

Design, Development and Deployment of Indigenous Gas Chromatographs

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Preamble:

The present article is aimed at documenting the effort at Chemistry Group, BARC, on the design, development and deployment of gas chromatographs for various in-house applications. The technology developed was transferred to several industries for commercial production.

Introduction:

Mikhail Semyonovich Tsvet, a Russian-Italian botanist, invented chromatography during his research on plant pigments. The method was presented in 1901 at the XI Congress of Naturalists and Physicians in St. Petersburg. Chromatography methods changed little after Tsvet's work until the invention of partition chromatography. In 1952 APJ Martin and RLM Synge invented liquid-liquid partition chromatography, which revolutionized the field of chromatography. They were awarded Nobel Prize in Chemistry for their invention of partition chromatography. Later Martin, in collaboration with A.T. James, went on to develop gas chromatography (GC), and in the mid 1950s commercial gas chromatographs came into the market and thereafter there was a rapid growth in it, particularly in terms of better detectors.

The Indian scientists also realized the potential of this technique and started development and manufacturing of GC instruments indigenously. Bhabha Atomic Research Centre was the pioneer in this effort. In Chemistry Group, dedicated efforts were made to develop a prototype GC in the laboratory for the first time in the country way back in early 1960s under the leadership of Dr R.M. Iyer. Soon collaboration with Indian entrepreneurs produced commercial instrument. Currently, in many laboratories Indian instruments are working as efficiently as the imported ones.

The present article is aimed at documenting the effort in Chemistry Group, BARC, on the design, development and deployment of gas chromatographs for various in-house applications. Initially, the technique of GC is described briefly. Subsequently, various custom-made instruments made for in-house use and also for outside agencies are described.

Back to basics:

GC is an analytical technique that is used to separate, identify and quantify components in a mixture. The analytes are required to be sufficiently volatile and stable at the operating

temperature. One of the great advantages of GC is the wide choice of the stationary phases, and the consequent possibility of separation of wide variety of mixtures.

A GC consists of a carrier gas, an injection port, separator column containing the stationary phase, detector, and data processing system. The sample to be separated is injected through an injection port, and is carried to the column by the carrier gas. Depending on the affinity of the analytes for stationary phase, they have different mobility, and thus get separated. As the analytes exit the end of the column, these are detected using a suitable detector at different times (called retention time) due to their different mobility. The retention time is characteristic of each component under the elution conditions. By comparing the retention time of the unknown compounds with that of the standard, identification is done. Other parameters affecting the order or time of retention, for a particular column and carrier gas, are the carrier gas flow rate, and the column temperature.

Mobile phases are generally inert gases, such as helium, argon, or nitrogen. The injection port is maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture. Since the partitioning behavior is dependent on temperature, the separation column is usually contained in a thermostat-controlled oven. Most of the columns contain a liquid stationary phase on a solid support, with large surface area, inside a glass or metal column. Gas liquid chromatography (GLC) is the terminology used when the stationary phase is a liquid. Here, the interaction is through partitioning (distribution), and the separation depends on partition coefficient K given by the ratio of analyte concentration in stationary phase to carrier gas. When the stationary phase is a solid, then the terminology used is gas solid chromatography (GSC). Here, the interaction taking place is adsorption, and the separation is based on adsorption coefficient.

Preparative chromatography has been used to obtain pure compounds from a mixture. The detector should be a non-destructive type, like thermal conductivity detector. Sample collectors are put at the outlet of the detector, and the instrument can be programmed, to collect the individual component (or sample of interest). Fig.1 (a) and (b) represent schematics of a typical gas chromatograph and separation process with different retention times, respectively.

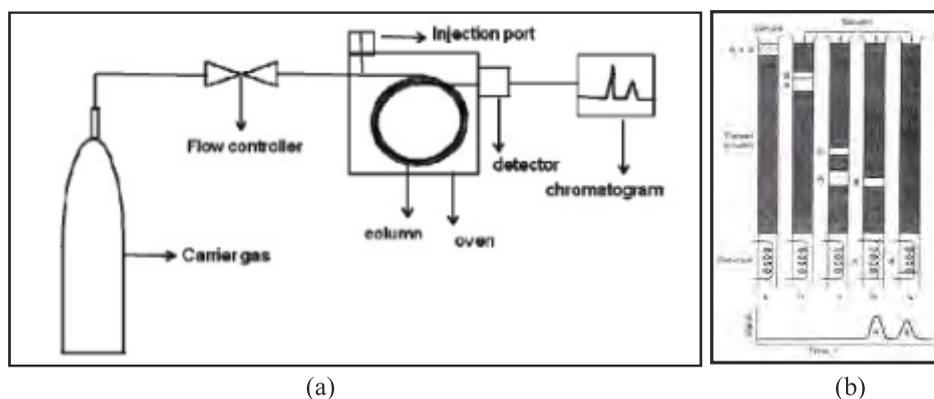


Fig. 1 : Schematics of a gas chromatograph (a) and separation process (b)

GC being a comparative method, standards are required for identification and quantitative analysis. Using the integrated peak area or height (for sharp peaks), a calibration graph is generated for different volumes of the standard. Knowing the analyte area or height, the amount of the component in the mixture can be obtained from the calibration plot.

A number of detectors, like thermal conductivity (TCD), flame ionization (FID), electron capture (ECD), nitrogen phosphorous (NPD), photoionization (PID), flame photometric (FPD), etc., are used in GC. The most commonly used detectors are FID and TCD, which have been developed at Chemistry Group. Both are quite robust, and sensitive to a wide range of components and concentrations. While TCDs are essentially universal, and can be used to detect any component (as long as its thermal conductivity is different from that of the carrier gas, at detector temperature), FID is sensitive primarily to hydrocarbons. Since TCD is non-destructive, it can be operated in-series before an FID (destructive), thus providing complementary detection of the same analytes. Another important detector (ECD) is very sensitive to halogen containing organic compounds. These three detectors could serve most of the requirements of Chemistry Group.

Custom-made gas chromatographs:

Gas chromatographs for routine analysis:

Following is a typical list of various units built in Chemistry Group over about four decades of intensive development for in-house and outside agencies' requirement.

- Fig. 2 shows the photograph of the first gas chromatograph built in Chemistry Group, BARC. It was a compact unit with high air flow fan, detector in the oven & injection port with preheated carrier inlet, and high sensitivity FID. Four units were made for IIT Bombay, NCL, Pune, FIPLY (BARC) and Chemistry Group (BARC) during 1968 – 1970.
- A portable Hydrogen Monitor to detect hydrogen in ambient air was delivered to Indian Navy during 1972-74, which could be operated in sample, hold and measure mode in the concentration range of 0-8%
- Thereafter, a 3-channel Hydrogen Monitor with alarms developed for the Tritium Lab of Isotope Division, BARC, during the year 1974. It was specially designed for round the clock operation, continuous sampling and direct reading, while each channel sensing a selected zone (Fig. 3).
- A Preparative Gas Chromatograph, with time based repetitive isothermal separation and collection of selected components in automated mode through repetitive cycles, was developed in the year 1975.

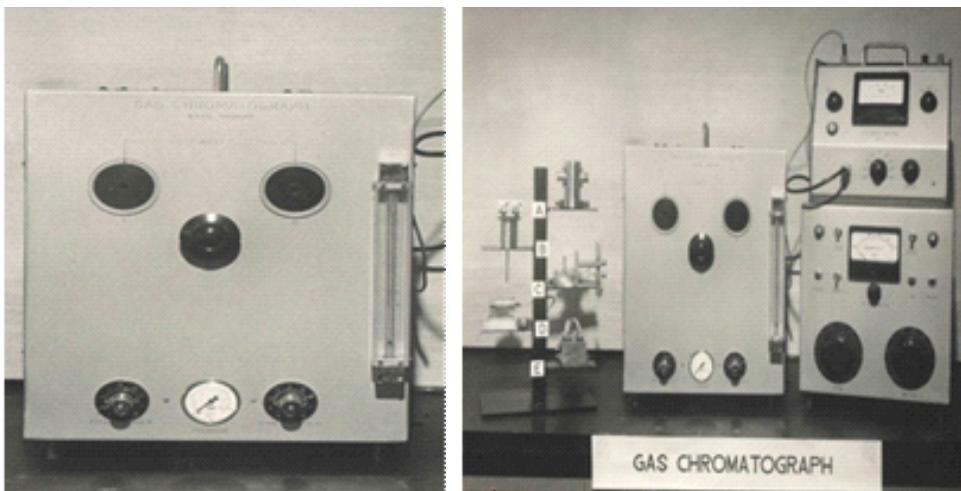


Fig. 2: Photograph of the first gas chromatograph



Fig. 3: Three channel hydrogen monitor

Gas chromatographs for special applications:

- During the operation of the CIRUS reactor, BARC, the control of the level of deuterium, oxygen and nitrogen in the blanket helium gas was required. Online analyzer for continuous monitoring of Reactor Cover gas Helium for deuterium, oxygen and nitrogen using TCD was developed, employing a simple and inexpensive gas chromatograph. Deuterium, oxygen and nitrogen impurities in helium were separated (Linde Molecular Sieve 5 A column) and determined (TCD using thermistors) at 0.05%, 0.01% and 0.01% (V/V), respectively, during 1972–1977.
- A GC was designed and developed for use in Power Reactors for sequential analysis of any or all EIGHT gas streams as selected by the operator in manual or auto mode. A prototype was installed in MAPS, and subsequently made by NPCIL (with ECIL) for KAKRAPAR power station. Fig. 4 shows the photograph of MAPS cover gas analyzer and gas flow control unit.



Fig. 4: MAPS cover gas analyzer developed at Chemistry Group, BARC

- Hydrogen Isotope Analyzer for $H_2 / D_2 / T_2$ mixtures for Isotope Division, BARC, was developed during 1990. The analyzer was provided with low volume ionization detector for tritium, an online hot copper oxide reactor ($400^\circ C$) was used to convert hydrogen isotopes into steam, and TCD ($120^\circ C$) was used to detect hydrogen isotopes in the steam. Analysis was carried out with column at liquid N_2 temperature with Helium as carrier gas. The column effluent passes through ionization detector, CuO reactor and TCD (Fig. 5).

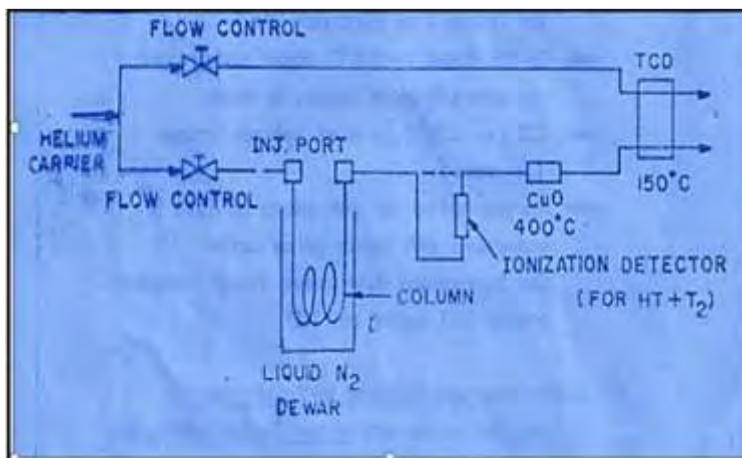


Fig. 5: Schematic of isotope analyzer

- Multi Stream Hydrogen Monitor for Heavy Water Plant, Vadodara, was developed in 1990. The unit has three independent fast response detectors, which can monitor twelve streams in about eight minutes. Microprocessor controlled operation can be made providing data acquisition, storage, display, stream selection, temperature control low and high level alarms (Fig. 6).

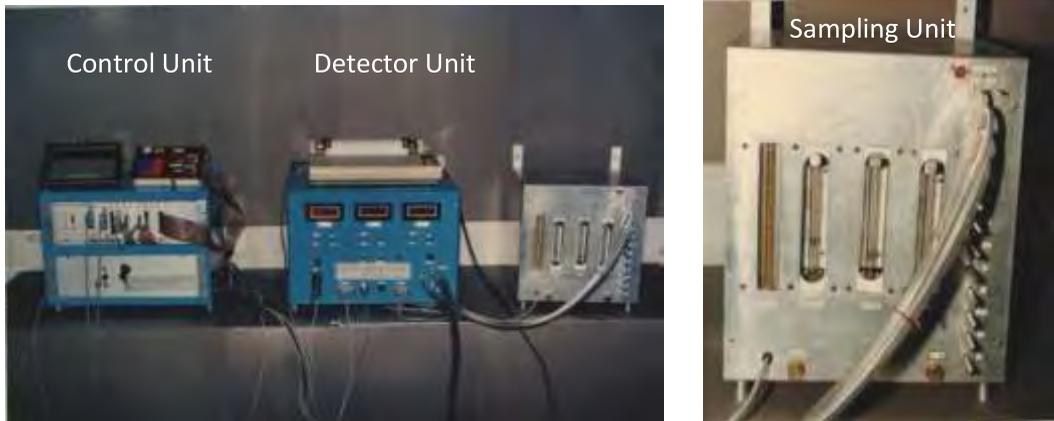


Fig. 6: Multi stream hydrogen monitor

- PC based Multi stream Hydrogen Monitor for H₂ mitigation experiments was developed in 1996. Based on previous expertise, a PC based Multi stream Hydrogen Monitor was delivered to Reactor Engineering Division (RED), BARC (Fig. 7).



Fig. 7: PC based multi stream hydrogen monitor for H₂ mitigation experiments

BARC-Industry interactions: Representative interaction during different years:

1	Basic GC with temperature programming, FID, TCD, and ECD; about 150 GC units were produced and sold by M/s Toshniwal Brothers (1968-71)
2	Analysis of dissolved gases in transformer oil; methodology to CPRI, Bangalore (1975)
3	Hydrogen Monitor to Indian Navy; Elico, Hyderabad (1976)
4	Online D ₂ , O ₂ & N ₂ analyzer for Power Reactors made by ECIL/NPCIL (1977 onwards)
5	Repair, testing & calibration of several CO ₂ & H ₂ monitors (Russian make) for Indian Navy
6	Calibration and testing of continuous flow H ₂ monitor (French make) for Mazgaon Dock
7	Calibration of gauge used for delivering Anesthesia in KEM and Nair Hospitals

In order to facilitate further development and academia-industry interaction, two workshops based on GC were organized by Chemistry Group in 1976 and 1980, which attracted good response and appreciation from the participants. The technology of the Gas Chromatographs developed at Chemistry Group was transferred to M/s Toshniwal Brothers and M/s AIMIL Industries for commercial production.

Deployment of gas chromatographs:

The development of gas chromatographs in Chemistry Group, BARC, can be considered as a model for design, development and deployment of scientific equipment for in-house applications, and subsequent transfer of the know-how to suitable vendors for commercial production. The Chemistry Group interacted with other industries, and the technology was transferred to them for large scale commercial production and sale inside and outside DAE. This entire process was done way back in late 1960s, and still remains a model to be emulated even at present. Similar model of design, development, deployment, interaction with industries and finally transfer of the technology to them should be followed for a R&D project.