ION VATAMANU

Doctor of Chemistry, Head of the Analytical Chemistry Department
(75 years after his birth)

Ion Vatamanu was a chemist, writer and public figure. He was equally passionate about both his chosen fields of activity: chemistry and poetry. Chemistry, with its perfect equilibrium of logic and precision, provided inspiration for lyrical creativity, whereas poetry writing enlivened his imagination and passion for chemistry. He loved his parents. He adored his wife Elena, whom he often gifted a sea of flowers. He loved his daughters Mihaela, Mariana, and Leontina. He loved life, and he loved people...

Ion Vatamanu was born on May 1, 1937 in the village of Costiceni of the Hotin County (now in the Chernivtsi Oblast, Ukraine). Following school graduation, he worked for one year as an assistant in the laboratory of chemistry of the local school. After that he became a student at the Department of Chemistry of the Chişinău State University (now the Moldova State University). Having obtained his college degree, Ion Vatamanu started his scientific career in the Analytical Chemistry Laboratory of the Institute of Chemistry of the Academy of Sciences of the Republic of Moldova, led by Professor Yuri Lyalikov. His research concerned the oscillographic polarography with linear variation of the electrode potential. The oscillographic polarography is a type of voltammetry that uses a dropping mercury electrode with oscillographic scanning of the applied potential. This technique is usually employed for measuring the concentration of electroactive species in solutions. An increased interest toward this method is explained by its great possibilities in the study of kinetics of electrochemical processes, such as high sensitivity and high resolution capability. The use of compounds able to form complexes with metal ions as background in the oscillographic polarography allows for a capacity augmentation in method resolution, an adjustment of mutual influence of ions, and facilitates the difficult task of analyzing mixtures of substances.

Dr. Vatamanu studied the composition and stability of complexes of metal ions with a series of organic and inorganic ligands, as well as the kinetics of their discharge on the electrode. Reversible reduction of complexes results in oscillographic characteristics based on the same theoretical principles as those used in classical polarography. A more difficult task consists in studying complexes that are discharged irreversibly on the electrode. Lack of methods for mathematical interpretation of experimental data precluded the use of oscillographic polarography for that purpose.

Composition and stability of predominant complexes in solution, as well as kinetics of discharge of complex species on the electrode can be characterized on the basis of the exchange current, equilibrium potential of reaction, and transfer coefficients α and β. These parameters were also necessary for approving the choice of complexation compound for analysis of metal ions that reduced irreversibly.

Ion Vatamanu proposed a set of mathematical expressions that employed experimental data for determination of the exchange current rate and equilibrium potentials. The deduced equations were then used to study the behavior of complexes in solution and kinetics of their discharge on the electrode. This method was employed to successfully characterize a wide series of reversibly reducing complexes of Bi^{3+} with chlorides, trioxyglutaric acid, tartrates etc., as well as compounds whose discharge on the electrode was irreversible, such as Zn^{2+} and Sb^{3+} complexes with ammonia and a series of organic acids.

For exact measurement of potentials, Ion Vatamanu developed a tandem instrument ensuring an accuracy of 1 to 2 mV. To experimentally verify the derived equations for determination of equilibrium potentials and exchange current, a novel and original construction of the universal cell was proposed. It allowed for simultaneous oscillo-polarographic determination, in the same solution, of small quantities of substances with accumulation on the mercury stationary electrode, and large amounts of compounds on the hanging mercury drop electrode.

The experimentally obtained values of equilibrium potentials were compared with data measured by other methods. It was proved that equilibrium potentials calculated through the use of equations proposed by Ion Vatamanu correlated satisfactorily with the most accurate results obtained by the thermodynamic method and differed from those by only $\pm$ 6 mV.

The research performed under the mentorship of Dr. E. Chykryzova was finalized in the PhD dissertation "The oscillographic study of complexes of Bi^{3+}, Zn^{2+} and Sb^{3+} with various ligands and their use in analysis", which Vatamanu successfully defended at the Department of Chemistry of the National University of Lviv (Ukraine) in 1971. Later, several PhD students of Professor A. Komlev (T. Vrublevsky, V. Marina and others) from Lviv University came to the Institute of Chemistry of the Academy of Sciences of the Republic of Moldova to train and study the

methods for calculating equilibrium potentials and exchange current, which they applied for data collection in their own research.

When studying the process of bismuth complex formation with trioxyglutaric acid (pH 2-4), it was observed that the oscillo-polarogram had the shape of an isosceles triangle. Such a shape is characteristic for processes of high complexity due to adsorption of depolarizator on the electrode. These processes can be influenced by a variety of experimental parameters.

Analytical application of phenomena of complex reduction from the adsorptive state opens the possibility for a significant increase in sensibility of polarographic identification of various metal ions, whereas the use of tensioactive compounds allows for individual detection of metals with comparable reduction potentials.

The use of tetrabutylammonia (as an inhibitor) and iodide ion (as an accelerator) for the polarographic determination of cadmium in the presence of palladium and indium, as well as lead in the presence of tin by I. Vatamanu and his co-workers (V. Mereanu, B. Pintilie, I. Grama and others) showed that tetrabutylammonia indeed inhibited the discharge of Cd, Pb, Sn, Pd and In, and the iodide ion is suitable as an accelerator for the detection of some metals in the presence of others. The system cadmium–lead–iodide ion is characterized by anion-induced adsorption, resulting in an accelerated discharge of cadmium and lead. At the same time, this acceleration is quantitative in nature, which allowed for the development of a quick, simple and sensitive method of determination of a series of metals in the presence of large amounts of other metals. These principles were employed in developing methods for determination of Pb in clays and limestone, and of Bi in the semiconductor system Bi-Sn, as well as of Bi and Pb in copper alloys. Dr. Vatamanu and colleagues contributed significantly to the development of polarographic and other electrochemical methods of analysis and proposed principles and concepts that led to substantial advances in analytical chemistry. Polarography (especially the oscillographic and alternative current versions) as a research method holds a distinctive place among electrochemical methods. Currently, polarographists are focused on the task of developing methods of analysis for difficult technical objects and implementing the newest experimental advances at the industrial scale.

Ion Vatamanu directed the collaborators of the Laboratory of Analytical Chemistry (V. Merean, L. Kopansky, L. Chiriac, I. Grama, B. Pintilie and others) to perform a series of important research studies of electrode adsorption processes involving numerous metal ions - As, Bi, Sn, Pb, etc. with organic ligands. The contribution of adsorption within the general electrode process was also estimated. Valuable information regarding the kinetics of discharge of adsorbed complex species was thus obtained. Selection of ligands favoring metal ion complex formation also contributed to the development of analytical methods of high sensitivity and selectivity. These methods were applied for analysis and accreditation of standards for heavy metal content in alloys and samples on the basis of Ni, Zn, Cu, and were summarized in the monograph “Polarography in the analysis of samples of heavy metals and alloys”. They found practical application in many plants of the former USSR for quality control of raw material and initial production. Drs. Ion Vatamanu and Ilie Fishtik studied a variety of complexes whose electrochemical reduction is characterized by prevalent adsorption processes. Experimental conditions and measurements were optimized in order to accelerate or inhibit surface processes. This research direction was based on a novel principle in polarography and opened up new perspectives in electro-analytical chemistry.

Theoretical studies conducted by Dr. Vatamanu and Dr. Fishtik in collaboration with colleagues at the Institute of Electrochemistry of the Academy of Sciences of former USSR aimed at developing new and diverse experimental models that would predict and closely approach real systems. These studies showed great promise in explaining the nature of highly complex processes. The expression for the isotherm of adsorption and chemical potential with the possibility of calculating different configurations of the binary complexes in the compact layer, as well as the expression for the electrostatic potential of chemically adsorbed particles were derived through this particular project. Ion Vatamanu had an essential contribution in the development of theoretical methods intended for optimization of conditions for performing chemical analysis (with Dr. I. Fishtik and Dr. I. Povar).

The theoretical group of researchers proposed a different approach to the problem of complex chemical equilibria. By introducing the definition of generalized equation of the reaction, Drs. Fishtik, Povar and Vatamanu managed to solve a series of problems of chemical thermodynamics as well as a number of problems in applied analytical chemistry. They proposed the use of change in Gibbs energy in real conditions instead of traditional approaches for calculation of complex chemical equilibria in solutions in the presence of solid phase. Besides a simplified calculation procedure, this method determined thermodynamic probabilities for chemical processes in solution to occur in the expected direction. The thermodynamic formulae for other functions such as enthalpy, entropy and heat capacity were also deducted.

The results of these studies were generalized in a monograph (written with Dr. Ilie Fishtik) and were presented in a PhD thesis (by Igor Povar). During the last years of his scientific activity Ion Vatamanu applied quantomechanical calculations (in collaboration with Dr. Tudor Spataru) to estimate the composition of complexes formed in solution and discharged on the electrode.

The research accomplishments of Dr. Ion Vatamanu were published in prestigious international scientific journals. Our narrative is only a brief summary of his many important contributions to analytical chemistry. His scientific legacy and vision is kept alive through the research successfully conducted by the collaborators of the Laboratory of Analytical Chemistry, now the Laboratory of Physicochemical Methods of Analysis and Research.

Dr. hab. I. Povar, Dr. L. Chiriac and Dr. T. Cazac