



Milestones in Chromatography

This "Milestones in Chromatography" column describes five small and very useful accessories developed 40 years ago to adapt gas chromatographs for special tasks.

Gadgetry for Gas Chromatography

Soon after the seminal 1952 paper of James and Martin describing gas-liquid partition chromatography, and particularly after the introduction of the first commercial gas chromatographs in the middle of the 1950s, various industrial and academic laboratories rapidly adapted the technique for analyzing gases and light volatile compounds. The situation was well characterized in the fall 1955 issue of *Instrument News*, the widely distributed quarterly magazine of Perkin-Elmer (Norwalk, Connecticut). An editorial in this issue — published just a couple of months after the introduction of the company's first gas chromatograph, the model 154 Vapor Fractometer — stated that "we have a wildcat by the tail [with this instrument]: its enthusiastic reception has us breathless, our lab engulfed by requests for applications studies and everybody happy" (1).

The major reason for the rapid acceptance of gas chromatography (GC) was the ease of operation of the instruments. Analysts soon realized that GC was the best laboratory separation technique because it permitted the analysis of a wide variety of sample types. They also realized that, even with more complex samples, some simple on-line manipulations usually made their analyses possible. This flexibility was one of GC's essential advantages. In fact, if we looked at the programs of the first major international GC symposia held in 1956–1957 in England and the United States, almost every other paper described some kind of sample treatment in direct combination with the instrument.

The second major feature of GC was the possibility of selecting a separation column according to the need. In less than a year after the introduction of commercial instruments, more than a dozen standard column packings were available, each of which facilitated the separation of a certain compound group. Chromatographers could also combine two or three columns to achieve optimum separation when analyzing more complex samples.

For both on-line sample handling and multicolumn use the instrument companies

soon developed and introduced various accessories. Their availability had a major role in the continuous exponential expansion of GC in its first decade. We affectionately called these accessories gadgets. I was introduced to this word in my first days after joining Perkin-Elmer in the fall of 1958. Having a poor command of English, I looked for the meaning of this word in my new Webster's dictionary. According to its 1958 edition (which I still have), a gadget is "a small contrivance, object or device for doing something." I believe this definition is an excellent characterization of our gadgets. They permitted us *to do something* — and I may add — to do it easily. These accessories were small items that could be easily mounted on the side of the instrument and used on-line with the system's column and detector.

Today, most of these gadgets are forgotten: they became superfluous because of the increased sophistication of our instruments. However, in some cases, their principles remained alive, either in the form of separate instruments or in modern systems.

I will devote this "Milestones in Chromatography" column to five of these gadgets, which were developed at Perkin-Elmer some 40 years ago. My co-workers and I did not invent them; the principles of their operation had already been described in earlier publications. What we did was engineer them by designing packages that could be easily added to existing instruments in the users' laboratories. These simple accessories greatly helped to extend the application of GC to new fields.

Parallel Column Adapter

One of the early frustrations of gas chromatographers was the realization that the simplest possible sample — air — could not be analyzed from a single injection. Only one column packing was available for the separation of oxygen and nitrogen: molecular sieve 5A. However, this material irreversibly adsorbed carbon dioxide, which is a standard component of air. On silica gel, which was the other commonly used adsorbent-type column packing, a well-

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separated carbon dioxide peak could be obtained; however, oxygen and nitrogen gave one peak. Thus, to analyze air, chromatographers needed to make two sample injections and change the column before the second injection.

(Although it is not the subject at hand, readers of this column might be interested to know that there is one substance that could be used as a partition-type stationary phase for the separation of oxygen and nitrogen: blood. Indeed, its use for this purpose had been demonstrated in 1959 by Gil-Av and Herzberg-Minzly [2]. A 2 m \times 1/4 in. o.d. column containing 33% blood on firebrick resulted in an excellent separation of oxygen and nitrogen at 30–40 °C. However, the use of blood as a stationary phase obviously is not practical.)

In 1958 the New York Academy of Sciences held a symposium on GC entitled "The Analysis of Mixtures of Volatile Materials" during which my colleagues N. Brenner and E.W. Cieplinski described a simple system permitting the simplification of this analysis (3). They split the carrier-gas flow after sample introduction into two parallel columns, one of which contained molecular sieve and the other contained silica gel, or, in the case of more complex samples, any proper column packing. The exit flows from the two columns were reunited and conducted to the thermal-conductivity detector, thereby presenting one unified chromatogram. By selecting the respective column lengths and adjusting the flow rates through them, chromatographers could ensure that the

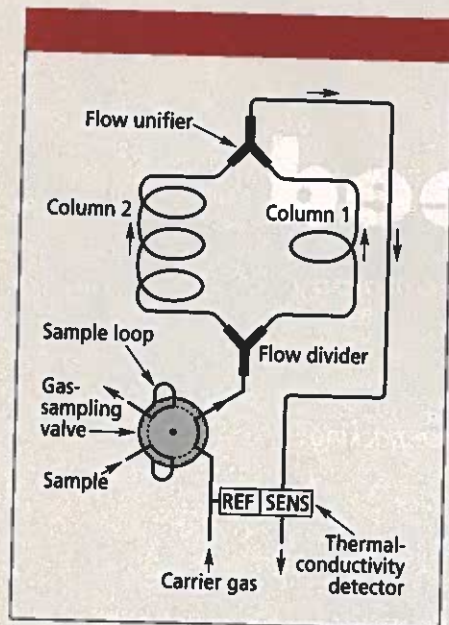


Figure 1: The principles of the parallel column adapter.

peaks coming from the individual columns would be properly spaced in the chromatogram.

Figure 1 shows the general schematic of the system. Its actual construction was very simple, facilitated by the design of the model 154 gas chromatograph, which was the most widely used instrument at that time. A large metal block located at the lower part of the column oven housed the thermal-conductivity detector, and one or two U- or W-shaped columns were directly attached to the block. The parallel column adapter simply consisted of two Y-shaped tube pieces inserted at the ports to which a single column normally would have been connected (Figure 2).

Figure 3 illustrates the use of the parallel column adapter for the analysis of an expired air sample. The first two peaks — air and carbon dioxide — are from the silica gel column, which does not separate oxygen and nitrogen, hence the air (nitrogen and oxygen) peak. The individual peaks of oxygen and nitrogen followed, now separated on the molecular sieve column. Note that because of the configuration of the potentiometric recorders, early chromatograms proceeded from the right to the left. The system could also be used for

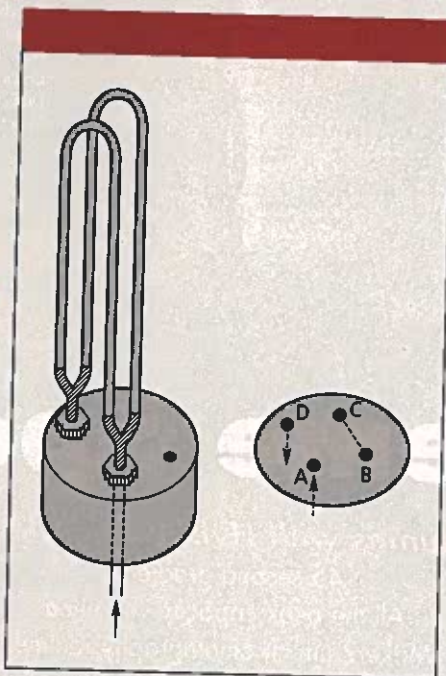


Figure 2: The detector block in the Perkin-Elmer model 154 gas chromatograph with the parallel column adapter installed. Port A received gas flow coming from the injector. Port D connected to the sensing side of the thermal-conductivity detector. Ports B and C are connected within the block. Normally, a single column would be installed to ports A and D, and two columns in series would be installed in ports A and B and ports C and D.

other, more complex samples. Reference 3 illustrated a few examples, such as the analysis of an anesthesia mixture containing cyclopropane and air as well as the analysis of a light gas mixture containing C₁–C₄ paraffins and oxygen and nitrogen. The latter analysis used a 4-m long partition column that contained di(2-ethylhexyl) sebacate as the stationary phase.

Naturally, one disadvantage of this arrangement was that the permanently retarded carbon dioxide slowly poisoned the molecular sieve, reducing its separation capabilities. Thus, periodic replacement with fresh material was necessary.

For years the parallel column adapter was quite popular with users of the model 154, particularly to clinical researchers investigating, for example, the breath of patients. It was a small gadget, easy to install and use.

Condensing System for the Analysis of Trace Impurities in a Gas Sample

The first universal detector used in gas chromatographs was the thermal-conductivity detector. This detector is based on the measurement of the thermal

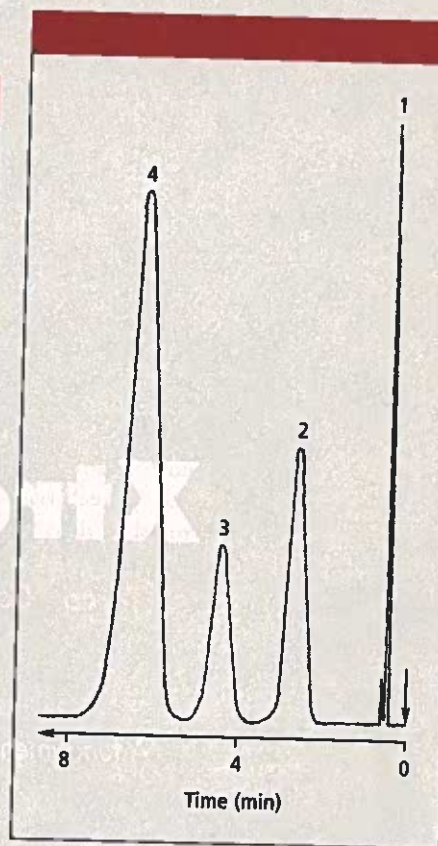


Figure 3: Analysis of expired air using the parallel column adapter. Columns: 2 m \times 1/4 in. o.d. molecular sieve 5A and 1 m \times 1/4 in. o.d. silica gel; column temperature: 22 °C. Peaks: 1 = air, 2 = carbon dioxide, 3 = oxygen, 4 = nitrogen. (Adapted with permission from reference 3.)

conductivity of the column effluent, comparing it with that of the pure carrier gas. It was only slowly replaced by the mid-1960s by the flame ionization detector. The thermal-conductivity detector was rugged and simple, and it did not need any additional gases. Its only drawback was that its sensitivity was limited to approximately 0.05–0.1% (500–1000 ppm). Within a couple of years after its introduction, GC became more and more desirable for the determination of trace impurities; however, the limited sensitivity of the thermal-conductivity detector represented a serious restriction. Various more-or-less complicated accessories have been described in the literature as partial solutions to this limitation; however, these accessories were unsuitable for average GC users in routine laboratories. To help them, in 1958 we developed a simple system that

could easily be adapted to the model 154. This accessory permitted the determination of trace impurities in gases, down to the parts-per-million level.

This system (see Figure 4) represented a modification of the standard Perkin-Elmer six-port rotary gas-sampling valve that was introduced in 1956. It was the first such sample introduction device, and all the present-day multiport rotary valves can be traced back to its design. This valve has two positions. In the first position, the gas sample flows through the sample loop, and the carrier gas connects directly to the column. By turning the valve to the second position, the carrier gas flushes the loop's content into the column. In the condensing system, a 50 cm \times 1/4 in. o.d. U-tube that contained an adsorbent or a partition-type column packing was substituted for the interchangeable sample loop of the

valve. In the first position (Figure 4a), a sample as large as 40 L in volume could be passed through the condenser, which was cooled by a mixture of dry ice and acetone to -80°C . The packing of the condenser tube retained the trace components of interest, and the matrix gas passed through it. After running a fixed volume of the sample gas through the condenser, the user closed it off from the sample source. Then, the exit of the tube was connected briefly to a vacuum to reduce the gas pressure in it and to remove part of the noncondensed matrix gas filling the tube. In some cases, the tube was also purged with helium while still cold. After sufficient purging, the coolant around the condenser column was replaced by a 50–60 $^{\circ}\text{C}$ water bath, which caused the rapid desorption of the condensed (adsorbed) trace components. After the condenser's temperature equilibrated, the gas-sampling valve was turned to the second position (Figure 4b), which flushed the desorbed solutes from the tube into the GC column for separation and analysis. Because large sample volumes passed through the condenser tube, the sample gas pressure and flow needed to be carefully regulated to assure good reproducibility.

We first presented our report on the device and its use at the spring 1959 National Meeting of the American Chemical Society in Boston, Massachusetts (4). We investigated a number of samples and could demonstrate remarkable reproducibility and sensitivity. For example, in analyzing 10 L of an air sample containing 4 ppm acetylene, we could reproduce the peak heights of acetylene with a relative standard deviation of $\pm 1.02\%$, and the minimum detectable limit for a 10-L sample was approximately 0.2 ppm. Even in a complex problem such as the determination of trace acetylene in ethylene gas — in which the matrix peak was close to the acetylene peak, other trace impurities were also present and clear baseline resolution was impossible (Figure 5) — we could reproduce the acetylene peak height (indicated in Figure 5) to better than $\pm 2\%$ with sample volumes as large as 40 L.

The correct operation of the system required some skill, however. The difficulties were not chromatographic, but rather they were purely technical and had to do with the state of art in GC instrumentation concerning the coupling of the thermal-conductivity detector with the potentiometric recorders, which were the standard devices of that period. These

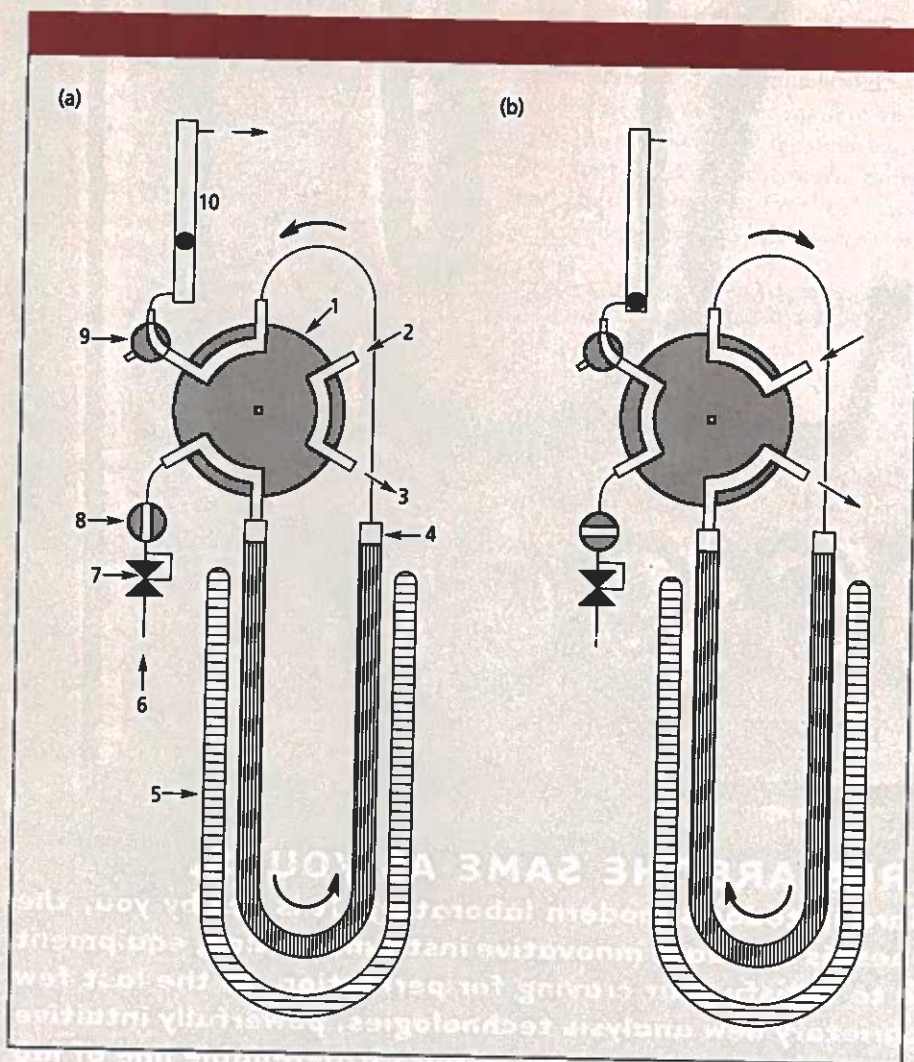


Figure 4: Condensing system for the determination of trace impurities in gases. The system is shown configured for (a) sampling and (b) transfer of the condensed sample to the column. 1 = gas sampling valve, 2 = carrier gas inlet, 3 = to column, 4 = 50 cm \times 1/4 in. o.d. condenser column, 5 = Dewar flask, 6 = gas sample inlet, 7 = pressure-flow regulator, 8 = on-off valve, 9 = three-way valve, 10 = flowmeter. (Adapted with permission from reference 4.)

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recorders used 10-in.-wide paper and had a 1- or 5-mV full-scale deflection at highest sensitivity (for trace analysis, we always used the 1-mV setting). The detector's electric circuit provided 10 attenuation levels that increased by factors of two from $\times 1$ to $\times 512$. The attenuation level was changed manually during a run. Unless we made a switch when the pen was at baseline, changing from a high to a low attenuation — that is, from a lower to a higher sensitivity — resulted in a baseline shift that made it difficult to measure peak heights accurately. Remember that at that time quantitation of a chromatogram was a manual task. Figure 5 illustrates this difficulty; we had to suddenly change from $\times 512$ (512 mV) to $\times 4$ (4 mV).

Our work had the dubious distinction of becoming obsolete almost at the moment it was completed. The flame ionization detector, which was introduced commercially in March 1959, was obviously a much better tool for trace analysis because it permitted the direct determination of parts-per-million concentrations without any preconcentration. However,

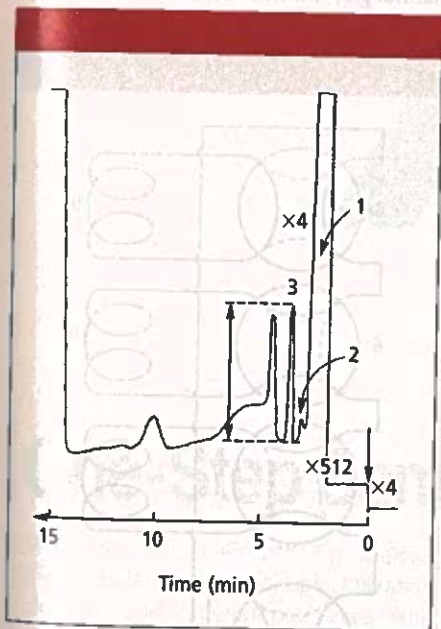


Figure 5: Analysis of trace acetylene in ethylene gas with the condensing system accessory. Column: 4 m \times 1/4 in. o.d. 20% dimethylsulfolane on Chromosorb; condenser column: 50 cm \times 1/4 in. o.d. containing 20% Carbowax 1540 on Chromosorb; sample gas volume: 40 L; condensation temperature: -80°C ; analysis temperature: 25°C ; carrier-gas (helium) flow rate during desorption and analysis: 90 mL/min. The acetylene concentration in the sample was less than 20 ppm. Values with an \times represent attenuation settings of a 1-mV recorder. Peaks: 1 = air, carbon monoxide, methane, ethane, and ethylene; 2 = carbon dioxide, 3 = acetylene. (Adapted with permission from reference 4.)

for inorganic sample components present in trace concentrations, the condensing technique is still valid.

Device for the Determination of Trace Components in an Essentially Nonvolatile Matrix

In the second part of the 1950s, an important analytical problem arose in the petroleum industry; namely, the GC analysis of dissolved gases, including oxygen, in petroleum fractions. A number of possibilities were proposed, but their fundamental principle was essentially the same: a shorter trap column and the analytical column were connected in series with provision to backflush the former. A 1-mL liquid sample was injected into the instrument's flash vaporizer, and the carrier gas transported the evaporated volatile components into the trap column. The dissolved gases were eluted from this precolumn well before the volatile hydrocarbons. By disconnecting the two columns at an appropriate time and backflushing the trap column, users could avoid the contamination of the separation column. However, a general problem with this approach remained: the injection block of the instrument became contaminated with the nonvolatile components, and frequent cleaning, a tedious and messy job, was necessary.

Based on our earlier work on the condensing system for the analysis of trace components in gases discussed above, we proposed a similar system in 1960 for liquid samples in which low concentrations of volatile components were present in an excess of essentially nonvolatile matrix (5). This device placed the trap column outside the gas chromatograph and connected it again to the gas-sampling valve in place of the usual interchangeable sample loop. However, one arm of this column was formed as an on-column injection port closed by a rubber septum through which the liquid sample could be injected directly on the top of the packing material with a long-needled hypodermic syringe (Figure 6). If desired, a water or oil bath in a Dewar flask could be used to heat the trap column, as in the condenser tube, to facilitate the evaporation of the solutes of interest.

After injection (Figure 6a), the carrier gas transported the volatile compounds through the trap column into the analytical column located in the gas chromatograph, and the packing material of the trap column permanently adsorbed the nonvolatile sample matrix. After transfer of



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the volatile compounds, the trap column could be backflushed (Figure 6b), using an auxiliary gas flow, conveniently, nitrogen. Naturally, the packing of the trap column eventually became saturated with the nonvolatile compounds and had to be replaced. The injection port of the gas chromatograph remained clean, however.

Besides the analysis of dissolved gases in petroleum fractions, this device was used successfully for the measurement of dissolved gases or light organic solvents in water. In essence, the device may be considered a predecessor of the present head-space samplers.

Multicolumn System for the Analysis of Complex Gas Samples

One of the important early GC applications was the analysis of natural gases. These gases represent complicated mixtures. In addition to methane, the main component, they contain a wide variety of other hydrocarbons, as well as air and other inorganic gases such as helium. Fur-

thermore, most of the impurities are present in low concentrations. Such samples could not be analyzed on a single column, so a combination of two or three columns was needed for a complete assay. By 1961 the Natural Gas Processors Association (NGPA) had described various column combinations for this purpose and also suggested the use of a multiport system permitting the transfer of the gas sample, or part of it, to the various columns and the release of their effluents to the detector in a controlled way so that the individual peaks did not interfere (6).

We at Perkin-Elmer immediately developed such a system that would fit the oven of the model 154. Figure 7 shows its schematic diagram. It comprised three columns, each connected to a four-port rotary valve, with a fourth valve directing the gas flow. This system made a number of operations possible. A user could have the columns in series, conducting the effluent from one to

another; individual columns could be bypassed or temporarily disconnected; and with help of the fourth valve, the carrier-gas flow could also be reversed, backflushing the columns still in the carrier-gas flow.

A variety of columns was recommended, depending on the actual task or the type of sample. Usually the third column contained molecular sieve 5A. In the beginning, the three columns were in series and the light components (oxygen, nitrogen, and methane) went rapidly through the first two columns and then entered the molecular sieve column. At this time, the third column was temporarily disconnected by turning the third valve. Next, the other sample components were separated in the first two columns and conducted to the detector. Finally, the third column was reconnected to the carrier-gas flow, and its content passed to the detector. Figure 8 shows the chromatogram of a natural gas sample. This example is from an American Society for Testing and Materials (ASTM) standard method (7), which is based on the original NGPA recommendations.

Although developed for the analysis of natural gas, this multicolumn system also

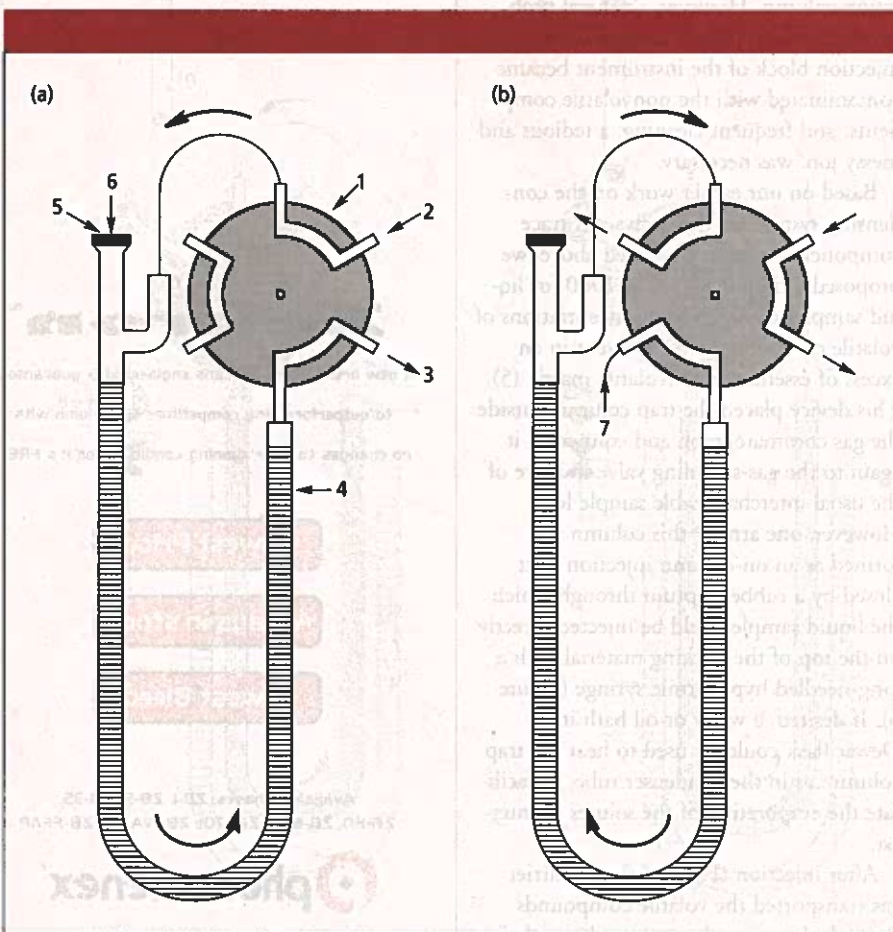


Figure 6: Schematic of a device for sampling volatile compounds in the presence of excess nonvolatile compounds. The device is shown configured for (a) sample injection and transfer to the column and (b) backflushing the trap column. 1 = gas sampling valve, 2 = carrier gas inlet, 3 = to the column, 4 = trap column, 5 = septum, 6 = sample injection, 7 = nitrogen gas inlet. (Adapted with permission from reference 5.)

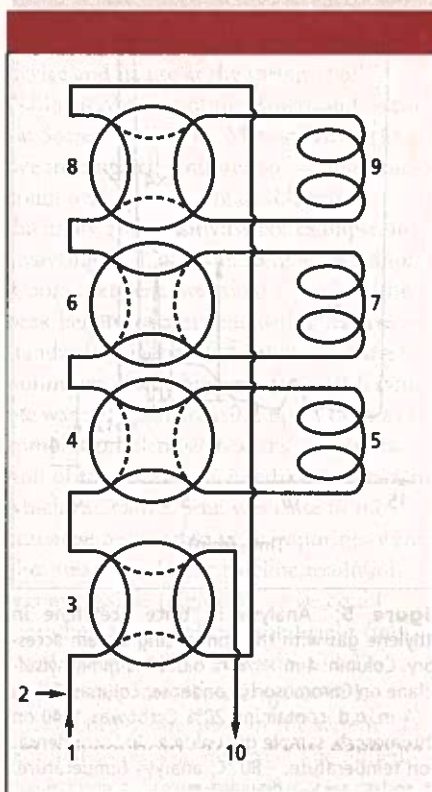


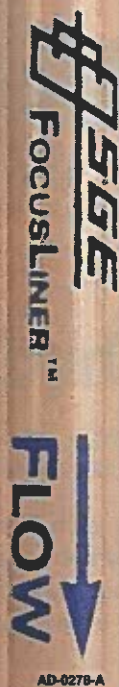
Figure 7: Multicolumn GC system for the analysis of natural gases and other complex gas mixtures. 1 = carrier gas inlet, 2 = sample inlet, 3 = reverse valve, 4 = valve 1, 5 = column 1, 6 = valve 2, 7 = column 2, 8 = valve 3, 9 = column 3, 10 = detector. (Adapted with permission from reference 8.)

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could solve a variety of other analytical problems in which column combinations or backflushing were necessary, and we pointed out some examples in a 1962 publication (8). The analysis of a gas mixture containing hydrogen, nitrogen, argon, and ammonia — an interesting and unusual application — was also mentioned by Csaba Horváth in a book chapter (9). The three columns used were Carbowax 1500 on PTFE support, alumina, and molecular sieve 5A. The columns were at room temperature, and the carrier gas was a mixture of helium and approximately 8% hydrogen. At start, the three columns were in series. Excluding ammonia, the sample components were permitted to pass through the first two columns and into the third column, in which they were separated on the molecular sieve and analyzed in the detector. During this process, ammonia remained in the first column. Subsequently, the flow direction was reversed to the first column and ammonia was backflushed into the detector. The second column did not participate in actual separation; its purpose was to protect the molecular sieve column from any ammonia that might have accidentally passed through the first column.

As mentioned earlier, we constructed such a multivalve system that fit the model 154 gas chromatograph's oven immediately after the issue of the NGPA procedure; to my best knowledge, this system was the only commercially available unit at that time. It was quite popular, and it actually prolonged the life of the model 154 for years. Because this instrument could operate only isothermally, we would have expected that its sales would come to an end after the introduction of gas chromatographs that enabled temperature programming. However, this event did not happen. Although Perkin-Elmer introduced its temperature-programmed gas chromatographs in the spring of 1962, the sales of the isothermal model 154 gas chromatograph remained significant. According to my notes, 981 of these instruments were still sold between August 1962 and July 1967, when its production was finally discontinued. These sales overwhelmingly represented purchases by laboratories involved in the routine testing of natural gas using the multivalve accessory, which was installed in the model 154.

These systems continue to be used in the GC laboratory practice. The best illustration is that the ASTM standard describ-

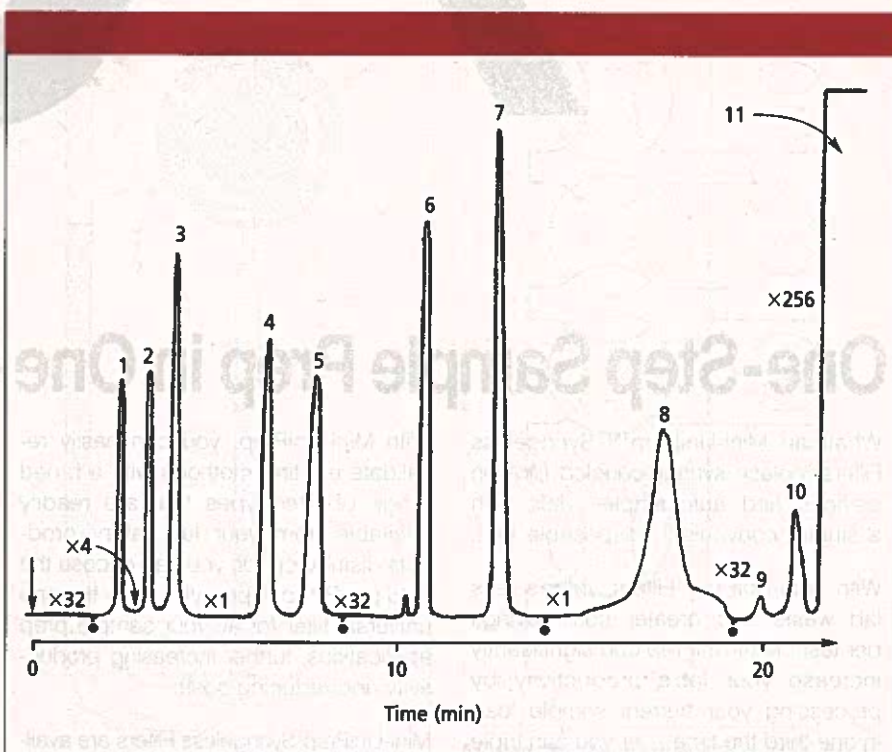


Figure 8: Analysis of a natural gas sample. Column 1: 3 m \times 1/4 in. o.d. 15% squalane on Chromosorb PAW 80/100 mesh; column 2: 2 m \times 1/4 in. o.d. Porapak N 80/100 mesh; column 3: 2 m \times 1/4 in. o.d. molecular sieve 5A 80/100 mesh. Values with an \times indicate attenuation settings of a 1-mV recorder. The symbol \bullet indicates valve switching. Peaks: 1 = propane, 2 = isobutane, 3 = *n*-butane, 4 = isopentane, 5 = *n*-pentane, 6 = carbon dioxide, 7 = ethane, 8 = C_6+ , 9 = oxygen, 10 = nitrogen, 11 = methane. (Adapted with permission from reference 7.)

ing its principles and use has undergone continuous refinement; its latest addition was issued in 1996 (7). Even today, instrument companies continue to market these multivalve accessories — naturally, they now have more sophisticated designs.

Microreactor System

The study of catalytic reactions on a laboratory or pilot-plant scale always represented a problem, not only due to the need for carefully designed systems but also because of the difficulties in sampling and analyzing the reactor effluent. In 1957–1958, I was also involved in such work in Germany, and I remember the difficulties we had in collecting the gaseous reaction products and introducing a representative aliquot into a gas chromatograph. A major breakthrough in this field came in

1955 when Kokes, Tobin, and Emmett (10) introduced microreactor systems directly connected to gas chromatographs that enabled researchers to carry out the experiments on a small scale and on the fly without the need of intermittent sample collection. Unfortunately, I was unaware of this research at that time — it could have spared me a lot of work. In the spring of 1959, when I was an associate of Perkin-Elmer, I attended the National Meeting of the American Chemical Society in Boston and heard a review presented by Emmett on instrumental techniques and the systems he and his colleagues used in the study of catalysis mechanism (11). I immediately realized that our six-port rotary gas-sampling valve could serve as the basis of a much simpler system that could be fitted not only to our model

154 but to practically any standard gas chromatograph and used for the study of catalysts and catalytic reactions.

We designed this type of unit within a few months, and I reported on it at regional meetings in fall 1959. Finally, I presented a detailed paper at the spring 1960 National American Chemical Society Meeting in Cleveland, Ohio, which was soon published (12). It was my good fortune that *Chemical & Engineering News* included my paper — with an illustration of the system — in its report on the meeting, creating a lot of publicity.

Figures 9 and 10 show a schematic of the microreactor system and the principles of its operation. It was built from two gas sampling valves, and the microreactor was placed in the second valve in lieu of the sample loop. The microreactor comprised a $4\frac{1}{2}$ in. \times $\frac{1}{16}$ in. i.d. ($\frac{3}{4}$ -in. o.d.) stainless steel tube connected by $\frac{1}{8}$ -in. o.d. tubes to the valve. It was contained within an electrically heated, temperature-controlled oven. The system permitted two types of investigations. In the *slug mode* (Figure 9), the reactant gas entered the second valve and flowed through a small three-way valve into the first valve's sample loop. After the top valve was turned, the carrier gas swept the gas volume present in the loop into the reactor and the reaction products into the gas chromatograph. The purpose of the small three-way valve was to bypass the reactor for direct analysis of the reactant gas. In this case, the sample gas was temporarily directed to the open port of this valve.

In the so-called *rail-gas technique* (Figure 10) a continuous catalytic reaction was carried out in the reactor, and the composition of the reaction products was periodically examined to study changes in the catalyst's activities over time. In this case, the reactant gas was continuously conducted through the microreactor, and the emerging reaction products passed through the sample loop of the top valve to vent. Periodic examination was performed by activating the top valve and purging the loop's content into the gas chromatograph.

The microreactor accessory could easily be mounted on the side of the model 154, and its operation was very simple. In the 1960s, such microreactor systems were quite popular, as demonstrated by the book chapter of Steingaszner published in 1969 (13). I did not follow up on this development, and thus, I am unaware of whether similar systems that combine a microreactor with a gas chromatograph are still in

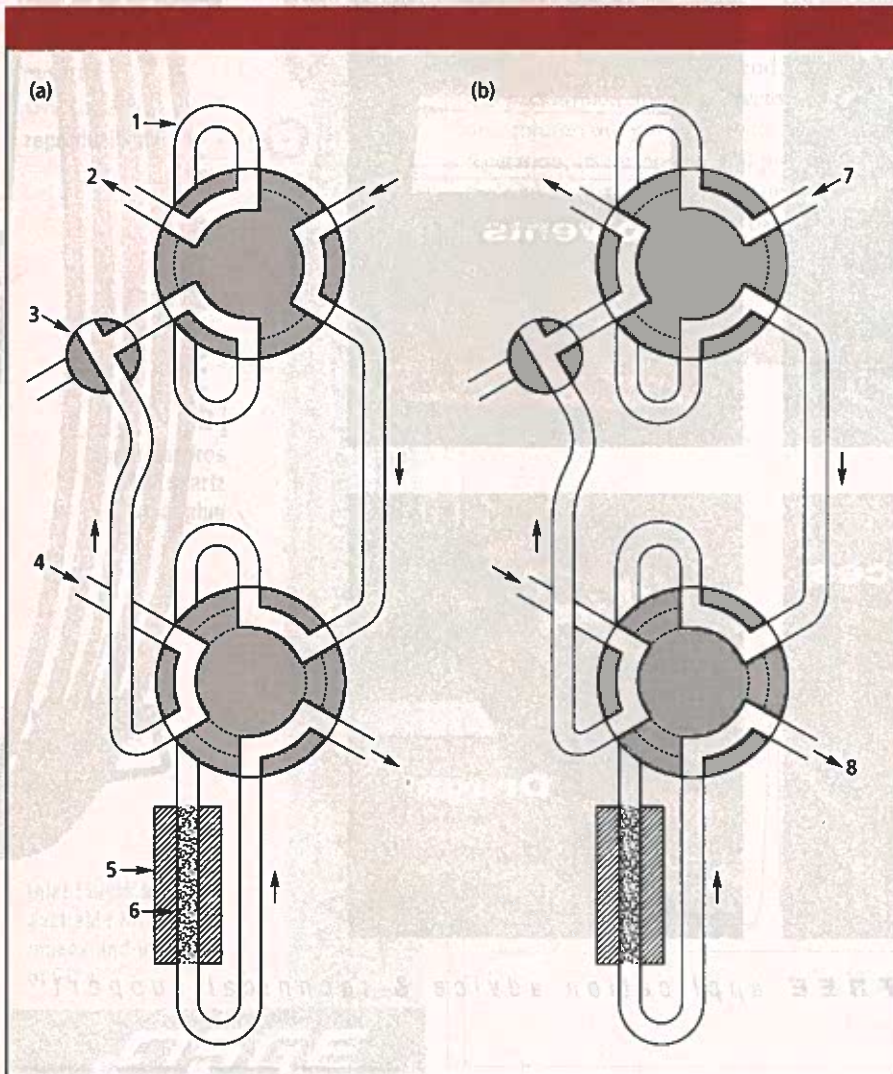


Figure 9: Microreactor-GC system set for periodic examination (slug technique). The system is shown configured for (a) sampling and (b) catalytic reaction and analysis. 1 = sample loop, 2 = exit, 3 = three-way valve, 4 = sample flow, 5 = microreactor, 6 = catalyst, 7 = carrier gas inlet, 8 = to the column. (Adapted with permission from reference 12.)

use. However, in any case, it was an excellent demonstration of the flexibility of GC.

Conclusions

I have discussed only five small accessories developed in the early years of GC. Naturally, these accessories were not the only ones available. These systems were very important in helping to extend the use of GC to a wide variety of applications and thus contributed to its rapid growth. These early systems had to be operated manually, and, thus, their successful use depended on the chromatographer's skill. Even today, a number of sampling accessories are available; however, these are mostly automated and free the users to perform other tasks. Present-day chromatographers generally take their successful operation for granted and no longer have the experience of analyzing each sample uniquely, which would

require the skill of the operators. With the brief description of these early gadgets, I hope that I was able to recount the early period of GC development.

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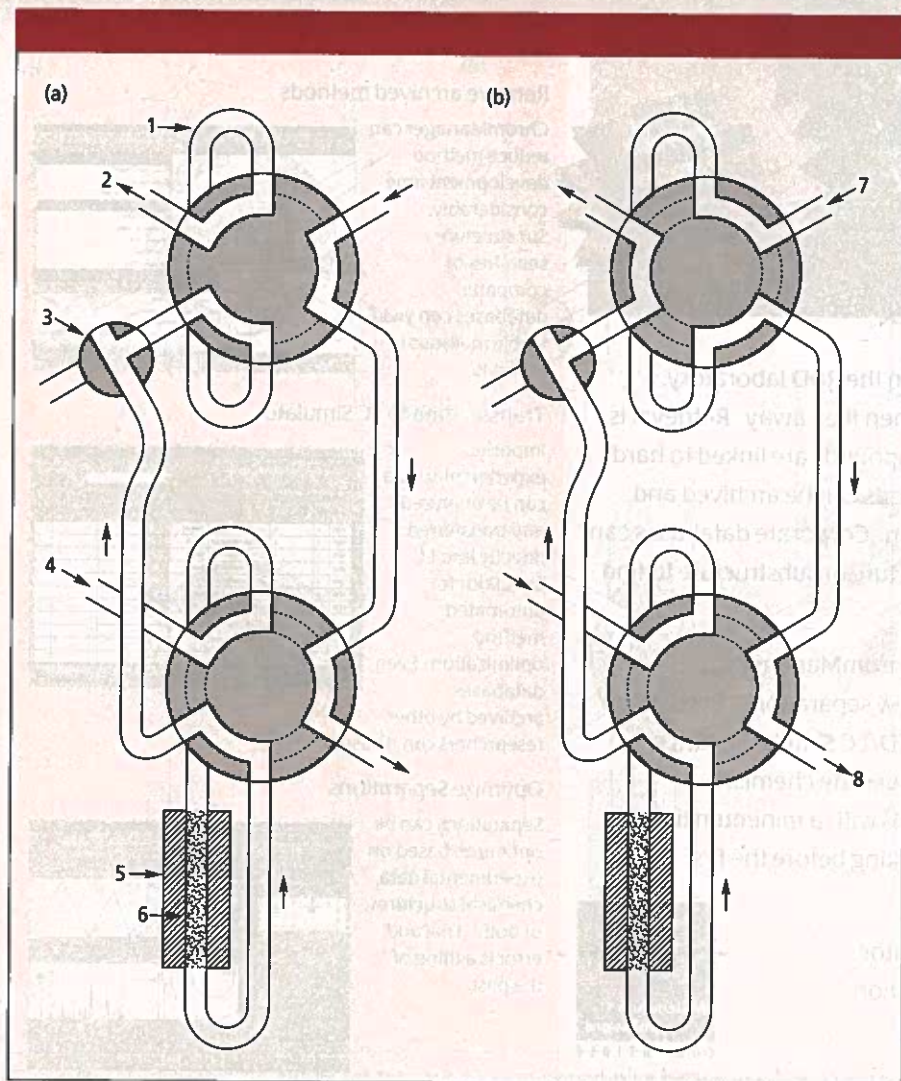
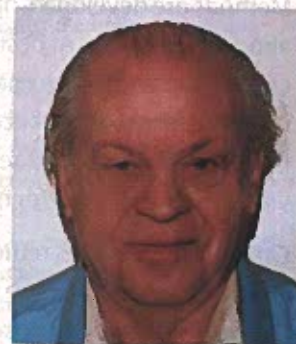


Figure 10: Microreactor-GC system set for the study of continuous catalytic reaction (tail-gas technique). The system is shown configured for (a) continuous reaction and (b) aliquot analysis. 1 = sample loop, 2 = exit, 3 = three-way valve, 4 = sample flow, 5 = microreactor, 6 = catalyst, 7 = carrier gas inlet, 8 = to the column. (Adapted with permission from reference 12.)



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