very little is known in the western world about the evolution of science in Russia and the Soviet Union. There are a number of reasons for this, such as the language barrier and the problem with Cyrillic script. However, in the split between the west and the east, the main problem was the secretive nature of the Communist system: contact with the capitalist countries was not only discouraged, but in fact, it was dangerous, and persons involved in it could easily be accused of collaborating with the enemies of the State. In the last decades of the Soviet Union the situation slowly started to change. Russian scientists began to publish more in western journals and also started to participate in international conferences and symposia. However, most of them could not establish the personal contact that characterizes the field of western international science.

The situation is very similar in the field of chromatography. In the past several decades a few key representatives of Russian chromatography finally became personally known to western scientists. However, still very little is known about the evolution of gas chromatography (GC) in the USSR although it had been significant, involving extensive studies on the theory and practice of the technique and in some aspects evolved on a different track than in the western world. The vastness of the field in the Soviet Union can be best illustrated by referring to the first two All-Union Conferences on Gas Chromatography held in Moscow in 1959 and 1962: the number of participants at either meeting was close to 1000, and more than 100 papers were presented at the second symposium.

One of the most prominent representatives of Russian chromatography was A.A. Zhukhovitskii. From the second part of the 1940s on, he was for decades the most prominent Russian scientist in GC development. During his long, productive life he developed a number of unique GC methods and was also involved in the development and construction of a number of gas chromatographs produced in the Soviet Union. However, outside his country very little is known about his activities. One of the main reasons for this is that, although he was invited a number of times to the international chromatography symposia dominating the field during the crucial period of the evolution of GC, he was not permitted to participate in them. In fact he was allowed to travel only once outside the Soviet bloc: in 1977, to the International Symposium on Advances in Chromatography, held in Amsterdam. Also, from the more than 300 scientific publications he authored or co-authored, only eight were published in western journals. A representative volume of GC papers published in 1961 in East Germany contained — among others — 19 papers by Russian authors, mostly by Zhukhovitskii and his associates (together with three papers by Chinese and 14 papers by Czechoslovak authors); however, this volume (1) had a limited distribution and is practically unknown in the western world. Thus, it did not help in the dissemination of his results to a broad audience. We believe that the activities of A.A. Zhukhovitskii and his school are even today of interest to the international chromatography community. Therefore, we devote the present “Milestones in Chromatography” column to some of his ideas and achievements.

**His Life**

Aleksandr Abramovich Zhukhovitskii (Figure 1) was born on 5 September 1908 in Rostov-on-the-Don, in southern Russia where the river Don flows into the Sea of Azov. He studied chemistry at the Polytechnic Institute of Novocherkassk, a town also on the Don, not far from Rostov. This college was founded in 1907 and was originally named the Donskoi Polytechnical Institute. Undoubtedly, Zhukhovitskii was an exceptional student because immediately
after graduation he was able to join the Karpov Institute of Physico-Chemistry in Moscow. This institute — named after L. Ya. Karpov (1879–1921), an active revolutionist and a very good chemical engineer — was for a long time the most prestigious research establishment for the chemical industry in the Soviet Union; it still exists as an important research institution. While at the Karpov Institute in 1933, Zhukhovitskii received the Candidate (Ph.D.) and in 1936 the Doctor of Science degree and also the academic status of a professor. He eventually advanced to the position of the assistant scientific director of the institute. In 1948 he was appointed to the chair of Physical Chemistry at the Steel and Alloys Institute in Moscow and remained affiliated with this institute for 30 years, until his retirement after his 70th birthday. However, he was also associated with some other industrial institutes such as the All-Union Research Institute for Geological Prospecting of Petroleum (VNIGNI), and from 1975 on, with the All-Union Scientific Research and Design Institute of Automation and Control Systems in the Oil and Gas Industry (VNIKANNEFTEGAS) (In Russia, they love these long names and acronyms!). His chromatography work was carried out under the auspices of these institutes. A.A. Zhukhovitskii died on 18 December 1991.

The study of adsorption of gases and vapors had a strong background in Russia, even in the period before World War I, due to the early production of petroleum in the Baku area (at that time one of the largest petroleum fields in the world) and then during that war, in connection with the development of the charcoal filters for gas masks (2). This work continued after the war and represented the basis of the generalized treatment in the books of M.M. Dubinin (1901–1993) and K.V. Chmutov (1902–1979) (3, 4). The initial work of Zhukhovitskii represented a continuation of these earlier activities and in the first years of his career he wrote a detailed treatise dealing with the adsorption of gases and vapors, which was published in 1937 (5). These investigations — just as those of Dubinin and Chmutov — already involved the use of adsorption on charcoal for the fractionation of certain vapors. This was, in effect, frontal and displacement chromatography; however, it was not identified as such. As expressed by Zhukhovitskii in an autobiographical discussion of his activities, “at that time chromatography … was little known to us” (6).

Zhukhovitskii’s early investigations were connected to his participation in the development of adsorption techniques for the protection of workers against unhealthy volatile compounds in industrial environments. In turn, these studies permitted him a quick comprehension of the chromatography concept. Within a decade he became engaged in chromatographic investigations, and in a short time he became the leading Russian scientist in this field.

The strong emphasis in Russia on research dealing with the various aspects of adsorption had important consequences. While a first-class Russian school on adsorption evolved, probably one of the best in the world, when they became engaged in gas chromatography (and as we shall see, this happened parallel to, or even earlier than in the west), Russian chromatographers inadvertently chose adsorption–desorption as the basis of separation, even for organic vapors, and switched to gas–liquid partition chromatography much later than western chromatographers.

Zhukhovitskii’s scientific interest covered a very broad field including various questions of physical chemistry and the processes related to the production of steel and alloys. However, chromatography was always his favorite field of science, and he developed a number of unique gas chromatographic techniques. It would be almost impossible to discuss all of his ideas; here we shall deal with only a few of the methods he developed, particularly with those which were also described — at least partly — in publications in western scientific journals.
Chromathermography

Zhukhovitskii started his cooperation with scientists in technological research laboratories (K.A. Gol’bert and N.M. Turkel’taub) in 1944, and together they developed some methods to analyze light hydrocarbons and other gases using adsorption—desorption on charcoal with an interferometer as the detector. However, the nonlinearity of the adsorption isotherms limited the possibilities of such analyses. In trying to eliminate the severe tailing observed, he, with Turkel’taub (1915–1965), eventually developed the elution chromatographic technique they called chromathermography. In this technique, a moving temperature field was applied along the adsorption column. Figure 2 shows a schematic of their original system.

In chromathermography the column is generally kept at an isothermal temperature; however, a small coaxial electric oven is applied that can move along the column in the direction of the carrier gas. A negative temperature gradient forms within this oven: its back is at a higher temperature than its front. At the beginning of a chromatographic run this small oven is at the column inlet and thus, the temperature gradually decreases along the column. As a result of this, the components of the sample injected into the carrier-gas stream will occupy different positions in the column according to their distribution ratios: solutes with high volatility will be toward the outlet of the column while those with low volatility will be near the column inlet.

By moving the small oven toward the end of the column, the solute bands move with it, at a rate equal to the velocity of the thermal wave (that is, the velocity of the oven). At the same time, because of the moving temperature field and the negative gradient within it, the back of a solute band is at a higher temperature than its front. This results in a focusing effect, sharpening the peaks and increasing the solute’s concentration at peak maximum.

In their basic textbook published in 1962, Zhukhovitskii and Turkel’taub (7) termed this variant stationary chromathermography. This was contrasted with the so-called nonstationary chromathermography, in which the small oven—that is, the higher temperature zone—moves in a direction opposite the carrier-gas flow.

In the original work of Zhukhovitskii and Turkel’taub, the column contained an adsorbent; later, however, they also extended the technique to partition chromatography utilizing column packings consisting of support particles coated with a liquid stationary phase.

The first paper on this technique was presented on 29 January 1951 at the meeting of the Physico-Chemical Section of the USSR Academy of Science and published soon after in the academy’s main and most prestigious journal (8). This was then followed by a number of other publications in various Russian journals: a review by A.P. Tudge (9) contains 47 titles through 1959. A somewhat sketchy discussion was included in a paper submitted by Zhukhovitskii to the 1960 International GC Symposium held in Edinburgh to which he was invited; however, he was unable to participate, and thus, his paper was simply included in the proceedings without any discussion (10). More recently the principles of chromatography were summarized by Vigdergauz, who discussed the early period of GC in the USSR (2), while a more detailed description of the various techniques developed by Zhukhovitskii employing a thermal gradient along the column was given by Berezkin et al. (11).

Based on the work of Zhukhovitskii and Turkel’taub, an instrument was also developed at VNIGNI and at KBAT (the Construction Bureau for Automation and Telemetry in the Petroleum and Gas Industries): the model KhT-2M gas chromatograph. This instrument was described at the First All-Union Conference on Gas Chromatography held in Moscow in 1959. In it the moving thermal field was produced by contact heating of the spiral chromatographic column and by blowing air along it, opposite the direction of the carrier-gas flow (12).

One of the major problems Russian chromatographers faced at that time was the lack of availability of helium and of sufficiently pure gases to be used as the carrier gas. For this reason their instruments contained an elaborate gas purification system consisting of a number of scrubbers. In addition to the usual detectors such as interferometers and katharometers, a unique detector was also developed by Russian chromatographers. In it the organic compounds were combusted over a hot platinum wire, and the heat of combustion was recorded against time.

Although we rightly consider Zhukhovitskii and Turkel’taub the inventors of chromatography, it should be noted that a moving heat zone along the column had been used earlier. In the so-called Turner-Burrell Adsorption Fractionator, a gas analysis instrument developed by N.C. Turner (13–15) and introduced in 1943 by the Burrell Corp. (Pittsburgh, Pennsylvania), a column filled with charcoal was used, and desorption was carried out by a combination of moving heat and displacement by mercury (16). Similarly in the very complicated GC system constructed by S. Claesson in the early 1940s at the University of Uppsala, Sweden, a small oven moving along an adsorption column made of quartz tube caused desorption.

Figure 2: The original apparatus for chromathermography, developed by A.A. Zhukhovitskii and N.M. Turkel’taub. 1 = carrier-gas (air) inlet, 2 = dust precipitator, 3 and 4 = scrubbers, 5 = three-way valve, 6 = flowmeter, 7 = calcium chloride drier, 8 = oven to preheat the carrier gas, 9 = sample inlet system, 10 = isothermal oven, 11 = small moving electric oven, 12 = chromatographic column, 13 = detector.
However, these systems are not related to the work of Zhukhovitskii.

Among the techniques developed by Zhukhovitskii, chromathermography was the only one that had also been investigated in the United States. In 1960 A.G. Nerheim of Standard Oil of Indiana carried out some exploratory work on the use of a moving heat field in partition chromatography (18). At the same time, a detailed study was carried out by W.W. Ohline and D.D. DeFord at Northwestern University (Evanston, Illinois) (19,20). Parallel to these investigations, A.P. Tudge of California Research Corp. further elaborated on the theory of the technique (9). However, these investigations had no follow-up at that time.

It is interesting to note that in the last decade the possibility of chromathermography started to be explored again, but now in a different form: Instead of a moving furnace, the temperature gradient along the column was created by applying resistive coating with a varying thickness along a relatively short fused-silica capillary column. In this way, with a given current, the temperature will be different at a given time at different locations along the column. By programming the electric current, progressively higher temperatures are moving down the column. In this way the solute bands are compressed because the rear of each band is at a higher temperature than its front. Such systems have been described by W.A. Rubey (21,22) and J.B. Phillips (23).

The potentialities of this method were also investigated in detail by R.E. Kaiser, who further improved it; he called it reversion gas chromatography (26). The system used was essentially identical to that shown in Figure 3. During sampling — conducting the sample gas into the column — the column inlet was kept at a sufficiently low temperature so that the sample components condensed there, adsorbed by the column packing. This sampling period can take a few minutes, but also a few hours; it is only important that all the solutes of interest remain on the column. For this reason Kaiser applied a fairly low (as low as −50 °C) temperature. Next, the sample gas flow was discontinued and the column was swept only by the carrier gas. At that point the oven was switched on, and, after it warmed the initial part of the column, its movement along the column started. As a result of this operation the individual solutes moved with the velocity of the

Figure 3: Chromatographic system of Zhukhovitskii and Turkel’taub, employing the heat-dynamic method. 1 = sample gas flow, 2 = carrier-gas flow, 3 = three-way valve, 4 = calcium chloride drier, 5 = circular column containing an adsorbent, 6 = coaxial moving heater, 7 and 8 = detectors.
centrations, and in the calibration care of the many variables, diffi-
tively pointed out the problems associated with this method, such as the need for
careful control of the many variables, difficulties in the identification of the individual compounds present in such small concentrations, and in the calibration necessary if quantitative data are desired.

**Chromatography without Carrier Gas**

The common characteristic of the techniques belonging to this group is that no carrier gas is used. The sample gas or its mixture with an inert gas acting as a diluent is continuously fed into the chromatographic column and manipulated there by different means. Zhukhovitskii devoted considerable time to the investigation of these methods.

In one of the variants of chromatography without carrier gas (CWCG), plugs of the carrier gas are periodically introduced into the sample gas flow. In this way a chromatogram is obtained, similar to the one that is obtained in the conventional form of GC operation, when a finite volume of the sample is introduced into the column, is connected to the main column's outlet. Zhukhovitskii called this variant *vacancy chromatography* (27, 28).

In a modification of vacancy chromatography, finite volumes of a standard mixture are periodically introduced into the sample gas stream; this standard mixture consists of some of the solutes present in the sample gas. If the compositions of the sample gas and the standard mixture are identical, no peaks are obtained. If the concentration of a solute in the standard is lower than in the sample stream, vacancies (negative peaks) are obtained, while the reverse case results in the usual positive peaks. The technique can also be carried out by having the standard mixture flowing continuously into the column and periodically injecting finite volumes of the actual sample. This version of CWCG was named *differential chromatography* (28–30). Differential chromatography is particularly suited for process control: by using a differential katharometer, for example, changes in the composition of a process stream can easily be established.

In addition to the techniques mentioned here, Zhukhovitskii was also involved in the development of other variants of CWCG, and these as well as the theoretical background of the method have been described in a number of publications (28, 31, 32).

**Chromarheography**

Chromarheography refers to elution analysis with a flow velocity gradient along the column. Various ways can be used to achieve this: the carrier gas may be gradually adsorbed or may permeate through the walls of the column tube. Velocity waves can also be created by moving an oven — followed by a cooler — downstream along the column or by moving the column itself slowly from a fixed oven into a cooler. The gas containing the impurities to be determined is continuously fed into the column. During the passage of the gas flow the weakly sorbable trace sample components will be enriched, producing peaks at the column outlet during each passage of the velocity wave along the column. To improve separation, sometimes an additional length of column, packed with the same adsorbent as is present in the main column, is connected to the main column's outlet. Zhukhovitskii demonstrated the use of this method for the determination of trace components present in a gas, such as hydrogen, methane, and air in carbon dioxide or helium, oxygen, and nitrogen in methane (33).

**Chromadistillation**

This method lies at the boundary between chromatography and distillation and may be considered as frontal distillation under chromatographic conditions, or as chromatography in which the sample components to be resolved and their solutions are used as the stationary phase. The column is packed with inert support particles and a negative temperature gradient is applied, with the column inlet at a higher temperature than its outlet. It is also possible to temperature program the whole column while maintaining the gradient along it. During the passage of the sample through the column a number of condensation and evaporation steps take place, resulting in the complete resolution of a mixture into separate zones of pure components (34–37). Because no liquid stationary phase is used, the determination is not restricted by the volatility of the phase; therefore, the range of the boiling points of the components to be resolved could be extended and the separation of mixtures representing a boiling point range of 60–800 °C could be demonstrated (38). The technique can be used for both the analysis of small sample volumes and preparative separation. Chromadistillation can also be combined with subsequent conventional chromatographic separation, allowing the direct analysis of organic trace components in water at parts-per-billion concentrations.

**Zhukhovitskii the Man**

In this report we tried to briefly summarize the most important gas chromatographic techniques developed by A.A. Zhukho-
vitskii. There are still many other ideas that he proposed; he always presented their theoretical background as well as a brief demonstration of the feasibility of realization. Unfortunately, however, most of these remained only proposals, outlines of possibilities, without any actual practical realization. Thus, many of his ideas are buried on the pages of Russian scientific journals and — like deposits of precious metals in the earth's crust — wait for the explorer who would dig for them; he would certainly be rewarded by rich findings.

We cannot finish this discussion without saying a few words about Zhukhovitskii, the human being and helpful colleague. His door was always open to everybody who needed help or advice, and he shared his ideas with his colleagues. He liked teamwork and always tried to have his junior collaborators be involved not only in carrying out the measurements but also in the evolution of the theory and the development of the concepts. This is best illustrated by the fact that his co-authors number more than 200. He was also an excellent teacher who could guide the research of young aspirants just starting in science. During his long career 150 post-graduate students prepared their Ph.D. theses and 20 scientists received their Doctor of Science degrees under his guidance. Such productivity is more common for a small institute but not for a single senior scientist. He was also very active in the chromatography associations and served as the chairman of the Gas Chromatography Section of the All-Union Scientific Council.
Zhukhovitskii helped to expand our knowledge through the use of chromatography and significantly improved the various chromatographic methods. He should be considered as one of those principal scientists who laid down the foundation of modern gas chromatography.

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Editor's note: In the spelling of Russian names we consistently followed the rules of Chemical Abstracts for transliteration from Cyrillic. This is in some cases different than used by other western journals: for example, in German publications the name of Zhukhovitskii is spelled as Schuchowitski.

The titles of books are given in both the original language and in English.

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