УДК 543.544

One hundred and ten years of Russian chromatography

Rudakova L.V.[1], Rudakov O.B.[2]

[1]*Voronezh State University of Architecture and Civil Engineering, Voronezh*
[2]*Voronezh State Medical Academy, Voronezh*

Received 28.01.2014

Аннотация

The stages of development of chromatography and existing scientific chromatographic schools in Russia are considered.

Keywords: chromatography, scientists of chromatography, scientific school.

Рассмотрены этапы развития хроматографии и существующих научных хроматографических школ в России.

Ключевые слова: хроматография, ученые хроматографии, научная школа

Chromatographic partition and analysis of substances and their compounds has become a widespread method determining research methodology and design for many natural sciences in recent fifty years.

The experimental methods of identification and quantity measurement of substances including electrochemical and spectro-optical methods, X-ray and structural analysis, mass spectrometry, NMR were successfully used by the middle of the 20th century. However, the store of traditional methods for compound substances partition have appeared insufficient to solve complicated research tasks facing modern analytical chemistry.

Overcoming of the disparity between the possibilities of an individual compound study and its partition from a complex mixture of compound is associated with the development of chromatography.

It is known that the first successful chromatographic tests were performed by the Russian scholar Mikhail Semenovitch Tsvet at the beginning of the XX century. He injected an extract of green leaves into the top of a packed column with calcite powder with a simultaneous transmission of petroleum ether. The result was that different zones of the column became coloured according to the extract colours. Tsvet's discovery of chromatography was recognized by the world expert society as of one of the hundred greatest discoveries of 20th century. A comprehensive article of V.A Shaposhnikov, a reputable historiographer in analytical chemistry and analytical chromatography, have thrown light to little known facts of Tsvet's career and discovery [1].

In the beginning chromatography was not much in demand. Its latent period lasted for 20 years, during which a number of reports about its application were published. In 1932 Richard Kuhn, a German chemist and biochemist, and his colleagues separated carotinoid (1931) by chromatographic method, which proved Tsvets' discovery effective.

An important landmark in chromatographic history became a discovery of thin-layer (technique in) chromatography, made by Soviet scholars N.A. Ismailov and M.S. Shraiber in 1938. That was followed by another significant discovery of the British scientists A. Martin and R. Sing. They introduced liquid partition chromatography illustrated by separation of acetyl derivates of amino acids on the column with silica gel and with chloroform as a solvent (1940). It was then noticed that not only liquid but also gas could be used as a mobile phase. Martin and Sing' discovery of partition chromatography was awarded by Novel Prize in chemistry in 1952.

Next R. Martin and A. James developed gas chromatography by partition of silicon DS-550 coating substance and stearin acid (1952 – 1953). Further modernization of gas-solid chromatography was offered by Y. Yanak in 1953. Nonspecific character, high sensitivity of detection and a high partition capacity of columns provided wide application for gas-solid chromatography as a method of organic nature objects' analysis. That was the time when gas-solid chromatography gained momentum most rapidly.

A valuable contribution to chromatography was made by G. Swab (Germany), a founder of ion exchange chromatography (1937-1940). This method was then developed in the works of Soviet scientists Y.N. Gapon and T.B. Gapon, who perform ion separation in solution (in collaboration with F.M. Shemyakin, 1947). Moreover, they implemented Tzvet's hypothesis on chromatographic separation of substances based on the difference in solution of poorly soluble precipitations (precipitation chromatography, 1948).

A contemporary stage in ion-exchange chromatography began in 1975 with the work of the American scientists G. Small, T. Stevens, W. Bauman. The researchers introduced an innovative analytical method called ion chromatography (high performance ion-exchange chromatography with conductivity detection).

The introduction of capillary column chromatography by the employee of Perkin-Elmer company M. Golay (United States of America) in 1956 was another exceptional event. This variant presupposed inner walls of a capillary tube coated by a stationary phase, which allowed to analyze trace amount of multicomponent mixture.

At the turn of 60-70th of 20th century there was a sharp rise of interest to liquid chromatography. The development of reliable and high precision pumps of high pressure allowed to implement High Performance Liquid Chromatography (HPLC). In the beginning it was called *high pressure liquid chromatography.* The beginning of the 21st century witnessed the introduction of high precision pumps able to function at 3000 bar pressure, which in turn gave an impulse to the development of Ultra Performance Liquid Chromatography (UPLC). Unique techniques of substance structure detection including NMR-spectrometry and mass-spectrometry were successfully combined with HPLC devices. MS-HPLC method, which seemed a fantastic breakthrough a few years ago, has become a wide spread practice in analytic laboratories.

The most important milestones in chromatography history are given below [3].

- 1902-1903 – beginning of chromatography as a separation process (M.S. Tsvet).
- 1931 – revival of Tsvet chromatography (R. Kuhn, A. Vittershtayn). Study of Natural Pigments.
- 1938 – development of *thin layer chromatography* (TLC) - N.A. Izmailov, M. Schreiber. Separation of herbal alkaloids on a glass plate with unfixed layer of aluminum oxide.
- 1941 – development of *liquid- liquid chromatography* - A. Martin, R. Synge. The separation of amino acids and its acetyl derivatives on silica gel.
- 1944 – introduction of *partition liquid chromatography on paper*. - A. Gordon, A. Martin

- 1951 – definition of affinity chromatography principles. - D. Kempbel, E. Lüscher
- 1952 – introduction of *gas-liquid chromatography* - A. James , A. Martin.
- 1956 – development of *amino acid analyzer* based on ion exchange chromatography principle - S. Moore, W. Stein.
- 1957-1958 - introduction of *capillary gas chromatography* - M. Golay. The development of chromatography for narrow long metal cooper and steel columns which inner walls are coated with stationary phase.
- 1959 – discovery of *size-exclusion chromatography* - J. Porath and P. Flodin
- 1961 – development of *ligand chromatography* .
- 1962 – beginning of supercritical fluid chromatography - E. Klesper, A. Corwin.
- 1968 -1970 - development of chiral chromatography - V.A. Davankov.
- 1982-1983 – discovery of liquid-gas chromatography - L.N. Moskvin , A.I. Gorshkov.

The monograph edited by B.A. Rudenko[2] dedicated to 100 anniversary of chromatography provides a general overview of the Soviet school of chromatography and its considerable contribution to the international science. The prominent Russian scholars, discussed in the book, are Y.N. Bogoslovskiy, M.S. Vigdergauz, D.A. Vyakhirev, E.N. Gapon, R.V. Golovnya, G.A Golbert, A.B. Davankov, M.M. Dubinin, A.A. Zhukhovitskiy, N.A. Ismailov, A.V. Kiselyev, N.I. Lulova, V. P. Meleshko, K.M. Olshanova, V.V. Ratchinskiy, V.A. Rotin, K.I. Sakodynskiy, K. M. Saldadze, G.V. Samsonov, M.M. Senyavin, N.M. Turkeltaub, G.A. Tchikin, K.V. Tchmutov, M.I. Yanovskiy. To our greatest regret, remarkable scientists B.G. Belenkiy, O.G. Larionov and B.A. Rudenko have deceased in recent years, having left significant heritage to Russian chromatography.

The contemporary period in chromatography is marked by the work of several academic schools. Some of them are based in Moscow (Moscow State University, RAS). The Chair of the Department of Analytical Chemistry, MSU, a corresponding member of Russian Academy of Science O. A. Shpigun leads one of the national schools of chromatography. Their academic interests involve the theory and analytical application of HPLC and capillary electrophoresis. O. A. Shpugun and his team have introduced new mobile phases based on amino acids and polyelectrolyte and zwitterionic sorbents for ion chromatography. They have also developed criteria for chromatographic partition optimization; innovative chiral selectors based on chitosan and antibiotics for the separation of optical isomers. The scholars have introduced a system of catalytic detecting for liquid chromatography, new pseudo stationary phases for capillary electrophoresis based on aliphatic polycations.

Moscow State University is an academic base for many prominent chromatographists. Among them there is S.N. Lanin, who has introduced absorption models of retention in liquid chromatography, and a living classic of Russian chromatography I.A. Revelskiy. His range of academic interests involves chromatic-mass-spectrometry, supercritical fluid extraction, sorption concentration, chromatic distillation, component identification in complex mixtures of organic compounds, detection of ultra-small concentrations of ecotoxicants, measurement of organic compound purity. Moscow chromatography school is also represented by G. I. Tsizin, who works on the theory of dynamic sorption analysis of elements and organic compounds concentration. He has also been developing new sorbates and high performance combined sorption-spectroscopic and sorption-chromatographic analysis, including both flowing and automatic methods.

BIOCHIMMAC ST corporation, founded as a start-up at the Moscow State University and headed by S.M.Staroverov has been developing preparative liquid chromatography, introducing chromatographic methods into pharmaceutical chemistry and creating new sorbent agents (coating substances). Ivanov V.A., an outstanding scientist

engaged with the problems of ion exchange, thermodynamics and ion exchange dynamics, a Head of Stable Isotope Laboratory of Physical Chemistry Chair in the Moscow State University, is at work over the problem to increase selectiveness in the separation processes (absorption and chromatographic processes are considered to be their particular cases).

Chromatographic methods are being developed in the Absorption Method Laboratory headed by Khamisov R.H., the Vernadsky Institute of Geochemistry and Analytical Chemistry. His range of academic interests is theory and practice of absorption process concentration and substance separation. Khamisov R.H. is one of the first to work over ion exchange processes, their kinetics and dynamics in multi-phase compound systems, in which there have been developed approaches to describe them. Dolgonosov A.M., one of the most prominent specialists in the country and abroad dealing with the ion chromatography issues, works in this laboratory. His range of academic interests is ion and molecular chromatography, adsorption, ion exchange, heterophase process kinetics, physics of interatomic relations. He has carried out a new type of sorbents for HPLC– centrally-localized sorbents; he has developed production process for ion chromatography sorbents; he has introduced a range of high-selective methods based on the bi-polarity of sorbent method developed by him to detect anions and cations simultaneously. Dolgonosov A.M. has developed and created software product IONCHROM on the basis of fundamental research in the field of ion exchange balance and kinetics to simulate and optimize chromatographic analysis of ion mixture. There has been developed heterogeneous electronic gas theory; its consequences in the sphere of physical adsorption allow to do aprior calculations of adsorption and chromatographic molecule characteristics based on their structural formula.

Buryak A.K., Kalinichev A.I. working in the A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Science (IPCE RAS) appear to be well-known scientists in chromatography. Buryak A.K., a Head of laboratory on Physicochemical Chromatography and Chromato-Mass-Spectrometry Fundamentals in the IPCE RAS, works in the field of chromate-mass-spectrometry. He has suggested a method to identify separate isomers in their compounds, based on combination of chromato-mass-spectrometric research data and molecular-statistic calculations, which allows to improve essentially identification reliability for isomers with equal mass-spectra. Methods of propellant component control have been carried out at his active involvement. Kalinichev A.I. has made a great contribution in the development of surface complex formation theory and its application for description of muli-component sorbent dynamic systems.

Berezkin V.G., Davankin V.A., Yashin Y.I. are outstanding chromatographists who have become masters for more than one generation of scientists. Professor Berezkin V.G. is the Head of the Chromatography Laboratory in the A.V.Topchiev Institute of Petrochemical Synthesis. He has carried out physical-chemical fundamentals to keep chromatograph compounds in the state of gas-liquid-solid phase chromatography. There has been demonstrated that in gas-liquid chromatography it is necessary to consider not only stationary liquid phase absorption but absorption of the surface partitions with gas-carriers and solid- carriers as well. He has made a significant contribution to the development and formation of reaction chromatography fundamentals and para-phase analysis. Berezkin V.G has been fruitfully working recent years and much of his research aim at the problems and new variants of chromatography. He is the author of 20 books; the translations of much foreign fundamental research in chromatography have been carried out under his edition.

Professor Davankov V.A. is a worldwide famous scientist, Nobel Prize Nominee, a Head of the Sorption Process Stereochemistry laboratory of the A.N.Nesmeyanov Institute

of Organoelement Compounds of the RAS. He has been awarded by M.S.Tsvet medal; he has invented new phenomena in stereochemistry. His range of academic interests is chromatography, methods of separation and concentration in analytical chemistry. He has described a new principle of enantiomer separation – ligand-exchange chromatography on chiral complex formation sorbents. For the first time in liquid chromatography process numerous class racemate compounds have been broken up with the help of this method; this fact has initiated development of enantioselective liquid chromatography field. There has been suggested principle of cross-over-linked styrene polymer synthesis; series of neutral new generation polymer sorbents has been created on their basis. Sorbents have high unique sorbent capacity towards organic substances in the water and air environment. They are widely used for trace contaminant concentration and for large-scale sorbent processes in food, chemical industries and medicine.

Professor Yashin Y.I. is a famous Russian chromatographist, a Head of the Research Technical Center "Chromatography" (Scientific Production Association "Chimavtomatika", Moscow). His range of academic interests is considered to be theoretical and practical issues of gas, liquid and ion chromatography. He has supervised numerous chromatographic methods of analysis in chemical, petrochemical, gas and food industries to control environmental contamination, and in medicine as well. He has introduced physic-chemical fundamentals of gas-adsorbent chromatography; he has investigated influence of the surface chemical nature and adsorbent geometrical structure on the separation selectiveness; he has established relation between molecule structure and containment parameters.

Moskvin L.N., Zenkevich I.G., Kartsova L.A., Krasikov V.D. are considered to be the most outstanding scientists in chromatography in St. Petersburg. Professor Moskvin L.N., a Head of the Analytical Chemistry Chair in the St. Petersburg State University, has founded his own scientific school; his range of academic interests is methods of separation and concentration, chromatographic and flow analysis methods, radio-analytical methods, chemical and radiochemical technologies in the atomic power engineering. Representatives of this school have carried out basic research in the sphere of extraction chromatography; have worked out continuing two-dimensional chromatography; have performed research in chromatography sphere on block (monolith) carriers and sorbents; liquid-gas chromatography has been invented.

Professor Zenkevich I.G., a Head of the Gas Chromatography Laboratory in the Chemistry Scientific Research Institute in St. Petersburg State University and a head of the Analytical Methods laboratory in the St. Petersburg Chemical-Pharmaceutical Academy, is one of the most active Russian scientists- publicists concerning chromatography issues. His range of academic interests is problems of organic compound chromato-spectral identification, chemometrics. He has suggested effective methods of analytical parameter calculations in the chromatography field; he has been developing theory of component identification in these methods.

Kartsova L.A. is a Professor of Organic Chemistry Chair of the Chemical Faculty in the St. Petersburg State University and is also one of the leading scientist-publicist on the chromatography issues. Her most significant works are devoted to one of the fundamental problems – increase of chromatographic separation selectiveness in organic compounds of different types due to introduction of macro cyclic agents as constituents of movable and stationary phases in gas and liquid chromatography, and as constituents of working buffer electrolyte in the capillary electrophoresis regimen.

Professor Krasikov V.D. has been developing the method of thin layer chromatography, strategy of mobile phase choice to separate effectively; is the author of numerous separation and quantitative analysis methods for a great number of compounds.

Voronezh academic school in chromatography and ion exchange is led by Selemenev V.F., a Head of the Analytical Chemistry Chair of the Voronezh State University, which is considered to be the basic organization of the unique periodical "Sorbent and Chromatography Processes" (State Commission for Academic Degrees and Titles - VAK list) and initiates national and international conferences in ion exchange and membrane process "Ionita". Professor Selemenev develops the theory of ion-exchanged balanced and unbalanced processes with elements of self-organization in sorption of physiologically active substances. Representatives of his scientific school are considered to be Professor Rudakov O.B., a Head of the Chemistry Chair in the Voronezh State Architectural Building University; Professor Slavinskaya G.V., Professor Khokhlov V.Y., Rudakova L.V., a Head of the Pharmaceutical Chemistry Chair in the Voronezh State Medical Academy. An outstanding scientist Professor Shaposhnik V.A. works on Selemenev's Chair; Shaposhnik is working over the problems of membrane electro-chemistry. He has discovered non-linear ion transformations under ampholyte electrodialysis: barrier and circulatory effects, stimulated bi-polar ion transport through ion-selective membranes; he has introduced new conceptions about elementary ion transport act in ion-exchanges, based on the determinative role of the transportation reaction of hydrogen bond between fixed ions. Professor Kotov V.V. (the Voronezh State Agrarian University) has been successfully researching separation processes with ion-exchanged membrane application for years. Professor Kravchenko T.A., an honorable lecturer of the Voronezh State University, has been developing theory of sorbent redox thermodynamics, kinetics, dynamics and electrochemistry on metalliferous electronic ion exchanges.

There is no avoiding mentioning such prominent scientists-chromatographists in other Russian scientific centers as Shtykov S.N., Sumina Y.G. (Saratov), Bulanova A.V., Onuchak L.A., Platonov I.A. (Samara), Krylov A.V., Kalmanovskiy V.I. (Nizhny Novgorod), Baram G.I., Sidelnikov V.N. (Novosibirsk), Deineka V.I. (Belgorod), Sychyov S.N. (Oryol). Scientific schools are preparing new generations of chromatographists whose names have already appeared in the Russian and foreign periodicals. Russian chromatography is developing successfully, looking forward to new achievements and inventions.

This article starts a series of publications devoted to history of Russian scientist and scientific school achievements in chromatography, ion exchange, adsorption and membrane processes; editorial staff of the periodical will be grateful to authors for their publications on the present topic.

References

1.Shaposhnik V.A. 110th anniversary of the discovery of chromatography by M.S. Tswett // Sorbtsion. Khromatogr. Protsessy, 2013, Vol. № 6.S. 541-550 [in Russian].

2.Larionov O.G., Kolomiets L.N., Senchenkova Y.M. Oni byli pervymi v otechestvennoi hromatografii. V kn. 100 let hromatografii. M. Nauka, 2003. P.21-31. [in Russian].

3.Dolgonosov A.M., Rudakov O.B., Surovtsev I.S., Prudkovsky A.G. Kolonochnaya hromatografiya kak obyekt matamaticheskogo modelirovaniya, Voronezh, 2013. 400 pp. [in Russian].

Rudakova Lyudmila V. – Doctor of Chemistry, Head of the Pharmaceutical Chemistry and Pharmaceutical Technology Chair, Voronezh N.N. Burdenko State Medical Academy

Rudakov Oleg B. – Doctor of Chemistry, Science and Innovations Vice- Rector, Voronezh State University of Architecture and Civil Engineering