

that, for large sample sizes, some decomposition is seen from the reheating of the cryotrap region between the two columns.

## Future Developments

High speed GC can probably be best described as currently being in an interim phase. It is in the process of moving from the research laboratory to the analysis laboratory. Most of the basic research demonstrating the feasibility of high speed GC and the instrumental modifications necessary for successful high speed analysis have been accomplished and the findings are well disseminated in the literature, yet the number of true applications remains small.

One technique, which has not been commented on in this article, is the combination of high speed GC with mass spectrometry (MS) as a detection method. The advent of fast scanning time-of-flight mass analysers has provided the data acquisition rates necessary for interfacing with high speed GC. Although the concept of coupling the two techniques together has been demonstrated, no real application articles using both techniques are currently available. Given the prominence of GC-MS analysis in many areas, this will surely change in the near future.

Other future developments will probably include the interfacing of other selective detectors with high speed GC and the subsequent expansion of high speed GC into the areas of analysis served by these selective detectors.

*See also: II/Chromatography: Gas: Column Technology; Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective; Historical Development; Multidimensional Gas Chromatography; Sampling Systems; Theory of Gas Chromatography.*

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## Historical Development

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In 1941 Martin and Synge published their classic paper on liquid–liquid partition chromatography in

which they pointed out that there was no reason why the mobile phase should not be a gas. This suggestion was not followed up until 1952 when James and Martin published their paper on the separation of fatty acids by gas–liquid chromatography. This paper generated a frenzy of activity, particularly within the petroleum industry where the method represented an

enormous advance in the separation and analysis of hydrocarbon mixtures. Gas chromatography has now matured into the method of choice for the separation of volatile, thermally stable compounds with an upper molecular weight limit of about 1000 Da and is one of the most widely used laboratory methods today.

The development of gas chromatography was unique in many ways in particular the fact that, although workers in some academic establishments made notable contributions, the major impetus came from industry and from instrument companies. Another factor in its rapid development was the establishment of discussion groups in many countries dedicated to disseminating information on new advances. The Gas Chromatography Discussion Group (now the Chromatographic Society) was established in the UK in 1956 and similar bodies were formed in other parts of Europe and in North America soon afterwards. The history of gas chromatography has been described a number of times; the book by Zlatkis and Ettore gives the reminiscences of some of the early workers.

Four papers are identified in **Table 1** that caused major advances in gas chromatography followed by periods of consolidation. These aspects are considered in more detail below.

## Column Development

### Packed Columns

For many years most gas chromatography was carried out with packed columns. Packed columns for analytical applications have internal diameters usually between 2 and 5 mm and lengths from 0.5 to 5 m, and contain particles around 100–250  $\mu\text{m}$  in diameter with a range of  $\pm 25 \mu\text{m}$ , carrying the liquid phase. Packed columns have been constructed of various materials but the preferred materials are glass and stainless steel. The packing can be a solid adsorbent such as silica, alumina or graphitized carbon for gas–solid chromatography or a porous support coated with a high boiling liquid for gas–liquid chromatography. The usual support for the liquid phase is diatomaceous earth, a form of naturally occurring silica, with a surface area of about 0.5–4.0  $\text{m}^2 \text{g}^{-1}$  and a capacity to retain physically 5–30% (w/w) of liquid phase. Celite, a commercial diatomaceous earth, was used by Martin and James in their early experiments and is still a common support for packed columns. Polar compounds such as those found in the biomedical field give severe tailing, possible decomposition and

**Table 1** Important advances in gas chromatography

1941	<i>Fundamental paper on partition chromatography</i> (Martin and Syngé)
1952	<i>Fundamental paper introduces gas chromatography</i> (James and Martin)
1955	First commercial GC instrument (thermal conductivity detector)
1955–1960	Rapid period of technological growth <ul style="list-style-type: none"> <li>Invention of ionization detectors (FID, ECD)</li> <li>Direct coupling to mass spectrometry</li> <li>Microsyringes</li> <li>Temperature programming</li> </ul>
1958	<i>Fundamental paper describes open-tubular columns</i> (Golay)
1960–1970	Period of technical advancement <ul style="list-style-type: none"> <li>Stainless steel open-tubular columns</li> <li>Transistors replace vacuum tubes</li> <li>Stable rubidium sources for AFID</li> <li>Improved FPD (several designs)</li> <li>Pulsed ECD</li> </ul>
1970–1980	Period of consolidation and refinement <ul style="list-style-type: none"> <li>Microprocessor-based instruments introduced</li> <li>Preparation of glass open-tubular columns mastered by some research groups</li> </ul>
1979	<i>Fundamental paper describes fused silica open-tubular columns</i> (Dandeneau and Zerenner)
1980–1990	Period of technical advancement <ul style="list-style-type: none"> <li>Gum and immobilized phases</li> <li>Thick-film open-tubular columns</li> <li>Wide-bore open-tubular columns</li> <li>On-column and PTV injection (greater understanding of the injection process)</li> <li>Large volume injection (LC-GC)</li> <li>Computing integrators for data handling</li> <li>Autosamplers</li> </ul>
1990–Today	Period of consolidation and refinement <ul style="list-style-type: none"> <li>Keyboard instrumentation (PC control of operation and data handling)</li> <li>Electronic pneumatic control</li> <li>Selectable elemental detection (AED)</li> <li>Sensitive and versatile spectroscopic detectors (MS, FTIR)</li> </ul>

structural rearrangements or even complete adsorption on untreated diatomaceous earth. Acid and/or base washing to remove metallic impurities and silanization of surface silanol groups are widely used to minimize these effects. Fluorocarbon powders have been used occasionally in the separation of reactive compounds such as hydrogen chloride and organometallic compounds. Glass beads have also been used in theoretical studies, but have no practical application.

With packed columns the only way to make a radical alteration in the selectivity is by changing the liquid phase. This gave rise to a large number of stationary liquids, many with similar separation properties. Rohrschneider developed an empirical classification method based on the comparison of Retention Index (see below) differences for a number of standard compounds on the liquid phase to be characterized, relative to squalane as a reference phase. The scheme was extended by McReynolds and although it had no fundamental basis it did allow a list of preferred liquid phases to be drawn up. By employing the Rohrschneider-McReynolds classification the number of liquid phases can be drastically reduced and seven phases can be recognized as preferred choices for packed column gas-liquid chromatography (Table 2). If sample volatility is also considered then a poly(dimethylsiloxane) such as OV-1 would have to be substituted for squalane.

Another factor in the move towards rationalization of the choice of stationary phase was the introduction by Kováts in 1958 of the Retention Index system for expressing retention times (or volumes) relative to a series of standards. This was not a new idea, but Kováts proposed that the normal paraffins be taken as the standards for the scale of reference. The Retention Index system took rather a long time to be accepted since it was originally published in an over-complicated form in German and it was not until it was publicized by Ettre in *Analytical Chemistry* some years later that the system received wider acceptance.

Much work has been carried out on the relationship between structure and Retention Index and the concept has proved so useful that it has been transferred in a modified form to liquid chromatography.

Current uses of packed columns include large scale separations, physicochemical measurement of compounds used as stationary phases (inverse gas chromatography), separations employing stationary phases not easily immobilized on fused silica surfaces (see below) and the routine analysis of simple mixtures in a dirty matrix not tolerated by open-tubular columns.

### Open-Tubular Columns

In 1958 Golay, wishing to simplify the mathematics of the flow of gas in a packed column with many tortuous paths, used a model consisting of a tube of capillary dimensions. He was able to demonstrate theoretically that such a capillary coated with a thin film of liquid would give columns with very high numbers of theoretical plates. The fundamental difference between packed and open-tubular columns is the much lower resistance to gas flow of the latter, which means that in practice very much longer columns can be used and very high efficiencies obtained. The reason for the need for a column of capillary dimensions can be understood from the equation derived by Golay stated in its modern form:

$$H = \frac{f_1[2D_{m,o}]}{u_o} + \frac{f_1[1 + 6k + 11k^2]d_c^2 u_o}{96(1 + k)^2 D_{m,o}} + \frac{f_2[2k]d_f^2 u_o}{3(1 + k)^2 D_s}$$

Here  $H$  is the height equivalent to a theoretical plate,  $f_1$  and  $f_2$  are pressure correction factors,  $k$  is the retention factor (frequently called the capacity factor),  $D_{m,o}$  is the solute diffusion coefficient in the mobile phase at the column outlet pressure,  $D_s$  is the solute diffusion coefficient in the stationary phase,  $u_o$  is the velocity of the mobile phase at the column

**Table 2** Selection of preferred stationary phases for method development at intermediate column temperatures

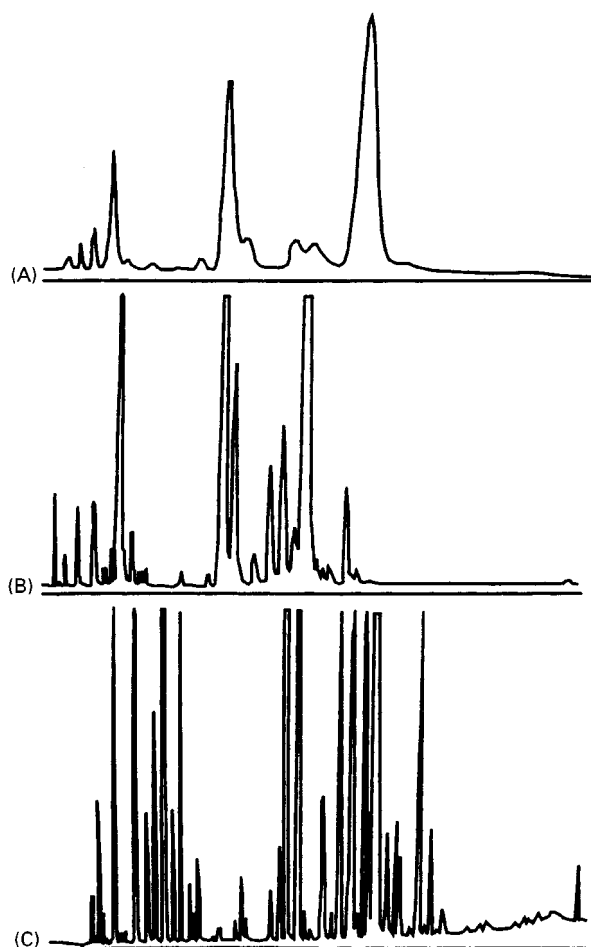
Representative phase	Solvent characteristics
Squalane	Low cohesion and minimal capacity for polar interactions
OV-17	Low cohesion with a weak capacity for dipole-type interactions and weak hydrogen-bond basicity
QF-1	Low cohesion and intermediate capacity for dipole-type interactions combined with low hydrogen-bond basicity
U50HB	Low cohesion and weak dipole-type interactions with interactions with intermediate hydrogen-bond basicity
CW 20M	Low cohesion and intermediate capacity for dipole-type interactions and intermediate hydrogen-bond basicity
QTS	Intermediate cohesion with a large capacity for dipole-type interactions and strong hydrogen-bond basicity
OV-275	Very cohesive solvent with a large capacity for dipole-type interactions and intermediate hydrogen-bond basicity

outlet,  $d_c$  is the column internal diameter and  $d_f$  is the thickness of the film of stationary phase.

The three additive components of the plate height represent the contributions of longitudinal diffusion, resistance to mass transfer in the mobile phase and resistance to mass transfer in the stationary phase, respectively. Open-tubular columns minimize the contribution from resistance to mass transfer in the mobile phase. The stationary phase mass transfer term becomes increasingly important as the liquid film thickness increases beyond about 1  $\mu\text{m}$ .

Soon after his theoretical investigation, Golay was able to demonstrate successfully the practical application of the theory. An important factor in the development of open-tubular (capillary) columns was the discovery of the flame ionization detector capable of giving adequate signals for the small sample sizes required by these columns. These early advances gave some spectacular separations, especially for complex hydrocarbon mixtures, but the general use of open-tubular columns evolved only slowly because many difficult problems remained that required a further 20 years of development. Stainless steel capillaries gave satisfactory performance for hydrocarbon mixtures but for more polar compounds they gave tailing peaks and poor efficiencies, owing to adsorption. Desty and co-workers described a glass-drawing machine capable of producing long lengths of coiled glass capillary tubing as early as 1960 but it was soon found that it was difficult to obtain uniform and stable thin films on glass columns. The surface was too smooth to allow good adhesion by physical adsorption of many of the phases commonly employed at the time, and the many metals included in glass, although at relatively low concentrations, gave rise to adsorption of polar analytes. Considerable effort was expended to overcome these problems, particularly notable being the work of G. and K. Grob. Leaching with aqueous hydrochloric acid to remove some of the surface metal ions followed by treatment with silanes was one approach. Deposition of a layer of barium carbonate to retain the stationary liquid was another practical solution. Such treatments, although successful in skilled hands, were regarded by many as a black art and the resulting columns were fragile and easily destroyed. **Figure 1** shows the separation of peppermint oil on three generations of Carbowax 20M columns up to 1980.

In addition to the work on true open-tubular columns, intermediate variants between these and packed columns were developed. These include micro-packed columns and support-coated open-tubular (SCOT) columns where a thin coating of a very fine diatomaceous support was deposited on the inner wall of a stainless steel capillary. Another



**Figure 1** Three generations in gas chromatography. Peppermint oil separated on (A) 6 ft  $\times$   $\frac{1}{4}$  in. i.d. packed column, (B) 500 ft  $\times$  0.03 in. i.d. stainless steel open-tubular column, and (C) 50 m  $\times$  0.25 mm i.d. glass open-tubular column. All columns contained Carbowax 20 M stationary phase and were operated under optimized conditions. (Reproduced with permission from Jennings W (1979) The use of glass capillary columns for food and essential oil analysis. *Journal of Chromatographic Science* 17: 636–639, Copyright Preston Publication, Inc.)

variant was the porous-layer open-tubular (PLOT) column with a thin coating of an adsorbent on the inner wall of the capillary. PLOT columns still find application for the analysis of low boiling mixtures such as light hydrocarbon gases, but the other types are now no longer used.

The introduction of open-tubular columns made from fused silica in 1979 made glass capillaries obsolete almost overnight and also caused packed columns to be displaced as the dominant type. Currently the dimensions of commercially available open tubular columns range from 100  $\mu\text{m}$  to 530  $\mu\text{m}$  in inner diameter and from 5 m to 100 m in length.

Today nearly all open-tubular columns are prepared from either fused silica or metal capillaries

lined with fused silica. Fused silica is essentially pure silicon dioxide containing less than 1 ppm of metallic impurities. When drawn, these capillaries are very fragile and must be protected from moisture and surface imperfections by the application of an outer coating of a polymer or aluminium layer immediately on production. After such treatment the tubing is rugged and sufficiently flexible to be coiled into a circle of 10 cm diameter or less. Typical performance characteristics of modern wall-coated open-tubular (WCOT) columns are summarized in Table 3 and compared those of classical packed columns.

To achieve a high separation efficiency in any type of open-tubular column it is essential that the stationary phase be deposited as a smooth, thin and homogeneous film that maintains its integrity without forming droplets when the column temperature is varied. Phases showing little variation in viscosity with temperature are preferred for this purpose. Many of the stationary phases developed for packed columns are of limited use for WCOT columns and have been replaced by specially synthesized poly(siloxane)s or poly(ethylene glycol)s.

A great advance in column technology that took place about the same time as the introduction of fused silica columns was the immobilization of phases by reaction with the column wall and crosslinking to form a three-dimensional polymer to further stabilize the poly(siloxane) films without destroying their favourable solute diffusion properties. Thermal condensation of nonpolar and medium polar poly(siloxanes) at high temperature with silanol groups on the fused silica surface results in chemical

bonding of the phase to the surface to give columns suitable for use up to 400–425°C. High polarity phases are more difficult to bond; they require careful surface preparation to avoid film disruption during the bonding process and generally yield columns of lower thermal stability. The general approach for immobilization of stationary phases is by free-radical cross-linking of the polymer chains initiated with peroxides, azo compounds, or  $\gamma$ -radiation. With increasing substitution of methyl by bulky or polar functional groups the difficulty of obtaining complete immobilization increases, and moderately polar poly(siloxane) phases are prepared with various amounts of vinyl, tolyl, or octyl groups that increase the success of the cross-linking reaction. Cross-linking is also important in enabling columns to be prepared with thicker films ( $> 0.5 \mu\text{m}$ ) than was possible with physically adsorbed stationary phases. Immobilization of polar phases remains a problem and so far cross-linking reactions are limited, in the main, to poly(siloxane)s and poly(ethyleneglycol)s, which limits the range of selective phases available for open tubular columns. The development of bonding and immobilization techniques facilitated large volume injection and online interfacing with liquid chromatography and supercritical fluid chromatography (or extraction), which require columns with a stationary phase resistant to solvent stripping.

## Instrumentation

The essential elements of instrumentation were developed by the early 1960s, but the advent of the

**Table 3** Chromatographic properties of commercially available columns

Column type	Length (m)	Internal diameter (mm)	Film thickness ( $\mu\text{m}$ )	Phase ratio <sup>a</sup>	H (mm)	N (column)	N/length
Classical	2	2.16	10% (w/w)	12	0.55	3640	1820
Packed	2	2.16	5% (w/w)	26	0.50	4000	2000
WCOT <sup>b</sup>	30	0.10	0.10	249	0.06	480 000	16 000
	30	0.10	0.25	99	0.08	368 550	12 285
	30	0.25	0.25	249	0.16	192 000	6400
	30	0.32	0.32	249	0.20	150 000	5000
	30	0.32	0.50	159	0.23	131 330	4380
	30	0.32	1.00	79	0.29	102 080	3400
	30	0.32	5.00	15	0.44	68 970	2300
	30	0.53	1.00	132	0.43	70 420	2340
	30	0.53	5.00	26	0.68	43 940	1470

<sup>a</sup>Phase ratio = volume of gas phase/volume of liquid phase in the column (columns with a low phase ratio are more retentive).

<sup>b</sup>Selecting a WCOT column: narrow-bore thin-film columns are used for high speed gas chromatography; columns with 0.25 and 0.32 mm internal diameters are used for general high performance applications; wide-bore columns with thicker films are used as replacements for packed columns; thin-film columns are employed for the separation of compounds of low volatility; and thick-film columns are used for separating volatile compounds and to obtain maximum sample loadability.

microprocessor has effected a radical change in design and use. Most gas chromatographs now have self-diagnostic software so that faults may be revealed and located. There has also been a revolution in the handling of the data produced (see below).

### Column Heating

The column heater is generally a forced-circulation air oven, the temperature of which can be changed in a controlled manner with time for temperature programmed separations. Good temperature control is essential to obtain reproducible retention times. A low thermal mass for the oven is also important since it allows rapid cooling after temperature programming. Air circulation ovens give a very satisfactory performance but they do have some limitations. Liquid thermostat baths were frequently employed in early gas chromatography and are still necessary if extremely accurate temperature control is required, as in theoretical studies.

### Sample Introduction

The most common method of sample introduction is by means of a microsyringe through a septum-sealed inlet. Microsyringes are useful for introducing liquid or gas samples, a technique developed by N.H. Ray in 1954. For quantitative work, gases are normally introduced by loop sampling valves, which are highly reproducible and readily automated. Solid samples may be introduced after dissolution in a suitable solvent. Direct introduction of solids is seldom used with open-tubular columns.

The limited sample capacity and low carrier gas flow rates associated with open-tubular columns makes sample introduction much more difficult than for packed columns. A thermostatted flash vaporization chamber in which the evaporated sample is mixed with carrier gas and divided between a stream entering the column (carrier gas flow) and a stream vented to waste (split flow) was the first practical solution to this problem. Split injection discriminates against high boiling compounds (bp > 250°C) owing to selective vaporization. Quantitative analysis of wide boiling range mixtures is difficult, and for the analysis of samples present in a dilute solution detectability is limited by the small amount of sample transferred to the column.

The so-called splitless injection technique was devised to overcome some of the deficiencies of split injection for the analysis of mixtures of compounds in a solvent (such as frequently occurs in environmental studies) through the transfer of relatively large volumes to the column. The gas flow through a splitless injector is relatively low, and the sample is introduced into the column over a comparatively long time

(30–60 s), relying on cold trapping and/or solvent effects to refocus the compounds at the head of the column. The importance of these refocusing mechanisms was not fully understood at first but splitless injection did demonstrate the possibility of performing trace analyses with open-tubular columns. It is also easy in practice to convert an injector from split to splitless operation by the operation of valves and minor hardware modifications.

The programmed-temperature vaporization (PTV) injector overcame many of the problems observed with the hot split and splitless injector. The PTV injector is designed to allow rapid heating and cooling and the sample is introduced at a low temperature. A rapid rise in temperature after introduction ensures rapid volatilization of the highest boiling sample components. The PTV injector may be used in both split and splitless modes and the accuracy and precision approach those obtained by cold on-column injection.

The production of wide-bore silica columns in the early 1980s allowed introduction of the syringe needle directly into the column and the use of immobilized phases eliminated the problem of removal of the stationary phase by large volumes of liquid sample. In cold on-column injection the sample is introduced as a liquid into the column inlet where it is subsequently vaporized. Discrimination based on volatility differences has been virtually eliminated and the risk of sample decomposition minimized. With secondary cooling of the injector, the oven temperature can be kept well above the boiling point of the solvent while maintaining the column inlet at a much lower temperature. This is important for using on-column injection in high temperature gas chromatography. Dirty samples present a problem owing to contamination of the sample introduction zone, which leads to poor chromatography and unreliable quantitation.

### Detectors

The thermal conductivity detector (TCD) was used extensively in early work and is still used in a much improved form which makes it compatible with wide-bore open-tubular columns. The relatively poor sensitivity of the early TCD meant that it was largely displaced by the flame ionization detector (FID). The combustion of carbon-containing compounds in a small hydrogen/air diffusion flame produces ions that can be detected by applying a voltage between the flame jet and a collector electrode situated around the flame. The detector has a low dead volume, a high sensitivity for nearly all carbon-containing compounds and an extremely wide linear range of response. As already pointed out, the discovery of the FID played a crucial role in the development of open

tubular columns. The FID is rugged, reliable and relatively insensitive to operating variable so that it is now by far the most widely used of all detectors.

The TCD and the FID are universal detectors; that is, they give a response for all substances. This is not strictly true for the FID since it gives no response for the permanent gases and water (which makes it very suitable for the analysis of aqueous samples). Another universal detector, now becoming much more widely employed, is the mass spectrometer. Coupling to a mass spectrometer (GC-MS) dates almost from the beginning of gas chromatography, but in the early days the practical problems and high cost meant that the combination was confined to a few research laboratories. The advent of the silica open-tubular column, improved designs of mass spectrometers, the availability of computers to handle the large amount of data produced and a considerable reduction in cost have resulted in the GC-MS combination becoming very widely used. The great advantage of the mass spectrometer as a detector is its ability to identify the compounds being separated. It is not quite ideal in this respect since isomers sometimes give almost identical spectra, but techniques such as tandem mass spectrometry (MS-MS) and different methods of ionization can overcome some of these problems. Another advantage is that the mass spectrometer can also be used in a selective mode, often with greatly increased sensitivity.

Fourier transform infrared spectroscopy detectors for gas chromatography are also available; their range of application is not as wide as the GC-MS combination but to some extent they are complementary.

In addition to the universal detectors, a number of selective detectors are commercially available. The nitrogen and phosphorus detector (NPD) is similar in design to a conventional FID but has an electrically heated rubidium-glass bead situated between the flame jet and the collector electrode and (for nitrogen compounds) uses a very small hydrogen flow so that there is a heated plasma in the working zone rather than a flame. This detector is widely used for the analysis of drugs and pesticides in environmental and biological research. Other variants of the FID such as the hydrogen atmosphere FID, which gives a response to some gases, and the O-FID for the selective detection of oxygen-containing compounds, also exist.

The electron-capture detector has an outstandingly high response for polyhalogenated compounds and so has found extensive application in pesticide and environmental analysis. Indeed, the start of the concern for the distribution of compounds such as DDT in the environment can be attributed to the development of this detector in the early 1960s.

Other selective detectors include the microwave plasma emission detector, which can detect a number

of elements simultaneously. The photoionization detector gives a high response for environmentally important compounds such as benzene and vinyl chloride and finds use as a portable field instrument. The flame photometric detector and the chemiluminescence detector have a high response to sulfur and are used extensively in the petroleum industry. Chemiluminescence detection has also been used for the selective determination of nitrosamines in foodstuffs. The Hall detector catalytically decomposes the compounds emerging from the gas chromatography column into simple inorganic gases such as hydrogen chloride (for chlorine) and ammonia (for nitrogen), which are absorbed in a circulating stream of aqueous organic solvent followed by monitoring the electrical conductivity of the solution obtained.

Although selective detectors find extensive application for particular problems they are all more demanding in the control of operating parameters than the FID.

### Data Handling

Data handling was originally by purely manual measurement of peak heights. It was recognized that peak area measurement was fundamentally better but areas could be obtained and approximately by measuring the peak height and the width at half height. Such an approach was satisfactory for simple mixtures but was totally impractical for mixtures containing perhaps 100 components in widely differing concentrations. Early integrators consisted of mechanical or electromechanical devices such as the ball and disk integrator and integrating amplifiers, but were very limited in range and speed of response. The mid-1960s saw the introduction of the first generation of electronic integrators and a little later the use of mainframe computers to handle data from a number of instruments simultaneously. The large amounts of data produced by open-tubular columns (especially when coupled to a mass spectrometer) can now be handled by a personal computer. The data can be acquired, manipulated and displayed in real time and can be stored electronically almost indefinitely for record purposes.

### Future Developments

Looking to the future, it is reasonable to expect continued evolutionary development. In this context it is interesting to note that several new selective detectors have become available in the last few years. The use of GC-MS will become more widespread as the real cost of such instruments continues to fall and the performance of the mass spectrometry detector shows continuous improvement in sensitivity and resolving power.

The gas chromatograph will develop into a module for more complex analysers for automated sample processing and plant control. The separation time will continue to decrease; in the past there has been limited interest in fast separations but this could change as automated sample processing is developed. Increasing use of coupled techniques such as GC-GC, liquid chromatography-GC, and supercritical fluid chromatography-GC for the separation of complex mixtures will give resolution unachievable by single column operation.

Columns with immobilized phases of a wider range of selectivity than currently exist will be developed. New sorbent (PLOT) columns and hybrid columns with low loadings of liquid phases, special application phases for separating enantiomers and isomers, and columns better able to withstand aqueous samples can be expected.

## Further Reading

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## Ion Mobility Mass Spectrometry

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### Introduction

J. J. Thompson made the first ion mobility measurements about a century ago. Modern ion mobility spectrometry (IMS), however, was first described in the early 1970s. The development of the electron-capture detector (ECD) had generated much interest with its impressive limits of detection, and this provoked thoughts of an ionization detector with an additional level of specificity that could operate as a stand-alone instrument. IMS was introduced initially as 'plasma chromatography', and sometimes as 'gaseous electrophoresis'. Such terms invited unrealistic comparisons between established separation techniques and IMS, with its modest resolving power. Superficial similarities to time-of-flight-mass spectrometry meant that IMS was also initially considered as an atmospheric pressure mass spectrometer, but poor mass-mobility correlations disproved this view too. Such unrealistic expectations arose from a lack of understanding of the principles of operation. Furthermore such misunderstandings confronted with com-

plex responses and memory effects observed in many investigations at that time resulted in disillusionment with the technique by many. IMS was generally dismissed as something of a curiosity.

By the late 1970s advances in sample handling (especially for trace levels) and better electronics led to renewed interest in IMS. Drift tubes were redesigned with heated components, which reduced memory effects, and sample introduction systems were re-evaluated, helping to avoid instrument overloads and allow quantitative work. Perhaps most importantly, IMS was evaluated on its own capabilities, rather than simply being compared with existing techniques.

The result was the appearance of the military chemical agent monitor (CAM) – a sensitive, highly selective, inexpensive, and fully portable instrument. The CAM also demonstrated that it was possible to produce IMS systems that could enable untrained personnel to make difficult chemical measurements in a hostile environment. The extent of the use of IMS in chemical agent monitoring is large. At the moment IMS instruments are issued at the platoon level across all the armies of the western alliance, thus making IMS arguably the most common trace VOC detection system in current use. Plans are underway to issue CAM devices to all military personnel.