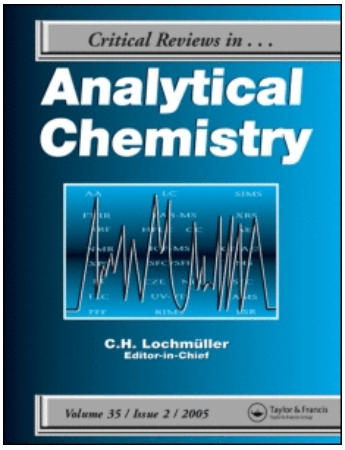

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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John N. Driscoll; Ira S. Krull

To cite this Article Driscoll, John N. and Krull, Ira S.(1987) 'Recent Advances in Gas Chromatography Instrumentation: An Historical Perspective', Critical Reviews in Analytical Chemistry, 17: 2, 193 — 212
To link to this Article: DOI: 10.1080/10408348708542794
URL: http://dx.doi.org/10.1080/10408348708542794

RECENT ADVANCES IN GAS CHROMATOGRAPHY INSTRUMENTATION: AN HISTORICAL PERSPECTIVE

Author: **John N. Driscoll**
HNU Systems, Inc.
Newton, Massachusetts

Referee: Ira S. Krull
Department of Chemistry and
The Barnett Institute
Northeastern University
Boston, Massachusetts

I. INTRODUCTION

The task that I set out to accomplish was to describe and contrast the early years of gas chromatography (GC) instrumentation development with those of the past 2 to 3 years. On the historical front, we will be concerned more with when a development was first commercially introduced rather than when it was first described in the literature.

James and Martin[1] first described the use of gas liquid partition chromatography (GLC) in 1951. Four years later, the first commercial GC, the model 154 vapor fractometer, was introduced by Perkin Elmer Corporation. This instrument had temperature control, utilized a carrier gas, and had a thermal conductivity detector (TCD). At about the same time, Burrell introduced a GC that was specifically for gas analysis, but had no temperature control. In early 1956, three more GCs were introduced in the U.S. by Fisher-Gulf, Podbielniac Inc., and Beckman Instruments.[2] It is interesting to note that of the original companies which produced the first GCs, Perkin Elmer is the only company that is still manufacturing GCs.

In the 1950s, the TCD was a simple reliable detector which dated back to 1880, and had been used in GC for more than a decade; however, it lacked sufficient sensitivity for trace analysis. As a result, considerable research was expended on detector technology during the mid to late 1950s. A number of significant advances in detector technology for GC were described in the period from 1957 to 1958.

A new sensitive flame ionization detector (FID) was first described in Australia by McWilliam and Dewar,[4,5] then shortly thereafter in South Africa by Hartly et al.[6] A mass spectrometer detector was described by Holmes and Morell.[7] Electron capture detectors (ECD) for GC were reported by Deal et al.[8] and Boer[9] in 1956 and 1957, respectively. Robinson[10] described a photoionization detector (PID) in 1957 also, and although a considerable effort was put into the development of this detector during the 1960s,[11] it did not become a commercial detector until 1976.[12] In 1957, Golay[13] described the first capillary column for GC that offered higher efficiencies and faster elution times than packed columns.

By the early 1960s, most of the above developments were commercially available and becoming more widely used in GC. Looking back, one might say that the 1950s were the most productive years in the development of GC since GLC, capillary columns, and all the major detection systems were developed during this time period. Therefore, one might conclude from the previous statement that little has been accomplished in GC during the past 30 years. This is far from the truth. During the early 1960s, the FID was improved through the use of a cylindrical collector and a polarized jet. In addition, the electronics were changed from vacuum tubes to transistors. This latter development led to improvements in reliability rather than performance.

The ECD, on the other hand, continued to develop into the 1970s through the efforts of Lovelock[14] and others. By changing from DC to pulsed operation, the linear range prior to

saturation was increased from 100 to 500 or more. A nickel 63 source was introduced by Microtek in the late 1960s. This source replaced tritium and allowed the utilization of this detector for pesticides as a result of the higher operating temperature (400°C). In 1972, Pye Unicam introduced the first commercial constant current ECD, which had been developed by Lovelock.[15] This ECD was a much more useful detector with a linear dynamic range of four to five orders of magnitude.

The alkali FID, also known as the thermionic or nitrogen phosphorus detector (NPD), was developed by Karmen and Guiffrida[16] in the early 1960s, but it was not until the early 1970s that the necessary modifications were made to ensure that this detector was stable enough to become routinely used in GC.

Perkin Elmer demonstrated in 1972 that by electrically heating the bead (containing an alkali salt) and using a cool flame, a stable NPD resulted. This was the predecessor of the present NPD.

In the following sections, we will discuss GC markets, the technology base for manufacturers in various parts of the world, and recent developments in detail.

II. WORLD GC MARKET/TECHNOLOGY BASE

The GC world market is still growing at a rate of 15 to 20% yearly, and sales (including accessories) are estimated at $350 million annually. The best estimate for the number of GCs sold annually is 18,000 units (1985 estimate) worldwide with approximately 200,000 to 250,000 instruments in use in the field. If we assume an average life of 10 years for a GC (which is probably too long), then the annual rate of replacement matches the annual sales rate and demonstrates that GC is a mature market.

There are three large distinct markets for gas chromatographs in the world: U.S. (40%), Asia (30%), and Europe (30%). Each of these markets has one or more manufacturers (Table 1), and different technologies and or philosophies have evolved in each area.

Of the 5000 units sold in Europe, Germany represents the largest market with about 25% of the total. During the 1970s, the European GC manufacturers and the many European scientists, with their extensive research laboratories, advanced the state-of-the-art in capillary GC to the point where the majority of separations were done on capillary columns. By the late 1970s, nearly 90% of the separations were done on capillary columns in Switzerland, 60% in Germany, and similar levels in France and Italy. Instruments were commercially available in Europe in the late 1970s using the Dean's switching techniques,[17] e.g., pressure balancing for capillary columns.

Many of the innovations in capillary GC now appearing in the U.S. such as Dean's switching, on-column injection, and programed temperature vaporizers were originally developed in Europe. The European GC manufacturers (each major country has a local GC manufacturer) have had an orientation toward capillary column innovation. One approach that many European GCs took was the use of a central GC with satellite capability. One such unit designed by Packard Instruments is shown in Figure 1. This type of unit was a trend in Europe in the early 1980s, which did not catch on in the U.S. Satellite capability was available in the U.S. on the Perkin Elmer model 2000 GC (introduced in 1982) or the Shimadzu 9A, but has not been very popular.

If it is possible to describe the emphasis of GC instrument development in Europe, then it would be on separations science and capillary column chromatography. The most recent advances in GC are most affected by a development about 12 years ago when the first microprocessor based GC (model 5830) was introduced by Hewlett Packard (HP) in 1973 and the improvements in computer technology over the past decade. The microprocessor chips for the HP 5830 were designed and manufactured internally, but recent HP GCs utilize commercial chips such as the Z80.

Table 1
MANUFACTURERS OF LABORATORY GAS CHROMATOGRAPHS IN EACH OF THE THREE MAJOR REGIONS

Region/country	Company	Location
Europe		
France	Delsi	Paris
West Germany	Siemens	Karlsruhe
Ireland	Accuspec	Dublin
Italy	Carlo Erba	Milano
	Dani	Milano
Holland	Packard Becker	Delft
Spain	Konik	Barcelona
U.K.	Pye Unicam	London
Asia		
Japan	Gasukuro Kogyo	Tokyo
	Hitachi	Tokyo
	Shimadzu	Tokyo
U.S.		
	Antek	Houston, Texas
	Carle	Anaheim, Calif.
	Gow Mac	Bound Brook, N.J.
	HNU Systems	Newton, Maine
	Hewlett Packard	Avondale, Penn.
	IBM Inst.	Danbury, Conn.
	Perkin Elmer	Norwalk, Conn.
	Tracor Inst.	Austin, Texas
	Varian Inst.	Walnut Creek, Calif.

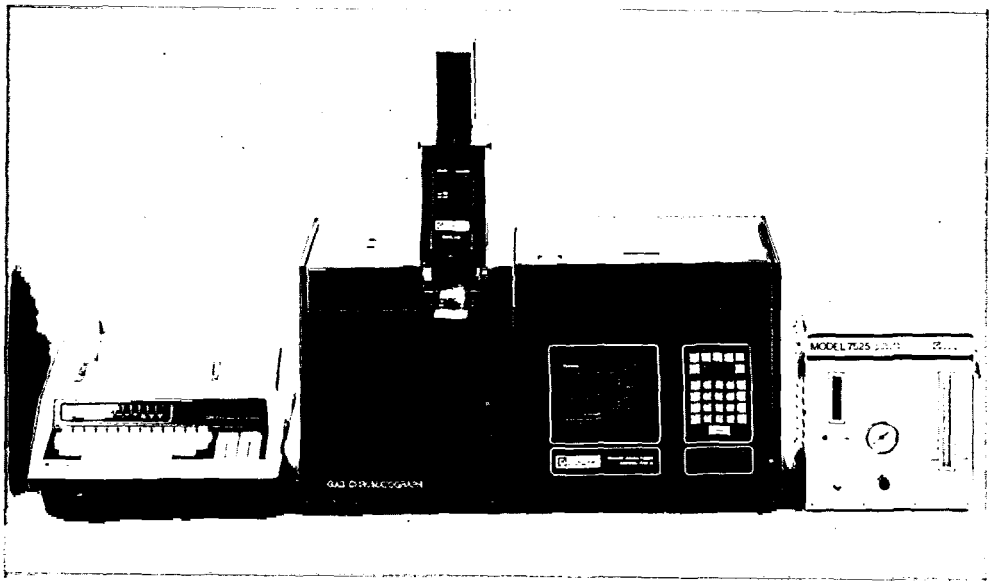
During the 1970s and early 1980s, the U.S. based manufacturers continued to advance in computer technology and, within the past 2 years, most of the these companies introduced new products, which utilized the microprocessor to develop and produce lower cost and more reliable instrumentation.

The U.S. manufacturers of GC instrumentation have concentrated on reliability and automation. Clearly, the automation aspect has led to the increased use of computers in GC instrumentation since computers are at the heart of any automation process. It is interesting to note that the company (HP) with the largest U.S. market share (40%) is also a computer company. The introduction of fused silica capillary columns in the late 1970s has started an upward trend in the use of capillary GC, to the point in 1985 where 50% of the units shipped have capillary capability. The fused silica capillary column has also decreased the significant lead that the European manufacturers possessed in the late 1970s.

Presently, the largest GC market in Asia is Japan, although within the decade, China will probably replace Japan as the largest market. In the Asian market, there are presently 5000 to 6000 units sold per year. Japan represents nearly 4000 units. The largest manufacturer in this area is Shimadzu, which maintains a 70% market share in Japan. Where are the Asians with regard to capillary column technology? Capillary GC sales have averaged 15 to 20% for the past few years, but are presently increasing at a brisker rate.

What concepts have the Japanese instrument manufacturers brought to the GC marketplace? Clearly, it is the Japanese management philosophy of the cost of production. The target of Japanese managers is to meet the target selling price and reduce costs where necessary.

It is interesting to now examine the newly developed GCs in view of the diversity of philosophies discussed above for the instrument manufacturers in the various regions. In



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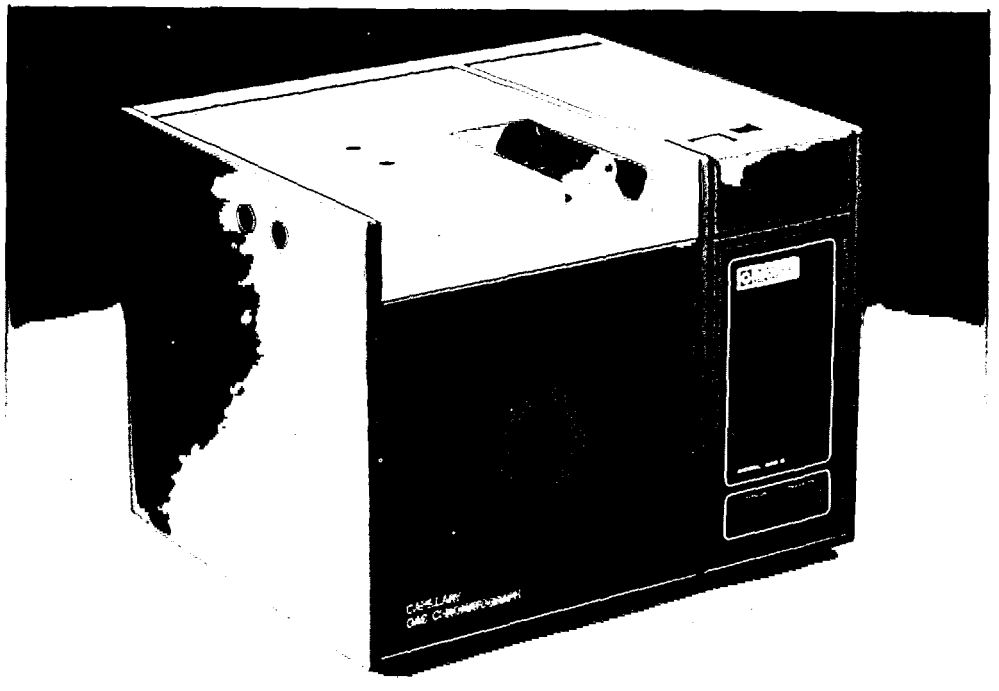

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FIGURE 1. (A) Photograph of Packard 412A (central unit) and (B) Model 436S satellite unit (courtesy of Packard Instrument Co. Inc.)

summary, the larger markets will tend to drive the technology base for GC instrument development; however, advances in peripherals such as injectors or detectors have come from any part of the world.

III. RECENTLY DEVELOPED GC INSTRUMENTATION

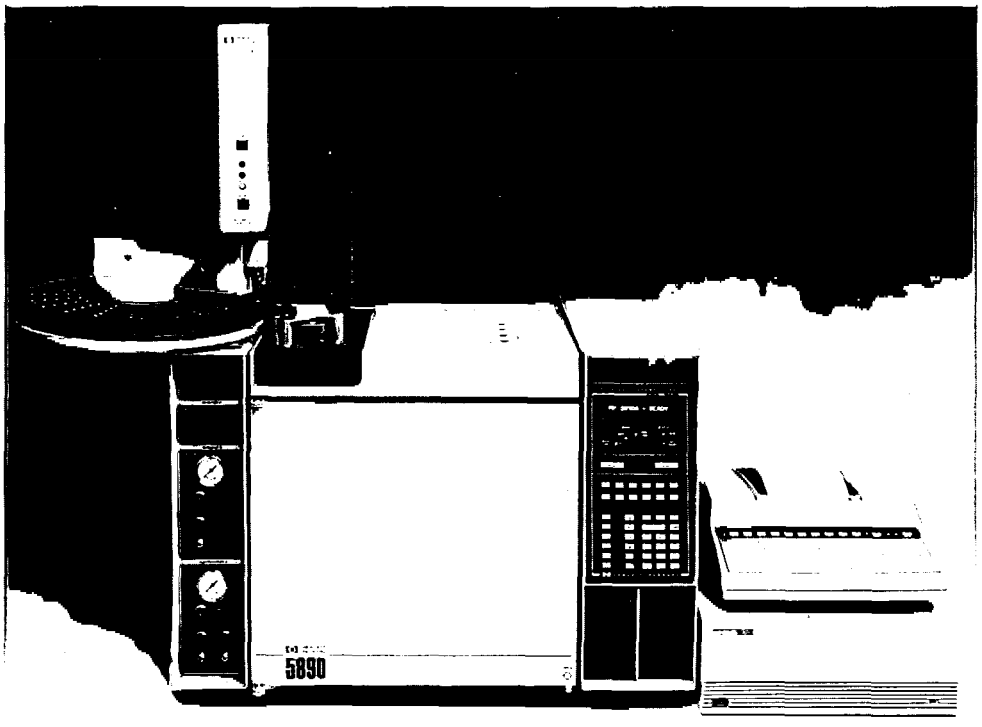
A request for information on GCs introduced within the past 2 years was sent to more than 35 companies worldwide who are listed as manufacturers of gas chromatographs. A response and literature was obtained from only two thirds of these companies. Some indicated that they did not manufacture GCs and one third did not respond. If a particular GC is not mentioned, it means that the product was either not introduced within the past 2 years or no information was sent. A list of GC manufacturers by region and country is shown in Table 1. The following sections do represent the current state-of-the-art in GC instrumentation. A recent article by McNair et al.[18] describes GC instrumentation available in 1983.

A. Routine Laboratory GCs

There were a considerable number of instruments introduced in the latter part of 1983 or early 1984. Some examples of these instruments are shown in Figures 2 and 4. These instruments are priced in the $6500 to $8500 range for packed column versions with an FID and can be considered a moderate price with high performance. Fifteen years ago I purchased a Perkin Elmer 900 GC with temperature programing and a FID and paid approximately $6000. The price in dollars today would be more than $10,000. In addition, the new GCs have microprocessor control, more reliable electronics, fewer electronic components, more precise control of the oven temperatures, ease of interfacing with computer systems, and troubleshooting capabilities not found in late 1970s version of these instruments.

The HP 5890A (Figure 2A) offers a single-ramp programer with no methods storage. Features such as multiramp programing and methods storage can be added via the 3392A or 3393A controlling integrators. All electronics in the 5890 (including the Z80A μp) are on a large single board with a few plug ins. Two detectors and two injectors are the maximum number on this GC. The injectors can be packed, split/splitless, or on-column capillary. Considerable emphasis is placed on communications through serial (bidirectional RS 232C) or digital (HP1B Bus) systems. The control link to other HP computers or equipment is the integrator (3392 or 3393). HP uses the analytical instrument network (INET) to connect their autosampler, integrator, and 5890A GC and to communicate with a large laboratory computer.

The HNU Systems model 421 GC (Figure 2B) is a flexible unit that has the electronics designed around the Standard (STD) Bus system. This is also referred to as the IEEE 488 Bus. The advantage of this system is based on the expandability of the design.[19] All of the positions (slots) in the Bus are equivalent so that new features, including hardware features, can be added by plugging in the new board and changing the software (chip), if necessary. This instrument has the capability of handling three detectors and three injectors (packed, split/splitless, and on-column). The GC comes with five-ramp temperature programing, stopwatch, and nine methods that are stored in E^2 PROM. With this latter feature, even if the power is turned off, the information will remain in memory for up to 3 years. The timed events options can be added by simply plugging a board into the STD Bus. The autosampler is controlled by the timed events card, ensuring that all timing and appropriate functions are on one-time base. Another option is the printer/plotter/integrator, which is also added via the STD Bus. All of these features are controlled via the same 8 bit Z80A microprocessor. A schematic representation of this is shown in Figure 3. Many of these new GCs can operate at temperatures just above ambient with excellent results as indicated in Table 2. One of the recent additions to this GC include bidirectional serial communication with an IBM PC.



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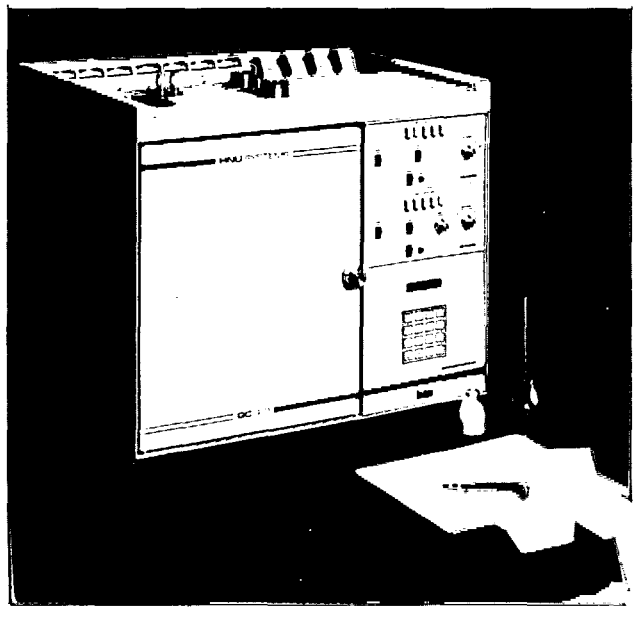

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FIGURE 2. Photographs of some of the new breed of moderate cost GCs. (A) Hewlett Packard Model 5890A (courtesy of Hewlett Packard Co., Avondale, Penn.) (B) HNU Systems Model 421 (courtesy of HNU Systems, Inc., Newton, Maine.)

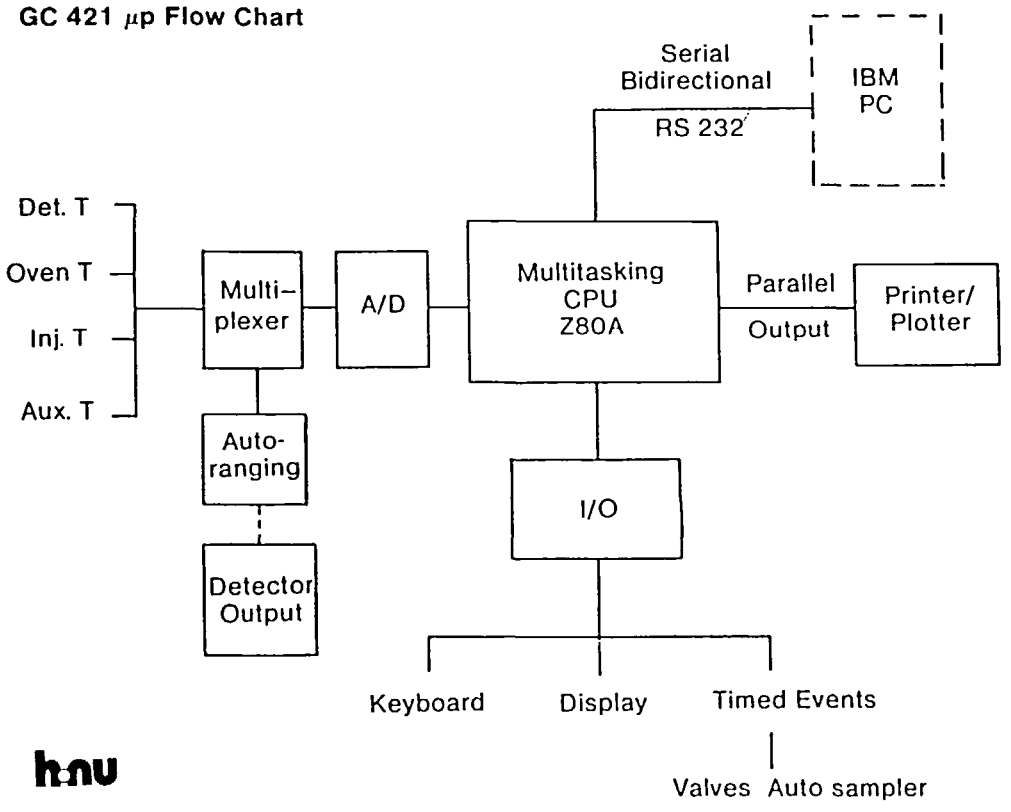
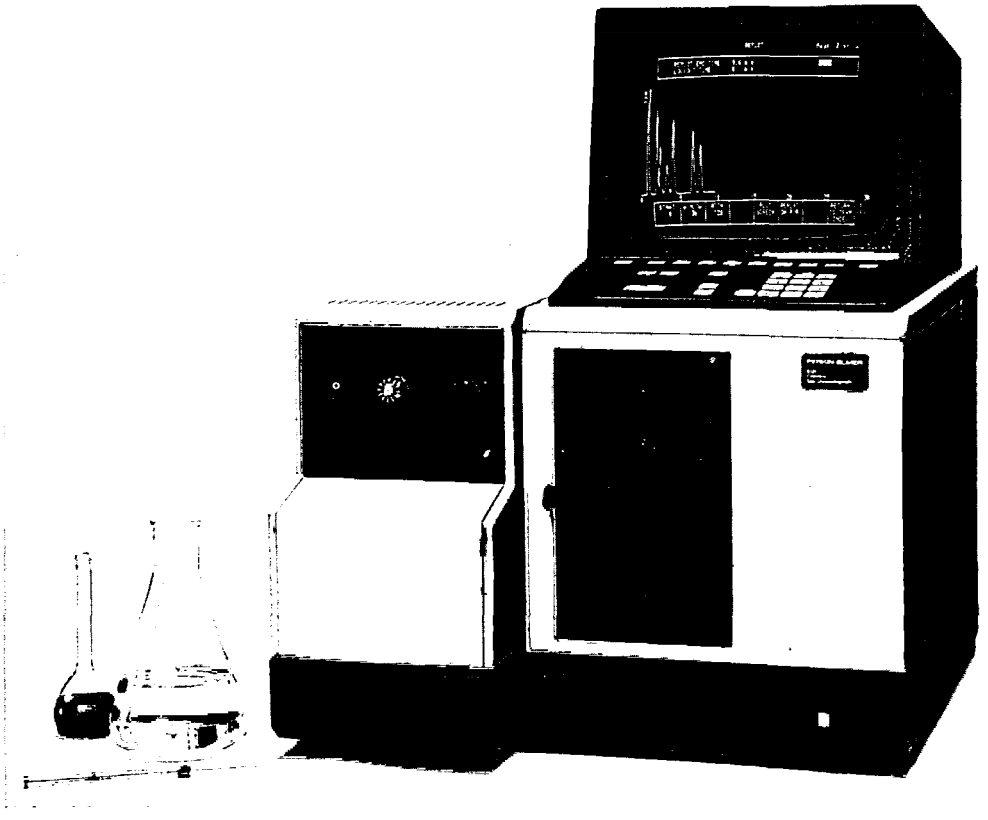


FIGURE 3. Block diagram of HNU Systems 421 GC. (courtesy of Research and Development, HNU Systems, Newton, Maine. With permission.)

The Perkin Elmer (PE) model 8321 GC (Figure 4A) was actually designed in England and has some European flavor although it is now being assembled in the U.S. It utilizes a 16 bit processor (Motorola 68000) and a CRT as a standard feature, which can display the chromatogram (with graphics option added) and calculate results. Data processing via the 16 bit processor is an option. Other options include times events and an RS 232C port. The 8300 can do real time and/or postrun data calculations. This instrument has a single packed or capillary column (split/splitless or on-column) and a single detector. It has multiramp temperature programing, methods storage, and automated bleed compensation. Perkin Elmer will shortly introduce the 8500 that will have two column and two detector capability. It will also have a new screen, which is similar to other CRT screens which PE produces.

Shimadzu Scientific Instruments model 9AM (Figure 4B) incorporates into a single module the injector, detector, and the column. Each of these modules can be interchanged quickly once the temperature cools down. Up to four analysis modules can be installed with either packed or capillary columns. There are ten methods in memory and five temperature ramps. The GC9AM and the Shimadzu integrator (CR3A) can be connected via a current loop and can communicate with each other (Optional board is required). Note that all the other GCs discussed used serial RS232 for communication.

Carlo Erba recently introduced the Vega 6000 GC (Figure 4C), which uses the popular 4100 GC series oven with new sheet metal and microprocessor control of the GC. The instrument is designed for capillary performance with 50 msec time response electrometers, but packed columns are also available. Two detectors and two injectors can be installed. This instrument has multiramp temperature programming, as well as RS232 and timed events capability. A small CRT is used to display the parameters.



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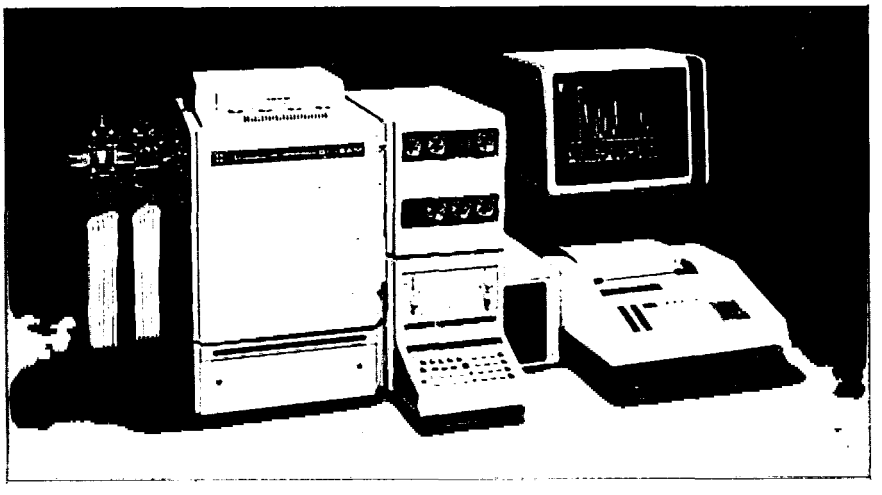

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FIGURE 4. Additional photographs of new GCs. (A) Perkin Elmer Model 8321 (courtesy of Perkin Elmer Corporation, Norwalk, Conn.) (B) Shimadzu 9AM (courtesy of Shimadzu Scientific Instruments, Inc., Tokyo.) (C) Carlo Erba Vega 6000 (courtesy Carlo Erba S.p.A., Milano, Italy.)

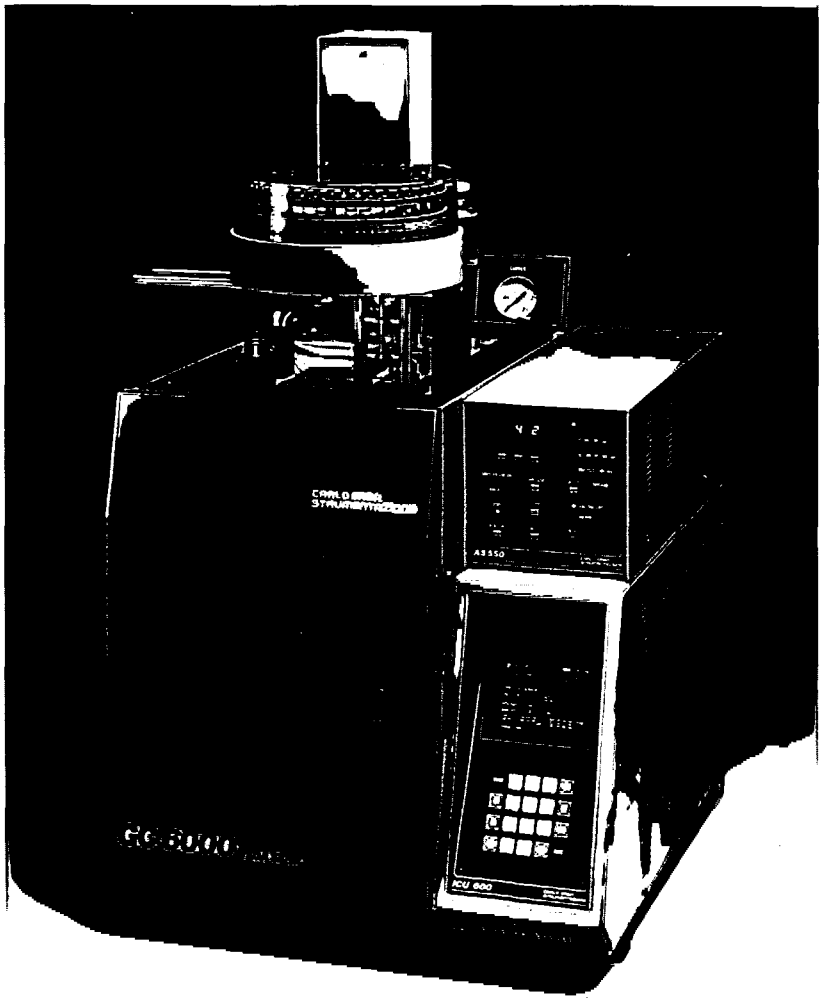


Figure 4C.

Packard Instruments has two new GCs; the model 436 and the model 421A. The former is a capillary GC, but can have two packed or capillary injectors. This GC has single ramp programing with nine methods in permanent memory (optional). The 412A is a special purpose GC designed for analysis of naphtha type samples.

Varian Instruments has three new GCs: the 3300, 3400, and 3500. These units have similar mainframes and electronics. The various features are controlled via software. The 3300 is the low-cost version for quality control or single dedicated application and does not have (four) methods storage, automation, or the optional printer/plotter, which are available only in the 3400. Each of these GCs have multiramp (four) temperature programing, capability for packed and capillary (split/splitless) columns, and will handle one or two detectors. A keyboard lock feature is included in all versions. The electronics for each major function, such as electrometer, temperature control, CPU, etc., are on a single board enabling fault correction by replacing one printed circuit board. A considerable effort has been put into self-diagnosis to minimize service problems. The 3400 also has optional timed events and RS-423/232C serial capability. Four of the 3400 GCs can be controlled by a Vista 402 system, although it is difficult to see any real utility for this option since the 402 does not

Table 2
MODEL 421
REPRODUCIBILITY OF RETENTION TIMES — MANUAL INJECTION — ON CAPILLARY COLUMN

	Isobutane	2,2 Dimethyl propane	2 Methyl butane	2,2 Dimethyl butane	2 Methyl pentane	3 Methyl pentane
	3.65	4.03	4.81	6.24	8.06	7.43
	3.65	4.03	4.82	6.24	8.07	7.44
	3.65	4.03	4.82	6.24	8.07	7.44
	3.66	4.04	4.83	6.26	8.09	7.46
	3.66	4.04	4.83	6.26	8.09	7.46
	3.66	4.04	4.83	6.26	8.09	7.46
	3.66	4.03	4.83	6.25	8.08	7.45
	3.66	4.03	4.83	6.25	8.08	7.45
	3.66	4.04	4.83	6.26	8.11	7.46
	3.66	4.04	4.84	6.27	8.10	7.47
	3.66	4.04	4.83	6.26	8.08	7.47
means	3.66	4.04	4.83	6.25	8.08	7.45
σ	0.005	0.007	0.008	0.011	0.015	0.013
CV (%)	0.14	0.18	0.17	0.18	0.19	0.17

Note: 10 $\mu\ell$ direct injection, conc. $\sim$ 15 ppm ea.
50 meters bonded phase QC methyl silicone, 35°C
detector — PID (11.7 eV)
carrier — N_2 — flow $\sim$ 2.9 cc/min.
retention times — minutes

Courtesy of Research & Development

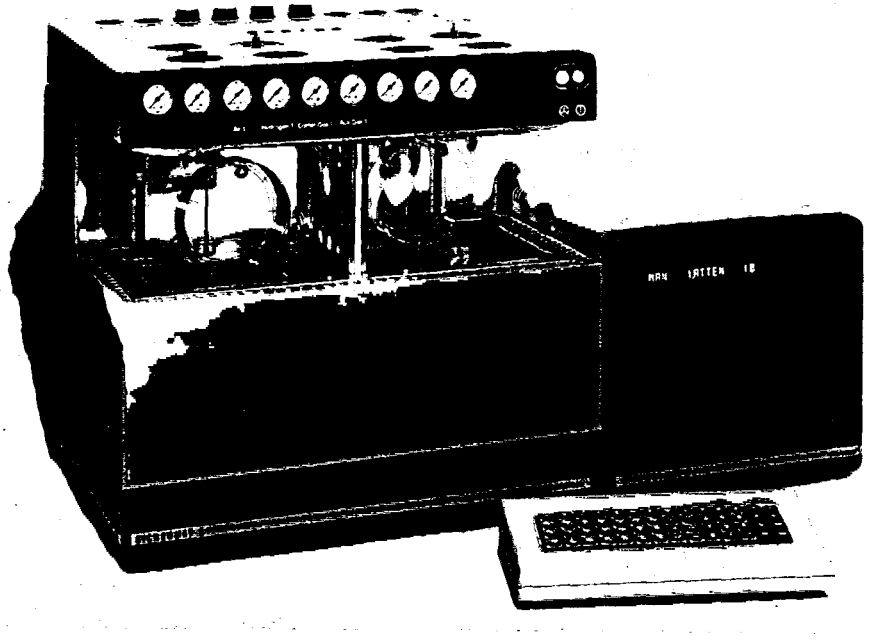
even have basic programing capability. The 3400 can also communicate with a DEC computer for use with the Laboratory Information Management System (LIMS). The 3500, which was introduced just recently, is a dedicated capillary unit. Some of the features include a compact FID with a rigid signal cable to reduce noise, a fast electrometer (50 msec), heated pneumatics, and back pressure regulated pneumatics. An optional feature pressure-flow measuremet can be used to display split ratio.

B. Research GCs

Many of the GCs described above would also fit into this category of research, although there is a considerable price difference between those units and some of the ones described below.

The Siemens Sichromat 2 has two oven systems in one instrument (Figure 5A). There are six ramps available for temperature programing for each oven. This instrument can handle four injectors and four detectors. One unique feature is the use of valveless column switching (Dean's technique described earlier) to reduce dead volume and prevent contact with any valve. A typical flow system for the low dead volume valveless switching system is shown in Figure 6. One example of the two oven column switching technique is shown in Figure 7, where the analysis on column 1 is isothermal with a packed column/TCD for the fixed gases, and column 2 is temperature programed with a capillary column and an FID for the alkanes. This system is complex, but extremely versatile. The capillary column will not separate ethane and ethylene, however, even with subambient programing. An RS232 serial output is available for communication with other computers.

Delsi Instruments model DI 700 (Figure 5B) can handle four detectors, four injector types



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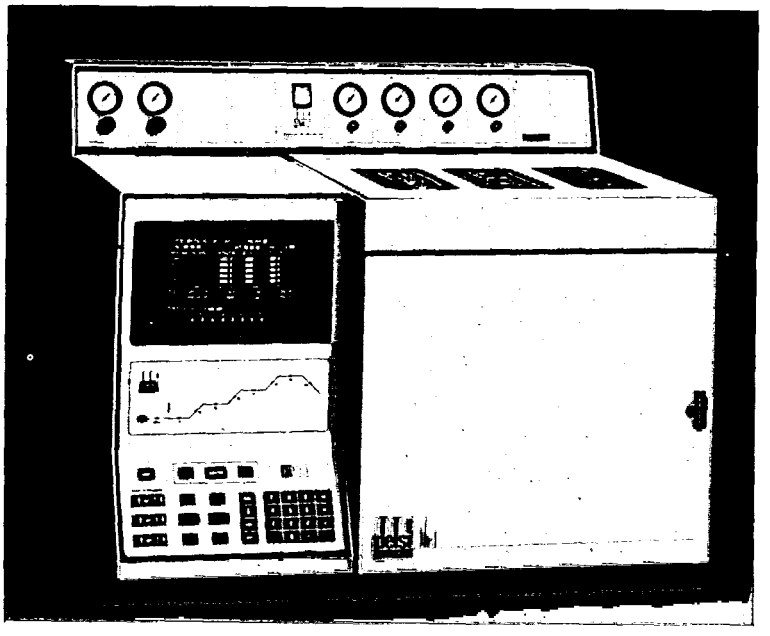

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FIGURE 5. Photographs of some new research GCs. (A) Photo of Siemens Sichromat 2 Dual Capillary Column GC (courtesy of Siemens AG, Karlsruhe, West Germany.) (B) Photograph of Delsi Model DI 700 GC (courtesy of Delsi Instruments, Paris.)

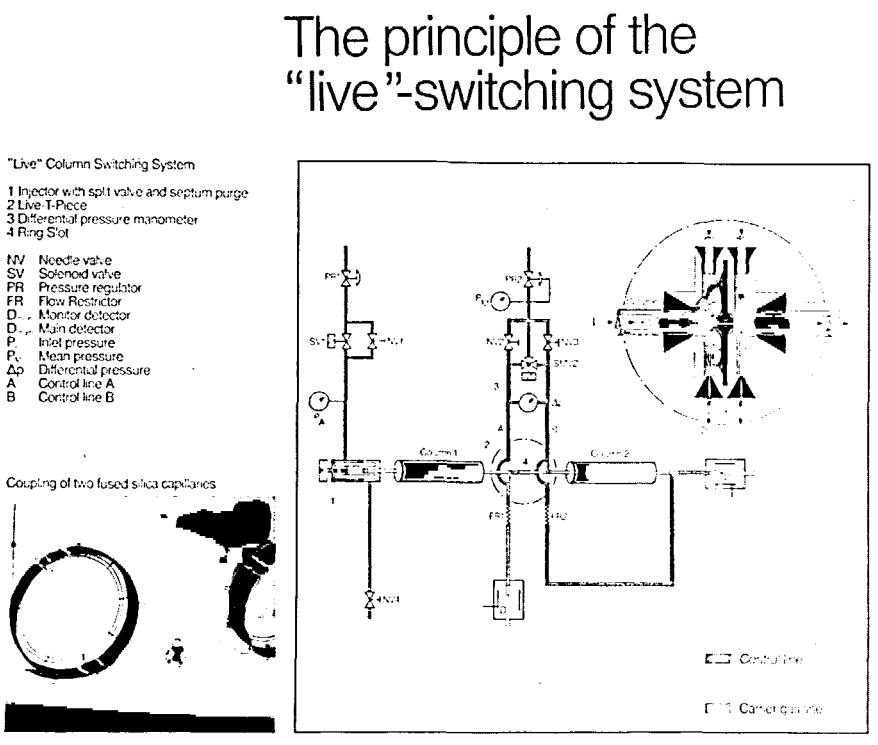


FIGURE 6. Schematic of "live" column switching system (courtesy of Siemens AG, Karlsruhe, West Germany.)

(including a gas sampling valve, packed or capillary), and four columns (large oven). This instrument has a three-ramp temperature programing, nine methods in memory, and a CRT for reading instrument parameters.

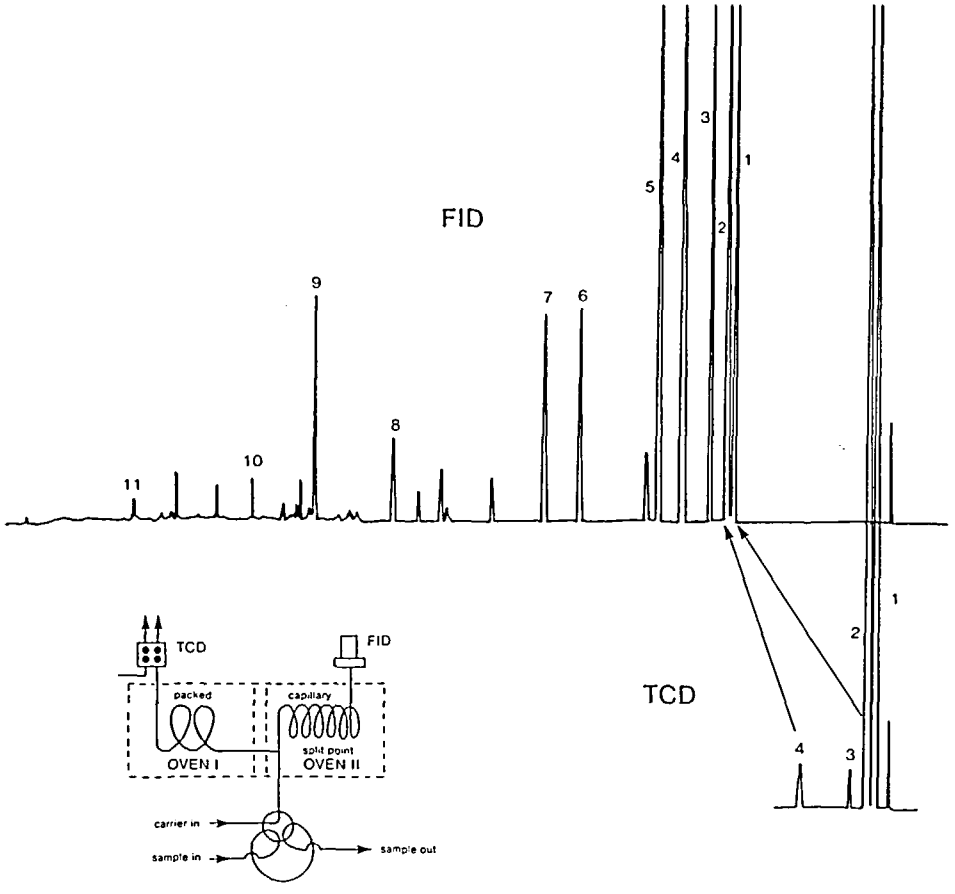
IBM Instruments recently introduced the model 9630 GC that features a dual oven design with four temperature ramps for programing. It would appear that this GC clearly has a European flavor. The instrument will handle up to three detectors including one TCD (per oven), and four packed (two per oven) or two capillary columns. Their concentration appears to be on capillary using column switching techniques, but with a valve instead of valveless described above. The GC has a CRT and keyboard for routine operation and can, of course, be easily interfaced to the IBM System 9000 for data acquisition and analysis.

C. Compact GCs

There are two new GCs in this category in which the instruments are one half to one third the size and weight of the routine lab GCs, one by HNU Systems and one by Shimadzu Scientific Instruments.

The Shimadzu unit is the Mini III (Figure 8A), which is a microprocessor-controlled unit with packed and/or capillary capability and one or two detectors. There is two-ramp temperature programing.

The HNU Systems model 301 (Figure 8B) is a flexible, versatile unit that can be used in the field (battery operated), as a simple low-cost isothermal instrument, or as a temperature programed (two-ramp) capillary GC. The instrument can be easily upgraded from isothermal by plugging in the microprocessor controller (STD Bus Compatible). The up controller takes over oven control from the 301. This instrument can handle packed or capillary columns and one or two detectors. Other options include timed events (plug in board), and a simple

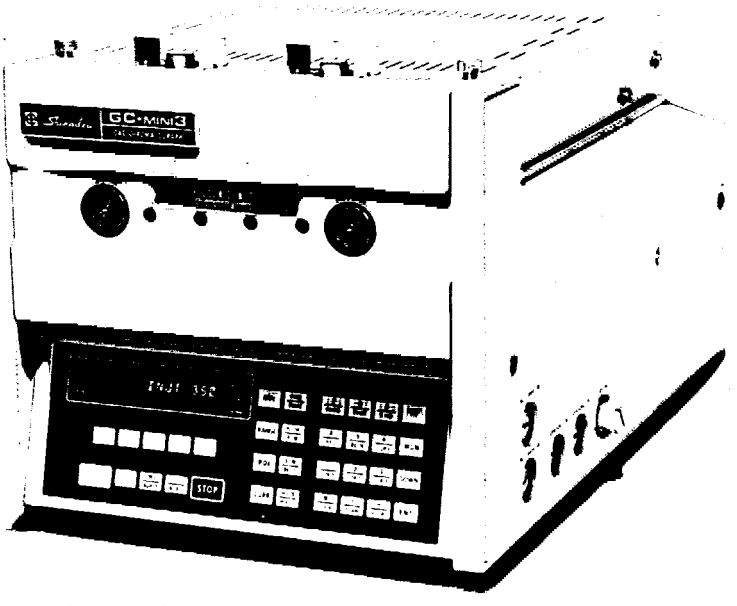


COMPLETE ANALYSIS OF NATURAL GAS BY
DOUBLE CHANNEL SEPARATION AND DETECTION

Columns	:a) 2m 1/8" Poropak R (separation of permanent gases: N_2, CH_4, CO_2, ethane) b) 100 m OV 1, 0.27 mm i.d., $d_f = 1\mu$ (hydrocarbons from CH_4 → decane)
Temperatures	:a) 60° C b) 40 - 200° C, 8° C/min
Detectors	:TCD - Siemens (coupled to Poropak column) :FID - Siemens (coupled to capillary column)
Carrier gas	:0.7 bar H_2
Instrument	:double oven chromatograph - Sichromat 2
Peak identification	:a) 1:N_2, 2: methane, 3: CO_2, 4: ethane b) 1:methane, 2:ethane, 3:propane, 4:i-butane, 5:n-butane, 6:i-pentane, 7:n-pentane, 8:hexane, 9:benzene, 10:heptane, 11:octane

G. Schomberg, F. Weeke, MPI für Kohlenforschung und Strahlenchemie, Mülheim a.d. Ruhr, 9/1981

FIGURE 7. Chromatogram of natural gas analysis on a dual oven instrument with different temperature profiles, different detectors (TCD and FID), and both packed and capillary columns (courtesy of Siemens AG, Karlsruhe, West Germany.)



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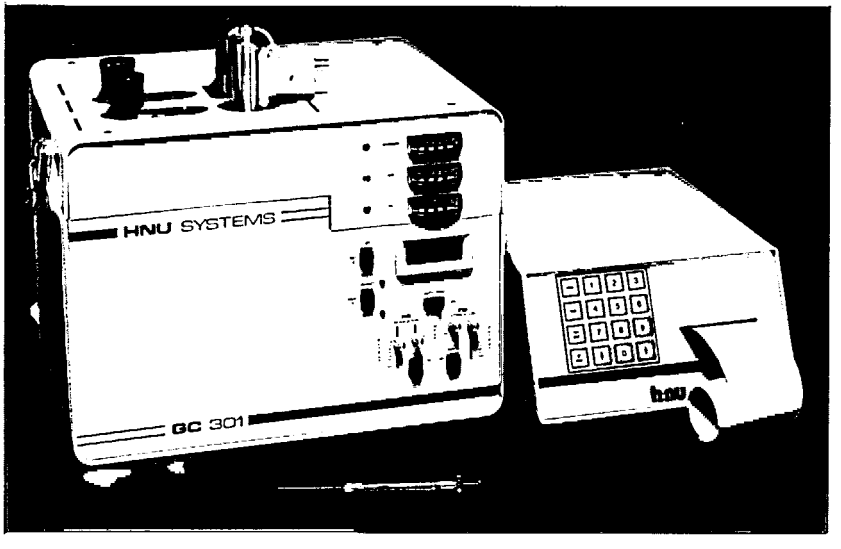


B

FIGURE 8. Photos of some compact GCs. (A) Shimadzu Scientific Institute Mini III (courtesy of Shimadzu Scientific Instruments, Inc., Tokyo.) (B) HNU systems Model 301. (Courtesy of HNU Systems Inc., Newton, Maine.)

two-channel data logger. Two new versions will be introduced shortly, i.e., the 321 and the 331. The former is a packed/capillary version with temperature programing and auto cool down as standard features. The latter is a dedicated capillary version with a fast (50 msec) electrometer and other optional features such as an RS232 for communications.

IV. GC ACCESSORIES

In this section, we will cover advances in detector technology as well as advances in sampling and data handling. McNair et al.,[20] in a review paper on recent advances in GC published several months ago, indicated that "Nothing revolutionary is occurring at present in GC instrumentation or applications." One could also argue that nothing revolutionary has happened in GC since the introduction of the microprocessor 12 years ago; however, it would be an oversimplication. McNair et al.[20] reviewed capillary column technology, including widebore thick film (megabore) and porous layer open tubular columns (PLOT). This latter column appears to be ideal for the separation of inert gases and other inorganics. The former area has changed the character of GC instrumentation significantly since Dandeneau and Zerenner[21] of Hewlett Packard introduced fused silica capillary columns in 1979. This development has caused the rapid rise in capillary column interest seen recently in the U.S. and Asian regions (Section II.). Since Duffy[22] has reviewed recent developments of widebore fused silica capillary columns and Ettre[23] recently reviewed the history and future prospects of open tubular chromatographic columns, there is little left to be said. As a result, capillary columns will not be reviewed in this paper.

Wright[24] described a multidimensional conversion system for capillary GC. This permits coupling of two columns in series, utilization of the heart cut technique, back flushing, fore flushing, and cold trapping. This system can be adapted to all GCs.

A. GC Injector/Detector

The Programed Temperature Vaporizer (PTV) was first introduced by Dani S.p.A. in 1981[25-27] and has only become popular in the U.S. during the past year. Perkin Elmer and Varian have introduced temperature programable injectors recently. The Perkin Elmer is the same as the Dani design, but the Varian is an on-column version, which will have many of the disadvantages of the on-column technique. The PTV (Figure 9) takes advantage of the broad application of the Grob split/splitless technique, which has problems with high molecular weight discrimination or thermally labile substances. A sample is introduced into the injector at ambient conditions in either the split or splitless mode. The inlet is rapidly heated (15 sec) to 350°C, and all substances, regardless of molecular weight, are rapidly eluted onto the capillary column. Other advantages of this technique are: the ease of automation, minimization of sample residue in column, and ability to inject a wide range of sample sizes and concentrations. This injector eliminates many of the disadvantages of on-column capillary injectors such as difficulty of automation, sample residues remaining on the column, and limited range of sample sizes and concentrations.

A new version of the stand alone PID was recently introduced by HNU Systems. The instrument has been optimized for capillary column applications with a low dead volume detector (40 $\mu\ell$) and fast electrometer. Proportional temperature control has been added to improve the stability. A review of photoionization detection for GC was discussed recently by Driscoll.[28] A schematic of the PID is shown in Figure 10A. With the low dead volume, PID sensitivity for aromatic hydrocarbons can be 100 to 150 times better than the FID, an important consideration for capillary column chromatography.

The far UV detector introduced by HNU Systems (Figure 10B) is one of a few new detectors for GC developed in the past decade. Driscoll et al.[29-31] describe some applications for the far UV detector. This detector uses a stable UV source, which emits at 120 nm and

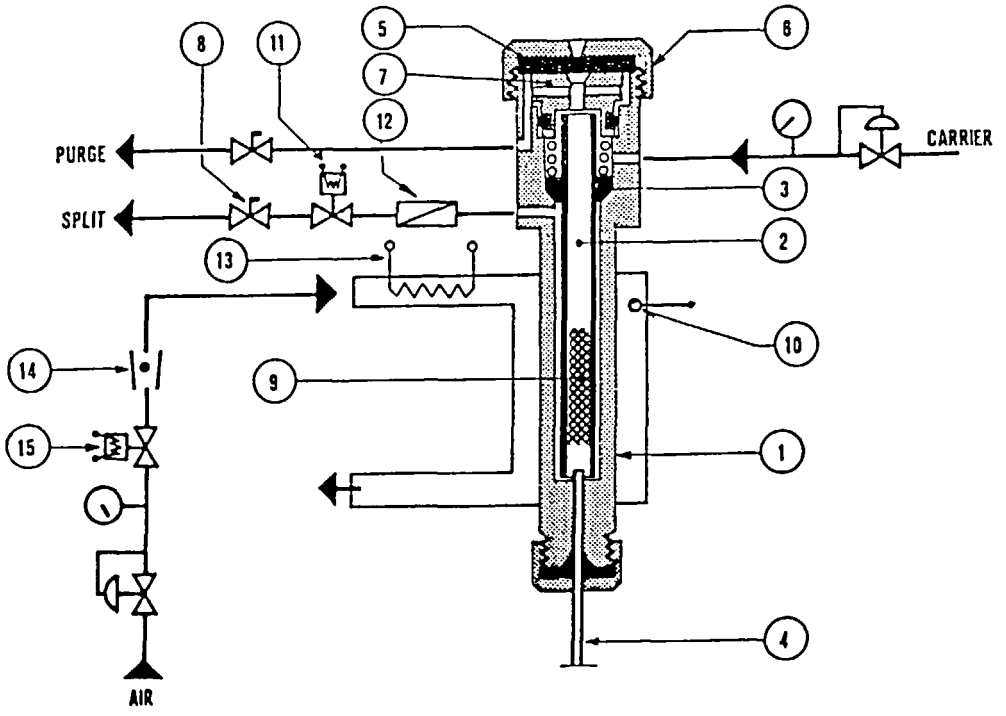


FIGURE 9. Schematic of the programmed temperature vaporizer (PTV) injection system (courtesy of Dani S.p.A., Milano, Italy.)

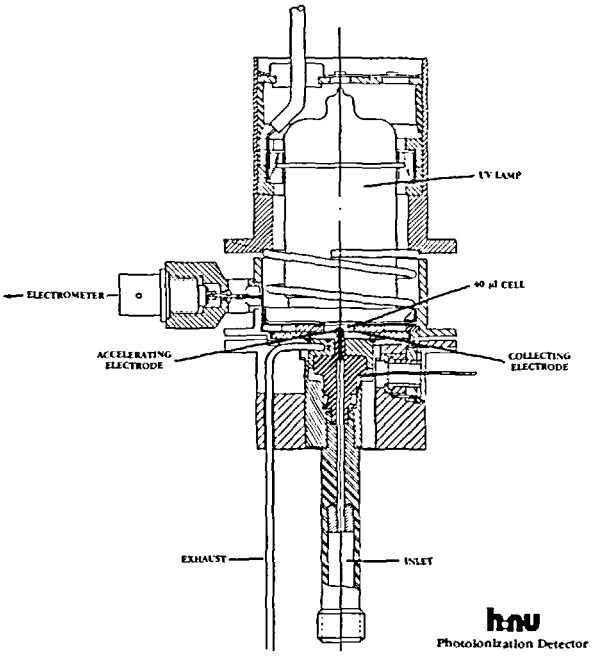
a novel UV photodiode to measure the absorbance. The detector has a universal response since all gases except the noble gases absorb in this region. A comparison of the responses for PID and far UV are given in Table 3. The far UV detector is a particularly interesting detector for capillary as a result of its low dead volume (40 $\mu\ell$), sensitivity, and concentration sensitive response (similar to the PID). With this latter feature, as the carrier flow is reduced, the sensitivity increases (C = 1/F where C = concentration and F = carrier gas flow rate), the sensitivity will improve at least 30 to 50 times (packed column flow vs. 0.5 to 1 cc/min for capillary). As a result of the sensitivity and universal response, this detector or the PID will become the detector of choice for capillary chromatography.

A new version of the electrolytic conductivity detector for chlorinated hydrocarbons was introduced by Oceanography International. This detector appears to have the sensitivity of the Hall detector, but is considerably easier to set up and use.

The mass spectrometer was first used on a GC in 1958,[7] the same year that the FID was introduced. Finnegan reintroduced the ion trap detector at the Pittsburgh Conference in 1985. This instrument is, in essence, a low-cost mass spectrometer that uses a three-dimensional quadrupole. In the ion trap, ionization as well as mass analysis occur in the same region, thereby eliminating the need for tuning.[32] As a result, the instrument is much simpler to operate and build. The ion trap is a powerful system, since it can combine the use of retention indexes with the mass spectrum. It can also utilize mass fragmentation search of NBS spectra to confirm the identity of the compound.

B. GC Sample and Data Handling

At the Pittsburgh Conference in 1985, Perkin Elmer introduced a laboratory robotics system that can be used for weighing, filtering, etc. prior to injection into a GC. A typical system is shown in Figure 11. Hewlett Packard introduced a system for coupling a Zymark



A

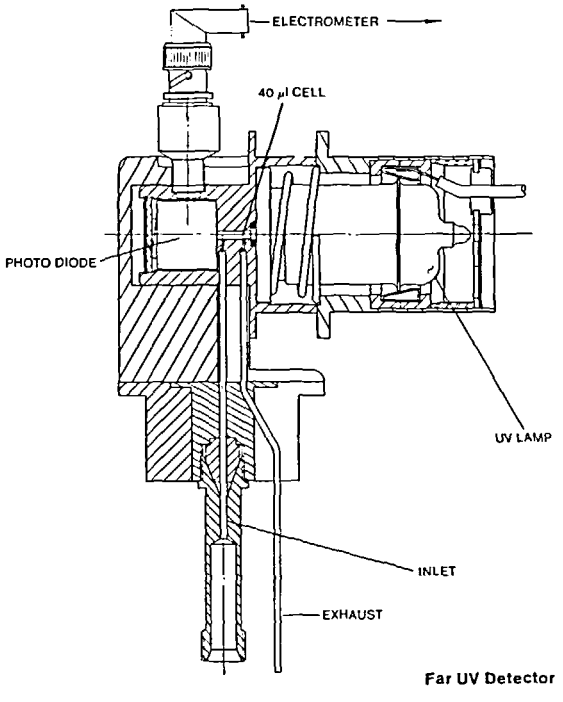


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FIGURE 10. Schematic drawings of two ultrasensitive detectors for capillary chromatography. (A) PID. (B) Far UV absorbance (courtesy of NHU Systems, Inc., Newton, Maine.)

Table 3
COMPARISON OF FAR UV AND PHOTOIONIZATION RESPONSE

Type of compound	Far UV response	Photoionization response
Atmospheric gases (CO, N_2, H_2O, O_2)	M	NR
Specific inorganic gases (NH_3, I_2, PH_3)	M	L—M
Aliphatic (C_1 — C_3)	H	NR
Aliphatic (> C_5)	H	L
Olefinic	H	M
Aromatic	H	H

Note: Far UV response: universal with small response range between classes; PID: selective (mostly HC) with wide response range between classes. H = High; M = Moderate; L = Low; NR = No Response.

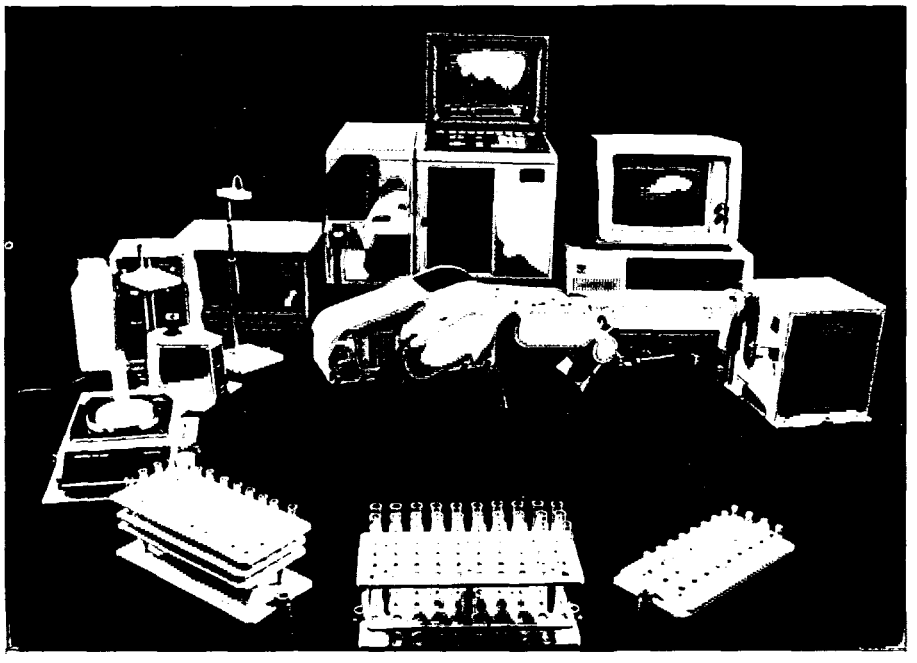

FIGURE 11. GC Robotics System. (Courtesy of Perkin Elmer Corporation, Norwalk, Conn.)

robot to an HP 5890A GC.[33] Although robotics have been around for more than 4 years, this year is the first time that they have appeared with GC instrumentation.

There are two types of integration systems that started very far apart and are coming closer together all the time. The first is the printer/plotter integration system, which is inexpensive, yet provides excellent performance. Typical units are manufactured by Hewlett Packard, Spectra Physics, Shimadzu, and Waters. With these units, the price has dropped dramatically over the past 2 years. Hewlett Packard recently introduced the 3393A system, which is used as the focal point of control for its 5890A GC. It has an optional floppy disk system so that chromatograms can be reintegrated. Similarly the Shimadzu C-R3A integrator has a floppy disk for reintegration as well as a CRT. These features are some of the more

important ones that set the PC based data systems apart from the stand alone integrators. Some of these integration systems were described in detail by Krull et al.[34]

The PC based systems have also changed dramatically in the past 2 years as a result of the rapid integration of the IBM PC into the analytical laboratory, and the relative ease of changing software as opposed to hardware. Several years ago, many of the programs were written for the Apple, now most have IBM PC compatible programs. Dynamic solutions have a system that has a pull-down menu with windowing that is used with a mouse. This system will handle four chromatographs with four detectors each. Winokur[35] and Batchelder and Lawler[36] describe some PC based data systems for data acquisition, control and optimization of chromatographic analyses. An article on managing chromatographic data[37] describes the choices micro, mini, or mainframe, databases, communication standards (?), and optimization. A buyer's guide to chromatography data systems[38] describes instruments/interfaces and/or software from 16 companies.

V. CONCLUSIONS AND FUTURE PROSPECTS

The past several years have seen many improvements in GC technology, particularly in the area of microprocessor control and communications with laboratory computers or PCs. We have already seen how many manufacturers have new GC models via software and some minor hardware changes. Expect to see considerably more of this in the near future. I would also expect to see a PC with every major piece of laboratory instrumentation, as a result of the increased automation, performance, and low prices of the various PCs. An excellent review of PC selection was written by Dessy.[39] As a result of the above, expandability and an RS232 port are essential for any new GC purchase.

The use of capillary columns will continue to expand, and within a few years a majority of all GC applications in the U.S. will be performed on capillary columns. The increased use of capillary columns will lead to a need for identification of components and hence the use of retention indices. With the advent of PCs in the laboratory, it would be advantageous to develop library search capabilities for this purpose. The need for more sensitive detectors will lead to increased applications for the PID and the far UV absorbance detectors. In addition, new selective and sensitive detectors will be required to solve the many complex environmental problems. The use of detector response ratios,[34,40] coupled with a retention index library program on a PC, could be a technique that rivals GC/MS for identification.

The development of new microchips will require new software, and hence additional improvements will result in this area as well.

We have seen significant improvements in GC performance and capabilities as a result of the advances in computer technology, and subsequent incorporation of these advances into gas chromatographs. The early 1980s should be remembered as a time period in the development of the GC that is every bit as important as the late 1950s.

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