenated hydrocarbons	C1–C3	good separation from hydrocarbon, possibly not inert for propylene oxide

\* Using short length column (e.g., 10 m) and high temperature (190°C continuously) expands the range.  
 † Water and alcohol will not affect retention.

its ability to separate volatile polar compounds from nonpolar ones. Another feature was that water eluted on the column with a sharp peak shape, thus resulting in reliable quantitation for water.

Figure 3 shows chromatograms of hydrocarbon separations on a PLOT U and a PLOT Q column. Hydrocarbons C1 to C5 were separated in the carbon number classes on both columns. C1 and C2 were separated, but the elution order was different for acetylene. On a PLOT Q column, it eluted before ethane; on a PLOT U column, it eluted after ethane. Propylene coeluted with propane on a PLOT U column, and it eluted before propane on a PLOT Q column. C4 isomers coeluted on both columns. Both types of the PLOT columns were more selective for alkenes and alkynes, which resulted in a sharp peak shape for both (but the peak shape of the branch alkanes was relatively broad).

Figure 4 presents the chromatograms of volatile polar solvents on both PLOT Q and PLOT U columns at 150°C. Different elution orders were found for acetone and ethyl acetate (as is expected because of increased polarity). It was found that acetonitrile and ethanol coeluted on a PLOT U column, and dichloromethane and ether were separated on a PLOT Q column. In fact, increased polarity will result in other coelutions. In comparison, Figure 5 shows a similar separation of common solvents on a wax-type column in which the other coelutions and elution order reversals were found. For example, methanol eluted after pentane and acetone, and ethanol almost coeluted with benzene. Consequently, if the selectivity of a polar compound is not adequate on a wax-type column, a porous polymer PLOT column may prove suitable. Additionally, an increased retention of porous polymer PLOT columns permits higher starting temperatures versus wax-type columns, thus reducing the GC cycle time.

## Applications

### Gases and light hydrocarbons

Perhaps, the most popular application for a PLOT U column would be the analysis of light hydrocarbons. This is because good separation of fixed gases and water from light hydrocarbons can be obtained on this type of PLOT column. Figure 6 shows a typical separation of a natural gas sample blended with water and hydrogen sulfide at 75°C on a PLOT U column. In this chromatogram, CO<sub>2</sub> was well-separated from methane and ethane, thus leading to the accurate methane and ethane quantitation for the British thermal unit determination of natural gas. Hydrogen sulfide (usually one of the odors added) was well-separated from ethane and propane with good symmetric peak shape. A similar application can be applied to the analyses of refinery gas and

other petroleum gases.

Figure 7 is the chromatogram of the separation of vinyl chloride and 1,3-butadiene. 1,3-Butadiene is the impurity presented in a vinyl chloride stream. Even at 100°C, vinyl chloride eluted much earlier than 1,3-butadiene, which left a significant separation for a main stream of vinyl chloride. However, Figure 7 is not a real analysis of vinyl chloride, it just illustrates this type of separation on a PLOT U column.

In Figure 8, an aqueous sample of ethylene oxide that was blended with hydrocarbons was analyzed on a PLOT U column. Ethylene oxide was present in many diverse samples such as industrial raw materials and spices. The baseline rise reflects the water disturbance on the FID signal. However, water elutes on a PLOT U column so that it will not have any effect on column performance. In terms of elution, ethylene oxide was found to be coeluting with isobutane on PLOT U columns.

### Common volatile solvents

Volatile solvent analysis is another major application area for the PLOT U column. Although the PLOT U column has increased polarity compared with the PLOT Q column, it is still nonpolar when compared with a wax-type column. This produces selective separations at above-ambient temperature, which is suitable for the analyses of impurities in some solvents. Furthermore, because most common solvents contain low-level water and water elutes much earlier with a sharp peak shape than these solvents on a PLOT U column, a PLOT U column is especially suitable for such analysis. Figure 9 and 10 present some of these analyses at above 100°C temperatures.

Figure 9 shows the analysis of HPLC-grade acetone performed by GC-TCD at 150°C. Water elutes before methanol and acetone with a sharp peak shape. In this sample, the water concentration is estimated as 0.1%. Based on the peak area and height, one can conclude that a low level of water down to 10 ppm or lower can be quantitated.

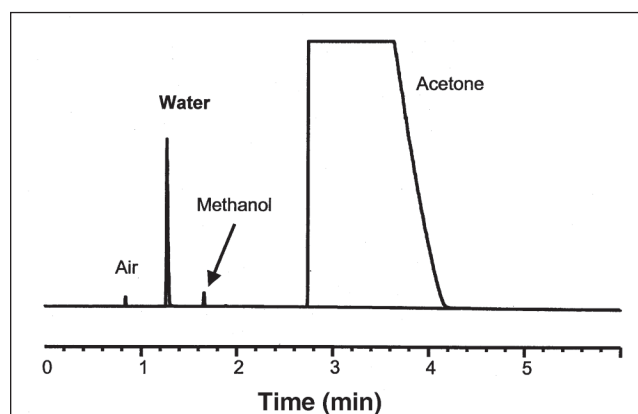
Figure 10 illustrates the selective separations obtained on a PLOT U column. The sample was acetic acid. The chromatograms were obtained on a GC-TCD and GC-FID. Formic acid as an impurity in acetic acid can be detected by GC-TCD; other impurities with hydrocarbons can be easily detected by GC-FID. In Figure 10A, formic acid is selectively separated (earlier elution) from acetic acid. As a comparison, formic acid eluted after acetic acid on a wax-type column (free fatty acid phase) (13). Because of the bonded phase of the PLOT U column, the analysis can be reproducibly repeated many times without any sign of column performance degradation (indicated by the flat baseline after acetic acid in Figure 10B in which acetaldehyde eluted as a symmetric peak before acetic acid).

Figure 11 demonstrates the separation of impurities (ethanol, methyl acetate, and others) from ethyl acetate. Low-level methanol and ethanol can be detected in this analysis (estimated to a 1–10-ppm level). Methyl acetate was far separated from

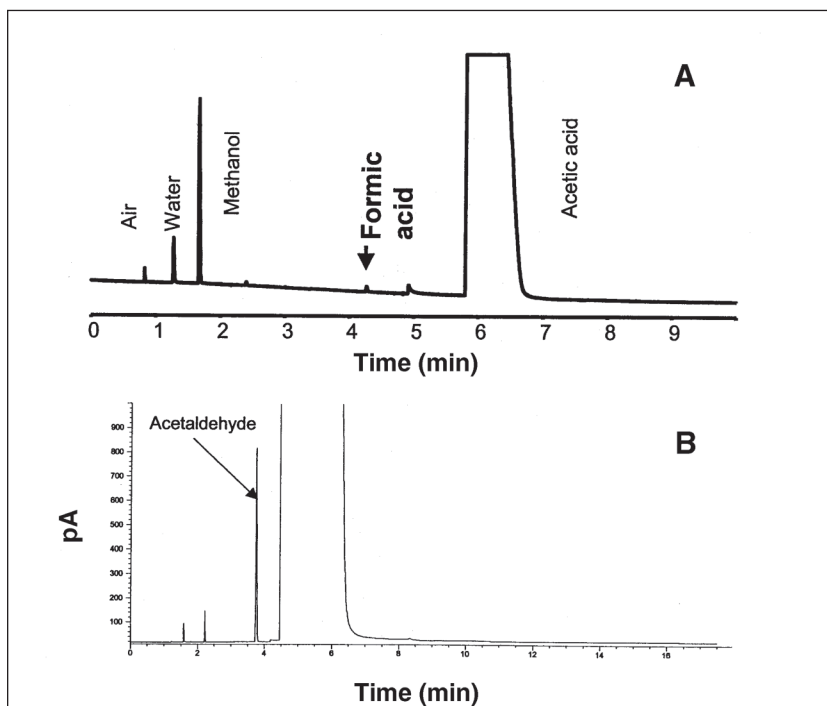
ethyl acetate. Several unknown impurities eluted after ethyl acetate. It is not understood why the baseline rose repeatedly after ethyl acetate.

### Amine and sulfur

Amine and sulfur would be good probes to test column inertness because of their basic and acidic properties. In the case using PLOT columns, the surface of the substrate had little effect on the amine and sulfur samples because its surface area was much smaller than the surface area of particle coating. Both the particles and the binding agent that are used (the coating) must be inert to these analytes (4,14). The new bonded PLOT U columns generally satisfy this requirement.



**Figure 9.** HPLC-grade acetone on an HP-PLOT U column (0.32 mm  $\times$  30 m  $\times$  10  $\mu$ m); oven, 150°C for 1 min then 10°C/min to 190°C and held for 4 min; inlet, 150°C; split ratio, 50:1; detector, TCD at 200°C; 10- $\mu$ L sample.



**Figure 10.** Acetic acid on an HP-PLOT U column (0.32 mm  $\times$  30 m  $\times$  10  $\mu$ m). (A) GC-TCD. (B) GC-FID: oven, 125°C for 1 min then 10°C/min to 190°C and held 5 min; inlet, 150°C; split ratio, 50:1; sample, 5  $\mu$ L of 99.8% acetic acid.

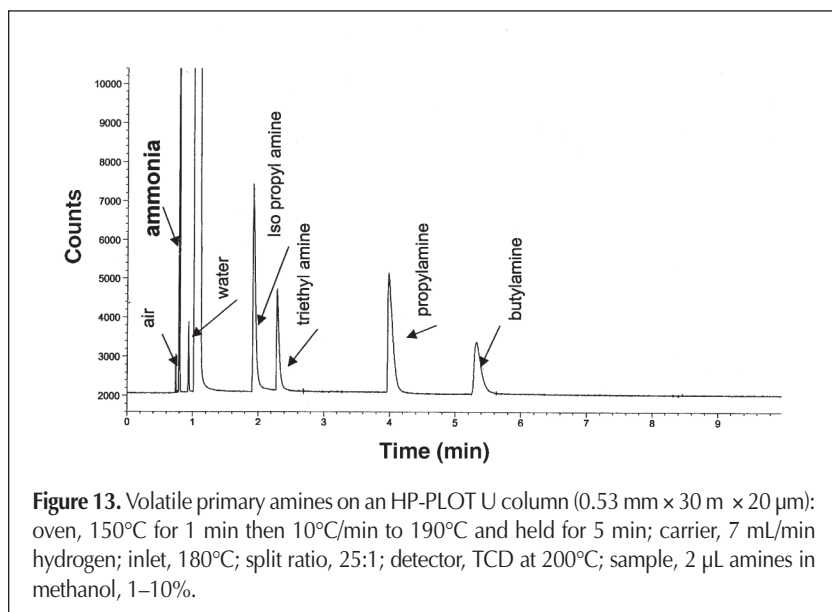
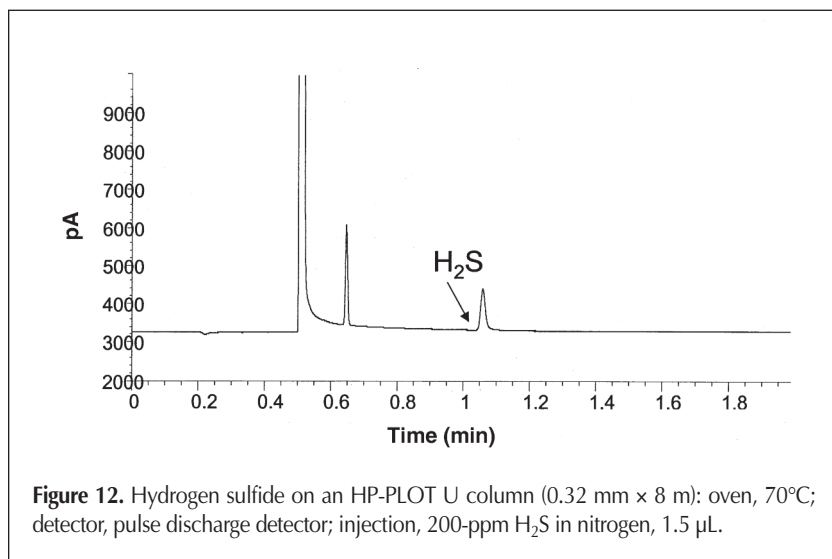
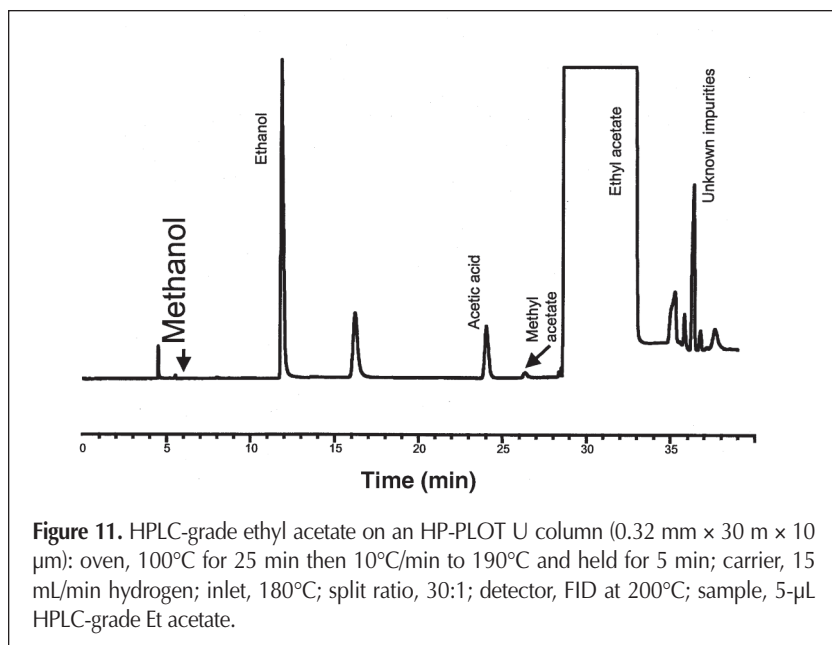


Figure 12 shows the chromatograms of 200-ppm hydrogen sulfide in nitrogen on a 8-m × 0.32-mm-i.d. PLOT U column at 70°C performed by a GC-pulse discharge detector. Hydrogen sulfide exhibited a symmetric peak shape (also shown in Figure 5 in which a large amount of hydrogen sulfide was introduced), which suggests less activity from the column coating. Figure 13 demonstrates the separation of ammonia and the primary amines C1 to C4 in methanol. In this extreme application, ten injections of the sample were introduced into the column at a temperature from 60°C to 125°C. No significant change in the column bleed, column selectivity, and column retention occurred. A relatively sharp peak was observed for ammonia that elutes before water. The four amines exhibited peak tailing because of column overloading.

## Conclusion

The new bonded HP-PLOT U column with increased polarity has demonstrated the ability to separate a wide range of apolar (light hydrocarbons), polar (water and volatile polar solvents), inert (nitrogen), and reactive (hydrogen sulfur and ammonia) analytes. This type of PLOT column possesses good column inertness and low column bleed because the phase is bonded. However, the column exhibits peak broadening for branched organic molecules.

Although this type of bonded PLOT U column can separate many small molecules, it still has an upper temperature limitation. If the upper temperature limit was increased to 250°C, it would be more useful in common solvent analyses (i.e., boiling point up to 180°C). In this case, more impurities would be separated and detected. Complete or more isomeric separations of hydrocarbons (such as C<sub>4</sub> isomers) would be another improvement for new PLOT U column development.

## Acknowledgments

This study was based on the presentation in the Pittsburgh Conference and Exhibition 2000 in New Orleans, LA (Paper number 112). Mr. P. Bucay and Dr. J. Destefano of Agilent Technologies provided valuable suggestions during the preparation. Dr. W. Wilson kindly provided the chromatograms used in Figure 1 and Figure 12, to whom the authors appreciate.

## References

1. O.L. Hollis and W.V. Hayers. Gas separations on microporous polymers. In *Gas Chromatography 1966*, A&B, Littlewood Ed., Elsevier, 1967, p 57.
2. S.B. Dave. A comparison of the chromatographic properties of porous polymers. *J. Chromatogr. Sci.* **7**: 389–99 (1969).
3. V.G. Berezkin and J. de Zeeuw. *Capillary Gas-Solid Chromatography*. Huthig, Heidelberg, Germany, 1997.
4. Z. Ji, R. Major, and E. Guthrie. Porous layer open-tubular capillary columns: preparations, applications, and future directions. *J. Chromatogr. A* **842**: 115 (1999).
5. J. de Zeeuw and J.C.M. Wessels. *Int. Lab. News* **December**: 18 (1992).
6. J.A. Peene, J.C. Buyten, and M. Mohnke. A new generation of PoraPLOT columns: the PoraPLOT S and PoraPLOT U. In *Proceedings of the 10th Int'l Symposium of Capillary Chromatography*. 1989, p 179.
7. T.C. Shen and M.M. Fong. In-situ polymerized PLOT columns III: divinylbenzene copolymers and dimethacrylate homopolymers. *J. Chromatogr. Sci.* **32**: 36–40 (1994).
8. Y. Yu, H. Liu, and X. Shen. *Sepu* **14**: 381 (1996).
9. Z. Ji. New porous polymer Q type PLOT columns with low column bleed and good immobilization. *Abstracts of Papers*, Pittsburgh Conference and Exhibition, New Orleans, LA, 1997.
10. Z. Ji and S. Hutt. New porous polymer Q type PLOT columns: low bleed, excellent immobilization and inertness. In *Proceedings of the 19th Int'l Symposium of Capillary Chromatography & Electrophoresis*. Wintergreen, Virginia, 1997, p 288.
11. J. de Zeeuw. The first chemically bonded PLOT column: 100% immobilized styrene-divinylbenzene porous polymer. *Abstracts of Papers*, Pittsburgh Conference and Exhibition, New Orleans, LA, 1998. Paper Number 054.
12. C<sub>3</sub> selectivity comparison of GS-Q megabore vs. packed columns. <<http://www.jandw.com/webpdf/c594.pdf>>.
13. *1998–1999 Hewlett Packard Chemical Analysis Columns and Supplies Catalog*. p 185.
14. K.K. Gaines, W.A. Chatham, and S.O. Farwell. Evaluation of PoraPLOT U column for sulfur analysis. *J. HRC* **13(August)**: 585–86 (1990).

Manuscript accepted June 20, 2000.