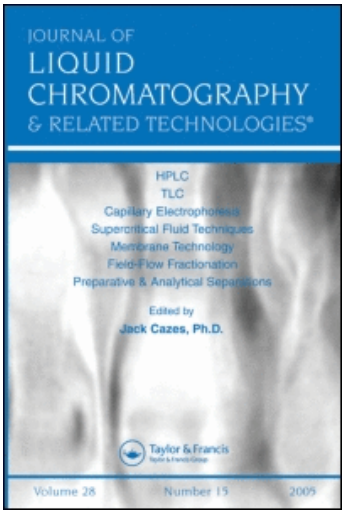

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A JOURNEY FROM MIKHAIL TSWETT TO NANO-LIQUID CHROMATOGRAPHY

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A JOURNEY FROM MIKHAIL TSWETT TO NANO-LIQUID CHROMATOGRAPHY

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□ *Today, chromatography is the back bone of separation science and is being used in all research laboratories and industries of the world. It has developed into nano liquid chromatography (NLC) modality through various kinds of chromatography. The present article describes a journey from Mikhail Tswett in 1903 to today of NLC. Attempts have been made to discuss the applications of newly developed NLC, especially for proteomic and genomic researches. Few chromatograms of NLC have been given for ready reference. The chromatographic journey is shown in the form of a chromatography tree. NLC is eco-friendly and may be referred to as green or clean chromatography. The future perspectives of chromatography have been highlighted.*

Keywords chromatograms, chromatography, journey, micro chips, nano liquid chromatography

INTRODUCTION

Nowadays, chromatography has become a powerful analytical technique for various scientific discoveries and industrial applications. Today, it is in its swing due to ample developments; capable of separating analytes ranging from simple to chiral molecules. Today, nano-liquid chromatographic devices are available which can detect any species at nano levels within a few seconds. It was really a miracle of Russian botanist Mikhail Tswett, who invented chromatography in 1903.[1] He separated plant pigments by passing their solution through glass columns packed with finely divided calcium carbonate.[2] The separation was as colored bands on

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the column and, hence, he called it chromatography [two Greek words, *chroma* (color) and *graphein* (to write)]. After this invention, not much work was carried out for a few years in this area but, after a few decades, Tswett's discovery was re-considered by a few scientists and various modalities of chromatography emerged.

Paper and Thin Layer Chromatography

In spite of the great discovery of Tswett, chromatography was not recognized considerably. But, later on, Martin and Synge[3] carried out some experiments on cellulose paper in 1941 and developed the theory of partition chromatography, based on certain calculations. In 1952, both these scientists shared Nobel Prize in Chemistry for their remarkable work.[4] The origin of thin layer chromatography is not clear but was probably first developed by Schraiber in 1939 with detection of spots by a fluorescence method.[5] Later on, in 1951, Kirchner[6] introduced the use of starch as a binder in the production of thin layer plates.[7] TLC gained popularity in 1956 by the introduction of an applicator by Stahl, called the Stahl type applicator.[8] As a result, TLC became a well established routine and rapid separation technique. Later on, several sorbents were developed for TLC coatings; TLC has achieved a good reputation with a wide range of applications.

Gas Chromatography

The work of A.J.P. Martin and R.L.M. Synge of 1941 encouraged the rapid development of several types of chromatography, including gas chromatography (GC). Based on Martin and Synge partition theory, Fritz Prior developed solid state gas chromatograph in 1947.[9] Later on, Martin and Synge published one paper on GC[10] and, from 1952 through the late 1960 s, GC evolved into a sophisticated analytical technique. Various stationary phases have been developed for GC, which were packed in open tubular columns and capillaries. The mobile phases were also developed as different pure gases. At present, GC is a well developed technique for the separation and identification of compounds that are volatile at its working temperature. This limitation of GC restricts its application and use in separation science.

High Performance Liquid Chromatography

As in the case of GC, partition theory gave birth to this widely accepted modality of chromatography, i.e., High Performance Liquid Chromatography (HPLC). First, Alm[11] reported the method of gradient elution

in 1952. In the late 1960s, liquid chromatographic theories and instrumentation were developed and quickly improved due to the development of columns and on-line detectors, leading to the first commercially available HPLC system in 1969.[12] Around 1973, packing technologies and development of reversed phase silica gel led to the first 10.0 μm (particle diameter) reversed phase HPLC columns.[13] Since then, HPLC has become powerful tool for the modern laboratory. Later on, several advancements have been developed for HPLC; these are discussed in the next section.

Other Modalities of Liquid Chromatography

After the development of HPLC, many modifications have been developed during the past three decades and some important hybrid techniques emerged, e.g., ion pair chromatography, ion chromatography, capillary electro-chromatography, size exclusion chromatography, supercritical fluid chromatography, micellar electrokinetic chromatography, etc. Basically, these chromatographic techniques differ slightly from HPLC only in stationary and mobile phases. Ion pair chromatography is similar to reversed phase HPLC; reversed stationary phases are used in both modalities. A counter ion is added to the mobile phase in reversed phase HPLC and the technique is known as ion pair chromatography. Ion pair chromatography is also known by the names of soap chromatography, ion interaction chromatography, and dynamic ion exchange chromatography.[14] In ion pair chromatography, if the counter ion is a surfactant molecule, a micelle is formed; this sort of liquid chromatography is referred to as micellar electrokinetic chromatography (MEKC). This technique was introduced by Terabe et al.[15] in 1984. It is useful for analysis of neutral analytes. Ion chromatography is the technique utilized to analyze ions by using cation or anion, or cation and anion exchange columns.

Capillary electrochromatography is a hybrid technique of HPLC and CE, which was developed in 1990 by Pretorius et al.[16] using packed columns. CEC is expected to combine the high peak efficiency which is characteristic of electrically driven separations with a high degree of separation selectivity. CEC experiments can be carried out on wall coated open tubular capillaries or capillaries packed with particulate or monolithic silica or other inorganic materials, as well as with organic polymers. It is useful for both ionic and non-ionic molecules. Another modality of HPLC is size exclusion chromatography, in which smaller species are retarded and the larger species pass through faster. It is useful for larger molecules such as metallic proteins, peptides, polymers, etc.

During the past three decades, supercritical fluids have been used as mobile phases in liquid chromatography; this modality of chromatography

is known as supercritical fluid chromatography (SFC). When both temperature and pressure of the system exceeds the critical values, i.e., of critical temperature (Tc) and critical pressure (Pc), the fluid is known as critical in nature. It is very useful for chiral separations.

Nano Liquid Chromatography

In spite of the medicinal properties of drugs, some drug residues remain in our body for a few days or months at low concentrations (~nano to pico levels). Sometimes, they accumulate in body tissues, leading to various diseases.[17,18] The concentrations of some species, such as hormones, RNAs, DNAs, antibodies, and other proteins are at very low levels. Also, detection of drugs at lower concentrations is required in the plasma of infants due to the limited availability of blood samples. Small sample volume is also a potential problem for some biological fluids such as cerebrospinal fluids. Besides, high-throughput screening (HTS) and drug discovery (combinatorial chemistry) need low level detection analyses. Moreover, low detection is a requirement for proteomic and genomic researches. Similarly, many xenobiotics are toxic, even at trace levels; they are also present in the earth's ecosystem[19–21] and they enter into our body via various pathways. Briefly, we assume the absence of these drug residues in our body and xenobiotics in the environmental matrices due to the lack of suitable analytical techniques capable of detecting them at nano levels, while these species accumulate in our body, resulting in various diseases and side effects such as carcinogenesis and failure of many vital body organs such as kidney, liver, and heart.[22–25] In such situations, it is essential to have analytical techniques which can detect drugs, pharmaceutical residues, and xenobiotics at very low concentrations in biological and environmental samples. Precisely, nano-analysis is becoming more important and scientists and regulatory authorities are requiring data on detection at nanogram levels.

Karlsson and Novotny[26] introduced the concept of nano-liquid chromatography in 1988. Since then, much advancement has been reported in this modality of chromatography; it was referred to as micro-total-analysis system (μ-TAS). It is being used as a complementary and/or competitive separation method to conventional chromatography. But, unfortunately, till 2008, no correct and scientific definition was put forward for this technique. Probably, this is due to the use of varied size columns (10–140 μm). Some definitions of nano-liquid chromatography have been found in the literature based on column diameter and mobile phase flow rates.[27–29] It has been reported that, when the chromatographic separation was carried out in capillary columns of 10 to 100 μm internal diameter, the

modality was called as nano-liquid chromatography.[30] On the other hand, some workers defined nano-liquid chromatography as the chromatographic modality having mobile flow rate at nano-mL per minute flows. But, no one has considered the detection aspect of this sort of chromatography, which is very important in analytical science. But, in 2009, Ali et al.[31] defined the exact and scientific detection of nano liquid chromatography. Taking all these facts into consideration, nano liquid chromatography (NLC) may be defined as 'a modality of chromatography involving samples in nano liter, mobile phase flows in nano milliliter per minutes, with detection at nano grams per milliliter.'[31] This definition is a complete one; it fulfills all the requirements of nano liquid chromatography. This sort of modality is generally carried out in micro chips and, hence, has also been termed as Lab-on-Chip Chromatography. Other modalities of nano liquid chromatography, such as electro-chromatography and micellar electrokinetec chromatography have been evolved to some extent. Nano liquid chromatography comprises the complete instrumental setup on a small chip (Figure 1). The micro chips may be made of silicon and other polymers. The interested reader should consult a recent book on this subject.[31] For ready reference and realization of NLC capabilities, Figures 2, 3, and 4 indicate the separation profiles of Nano-HPLC (NHPLC), Nano-CEC (NCEC), and Nano-MKEC (NMKEC), respectively.

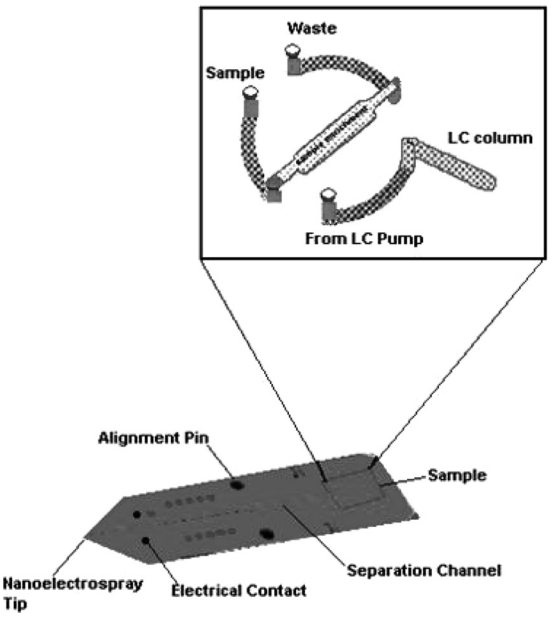

FIGURE 1 A schematic representation of Nano-HPLC micro chip.

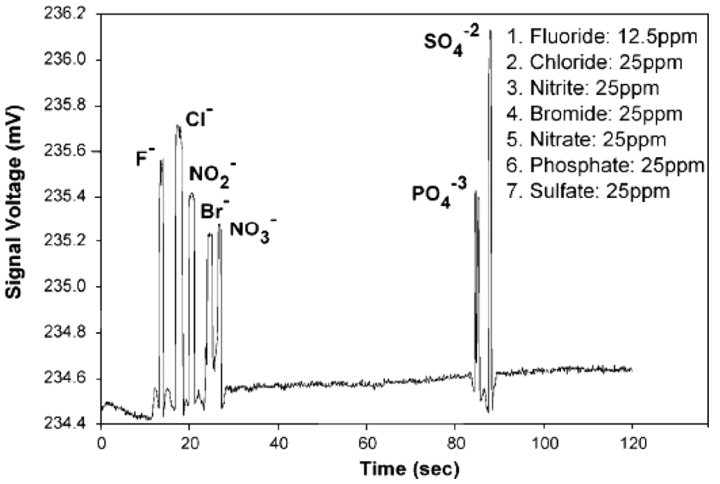

FIGURE 2 Chromatogram of seven anions by using Nano-HPLC [32].

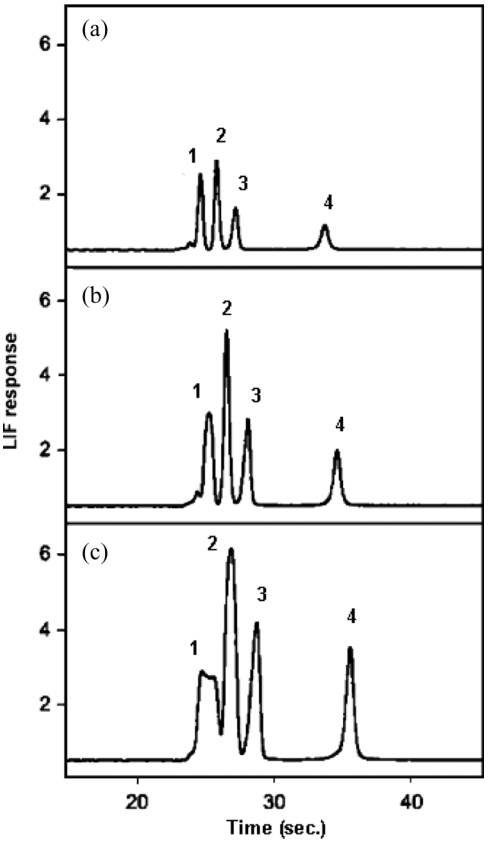

FIGURE 3 Chromatograms of the separation of 1. anthracene, 2. pyrene, 3. 1,2-benzofluorene and 4. benzo[a]pyrene in Nano-CEC coated with octadecylsilane [33].

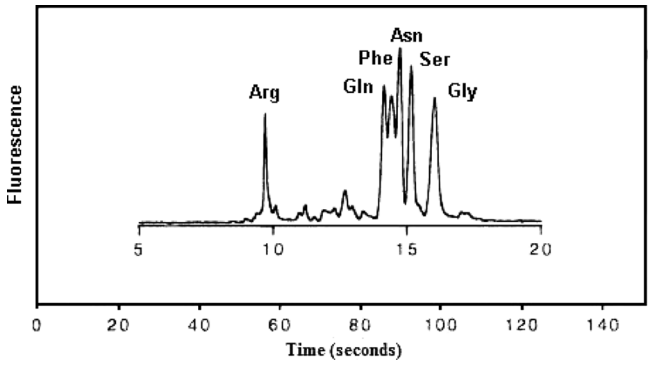

FIGURE 4 Chromatograms of fluorescein isothiocyanate labeled amino acids in Nano-MKEC.

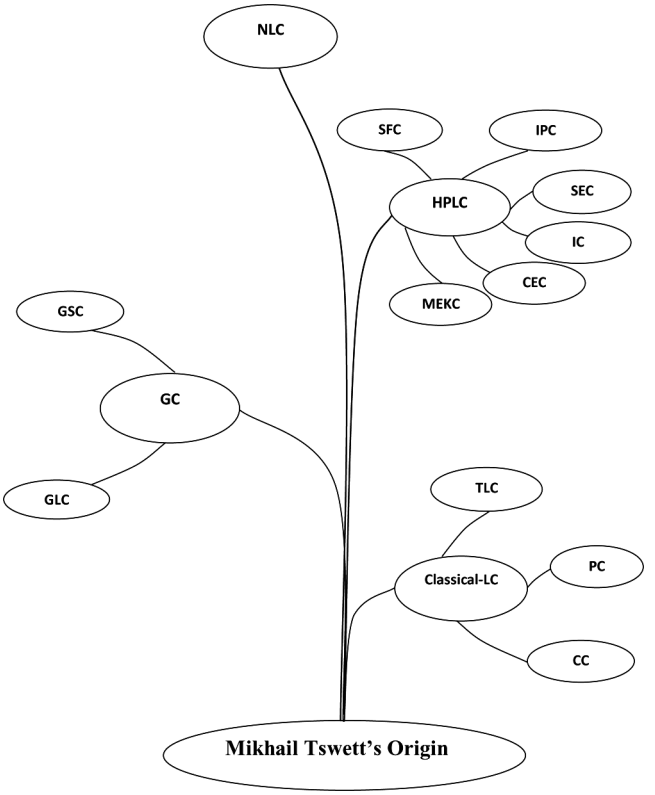

FIGURE 5 A chromatographic tree. CC: Column Chromatography, TLC: Thin Layer Chromatography, PC: Paper Chromatography, GC: Gas Chromatography, GSC: Gas Solid Chromatography, GLC: Gas Liquid Chromatography, HPLC: High Performance Liquid Chromatography, CEC: Capillary Electro-Chromatography, SFC: Super Critical Fluid Chromatography, IC: Ion Chromatography, SEC, Size Exclusion Chromatography IPC: Ion Pair Chromatography MEKC: Micellar Electrokinetic Chromatography and NLC: Nano Liquid chromatography.

CONCLUSION

Our journey of chromatography started in 1903 with the discovery by Tswett and has reached to NLC in 2009. A chromatographic tree of this journey is shown in Figure 5. The period of this journey has been interesting and remarkable. Chromatography has advanced research to a great extent and become the back bone of separation science. Nano liquid chromatography is a miracle; it can be used to measure nano amounts within a few seconds at relatively low cost. The pollution due to hazardous liquids and gases in this modality is almost zero and we can call it green or clean chromatography, being eco-friendly in nature. Furthermore, more chromatographic advancements in the coming years will be a boon for our challenging research in this century.

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