Review

Porous layer open-tubular capillary columns: preparations, applications and future directions

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Abstract

Porous-layer open-tubular (PLOT) columns, first suggested by Golay in the late 1950s, have been developed and commercialized successfully. PLOT columns have since become powerful and routine tools in gas chromatographic analyses of fixed gases, light hydrocarbons and volatile solvents. They often replace traditional packed columns. However, there are still many unknowns in the development and the applications of PLOT columns. The future of PLOT columns seems less clear. This paper reviews the history of PLOT column development and its applications including practical aspects of PLOT columns. Some speculation of future development is also provided. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Porous layer open-tubular columns; Stationary phases, GC; Column technology; Coating; Fixed gases; Hydrocarbons; Volatile solvents

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1. Introduction

Gas chromatographic separation is achieved by analyte partition between two phases: the mobile phase and the stationary phase. Partition mechanism results in two types of gas chromatography (GC): gas–liquid chromatography (GLC) and gas–solid chromatography (GSC) [3]. Although GLC dominates the GC applications, GSC has its place in separation laboratories for more specialized applications. In recent years, there has been a renewed interest in GSC because it enables effective separation of gaseous molecules such as fixed gases and light hydrocarbons at above ambient operating temperatures, as predicted by Ettre in 1985 [4]. Also solid surfaces often are very stable and free of bleed associated with liquid phases, and they often display a unique selectivity based on molecular shape and size [5].

GLC and GSC have used packed columns for quite some time. However, chromatographic resolution with packed columns is not sufficient for many separations. The development of capillary columns, particularly fused silica capillary columns, enabled very high-resolution GC to be achievable routinely. Development of capillary GC led to the porous-layer open-tubular (PLOT) capillary columns widely used in GSC, starting with Golay's suggestion [1,2,6,7], Halasz and co-workers [8–12], Ettre and Purcell's [13] earlier pioneering work, and other earlier PLOT column preparations by Kirkland [14], Scott [15,16], Hollis [17–19], Nikelly [20, 21], Schneider and co-workers [22, 23], just to name a few. Additionally, PLOT columns provide greater efficiency (<0.1 mm height equivalent to a theoretical plate, HETP), faster separations (seconds),

quicker column regeneration (<30 min) and fewer instrumentation requirements, compared to the packed column technology.

Owing to great efforts from column manufacturers, PLOT columns have become routine tools in gas analysis by GC from laboratory operation to in-process monitoring. PLOT column applications have been extended to a wide range of analytes from fixed gases (hydrogen) to volatile liquids (tetradecane), from nonpolar compounds (hydrocarbons) to very polar (water), and from very inert analytes (noble gases) to very active ones (hydrogen sulfide).

With growing interest in GSC from research and applications and continuing development in the column manufacturers to apply PLOT columns to a wider range of applications, many papers have been published during the last four decades. Ettre [4], De Zeeuw et al. [24], Henrich [25], and others reviewed earlier works in the PLOT column development. More recently, Bruner et al. [26] reviewed the preparation and application of graphitized carbon black columns. De Zeeuw and Wessels [27] reviewed the technology of PLOT columns developed by Chrompack, Tuan et al. [28] reviewed the determination of sulfur components in natural gas by using different GC techniques including PLOT columns. Berezkin [29, 30] reviewed the current status of capillary GSC including many references. He also discussed the history, column preparation, retention theory and practical applications of open-tubular GSC columns. Ji and Majors [31] reviewed the practical aspects in the use of PLOT columns.

This paper will provide an overview PLOT column technology from column preparation to recent application with special attention focusing on commercial PLOT columns. Practical aspects in the use

of PLOT columns will be discussed. Some future developments of PLOT columns will be also speculated.

2. Present status of PLOT column technology

2.1. Definition of PLOT columns

PLOT columns stand for porous-layer open-tubular capillary columns in a generalized way. A porous layer of the stationary phase (sorbent) is constructed over the inner surface of an open-tubular capillary tubing, either metal or fused silica tubing. The column should maintain open-tubular structure after completion of column preparation step. The term PLOT column often causes confusion in today's commercialized PLOT columns and the previous, widely studied support-coated open-tubular (SCOT) columns. Presently PLOT columns may be more precisely called adsorption solid-phase open-tubular (ASPOT) columns.

In this paper, PLOT columns are narrowly defined as the capillary columns used exclusively for surface adsorption-type GSC, in accordance with almost all commercialized PLOT columns. Inside these columns, the porous layer is constructed by amorphous, porous, and fine particles (sorbent) that are immobilized by means of bonding chemically, either to the

inner surface of capillary column or to the surfaces of particles themselves, or binding physically (gluing). In this sense, it excludes SCOT columns and wall-coated open-tubular (WCOT) columns that possess microcrystalline structure, although both fall into the generalized PLOT column category. The mechanism of the separation on a SCOT column is gas–liquid partition due to liquid phase coated over the solid support, which is often porous (Jennings) [32], whereas most commercialized PLOT columns use strict surface adsorption GSC.

2.2. Stationary phase and preparation

PLOT columns have been developed in the tail of the packed column technology used in GSC. Therefore, all known packed materials are available as the stationary phases of PLOT columns. Table 1 lists the phases used in commercialized PLOT columns and their typical separations. Other materials used in the preparation of commercial PLOT columns include proprietary materials such as GS-GasPro (J&W Scientific, Folsom, CA, USA) [33], ZeoColumn (UOP, El Dorado Hills, CA, USA), and CP-Lowox (Chrompack, Middelburg, Netherlands) [34]. Some inorganic salts as adsorption type stationary phase had been reported in the past [35,36]. Eiceman [37] gave many sorbents used in GSC. Generally, these stationary phases can be classified as inorganic (such

Table 1
Stationary phases of PLOT columns

Stationary phases	Temperature ranges[a] (°C)	Separations
Aluminum oxide modified with deactivation agents: Al_2O_3/KCl,/Na_2SO_4,/"S"/"M"	−50 to 200	Mostly light hydrocarbon gases C1 to C10s and halogen hydrocarbons C1 to C2s. Good for separation of isomers
Divinylbenzene base porous copolymers: Q type DVB–styrene copolymer or DVB homopolymer S type DVB–vinyl pyridine U type DVB–ethylene glycol dimethyl acrylate	−50 to 310, Q type, bonded phase −50 to 250, S type −50 to 190, U type	Light hydrocarbons C1 to C10s, halogen hydrocarbons C1 to C2s, volatile oxygenated solvents C1s to C6s including alcohols, ketones and aldehydes esters, ethers, acids, thiols, amines, inorganic gases. Good separation of nonpolar and polar compounds
Carbon sieve or carbon	−50 to 350 (carbon) −50 to 150 (carbon sieve)	Inorganic gases and light hydrocarbons C1s to C5s. Good separation of C2 isomers from fixed gases
Molecular sieves, Zeolite, 5A, 13X, and others	−50 to 350	Oxygen, nitrogen, noble gases, CO, SF6, hydrocarbon C1 to C3s and paraffin C1 to C10s
Porous silica with/without surface modifications	−50 to 250	Light hydrocarbons C1 to C10s for GasPro, C1 to C4s for Silica PLOT, halogen hydrocarbons C1 to C2s, inorganic gases, volatile oxygenated solvents

[a] −50°C is a temperature obtained easily in a laboratory, although much lower temperature separations may be needed.

as alumina, molecular sieve, zeolites, silica and carbon sieves) and organic (porous polymers).

2.2.1. Alumina

Alumina has been used as an effective GSC sorbent for the separations of hydrocarbons and other organic molecules. It is obtained by heat-treating aluminum oxide hydrate (dehydration) at temperatures from 300°C [23,24] to 1000°C [38–40]. Temperature of the heat treatment yields different crystal structures, namely α, β and γ of alumina [41,42]. Dehydration of aluminum oxide hydrate at low temperature (below 700°C) is not a complete and irreversible step, aluminum oxide hydrate will regenerate with water during column preparation. The presence of aluminum oxide, hydrate, controls not only the surface area and surface activity of the particles but also the chromatographic properties of the column such as column selectivity and retention time. The particle size of alumina ranges from 60 mesh for packed columns to 2 μm or less for capillary PLOT columns [23]. Because alumina has too many active sites, it requires deactivation to block excessive active sites to reduce peak tailing and to improve column selectivity and separation. The deactivation agents are water [15,43,44], liquid phases used for GLC, and inorganic salts. Liquid phases include silicon oil [5], squalane and carbowax [23], diphenyl phthalate [45], and so on. Inorganic salts are sodium iodide and sodium hydroxide [16], sodium or potassium chloride [23], potassium hydroxide [42], potassium carbonate and dipotassium hydrogenphosphate [38–40] or fluoride [46], and others.

Scott [15] studied alumina packed columns deactivated with water for analysis of C1 to C5 hydrocarbons. Halasz and Heine [9] described a packed glass capillary column containing alumina that was deactivated with saturated sodium sulfate decahydrate vapor in carrier gas flow. Kirkland [14] probably first prepared the aluminum oxide open-tubular columns (0.2 mm to 0.5 mm internal diameters, 25 ft length, 1 ft=30.4801 cm) for fluorinated hydrocarbon separation at room temperature. Petitjean and Leftault [47] described the preparation of a 5 μm thick alumina PLOT column from oxidation of aluminum capillary tubing of I.D. ca. 0.5 mm (in situ). They noticed some loss of olefins on the highly active alumina layer they obtained. Scott and Phillips [16] investigated the modification of aluminum oxide with inorganic salts to improve the separation of hydrocarbon isomers, C6 to C14, and aromatics. Moore and Ward [48] used an alumina column to separate spin isomers of hydrogen, and Genty and Schott [49] used an alumina packed column deactivated with $Fe(OH)_3$ to separate hydrogen isotope. Both separations were performed at −196°C. Al-Thamir et al. [50] used an alumina packed column to attempt a complete but slow separation of C1 to C4 hydrocarbons. They modified the surface by coating it with conventional liquid phases. Schneider et al. [23] developed the alumina PLOT columns deactivated with potassium chloride, squalane and carbon wax. They obtained the separation of ppt-level hydrocarbon C1 to C10s. De Nijs [51] reported the preparation of alumina PLOT columns deactivated with saturated $CuSO_4 \cdot xH_2O$ vapor in carrier gas flow. They achieved the separation of C1 to C5 hydrocarbons at 60°C.

Snyder and Fett [43] reviewed the earlier work in alumina packed column technology. De Nijs and co-workers [24,52] reviewed the general preparations and applications of Al_2O_3 PLOT columns and other PLOT columns they developed. Ji and Chang [54] examined the column selectivity for several commercially available alumina PLOT columns.

Alumina PLOT columns were introduced by Chrompack in 1983. De Nijs and De Zeeuw [52] reported the separation of 22 hydrocarbons (C1 to C10) on a 50 m×0.32 mm fused silica Al_2O_3 PLOT column. Separation of C1 to C4 hydrocarbons was achieved within 100 s. Benzene (100 ppm) in cyclohexane was also analyzed. Following Chrompack, J&W Scientific in 1990, Hewlett-Packard in 1994, Restek in 1995, and Supelco in 1995, introduced their own alumina PLOT columns. These alumina PLOT columns are deactivated with potassium chloride [52], sodium sulfate [53], mixed salts, or some proprietary agents. Therefore, these alumina PLOT columns exhibit different column selectivity.

2.2.2. Molecular sieve, zeolites

The molecular sieve, zeolite, is rather general. Unless otherwise qualified, it is taken to refer to artificially prepared zeolites, which are the aluminosilicates of sodium, potassium, or calcium. Those

most commonly used in GC are type 5A, calcium alumino-silicate, with an effective pore diameter of 5 Å, and type 13X, sodium alumino-silicate, with an effective pore diameter of 10 Å [55,56].

Because of its strong hydroscopicity (excellent drying agent) property, molecular sieve requires activation by heat treatment to remove adsorbed water. The temperature and duration of the heat treatment control both the elution order and the separation of fixed gases such as CO and CH_4, O_2 and N_2 [56]. The condition of the activation was reported as 250°C (for 5A) and 350°C (for 13X) for 18 h (weak activation) [56] and 450°C for 5 h (strong activation) [57]. The particle size of these molecular sieves ranges from 10 nm [58] for in situ column preparation, 1–2 μm [59–61] for coating, to mesh size for packed columns. Their surface areas may range from 100 to 800 m^2/g. Acidity of zeolite can be reduced by pretreatment with sodium hydroxide [60], nickel nitrate, or silver nitrate [62].

The popularity of molecular sieves results from their unique ability to separate fixed gases, such as O_2, N_2, noble gases, NO, CO and CH_4, at above ambient temperature. Janak et al. [63] studied molecular sieve 5A and found the activation temperature affects the elution order of more retentive molecules such as CO and CH_4. Karlsson [64] showed that the separation of argon and oxygen was obtained by high-temperature activation (500°C for 30 h) of 2 m molecular sieve 5A and 13X packed columns. Dietz [65], and Clay and Lynn [66] developed a column pretreatment procedure for the analysis of nitric oxide. This pretreatment was to saturate the columns with nitric oxide prior to the analysis. Simmonds et al. [67] studied the effect of the activation of 5A on the elution order of sulfur hexafluoride and iso-butane. Deans et al. [68] obtained the separation of CO and CH_4 on 13X with different elution orders at different activation conditions. Brunnock and Luke [69], Garilli et al. [70], Soulages and Brieva [60], Zou and co-workers [71,72] reported the separation of paraffins and naphthenes (C1 to C12) on 13X packed and PLOT columns. Finkelson [73] used a Porapak Q packed column and a molecular sieve zeolite, 13X packed column to analyze medical gas containing O_2, N_2, NO, CO_2 and C_2H_4. Mohnke and Heybey [61] obtained the separation of low boiling point gases (Ar, O_2, N_2, He) and isotope molecules

(hydrogen, methane and ethane) on a 67 m×0.33 mm I.D., 30 μm 5A PLOT column. The temperatures used were 22.3°C for deuterated methane and ethane, and −78.5°C for hydrogen isotopes, respectively.

In the late of 1980s and early of 1990s, molecular sieve, zeolites, PLOT columns became commercialized from most column manufacturers [24]. Since then, these PLOT columns have been widely used for the analysis of fixed gases.

2.2.3. Active carbon, carbon sieve and graphitized carbon black

It is necessary to distinguish these carbons morphologically to understand its use in chromatography. Active carbon is an amorphous form of carbon with high adsorptivity for many gases, vapors and colloidal solids. It is obtained by the destructive distillation of carbonaceous material and activation at 800–900°C with stream or carbon dioxide that results in a porous structure. Carbon sieve is carbonaceous particle that is obtained typically from pyrolysis of poly(vinylidene chloride) or other products. Carbon sieve is inert, very apolar and has very high surface area. Graphitized carbon black (GCB) is a nonporous and very fine particle with a large surface area and regular crystal structure. It has a high affinity for hydrocarbons.

Active carbon has been used since the beginning of GC [74]. Ray [75] showed the separation of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane and acetylene at 20–40°C. Madison [76] used a 20 ft column at 20°C to obtain the separation of oxygen and nitrogen and others. Tsuji et al. [77] analyzed breath gas on an active carbon column. It has been noted that few GC applications have been published since then.

Kaiser [78] reported the use of carbon sieve in GC for light gas analysis. He obtained the separation of hydrogen, oxygen+nitrogen, carbon monoxide, water, methane, carbon dioxide and acetylene, ethylene and ethane. Yu et al. [79] pyrolyzed a divinylbenzene–styrene polymer to form an active carbon layer inside a column. They achieved the separation of fixed gas and C1 to C3 hydrocarbons. Yang and Lu [80] prepared a carbon sieve PLOT column by dynamic coating and separated fixed gases at −4°C on that column. Some commercialized

carbon PLOT columns probably use carbon sieve as stationary phase [33,81].

GCB has been studied quite extensively in gas chromatography. Griffiths et al. [82] studied the retention times of polar solvents and hydrocarbons on carbon. Eggersten et al. [83] deactivated GCB with squalane to reduce peak tailing. Halasz and Horvath [11] obtained n-alkanes up to C13 on a glass bead coated with carbon. Simmons and Snyder [84] and Schneider et al. [22] investigated the elution order of hydrocarbons on carbon, they found that alkenes and aromatics follow the elution order in carbon number. DiCorcia and Samperi [85,86] studied the separation of C4 isomers on a modified carbon black column. Kalashnikova et al. [87] published retention indices of various compounds on GCB. Vidal Madjar et al. [88] used carbon black for making a selective glass column. Liberti and co-workers [89–92], and Engewald and co-workers [93,94] studied the separation of volatile polar solvents including amines and xylenes. Bruner and co-workers [95,96] modified (monolayer) GCB (Carbopack) with different liquid phases such as carbon wax and FFAP to separate a wide range of volatile polar and apolar solvents. Similar work was reported by Krawiec et al. [97], Xiang [98], and Lattanzi et al. [99] for various hydrocarbon separations. Sidisky and Robillard [100] reported the preparation of carbon-layer open-tubular (CLOT) columns using Carbopack B.

CarboPLOT columns are now commercially available from Chrompack, Supelco and J&W Scientific and other column manufacturers. CLOT columns are available from Supelco. The morphology and structure of the carbon used in these PLOT columns are not disclosed. These columns are used mostly for the separation of fixed gases and hydrocarbons C1 to C2.

2.2.4. Silica gel and silica

The silica used in chromatography includes silica gel and porous silica. Silica gel has been used since the early days of GC. Janak [74] mentioned the columns of silica gel and active carbon. Silica gel can be made by poly-condensation, Arshady [101]. Further gelation and drying of silica gel leads to porous silica particles (microbead), available as Spherosil, Porasil, or other brands. These silica beads

are widely used in packed columns. Both types of silica are porous in a variety of surface areas and pore diameters. They often contain many silanols on the surface. The activation by heat treatment can remove silanol groups [102]. Other treatments with deactivation agents such as inorganic salts may be used [102].

Green and Pust [103] reported the separation of hydrogen, air, carbon monoxide, carbon dioxide, C1 to C4 alkanes and alkenes on silica gel column. Mohnke and Saffert [104] developed silica PLOT columns by the reaction of glass (tubing) with ammonia at 170°C. They separated hydrogen isotopes on this column. Bruner and Carton [105] prepared silica columns using a similar in situ technique. Schwartz et al. [106] reported the separation of hydrocarbon C1 to C7s at room temperature on plastic and metal columns coated with Nalcoag 1022 colliodal silica. Fish et al. [107] used silica gel to separate combustion gases containing phosgene, hydrogen chloride and chlorine. Kiselve et al. [108], and Purcell and Ettre [109] used silica gel to accomplish the separation of n-alkanes through C29 in a reasonable time. Thornsbury [110] described its use in Claus plant gases that include air, carbon dioxide and sulfur gases. Guillemin and co-workers [111,112] and Cirendni et al. [113] studied the separation of C4 isomers with symmetric peak shapes on porous silica beads that were modified with water and liquid phases. Treatment with other agents including liquid organic agents and inorganic salts were reported by Mathews et al. [114], Aue and Wickramanayake [115], Barry and Cooke [116], Kopecni et al. [117], Prochazka and Smolkova [118], and others [119,120,122].

Chrompack introduced commercial silica PLOT columns in 1997 [121]. Similar silica phase PLOT columns were introduced first by Astec (GasPro) [123] and are now available from J&W Scientific [33].

2.2.5. Porous polymers

The term porous polymer is used for distinguishing divinylbenzene (DVB) based copolymers from Porapak, Chromsorb Century and Hayesep that are widely used for preparation of packed columns. The porous polymers, possibly first suggested, synthes-

ized and used in GSC columns by Hollis and co-workers [17–19], have similar structures to Porapak and Chromsorb Century materials. They are classified as Q, S, U type, and others, and their polarity is in a Q <S <U order, based on the monomers used. However, the column selectivity with these porous polymers is slightly different from packed columns prepared with Porapak, Chromsorb Century, or Hayesep materials.

Porous polymers used for the preparation of commercial PLOT columns are made of DVB homopolymer (J&W GS-Q, HayeSep Q) or DVB-based copolymers. Because of their highly crosslinked structure, these polymers are very porous, ranging from meso- to microporous. Because emulsion polymerization is a conventional technique to synthesize the polymers, the particle size is often less than 2 μm [101]. Surface area can range from 250 to 1000 m^2/g [124]. DVB–styrene copolymer is named as Q type [124,125], DVB–pyridine copolymer is classified as S type [126,127] and DVB–ethylene glycol dimethyacrlate [128–133] copolymer as U type. Corresponding commercial brands are GS-Q, CP-PoraPLOT Q, S, U, and HP-Q, and others. These porous polymers can be modified with a basic agent such as KOH for amine analysis. Lindsay et al. [134], Mohnke et al. [135], and others reported the modification of polymer and the separation of primary amines.

Many studies have reported the characteristics of similar porous polymers used in packed columns [17–19,131,136–141]. These characteristics include the retention volume, retention index, water resistance, and separation of hydrocarbon isomers, fluorinated compounds, and fixed gases. Pankow et al. [142] investigated gas–solid chromatographic property of these polymers or similar ones. They reported the retention volumes of aliphatics, halids, aromatics, ketones, amines, alcohols, phenols, acids and others on these polymer beads. De Zeeuw et al. [124,143], and Ruan and Liu [126] discussed selectivity (retention indices) of porous polymers they developed. Yang et al. [132] described the modification of porous polymer by polar liquid phase, β,β-oxydipropionitrile and PEG-20M, to improve the separation of isomers. Yu and Liu [133] synthesized the polymer of acrylonitrile crosslinked by DVB. Its polarity is similar to the porous polymer, U type.

2.2.6. Others

Smolkova and co-workers [144,145] investigated the possible use of cyclodextrin as GSC stationary phase for a wide range of separations in hydrocarbons (>C5), alcohols and halocarbons. Armstrong and his group [146–153] have extensively studied the GSC separations of cyclodextrin including fixed gas, light hydrocarbons, and halocarbons. Their work led to the commercial GasPro PLOT column [123]. Other studies are been reported in [154–157].

Many researchers have reported other sorbents as stationary phases and their separation ability in fixed gas and hydrocarbons. These sorbents include polyurethane [158], alkali chlorinate salts [159,160], cobalt phthalocyanine on GCB [161], Kaolin [162,163], natural magnetite and NH_4-clinoptilolite [164,165], mercury sulfide [166], rubidium chloride over silica [167], rhodium (I) and ruthenium (II) on silica [168], ammonium tungstosilicate on glass beads [169,170], titanium phosphate [171] and charcoal [172]. The separations on these sorbents are rather limited and specific, compared to ones used in commercial PLOT columns.

2.2.7. General requirement for stationary phase

The sorbent to use in chromatography must meet certain requirements. Kiselev and co-workers [35,36] investigated the structures and properties of many sorbents widely used in chromatography. De Zeeuw et al. [24] discussed general requirements for PLOT column stationary phase materials. Specifically, these materials must have homogeneous and uniform properties in the distribution of pore size, particle size, and surface area. Any imhomogeneity in material properties will result in decreased column efficiency, broadening peak, and changing elution order. Additionally, the materials should be inert for chromatographic purposes [31].

2.3. Separation mechanism

It is important to clarify the basic principles of GSC separation to predict the application of PLOT columns. The theoretical works of Giddings [173] are almost solely with column efficiency in GSC. In Giddings' theory, the coefficients of the linear velocity (*u*) term, C_m and C_s, are inversely proportional

to the diffusion rate of the analyte molecules in both the mobile and the stationary phases. If the coating layer of a PLOT column is highly porous, the diffusion rate of molecules inside the coating layer is fast, just like in the mobile phase. Then the C_s becomes smaller, so it increases the column efficiency. A similar conclusion applies to the thinner coating case. The coatings of most PLOT columns are relatively thick, e.g., 50 μm, making their efficiency relatively lower than conventional WCOT columns that have much thinner coating, e.g., 5 μm. Because of the relatively strong interaction of sorbents inside PLOT columns with polar molecules of the analyte, the diffusion rate of these polar ones is slower than less polar ones. Thus, the column efficiency for less polar molecules would be higher than polar molecules. So it is true for the molecules with different boiling points. Moreover, the rate of adsorption–desorption on the surface of the sorbent for the analyte molecule (affinity) clearly determines the diffusion rate inside the stationary phase. If the rate is high, column efficiency would be higher, too. In conclusion, properties of the coating layer of the PLOT column and the analyte molecule determine the column efficiency. Such properties include coating thickness and column diameter, porosity and surface activity of sorbent, boiling point, polarity, molecular size and shape of analyte.

Like GLC, the elution order of analytes on PLOT column basically follows the boiling point or the carbon number of analyte molecules. An exception is observed for aluminum oxide PLOT columns for which alkenes and alkynes may elute after the next alkane. Basically, the retention of analyte molecules is achieved by adsorption–desorption onto the different activity sites of the sorbent surfaces (both inner and outer if the sorbent is porous). The chromatographic separation is obtained by the transportation of carrier gas flow. The rate of adsorption–desorption, which may not be the same, and the interactions of analyte molecules with activity sites on the sorbent surface (affinity), determine the column selectivity.

Column selectivity is classified approximately by three types of interactions of sorbent with analyte: size, strong dipole (polar) and polarizable. Molecular sieves such as 5A, 13X, carbon sieve and porous polymer provide separation by sizing or sieving. The particles have small pores of only a few angstroms that allow the selective permeation of small gas molecules. Larger molecules such as sulfur hexafluoride and isobutane elute earlier than smaller molecules (helium and nitrogen).

Aluminum oxide provides a separation based on strong dipole interactions. Both the deactivation agent (mostly inorganic salt) and aluminum oxide have very strong and permanent dipole that weakly interacts with nonpolar compounds such as hydrocarbons, so separation of hydrocarbons can be obtained within a relatively short time. This dipole effect enhances the separation of light hydrocarbon isomers and causes the elution order of alkene and alkyne not to follow their carbon number or boiling point. However, polar or polarizable molecules such as oxygenate hydrocarbons are strongly retained, which makes the separation of these molecules nearly impossible within a short time at a practical operating temperature.

Interactions of analyte with porous polymer PLOT columns involve polarizable selectivity. The induced dipole at the phenyl group interacts with the analyte molecules. However, it is much weaker than that in the aluminum oxide case. Therefore, the separation of polar molecules such as light alcohols, thiols, ketones, ethers and esters can be achieved. Because of the weaker induced dipole effect, the non-polar light hydrocarbons can be separated, but the separation of the isomer is poor compared to aluminum oxide.

In actuality, the separation mechanism on PLOT columns cannot always be classified simply as one of the above three types. More often, all these types of mechanisms may occur simultaneously to produce a bimodal or trimodal separation. GS-GasPro PLOT columns could be a good example of columns with multimodal separation characteristics: sieving for fixed gas separation (−70°C), dipole for improved separation of isomers and polarized selectivity for general separation of hydrocarbons and solvents. Detailed discussions of the separation mechanism can be found in Refs. [144–153].

2.4. Coating techniques

The successful preparation of PLOT columns depends greatly on coating techniques. The column

properties such as capacity factor (k'), coating efficiency, column selectivity and column inertness are directly affected by the coating technique. The coating techniques used to make PLOT columns are in situ polymerization, dynamic coating, and static coating.

PLOT column preparations with in situ polymerization were reported for porous polymers [17–19,125,128–133], molecular sieve, zeolite [174], silica [122,158,175] and others. In this technique, the solution of monomer, catalyst, and solvent is first filled into or pushed out of a column. The column is then heated (if necessary) for certain time to complete reaction (polymerization), producing a porous layer structure inside column. After reaction, the residue solvents and monomers are removed by either purging with gas or rinsing with another solvent rinsing followed by gas purging. Heating also helps to speed up the solvent removal.

Dynamic coating, possibly first started by Dijkstra and DeGoey [176], has been used for the preparations of alumina [14,20,21,23,52] and molecular sieve, zeolite, [71] PLOT columns. For this technique, a slurry-like suspension solution plug is first filled into the capillary column under high gas pressure, and then is pushed through the column at a steady speed, leaving a wet coating layer behind the meniscus of the plug. To avoid acceleration of the solution plug near the exit of the column being coated, a buffer tube is attached to the column end as a restrictor. After coating, the column is allowed to settle for certain time, e.g., overnight, to let the coating thicken. Then the wet coating layer is dried by continuous gas purge.

Static coating has been used to prepare molecular sieve [58,61], silica [106], and porous polymer PLOT columns [124]. For this technique, the column is filled with a dilute, stable suspension solution. The solvent (suspension agent) then is evaporated under vacuum, producing a semi-wetted coating layer.

Columns made by any of these coating techniques are required to condition under gas purge for up to 24 h. The conditioning serves multiple purposes: to remove solvent residue and low-molecular-mass compounds resulting from thermally decomposed polymer or compounds adsorbed on the surfaces of sorbents, to immobilize the coating particles, to activate porous layer (particles), and to tune up

column selectivity. Effects of the conditioning temperature and time on a column property (capacity factor, efficiency, retention indices) have been discussed [52,124–126].

The coating thickness of PLOT columns directly controls column retention property based on the partition theory [3,5]. For most commercial PLOT columns, the thickness ranges from 5 to 50 μm, to meet the requirement for separating very small molecules. De Zeeuw et al. [24] and Mohnke and Heybey [61] discussed the requirement of coating thickness.

The thickness (D_f) of coating layer can be modeled by the following equations. In the dynamic coating case, the thickness (D_f) of coating is related to the coating speed (U_f) by:

$$(U_m - U_f)/U_f = 4(1 - x) = f(Ca) \tag{1}$$

where U_m is the speed of the meniscus. $x = D_f/r$ is non-dimensional thickness scaled by the radius (r) of the capillary column, and Ca is the capillary number of the suspension solution defined as

$$Ca = U_m \eta/\sigma \tag{2}$$

where σ is the surface tension and η is the viscosity.

For a Newtonian fluid (for example, water, solvent and milk) $f(Ca) = Ca^m$, $m = 1/2$. The suspension solution to coat a PLOT column is usually non-Newtonian fluid (shearing thinning). Thus, the m is less than $1/2$.

The coating thickness by dynamic coating over length (L) can be determined also by the consumed solution plug length (L_1) as:

$$D_f/r = 1 - (1 - L_1/L)^{1/2}$$
$$= 1/2 \, L_1/L\left[1 + L_1/4L + 1/8 \, (L_1/L)^2 + \ldots\right] \tag{3}$$

and L_1 is related to the coating speed as

$$U_m = U_f - dL_1/dt \tag{4}$$

When L_1/L is small, it leads to:

$$D_f/r = L_1/2L \tag{5}$$

The mass per unit length M/L is given by

$$M/L = cAL_1/L \tag{6}$$

where L is the length being coated, c is the concentration of the solution (w/v), and A is the cross-section area of capillary tubing.

In the case of static coating, the concentration (c=w/v) of particles determines the coating thickness by [61]:

$$D_f/r = 1 - (1 - c/\rho)^{1/2}$$
$$= c/2\rho[1 + c/4\rho + 1/8(c/\rho)^2 + \dots] \qquad (7)$$

when c/ρ is small, it leads to

$$D_f/r = c/2\rho \qquad (8)$$

where ρ is the density of drying porous layer. ρ is less than the true density of particles due to packing and shrinkage after drying.

Therefore, both the coating thickness and the coating mass per length are proportional to the concentration of suspension solution.

Both dynamic and static coating techniques require the preparation of solution suspended with fine particles. Many difficulties associated with the preparation of PLOT columns are related to the solution preparation, based on the experience of the authors. The requirement for the preparation of suspension solution would be:

(i) The solution must be rheologically stable at least for a couple days so that both coating and drying can be completed. Some rheological problems are sedimentation, agglomeration, and plugging. These problems produce either non-uniform coating (clogging) or failure in completion of coating.

(ii) The solution should have adequate concentration to determine the coating thickness (mass) governed by the above equations as well as rheology of the solution. As the concentration of the suspension is increased, the viscosity and surface tension are also increased. Sometimes this increase leads to plugging during coating.

(iii) Solvent (suspension agent) in the suspension solution must be compatible with the suspended particles and be completely removed by using conventional drying techniques. Any incompatibility of solvent to the surfaces of particles will result in phase separation of the suspension solution. As a result, it will either cause plugging during the coating or destroy the coating layer during the drying (clogging). The surface tension of solvent also directly affects the coating thickness. The variation

in coating thickness mostly relates to the variation in surface tension of water as solvent, which changes greatly.

(iv) The solution may contain some binder agent to bind fine particles after coating and drying to prevent particle regeneration and to maintain column open-tubular structure. In addition to the binding purpose, the binder may act as the surfactant or stabilizer of the suspension solution. However, the binder used often changes the chromatographic property of columns such as elution order and column inertness.

Effective approaches to overcome the rheological problems in the preparation of suspension solution are to use smaller size particles, to well-disperse the suspension solution, to change solvent, and to even change the concentration of solid particles.

With good progress in coating technology, the reproducibility of PLOT columns once questionable at the earlier development stage has improved greatly. De Nijs and co-workers [24,52], Sidisky and Robillard [100], Ji [177], and others have reported satisfactory reproducibility in retention time and peak area for some commercial PLOT columns. Similar results can be found in the applications of PLOT columns given by many chromatographers.

2.5. Column dimensions and manufacturers

Most of the improvements in GSC and PLOT columns have been made in the commercial sector. Table 2 lists typical examples of the modern PLOT columns representative of these developments.

With the progress in coating technology, 0.53 mm, 0.32 mm and 0.25 mm I.D. capillary PLOT columns with lengths up to 100 m can be prepared routinely. It is also feasible to prepare alumina PLOT column down to 30 m×100 μm I.D. The theoretical plate value of this column can be 5000 plate/m (pentane, 100°C).

3. Practical aspects of PLOT columns

3.1. Practical maintenance and use of PLOT columns

It cannot be overstated that careful maintenance and correct operation are necessary to fully use the

Table 2
PLOT column manufacturers

Manufacturer[a]	Product name	Stationary phase	Film thickness (μm)	Internal diameter (mm)	Length (m)
Alltech	At-Alumina	Aluminum oxide	Not available	0.53	30
Alltech	At-Mole Sieve	Molecular sieve 5A	Not available	0.53	30
Chrompack	CP-Al$_2$O$_3$ PLOT	Aluminum oxide deactivated by potassium chloride or sodium sulfate	4–10	0.25, 0.32, 0.53	10–50
Chrompack	CP-Silica PLOT	Silica gel	4	0.32, 0.53	15, 30
Chrompack	CP-PoraPLOT, Q, S, U, Q-HT, Amines, CP-PoraBond Q	Porous polymer, DVB base copolymer	8–20	0.25, 0.32, 0.53	10–50
Chrompack	CP-CarboPLOT P7 CP-CarboBond	Carbon sieve	25	0.53	10, 25
Chrompack	CP-Molsieve 5A	Molecular sieve, 5A	10–50	0.32, 0.53	10–50
Hewlett-Packard	HP-Al$_2$O$_3$ PLOT, "KCl", "S", "M"	Aluminum oxide deactivated with different salts	5–25	0.25, 0.32, 0.53	10–50
Hewlett-Packard	HP-Molesieve 5A	Molecular sieve, 5A	10–50	0.32, 0.53	15, 30
Hewlett-Packard	HP-PLOT Q	Porous polymer, DVB base copolymer	10–50	0.32, 0.53	15–30
J&W Scientific	GS-Alumina, GS-Alumina/KCl	Aluminum oxide deactivated with different salts	Not available	0.32, 0.53	15–50
J&W Scientific	GS-Molesieve	Molecular sieve, 5A	Not available	0.53	30
J&W Scientific	GS-Q	Porous DVB polymer	Not available	0.32, 0.53	30
J&W Scientific	GS-CarbonPLOT	Carbon	1.5–3	0.32, 0.45, 0.53	15–60
J&W Scientific	GS-GasPro	Not specified	Not available	0.32	5–60
Quadrex	PLT-5A	Molecular sieve 5A	Not available	0.53	15, 30
Restek	Rt-Alumina PLOT	Aluminum oxide deactivated with different salts	Not available	0.32, 0.53	10–50
Restek	Rt-Msieve, 5A, 13X	Molecular sieve, 5A, or 13X	Not available	0.32, 0.53	5–30
Restek	Rt-Q and S PLOT	Porous polymer DVB base copolymer	Not available	0.32, 0.53	15, 30
Supelco	Alumina PLOT Alumina-KCl PLOT	Aluminum oxide	Not available	0.32, 0.53	30
Supelco	MolSieve 5A	Molecular sieve 5A	Not available	0.32, 0.53	30
Supelco	Supel-Q PLOT	Porous DVB polymer	Not available	0.32, 0.53	30
Supelco	Carboxen-10xx PLOT, CLOT	Carbon sieve or carbon	Not available	0.32, 0.53	15, 30, 60
UOP mat/sen	ZeoColumn	Aluminum oxide zeolite	Not available	0.3	35

[a] Alltech (Deerfield, IL, USA), Chrompack (Middelburg, Netherlands), Hewlett-Packard (Wilmington, DE, USA), J&W Scientific (Folsom, CA, USA), Quadrex (New Haven, CT, USA), Restek (State College, PA, USA), Supelco (Bellefonte, PA, USA) UOP mat/sen (El Dorado Hills, CA, USA).

unique features of PLOT columns and prolong their lives. Both column selection and sampling are crucial for a successful application, particularly for inorganic type PLOT columns. It is not unusual for liquid samples accidentally being introduced into aluminum oxide or molecular sieve PLOT columns. Occasionally, inorganic type PLOT columns are deactivated continuously or repeatedly by carbon dioxide, water or even acids contained in the sample. As a result, such columns can be damaged easily.

The practical precautions for maintenance of PLOT columns are adequate conditioning, proper connection to the GC, idling inside the GC oven and recovery after contamination.

After a column is received from a supplier and the box is opened, the first requirement for PLOT columns is thorough conditioning. During its storage

time, PLOT columns adsorb almost anything from air, thereby decreasing its retention property. The conditioning time is usually 10 to 24 h at the column's upper temperature limit. Conditioning also reduces the column bleed for porous polymer PLOT columns, silica PLOT columns, and some types of carbon sieve PLOT columns.

When a PLOT column is connected to a GC inlet, manufacturers recommend slowly increasing the head pressure, 2–3 p.s.i. for each step, to the setting one. In addition, the column should be purged for 5–10 min before connecting it to the GC detector (1 p.s.i.=6894.76 Pa). Purging will remove any particles that may have been dislodged. Additionally, oxygen adsorbed inside column should be purged to prevent oxidation of the stationary phase.

PLOT columns must be operated at a temperature

below their upper limit. Oxidation or thermal de-struction may occur for porous polymer PLOT columns if the temperature is higher than their upper limit. The results of phase oxidation are high column bleed and reduced retention time. To prevent phase oxidation, the carrier gas must be oxygen-free. Retention time and column selectivity will shift significantly for Al_2O_3 PLOT columns if they are heated to a temperature higher than 250°C for more than 2 h since the generation of more active sites occurs. For molecular sieve PLOT columns, high temperature conditioning will activate their surface and decrease their inertness for oxygen and some hydrocarbons. When the column is idling inside the GC oven, the oven temperature should be maintained to a range of 150–200°C.

In case of column contamination by improper sampling, column performance can be recovered by either conditioning or solvent rinsing. Solvents in-clude water or methanol for inorganic type PLOT columns and volatile organic solvents for chemically bonded porous polymer PLOT columns. The res-idues of these solvents can be removed by both purging with gas and conditioning. After solvent rinsing and drying, the column needs to be con-ditioned at its upper temperature limit for 1–24 h, depending on the column dimensions and rinsing solvent.

A more effective way to prolong column lifetime is to use proper sampling technique. PLOT columns, in general, are only good for "clean" samples. Table 3 lists compounds that may damage PLOT columns, based on the authors' experience.

The use of a trap PLOT column is a practical sampling technique that prevents damage to ana-lytical PLOT columns. Often this trap column is a porous polymer Q type column [178,179]. Water, solvents and thiols in a hydrocarbon stream are trapped on porous polymer sorbent of the trap column and retained while the other hydrocarbons and fixed gases are directed to column by a timed valve switch and separated by an aluminum oxide or molecular sieve PLOT column. However, the re-liability and reproducibility of this technique depends on the column reproducibility (because of timed switch) and the degree of particle immobilization inside the column (particle generation and signal noise). The details of the valve switch and the column connection for such a purpose are given in Ref. [56].

Table 3
Compound compatibility with PLOT columns

Compound	Aluminum oxide	Molecular sieve, zeolite	Porous polymer	GasPro	Carbon sieve	Silica
Carbon monoxide	a, b					
Carbon dioxide	a, b	a, b				
Water	a, b	a, b		c	b, c	b, c
Hydrogen sulfide	f	f	c		c, f	
Carbonyl sulfide	f	f			c, f	
Carbon disulfide	f	f	c		c, f	c
Thiol	f	f	c		c, f	
Alcohol-ketone and other solvents	f	a, b, f	d	c	b, f	
Hydrocarbons C2 and higher		d, e, f			d, e	
Hydrocarbons C6 and higher		d, e, f	e		e, f	e
Hydrocarbons C10 and higher	e	e, f	e	e, f	f	e
Hydrochloride acid	f	f	a, b, c	a, c	f	f
Halids	c	f			c, f	

[a] Strongly or permanently adsorbed, slightly or slowly damages column.
[b] Decrease the retention time, but some of that loss recovered by conditioning.
[c] Some irreversible adsorption, not good for trace analysis.
[d] Quantitation problem on some brand of columns.
[e] Not recommended but usable.
[f] Avoid.

3.2. Limitations and disadvantages of existing PLOT columns

After a wide range of use, limitations and disadvantages of PLOT columns have been identified. Compared to WCOT columns, some of them have lower efficiency and sample loading capacity. For some separations, column inertness is unsatisfactory. Also, reproducibility–stability problems may appear over time. Moreover, the immobilization of the coating in the early-developed PLOT columns was insufficient, and particle dislodging occurred. Some of these disadvantages have given misleading, while others limit the application scope of PLOT columns.

3.2.1. Efficiency

Aluminum oxide and GasPro PLOT columns have relatively high efficiency comparable to WCOT columns. However, porous polymer, silica, carbon sieve, and molecular sieve PLOT columns have much lower efficiency. Most PLOT columns are very selective (thus separate) for specific analytes such as fixed gas and light hydrocarbons, the low column efficiency has less impact on high-resolution chromatography. Factors such as conditioning and coating affecting the column efficiency have been investigated [52,126,143].

3.2.2. Sample loading capacity

In general, all PLOT columns have limited sample-loading capacity compared to WCOT columns and packed columns. PLOT columns have only about 1% of the loading capacity of WCOT or packed columns [54,180].

Low sample-loading capacity of PLOT columns has been overcome by increasing column selectivity. This is why various PLOT columns with different selectivity have been developed. For aluminum oxide PLOT columns, deactivation agents such as potassium chloride, sodium sulfate, and other salts or mixture control the column selectivity [54]. For porous polymer PLOT columns, different monomers, styrene, pyridine, and acrylate, are co-polymerized with divinylbenzene to adjust the column selectivity and optimize the separation. Table 4 lists the retention indices for different types of PLOT columns in an increasing order of column selectivity.

Table 4
Retention indices (RIs) of PLOT columns

Column	RI (propylene)[a]
Porous polymer Q type	292
Porous polymer S type	300
Porous polymer U type	310
Silica	320
GasPro	350
Al_2O_3/KCl	352
Al_2O_3	360
Al_2O_3/Na_2SO_4, HP S	365
HP-Al_2O_3 M	375
GS-Al_2O_3	380
Carbon Sieve	NA
Molecular sieve, 13X	NA
Molecular sieve, 5A	NA

[a] Typical values at 100°C.

3.2.3. Inertness

Lack of inertness for non-hydrocarbon compounds, is the most challenging problem for some PLOT columns. Such compounds include sulfur gases [181], amine and nitrous gases [182], alkenes or halocarbons [183], water [54], and volatile acids. Lack of inertness of PLOT columns not only produces difficulty for trace analysis but also causes poor reproducibility of analysis. As a result, active or reactive compounds deactivate the sorbent inside the PLOT column, thereby decreasing retention time and producing irreproducible peak areas over multiple runs.

The physical properties of the stationary phases cause this problem. Some sorbents such as aluminum oxide and molecular sieve zeolites are made in a large-scaled industrial batch size for non-chromatographic purposes and are not totally chromatographic inert. The localized surface energy of the enormous amount of fine particles in the sorbents can be very high, causing a catalytic effect. Most sorbents are not free of chemical reactions or irreversible surface adsorption with analyte molecules. Such reactions and adsorption problems include:

(i) The irreversible adsorption of carbon dioxide, and nitrous gases occurs on aluminum oxide because of the Lewis acid–base reaction [182].

(ii) When using hydrogen as a carrier gas, the hydroxyl bond from sol-gel glue used to immobilize molecular sieve particles presumably catalyzes the

reaction of a small amounts of oxygen in the sample with hydrogen to form water, which is strongly adsorbed by the molecular sieve particles. A similar phenomena is observed for halocarbon dehydration on aluminum oxide [183–186].

(iii) Hydrogen sulfide can be adsorbed by porous polymers [181,187] because of free radicals present inside the highly crosslinked polymer caused by thermal destruction.

Table 5 shows the typical trace-level capability of most PLOT columns under direct sample introduction, i.e., without sample enrichment. Large-size sample introduction may extend this capability.

3.2.4. Reproducibility/interchangeability

Generally, PLOT columns have good reproducibility in retention time and peak area count compared to packed columns. Typical retention time variation would be 1% relative standard derivation (RSD). Peak area variation for non-trace level analysis would be less than 5% RSD. Poor sampling techniques, sample shelf life, and column inertness cause higher RSD in peak area count. Deactivation by continuously sampling of samples containing active reactive compounds produces the shifting in retention time. These derivations cause difficulty for routine analysis and monitoring.

Lack of interchangeability of different brands of PLOT columns is a major problem for routine applications. This problem is associated with a different retention time factor (k') and column selectivity of similar stationary phase PLOT columns. For example, k' (pentane, 100°C) of the commercial aluminum oxide PLOT columns ranges from 2.5 to 6.5, and the retention indices of propylene for several porous polymer Q type PLOT columns ranges from 287 to 298. Interchangeability requires standardization in sorbent characteristics and coating thickness, but this would be extremely challenging for column manufacturers, who prefer to have uniquely different columns.

3.2.5. Immobilization

The porous particles of early PLOT columns were poorly immobilized, causing detector spikes when particles were dislodged from the column. Also, particles had a tendency to move under carrier gas flow and temperature programming conditions. All these problems caused baseline noise or spiking, which decreased detection sensitivity or generated ghost peaks [186].

With the progress in binding technology used for modern PLOT columns, the immobilization of porous layer has been improved greatly. The binding technology can be classified into two approaches: chemically bonding particles, or physically "gluing" of particles with a binder. Chemically bonding produces superior immobilization of particles. Chemically bonded columns can withstand higher gas flows and head pressures as high as 80 p.s.i.g. Some PLOT columns even can be rinsed with solvent without particle loss. HP-PLOT Q and HP-PLOT/Al_2O_3 PLOT columns (Hewlett-Packard), CP-PoraBond Q, CP-Carbobond and CP-silica PLOT columns (Chrompack), GS-GasPro, and GS-CarboPLOT (J&W Scientific) are examples of chemically bonded columns. Physically "glued" columns include some of porous polymer PLOT columns, molecular sieve zeolites PLOT columns and carbon sieve PLOT columns. Although most of these columns are well immobilized at low carrier gas

Table 5
Trace-level capability of PLOT columns without sample enrichment

Column	Typical trace level (ppm)[a]
Al_2O_3	1 hydrocarbon
Molecular sieve, 5A	1 oxygen, 10 hydrogen
Carbon sieves	10 fixed gases
Porous polymer, Q type	10 hydrocarbon, 100 hydrogen sulfide, 10 oxygenate
Silica	1 oxygenate, 10 hydrocarbon, 1 sulfur gases
CP-Lowax	0.1 oxygenate
GS-GasPro	0.1 hydrogen sulfide, 1 hydrocarbon

[a] Authors' estimate. Typical sample size: 0.25 ml, split ratio 20:1.

pressure, they cannot withstand vibration during handling or when installed inside GC oven, nor can they withstand the high-pressure carrier gas flow in a fast GC analysis or a valve switching operation. The result is the particle dislodging or *snowing*.

4. Applications

PLOT columns have been used successfully for many gas analyses [5]. A good source of these successes can be found in the presentations of column manufacturers in the proceedings of the Pittsburgh Conference, 1985. Another one is the applications of PLOT columns appeared in the WEB pages of each column manufacturer. Very practical guidance of gas analysis by chromatography is referred to by Cowper and DeRose [56], though it was based on packed column technology. This paper illustrates and reviews typical applications of PLOT columns.

4.1. Fixed gases

Fixed gases are inorganic molecules that are presented as gaseous phase at ambient condition. These molecules include oxygen, nitrogen, noble gases, carbon mono-/dioxide, sulfur gases such as hydrogen sulfide, methyl mercaptan, ammonia, nitrous gases and others. These are analyzed either as a matrix, mixture, or minor compounds from a major matrix such as ethylene. Because air with carbon mono-/dioxide is present everywhere, almost all gas analyses inevitably deal with it.

Fixed gases can be separated on many types of PLOT columns. Fig. 1a shows such a separation on a molecular sieve 5A PLOT column. As shown in this chromatogram, molecular sieve 5A PLOT columns can produce the highest resolution of oxygen and nitrogen, thereby making it the most popular column used in gas analysis. Noble gases including helium, argon, neon, krypton and xenon can be separated on the molecular sieve PLOT column at above ambient temperatures. However, such an analysis requires
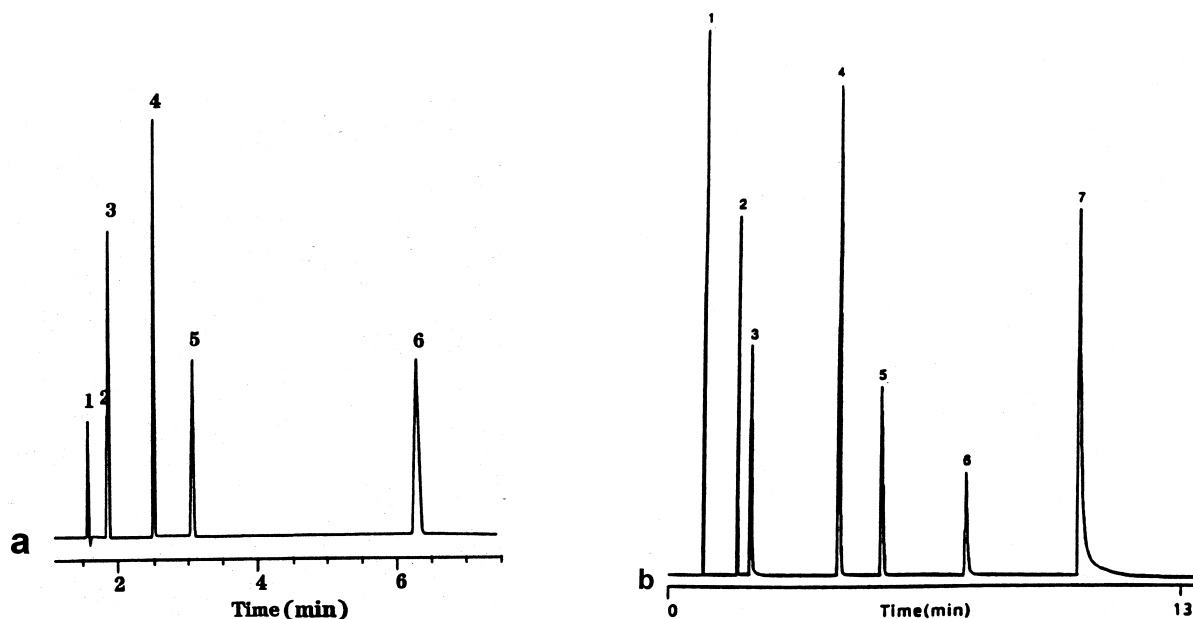

Fig. 1. Separation of fixed gases. (a) HP-PLOT Molesieve 5A, 30 m×0.32 mm. Oven: 40°C. Carrier: Helium. Injection: 5 μl fixed gas sample, split. Detection method: TCD. Peak identification: 1=neon, 2=argon, 3=oxygen, 4=nitrogen, 5=methane, 6=carbon monoxide. (b) GS-GasPro, 30 m×0.32 mm. Oven: 25°C (3 min) 10°C/min to 200°C (hold). Carrier: helium. Injection: 50 μl, split. Detection method: TCD. Peak identification: 1=nitrogen, 2=carbon dixoide, 3=sulfur hexafluorine, 4=carbonyl sulfide, 5=hydrogen sulfide, 6=ethylene oxide, 7=sulfur dioxide. Courtesy of J&W Scientific.

longer and thicker film columns. Molecular sieves 5A and 13X strongly but not irreversibly adsorb carbon dioxide [188], chlorine, sulfur and nitrous gases. If these gases are presented in a sample, GS-GasPro PLOT columns could be used. Fig. 1b shows the chromatogram of separation of sulfur gases from other fixed gases on a GS-GasPro column. This column possesses the excellent column inertness for sulfur gases. However, it cannot separate oxygen and nitrogen at above ambient temperatures. Carbon sieve PLOT columns can separate carbon monoxide and carbon dioxide from air, but the limited resolution in oxygen, nitrogen, carbon monoxide is problematic in some applications. Fixed gas separation including argon and oxygen on a porous polymer, Q type, packed column was reported by Hollis [19] at a near sub-ambient temperature. For the analysis of a sample containing water and CO_2, this type column can be used [179].

Table 6 lists the elution order for fixed gases on different PLOT columns.

Analysis of deuterated gas including isotopes that is present in natural gas can be also performed on molecular sieve PLOT columns [61]. However, for the isomer separations, the analysis is usually done at a low cryogenic temperature (e.g., $-70°C$) using a long column (e.g., 100 m) to obtain satisfactory separation. As a result, the analysis time is relatively long (70 min). Argon and oxygen separation also requires a long length and thick coat PLOT column operating at ambient temperature, otherwise it will be obtained at much lower cryogenic operation ($-60°C$) on short length (<30 m), thin-coat PLOT columns. Ji [189] reported separation of 99% argon from oxygen by using three 30 m×0.53 mm I.D., 50 μm thickness molecular sieve 5A columns at 30°C. Carbon dioxide eluted on a molecular sieve 5A column at high temperature (250°C), but the peak shape showed extreme broadening and tailing [188]. Sulfur hexafluoride will elute on a molecular sieve earlier than oxygen [189].

One of the difficulties in this kind of analysis is that there is no single known PLOT column that can separate all fixed gases completely. Multidimension GC using two or more PLOT columns is usually required [179]. Hence, valve switching and column connections are usually complicated [56,190,191]. Success of this analysis depends greatly on the reproducibility of the PLOT columns. An example of natural gas analysis using such multidimension GC technique is given [190].

4.2. Hydrocarbons C1 to C10

Light hydrocarbons (C1 to C10) are present in many petroleum products and feedstock as well as in our living environment. Thus, the analysis of hydrocarbons has a practical importance in our life. The

Table 6
Elution order of fixed gases

Compound	Molecular sieve 5A	Molecular sieve 13X	Carbon sieve	GasPro	Porous polymer
Neon	1	1	1	1	1
Hydrogen	2	1 or 2	1	1	1
Argon	3	2	2	2	3
Oxygen	3 or 4	2	2	2	4
Nitrogen	5	3	3	3	5
Krypton	6	NA[a]	NA	NA	NA
Methane	7	4 or 5	5	5	6
Carbon monoxide	8	5 or 4	4	4	2
Carbon dioxide	10 or NA	NA	6	7	7
Ethane	9	6	8	6	8
Isobutane	2 or 5	7	NA	NA	NA
Water	NA	NA	7	NA	11
Hydrogen sulfur	NA	NA	NA	9	9
Carbonyl sulfide	NA	NA	NA	8	10
Sulfur dioxide	NA	NA	NA	10	12

[a] NA: Not applicable.

analysis of hydrocarbons has used the chromatographic technique since the beginning of GC.

Light hydrocarbon analysis is perhaps the greatest class of PLOT column applications. Their separations can be achieved virtually on all PLOT columns, with a primary choice being the alumina PLOT columns because of its capability in isomer separation. Table 7 lists hydrocarbon separation on different types of PLOT columns. Figs. 2a–dshow the hydrocarbon separations on commonly used PLOT columns such as HP-PLOT/Al$_2$O$_3$, GS-GasPro, CP-Silica and HP-PLOT Q. The C1–C4 isomers are separated completely on the alumina PLOT column. Less co-elutions are found for C4s and above on the GasPro PLOT column; more co-elutions of C4 isomers occur on the other columns, particularly on porous polymer Q type.

More detailed separation of hydrocarbons C1 to C10 were reported on alumina PLOT columns [23,24,192–194] and on GasPro columns [33,148,152]. Armstrong et al. [148] compared the hydrocarbon separations on both types of PLOT columns.

The requirements for hydrocarbon analysis include column selectivity, column inertness and separation ability. Since hydrocarbon gas is relatively stable, column inertness is less problematic for most of hydrocarbons. Low level (low ppm) of dienes, such as butadiene and pentadiene is an exception. The separation of C4 or above dienes demands high column temperature; often making them polymerize on aluminum oxide (catalyst by acidity of aluminum oxide). Analysis of natural gas and other feedstock gases requires column's separation ability of C1 to C10 alkanes or above. The analysis time should be as short as possible, e.g., 2 min for up to C6 [189]. Samples such as ozone precursor, engine exhaust,

and gas of storage and package of vegetable/fruit contains low level of alkenes and alkynes [24,33,179,192–196]. Such analyses demand a good column inertness as well as column ability of isomer separation. Analysis of refinery gas, BTEX (benzene, toluene, ethylbenzene and xylenes) and other isomer separation needs sufficient column selectivity for alkenes, alkynes and aromatics. In general, both alumina and GasPro PLOT columns are able to meet these requirements, making them most popular choice for hydrocarbon separations.

The elution order of light hydrocarbons on different types of alumina PLOT columns is almost the same. The only exception is alkynes and dienes on Al$_2$O$_3$/KCl column. Their elution orders are sensitive to the column temperature program, particularly to the sample containing water and carbon dioxide, and often change between C3 and C4 alkanes. This change in elution order makes this type of PLOT column difficult to use in a routine analysis with a developed method.

Although alumina PLOT column is most selective PLOT column for hydrocarbon analysis, it is still not adequate selective for some hydrocarbon separations. This is demonstrated by the chromatogram in Fig. 2a. Any sample over-loading will affect the separation of the neighboring hydrocarbons from the matrix, such as ethylene, propylene, 1,3-butadiene. These effects include masking minor compounds due to peak tailing, elution time change, and oven temperature program. The minor compounds usually are ethane from methane, propane from ethylene, cyclopropane, possibly acetylene and propadiene, and isobutane from propylene, 1,2-butadiene and propyne from 1,3-butadiene, and so on.

This selectivity requirement leads to different brands of alumina PLOT columns, namely Al$_2$O$_3$/

Table 7
Hydrocarbon separation on different types of PLOT columns

| PLOT column	Largest hydrocarbons	Comment
Molecular sieve 5A	C3	C6 for branched alkanes. Not good for alkenes and alkynes.
Molecular sieve 13X	C12	Only for alkanes
Carbon sieves	C5	Good isomer separation up to C3.
Silica	C4	Improved isomer separation over carbon sieve PLOT columns
GS-GasPro	C10	Improved isomer separation over silica PLOT columns
Porous polymer Q type	C14	High temperature operation for C10 alkanes and above. Good separation up to C3 isomers
Aluminum oxide	C10	Optimized separation for alkane, alkene, alkyne and aromatics isomers
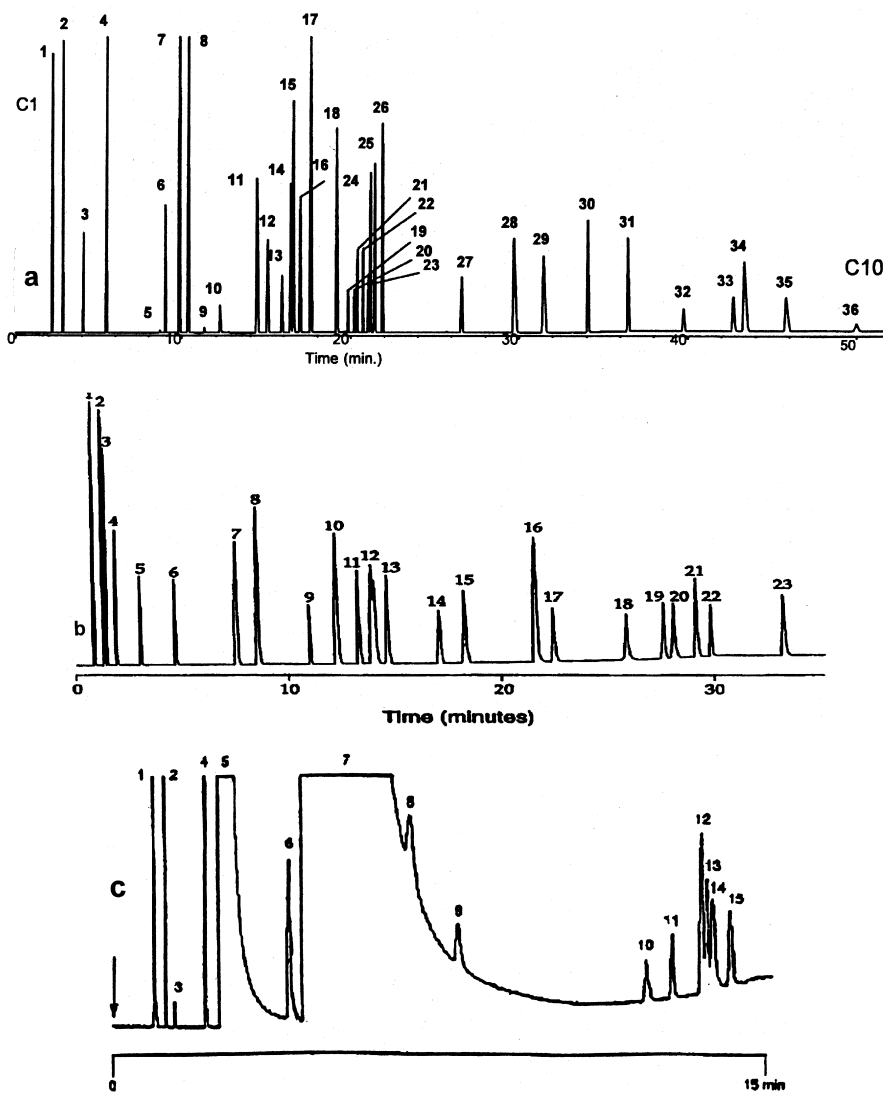
Fig. 2. Separation of hydrocarbons. (a) HP-PLOT Al_2O_3 "S", 50 m×0.53 mm. Oven: 40°C (2 min) 7.5°C/min to 100°C (5 min) 12.5°C/min to 180°C (10 min) 15°C/min to 225°C (20 min). Carrier: helium. Injection: 5 µl splitless. Detection method: FID. Peak identification: 1=methane, 2=ethane, 3=ethylene, 4=propane, 5=cyclopropane, 6=propylene, 7=isobutane, 8=n-butane, 9=propadiene, 10=acetylene, 11=t-2 butene, 12=butene-1, 13=isobutylene, 14=c-2 butene, 15=cyclopentane, 16=isopentane, 17=n-pentane, 18=1,3-butadiene, 19=t-2 pentene, 20=2-methyl-2 butene, 21=pentene-1, 22=c-2 pentene, 23=unknown, 24=cyclohexane, 25=2-methyl-pentane, 26=n-hexane, 27=n-heptane, 28=benzene, 29=isooctane, 30=n-octane, 31=toluene, 32=nonane, 33=ethylbenzene, 34=o- and m-xylene, 35=o-xylene, 36=decane. (b) GS-GasPro, 15 m×0.32 mm. Oven: 60°C, 2.5°C/min to 160°C. Carrier: helium. Detection method: FID. Peak identification: 1=methane, 2=ethane, 3=ethylene, 4=acetylene, 5=propane, 6=propylene, 7=isobutane, 8=n-butane, 9=propadiene, 10=butene-1, 11=1,3-butadiene, 12=t-2 butene and isobutylene, 13=c-2 butene, 14=isopentane, 15=n-pentane, 16=butyne-1, 17=pentene-1, 18=2,2-dimethyl butane, 19=2-methyl pentane, 20=3-methyl pentane, 21=hexane, 22=2-butyne, 23=1-hexaene. Courtesy of J&W Scientific. (c) CP-Silica PLOT, 30 m×0.32 mm. Oven: 50°C (5 min) 5°C/min to 180°C. Carrier: helium. Injection 100 µl, split. Detection method: FID. Peak identification: 1=methane, 2=ethane, 3=ethylene, 4=acetylene, 5=propane, 6=cyclopropane, 7=propylene, 8=isobutane, 9=n-butane, 10=butene-1, 11=propyne, 12=1,3-butadiene, 13=t-2 butene, 14=isobutylene, 15=c-2 butene. Courtesy of Chrompack BV. (d) HP-PLOT Q, 30 m×0.53 mm. Oven: 60°C (5 min) 20°C/min to 200°C (1 min). Carrier: helium. Injection: 0.25 ml or refinery gas sample, split. Detection method: TCD. Peak identification: 1=air/CO, 2=methane, 3=CO_2, 4=ethylene, 5=ethane, 6=H_2S, 7=COS, 8=water, 9=propylene, 10=propane, 11=methanol, 12=isobutane, 13=t-2 butene, 14=n-butane, 15=c-2 butene, 16=isopentane, 17=n-pentane.

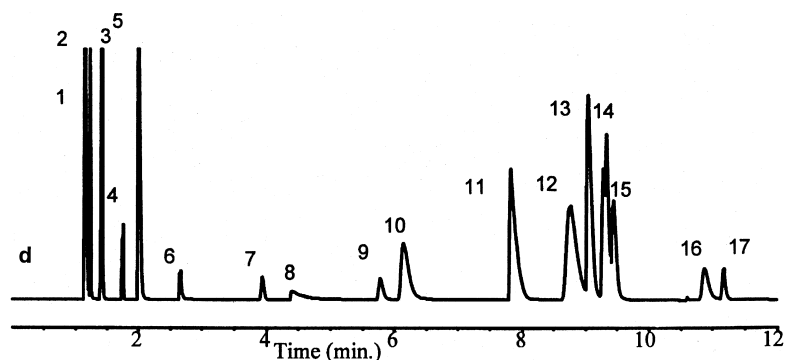Fig. 2. (*continued*)

KCl, Al$_2$O$_3$/Na$_2$SO$_4$, Al$_2$O$_3$ "S" and "M" and GS-Alumina and others. Based on the retention indices listed in Table 4, the Al$_2$O$_3$/KCl column is the least selective, even less selective than non-deactivated alumina PLOT column, and the GS-Alumina is the most selective. Variety in column selectivity provides multiple choices for many applications, but it sometimes results in difficulty of interchangeability, e.g., Al$_2$O$_3$/KCl to Al$_2$O$_3$ "S" or "M" or/Na$_2$SO$_4$, et al., because of different elution order and retention time in alkynes and alkenes.

4.3. Halocarbons C1 to C2

Analysis of halocarbons or less precisely chloro-fluorocarbons (CFCs) has the significance in environmental protection. CFCs destroy stratospheric ozone and are currently being phased out in the use of refrigerant fluids. Therefore, the demand for such an analysis is increasing worldwide.

CFC analysis is a much more complex task than any other known analysis done on PLOT columns. It has been shown that complete separation of C1s and C2s cannot be achieved on PLOT columns or WCOT columns. This is because isometric structure becomes more complicated as more substitute positions of halogen atoms are possible. It may require more selective PLOT column than the alumina columns, or multi-dimension GC, to achieve a complete separation of CFCs.

Known separation of CFCs on PLOT columns have been reported on alumina PLOT columns [197–199], porous polymer PLOT columns [200,201], silica PLOT columns [202] and GS-GasPro PLOT

columns [33, 153]. Alumina columns produce less co-elution separation, however, catalytic effect or dehydrohalogenation have been observed, principally with 1,1,1-trichloroethane, CHF$_2$Cl (HCFC 22), CH$_3$Cl, CH$_3$CF$_2$Cl (HCFC142b), CHCl$_2$CF$_3$ (HCFC123) [197–199]. Porous polymer PLOT columns have less activity problems than alumina columns, but the isomer separation is very poor due to low efficiency and lack of adequate column selectivity. Moreover, the less volatile halocarbons are too retained. They require high column temperatures to elute out of column, making it less practical [200]. GS-GasPro [33,153,202] and silica PLOT columns [202] produce better quantitative results while producing less co-elution separations. Greally et al. [202] discussed the detailed separation on these PLOT columns.

Figs. 3a and b show the chromatograms of CFCs on a CP-silica PLOT and a GS-GasPro column. With a careful instrumentation in sampling, analysis of CFCs at a low to sub ppm level is possible [202]. Co-elutions occurring on Gaspro PLOT columns include CFC12 and HFC125, HCFC 142b and HCFC 124, and others. Poorly resolved pairs and co-elutions occurring on silica PLOT column are HCFC 124 and HCFC 142b, HCFC 134a and CH$_3$Cl, HFC 32 and CFC115, CFC 12 and HFC 125, and others [202].

4.4. Volatile organic solvents

Volatile organic solvents are widely used in chemical processes, from laboratory synthesis to industrial process. Their vapors and residues also
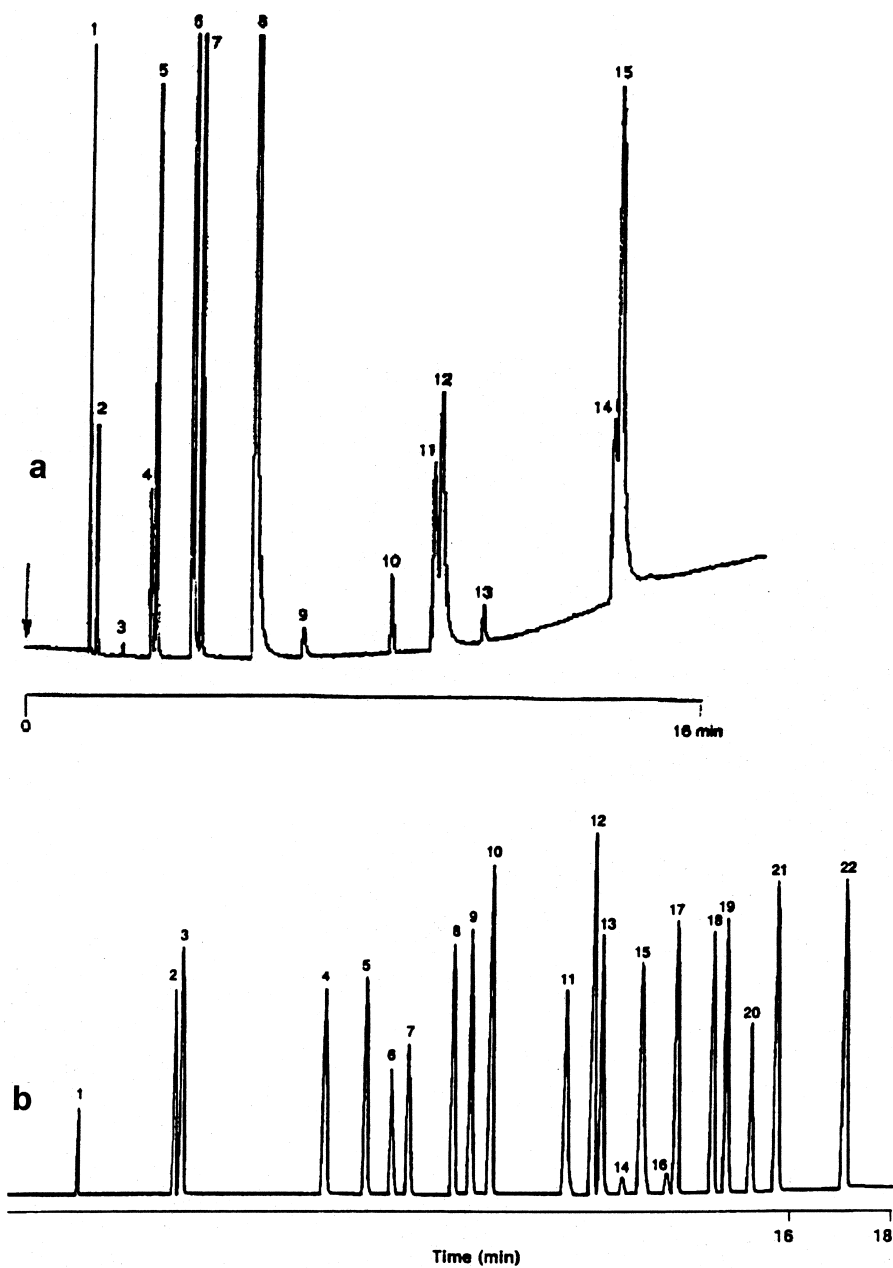
Fig. 3. Separation of halocarbons. (a) CP-Silica PLOT, 30 m×0.32 mm. Oven: 60°C (1 min) 10°C/min to 200°C. Carrier: helium. Injection: 100 μl split. Detection method: FID. Peak identification: 1=methane, 2=ethane, 3=CFC 116, 4=CFC 12, 5=CFC 22, 6=CFC 134a, 7=CFC 40, 8=CFC 114, 9=CFC 11, 10=CFC 30, 11=CFC 113a, 12=CFC 113, 13=CFC 20, 14=CFC 112a, 15=CFC 112. Courtesy of Chrompack BV. (b) GS-GasPro, 30 m×0.32 mm. Oven: 130°C (4 min) 10°C/min to 225°C (hold). Carrier: helium. Injection: 1 μl, split. Detection method: FID. Peak identification: 1=methane, 2=Freon 22, 3=Freon 12, 4=Freon 114, 5=Freon 21, 6=Freon 11, 7=Freon 12B2, 8=CH_3 I, 9=CH_2C_l2, 10=trans-ClCH=CHCl, 11=Freon 113, 12=cis=ClCH=CHCl, 13=$CHCl_3$, 14=unknown, 15=CCl_4, 16=unknown, 17=CH_2CH_2I, 18=CH_2Br_2, 19=$CHCl_2Br$, 20=C_4F_9I, 21=$CHClBr_2$, 22=$CH_3CH_2CH_2I$. Courtesy of J&W Scientific.

present in many areas including air and water. Although analysis of organic solvent samples is dominantly done on WCOT columns such as HP624, DB624 or Innowax columns, analysis of gas samples containing volatile organic solvents or their residues can be done particularly well on porous polymer, silica, carbon sieve and other PLOT columns. Table 8 lists typical these applications on PLOT columns.

Most popular PLOT columns used for volatile solvent analysis are porous polymer type PLOT columns because these columns possess good retention and selectivity at above ambient temperatures. Many column manufacturers have reported the separations of a wide range of polar/nonpolar volatile solvents on porous polymer PLOT columns [124,189,203].

Fig. 2d is the chromatogram for the separation of water and methanol from hydrocarbons on a PLOT Q type column. Water elutes after C2, while methanol elutes after C3. Fig. 4a is the chromatogram of common solvents to illustrate separations of hydrocarbon, alcohol, halocarbon, ketone, ether, ester, nitrile and arene at relatively higher temperature, starting from 150°C. Fig. 4b shows analysis of acetone on a CP-PoraPLOT U column. Note that water peak shape in this chromatogram is much

better than that on Fig. 2d. In spite of different column temperatures used in both cases, U type column usually produces much better peak shape for water than Q type, indicating reliable quantitation of water on it.

One of unique features of porous polymer PLOT columns is that water in a sample will not affect the column performance [16,17]. However, it had been reported that water and alcohol in a sample cause a problem by shortening the column lifetime of porous polymer PLOT columns as well as poor analysis repeatability, possibly resulting from the interaction of water with the binders inside the columns. New binding technology in the preparation of these PLOT columns overcomes this problem. Ji [189] reported that a Q type PLOT column had not shown any sign of degradation after 1800 injections with a water–alcohol sample. A similar result was also reported by De Zeeuw [203].

One of disadvantages of porous polymer PLOT columns in the applications of solvent analysis is that column efficiency is much lower than WCOT columns. For example, the theoretical plates of benzene may be as low as 300 plates/m. This low efficiency problem may cause a resolution problem. Another disadvantage is that high column temperature is

Table 8
Separation of solvents on PLOT columns

| Solvent	Typical PLOT columns	Comment
Water	Porous polymer, Q and U type, silica	Excellent water resistance on Q type columns, excellent water peak shape on U type columns
Alcohols C1 to C6	Porous polymer, Q and U type, silica, GasPro, Lowox	Chemically bonded Q type gives out more separations of alcohols, while Lowox provides excellent selectivity for low level alcohols (C1 to C5) and other oxygenates
Ketones, C1 to C6	All porous polymers, silica, and carbon sieve	S type provides more separations of ketones, others have small separation range
Esters, C1 to C6	All porous polymers, and carbon sieve	Q type is most popular
Aldehydes, C1 to C6	All porous polymers, carbon sieve	Q type offers a wider separations than any other porous polymer PLOT columns
Ethers, C1 to C5	All porous polymers	Q and U work better
Halogalkanes C1 to C2	All PLOT columns except molecular sieve, zeolites	GasPro and Silica work better than others because of less activities. Al_2O_3 gives out more separations
Nitriles/nitro-compounds C1 to C6	Porous polymer U type, and Al_2O_3,	Al_2O_3 column has an activity problem
Thiols C1 to C6	All porous polymer, silica, GasPro	GasPro is the best. Silica works better. U type has smaller separation range. Q is not inert enough
Amines, C1 to C6	PoraPLOT-amine and U type	Good separation of amines from air
Arenes	Al_2O_3 and porous polymer Q type	Excellent separation on Al_2O_3 columns
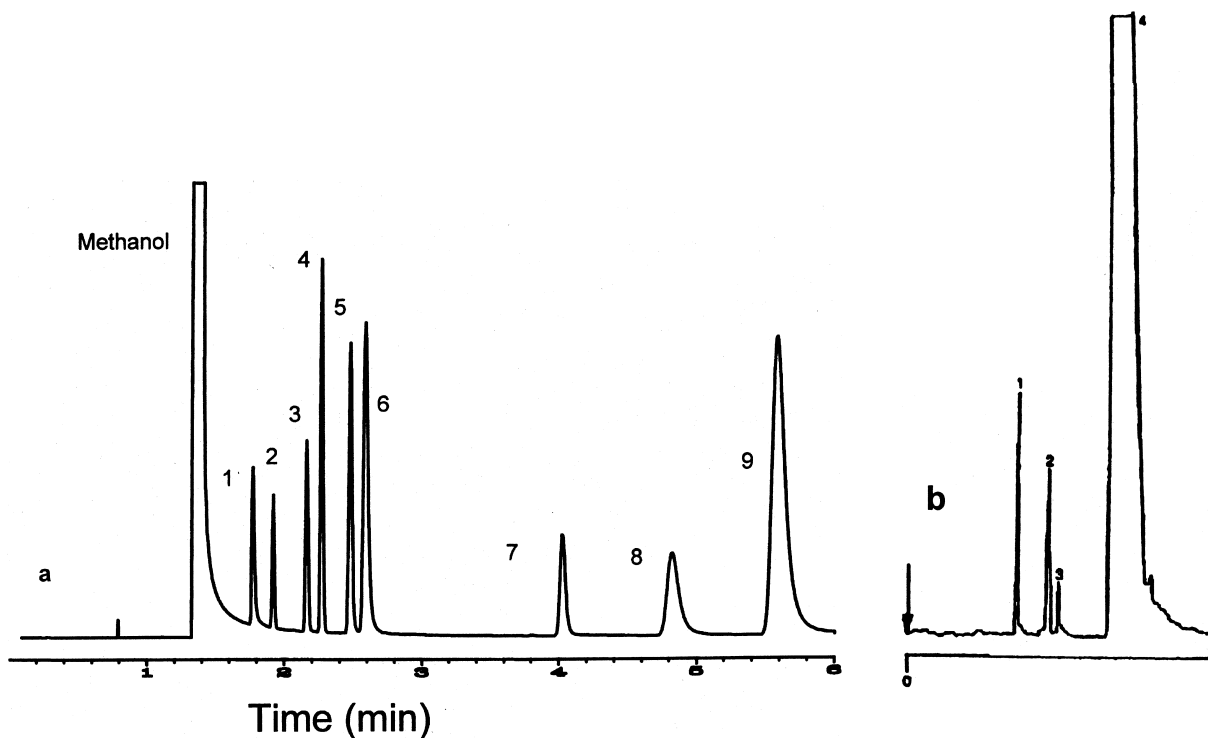
Fig. 4. Separation of volatile organic solvents. (a) HP-PLOT Q, 30 m×0.53 mm. Oven: 150°C. Carrier: hydrogen. Injection: 5 μl split. Detection method: FID. Peak identification: 1=ethanol, 2=acetonitrile, 3=acetone, 4=dichloromethane, 5=diethyl ether, 6=pentane, 7=ethyl acetate, 8=hexane, 9=benzene. (b) CP-PoraPLOT U, 25 m×0.32 mm. Oven: 175°C. Carrier: helium. Injection: 0.5 μl split. Detection method: TCD. Peak identification: 1=air, 2=water, 3=unknown, 4=acetone. Courtesy of Chrompack BV.

required for the elution of halocarbon, aldehyde, and others. This requirement will produce column bleed.

4.5. Sulfur gases

Analysis of sulfur gases has its significance from the process industry to environment. If sulfur gases are presented excessively in a feedstock stream, they poison the catalyst. The cost of replacement of catalyst and downtime of the process may be enormous. Food and wine contains some sulfur compounds as flavor and antioxidants, and their content should be accurately determined [204].

Analysis of sulfur gases is one of the most difficult tasks in gas analysis. Sulfur gases are hydrogen sulfide, sulfur dioxide, carbonyl sulfide, carbon disulfide and light mercaptans. These gases are very active–reactive, often being adsorbed onto surface and forming radicals. It requires special attention to

the sample preparation and introduction, separation and detection in a GC analysis [56]. Since in most cases, the sulfur gases are presented in samples at very low level (ppm or even ppt level [205]), reliability of GC analysis depends greatly on the column inertness [181]. Tuan et al. [28] reviewed the determination of sulfur gas in natural gas by using different capillary columns including several types of PLOT columns. They found that both porous polymer and carbon PLOT columns were not sufficiently inert, particular for hydrogen sulfide and sulfur dioxide. Other studies of the determination of low level sulfur gas with using of PTV technique was reported by Sye and Cheng [206].

Selectivity of porous polymer PLOT columns for sulfur gases presenting in a hydrocarbon stream is satisfactory, as shown in Fig. 2d. Hydrogen sulfide and carbonyl sulfide elute before propylene and relatively far after ethylene. Mercaptans are similarly

separated from hydrocarbons. However, these columns are insufficiently inert for trace analysis down to low ppm levels.

Both GS-GasPro and CP-Silica PLOT columns display better column inertness, making them suitable to trace level analysis of sulfur gases. With a careful sample preparation (e.g., cyrofocus), about 100 ppb level of sulfur gases can be analyzed [206]. Porous polymer, Q type, PLOT columns are sometimes used when column inertness is not critical for analysis. As shown in Fig. 2d, Q type PLOT columns provide satisfactory column selectivity for sulfur gases including mercaptans that are often used as odorants. Fig. 5a is the chromatogram of typical sulfur gas including light mercaptans, on a porours polymer Q type column, and Fig. 5b shows the separation of C2–C6 mercaptans on a GS-GasPro column.

Even though the column inertness has been improved, there is still a need to improve the column selectivity for sulfur gases. As shown in Figs. 1b and 2d, H_2S and COS peaks would be affected (mask-

ing), if ethylene or propylene is overloaded and these peaks become broadened. Additionally, when selective detector such as flame photometric detection (FPD) is used, the quenching effect of hydrocarbons will affect the accuracy of determination of sulfur gases. The ideal separation of sulfur gases on a PLOT column should be favorably separated away from hydrocarbons.

4.6. Others

A series of papers have reported specific applications of PLOT columns. Do and co-workers [182,207–209] investigated in series the cyanogen composites of outer space (Titan) gases by using alumina, porous polymer and molecular sieve 5A PLOT columns. They found that C1–C5 nitrous gas in the samples containing hydrocarbons, CO, CO_2 and air are well retained on a long Al_2O_3/KCl column. But nitrous gases have little effect on the separation of other fixed gases on the molecular sieve 5A PLOT column. The analysis of nitrous
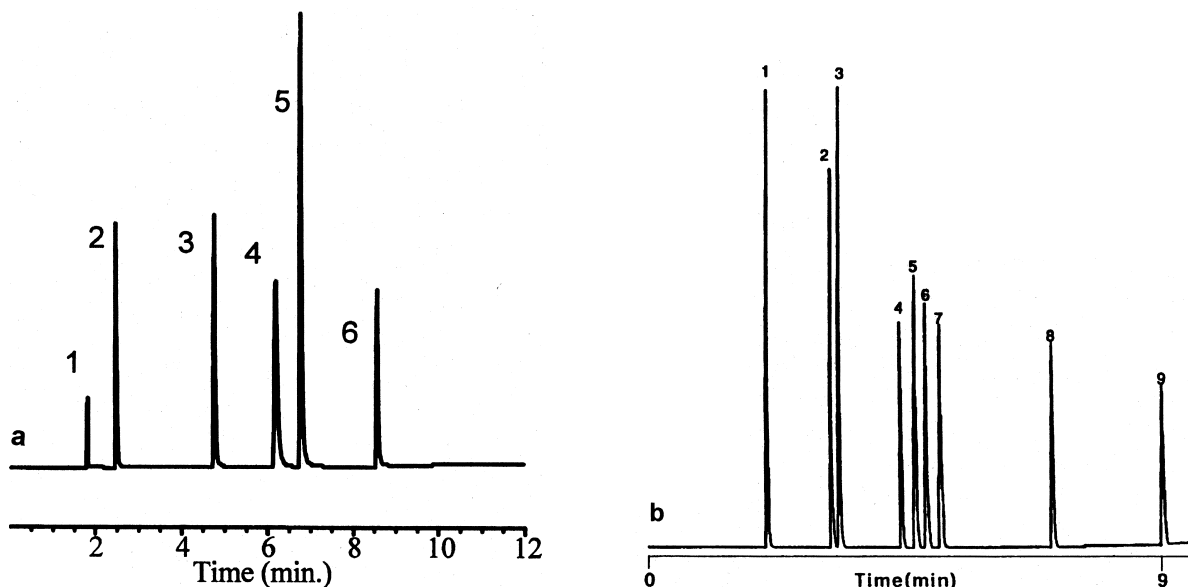

Fig. 5. Separation of sulfur gases. (a) HP-PLOT Q, 30 m×0.53 mm. Oven: 105°C (1 min) 15°C/min to 240°C (2 min). Carrier: hydrogen. Injection: 0.25 ml, split. Detection method: FID. Peak identification: 1=hydrogen sulfide, 2=carbonyl sulfide, 3=ethanelthiol, 4=isopropyl mercaptan, 5=n-propyl mercaptan, 6=n-butyl mercaptan. (b) GS-GasPro, 30 m×0.32 mm. Oven: 175°C (2 min) 10°C/min to 260°C (hold). Carrier: helium. Injection: 0.2 μl, split. Detection method: FID. Peak identification: 1=ethyl mercaptan, 2=2-propyl mercaptan, 3=1-propyl mercaptan, 4=2-methyl-2-propyl mercaptan, 5=2-methyl-1-propyl mercaptan, 6=1-methyl-1-propyl mercaptan, 7=1-butyl mercaptan, 8=1-pentyl mercaptan, 9=1-hexyl mercaptan. Courtesy of J&W Scientific.

gases is improved on a porous polymer PLOT columns [209]. Shen and co-workers [128–130] developed porous polymer PLOT columns to separate outer space gases in order to look for ammonia, water and CO_2 for tracing life origin in outer space. Their columns are similar to U type columns. Analysis of amines on a PLOT–amine phase column was reported in Refs. [135,216]. The separation of *n*-hexane, cyclohexane and benzene was obtained on a molecular sieve, ultrafine zeolite, ZSM-5 type, PLOT column [174]. Methyl bromide in air from pest control fumigations had been determined by using a PLOT column [210]. Volatile metabolites in human breath were analyzed by using PLOT column or packed column with Dexsil and detecting by an ion trap detector [211,212]. The separation of ethylene oxide in a spicy vapor on a Q type PLOT column was reported by Woodrow [213]. Medical gas and anaesthetic gas containing nitrous gases, carbon dioxide and others were analyzed [214,215] on porous polymer and carbon sieve PLOT columns. Dissolved gas in transform oil [217–219] and in jet fuel [179] had been analyzed by using two-dimensional GC with PLOT columns.

5. Future directions

Existing PLOT columns were developed as extensions to traditional packed column technology. After a long time of use, their applications have been firmly established. Meanwhile, their disadvantages and limitations also have been identified. To address these known problems, the development of PLOT columns should proceed in three directions. The first direction would focus on the column performance improvement. The second direction could be the change of column. And the third direction is to expand and explore new applications.

The development of PLOT columns using GasPro, carbon, silica, chemical bonded porous polymer, CP-Lowox and renewed Al_2O_3/KCl illustrates the first direction. The performance of these columns has been improved in column inertness, immobilization, column selectivity and column upper temperature limit. Their application scopes have been extended too. Since a significant part of analyses using PLOT columns is trace level analysis, perhaps more development efforts would be directed on improving column inertness.

The second direction would lead to faster GC and wider applications. The micro-GC system of Hewlett-Packard, producing quick separations (s) of many gases, utilizes short length and small I.D. PLOT columns. Present commercial PLOT columns have been designed primarily for gas analysis, leading to offering thick film and long columns. Large sized molecules can elute on these columns at higher temperatures and with longer time. For example, hydrocarbons of C6 and above are usually eluted after 10 min at above 150°C on most existing PLOT columns. If the coating thickness were reduced by one-third, these compounds would be eluted within 5 min or less. With use of shorter, thinner and smaller PLOT columns, the separation of C6 to C10 isomers including polar organic solvents would be improved, possibly replacing conventional WCOT technology in this area. Thinner coat also reduces the column activity and column bleed, as the result, the trace level of analysis can be increased.

Earlier works illustrate the third direction. Some C6 isomers can be separated on innovative molecular sieve PLOT columns. Sulfur compounds and amine compounds have been demonstrated to separate on some PLOT columns, but both column inertness and column selectivity are problematic. These would lead to developing more specific application oriented PLOT columns, as shown by Lowox PLOT column (Chrompack), that is suitable for the analysis of low level oxygenates presenting in hydrocarbon streams [34]. Finally, alumina, carbon, silica, molecular sieve and porous polymer have been long used in liquid–solid chromatography. It is well known that biomolecules can be separated on most known porous materials used for current PLOT columns. Can an open-tubular liquid chromatography capillary column be prepared by using PLOT column technology in a near future for bio-separation? Is there any good advantage to utilize very fine particles (down to 10 nm) used in today's PLOT columns to prepare a LC column for more efficient and effective bio-separation? If so, the pressure of the mobile phase would be very low, possibly impacting both the instrument and the instrumentation.

Acknowledgements

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