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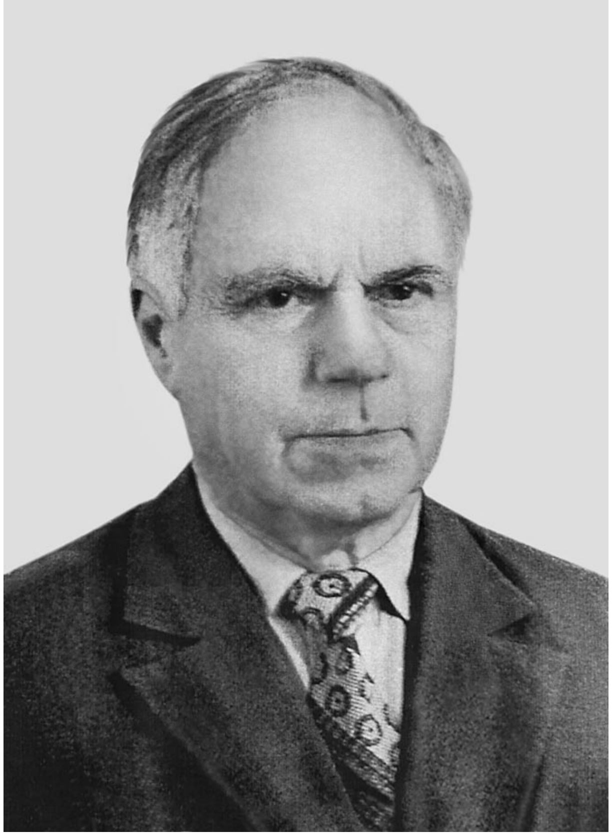
CHRONICLE

A Life in Science: I.M. Korenman (On the 100th Anniversary of His Birth)



Korenman held a prominent place among Russia's outstanding analysts. The development of microcrystal tests, microanalysis, ultramicroanalysis, radiometric analysis, extraction and coprecipitation methods, and organic analytical reagents are all associated with his name. He was a talented researcher and a brilliant teacher. His books served as handbooks for analysts for many years.

Izrail' Mironovich Korenman was born on January 5, 1904, to a photographer's family in Aleshki (at present, Tsyurupinsk). After leaving primary school in 1923, he attended Odessa Chemical and Pharmaceutical Institute, graduating from it in 1927. After finishing the institute and a post-graduate course under the supervision of analyst Prof. A.G. Fisher (at that time, the post-graduate course did not require the defense of a thesis), Korenman worked as head of the chemical laboratory of the Odessa regional Division of Labor (later, this laboratory joined the Research Institute of Labor Protection).

An examination of the research papers published by Korenman in these years shows the diversity and thoroughness of his work and its practical orientation. The lack of manuals on forensic chemistry in the Russian literature and an insistent demand for them prompted Korenman to translate *Chemical Detection of Poisons* by F. Sabalicka (1926) from the German. This book was necessary both for students and trainees studying forensic chemistry and for experts. Professional hygienists were extremely interested in the acrolein present in the air of plants where fats and fat-containing materials were heat-treated. It was necessary to develop a simple procedure for determining its traces, especially because the distinctive smell of acrolein could be masked by other odorous substances. Korenman developed a procedure for the determination of acrolein in the presence of acetaldehyde. Trichloroethylene used in extraction processes in the production of fats and oils forms dark products in iron process vessels. Korenman found an explanation for this fact and proposed the con-

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tinuous monitoring of the production processes that use trichloroethylene. He also drew attention to an imperfection of the Volhard titration of trichloroethylene (an ~85% error). Korenman also developed a procedure for the determination of 0.001 mg/dm^3 furfural vapors in air. (Before this, there was no method for the determination of furfural).

Microchemical methods were at that time being introduced more and more widely into the practice of factory laboratories. The problem facing chemists was not only to reduce the mass of the analyte but also to minimize the number of analytical operations and to simplify them. The microchemical societies organized in Austria and Great Britain and the microchemical division established in the American Chemical Society during these years point to the increased interest of analysts in microchemical methods. In some countries, special courses were organized, for example, at the University of New York, in Stockholm, etc. Korenman urged that the introduction of microchemical methods into the practice of factory laboratories be promoted by all means. His own research in the field of microchemical methods was widely diversified. He modified the Komarovskii method for the determination of alcohol to increase the sensitivity of the determination of amyl alcohol and amyl acetate in ethanol and alcoholic drinks. Korenman proposed a microchemical reaction for the titration of 0.001 M methyl orange solution that can be used for the determination of chlorine in chlorine water and chlorinated tap water. In collaboration with A.L. Teneiboim and S.I. Lyamoshko, he developed a microchemical modification of a procedure for the determination of nickel; in collaboration with Z.A. Anbrokh, he developed a procedure for the determination of antimony, arsenic, iodide, and thiocyanate traces with an error of 1.5–2%. In 1931, Korenman published the manual *Kratkoe posobie po kachestvennomu mikrokhimicheskomu analizu* (A Short Guide to Qualitative Microchemical Analysis), in which the most important microchemical reactions were described and the shapes of the resulting crystals for most cations and anions were shown in figures.

In 1936, a department of analytical chemistry was organized at Gorky (now Nizhni Novgorod) University. As was proposed by Prof. S.I. D'yachkovskii, who was dean of the Faculty of Chemistry at that time, the leadership of the department was offered in 1937 to the 33-year-old Korenman. From this time on, the scientific activities of Korenman were associated with Gorky. There he successfully investigated microanalysis and ultramicroanalysis, photometry, the theory of organic reagents, the solvent extraction of chelates, coprecipitation, radiometric analysis, and electrochemical methods. In 1939, Korenman defended his doctoral thesis on microcrystal tests at the Mendeleev Institute of Chemical Engineering, Moscow.

The research of Korenman always responded to the requirements of industry. During World War II, he solved the problems of the monitoring of technological processes and the analysis of alloys. He developed procedures and instruments for microanalysis and ultramicroanalysis. The production of microburettes and ultramicroburettes was commercialized, and designs for ultramicro scales were developed. During the war, Korenman wrote the book *Indikatsiya boevykh otravlyayushchikh veshchestv* (Detection of Chemical Warfare Agents). The book described methods for chemical detection and pointed out the possibility of the organoleptic detection of poisonous substances.

Shortly after the war, Korenman published five collections of articles titled *Analiz vozdukha promyshlennykh predpriyatii* (Analysis of Occupational Air), in which many methods for the detection and determination of air pollutants were described and critically reviewed. Special attention was paid to studies performed in Soviet labor hygiene institutes and laboratories, in particular, at the Nizhni Novgorod Institute of Occupational Hygiene and Occupational Diseases (Ministry of Public Health of Russian Federation), where Korenman was a scientific consultant for more than 30 years. Under his supervision, E.V. Gernet, O.K. Ardasheva, A.A. Belyakov, A.Ya. Tubina, A.M. Petrov, A.A. Korshakova, E.Sh. Gronsberg, M.D. Skopova, and many others defended their theses there.

At the same time, Korenman pursued the development of microanalysis and ultramicroanalysis. These studies were performed in the laboratory of microanalysis at the Research Institute of Chemistry, Nizhni Novgorod State University. This institute was organized on the initiative of Prof. M.B. Neiman in 1944. Korenman was the organizer and scientific advisor of the laboratory of microanalysis until 1960. In 1949, he published the monograph *Kolichestvennyi mikrokhimicheskii analiz* (Quantitative Microchemical Analysis), and in 1963, the monograph *Vvedenie v kolichestvennyi ul'tramikroanaliz* (Introduction to Quantitative Ultramicroanalysis), which was translated into English, Japanese, Romanian, and Polish.

In the late 1940s, the intensive development of the nuclear industry began. This field encompassed Dr. Korenman's scientific interests. Both the laboratory of microanalysis of the Research Institute of Chemistry and the department of analytical chemistry at the university performed investigations on the application of radioactive species for the solution of theoretical and practical problems in various fields of analytical chemistry: the composition and solubility of poorly soluble precipitates of metal cations, the coprecipitation of traces of metal cations with organic precipitating agents, the solvent extraction of complexes, quantitative determination with radioactive and nonisotopic indicators, etc.

Under Korenman's supervision and with the participation of F.R. Sheyanova, the composition and solubility of poorly soluble cobaltinitrites of Na^+, K^+, NH_4^+, Tl^+, Ag^+, and Pb^{2+} were studied. Conditions were found at which the ratio between different cations in the complexes remained constant, and the solubility of the complexes in water and some electrolyte solutions was studied. As a result, procedures for the radiometric determination of small amounts of potassium, thallium, silver, and lead were developed. These methods were used in the analysis of chamotte refractories from Dzerzhinsk industrial center (^{60}Co was used as an analytical indicator). One of the papers on the determination of cobaltinitrites by radioactive indicators was awarded the prize of the Academy of Sciences of the USSR in 1954.

The properties of the poorly soluble tetrathiocyanatomercurates yielding precipitates of calcium, cadmium, zinc, cobalt, and other complexes were extensively studied in complex aqueous media containing various electrolytes. Similar studies were performed for rhodizonates, thionalidates, and chromates. A study of the solid phase of tetrathiocyanatomercurates resulted in the development of a method for the determination of microgram amounts of certain metals by radiometric titration. A titration technique was used in which the titrant was not continuously introduced into the analyte solution; instead, a series of samples with equal concentrations of the target ion were prepared, and different amounts of the titrant were added to them. With the use of this technique, it was possible to monitor the progress of titration by the specific activity of both the liquid phase and the resulting precipitate. Comparison of the results increased the accuracy of the analysis.

The school of Academician V.G. Khlopin studied the theoretical and practical problems of coprecipitation mainly with examples of inorganic compounds. The manuals devoted to the action and practical application of organic precipitating agents published at that time did not mention the possibility of coprecipitation. Apparently, because of the lack of systematic studies of coprecipitation, it was believed that the coprecipitation of foreign substances under the action of organic precipitating agents was negligible. This might have been an advantage of organic precipitating agents. However, the investigations of Korenman with A.A. Tumanov, M.N. Baryshnikova, Z.I. Glazunova, and Z.V. Krainova showed that, for organic precipitating agents, coprecipitation is the rule rather than the exception. In some cases, coprecipitation is so significant that it should be taken into account in quantitative determinations. It was shown that in some cases, coprecipitation is adsorption in nature, and in other cases, it is isomorphous. Isomorphous coprecipitation in the studied cases is much higher than adsorption coprecipitation. Sometimes mixed coprecipitation is observed. The use of radioactive species for the study of coprecipitation, especially by microchemical methods, was very effective. Studying the influence of various complexing agents on coprecipitation led Korenman and Tumanov to the use of coprecipitation for the quantitative determination of certain elements. This technique was experimentally confirmed by the precipitation of cerium and zirconium with 8-hydroxyquinoline and anthranilic acid in the presence of fluoride, oxalate, citrate, and EDTA.

A large series of papers by Korenman was devoted to organic reagents for metal ions. In his first reviews, Korenman systematized analytical properties of more than 100 organic compounds of various classes and proposed a classification of organic reagents based on the composition of the resulting chelates (1946). While F. Feigl found about ten specific groups, including one for nickel, Korenman recommended about ten various functional groups for nickel, which were combined into one group according to the proposed classification. Based on the statements formulated, the mechanism of reactions of many metal ions was explained and the composition of the resulting products was predicted. Sulfur-containing reagents and acetylacetone derivatives were considered for the first time.

In November 1950, the priority problems of the theory and practice of organic reagents in inorganic analysis were formulated at a meeting on the classical methods of substance analysis in Moscow. The following priority areas were recognized: selectivity, masking ligands, and steric factors; organic coprecipitating agents; extraction processing for preconcentration of impurities or matrix elimination; color reactions and their contrast, solid-phase reactions, masking buffer solutions, and heterogeneous color reactions; and colorimetric methods for the determination of various element traces. After considerable discussion, the conclusion was that it was necessary to develop several determination methods for each element based on different principles.

The development of these areas was in fact the subject of all Korenman's subsequent activities. This is confirmed by his monographs *Fotometricheskii analiz. Metody opredeleniya organicheskikh soedinenii* (Photometric Analysis. Methods for the Determination of Organic Compounds, 1975), *Ekstraktsiya v analize organicheskikh soedinenii* (Extraction in Analysis of Organic Compounds, 1977), *Organicheskie reagenty v neorganicheskom analize. Spravochnik* (Organic Reagents in Inorganic Analysis. A Handbook, 1980), and *Novye titrimetricheskie metody* (New Titrimetric Methods, 1983).

At present, numerous disciples of Korenman are successfully developing the ideas of their teacher in the field of the theory and practice of organic reagents.

In addition to the fields of analytical chemistry mentioned above, studying extraction processes was an important part of Korenman's work. In 1956–1957, he published a series of papers in collaboration with F.R. Sheyanova concerning the extraction of chelates of certain metal ions. Solvent extraction as a method for separation, preconcentration, identification, and determination is especially promising for the determination of organic compounds with similar properties. His first papers on the extraction of the ion pairs of nitrophenol with basic dyes (in collaboration with F.R. Sheyanova and S.N. Maslennikova) were published in 1966. Later, the regularities of extraction of the ion pairs of basic dyes with aromatic acids (in collaboration with A.A. Kalugin) and higher aliphatic acids (in collaboration with I.A. Borisova) were studied.

The distinctive feature of these papers was that organic reagents were used for the determination of organic compounds. With the proposed procedures, some organic acids could be determined at a level of 10^{-5}–10^{-7} M; that is, these methods were applicable to the determination of impurities in high-purity organic compounds. Many recommendations of Korenman and his disciples found their practical application, for example, the determination of phthalic acid in benzoic acid, picric acid and dinitrophenols in mononitrophenols, higher fatty acids in various samples; the analysis of mixtures of nitrosubstituted salicylic acids; and many others.

Almost immediately after this series of papers was started, it became obvious that the extraction of ion pairs of organic compounds could not be studied thoroughly unless the phase distribution of individual substances was known. Therefore, much effort was aimed at the study of the extraction of various classes of compounds (L.N. Karyakina studied naphthylamines; T.M. Kochetkova, toluidines; B.A. Nikolaev, benzidine; A.A. Gorokhov, pyridines; V.V. Boyarkina, aminobenzoic acids; I.A. Gur’ev, aliphatic acids; T.D. Klyukvina, furfurol; G.M. Lizunova, aniline; etc.). Thus, the role of the acidity of the medium, the type of the solvent, and its physicochemical properties was studied, and the relationship between the structure of a compound and its extractability was found. The properties of extraction by mixed solvents were studied. Synergistic systems were found. Much attention was paid to the salting-in and salting-out of organic compounds in extraction.

The study of the distribution of organic compounds between two immiscible solvents formed a basis for the two-phase titration method, in which the equilibrium extraction of individual components of the extraction system is superimposed on the main chemical reaction. The use of the redox properties of some two-phase systems involving antimony(V) and chromium(VI) led to the development (in collaboration with G.M. Sergeev) of the promising field of the extraction–photometric determination of many substances, such as those that contain sulfur.

From 1977 on, a great many of Dr. Korenman’s papers were concerned with potentiometry with ion-selective electrodes. Liquid electrodes were developed for the determination of organic and inorganic substances, and their properties and field of application were studied. This was a logical development of the studies of extraction rather than an accidental change of the subject, because the electrodes used the electrochemical properties of the extraction systems studied earlier. A new method, titration in two-phase systems using liquid ion-selective electrodes, appeared on the boundary between potentiometry and extraction. This was not a formal combination of the two fields. The combination gave a new quality to the method: increased selectivity and a lower detection limit. New titration systems were proposed. The theoretical and practical principles of the new analytical method were developed, and the method found its practical application immediately.

Korenman performed his versatile investigations with his numerous disciples and shared his almost encyclopedic knowledge and scientific experience with them. Workers of factory laboratories often consulted him and always got an irrefragable opinion and practical help. With his participation, the way from conceptual design to the practical implementation of one’s results in industry became shorter.

Korenman was the author of the monographs *Analiticheskaya khimiya talliya* (Analytical Chemistry of Thallium, 1960) and *Analiticheskaya khimiya kaliya* (Analytical Chemistry of Potassium, 1964). He wrote 25 books; many of them were translated into foreign languages and published in the United States, Great Britain, France, Japan, Israel, Poland, Romania, China, and other countries. Korenman was the author of more than 800 papers. About 60 Ph.D. theses were defended under his supervision. At present, his disciples are successfully working in different regions.

The scientific and organizational activities of Korenman were also very productive. In 1939–1944, he was dean of the Faculty of Chemistry of Gorky State University. During the war, not only did he organize work on defensive positions, he also took a direct part in this work. The following is an interesting episode from Dr. Korenman’s life: By order of a member of the State Committee of Defense, S.V. Kaftanov, a captured object of unknown composition was brought to the laboratory. The object presumably contained a potent poison gas. The task was to open the object and find out its composition. On Korenman’s request, all the workers of the institute were evacuated from the building; he stayed in the laboratory alone. The analysis took an entire day and night, and the composition of the substance was found correctly.

Korenman was head of his regional organization of Mendeleev Chemical Society. For many years, he directed the urban philosophy workshop at the House of Scientists. He was the editor of *Uchenye zapiski* and the interuniversity collections *Khimiya i khimicheskaya tekhnologiya,* a member of the Commission on Analytical Chemistry of the Academy of Sciences of the USSR, and the organizer and chair of the regional workshop on analytical chemistry. Korenman’s contribution was recoghized with the Red Banner Order of Labor and a number of medals. He was awarded the title of Honored Worker of Science and Technology of the Russian Federation.

After his wife’s death, being seriously ill, Korenman moved to his son’s in Voronezh in 1984. There, he began to write the handbook *Metody kolichestvennogo khimicheskogo analiza* (Methods of Quantitative Chemical Analysis). He did not live to see its publication. This book of a little over 100 pages gives an extremely concise presentation of the principles and range of application of almost all methods of analysis.

Izrail’ Mironovich died on October 1, 1988, and was buried in Odessa.

A. A. Tumanov