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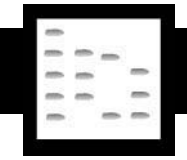
GAS ANALYSIS: GAS CHROMATOGRAPHY



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Introduction

If gases are defined so as to be distinguished from vapours, which is to say only those gases whose critical temperatures are below ambient, and hence cannot be liquefied by pressure at ambient temperature, then the task of gas analysis appears to be a simple one. Applying the criterion of a critical temperature below, say 15°C, produces a very small list of elements and compounds, ranging from helium to ethene. It is, of course, more appropriate to define gases as those which are handled in the gas phase at ambient conditions. Widening the criterion to allow components with boiling points below 15°C produces a rather larger list, ranging from xenon to cyclobutane.

Any gas mixture will be based on one or more of these components, but can in addition contain higher boiling compounds whose low concentration allows them to be present without condensing out from the mixture. As an example, natural gas is treated before it is distributed so that it remains stable in the gas phase over a wide range of temperatures and pressures. It consists predominantly of methane, but contains a large number of other hydrocarbons, up to and including decane, at concentrations which are amenable to direct analysis by gas chromatography.

Analysis for decane and similar components in liquid hydrocarbon mixtures is well established, and similar analytical procedures can be applied to its measurement in natural gas. The main difference is in sample handling and introduction. This will generally be true for other low concentration components of gas mixtures which would normally be liquids or solids. Where techniques exist for analysis of such materials as liquid or solid samples, they can be modified to handle those components in a gas mixture.

This article is not intended to give details of how to analyse all the chlorofluorocarbons or the hydrides of germanium, but aims to show the characteristic differences in equipment and procedures used for gas analysis.

Equipment and Procedures

A chromatograph which is configured for gas analysis will differ in a number of respects from one designed for liquids' analysis. Sample injection will almost invariably be by valve, and other valves may be used to alter the relative positions of different columns during the analysis. Some columns are specifically used for gas analysis, and others may be used in a different way from that for other applications. Carrier gas must be chosen with some care, as it may be a component of the sample, or have properties which do not favour the measurement of sample components. The thermal conductivity detector (TCD) is likely to play a major role; the flame ionization detector (FID) may be regarded as a selective detector in this context.

Sample Handling and Injection

A packed column will handle sample sizes typically in the region of 0.1 to 10 mg. For samples which are liquid, or solids dissolved in a solvent, this means volumes of 0.1 to 10 μL, which are conveniently measured and injected using microsyringes. For gas samples, this mass range approximates to volumes of 0.1 to 10 mL at ambient conditions.

Gas-tight syringes will easily cope with such sample sizes, but the main drawback with using them is poor repeatability, due to injection of a

compressible sample into an already compressed carrier gas. Most chromatographs equipped for gas analysis will be fitted with a gas sampling valve, sometimes referred to as a bypass injector. **Figure 1** shows a typical design of a six port valve. It consists of a base through which six holes or ports are drilled, equally spaced around the circumference of a circle, and a rotor, which rotates around the axis of the same circle. The rotor has three grooves machined into it, which connect adjacent pairs of ports. Rotation of the rotor through 60° alters the internal plumbing by connecting different pairs of ports. The ports are connected into the chromatograph by small bore tubing.

In **Figure 1**, the carrier gas inlet is connected to port 1, and port 2 goes to the column. Sample gas enters and exits through ports 5 and 4 respectively. A sample loop is connected between ports 3 and 6. The sample loop, usually a length of 2 mm i.d. tubing, defines the size of sample injected. **Figure 1**A shows the sample loading position, with the carrier gas going directly to the column, and **Figure 1**B shows the inject position. Here, the carrier gas sweeps the entire contents of the sample loop on to the column. Provided that the temperature and pressure of the sample gas in the loop are constant just before injection, the technique is capable of excellent sample size precision, and hence very good quantitative behaviour.

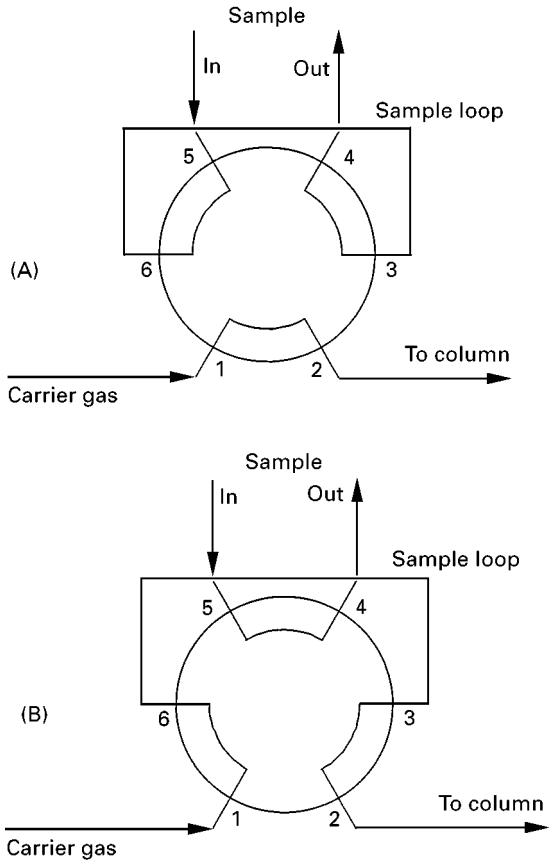

Figure 1 Gas sampling valve. (A) Sample loading. (B) Sample injection.

Gas sampling valves can use other configurations – the motion can be linear rather than rotary, but the principle of isolating the sample in a defined volume and then purging it on to the column with carrier gas remains unchanged. Valves with more ports can also be used, to combine gas sampling with other switching operations which may be required.

Capillary columns need much smaller sample sizes for efficient operation, and hence the proliferation of techniques for liquid samples, ranging from sample splitting to solvent effects and retention gaps. It is possible to minimize the dead volume in a gas sampling valve to allow direct injection, but this becomes more difficult as the column i.d. is reduced. If a gas sample is stable when introduced into the chromatograph, it is most likely that splitting the carrier gas flow downstream of the valve will give a representative sample on to the column. In most instances this would be the preferred option.

Columns

Gas chromatographic separations are mainly influenced by the volatility of the components of the mixture. By using selective stationary phases, groups of components of higher polarity can be retained in the column for longer than components of lower polarity. Within similar groups, however, the order of elution will be dictated by boiling point. It is also the case that an isothermal analysis would use a column temperature of somewhere around the middle of the boiling range of the sample, and a temperature programme would very approximately mimic the distillation characteristics.

Permanent gases in particular do not have boiling points which would suggest a convenient choice of column temperature, and polarity differences do not appear to be strong enough to be helpful. Although columns have been operated at liquid nitrogen temperature for the separation of hydrogen isotopes, in general subambient operation is unattractive. Gas analysis, therefore, requires different separation mechanisms to allow use of more or less standard equipment at normal temperatures. The principle difference is the use of adsorption onto stationary phases with active surfaces as the means of separation, rather than partition into a dispersed liquid phase. Such adsorption phases separate, at least in part, by molecular size or shape. As a consequence, some have relatively limited applicability, and are used as part of a range of columns required for a complete analysis.

Molecular sieve The term is general, but in the context of gas analysis it refers to aluminosilicates of the alkali and alkaline earth metals. The most commonly used are type 5A, based on calcium, and 13X, based on sodium. They have average pore diameters of 0.5 and 1 nm respectively. Molecular sieves are the only materials available which can separate oxygen and nitrogen at normal chromatographic temperatures (35–100°C). On the other hand, they retain carbon dioxide under the same conditions for so long that it is sometimes regarded as being permanently absorbed. They also strongly adsorb water, and are widely used as drying agents.

Molecular sieves must be activated before use, to drive off water and other strongly adsorbed materials and to make the pores available to sample components. This can be done *in situ*, by heating the column to around 300°C for several hours with dry carrier gas flowing. During use, a column will slowly lose separating power due to adsorption of moisture from samples or carrier gas, and will eventually need to be conditioned again. With reasonable precautions, a column should continue to give good separations for a year or longer.

5A and 13X sieves have broadly similar behaviour, with some detail differences which may cause one to be preferred over the other for particular applications. When each is packed into a typical 2 m column, 5A sieve will give longer retention times, most evidently for carbon monoxide. **Figure 2** shows a chromatogram, from a 5A molecular sieve column, of helium, hydrogen, oxygen, nitrogen, methane and carbon monoxide, using argon carrier gas at 50°C. Under these conditions, rare gases can also be analysed, with neon eluting just after hydrogen, argon co-eluting with oxygen, krypton just before nitrogen, and xenon after carbon monoxide. Component relative retention times are influenced by the temperature and time of activation, and so in the unlikely event of rare gases being significantly present in a mixture such as that in **Figure 2**, it should be possible to find an activation procedure which will allow all to be separated.

Argon is the most abundant rare gas (0.93% v/v in air), and so its co-elution with oxygen can create a problem. It can be resolved before oxygen by using, for example, a 2 m column at −50°C, or a 5 m column at 0°C. The obvious drawback is the excessive retention times for other components. An alternative way of measuring oxygen without interference from argon is to use argon as carrier gas, as in **Figure 2**.

Capillary columns containing 5A sieve are available. The finely divided material is dispersed as a layer on the wall of the capillary. This is known as a porous-layer open-tubular or PLOT column. The combination of high efficiency and high carrier gas linear velocity means that argon and oxygen can be separated within an overall analysis time comparable to that of a 2 m packed column.

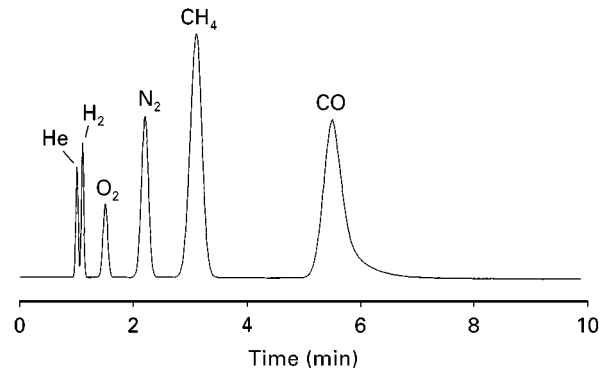

Figure 2 Molecular sieve 5A.

5A molecular sieve is also capable of exclusion chromatography, based on molecular shape. Ethane, propane and n-butane have increasingly longer retention times, so as to be unmeasurable, under the conditions of **Figure 2**. However, isobutane (2-methylpropane) elutes as a tailing peak just before methane; **Figure 3** shows this effect. Similar behaviour is found for neopentane (2,2-dimethylpropane), although it is less of a problem, since neopentane is likely to be at much lower concentration than isobutane. A further example is sulfur hexafluoride, which elutes before oxygen. This can be used where SF_6 is measured as an atmospheric tracer by electron-capture detector; oxygen is mildly electron-capturing, but does represent 21% of the atmosphere, and so having the trace of SF_6 eluting first makes detection easier.

Under the same conditions, 13X molecular sieve gives more uniform separation of components, with rather shorter retention times, as shown in **Figure 4**. 13X sieve does not display the exclusion mode of

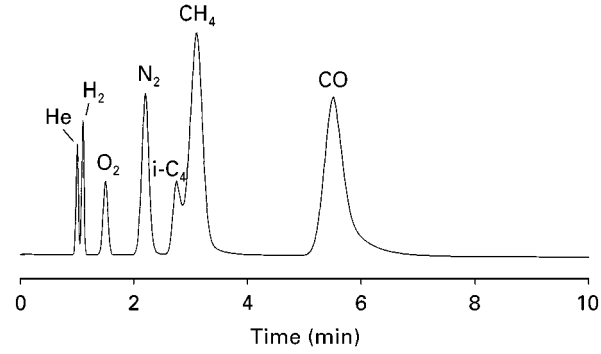

Figure 3 Molecular sieve 5A.

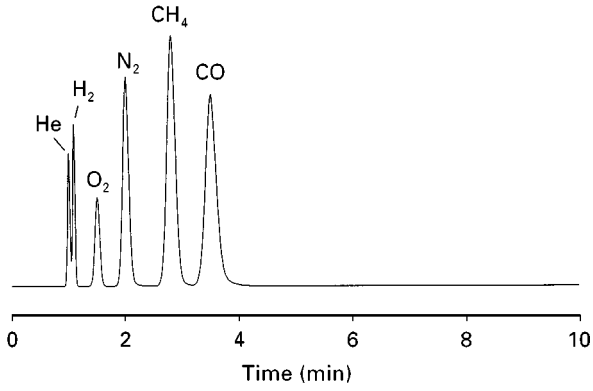

Figure 4 Molecular sieve 13X.

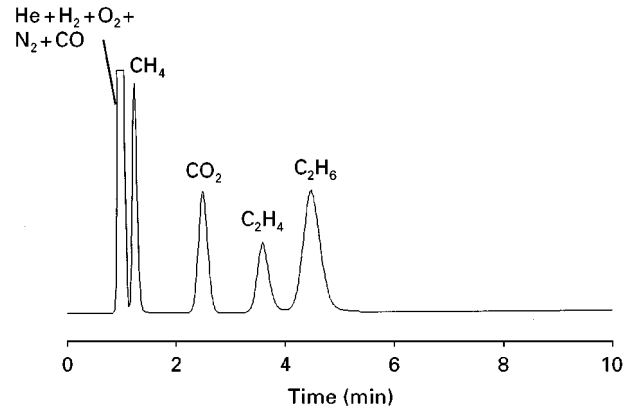

Figure 6 Porous polymer beads as packing material.

behaviour shown by 5A. Another difference is that the order of elution of methane and carbon monoxide can be reversed. If the temperature of activation is limited to 150°C, then a chromatogram similar to that in **Figure 5** is produced. With this reduced level of activation, the long-term stability of the column is excellent. With the higher activation temperature required for **Figure 4**, the column performance, as with 5A sieve, slowly deteriorates. 13X sieve must have at least two types of pores, from one of which water is removed at relatively low temperature, giving the chromatogram in **Figure 5**; the other requiring higher temperatures to give the performance in **Figure 4**. Obviously, at some intermediate activation temperature, methane and carbon monoxide will co-elute.

Porous polymer beads Porous polymer beads are based on polyaromatic cross-linked resins. They have a regular pore size and form beads of uniform diameter, making a good packing material. They are available in a range of polarities, according to the method of preparation, which allow differences in elution order. They are not hygroscopic and hence need no activation before use, although treatment overnight near the maximum operating temperature will remove residual low relative molecular mass material and give more stable baselines. With operating temperatures from subambient to around 250°C, the range of samples to which they can be applied is large. Since there is no change in activity due to adsorbed moisture, porous polymers are frequently used in temperate-programmed applications, which considerably increases their flexibility.

A 2 m column packed with nonpolar material at 50°C does not separate oxygen, nitrogen and carbon monoxide, which elute at the beginning of the chromatogram, closely followed by methane. It does separate carbon dioxide, ethene and ethane in that order, which makes it a natural complementary column to molecular sieve for light gas analysis (**Figure 6**). Propene elutes just before propane, but C_4 saturated and unsaturated hydrocarbons are mixed together. At higher temperatures, porous polymers can analyse hydrocarbons to C_8. They are also good for sulfur-containing gases, separating H_2S, COS and SO_2 in that order. With temperature programming, organic thiols and sulfides can be included.

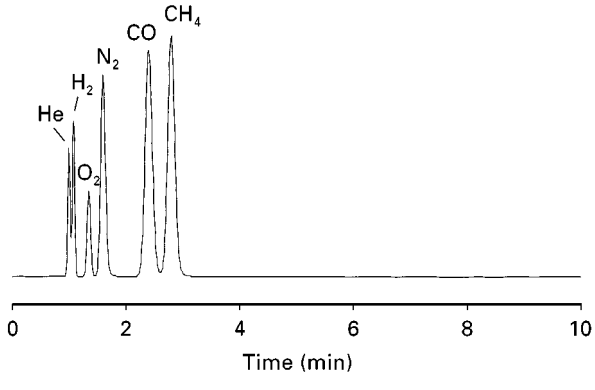

Figure 5 Molecular sieve 13X – partially activated.

Alumina Activated alumina has a high polarity which is suitable for mixtures of saturated and unsaturated hydrocarbons. To avoid tailing peaks for unsaturated components, some controlled surface deactivation is necessary. Originally this was done with water, or a mixture of water and silicone oil to obtain the desired polarity. The water would slowly be stripped off by the dry carrier gas, increasing polarity and the tendency to tailing peaks. Alumina PLOT columns are now available, deactivated with inorganic salts, and these offer the optimum solution for this type of analysis. **Figure 7** shows a chromatogram of C_1 to C_4 saturated and unsaturated hydrocarbons. This was produced using an FID, so the lack of

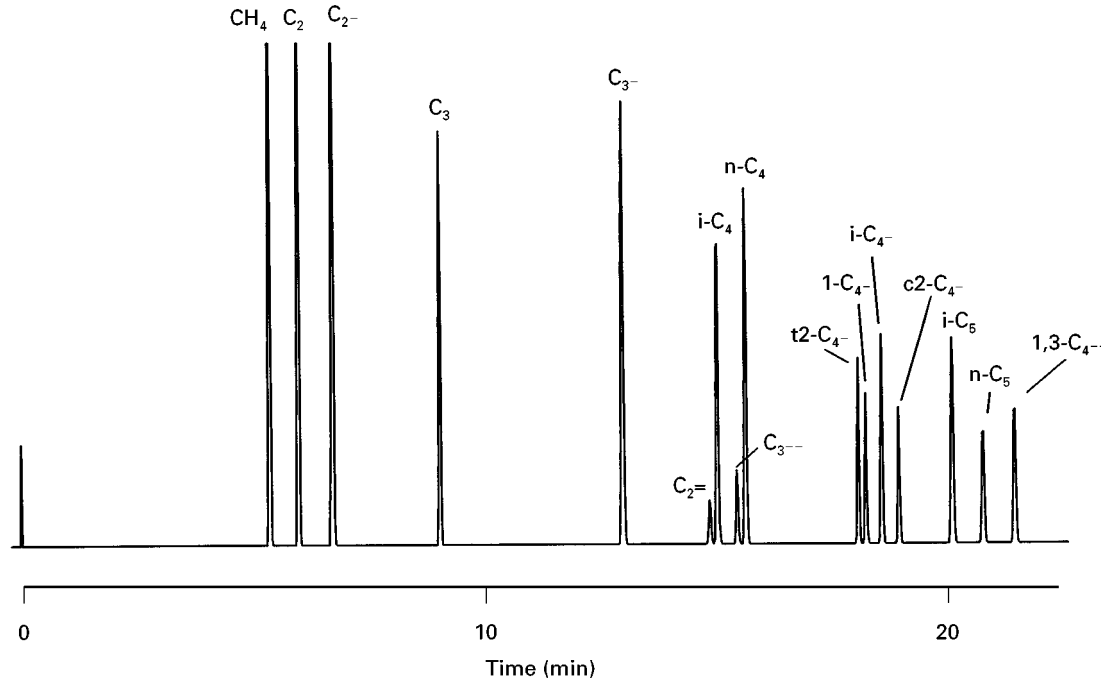

Figure 7 Porous-layer open-tubular (PLOT) alumina column.

separation between methane and inorganic gases is not a problem.

Carbon Active carbon has been used as a packing since the introduction of gas analysis by chromatography. Modern packings are based on graphitized carbon black or on carbon molecular sieve. Both have similar retention characteristics to porous polymers, but carbon molecular sieve, with a high surface area, requires higher temperatures. Another characteristic of carbon molecular sieve is its very low retention for water, typically eluting before CO_2. Either type of packing is used for samples containing adsorptive components, in which case the inert nature of all the materials in the sample path, not just the packing material, must be considered.

Column Switching

Most gas analyses require the use of more than one column, given the restricted applicability of each. Rather than use the columns individually in separate chromatographs, they can be combined in a single unit by means of switching valves. Such valves are similar to the gas sampling valve described earlier, but configured for different uses.

Figure 8 shows a configuration suitable for the common combination of molecular sieve and porous polymer columns. V1 is the gas sampling valve and

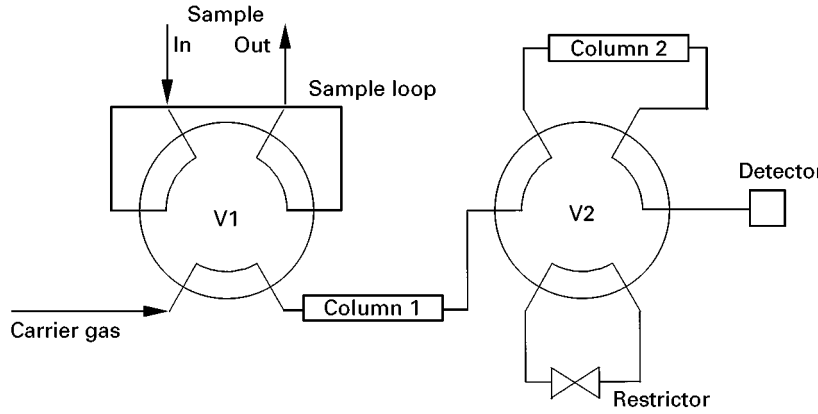

Figure 8 Column isolation.

V2 the column switching valve. Column 1 is porous polymer and column 2 molecular sieve. The restrictor on V2 is adjusted so that the carrier flow to the detector is the same for both positions of V2. Those components for which molecular sieve is appropriate (O_2, N_2, CH_4 and CO) are rapidly eluted from the porous polymer column with little or no separation. With V2 in the position shown, they pass into the molecular sieve column. Before CO_2 and other components have reached the end of the porous polymer column, valve V2 is switched, allowing them to bypass the molecular sieve and pass directly to the detector. Switching V2 also isolates the light components in the molecular sieve column, with no carrier gas flow. After the components directly eluted from the porous polymer column have been detected, V2 is switched back, and the light gases are measured. **Figure 9** shows a chromatogram.

Another procedure is possible. If the gap on the porous polymer column between the initial unresolved components and CO_2 is sufficiently large, then the flow can continue through the molecular sieve to allow the light components to be measured before CO_2 reaches V2. V2 is then switched, allowing CO_2 and the other components to be measured.

Combined use For certain applications, one 10-port valve can be used in place of two 6-port valves. **Figure 10** shows the configuration which would allow the second procedure described above to be achieved with one valve. With the valve in the first position, sample is being purged through the loop, and the carrier gas is following the sequence column 2 → column 1 → detector. Switching the valve injects the sample on to column 1 (porous polymer). After the light gases from column 2 have been measured, the valve is returned to the sample load position for measurement of CO_2 and other components.

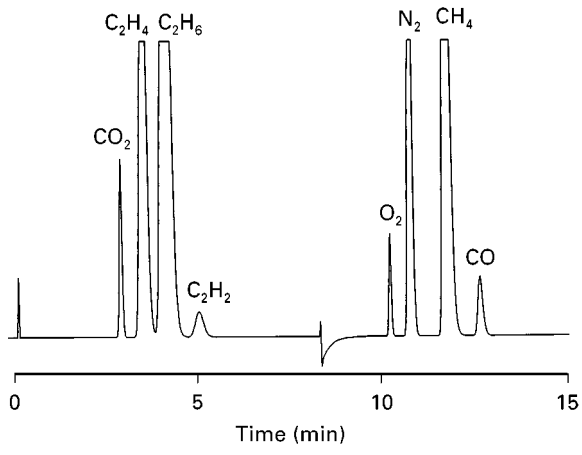

Figure 9 Combined column chromatogram.

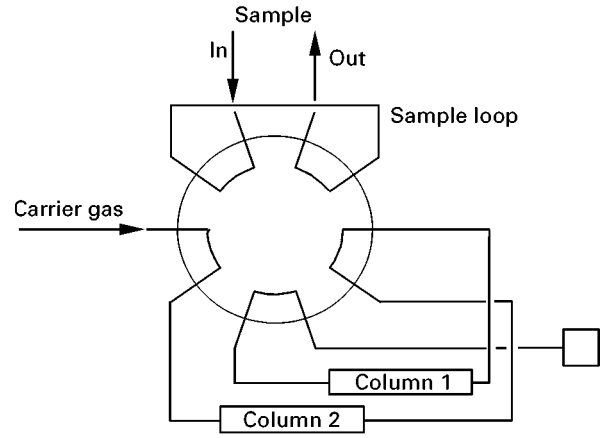

Figure 10 Combined injection and switching.

Multiple systems Natural gas and refinery gas are two examples of complex mixtures which require more elaborate systems than those described above. Although neither mixture should contain oxygen, a molecular sieve column is recommended because air contamination of the sample is always possible; measurement of the oxygen concentration allows the air content to be calculated and allowed for. A porous polymer column allows optimum separation of carbon dioxide, ethane and, if present, ethene. C_3, C_4 and C_5 hydrocarbons can be dealt with by an appropriate liquid-phase column, and in a common implementation all heavier hydrocarbons are measured as a backflushed C_6+ group.

Figure 11 shows the configuration. Column 1 is divided into two sections, the longer 1B, on which C_3, C_4 and C_5 hydrocarbons are separated, and the shorter 1A, from which C_6+ is backflushed. Valve V1 injects the sample and also alters the sequence of columns 1A and 1B. Valve V2 isolates and reconnects the porous polymer (column 2) and molecular sieve (column 3), and V3 does the same for column 3 alone.

After sample injection, V1 is left in that position until the C_5 components have passed on to column 1B, while the C_6 and heavier are still on column 1A. This time is found by trial and error. At this point, V1 is returned to the sample load position, which also reverses the flow through column 1A and places it directly before the detector. All heavier components are rapidly measured as a recombined C_6+ peak. After the light gases have been eluted from column 1B, rotation of V2 isolates them in columns 2 and 3. The timings and column lengths are chosen so that each group of light gases is isolated on the appropriate column. C_3, C_4 and C_5 hydrocarbons elute from column 1B, pass through column 1A for the second time, and are detected. After that, valves V2 and V3

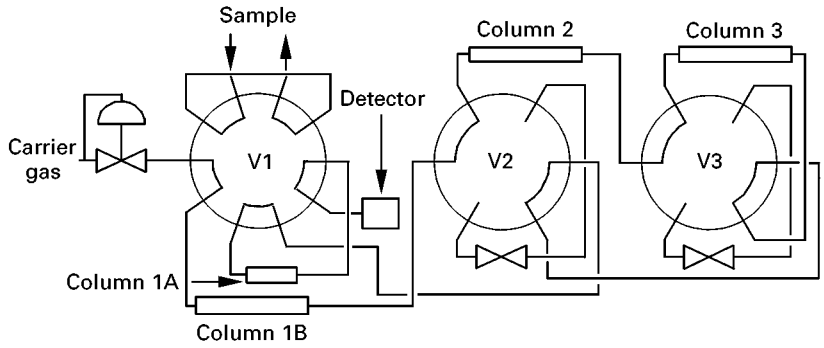

Figure 11 Multiple column analysers.

are rotated to reconnect column 2, and CO_2 and C_2 hydrocarbons are measured. Finally, V3 reconnects column 3, and the components from the molecular sieve column are measured. **Figure 12** shows a chromatogram of natural gas.

Carrier Gas

Since the TCD is normally used for the major components of gas mixtures, the thermal conductivity of the carrier gas is one of its most important properties. Helium and hydrogen have similar high thermal conductivities, and allow other components to be detected with good sensitivity. All other things being equal, helium would be preferred for its inertness. Unfortunately, the thermal conductivities of helium/hydrogen mixtures have a significantly nonlinear relationship to concentration, which makes quantitative measurement of hydrogen in helium carrier gas difficult. Argon or nitrogen is suitable for the measurement of hydrogen and/or helium. As described above under 'Molecular sieve', argon can be used to measure oxygen without interference, and nitrogen may be the best choice for measurement of other trace components in air.

When other detectors, such as the FID, are used, the choice of carrier gas is less critical. Maximum sensitivity from the FID is obtained with nitrogen or argon, but this is rarely the most important need. Helium allows higher carrier gas linear velocities without loss of efficiency, and is also preferred in cases where both TCD and FID are used in series.

Detectors

For specific applications, most types of detector are used or have been used. Electron capture, helium ionization, ultrasonic and flame photometric detectors are applicable where the properties or very low concentrations of sample components require them. For the majority of applications, however, the TCD is the most popular, followed by the FID. TCDs use either filaments or thermistors as sensing elements. Thermistors give greater sensitivity at lower detector temperatures, but are less good if the application demands a high detector temperature. When

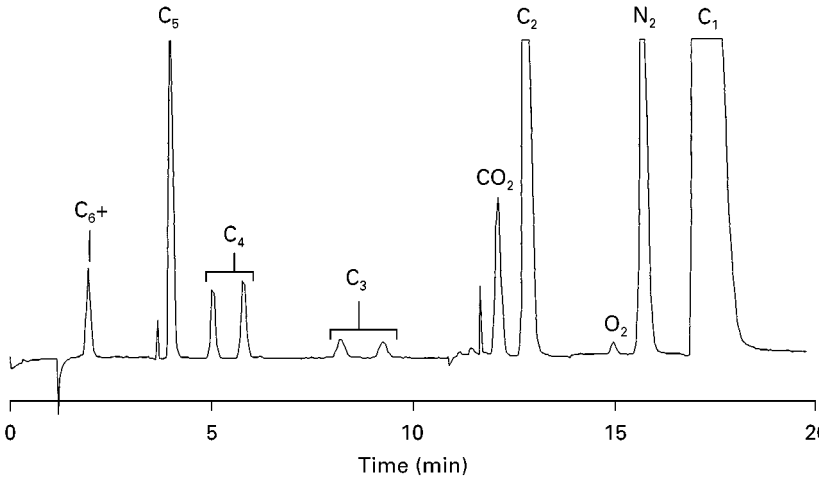

Figure 12 Natural gas chromatogram.

using adsorption columns, it is not always necessary to maintain a detector temperature higher than that of the column oven, and thermistors may still be preferred. The higher temperatures of filaments can cause sample components to react with them. As an example, a sample containing both oxygen and hydrogen sulfide can cause step baseline changes in opposite directions as each component in turn passes through the detector.

Quantitative Analysis

The importance of calibration is as great for analysis of gases as it is for liquid samples. In some respects it is even greater, since the TCD, which is used for the major components of gas samples, does not share the 'carbon counter' characteristic of the FID. If, for example C_3 to C_5 hydrocarbons in a gas are analysed using an FID, it would be possible to calibrate using a standard gas containing C_3 alone, and then quantify the other components by means of relative response factors. This is not the case when using TCD; while the relative response for a particular detector will be stable, they are not predictable as for the FID, and there is not a sufficient basis of knowledge to allow them to be transferred to other models of TCD from other suppliers.

Calibration gas mixtures of the highest accuracy can be prepared in cylinders gravimetrically. Although the mass of the cylinder is very much greater than the masses of the added components, the discrimination and accuracy of weighing are such that the uncertainties of the composition are very small. Such mixtures are, of course, expensive, and for regular use certified calibration mixtures, which have been analysed against a gravimetric mixture, are normal. If components are likely to react with or adsorb on to cylinder walls, then calibration mixtures can be prepared dynamically, at the time and place of use. Permeation tubes, where a component diffuses through a membrane into a measured diluent gas flow under controlled conditions, are widely used for trace analysis.

If only a few specific components are to be measured, then the individual response factors calculated from the calibration gas are critical. It is necessary to calibrate with sufficient frequency that uncontrollable effects, such as that of barometric pressure on TCD response, do not degrade the result. Consistency of sample size between calibration and analysis is also important. A gas sampling valve (see above under 'Sample handling and injection') allows this, but the operator must ensure that the temperature and pressure of the calibration gas and sample are uniform.

If the analysis is comprehensive, as in the natural gas example shown in **Figure 12**, then the resulting composition will be normalized to 100%. This procedure effectively converts the individual response factors to relative ones. Since relative response factors for a single detector remain stable over long periods, consistency of sample size is less critical. Regular calibration is still important, but is used as much as a quality control test as for calibration in the traditional sense.

Further Reading

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GAS CENTRIFUGE: ISOTOPES SEPARATION

See **III / ISOTOPE SEPARATIONS: Gas Centrifugation**

GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN MEDICINE

See **III / BIOMEDICAL APPLICATIONS: Gas Chromatography–Mass Spectrometry**