determined for the slope of the standard curves, with concentrations between 80 and 2000 p.p.m.

These between-days RSD values were 4.0% for diethyl sulfide, and 5.0% for methanethiol. These results include the errors arising from the dynamic dilution system used. In this case a photo diode array type detector was employed, which has the advantage of having a low wavelength drift.

Applications

GC–UV is a general method of analysis with numerous possible application areas. So far, the method has been little used and most investigations have been concerned with the fundamentals of the analytical principle. Nevertheless, a number of works have been published, for example the determinations of nitric oxide adsorbed on mineral fibres and isoprene and acetone determinations in exhaled breath. A method, using GC–UV for the determination of alcohols, denoted as GC–GPMAS (gas chromatography with gas-phase molecular absorption spectrometry) has been reported. These are short reports concerning determinations of single, double and polyaromatics in petroleum products, volatile compounds at low concentrations in air, irritants adsorbed on dust particles, determinations of compounds present in cigarette smoke, identifications of compounds in flavour samples, analysis of methanethiol, diethyl sulfide and hydrogen sulfide in paper industry, and identifications of congenes and isomers of polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs).

Future Developments

UV absorption spectra are basically electronic spectra which arise from transitions between electronic states and are accompanied by simultaneous changes in the vibrational and rotational states. Thus, an absorption spectrum is a function of the whole structure of a molecule and an expression for its fundamental chemical properties. UV absorption spectra in the gas phase are very well defined and can be denoted as finger-prints of organic as well as inorganic compounds. They have considerably higher absorptivities than their counterparts in the infrared wavelength region and are very well suited for computer-based spectral search systems. The size of reference spectra presently available is much smaller compared with that available for GC–FTIR and particularly for GC–MS. Future development of the GC–UV method will include continuous extension of the reference spectrum library.

One of the main advantages of UV gas-phase spectra might be to make detailed classification of functional groups. At present ~ 50 groups with characteristic features can be identified. However, this will certainly be extended and will also include a number of groups with mixed functionalities.

Concerning further instrumental development, recordings of spectra at lower wavelengths than 168 nm will probably be possible. Another instrumental development that can be expected is matrix isolation and direct deposition techniques similar to the ones developed for GC–FTIR measurements. Furthermore, the GC–UV spectrophotometer will, in the near future, be adapted to online measurements in industrial process monitoring and control.

See also: **II/Chromatography: Gas:** Derivatization; Detectors: Mass Spectrometry; Detectors: Selective; Gas Chromatography-Infrared.

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Gas–Solid Gas Chromatography

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Introduction

Gas–solid chromatography (GSC) has been used since the earliest days of gas chromatography and preceded gas–liquid chromatography. Through this early work the limitations of GSC were well recognized and, although the advantages of GSC were also apparent, it was quite some time before reliable and reproducible GSC columns became commercially available. There are many methods in the literature describing the application of GSC to specific analyses, for example the UK Institute of Petroleum method

IP345/80 describes the use of a 3 m × 2.3 mm stainless-steel column containing Porapak R for the separation of nitrogen, oxygen and carbon dioxide and hydrocarbons up to C_8 in the gas above crude oil. The method requires programming the column from $-50°C$ to $240°C$, which is unattractive in that it requires a supply of coolant such as liquid nitrogen.

Although the superior separation characteristics of adsorption materials in porous-layer open-tubular (PLOT) columns were recognized, the main problem was that the preparation procedures for PLOT columns are complex and difficult to implement. However, with the introduction of new capillary column coating technology it is now possible to deposit stable layers of adsorbents on the inner wall of fused silica capillaries. These columns give better separations in a shorter time than the older packed columns.

Adsorption materials that are now commercially available in capillary columns are aluminium oxides, molecular sieves, activated carbon such as graphitized carbon black, porous polymers and silica. Besides fused silica capillary columns, the adsorbents are also deposited in metal columns, expanding the application of adsorbents in the area of process analysers and portable equipment.

Each adsorbent has its own specific application field, as summarized in **Table 1**. In general the application field of PLOT columns covers the permanent gases and volatile mixtures with boiling points up to *c.* 225°C.

Molecular Sieves

Molecular sieves are synthetic and naturally occurring zeolites with well-defined structures that have found extensive use for the separation of permanent (or fixed) gases. Molecular sieves have a pore size that is defined by the particular ion used in the preparation

Table 1 General application fields of adsorbents

Absorption material	Applications
Molecular sieves	Permanent gases, hydrogen isotopes, CO, N_2O
Porous polymers	Volatile polar and nonpolar compounds; samples containing water; CFCs; solvents
Alumina	Hydrocarbon impurities in C_1–C_5 hydrocarbons
Carbon	CO and CO_2 in air; impurities in ethylene
Silica	C_1–C_3 hydrocarbons, sulfur gases; hydrocarbon and semipolar impurities; samples containing water

CFC, chlorofluorocarbon.

of the material – calcium aluminium silicate gives a pore size of 0.5 nm, whereas sodium aluminium silicate gives a pore size of approximately 1 nm. These are the two commonest molecular sieves; other pore sizes are available but are less widely used. The separation on a molecular sieve is based on more than one retention mechanism. The first selection depends on size – molecules that are smaller than the pore size will diffuse inside the pores. Once inside the cavities, the small molecules can interact with a large surface area, which means that they will have relatively long retention times. Large molecules such as branched alkanes or sulfur hexafluoride (SF_6) are too big to enter the pores and these compounds will elute earlier. Compounds that are too large to enter the pores will only be retained by relatively weak adsorption on active sites on the outside of the particles, and thus give shorter retention times.

The retention of components with dipole interaction and hydrogen bond formation, like water and carbon dioxide, is very high. Carrier gas and samples should be as dry as possible. Water is absorbed by the molecular sieve and will cause a reduction of retention times. The water can be removed by heating for a few hours at 300°C. A molecular sieve of pore size 0.5 nm is an ideal adsorbent for the separation of permanent gases; this is also the main use of the column. Normally molecular sieves are not used for separations above C_2 except for hydrocarbon type analysis. Higher boiling compounds are strongly adsorbed and can only be eluted by using undesirably high temperatures (molecular sieves are good catalysts!), vicinal exchange coupled with backflush techniques or even destruction of the sieve with hydrogen fluoride. A typical separation of a permanent gas mixture is shown in **Figure 1**. The 0.53 mm fused silica column is usually coated with a 50 μm layer of 0.5 nm molecular sieve to generate sufficient retention to make a high resolution separation possible at temperatures above ambient. The separation of argon and oxygen is baseline. The 50 μm layer provides a relatively high retention for carbon dioxide. If the separation of argon–oxygen is not important, a 15 μm film can be used. For a comparison of the separations with 50 and 15 μm layers, see **Figures 1** and **2**. Several other applications have been reviewed. Molecular sieves are also successfully coated onto Ultimetal capillary columns of 0.53 mm i.d. Applications of these columns are especially of interest for analyser systems where reliability is a major issue (see metal PLOT columns below).

Molecular sieves of the 13X type are also used. These materials have a lower absolute retention due to the larger pores. They are used in the petroleum

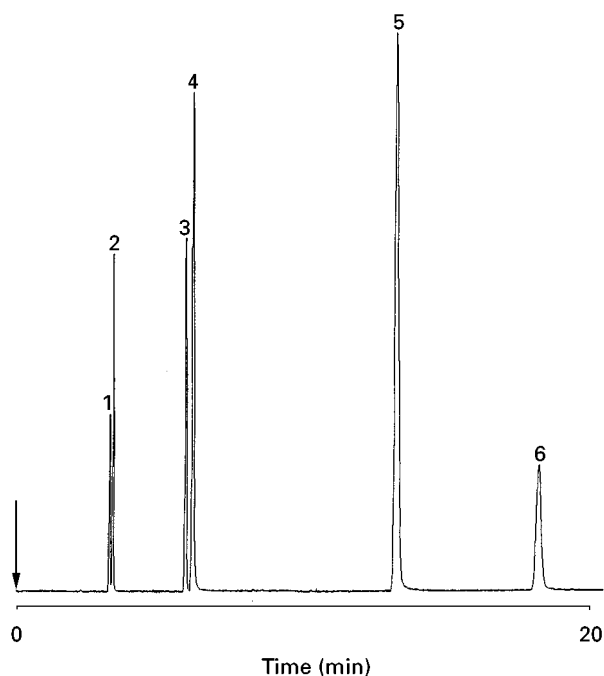**Figure 1** Permanent gases on a 50 μm Molsieve 0.5 nm PLOT column. Experimental details: column, 50 m × 0.53 mm fused silica; oven, 30°C; carrier gas, hydrogen; injection, split; detection, TCD. Peaks: 1, helium; 2, neon; 3, argon; 4, oxygen ; 5, nitrogen; 6, methane.

industry for the type separation of naphthenes from paraffins, olefins, naphthenes and aromatics (PONA analysis), mainly in packed column configurations.
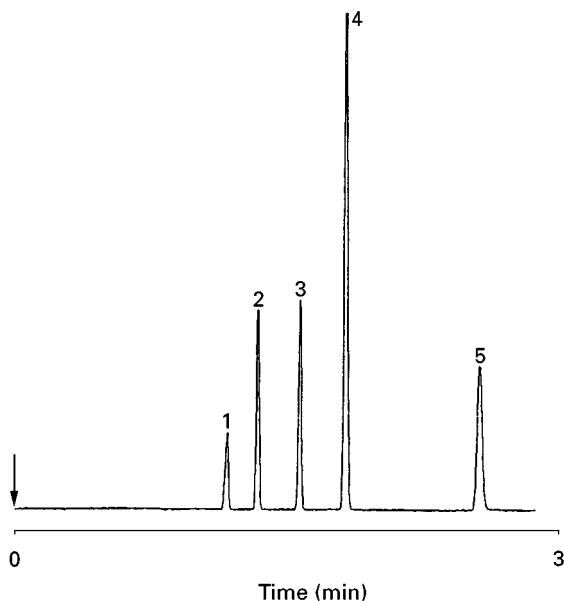

Figure 2 Fast separation of permanent gases on a 15 μm Molsieve 0.5 nm PLOT column. Experimental details: column, 30 m × 0.53 mm fused silica, Molsieve 0.5 nm d_f = 15 μm; oven, 50°C; carrier gas, hydrogen; injection, split; detection, TCD. Peaks: 1, helium + neon; 2, argon + oxygen; 3, nitrogen; 4, methane; 5, carbon monoxide.

Alumina Adsorbents

Alumina adsorbents in capillary columns were introduced as long ago as 1963 and were made commercially available in fused silica capillary columns in 1981. Alumina has a very high activity and will retain components as light as ethane. To make the highly active alumina work as stationary phase in GC, it has to be deactivated. Deactivation can be done in many ways, but the most practical and reproducible method is deactivation with inorganic salts.

Alumina deactivated with potassium chloride (KCl) provides a general nonpolar adsorbent that is widely used. Such a column will elute acetylene before butane (**Figure 3**). The alumina surface can be made more polar by deactivation with sodium sulfate instead of KCl. The resulting alumina layer will elute acetylene after the butane peaks, indicating the higher polarity.

The selectivity of alumina for hydrocarbons is very high. All C_1–C_4 hydrocarbons can be baseline separated. The resolution between the different hydrocarbons is sufficient to be able to measure many trace amounts of C_1–C_4 hydrocarbons in a main stream of any one of these hydrocarbons (**Figures 4–6**). For this reason alumina is one of the most widely used columns in petrochemistry for analysing hydrocarbon impurities in ethylene, propylene (Figure 5) and 1,3-butadiene (Figure 6).

Although alumina has unique separation characteristics, it also has limitations. The activity of the adsorbent is such that it will adsorb any moisture, carbon dioxide or other polar impurity in the sample. When
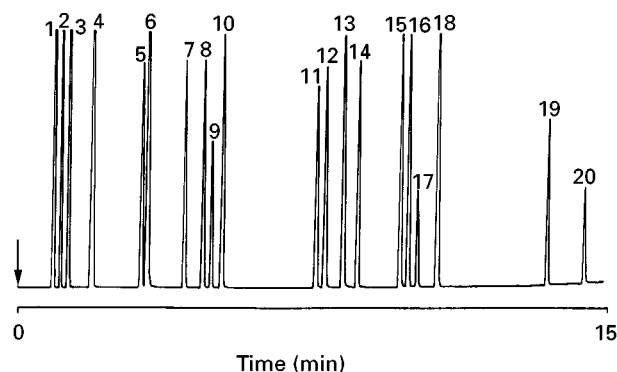

Figure 3 C_1–C_6 hydrocarbons on an Al_2O_3, KCl PLOT column. Experimental details: column, 50 m × 0.32 mm fused silica, Al_2O_3/KCl, d_f = 5 μm; oven, 70°C (4 min) → 180°C, 10°C min^{-1}; carrier gas, helium; injection, split; detection, flame ionization detection (FID). Peaks: 1, methane; 2, ethane; 3, ethylene; 4, propane; 5, cyclopropane; 6, propylene; 7, acetylene; 8, isobutane, 9, propadiene; 10, butane; 11, *trans*-2-butene; 12, 1-butene; 13, isobutene; 14, *cis*-2-butene; 15, isopentane; 16, methylacetylene; 17, pentane; 18, 1,3-butadiene; 19, ethylacetylene; 20, hexane.
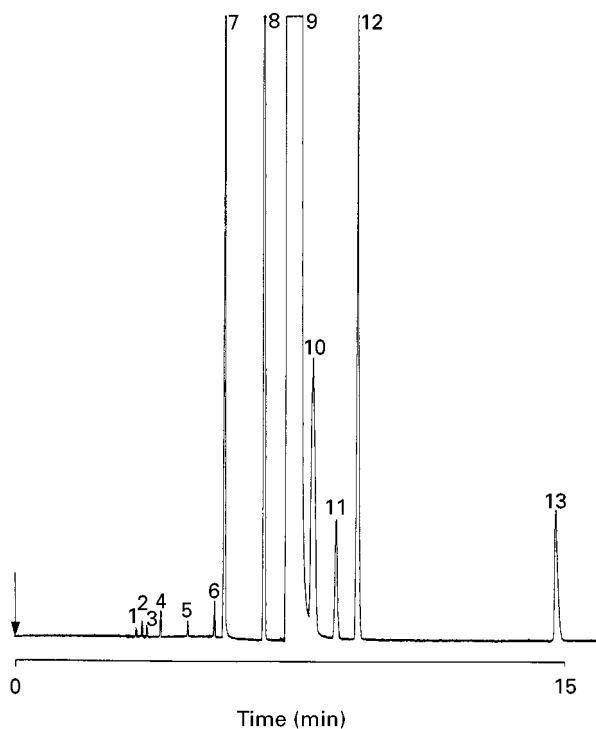
Figure 4 Impurities in *trans*-2-butene on an Al_2O_3/Na_2SO_4 adsorbent PLOT column. Experimental details: column, 50 m × 0.32 mm fused silica, Al_2O_3/Na_2SO_4, $d_f = 5$ μm; oven, 110°C; carrier gas, nitrogen; injection, split; detection, FID. Peaks: 1, methane; 2, ethane; 3, ethylene; 4, propane; 5, propylene; 6, isobutane; 7, butane; 8, cyclobutane; 9, *trans*-2-butene; 10, 1-butene; 11, isobutene; 12, *cis*-2-butene; 13, 1,3-butadiene.

Figure 5 Impurities in propylene on an Al_2O_3/KCl PLOT column. Experimental details: column, 50 m × 0.53 mm fused silica, Al_2O_3/KCl $d_f = 10$ μm; oven, 40°C (10 min) → 160°C, 5°C min^{-1}; carrier gas, helium; injection, split; detection, FID. Peaks: 1, methane; 2, ethane; 3, ethylene; 4, propane; 5, propylene; 6, isobutane; 7, acetylene; 8, butane; 9, propadiene; 10, *trans*-2-butene; 11, 1-butene; 12, isobutene; 13, *cis*-2-butene; 14, isopentane; 15, methylacetylene; 16, pentane; 17, 1,3-butadiene.

alumina is exposed to water, the retention times for hydrocarbons are altered and resolution is degraded. The water will deactivate the surface and, as a consequence, the column will have lower retention. The water can simply be removed and the column performance regenerated by heating to 200°C for a short time. If an isothermal setup is required, a polar precolumn that retains the water can be employed. A polyethylene glycol-coated column with a 1.2 μm film works very well as the C_1–C_6 hydrocarbons will elute from this column before the water and by simple backflushing or a vent switch the water peak can be removed. For more polar impurities, regeneration may take longer, but it is possible. Alumina columns are difficult to destroy and oxygen in the carrier gas will not harm the column. It has been found that sulfur impurities present up to 2000 ppm do not seriously interfere with the retention characteristics of alumina. The maximum temperature of alumina columns should not exceed 200°C; above this temperature recrystallization of the deactivating compound will occur, causing changes in selectivity. Alumina layers coated in Ultimetal tubing are very stable and find wide application in hostile environments.
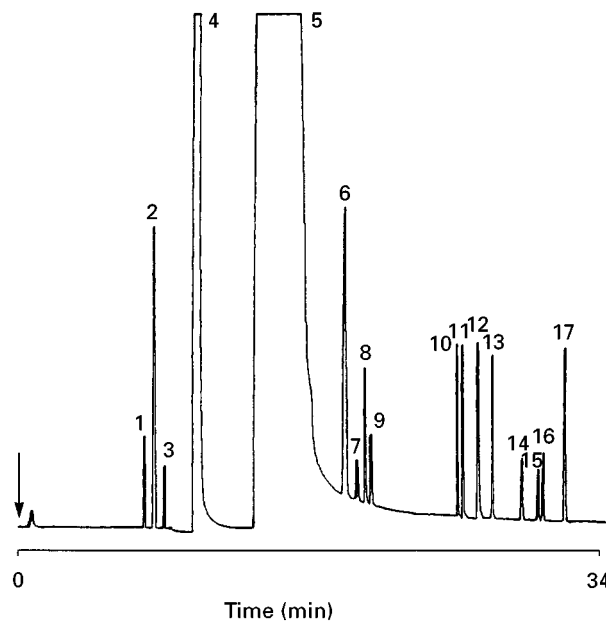
Porous Polymers

The preparation of capillary columns with porous polymers synthesized *in situ* was described by Hollis in 1973. These columns were quite active and only worked well for hydrocarbons; polar compounds elute with severe tailing. Using new coating techniques, it has become possible to coat porous polymers very efficiently on fused silica capillary columns.

Porous polymers are prepared by the copolymerization of styrene and divinylbenzene or other related monomers. The pore size and specific surface area can be varied by the amount of monomer added to the polymer. Several types of porous polymers have become commercially available under different names, including GS-Q, PoraPLOT Q and Supel-Q. It should be noted that the selectivity of some porous polymers in capillary columns does deviate strongly from the original polymer consisting of 100% styrene–divinylbenzene.

In general the polymer-coated capillaries are highly efficient and inert. **Figure 7** shows the separation of a range of solvents with different functional groups; all the different types of compounds elute with good peak symmetry. A typical application for a porous polymer of the 'Q' type is shown in **Figure 8**, where
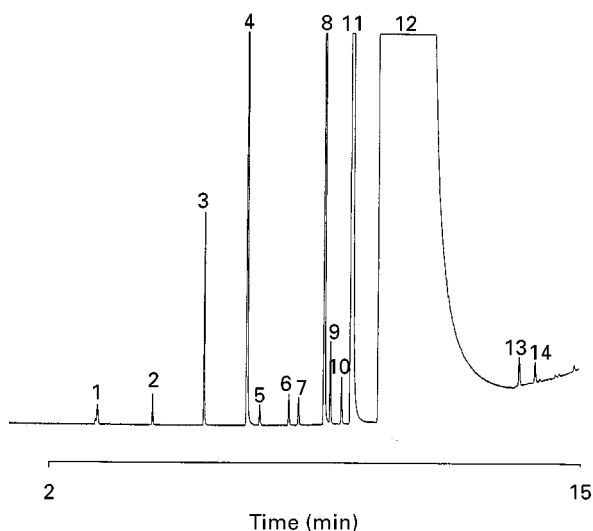
Figure 6 Impurities in 1,3-butadiene on an Al$_2$O$_3$/KCl PLOT column. Experimental details: column, 50 m × 0.25 mm fused silica, Al$_2$O$_3$/KCl, $d_f = 4$ μm; oven, 50°C (1 min) → 200°C, 10°C min^{-1}; carrier gas, helium; injection, split; detection, FID. Peaks: 1, methane; 2, propane; 3, propylene; 4, isobutane; 5, butane; 6, cyclobutane; 7, unknown; 8, *trans*-2-butene; 9, 1-butene; 10, isobutene; 11, *cis*-2-butene; 12, 1,3-butadiene; 13, ethylacetylene; 14, hexane.

Figure 7 Solvents on a porous polymer PLOT column. Experimental details: column, 10 m × 0.53 mm fused silica, PoraPLOT Q, $d_f = 20$ μm; oven, 100°C → 200°C, 10°C min^{-1}; carrier gas, hydrogen; injection, split; detection, FID. Peaks: 1, methanol; 2, ethanol; 3, acetonitrile; 4, acetone; 5, isopropanol; 6, dichloromethane; 7, methylacetate; 8, pentane; 9, ethyl acetate; 10, hexane; 11, benzene.

traces of acetaldehyde are measured in a hydrocarbon matrix.

Porous polymers are also available with different selectivities. By the incorporation of vinyl pyridine or methacrylate groups, the general selectivity can be changed and the polymer can be made much more polar.

Porous polymers have become very popular because of the high retention, the inertness and the selectivity that these materials provide. With porous polymers very volatile components can be separated at temperatures above ambient. In addition, one of the unique characteristics of porous polymers is their highly hydrophobic behaviour. The interaction with
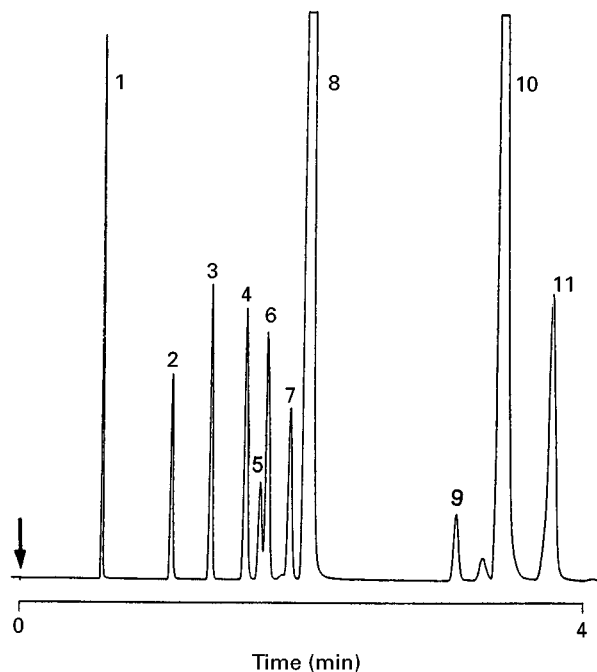
water is very low, which results in a fast elution of water so that, for example, water elutes on a 100% styrene–divinylbenzene column before acetone and methanol.

The porous polymers are also recognized to be very inert, which makes them applicable for a wide range of compounds. A series of porous polymers of different selectivity has been commercialized and is nowadays available in 0.53, 0.32 and also 0.25 mm internal column diameter. Porous polymers have recently
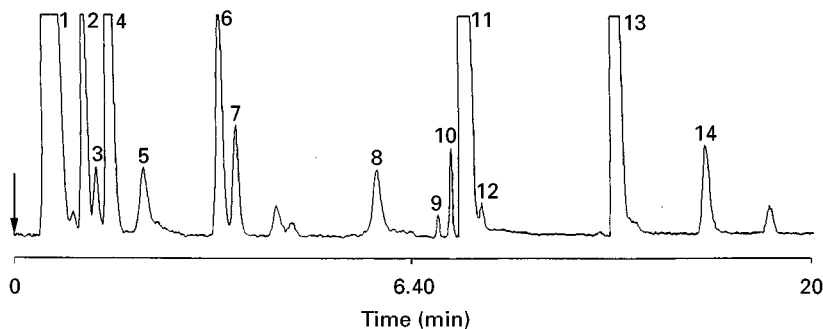

Figure 8 Trace acetaldehyde in a hydrocarbon matrix. Experimental details: column, 25 m × 0.32 mm fused silica, PoraPLOT Q, $d_f = 10$ μm; oven, 140°C, carrier gas, helium, injection, split; detection, mass selective detection (MSD). Peaks: 1, air, argon and methane; 2, sulfur hexafluoride; 3, ethylene; 4, ethane; 5, water; 6, propylene; 7, propane; 8, acetaldehyde; 9, isobutane; 10, butane; 11, *cis*-2-butene; 12, acetone; 13, isopentane; 14, pentane.
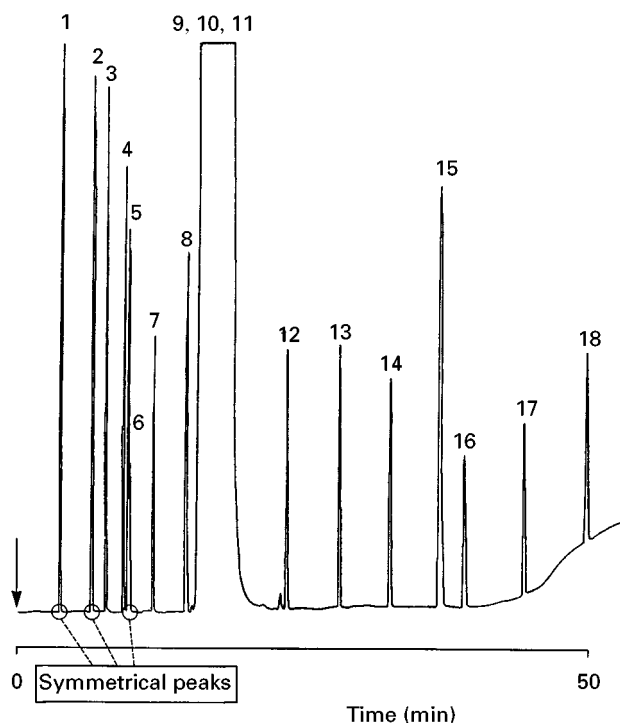
Figure 9 Solvents on a porous polymer PLOT column. Experimental details: column, 25 m × 0.53 mm fused silica, PoraPLOT Q-HT, d_f = 20 μm; oven, 100°C → 250°C, 5°C min^{-1}; carrier gas, hydrogen; injection, split; detection, FID. Peaks: 1, methanol; 2, ethanol; 3, acetonitrile; 4, acetone; 5, isopropanol; 6, dichloromethane; 7, pentane; 8, ethyl acetate; 9, hexane; 10, benzene; 11, cyclohexane; 12, toluene; 13, ethylbenzene; 14, propylbenzene; 15, decane; 16, butylbenzene; 17, undecane; 18, dodecane. Note the elution of volatile solvents.

become available in metal tubing, which has expanded their application even more as PLOT columns can now also be used in a process-type environment.

One of the latest developments is the improved stabilization of the 100% styrene–divinylbenzene porous polymers, which has resulted in the introduction of a high temperature material, called PoraPLOT Q-HT. This porous polymer can be used up to temperatures of 290°C, an increase of 40°C over the previously available material, and the bleed level of the polymer at lower temperatures has been reduced. The selectivity and inertness of the new polymer is not influenced by the stabilization process (**Figure 9**).

Carbon Adsorbents

Unique selectivity is found with the carbon adsorbents. This type of material has been used for many years in packed columns. One of the problems associated with the material available in the early days was its lack of reproducibility; the introduction of graphitized carbon black has improved this situation. The graphitized carbon adsorbent often has its separ-

ation properties modified by the incorporation of a small quantity of a stationary liquid such as Carbowax 20M. Two commercial materials currently available are known as Carbosieve and Carbopack. Much elegant work has been done on graphitized carbon black capillary columns by Bruner and his co-workers at the University of Urbino, who have demonstrated that such columns can give good separations of hydrocarbons and amines with short analysis times (see Further Reading). Their suggestion of the name GLOT (graphitized-layer open-tubular) columns has so far met with little recognition.

The Carboxene and CarboPLOT columns have comparable characteristics and are useful for the separation of carbon monoxide, carbon dioxide and air from C_1 and C_2 in coke oven gas (**Figure 10**). The main restriction to the application of carbon-coated PLOT columns is their limited temperature range. Carbon layers become extremely active on heating and application of these materials is limited to about
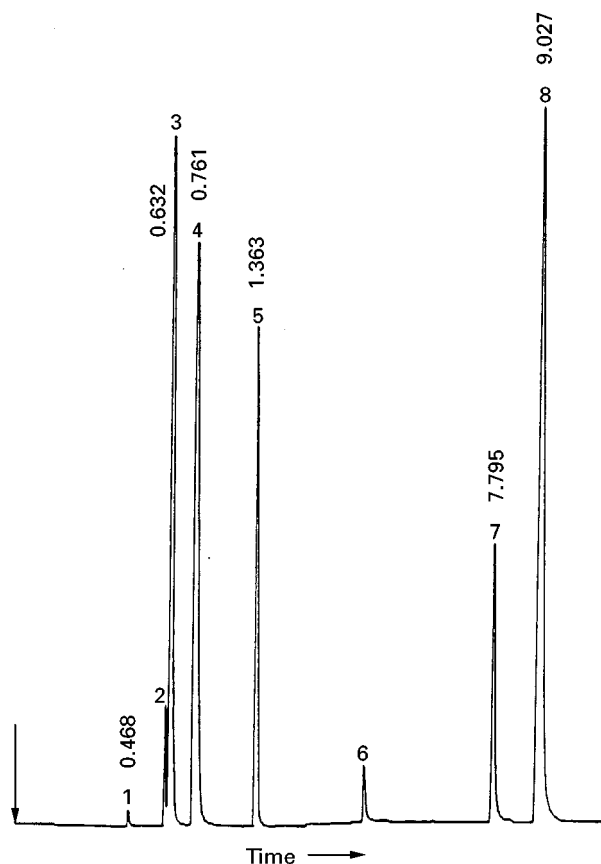

Figure 10 Coke oven gas on a carbon PLOT column. Experimental details: column, 25 m × 0.53 mm fused silica CP-Carbo-PLOT P7. d_f = 25 μm; oven, 35°C → 115°C, 15°C min^{-1}; injection, split; detection, TCD/FID. Peaks: 1, hydrogen (51%); 2, oxygen (0.5%); 3, nitrogen (6%); 4, carbon monoxide (10%); 5, methane (25%); 6, carbon dioxide (2.5%); 7, ethylene (1%); 8, ethane (2%) (signal ethylene and ethane by FID).
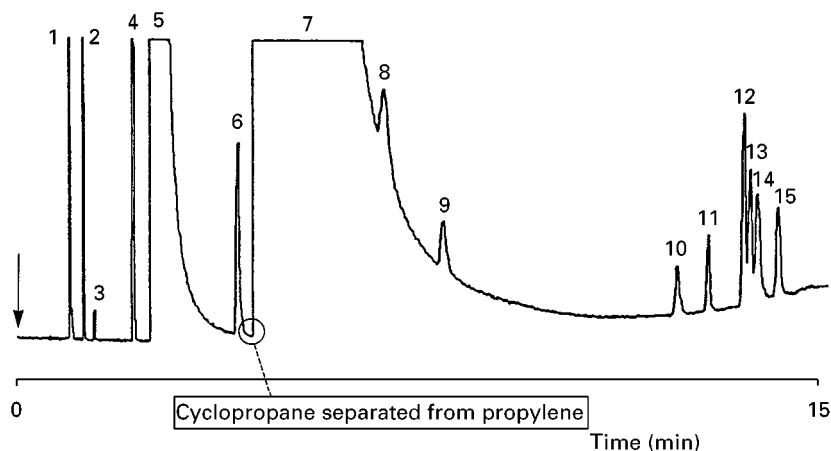
Figure 11 Impurities in propylene on a silica PLOT column. Experimental details: column, 30 m × 0.32 mm fused silica CP-Silica-PLOT, $d_f = 4$ μm; oven, 50°C → 180°C, 5°C min^{-1}; carrier gas, helium; injection, split; detection, FID. Peaks: 1, methane; 2, ethane; 3, ethylene; 4, acetylene; 5, propane; 6, cyclopropane; 7, propylene; 8, isobutane; 9, butane; 10, 1-butene; 11, methylacetylene; 12, 1,3-butadiene; 13, trans-2-butene; 14, isobutene; 15, cis-2-butene.

200°C. Higher temperatures may be possible but require specifically deactivated layers, which involves a risk of altering the selectivity.

Silica

The application of silica as adsorption material was established from the very earliest days of GSC. Later publications have shown the high separation and inertness of silica in PLOT columns but absolute retention and capacity were always the limiting factors in successfully applying silica as an adsorbent for these columns. The deposition of a layer of silica in a capillary column could not compete with the high selectivity and retention provided by alumina or the inertness and retention of porous polymers. Theoretically, silica should be a very interesting adsorbent because it has a very low catalytic activity.

The silica layer in a silica PLOT column is activated at 250°C and can be used for a wide variety of compounds such as C_1 to C_8 hydrocarbons, volatile sulfur compounds and halogenated compounds in the C_1 to C_6 range. The hydrocarbon selectivity of a silica PLOT column is shown in **Figure 11**. Note the high separation efficiency of the C_1–C_3 compounds. Also cyclopropane elutes before propylene, making low level quantification in propylene possible.

Sulfur compounds are well separated from hydrocarbons and there is, therefore, no risk of quenching if a flame photometric detector is used. Silica adsorbents also produce very sharp peaks for sulfur compounds, making low level measurement possible. Determination of carbonyl sulfide and hydrogen sulfide in pure propylene is possible down to low ppb levels using sulfur selective detection as shown in **Figure 12**. Sulfur dioxide also elutes as a sharp peak.

Figure 12 Volatile sulfur impurities in propylene on a silica PLOT column. Experimental details: column, 30 m × 0.32 mm fused silica CP-SilicaPLOT, $d_f = 4$ μm; oven, 50°C → 120°C, 10°C min^{-1}; carrier gas, helium; injection, valve, 375 μL propylene; detection, sulfur chemiluminescence detection. Peaks: 1, carbonyl sulfide (34 p.p.b.); 2, hydrogen sulfide (108 p.p.b.).
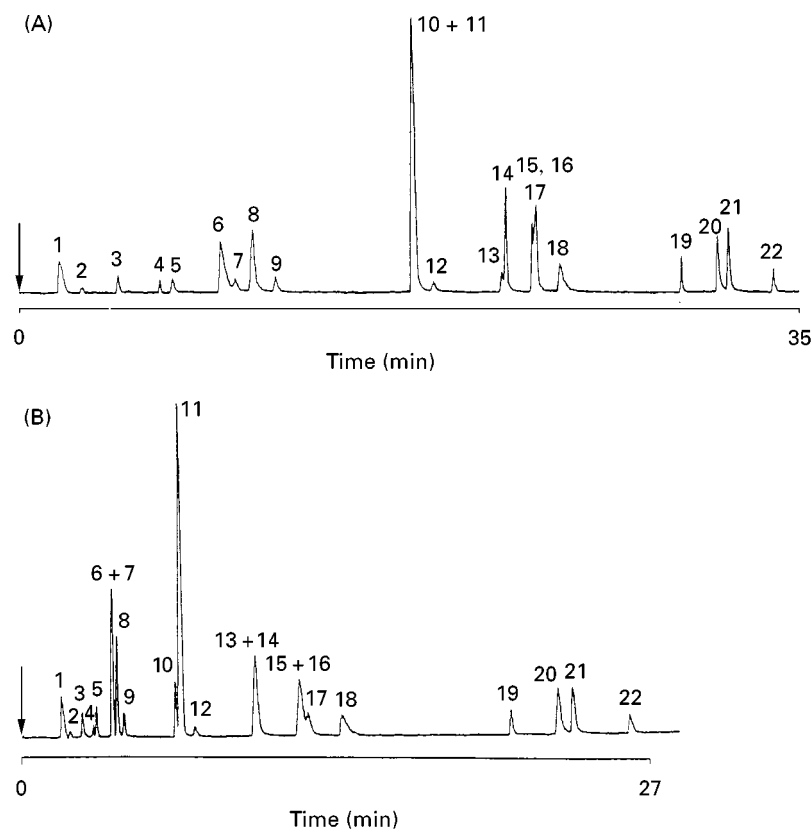
Figure 13 Chlorofluorocarbons on a silica PLOT column. Experimental details: column: 30 m × 0.32 mm fused silica CP-Silica-PLOT, d_f = 4 μm; injection, split; detection, FID. Chromatogram (A): oven, 35°C, 12 min → 150°C, 4°C min^{-1}; carrier gas, helium, 2.5 mL min^{-1} Chromatogram (B): oven, 70°C, 12 min → 150°C, 4°C min^{-1}; carrier gas, helium, 2.0 mL min^{-1}. Peaks: 1, nitrous oxide; 2, CFC-23; 3, CFC-13B1; 4, CFC-32; 5, CFC-115; 6, CFC-12; 7, CFC-125; 8, CFC-143a; 9, CFC-22; 10, CFC-134a; 11, chloromethane; 12, CFC-12B1; 13, CFC-114; 14, CFC 152a; 15, CFC-142b; 16, CFC-124; 17, bromomethane; 18, CFC-11; 19, dichloromethane; 20, CFC-141b; 21, CFC-123; 22, trichloromethane.

The selectivity of silica for separation of volatile halogenated hydrocarbons like the CFCs, is very specific. Unlike alumina, the CFCs do not decompose or react on silica, which makes their quantification possible at low levels (**Figure 13**). The low catalytic activity is also important for the analysis of pentadienes. On alumina these compounds polymerize due to the catalytic activity of the surface, while on silica these compounds elute as symmetrical peaks.

One of the key benefits of deactivated silica as an adsorbent is a more reproducible retention behaviour in the presence of water. Although water is retained by silica, the water will elute from the column and the influence on retention is small. Because of this, samples containing moisture can be analysed at lower temperatures. This is especially important if isothermal or fast analysis conditions are required, as in a plant analyser.

Metal PLOT Columns

The maximum temperature of polyimide-coated fused silica columns is limited to *c.* 350°C owing to the stability of the polyimide protective outer coating. For higher temperatures a more stable tubing material is required. Metal capillary columns would be ideal but are very active. Several companies have been successful in deactivating metal to make it almost as inert as fused silica, and these deactivated metal columns have been successfully coated with alumina adsorbents, molecular sieves and 100% divinylbenzene porous polymers.

In comparison with fused silica columns, the metal column provides higher mechanical stability and offers, therefore, better mechanical reliability. Besides the high temperature capability, metal columns are especially applicable to process monitoring, on-line analysis and portable instrumentation.

Conclusion

Although it is likely that gas–solid chromatography will always represent something of a niche market in the gas chromatographic field as a whole, it is nevertheless of vital importance, particularly for gas analysis.

In the field of gas analysis, adsorbents offer the possibility of very selective separations that depend on the geometry of the molecules to be separated rather than the more generalized solubility mechanisms acting in gas–liquid chromatography. It should be theoretically possible to design adsorbents for particular separations. In the branch of liquid chromatography known as affinity chromatography, for example, it is already possible to manufacture stationary phases of exquisite specificity. An analogous approach might be possible in gas–solid chromatography and considerable work is in progress on the preparation and properties of molecular sieves with different dimensions to the well-established materials.

Further Reading

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Headspace Gas Chromatography

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Introduction

The term 'headspace analysis' was first applied to the analysis of gases in sealed cans and was later applied to the general analysis of vapours in contact with the sample from which they come. Gas chromatography was the technique of choice for this type of analysis; the combination is therefore called *headspace–gas chromatography* (HS-GC).

For quantitative analysis calibration of the volatiles in the vapour is necessary. This is achieved preferably, but not necessarily, in a state of equilibrium. To reach this state the sample is placed in a glass vial and thermostatted. When equilibrium is achieved, an aliquot of the gas phase above the sample is rapidly transferred onto the GC column. The term *equilibrium HS-GC* is commonly used for this sampling technique. However, since under certain circumstances calibration for quantitative analysis may also be performed in a nonequilibrium system, the term *static HS-GC* is more appropriate to distinguish this sampling technique from the so-called *dynamic HS-GC* techniques. In dynamic HS-GC analysis, the volatile compounds are stripped off completely from the sample by a continuous flow of an inert gas. This takes some time and the continuously delivered volatiles need to be concentrated in a trap, either by absorption or by cold trapping. The trapped compounds are released from the trap by thermal desorption and transferred to the gas chromatograph. This technique, also known as *purge and trap*, is thus an off-line procedure, in contrast to the static headspace technique, where the headspace gas is transferred directly and on-line to the gas chromatograph. Thermal desorption is also used for sample transfer with a technique called *solid-phase microextraction* (SPME), where a thin rod or a small fibre, coated with a nonvolatile liquid phase, is inserted into a liquid sample or into the gas space of a headspace vial. The volatile compounds in the headspace are absorbed into the liquid-phase coating. After transfer into the heated injector of a gas chromatograph, the trapped compounds are released by thermal desorption. Off-line techniques, dynamic HS-GC and SPME are not discussed here, but all the important considerations regarding sample properties, such as matrix effects, necessary equilibration time, diffusion processes and sampling pretreatment, are common to all headspace techniques.

Fundamentals of Static HS-GC

The theory of static HS-GC is best explained using the example of a liquid sample present in a closed vial, as shown in **Figure 1**. The volatile analyte present in the liquid sample will evaporate into the gas phase until the concentration in both phases (C_S and C_G) remain constant. Equilibrium is achieved by diffusion from the sample into the gas phase and vice versa. The equilibrium constant is called the partition coefficient (K), and can be split into the mass ratio (k) and the phase ratio (β).

The aim of every quantitative analysis is the determination of the original concentration of the analyte (C_0) in the sample. The peak area (A) in a headspace