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Early Stages in the History of Gas Chromatography

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Highlights

The history of gas chromatography began earlier than famous Archer Martin's works

Most of the earlier chromatographic studies dealt with gas-adsorption chromatography

Early studies were carried out mostly in Germany, Austria, UK and USSR

Abstract

The creation of gas chromatography is traditionally associated with the names of Nobel Prize winner Archer Martin and his colleagues Richard Synge and Anthony James. However, sometimes references to their predecessors can be found. An investigation conducted by the authors of this article not only confirmed the reliability of these references; but in fact led to the conclusion that by 1952, which is commonly believed to be the year when gas chromatography was born, many research papers had already been devoted to this method, mainly, in its gas-solid version. These papers are considered in this article.

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Keywords:
gas chromatography,
gas-solid chromatography,
gas-liquid chromatography,
history of chromatography

The creation of gas chromatography is traditionally associated with the names of Nobel Prize laureate Archer Martin and his colleagues Richard Synge and Anthony James. Martin and Synge experimented with separation of amino acid mixtures and, while conducting experiments in 1941, they developed liquid partition chromatography [1]. In the same work, they have noted that chromatography could also be used to separate gases, although no experimental proof was provided. When developing partition chromatography, Martin and Synge invented paper chromatography in 1944, a method that received widespread use but was later almost completely supplanted by thin-layer chromatography. Later, Synge dedicated himself to the analytical protein chemistry and practical problems in the chromatographic separation of biologically important substances. Martin, however, continued his work with James, and in 1952, they invented gas-liquid chromatography [2], a method with an inert carrier gas used as the mobile (or moving) phase and an involatile liquid on a solid support used as the stationary phase. Paper [2] generated extensive interest, and since then Martin, Synge, and James have been considered pathfinders in the area of gas chromatography. The awarding of the Nobel Prize to Martin and Synge only strengthened this opinion.

There was some evidence that Martin and his colleagues had predecessors. L. Ettre [3] pointed out several researchers who, in his opinion, had conducted the first experiments on gas chromatography long before Martin. For example, Ettre mentions American scientist N.C. Turner (1943), who created, in cooperation with Burrell Co., something that can be called the world's first industrial gas chromatograph. This device could be used to partially fractionate natural gas. The device was a nearly two-meter column filled with charcoal; a heated reservoir full of mercury was attached to the bottom of the column. Mercury vapor was used as the displacer. Unfortunately (or luckily, bearing in mind that it was mercury), the device was not common. In the 1940s in Uppsala, Stig Claesson, a student of Nobel Prize laureate Arne Tiselius, created a device that made it possible to examine liquids and gases on charcoal columns using the chromatographic technique. Ettre claims that the installation, which was big enough to fill an entire room, was recognized as operational; there was an article written about it [4], but then it was completely forgotten. Claesson himself told a story, that in 1947, Arnold Beckman, the founder of company Beckman Instruments, was intrigued by the device and even was going to produce it, but later abandoned the idea because he considered the apparatus too complex and gas chromatography itself a dead end.

We set ourselves the task of studying the prehistory of gas chromatography in greater detail. In pursuing this goal, we had absolutely no attention to lessen the significance of the works by Archer Martin and his colleagues; these works did their important part.

Below, several different modes of chromatography arediscussed; we would like to clarify some of the used terms, especially the rarely used ones. Gas chromatography is considered here as a dynamic method of separation of gas (or vapor) mixtures; method is based on the movement of a mobile gas phase through a stationary phase and on different distribution of mixture components between mobile and stationary phases. Carrier gas and detector are not required for separation itself, but they are usually used in modern versions of the technique. Two types of stationary phases can be used in gas chromatography: solid adsorbents (gas-adsorption chromatography mode) or viscous and highly boiling liquids immobilized on a solid carrier (gas-liquid chromatography mode). There are several modes of gas chromatography separation. In elution mode (which is more important for analytical purposes), analyzedsample is injected into the column and then is moved along the column by the carrier gas In this mode, chromatogram (or elution curve)consists of a group of peaks. In ideal case every peak corresponds to single component of the sample. In displacement mode, a substance, which adsorbs more strongly than any component of the separated mixture, is introduced into the column (with or without the carrier gas). It is possible to obtain pure fractions of the components. In this mode, in contrast to elution mode, absorbents with high capacity can be used for preparative purposes. The third mode is a so-called frontal analysis. A mixture to be analyzed is continuously introduced into the column, and the most strongly retained component displaces the others. however, in this case, only the least retained component can be obtained in a pure form. The second zone consists of two components, the third – of three ones, and so on. In thermochromatography mode a mixture of components is injected into the column; their movement is stimulated by sequential heating of the column (by an oven moving along the column); the effect of the change of temperature is "similar" to the change of adsorbent.

1.Early works

The first known use of gas chromatography was perhaps a work by Hieronymus Brunschwig, found by A. Bittel [5]. It dates back more than 500 years ago (1512). Brunschwig described a technique for purifying alcohol by passing a mixture of alcohol and water through a metal column filled with a cotton or sponge, prewetted with olive oil. With this technique, Brunschwig managed to obtain a certain amount of pure alcohol. The sponge served in this case as the stationary carrier, while olive oil was the liquid stationary phase. Alcoholic fumes acted as the mobile phase (the same role is often performed by one of the components of a mixture in frontal analysis). It is of interest that in 1962, E. Bayer and F. Born experimentally confirmed the veracity of Brunschwig's results. It is useful to note that, in fact, it was the gas-liquid version.

Since the nature of separation in a number of chromatography versions is related to the phenomenon of adsorption, we need to make a digression about the history of studying this phenomenon and techniques based on it. At the end of the 18th century, Tobias Lowitz [6] discovered absorption of substances by charcoal. This was not the first observation of the kind, but Lowitz was the one who introduced it into science. Here is how Senchenkova [7] described this discovery. "Working at a pharmacy, Lowitz lacked reliable techniques for purifying substances from impurities. On June 5th, 1785, he accidentally came to the development of a technique based on adsorption. While evaporating a solution of tartaric acid to produce brown crystals of it, Lowitz allowed its partial carbonization due to an oversight. After stirring a coal-like sediment and allowing it to settle for another eight days, Lowitz obtained a clear solution with colorless crystals, which he had not been able to obtain by any means before. Then Lowitz started to study the phenomenon that he discovered. He used charcoal to purify medicines, drinking water, vodka, honey and other sweeteners, saltpeter,, as well as to absorb various volatile substances such as carbon dioxide, hydrogen, hydrogen sulfide, onion and garlic odors (i.e., phytoncides). The practical impact was rather large: the author's name became widely known abroad..

In the 19th century, the use of adsorbents (coals, etc.) had already been widespread for purifying various solutions as well as gaseous substances. The Genevan naturalist Nicolas-Théodore de Saussure had been studying properties of some gases and vapors coming into contact with solid adsorbents [5]. He established in 1812 that porous bodies such as pumice stone, asbestos, cork, or coal are capable of adsorbing many gases. De Saussure conducted a study of the dynamics of the process, finding that grinding the coals into powder does not always enhance adsorption. In his experiments, the adsorptive power of coal varied depending on the coal humidity and the temperature and pressure at which adsorption occurred.

Later (1863–1870), J. Hunter studied different adsorbents capable of absorbing ammonia, carbonic acid, and cyanogens (oxalic acid dinitrile). In order to determine the adsorptive capacity, he used the same method as de Saussure and described it [7] as follows: “Carefully dehumidified gas was collected in a tube overturned above mercury, and the mercury level was marked. Coal was brought to red heat and, in this condition, immersed in mercury. The mercury level was marked again 24 hours later.”

At the beginning of the 20th century, interest in the separation of gases and vapors has awakened; this, in turn, led to intensive study of gas-phase sorption. The development of gas-mask production, recuperation of solvents, and other practical problems stimulated research in the area known today as frontal analysis. The book *Chapters in the Evolution of Chromatography* [5] names such people as E. Berl, K. Andress, G.S. Bohart, E.G. Adams, and O. Schmidt.

2.Research in the 1930s

Some researchers [8] believe that Paul Schuftan (1896–1980) was the first scientist to apply gas-solid chromatography as we know it today. He was born in Breslau (Germany) but moved to England in 1936, after Hitler's rise to power. Schuftan described his research in the book *Gas Analysis in Technology* (1931) [9], originally written as a chapter for a five-volume manual on petroleum products. Starting in 1922, Schuftan worked in the area of separation of gas mixtures in industrial cracking and also engaged in extraction of hydrogen/nitrogen mixtures for ammonia synthesis and hydrogen production and for hydrogenation of coal to yield ethylene [8]. Solving these problems required appropriate gas-analysis methods, which were practically absent.

In the early 1930s, Schuftan proposed (and implemented) the method of the "adsorption analysis" (the term introduced by Schuftan) of a multicomponent gas mixture consisting of hydrogen, nitrogen, oxygen, carbon monoxide, methane, ethylene, ethane, propylene, and propane, as well as *n*-butane and isobutane. Schuftan described the procedure for separating the mixture in great detail [8]. First, he separated the mixture into several fractions by means of low-temperature activated-carbon adsorption, in which the gas with the lower boiling point and molecular weight was displaced by the fractions with higher boiling temperatures and molecular weights. Schuftan used an interferometer (see Fig.1) to observe the breakthrough of every next component. In this case, the interferometer had not yet been used as a detector in the purest sense (an interferometer was used as a quantitative device only

10 years later, in 1942, by Tiselius and Claesson). In addition, Schuftan suggested the possibility for using devices based on thermal conductivity to detect effluent gases.

Schuftan's device contained several receiving vessels (Fig. 1). The analyzed gas mixture was loaded into a coal-filled tube where hydrocarbons were adsorbed by coal, while hydrogen, nitrogen, carbon monoxide, and oxygen were immediately, without being adsorbed, fed to the first vessel until methane breakthrough. Afterwards, a carbon dioxide flow (the mobile phase) was supplied, and methane was collected in the same first vessel along with CO_2, which was absorbed by an alkali. Ethylene and ethane were the next fractions and were consecutively collected in the second and third vessels. Hydrocarbons C_3 and C_4 were collected in the fourth receiving vessel. Thus, at the end of the analysis (ideally), the following four fractions were collected: (a) H_2, N_2, O_2, CO, CH_4; (b) ethylene; (c) ethane; and (d) other hydrocarbons. Certain overlapping was of course inevitable in practice.

This methodology can be considered as the starting point in the applications of the principles of chromatography to gas analysis [8]. In fact, a combination of frontal and displacement chromatography had been used here, change of temperature was also used. Schuftan himself did not use the concept of "gas chromatography," since this term (and the concept itself) simply did not exist then. Even liquid chromatography, discovered by Mikhail Tswett 20 years earlier, was only known to a limited group of researchers. At the same time, industrial processes of gas separation and their extraction by adsorption or desorption had already been known, for example, in the extraction and purification of benzene or light hydrocarbons. Schuftan deserves great respect for implementing the method of adsorption and selective desorption in gas analysis and demonstrating the merits of gas separation.

In the 1930s, considerable research on adsorption was conducted in the USSR, mainly aimed at the development of gas masks (mostly frontal version). A special scientific research institute of sorption technologies was even created. Starting with the works by Nikolay

Zelinsky, activated coal was used as a sorbent. Nikolay Shilov, one of Zelinsky's teammates, also worked intensively in this area. He contributed to the then nonexistent gas chromatography by deriving the so-called "Shilov formula" that can be used to determine the "time of protective effect" in gas mask or what is known as the "retention time" in gas chromatography, $\theta = kL - \tau$, where θ is the time of the protective effect, L is the layer length, and k is the coefficient of the protective effect, with τ being the loss in the time of protective effect, that is, simply a correction factor [10]. This was not the only contribution from this researcher to the theory of sorption and chromatography. Shilov also trained many well-known scientists, including Mikhail Dubinin, Konstantin Chmutov, and Andrey Kiselev, who subsequently became outstanding chromatographers. Dubinin headed a department at the Military Academy of Chemical Protection and wrote a book about Shilov [11]. Jointly with Chmutov, Shilov published a number of articles on the theory of sorption. Starting in 1932, Chmutov worked at Dubinin's department. By 1950, he became one of the leading researchers in the area of chromatography and ion exchange. In 1951, Chmutov created and headed the chromatography laboratory at the Institute of Physical Chemistry of the USSR Academy of Sciences. He made significant efforts to develop and popularize this method. For example, most articles on chromatography in *The Concise Encyclopedia of Chemistry* (1967) had his name attached.

However, let us return into the 1930s, particularly, to the works by Mikhail Dubinin. In 1935–1936, Dubinin applied frontal analysis to analyze gases. He conducted research in the area of the kinetics and dynamics of sorption. As a coauthor with S. Yavich and M. Khrenova the theoretical foundations for calculating adsorbers in the fractional separation of a mixture of gases or vapors was developed [12–16]. The authors analyzed the dynamic operation of the sorbent layer, firstfor the sorption of just one vapor from the airflow. The analysis led to simple notions about using the static capacity of the layer and the linear dependence of the layer period of action on its length. WIn the presence of several vapors, the dynamics of sorption is, of course, more complicated. These theoretical considerations were tested [13] experimentally in 1936. Sorption of alcoholic and toluene fumes and their mixtures by activated carbon was studied, as well as the distribution of retained components along the length of the carbon layer [16].

The authors conducted several experiments, one of which is particularly notable. They separated several layers (1 cm each) with a thin wire mesh “in the face part and … trailers of a coal charge” (i.e., column) and passed a steam–air mixture through this construction up to the precalculated point of the complete adsorption of the components and coal-layer “saturation”. Then, these layers were removed and subjected to inert-gas thermal desorption, the sorbate was frozen, and the contents of the components in the mixture were determined “by means of chemical analysis or refractometry” (Tswett was extracting individual substances from his column in more or less the same way, but he worked with liquid components, whereas a gas was extracted here). Thus, in fact one of the world’s first analyses of a gas mixture was carried out by gas chromatography. Later, Dubinin continued developing the idea of fractional separation of multicomponent mixtures of vapors and described the principle of frontal-type gas chromatography. He talked about “the front of each component moving at a constant speed along the sorbent layer,” and in his work he presented a graph that was later coined as an external (frontal) chromatogram. The developed arrangement of the process was generalized by the authors to include the case of multicomponent mixtures of gases and vapors, a case that is of interest for fractional separation. Dubinin finished one of his papers by describing the method of fractional separation of gas and vapor mixtures with a system of adsorbers and provided the required formulas.

Some details deserve attention. Dubinin and his colleagues used an activated-coal sorbent but not in the form of coarse granules, as in the case of recuperation techniques, but in the form of fine-dispersed particles with a grain diameter of approximately 3 mm, a size that in itself makes this system similar to a gas chromatograph. Authors unambiguously indicated the applicability of the above-mentioned Shilov equation to the dynamics of sorption of separate components in the mixture. Even though the word “chromatography” did not appear in Dubinin’s two above-mentioned papers and no reference was made to Tswett’s works. Dubinin, in cooperation with Yavich and Khrenova, not only performed experiments in the yet to be discovered area of gas chromatography but also contributed to the theoretical foundations of this method. In 1952, Dubinin was offered to edit the book of collected articles *Research in the Area Chromatography* [14]. In his foreword, the editor wrote about chromatography confidently and knowledgeably.

3.Research and developments of the 1940s

In 1941 appeared several works of G. Hesse, who is considered the first to use a carrier gas [17–20], and Claesson, who is viewed by many as the father of the displacement method,. In 1941, Hesse described [18] his first experiments on applications of gas chromatography. A stream of nitrogen with bromine and iodine vapors was fed through a starch-filled tube, and a bromine-containing brown and iodine-containing blue bands could be observed. In addition, preparative separation of certain esters not amenable to separation by distillation was carried out, with silica gel used as the stationary phase and carbon dioxide as the mobile phase. The device was rather simple, as illustrated in Fig. 2 [19].

The history of this work, described by Hesse himself in [20], is curious. Then it was not rare to hear that gas chromatography has no prospects. Meanwhile, Hesse always recalled the words of Hans Meerwein, a venerable scientist, to his young colleagues: “The poor man is too educated. As soon as he has an idea, he immediately knows why it should not work and, therefore, he never tries anything”. Hesse was brave enough to try the “impossible.” The thought of replacing a liquid with a gas seemed only natural, and he began to prove it. Further research by Hesse and his collaborators trying to separate azeotropic mixtures and *cis-trans*-isomers was disrupted by his departure for war and the subsequent devastation.

Two publications by G. Damköhler and H. Theile appeared a bit later, in 1943 and 1944 [20], in which they reported separation of methanol and ethanol, as well as cyclohexane and benzene on broken brick (the adsorbent), while using a carrier gas in the role that it commonly plays in elution chromatography. In addition, they used a glycerol-charged adsorbent; in fact, this was the first (setting aside Brunschwig's experiments) example of gas-liquid chromatography (it was 1942!). However, nobody was able to learn about these works, because the editions in which they were published were not so well known. In addition, the authors worked in industrial and, most likely, secret laboratories and did not intend to develop gas-liquid chromatography as such.

The story of works [21–26] by German–Austrian chemist Erika Cremer (1900–1996) and her students that unfolded in the late 1930s–early 1940s was rather dramatic. Cremer was born in Berlin, and starting from 1940, she worked in Innsbruck (Austria). The first time she heard about chromatography was at a Hesse lecture in 1935, and in 1943, she had studied his monograph. In those years, she was interested with adsorption of gaseous substances. When she needed to find a quick and accurate method for determining acetylene and ethylene (to study the kinetics of acetylene hydrogenation), the chromatographic method proved a rather natural choice. After she had finished the work, Cremer sent it to the journal *Die Naturwissenschaften* in 1944 and soon received a galley proof of the article. However, the print shop in Vienna where the journal should have been printed was destroyed by bombing. As a result, her data were eventually published only 30 years later, in 1976, along with the history of the twists and turns of the works with her postgraduates Fritz Prior and Müller [22, 23].

Immediately after the end of hostilities, while enduring postwar recovery, lacking financing and picking many components literally from the ashes, Cremer and Prior mounted a system that possessed all the features of a gas chromatograph. A prepurified carrier gas (hydrogen) could be streamed along a column at different rates, the column was temperature-controlled, and the time of elution and the amount of a component were determined by a detector based on the difference in the heat conductivities of the components (Fig. 3) [24]. The stationary phase was activated coal, kieselguhr, or silica gel of different graining. Air–carbon dioxide, carbon dioxide–acetylene, and acetylene–ethylene mixtures were separated [25,26]. These works were presented as Prior's dissertation in 1947 and as Müller's dissertation in 1950. It was pointed out in the dissertations and in [25,26] that the proposed method (an elution technique for the first time in gas chromatography) made it possible to carry out quick and highly accurate analysis, both qualitative and quantitative, as well as to determine isotherms and adsorption heats. In addition, a relationship was revealed between the adsorption heats of separate components and the sequence of their elution.

Cremer's energy and perseverance in asserting the priority of her works, as well as the priority of other scientists (Hesse and Damköhler) via speeches at conferences, participations in discussions, etc., command respect and even admiration. In 1965, a branch of the Deutsches Museum—probably the world's biggest museum of technology—was opened in Bonn. One of the exhibits was (and perhaps still is) a device for gas-chromatographic analysis designed by Cremer and Prior. The organizers planned to present the original device dating to 1945–1947 but it had already been lost. Then, the description of this system provided by Prior in his dissertation was used to replicate the model exactly, including the homemade detector. The exhibit was demonstrated side by side with the original copy of Prior's dissertation.

Development of the theoretical foundations of adsorption chromatography is associated with the names of J.N. Wilson, D. de Vault, and E. Glueckauf. It was clear at the infancy stage of chromatography that there was a dependence between the chromatographic behavior of a retained substance and the adsorption isotherms, but a quantitative relationship between the two was considered for the first time by Wilson in 1940 [27, 28]. Wilson assumed that there was a dynamic equilibrium between the substance retained by the solid phase and the substance in its gaseous state. He used the condition that the adsorption of the substance is the only process that occurs in the column. In other words, Wilson was considering a "ideal" chromatography, in which the amount of substance retained from the gaseous state is proportional to its concentration in this phase. His ideas were furthered by de Vault in 1943 [29], who considered the possibility of obtaining the adsorption isotherms from chromatograms with tailed band edges, but also only for a single component.

Glueckauf (1908–1981) rendered a more significant contribution to the theory of gas chromatography. He was born in Germany but relocated to England when the Nazis came to power

The earliest gas-chromatographic study by Glueckauf in 1948–1949 [30] was related to separating ^{22}Ne and ^{20}Ne neon isotopes by adsorption on charcoal at –196 °C. This was the first gas-chromatographic isotope separation. The principle of operation and the apparatus described by Glueckauf are rather simple. A V-shaped tube with coal precharged with nitrogen was connected at the bottom to a neon inflow and was gradually immersed in liquid nitrogen. A small amount of nitrogen in the tube was retained, which led to a constant inflow of neon passing through the low-temperature area. Since the ^{22}Ne isotope is much better retained on coal than ^{20}Ne, the top of the column was enriched with the ^{20}Ne isotope (mass-spectrometric analysis data). Also in 1948–1949, Glueckauf succeeded in using activated coal and hydrogen as a carrier gas to determine the content of krypton and xenon in the atmosphere and, a bit later, under radioactive decay. Common elution was used. However, this work could not be published until 1956 (most likely, for reasons of secrecy) [31].

Since Glueckauf's work dealt with separation of isotopes, i.e., with a system that contains more than one component. Glueckauf provided a complete analysis of the separation processes in a binary system [32] (1946), [33] (1949). He derived a number of equations that, after determining the concentration of extracted substances (by the elution method) and having some other constants such as the column length known, could have been used to construct the adsorption isotherm as well as to determine the purity of the extracted substances based on the adsorption curves. The condition here is that separation should occur slowly enough so that local equilibrium is established between the solution and adsorbent over the entire tube length [32]. Glueckauf also suggesteda version of elution chromatography in which the component is a coloring agent (1947) [34]. In this case, the propagation rate along the column can easily be measured and the adsorption isotherm can be constructed with high accuracy.

M.M. Senyavin was the first or one of the first scientists, who carried out chromatographic studies in the USSR in 1947–1949 [35]. He used gas-adsorption mode with silica gel as a stationary phase and nitrogen as a carrier gas. Effect of different factors, namely, temperature, length of adsorbent layer, and rate of the carrier gas flow, on the separation of benzene and cyclohexane mixtures (50/50%) was studied.

At that time, Mark Moiseevich Senyavin (1917–1989) worked in Karpov Physico-Chemical Institute in Moscow. Later, he was a head of the laboratory of sorption methods in Vernadsky Institute of Geochemistry and Analytical Chemistry also located in Moscow.

In the same years (1930s–1940s), the oil, petrochemical, and gas industries in the Soviet Union needed methods for separating and analyzing hydrocarbons, such as methane, ethane, and propane. It was necessary to develop appropriate procedures and apparatus for geological oil and gas prospecting (the method was created by V.A. Sokolov). Nusin Motelevich Turkeltaub (1915–1965) made a great contribution to this. He was born in Lübeck and, having graduated from the gymnasium, enrolled in the department of chemistry at the University of Warsaw. In 1939, after the division of Poland, he relocated to L'vov, where he continued his university studies. In June 1941, German planes bombed the university dormitory. Turkeltaub volunteered for the Red Army, only to be dismissed in September 1941 for "bourgeois origins." He was sent to work in Saratov, where an oil deposit was discovered and chemists were in demand. In 1944, Turkeltaub moved to Moscow to become the head of Neftegazos'emka, an organization that later became a leader in gas chromatography. It is at this organization that Turkeltaub began to develop a chromatographic technique for separate determination of microconcentrations of hydrocarbons in air [36]. In 1949, Turkeltaub published an article "Chromatographic titrimetric gas analyzer," in which he described the design of a device created for the analysis of soil air and which used the gas chromatography [37]. Turkeltaub was confident that he was the first to realize "separation of gases with concentrations on the order of thousandths and ten thousandths of a percent." He called his device a "simple gas analyzer immediately applicable in field conditions" and provided a schematic of the device (by the way, the author mentioned that the previous, TG-5A device also made partial use of chromatography to separate methane from a mixture of hydrocarbons). Water-moistened activated coal was used as the stationary phase, with air being the carrier gas. Afterwards, Turkeltaub replaced coal with a more promising, as he believed, silica gel. There was no detector. The determination was carried out (after separation) using the combustion of hydrocarbons to CO_2, its absorption by alkaline solution and titration. Turkeltaub's chromatographic titrimetric gas analyzer was the first device in Russia and one of the first in the world to use the principle of gas chromatography (Fig. 4).

Turkeltaub studied the dependence of the beginning and end of elution of methane, ethane, and propane on the total concentration and composition of the hydrocarbon mixture, the humidity of the adsorbent, and the temperature at which analysis was carried out. In addition, he studied the methane and ethane adsorption isotherms on dry and humid coal and the dependence of the shape of the elution curves on the graining of the adsorbent and the air flow rate. As a result, he established that the optimum conditions for analyzing the above-mentioned mixture are ensured with chromatography using KAD-grade activated coal with a humidity of 12 wt % at a temperature of 20°C. Articles [37,38] describe in detail both the gas analyzers and the analysis procedures.

In his book *Outline of a Novel* [39], Turkeltaub’s son-in-law Sergei Il’in briefly depicts the life of his father-in-law. Turkeltaub’s son Georgii Nusinovich has become a chemist and also works in the area of gas chromatography. A collection of articles [40] was published in memory of N.M. Turkeltaub.

The most productive period of Turkeltaub’s scientific activity was when he worked together with Aleksandr Zhukhovitskii, who was interested not so much in solving applied problems as in developing the methodology of gas chromatography itself.

Aleksandr Abramovich Zhukhovitskii (1908–1990) was born in Rostov-on-Don. For 18 years, he worked at the Karpov Physical–Chemical Institute in Moscow; and starting from 1948, he headed the department of physical chemistry at the Moscow Institute of Steel and Alloys. He conducted research in the theory of chromatographic band tailing and separation of substances and studied detection and new methods in chromatography. Zhukhovitskii considered the thermal factor as the most important due to its ability to alter the sorption properties of a sorbent over time and column length; he therefore placed special emphasis on the development of thermal methods.

In cooperation with Turkeltaub, Zhukhovitskii studied the effect of temperature variations on the chromatographic process; in 1951, the two of them developed chromatographic analysis, which they called chromathermography. This method combined the advantages of thermal desorption and elution chromatographic analysis, which on their own had been unable to ensure an acceptable level of separation of components in various mixtures (band “smearing,” etc.) [41,42]. The method consisted in simultaneous movement of the furnace and passing of a “solvent” flow along a layer containing the mixture being separated at its front edge.

The mixture of substances to be separated is sorbed ona silica gel in a vertical colum. The column with the silica gel is loaded into a large furnace that contains a small moving cylindrical furnace that can heat separate zones. Air (the carrier gas), prepurified and heated to the needed temperature, is sucked through the column at a certain rate (measured by a rheometer), while the small furnace is lowered along the layer (the column is vertical). The gas flow leaving the column is fed to a recording gas interferometer. This technique makes it possible to vary not only the adsorbent, the flow rate, and the absorber temperature, but also furnace’s movement rate. The propagation rate of the separate components of the probe is influenced by the temperature field such that each component soon reaches the spot of the temperature field where its characteristic temperature prevails. The characteristic temperature is the temperature when the rate of moving component band is equal to the rate of oven moving. It is connected with the adsorption heat. Starting from this moment, the zone of this component moves at the speed of the field until it reaches the end of the column. The relative position of each component is fixed, with all of them moving at the same speed. This predetermines the presence of a maximum on the elution curve for each component at a certain spot. The lack of a maximum at this spot unambiguously indicates the absence of a component. The bandwidth depends on the temperature gradient of the field rather than on the rate of advancement along the column. It is interesting that a similar idea was at some point used in the USA, although to some degree unsuccessfully and for other purposes.Figure 5 shows the elution curves for chromatographic separation of a methane–ethane–ethylene–propane–propylene–butene–isobutylene mixture [42]. The volumes of the air (in cm^3) let through are plotted as the abscissae, while the ordinates are the concentrations of hydrocarbons (immediate readings of the interferometer). A very good separation of saturated and unsaturated hydrocarbons can be seen from the figure.

Another version is the heat-dynamic method, in which steady-state chromatography is coupled to frontal analysis [43]. In this case, sample was introduced continuously to the column, and temperature field (oven) moves simultaneously along the adsorbent layer. When gas portion is removed, the oven is lifted automatically and quickly, and again, moves slowly along the adsorbent layer.

A great contribution to the development of gas chromatography was made by a British scientist C.S.G. Phillips [44]. His research in this area, as well as works by Shilov and Dubinin, find their origin in the development of gas masks during the period of World War I. Phillips himself could not take part in this development, because he was born in 1924, but his college curator B. Lambert became famous precisely owing to the implementation of a gas mask device [44].

In 1946, Phillips started working on the transformation kinetics of gaseous hydrocarbons. While searching for a suitable analytical method, Phillips and Lambert turned their attention to the technique of charcoal adsorption separation of gases and designed a glass-made system for solid-phase separation of hydrocarbons by the elution method. However, soon after, they read an article by one of their colleagues to find out about the work by Claesson on the charcoal separation of hydrocarbons by the elution method. Phillips and Lambert contacted Claesson, followed his advice, and properly modified their system. The first publication on the subject appeared in 1949 [45]. Phillips was evaporating a mixture of hydrocarbons into the column with an adsorbent and then introduced a much stronger adsorbent in a nitrogen flow. The detector was based on a difference in heat conductivities. The (amount/time) chromatogram was a series of steps, each corresponding to a component (Fig. 6).

The step height characterizes the component, while the step length is directly proportional to the component content in the original mixture. Phillips was conducting these experiments with the use of columns at room temperature with substances that boil at temperatures in the range from –100ºC to 100ºC. Later, having introduced some improvements, Phillips carried out separation on a column at 100ºC; this made it possible to operate with substances that have boiling points of up to 210ºC (1952) [46]. In this way, two-, three-, and multicomponent mixtures were analyzed by charcoal gas chromatography for a number of aromatic substances (benzene, toluene, chlorobenzene, thiophene, etc.), acetates, and other organic compounds, with bromobenzene used as the displacer.

Phillips successfully applied the elution method as early as 1946, when he encountered "poisoning" of charcoal by an involatile liquid but (as he admitted himself) did not mention this data in the 1952 article [46]. When he learned about the article on gas-liquid elution chromatography by James and Martin, then (ex post facto!) it became clear to him that, first, he underrated his first experiments and, second, his knowledge of the work by the famous Claesson "put a crimp in" his appreciation of them. Not without humor, Phillips wrote [44] that one should not read too much literature before embarking on experiments in a new field. This recalls the above quote from Meerwein.

The story of how another British scientist N. Ray "entered" gas chromatography is related to the chemistry and applications of polyethylene [47]. Polyethylene was obtained in England in 1933, and in 1939, its industrial applications commenced. During the first postwar years, the efforts of many researchers were directed toward purification of ethylene to produce high-quality polyethylene. In 1949, Ray started his work in this area with fractional distillation and analysis of over one hundred fractions of unsaturated hydrocarbons [47]. The analysis procedure consisted of ozonization and transformation of the resultant carbonyl compounds into their crystalline derivatives. As successful as it was, this analysis was of little use in practical terms. At this time, Ray heard about Phillips' work on displacement gas chromatography [45] and immediately (after a conversation with Phillips) began implementing this method as applied to ethylene purification, attaining good results in the end. However, he had to pass 56 L of ethylene through a column at –80ºC and then displace impurities by slow heating to room temperature. It was Phillips again who advised Ray to speak to Martin, and in 1950, when they met, Martin and James told Ray in detail (prior to their first publication!) about the method of gas-liquid partition chromatography they had been developing to analyze a mixture of fatty acids. In November of the same year, Ray designed the first gas chromatograph capable of separating hydrocarbons by means of partition chromatography with a detector that measured heat conductivity. The stationary phase was kieselguhr coated with bis(3,5,5-trimethylhexyl)phthalate. This chromatograph was used to separate and analyze milligram amounts of mixtures of volatile organic compounds of different composition, including hydrocarbons, alcohols, simple and compound ethers, aldehydes, and ketones (1954) [48].

One of Ray's achievements was to use a syringe to insert the sample into the column. When Ray came up with this idea, he went to a hospital and a nurse gave him a set of syringes. Ray with humor described [47] the following situation with a catharometer. When talking to Martin, Martin suggested using a catharometer to detect the substances being separated. Martin thought that it was his idea. However, in fact, Ray had already been using "a pair of thermal conductivity cells" as a monitor, which he had copied from Phillips. At that time though, Ray said nothing to Martin, as he was merely unaware of what exactly a catharometer was and did not feel it appropriate to ask, because the discussion was interrupted by the news that Martin's son was involved in a serious accident.

It is fitting that this article concludes with the works by Dmitrii Vyakhirev (1909–1984). Starting from 1950, Vyakhirev headed the laboratory of gas chromatography at

Lobachevsky Gorky University. In the early 1950s, he developed the so-called volume-chromatographic method of gas analysis [49]. The method is essentially as follows. The column with an adsorbent is blown through with a current of CO_2; a gauged amount of the studied gas mixture (binary ethane–propane mixture) is inserted; and CO_2 is again used to elute the column. The gas leaving the column is fed into a special burette filled with a 30% solution of KOH, where CO_2 is completely absorbed, while the components of the separated mixture that are washed out by the CO_2 current are gradually accumulated in the burette. A probe of the gas being analyzed is inserted into the column from the same burette. Accumulation proceeds in steps, with the graph of the dependence of the volume of the gas accumulated in the burette on the volume of CO_2 passed through the column being a stepwise curve. A similar device was simultaneously proposed by a Czech scientist Jaroslav Janak, a fact that he reported many years later [50].

In summary, we can conclude that the materials provided in this paper demonstrate that even prior to 1952, which is commonly taken as the year gas chromatography was born (the article [2] by James and Martin), a lot of publications had been devoted to this method. Martin’s works just earned greater fame and gave a powerful impetus to the development and application of the method.

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Figure captions

Fig.1. Schuftan apparatus for gas adsorption analysis: *1* gas burette (circ. 1,200 mL) for analyzed probe, equipped with a balancing flask containing saturated $CaCl_2$ solution; *1c* three-way valve; *2* bubble counter, filled with saturated $CaCl_2$ solution; *3* tube with P_2O_5 for desiccating gas stream; *4* tube with activated coal (circ. 3 g), placed in a Dewar vessel containing denaturated alcohol; *4a, 4b* vacuum valves; *5a, 5b* interferometer measurement and comparison dishes; *A*, *B*, *C*, *D* flasks (approximately 500 mL each) for collecting gas fractions, each dish equipped with a balancing flask (*6a–6d*) that contains an alkaline solution; CO_2 source; *6e* valve; *7e* manometer.

Fig.2. Hesse inbstallation for the first gas-chromatic separation. The column was heated with steam.

Fig. 3. Cremer and Prior device (1945–1947): *A* adsorbent for purifying carrier gas (H_2); *B* probe insertion system; *C* burette containing mercury with niveau glass for probe insertion; *D* Dewar vessel; *E* separation column (outer diameter 1 cm, with 20-cm-high layer of silica gel or activated coal); *F* heat-conductivity detector; *1–8* glass valves. The vacuum pump was connected to the system via valve *8*.

Fig. 4. Diagram of chromatograph by Turkeltaub.

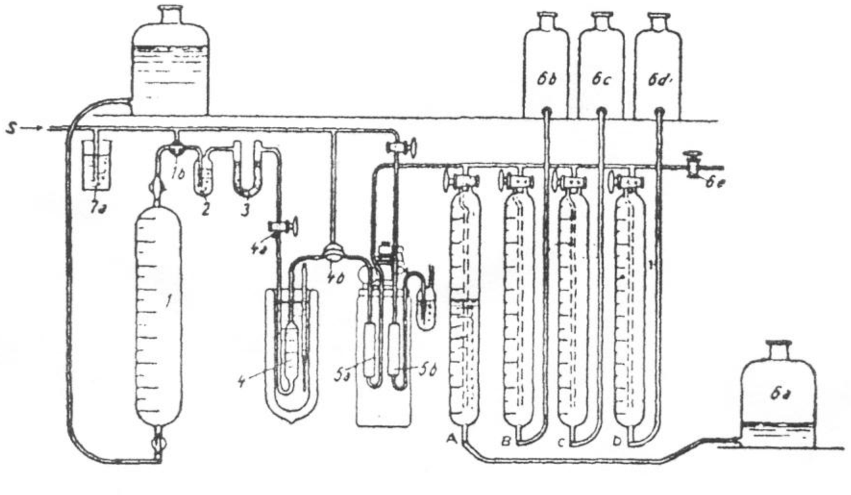
Fig. 5. Chromatogram of mixture of methane, ethane, ethylene, propane, propylene, and butene-isobutylene

Fig. 6. Chromatogram obtained by Phillips (displacement analysis).

The numbers mean different hydrocarbons:

The left graph: Water (1), iso-Pentane (2), n-Pentane (3), n-Hexane (4) , Benzene (5) . n-Heptane(6),Toluene (7) , Chlorobenzene (8)

The right graph: Water (1) ,Ether (2) ,Chloroform (3),Ethyl acetate (4), Thiophene (5) Dioxane (6) ,Pyridine (7) ,Butyl acetate (8), Chlorobenzene (9)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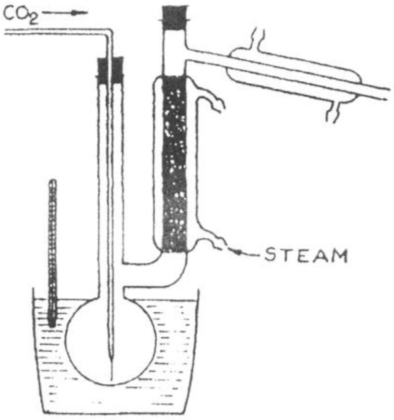
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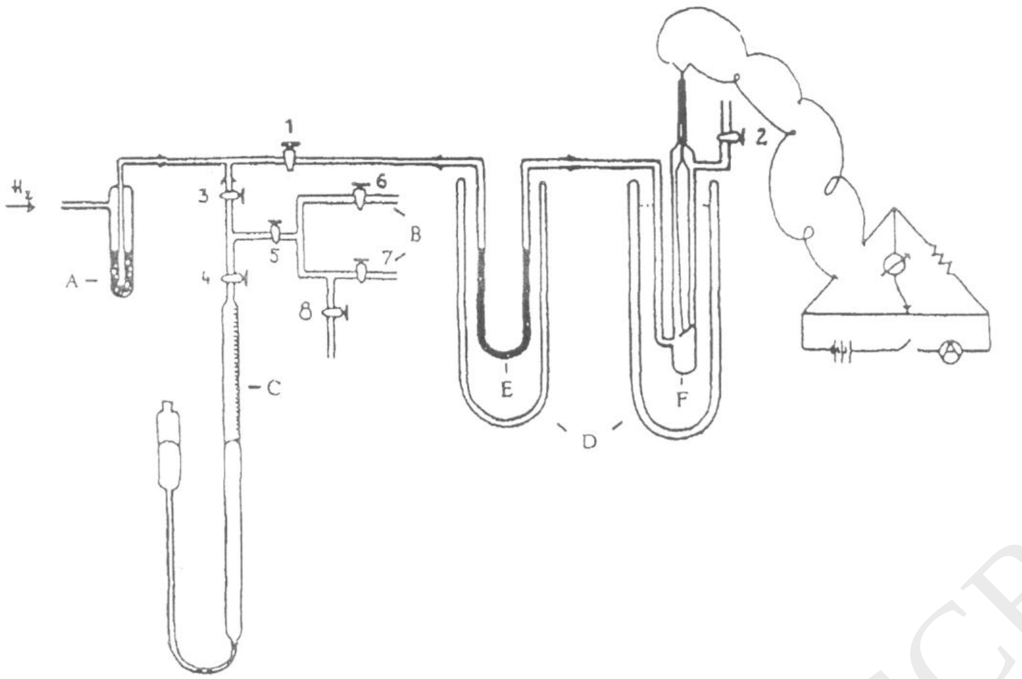
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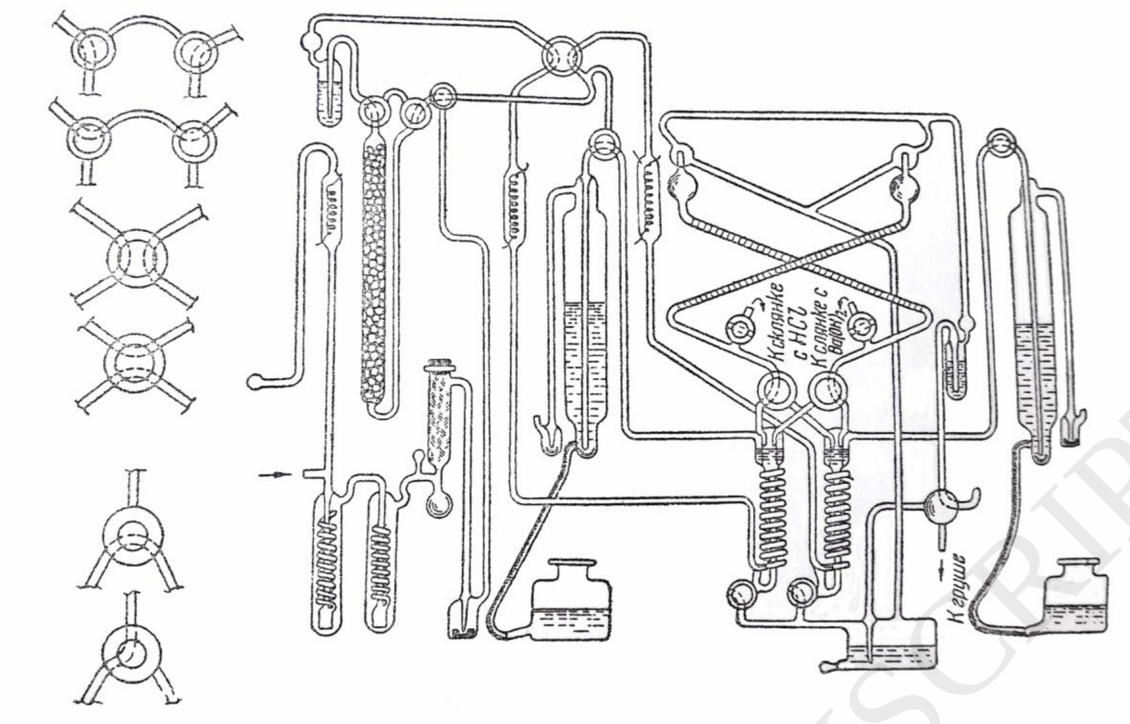
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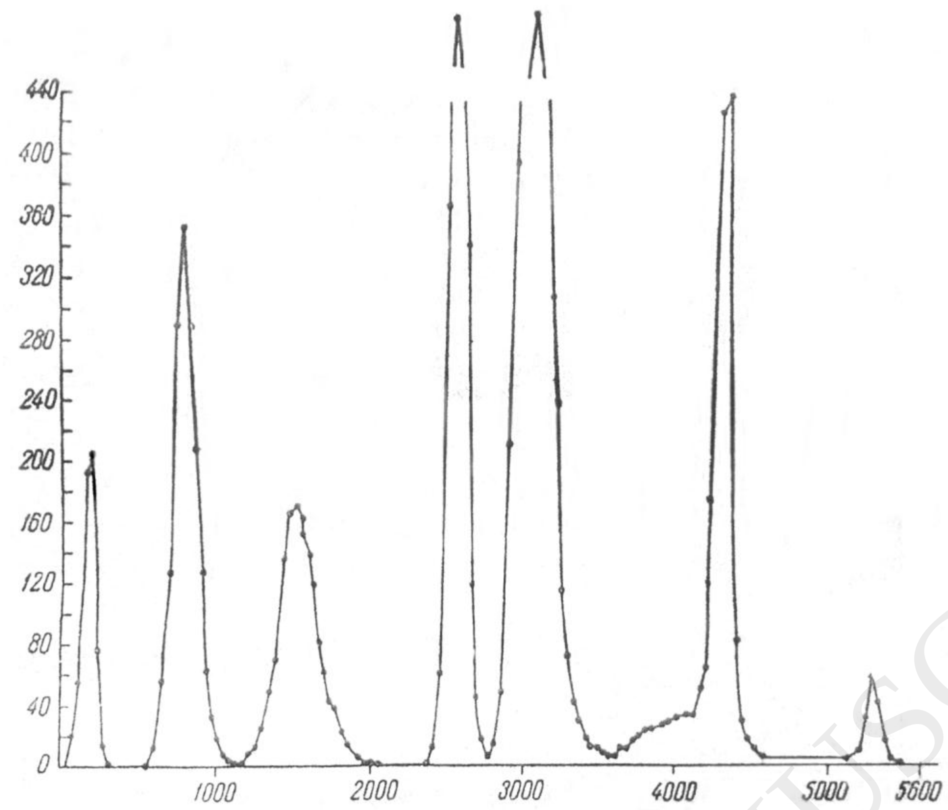
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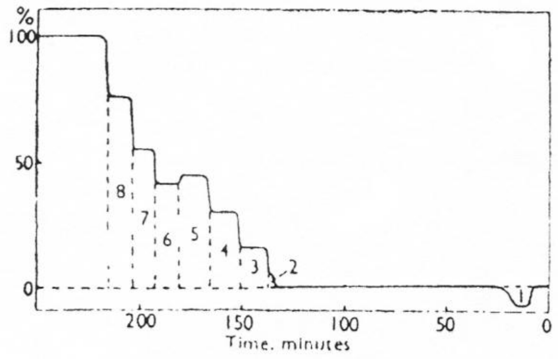
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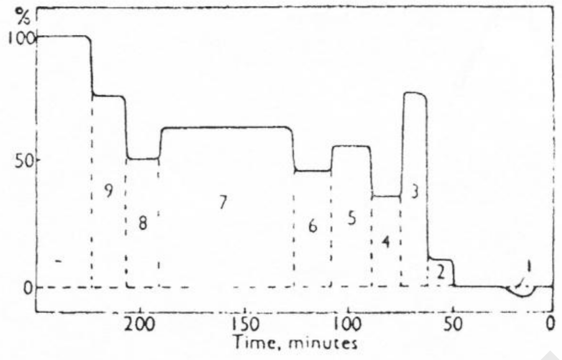
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