

Evolution of Gas Chromatography in India

- B. Sitharaman

Introduction

Some Basic concepts about the GC technique

Major Aims of analytical scientists are separation, identification and quantitative analysis. The classical methods were used by the analytical scientists since ages; however, they were not suitable for handling the analysis of complex mixtures of organic compounds. The discovery of chromatographic methods and subsequently the Gas chromatographic technique offered a major breakthrough in solving the complex analytical problem. GC is a chromatographic technique in which mobile phase is gas and stationary phase is of solid particles (GSC) or the solid support particles coated with liquid having low volatiles (GLC). When such particles are packed inside the tubular columns they are called as packed columns. The separation takes place inside the column because of the differences in the partition coefficients in case of GLC and in adsorption coefficients in case of GSC. The major parts of GC are Injector, column in an oven and detector. A significant advancement in technology was brought out by the scientists with the concept of capillary columns with fused silica wall material having the stationary phase liquids coated on the inside surfaces of Open Tubular Columns (OTC) having very small diameters. With capillary GC the analyser can achieve the high resolution in shorter time at trace levels of the concentration of the analytes.

Natural Chromatographic Processes

In nature various interactions and equilibrious and nonequilibrious processes occur practically in the same form

SITHARAMAN



Sitharaman joined Chemito Technologies in January 1972 as a junior engineer and was involved in the development of Gas Chromatograph. Later he took charge of the new manufacturing facility at Nasik in 1980 as a production manager. He was elevated as General Manager and Vice President over the years and is presently the Director since 1999. Sitharaman is a graduate in Chemistry and has under

gone Management Course at IIM Ahmedabad. He was responsible for initiating Kaizen movement at the company in 1996 and for various other recognitions Chemito Technologies got over the years. Sitharaman has traveled extensively abroad for business negotiation and seminars.

Market Dynamics in India

- ⇒ India beats the global average of 2% with 8 - 10% growth in recent years.
- ⇒ About 1000 – 1200 units of GCs are supplied per annum.
- ⇒ 50% of the market is owned by domestic manufacturers, Chemito leading with major share.
- ⇒ Agilent, Shimadzu, Perkin Elmer, Varian and Thermo share the balance almost equally.
- ⇒ The visible trend is more customers are moving towards GCMS.

as we are realizing them scientifically in the laboratory. Some of the existing natural chromatographic processes are:

- Formation of treasures in the soil during geological eras such as gold, nickel, iron, copper etc.
- Formation of petroleum sources, with partial fractionation of heavier and lighter hydrocarbons through the altitude of regions as a result of migration through soils and minerals.
- Formation of mineral water
- Flow of blood through the blood channels with redistribution of oxygen and flow of sap through vegetable fibres just as in capillary columns
- Process of respiration similar to those in the huge chromatographic system of lungs with enormous surface of exchange with blood as the partition stationary phase, air as the mobile phase and a pump system.

Brief History of the evolution of GC

Chromatography began its role from the beginning of 19th century (1905) when Ramsey separated mixtures of gases and vapors and adsorbents like active charcoal. Michael Tswett separated plant pigments by liquid chromatography (1). The important seminal work pertaining to GC was first given by Martin and James in 1952 belonging to GLC, though the first published paper on GSC was by Hesse et.al. in 1941(2). Martin and Synge in 1941 revolutionised liquid chromatography and had set the stage for the development of GC technique. One of the most important names in the evolution of GC is the well-known German chemist Prof. F.F.Runge.



A.J.P. Martin



M.S. Tswett



F.F. Runge

Technological advancements in GC instrumental technique International/ World scenario

Since its introduction over 60 years ago, GC has become a premier technique of organic analytical chemistry. While the basic components/parts of GC have not changed since its introduction by Martin and James in 1952, instrumentation refinement has answered the demands of the analysers for faster, more sensitive selective and high resolution capabilities of the GC.

Hardware advances include new injection techniques, advances in heating technology (including) resistive heating and two source heating for GC ovens. Some important injection systems which were developed could be mentioned such as :- Packed Injector, Split/ Split less Capillary injector, PTV, HSS, Auto liquid samplers, Pyrolysers, Thermal desorbers, Purge and Trap, SPME, Sampling Valves, Cryogenic attachments, Methanator etc. The largest volume of work was being done in the development of new detectors. Several detectors are reported in the literature, the prominent ones are Flame Ionisation Detector (FID), Thermal Conductivity detector (TCD), and Micro (u TCD), Electron Capture Detector (ECD), Thermionic Ionisation Detector (TID), Flame Photometric Detector (FPD), Pulsed (PFPD), Photo Ionic Detector (PID) and Discharge Ionisation Detector(DID). The latest detector is the Electrolyser FID (EFID) where hydrogen and air cylinders are not required for the FID. Some special configurations of GCs were also developed such as: Natural Gas Analyser (NGA), Refinery Gas Analyser (RGA), Dissolved Gas Analyser (DGA), PONA/PIONA/DHA, (SIMDIS), BTEX Analyser, Online GC Reactor systems etc. Commercial portable GCs were also developed. Advances in the realm of column technology is evidenced through the commercialization of high temperature sustaining fused silica capillaries and stationary phases development has incorporated, stable material such as Sol-Gel Polyethylene Glycol, nanoparticles, ionic liquids and copolymers.

Early GC instrument in the international scenario was the model 154 (of Perkin Elmer) was introduced in 1955 and their model 900 was introduced in 1967. The model 900 was initial sophisticated model of GC; its front panel had over 30 switches, knobs and dials. Oven temperature was controlled by separate dial setting the initial and final temperatures (each in steps of 5° C between -75° C and +400° C by using suitable accessories) and the program rate (providing 15 rates between 0 and 32° C/min). Separate dials permitted the setting of the initial and final isothermal periods and even the rate of the cooling at the end of the program. During the actual programming the large

middle dial was slowly turning, indicating the actual temperature. These were analog systems relying on manual and mechanical controls (3). The first 3 companies involved in manufacturing GC in 1955 were Burrell corpn, Podbielniak and Perkin Elmer. The first two companies are unknown to the present day chromatographers. From 1955 for almost 20 years the analog systems reined the GC instrumentation, till in 1977 PITCON microprocessor controlled digital systems were introduced. In these instruments, oven temperatures and analytical conditions were set from a central keyboard and not with the help of many knobs and dials. Also the conventional packed columns were replaced by capillary columns for several applications. At the same time a new generation of chromatographers started emerging, who were not involved in the early development of GC technology (3).

Evolution of GC manufacturing technology on the Indian stage

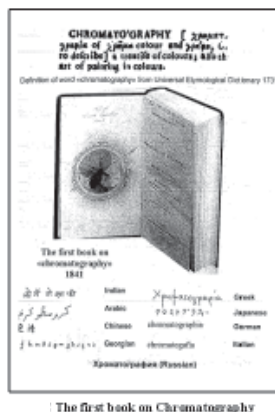
Very close to the international where the model 900 of PE was introduced in 1967 on the Indian stage in just 1969, Chemito Technologies Pvt. Ltd. (that time Toshniwal Instruments Pvt.Ltd.) introduced the first Gas Chromatograph under the license from the Bhabha Atomic Research Centre (BARC) as their "RLO4" model. At about same time AIMIL / Nucon also introduced their initial GC models under license from National Chemical Laboratory, which were manufactured in India. CIC (Chromatography Instruments & Co.) lead by Dr. M.K Shingari introduced their first Gas Chromatograph in 1972. Netel India Ltd. also introduced the first Gas Chromatograph in the late 1970s.

The electronic configurations in the analytical instruments / GC were stepwise developed as follows (4):-

1. Hybrid electronic system of valves and Vacuum tubes
2. Transistor and Semiconductors
3. Micro processor based electronics with PC control.

With the advent of Microprocessors the information technology and PC based library facilities that flowed from it made possible totally new approaches to chemical measurement via GC instruments such as speedy and accurate analysis even at trace levels with high precision and reproducibility was made possible. The sizes of initially developed GC instruments were quite bigger, required lot of space to accommodate them having heavy weights. Initially Strip chart recorders were used for Data Acquisition. They were subsequently replaced by dedicated electronic integrators. Presently PC based data acquisition software s are used extensively. By

using the features like speed and memory storage of PC Multiple GCS are connected through Net work. Even Trouble shooting of Gcs are done through Network. However, the PC



The first book on Chromatography

microprocessor based instruments could be packaged in attractive, small convenient, decent and affordable units. These computerized windows based GC instruments initially with 16 bits software and later with 32 bit software, became extremely popular and handy since they were easy to operate and customer friendly. Techniques resting on the use of mathematical transformations, methods requiring immediate access to data bases, protocols involving precise multistep sample handling, automation of complex measurements along with autosamplers and autoinjection devices, measurements of large number samples even at trace levels with high precision and accuracy suddenly became practically possible.

Further to introduction of RLO4 model in 1969 by Chemito, the company developed model GC 3800 with a technical know-how from DANI s.p.a, Italy, in 1980. Subsequently, they introduced microprocessor based model GC 3865 in 1985, GC 8510 in 1988. In 1992 GC 8610 with high temperature analysis facility was developed. In 1996 totally automated GC with keyboard controlled with EPC model GC 1000 was introduced. The latest model of Chemito GC Ceres 800 plus was introduced in 2004 which has complete computer control facility for setting all the instrumental conditions along with data acquisition and data processing facilities. This model has a graphical LCD display which shows all important parameters. The various GC models of Chemito have reached the international level of quality in technological aspects.

Marketing perspective of GC

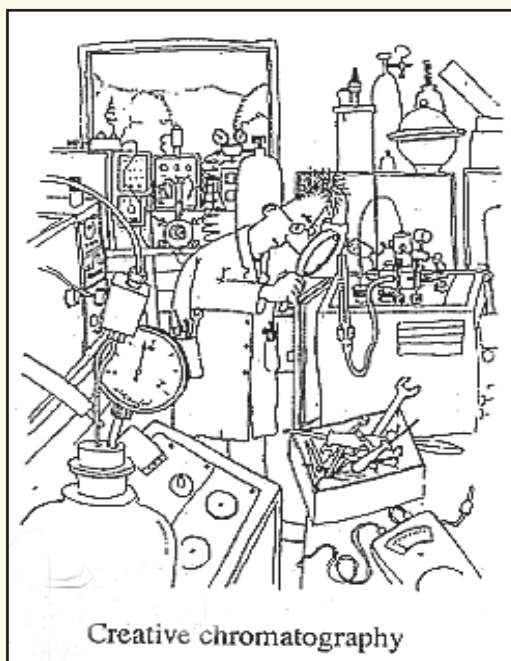
In the eighties and nineties the high resolution capillary GCs and GC MS technology progressed at the amazing pace which revolutionised the field of analytical chemistry. The above said advancement of technology in GC became very popular and was favourably accepted by the customer/ market, specially in the QA/QC/R&D labs of following market fields, where GC became the integral part world over and of course also in India.

- Organic Industrial Chemicals
- Pharmaceuticals & drugs
- Environment Sciences
- Petroleum & Petrochemical industries
- Pesticides & their residues
- Clinical Chemistry
- Bio- Chemistry & Bio-technology
- Foods & beverages
- Vegetable Oils, fats & soaps
- Forensic Sciences
- Explosives & their residues
- Dangerous drugs, narcotics etc
- Agricultural sciences
- Soil Analysis
- Water Analysis
- Paints
- Dyes/textiles etc
- Thinners
- Alcoholic beverage industries
- CSIR & Research organization
- University departments and colleges
- Central and state govt. organizations involving chemical analysis

The Chromatographer's Lament

- By R.G. Mathews

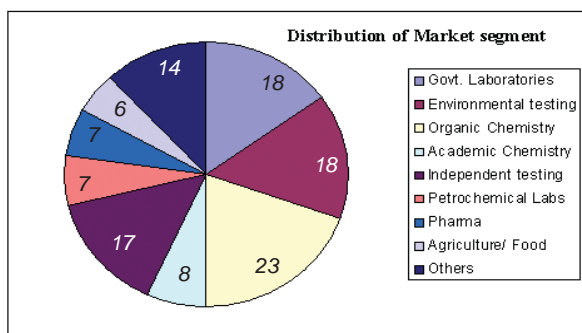
*"I've heard of chromatograph systems that give separations so fine,
But the beautiful peaks in those pictures bear little resemblances to mine.
We bought a new phase for our column with a high temperature guarantee...
They said we could cook it forever, but it conked out at 200 ° C.
We coated it ever so slowly; Conditioned with greatest care....
But the baseline kept rising and rising and our sample got lost way up there.
Now the oleate's in with the stearate, and the peak shapes are slightly askew.....
The flow rate just fell off to zero. So I really don't think it will do
We've avidly read all the journals, advise we have never refused...
But after you've plugged all that stainless, It's hard to stay really enthused.
We've tried this thing over and over and we feel that success must be near...
All we need are a few more good substrates and a couple more bottles of beer.
To-morrow, To-morrow,
We'll coat the new phase that they say is the best....
But I'll still bet you
It'll bleed even worse than the rest."*





A 1961 survey by Chemical & Engg. News (5) estimated a world over annual GC business to be close to \$ 4 million and for the mid 1970s conservative estimates put the annual GC business over \$ 100 million. A recent survey indicated the GC business (without GC-MS) at \$ 1.324 billion in the year 2006 and projected US \$ 1.433 Billion by 2010. Even though the CAGR globally is only 2%, in India the growth is expected to be around 8 – 10%. One of the visible trends is customers moving to GC MS in more numbers.

Distribution of GC according to market segments world over are as follows (3):



Agilent (successor of HP) has the major market share at around 60 % at the International levels. The other GC manufacturing companies recognized at the International levels are as follows: Perkin Elmer, Varian (the successors of Wilkens Instrument), Shimadzu and Thermo- Electron.

In the Indian market totally 1000 – 1200 GC units are sold per annum approximately. Amongst them estimated market share of the Indian GC manufacturing companies would be roughly around 50%; Chemito having the major share of the market. Balance 50% share is taken up foreign manufacturers like Agilent, Perkin Elmer, Shimadzu, Varian and Thermo almost equally catering to specific industrial segments.

Future Trends in Gas Chromatography

- GC instruments will be made portable. Miniaturization will be the trend. Probably the column may be eliminated by heating the capillary column by contact heating.
- More towards application specific areas.
- Mass detectors will become more popular.

Conclusion

The meteoric rise of GC in the past 45 years was unparalleled in the history of Analytical science. The evolution of GC to the present mature status has revolutionised the capabilities in the field of Analytical Chemistry. By the second part of 1960s it started to branch out, giving rise to the development of other chromatographic techniques (e.g HPLC and electro Chromatography). This phenomenal and amazing growth would not have been possible without the outstanding contributions from the instrument manufacturing companies.

Therefore, we should pay tribute to first seminal paper by James and Martin on Gas Liquid partition chromatography for their pioneering contributions towards the development of such a useful technique as GC.

One final quote on Chromatography

“Chromatography existed, exists and will exist. Before human society, simultaneously with it, besides of it. That is true!”

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- Mr.Devraj Aiyar Ex General Manager- Marketing Toshniwal Instruments Pvt.Ltd, presently General Manager, SGE India Ltd.

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