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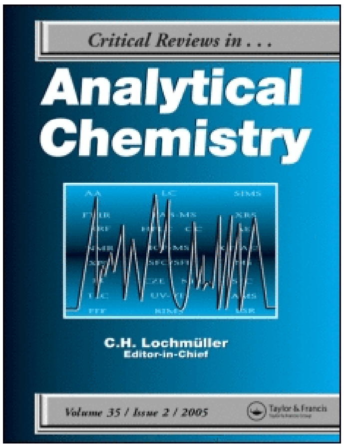

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HYDRODYNAMIC VOLTAMMETRY

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I. INTRODUCTION

During the 55 years since its discovery, polarography has become one of the most important techniques in analytical chemistry. The large hydrogen overpotential on mercury allows the measurement of anodic and cathodic currents of numerous organic and inorganic materials, and thereby, the determination of their concentration. In terms of a theoretical description of this process, the mass flux, and thus the voltammetric current, formed on the surface of the slowly moving electrode surface of the dropping mercury electrode, in a static solution, can be described with good approximation using the equations of diffusion mass transport.

However, even at the beginning of the development of the voltammetric technique, besides the dropping mercury electrode, other electrodes, first of all noble metal, and later on, graphite electrodes had also been used. From Fick's laws considering the actual experimental conditions, a relationship (Randles-Sevcik equation[1,2]) had been deduced for electrodes of constant surface area by assuming linear diffusion.

A measurement system does not have to have a static solution, however. As long as the system has linear diffusion to the electrode surface, the current can be described by the appropriate equations. One such system is where the solution flows past the electrodes.

In the first application of voltammetric methods to flowing systems, it was observed that the measured voltammetric signal depends on the hydrodynamic parameters of the measuring system. As the voltammetric signal is a result of a mass transfer process, this observation was not surprising; the theoretical study of the phenomenon had been preceded by the description of much empirical data, and many detailed experimental works.

Around the 1940s, the voltammetric method was applied under convective conditions. Various problems arose in those days which persuaded the researchers to deal with these investigations. The already mentioned empirical examination of the phenomena is characteristic for the same period of time, too.

Though Levich began to publish his papers of fundamental importance regarding the theory of this topic at the end of the 1940s, his works became widely known in the English speaking world only in 1962, when the book on "Physicochemical Hydrodynamics" appeared in English.[3]

In the 1960s and early in the 1970s, investigations were published which, mainly based upon the works of Levich, contained the theoretical derivations of limiting current relationships valid for systems with electrodes of different geometry. In certain cases these papers also contain the experimental justification of the theories.

In the 1970s, the theoretical studies of more and more complicated systems, on the one hand, and, on the other, significant developments in the practical application of hydrodynamic voltammetry are characteristic. An important trend in the development is the intensive study of the conditions of turbulent flow. Practical problems—as well as the possibilities of application—necessitated the theoretical descriptions of complicated hydrodynamic conditions as well as of the current intensities resulting from these conditions. Nowadays many attempts are being made to solve these problems.

The two trends of development, theory and practice, were separated from each other rather significantly, as it is often found in the different fields of science. Researchers dealing with theoretical problems seldom are occupied with practical problems, while the users of the methods are rarely interested in theoretical questions.[4]

In our present work we wish to deal with both domains. However, the volume of the paper does not permit us to treat every aspect of hydrodynamic voltammetry. We will examine primarily analytical aspects, so that electrochemical and electrode kinetic problems are reviewed only superficially, or not at all.

II. THEORY OF HYDRODYNAMIC VOLTAMMETRY

A. Mass Transport Processes Under Hydrodynamic Conditions

In voltammetry, the measure of the rate of a heterogeneous chemical reaction — the current density — provides information on the concentration of the component(s) taking part in the given reaction.

As is well known, the rate of a heterogeneous chemical reaction consisting of consecutive reaction steps — like an electrode process — is governed by the rate of the slowest step. In the case of electrode processes, the slowest step is most often a mass transport process involving the diffusion of reactants or products to or from the electrode surface. Mathematical descriptions of mass transport by diffusion to electrodes of different geometries results from the application of the fundamental diffusion laws. When convection accompanying the diffusion mass transport cannot be neglected, the process becomes much more complicated.

The first and so far most commonly used theory concerning the kinetics of heterogeneous chemical reactions taking place in stirred solution has been developed by Nernst.[5] According to the Nernst theory, there is a thin layer of static liquid immediately adjacent to the surface of the solid body — a layer through which diffusion of the reacting species takes place.

Beyond this layer, called the diffusion layer with thickness δ, the substance is transported by convection. Inside the diffusion layer, the solution is assumed to be unstirred, and the concentration distribution within the layer is linear. On the basis of these assumptions the flux of component taking part in the heterogeneous chemical reaction can be given as follows:

$$j = D \frac{c - c_0}{\delta} A \tag{1}$$

(For a definition of these and subsequent terms, see the glossary of symbols at the end of this review.)

The experimental observations have not proved Nernst's assumptions, namely the liquid is not stationary in the vicinity of solid surfaces ($\delta \simeq 10^{-5}$ cm), and the concentration distribution is not linear. In spite of these limitations, the Nernst relationship described by Equation 1 is an acceptable approach still being used. From Equation 1, it can be seen that every effect that decreases δ, such as an increase of the rate of flow of the solution, a viscosity decrease, etc. increases the mass flow; however, even though this description is qualitatively correct, the relationship is not suitable for the quantitative description of the effect of the above parameters.

The exact treatment of the mass transport involving convection and diffusion was given by Levich.[6] He treated the heterogeneous chemical reaction taking place in stirred solutions as being similar to heat transfer and mass transfer processes. On this basis, he derived an equation to describe the mass transport process taking place in stirred or flowing solutions, thereby considering both the diffusion and convection processes.

The fundamental statement of Levich's theory is that "the transport of a solute in a liquid is governed by two quite different mechanisms. First, there is molecular diffusion as a result of concentration differences; second, solute particles are entrained by the moving liquid and are transported with it. The combination of these two processes is called convective diffusion of solute in a liquid." Either of the two strongly differing processes, convection and diffusion, can be predominant in one or another point of the liquid. In the vicinity of the solid surface, however, both processes play significant roles. Due to this phenomena, descriptions of the mass flux must take into account both processes.

In a general case in addition to the convective diffusion, the migration of ions due to the effect of electrical attraction plays a role in an electrode process. Furthermore, the rate of a homogeneous chemical reaction may depend upon a heterogeneous chemical reaction in which it is involved. Thus, the concentration distribution relating to a heterogeneous chemical reaction can be given as follows:

$$\frac{\partial c_i}{\partial t} = \nabla(D_i \nabla c_i) - V\nabla c_i + z_i F \nabla (u_i c_i \nabla \phi) + R_i \qquad (2)$$

where D_i is the diffusion coefficient of species i, c_i is the concentration of species i, V is the flow velocity vector, z_i is the number of charges transported by i, u_i is the ionic mobility, ϕ is the strength of the electric field, and R_i is the rate of the homogeneous chemical reaction.

The first term relates to the concentration gradient of species i, and the second to the macroscopic flow velocity of the fluid and on the concentration of i. The third term relates to migration, and the fourth one is the rate of the homogeneous chemical reaction.

Equation 2, as a partial differential equation containing variable coefficients, can be exactly solved only in a few cases, usually in the cases of systems with very simple geometry. However, there are special cases in which reasonable assumptions can be made that lead to simpler equations.

Thus, in a system containing a noncompressible liquid with the electrode process being the only reaction, the value of R_i is zero. If migration can be neglected, and the diffusion coefficient is considered to be independent of the concentration, the following, much simpler relationship is obtained:

$$\frac{\partial c_i}{\partial t} + V \nabla c_i = D_i \nabla^2 c_i \qquad (3)$$

In many electrochemical problems — in addition to the above — it can reasonably be assumed that the process is steady-state when the potential of the electrode is constant.

Then, the steady convective diffusion equation is

$$V \nabla c_i = D_i \nabla^2 c_i \qquad (4)$$

The solution of the convective diffusion equation for a given system requires knowledge of the flow-velocity distribution functions. These can be obtained by solving the hydrodynamic equations of Navier-Stokes and continuity equations relating to the given system.

The systematic solution of the problems of mass transport in steady-state, such as may appear in hydrodynamic voltammetry, according to Marchiano and Arvia[7] comprises the following steps:

1. Choose a coordinate system most closely fitting the given system and base the convective diffusion equation on this.

2. Substitute the flow-rate components included by the convective diffusion general equation by the flow-velocity distribution functions.
3. Give the boundary conditions of the convective diffusion equation.
4. Transform the partial differential equation to a total differential equation.
5. Determine the concentration distribution of the component i in question by solving the differential equation.
6. Determine the rate of mass-flow with the help of the equation that describes the concentration distribution and Fick's law.
7. Determine the rate of mass transport at the surface (j). In the case of an electrochemical reaction the rate of mass transport and the current density are in correlation with each other on the basis of Faraday's law:

$$i = n_i F_i j_i$$

Boundary conditions for the equation of convective diffusion, Equation 4, most often used in hydrodynamic voltammetry are as follows:

- The concentration of the species i is constant in the bulk of solution.
- The concentration of the species at the reaction surface is zero.

Considering these boundary conditions, limiting current equations can be obtained for mass-transport-controlled electrode processes. These equations are independent of the electrode potential; that is, the potential applied to the electrode is large enough to ensure the maximum rate of electron transfer, a condition in which the concentration at the electrode surface is an equilibrium concentration approaching zero.

In electrochemical kinetics, there are also electrode processes under mixed or intermediate control, as well as under pure activation control. In the latter case, obviously, the hydrodynamics of the electrochemical system can in principle be ignored.

In the case of electrode processes under mixed control, the limiting current values measured at different hydrodynamic conditions are suitable for the calculation of the rate of heterogeneous chemical reaction, if the appropriate limiting current equations are available.

The convective diffusion limiting current equation with respect to some systems of simple geometry have been given by Levich. Later on, several other authors have treated this subject for many kinds of systems. The current equations obtained are often different, even in the case of systems of the same geometry. This originates from several factors, e.g., the hydrodynamic equations valid for a system of special geometry can be solved considering different boundary conditions and by different mathematical approaches.

The equations obtained as a result of different approaches must be considered as trials to describe reality more and more precisely.

When deciding which equation to use, the experimenter must use the equation whose boundary conditions most closely match those of the case at hand.

Most of the equations reported in literature refer to laminar flow. However, recent studies on turbulent flow have significantly extended this method in terms of theoretical knowledge and applications.

Many attempts have been made by several researchers to consider migration in hydrodynamic electrochemistry. Additionally, natural convection was also taken into account by various authors dealing with the theory of hydrodynamic voltammetry, (e.g., References 54 to 56).

B. Limiting Current Relationships for Systems Having Simple Geometry with a Laminar Flow Region

1. Rotated Disk Electrodes

Theoretically, the most amenable treatment of an electrode system is the rotated disk electrode. Levich used the solution of the Navier-Stokes equation given by Cochran-Kărmăn.[8,9] Thus, by solving the convective diffusion equation he derived the following relationship for the limiting current:

$$i_L = 0.62\, nFAD^{2/3}\, \nu^{-1/6}\, \omega^{1/2} c \tag{5}$$

On this basis the diffusion layer is

$$\delta_d = 1.61\, (D/\nu)^{1/3}\, (\nu/\omega)^{1/2} = 0.5\delta_h\, (D/\nu)^{1/3} \tag{6}$$

where δ_h is the hydrodynamic boundary layer. From a practical point of view, the equation supplies an extremely important fact, namely, that the thickness of the diffusion layer is independent of the radius, which means that the diffusion layer on the surface of the rotating disk is uniform. This property of the electrode system makes it especially suitable for obtaining reliable limiting current values, which then may serve for theoretical calculations.

In addition to Levich, several other authors[10-15] found solutions of the convective diffusion equation that are valid for the rotated disk electrode. These relationships are dealt with in detail by Riddiford[16] in his comprehensive work. Gregory and Riddiford[17] derived a current equation for the electrode by applying Cochran-Kărmăn hydrodynamic equations, but in the velocity distribution function, terms of higher order have also been taken into account. Consequently, their relationship is closer to reality than the others.

When the rate of the electrode process is controlled by both the rate of electron transfer and mass transport process, the equation obtained is the following:

$$i = \frac{nFAcD}{1.61 \cdot D^{1/3}\, \nu^{1/6}\, \omega^{-1/2} + (D/k)} \tag{7}$$

where k is the rate constant of the heterogeneous chemical reaction. On the basis of these relationships, the study of kinetics and mechanisms of different electrode processes are conveniently followed by using a rotated disk electrode.

The rotated ring-disk electrode, like the rotated disk electrode, has been deeply and frequently studied by researchers. However, the rotated ring-disk electrode, except for a few analytical applications, is used mostly for investigating the mechanisms of electrochemical processes. In the most frequently used operation, the disk and the ring are connected to two separate electrical circuits. The product of the electron transfer reaction taking place on the rotated disk electrode can be investigated as it sweeps over the ring — possibly after a chemical reaction. This technique affords an opportunity to investigate electrode processes involving generation of radicals of short life time.

According to Levich and co-workers[6,18,19] the mass flux, j_r, reaching the ring (Figure 1) is given by the following correlation:

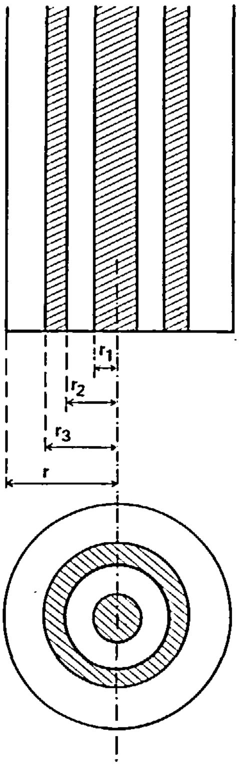

FIGURE 1. Schematic design of the rotated ring disk electrode.

$$j_r = \frac{0.4\, j_d}{1 + k_2\, \delta_{d,r}/D_2}\ \frac{r_1{}^2 r_2}{r^3}\ \frac{[1 - \tfrac{3}{4}(r_1/r_2)^3]^{1/3}}{[1 - (r_2/r^3)]^{1/3}[1 - \tfrac{3}{4}(r_1/r)^3]} \tag{8}$$

where k_2 is the rate constant of heterogeneous chemical reaction occurring at the disk, j_d is the mass flux reaching the disk, and D_2 is the diffusion coefficient of the intermediate diffusing toward the disk. (Other symbols are given in Figure 1.)

The current-potential relationships regarding the reversible electrochemical processes at rotated ring and ring disk electrodes, respectively, have been described by Albery et al.[20] Recently, a very comprehensive review on rotating disk and ring-disk electrodes with more than 700 references has been published by Opekar and Beran.[461]

2. Tubular Electrodes

For investigating streaming solutions, those systems most frequently used (both in practice and in theory) are where one section of the flow-through channel, the tube in which the solution is streaming, serves as the working electrode. The first exact description of the mass transfer problem and the solution of convective diffusion equation relating to the tubular electrode is due to Levich.[6] The most intensive theoretical studies concerning this type of electrode have been performed by Blaedel and co-workers, also employing tubular electrode in a large number of practical tasks. In addition to these investigators, several authors have studied the problem of tubular electrodes.[21-26]

If, in a tubular electrode having circular cross section there is a laminar flow, then the total tube can be divided into two parts: the so-called entrance length and the section of Poiseuille flow. In the entrance length section, friction on the tube wall slows down the flow of the solution entering the tube. After the solution is slowed down, Poiseuille's rate distribution gradually appears. If, in the tube, there is also a diffusion process, then the tube can be further divided into another part. Besides the entrance and Poiseuille's sections, there is also the section of stationary diffusion.

In the first zone, both the hydrodynamic and diffusion boundary layers begin to be formed. For the diffusional flow to the surface of the conduit the same correlations are valid as in the case of a flat plate (see below), since the radius of the tube is much greater than the thickness of the diffusion boundary layer. In the second zone, the Poiseuille profile is fully developed, but the thickness of the diffusion layer is still small as compared to the tube radius.

Different voltammetric equations have been derived related to the flow in the Poiseuille's section of the tube. The tube sections used as electrodes are generally too short to produce a stationary diffusion within them, so the current relationship concerning the Poiseuille flow is valid for the generally used electrode systems. This relationship is

$$i_L = 2.01 \cdot nFcD^{2/3} R^{2/3} X^{2/3} V^{1/3} \qquad (9)$$

where R is the radius of the tube and X is the length of the tube.

It is to be noted that the $V^{1/2}$ flow rate dependence obtained experimentally by several authors, (e.g., Reference 121) can be explained by the fact that the boundary layer along the tube section serving as the electrode is negligibly thin compared to the tube radius, therefore the wall of the tubular electrode behaves like a planar electrode (see below).

Relationships valid for tubular electrodes in the case of reversible,[28,29] quasi-reversible, and irreversible[30] electrode processes, in addition to catalytic process[31] occurring on the tubular electrode are given by Blaedel and co-workers. Their theoretical results have always been experimentally proved.

A very exciting paper has been published by Flanagan and Marcoux[32] concerning tubular electrodes. To describe the limiting current under diffusion and convective diffusion conditions, digital simulation was applied by the authors. In general, their results show very good agreement with those obtained by other types of mathematical solutions. From the point of view of the theory of hydrodynamic voltammetry, their investigations are considered to be very important, because the digital simulation technique developed by Feldberg[33] and widely employed in practice is a significant help in solving complicated electrochemical problems — like the convective diffusion.

3. *Flat Surfaced Electrodes*

A relatively simple geometric shape is the flat plate first examined by Levich.[6]

The assumptions applied when deriving equations of convective diffusion to a flat plate are generally difficult to fulfill in practice. Nevertheless, those kinds of electrodes which are usually regarded as flat have been extensively applied in practice. In his deduction, Levich assumed the following: the flow with a velocity V is laminar in the vicinity of the plate and the length *h* and width *b* of the plate is much greater than the thickness of the hydrodynamic boundary layer. The following relationship was obtained for the limiting current:

$$i_L = 0.63\, nFD^{2/3}\, \nu^{-1/6}\, bh^{1/2}\, V^{1/2}\, c \qquad (10)$$

Trümpler and Zeller[34] carried out experiments which verified the above equation, while Wranglen and Nilsson[35] proved it both for laminar and turbulent conditions. Suzuki[36] dealt with and described the diffusion limiting current equation in the case when only a part of the plate placed into the laminar flow served as the working electrode.

4. *Conical Microelectrodes*

One of the very first electrodes examined in flowing streams was the conical microelectrode. The work of Jordan and Javick,[37] in which they discussed the use of the electrode in flow systems in detail, nowadays is considered to be classical. They were the first to use the name "hydrodynamic voltammetry" for this field. Utilizing the similarity principle between the heat transfer and mass transfer processes, they derived an equation for the convective diffusion limiting current formed on the conical microelectrode.

Jordan and Javick directly used the heat transfer equation of a conical shape body, expressed with dimensionless numbers.

Dimensionless Numbers used in Heat and Mass Transfer

Heat transfer			Mass transfer		
Nusselt number	Nu =	$\frac{q_oL}{k(T-T^\circ)}$	Nusselt or Sherwood number	Sh =	$\frac{jL}{D(c-c^\circ)}$
Prandtl number	Pr =	$\frac{\nu s\varrho}{k}$	Schmidt number	Sc =	$\frac{\nu}{D}$
Reynolds number	Re =	$\frac{VL}{\nu}$	Reynolds number	Re =	$\frac{VL}{\nu}$

They substituted the dimensionless numbers existing in the relationship relating to heat transfer, by those holding for mass transfer.

$$Nu = \frac{4}{3\sqrt{3}} \cdot Re^{1/2}\, Pr^{1/3} \qquad (11)$$

$$Sh = \frac{4}{3\sqrt{3}} \cdot Re^{1/2}\, Sc^{1/3} \qquad (12)$$

This kind of treatment, i.e., the direct application of the heat transfer equations, is often used in hydrodynamic voltammetry. The deduction and solution of the convective diffusion equation valid for the given system, however, generally gives more reliable results, as the special constructions of the hydrodynamic system can better be taken into consideration.

Substituting the dimensionless numbers, Jordan obtained the following equation:

$$i_L = \frac{4}{3\sqrt{3}} \cdot nFAcV^{1/2}\, D^{2/3}\, L^{-1/2}\, \nu^{-1/6} \qquad (13)$$

where L is the slant height of the cone.

The equation relating convective diffusion to current for conical microelectrodes was derived and solved by Marchiano and Arvia[38-40] and Matsuda,[41] respectively. Their results show complete agreement with those of Jordan, with exception of the numerical constant.

5. Disk Electrodes with Perpendicular Flow

The theoretical and experimental investigations of convective diffusion processes occurring on the disk electrode placed perpendicular to the flow were done by Marchiano and Arvia.[38-40] The same problem was examined theoretically by Matsuda,[42,43] and experimentally by Bardin and Dikusar.[44]

6. Cylindrical Electrodes

Generally the system consisting of a cylindrical electrode is constructed from a flow tube, the inner wall of which serves as a reference electrode (or in certain cases as auxiliary electrode), while the cylinder placed in the tube parallel to its axis serves the working electrode. Such kinds of investigations were carried out by Bazan and Arvia,[45] Gurinov and Gorbachev,[46] Štrafelda and Kimla,[47] and by Newman.[48] From among the above works, that of Newman contains an exact theoretical treatment of the problem.

7. Spherical Electrodes

Štrafelda and Kimla,[49,50] Newman,[51] as well as Matsuda[52] derived relationships of current to boundary conditions on spherical electrodes placed in a flowing electrolyte. The frequency of spherical electrode applications in practice is negligible.

8. Dropping Mercury Electrode in Flowing Solution

The experimental work in hydrodynamic voltammetry started with the use of the most popular voltammetric electrode, namely the dropping mercury electrode. However, the theoretical treatment of the problem is complicated, and is not yet solved.

Levich's monograph, "Physicochemical Hydrodynamics",[6] deals with the problem of a falling sphere moving by the effect of force of gravity in a stationary liquid. The limiting current equation for the dropping mercury electrode placed into flow stream was given by Kimla and Štrafelda[53] on the basis of a half-empirical treatment.

C. Relationships in Turbulent Flow Systems

1. General Introduction

For a significant part of practical problems, one has to deal not only with laminar flow, but often also turbulent flow.

According to Levich,[57] turbulent flow in a fluid layer near solid surfaces occurs:

1. When the surface of the body has a nonstreamlined shape such as a sphere, cylinder, or at a corner or roughness, etc.
2. In the case of flow along a streamlined body, such as a disk or plate, if the Reynolds numbers are higher than 10^5, or according to Dreesen and Vielstich,[58] if $Re > 2 \times 10^3$ in a tube

A characteristic property of turbulent flow is the strong and disordered mixing of the fluid. Furthermore, the distinguishing feature of the turbulent flow is the chaotic and distinctly unsteady nature of the motion of the fluid. Therefore, analysts in general try to avoid the phenomenon of turbulence in their measurements. However, several authors pointed out that in many cases an advantage appears, the increased sensitivity of the measurement, as a consequence of the increased rate of mass transport.[59,60]

2. *Turbulence Frequencies of Flow*

In the case of turbulent flow, the rate of the flow unsystematically fluctuates about an average value and the disordered disturbances become superimposed on the systematic motion of the liquid. At $Re < Re_{cr}$ the disturbances occurring in the fluid are rapidly damped, but in the case of $Re > Re_{cr}$ the disturbances are not damped, moreover they reinforce each other. Even if these disturbances are of periodic nature, the superimposition of the many disturbances of various frequencies and amplitudes may lead to the establishment of a chaotic regime.

Different methods have been developed to follow the path of the fluid particles. The mixing of added dyes was observed, the moving of solid particles was examined with an ultramicroscope, or a hot wire anemometer was applied to follow the turbulent pulsations etc. A difficulty in these methods is that, with visual techniques, quantitative measurements are not possible, while the hot wire anemometer itself causes a disturbance in the flow of the fluid. The measurement of the frequencies of turbulent pulsations can be performed with the application of the Doppler effect of a laser ray, but the voltammetric technique is also very suitable for this purpose. Lewis[61] investigated the fluctuations taking place in the middle of a tube with about a 20 mm inner diameter — with the help of the Doppler effect. He found the frequency of the average fluctuation to be about 20 c/sec in the case of water flow at a 6500 Re number. According to Davies,[62] if, in this system, fluctuations with still perceivable amplitude are taken into consideration, the maximum frequency is about 50 c/sec.

The voltammetric examination of the frequency of turbulent pulsations is based on the fact that the fluctuation in the flow rate of the fluid establishes a current fluctuation on the working electrode in those cases when the mass transport solely defines the intensity of the current. Reiss and Hanratty[63] placed nickel wire electrodes of 0.13 to 1.63 mm diameter at the wall of the tube in such a way that they should not disturb the flow pattern. They examined the fluctuations of the reducing current of ferricyanide. According to their measurements, at low Re numbers, (i.e., in the case of laminar flow) no fluctuation could be observed in the current. At 2340 Re number they observed the transition interval between laminar and turbulent flow. At Re number higher than 3740 they observed a total turbulence, whereupon by increasing the Re number, the frequency of the fluctuations also increased. The aim of the above mentioned researchers was to study the conditions of flow in the viscous sublayer being formed in the vicinity of a solid surface, since this layer plays a very important role from the point of view of the determination of mass transfer taking place between a solid surface and a liquid.

Bardin and co-workers[64] investigated, in mixed solution, the Re numbers region between 4×10^3 to 5.7×10^4 with the current fluctuations taking place on a disk electrode. The electrode of 3 mm diameter was made of platinum. Their results proved that current fluctuations measured via an electrode depend on the intensity of mixing and viscosity of the solution. In the case of greater viscosity, frequency and amplitude of the oscillations decreased, while with more intensive mixing, frequency and amplitude of the oscillations increased. If stirring of the solution was stopped, the current fluctuations ceased. These experiments prove that the turbulent flow disturbs the viscous sublayer.

By means of an oscillograph Bardin and Dikusar[65] examined the limiting current for the case of turbulent flow on a disk electrode placed in the tube. They observed a current fluctuation originating from turbulent pulsations. Dikusar and Petrenko[66] measused a 10 to 15% fluctuation in the amplitude of the limiting current in the region of $2000 < Re < 3000$ on a disk electrode. With an increase in the Re number, the frequency of oscillations increased, while their amplitude decreased to ± 3 to 7% of the original value. Their result was explained by assuming oscillations of high amplitudes in the transition range.

In order to study the boundary layer forming at the electrode surface, Pungor and co-workers[67] examined the current fluctuations caused by an electrolyte solution streaming out from a jet of 0.5 mm diameter onto a microelectrode. The microelectrode of 1.2 mm diameter was placed perpendicularly to the direction of flow, and 37.7 cm/sec linear flow rate was used. By performing Fourier analysis on the current signal, they stated that a hyperbolic relationship exists between the frequency and amplitude of fluctuations in the current intensity caused by the turbulence.

They have theoretically interpreted the empirically obtained results using the turbulent dissipation of kinetic energy. In this way the following equation was obtained for the fluctuating current i_{df} superimposed on the voltammetric signal.

$$\tilde{i}_{df}(\nu) = \frac{A_R n \, FDC \left(E_{kin}\right)^{1/2}}{\pi (2)^{1/2} \delta_m^2 \, p} \nu^{-1} \qquad (14)$$

where A_R is a part of the electrode surface, δ_m is the effective thickness of the boundary layer, and p is an integer. This relationship is in good agreement with the results obtained empirically.

Accordingly, in the examination of turbulent fluctuation, the analysis of frequencies has a double significance. On the one hand, it offers a possibility of studying the structure of the boundary layer being formed between the surface of a solid substance and the liquid, and to obtain through this examination an answer to mass transfer problems. On the other hand, it makes possible the ability to decide whether or not it is necessary to use a frequency filter in analytical measurements for the elimination of the noise originating from turbulence.

3. *Characterizing Parameters of Turbulence*

For describing the transfer of momentum and mass in the case of turbulent flow, Levich introduced the concept of the coefficients ν_{turb} and $D_{turb} \cdot \nu_{turb}$ is the so-called eddy viscosity and D_{turb} is the turbulent diffusion coefficient.

According to Levich, using the known relationships of kinetic theory of gases or the similarity theory,

$$\nu_{turb} = s \Delta V$$

where s is the distance over which the velocities of turbulent pulsations change significantly. ΔV is the change in the average velocity over the distance s and D_{turb} is proportional to ν_{turb}.

Since the Re number is always very large for large scale eddies, viscosity does not play a significant role and so there is no significant energy dissipation. Thus large scale eddies are the major contributors to the kinetic energy of turbulent motion. However, superimposition of large scale eddies causes small scale eddies, whose Re number rapidly decreases. In this case, viscosity begins to exert a significant effect upon the motion of the liquid, leading to considerable dissipation of energy. The small scale eddies remove energy from the large scale eddies until all the energy from turbulence is converted into thermal energy. In a steady-state fluid flow, the process of energy transfer is also steady-state in nature. Eddies of a moderate scale receive as much energy from large scale eddies as they pass on to smaller scale eddies.

With the help of the eddy viscosity, the energy losses ε occurring in the flow per second per volume unit can be expressed by the equation

$$\epsilon = -\frac{dE}{dt} = \rho \nu_{turb} \left(\frac{\Delta V}{s}\right)^2 \qquad (15)$$

The effective eddy viscosity is very large in comparison with the ordinary viscosity

$$\frac{\nu}{\nu_{turb}} = \frac{\nu}{\Delta Vs} \approx \frac{1}{Re} \ll 1 \qquad (16)$$

By applying the coefficient of turbulent diffusion, j_{turb}, the mean material flow transferred by turbulent eddies onto 1 cm^2 surface can be expressed in the following way:

$$j_{turb} = D_{turb} \frac{\partial c}{\partial y} \qquad (17)$$

Where $\partial c/\partial y$ is the concentration gradient. The coefficient of turbulent diffusion is not the same as the coefficient of the molecular diffusion. The coefficient of turbulent diffusion characterizes the mass flow transferred by chaotic turbulent motion, while the coefficient of molecular diffusion is characteristic of molecular motion. The coefficient of turbulent diffusion is orders of magnitude larger than the value of the coefficient of molecular diffusion.

Boussinesq[68] introduced a concept analogous to the coefficient of turbulent diffusion, the so-called exchange coefficient for describing the turbulent mass transfer. Prandtl[69] defined the apparent eddy viscosity and the coefficient of apparent turbulent diffusion by interpreting the turbulent motion on the basis of kinetic gas theory.

4. Structure of the Boundary Layer

In the case of turbulent flow, the structure of the boundary layer formed in the vicinity of the surface of a solid body is far more complicated than in the case of laminar flow.

According to the Prandtl-Kărmăn[69,70] model, three zones are formed at the surface of a solid body. Adjacent to the wall, the flow is laminar and the region is the ordinary diffusion boundary layer. In the zone furthest from the wall, the fully developed region of turbulence is formed. Between the two zones is the transition zone, the viscous sublayer where turbulent pulsations become damped and molecular viscosity plays a role. Levich[57] also suggested a similar structure consisting of several layers, and he too suggested the existence of a turbulent sublayer. The structure of the boundary layer according to Levich is shown in Figure 2.

Far from the surface of the solid body ($y > \delta_h$) is the zone of developed turbulence in which the concentration is constant.

$$c_I = \text{constant} = c_o \qquad (18)$$

Both momentum and mass are transferred with the help of turbulent eddies. Closer to

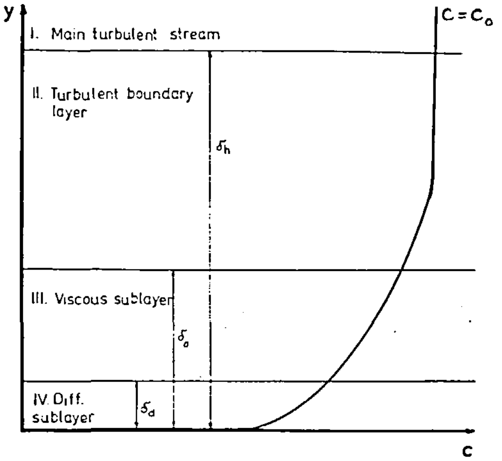

FIGURE 2. The structure of the boundary layer according to Levich, for turbulent flow.

the wall ($\delta_o < y < \delta_h$) in the turbulent boundary layer, the average velocity and concentration decrease according to a logarithmic relationship. For the latter case, the following relationship is valid:

$$c_{II} = \frac{j}{a \cdot v_o} \ln\left(\frac{y}{\delta_h}\right) + c_o \qquad (19)$$

where a and c_m are constants, v_o is the velocity of eddies characteristic of the flow, and j is the mass flux. In this region, molecular viscosity and diffusion do not play a significant role.

Still closer to the wall ($\delta_d < y < \delta_o$), in the viscous sublayer, turbulence eddies become so small that the momentum transferred by molecular transport exceeds that transferred by turbulence eddies. But since the diffusion coefficient D is smaller than kinematic viscosity, even the remaining turbulence eddies transfer substantially more material than molecular diffusion. Approaching the surface D_{turb} decreases with the fourth power of the distance. Only in the innermost part of the viscous sublayer ($y < \delta_d$) does the molecular diffusion mechanism predominate over the turbulence mechanism. In this region, the linear relationship for concentration is valid:

$$c_{III} = \frac{j}{D} y \qquad (20)$$

Levich obtained the following relationship for the thickness of diffusion sublayer:

$$\delta_d \sim \delta_o \, Pr^{-1/4} \qquad (21)$$

For example, at Pr $\sim 10^3$ the value of δ_d is about one sixth of δ_o. The validity of the formula was proved by Bagotskaya[71] with electrochemical measurements.

The Prandtl-Kármán and Levich model is summarized in Figure 3.

	LAMINAR		TRANSITION	TURBULENT
Prandtl-Karman model	Concentration Boundary Layer $\nu > \nu_{turb}$ $D > D_{turb}$		Viscous sublayer $\nu \leq \nu_{turb}$ $D \leq D_{turb}$	Fully developed turbulence $\nu < \nu_{turb}$ $D < D_{turb}$
Levich model	Diff. sublayer $\nu > \nu_{turb}$ $D > D_{turb}$	Viscous sublayer $\nu > \nu_{turb}$ $D < D_{turb}$	Turbulent boundary layer $\nu < \nu_{turb}$ $D < D_{turb}$	Fully developed turbulence $\nu < \nu_{turb}$ $D < D_{turb}$

FIGURE 3. Comparison between the Prandtl-Karman model and the Levich model.

Both the Levich, as well as the Prandtl-Kårmån several-layered structure is widely accepted. Diessler[72] described the relationship regarding eddy viscosity for three zones. Gabe,[73] supposing a three-layered structure, deduced the relationships concerning mass transfer in a cell containing a rotating cylinder.

Dreesen and Vielstich[58] demonstrated the formation of the several-layered structure in the direction of flow by using flat and tubular electrodes. In contrast to Levich, they assumed that the diffusion coefficient changes with the third power of the distance to the wall, which was experimentally proved (see also Reference 91).

5. *Mass Transfer Equations*

In the case of turbulent flow, Equation 4 describing the convective diffusion is modified as follows:

$$V \nabla C = (D + D_{turb}) \nabla^2 C \qquad (22)$$

where the term in the parentheses expresses the mass transfer caused by diffusion and by turbulent eddies. The exact mathematical description of turbulence is not known, because there does not exist a correct, proven physical model for the description of turbulent motion. In general, authors apply initial and boundary conditions starting from their special models and thereby solve the appropriate equations for a given geometry.

Many researchers apply the empirically derived Chilton-Colburn equation[74] for the determination of material transport.

The solution of the above equation, the rate of the mass transfer, and thus the density of the diffusion limiting current, is generally characterized by the following dimensionless equation:

$$Sh = \alpha\, Sc^{\beta}\, Re^{\gamma} \qquad (23)$$

where α, β, and γ are constants.

Many publications report the relationship regarding the Sh number in the case of bodies of various geometries. Examinations were carried out with plate, tube, conical, ring, and spherical electrodes, as well as rotating disk, ring, cylindrical, and hemispherical electrodes. The constants determined by various authors show little difference in general.

a. Plate Electrode

The deduction of the relationship concerning plate electrodes parallel to the direction of flow is rather difficult, because the turbulent boundary layer does not immediately start at the point of contact of the stream and the solid body, but only at a certain distance downstream. Thus the expression of mass transfer towards the plate will be a combination of the flow taking place in the laminar section and that occurring in the turbulent section. According to Levich, the mass transfer can be characterized by the following equation:

$$\mathrm{Sh} \sim \mathrm{Re}^{0.9}\ \mathrm{Sc}^{0.25} \tag{24}$$

The theoretically defined expression of Sh is based on the supposition that in the laminar sublayer there is no turbulent motion. This is why its correlation with experimental result is not satisfying.

For the turbulent region, Wranglen and Nilsson[75] deduced the following correlation:

$$\mathrm{Sh} = 0.143\ \mathrm{Re}^{0.6}\ \mathrm{Sc}^{0.33} \tag{25}$$

According to their experiments, however, the limiting current increases with the 0.5 power of the Re number, similar to the laminar region. The slope of the straight line in the plot of ln Sh vs. ln Re is larger than theoretically justified. The difference between theory and practice is attributed, by the authors, to the disturbing effect caused by the wall of the cell.

Tobias and Hickman[76] also investigated mass transfer to a horizontal plate electrode and found that for an Re number larger than 4000, the effect of "free convection" from the point of mass transfer can be neglected.

Bardin and Dikusar,[65] using disk electrodes perpendicular to the direction of flow, found a good agreement with the equations deduced by Matsuda[77] for laminar flow in the Re number region of 244 to 1.03×10^4, i.e.,

$$\mathrm{Sh} = 0.85\ \mathrm{Re}^{0.5}\ \mathrm{Sc}^{0.33} \tag{26}$$

The average value of the ratio of the Sh values obtained theoretically and experimentally was 1.007, while the maximum deviation amounted to 8.2%. These results support the suggestion that a solid body placed into a turbulent flow is surrounded by a laminar layer. At the same time, by means of suitable experimental equipment, it was shown that for fluctuations that can be observed at high flow rates, the turbulent eddies penetrate into the viscous sublayer.

Dikusar and Petrenko[66] empirically determined the value of the α constant in the equations regarding the Sh number. Their system was a disk electrode with turbulent flow, where the ratio of electrode to tube diameter is larger than 0.35. According to their expression, the value of the constant depends on the ratio between electrode diameter and tube diameter.

b. Conical Electrode

The experiments of Dikusar and Bardin[78] carried out with conical electrodes proved that the equation of Matsuda[79] also describes, in a satisfying way, the mass transport in the case of turbulent flow

$$Sh = 0.82\ Re^{0.5}\ Sc^{0.33} \left(\frac{1}{L}\right)^{m/2} \tag{27}$$

where m is a constant whose value depends on the angle of the conus of the electrode.

c. Tubular and Ring Electrode

According to Devanathan and Gurusvami,[80] the tubular electrode possesses significant advantages over other types. Also, at smaller Re numbers, the turbulent space within the tube can be achieved and be mathematically described with sufficient accuracy. The authors proved, with measurements of high accuracy, the validity of the relationship between the voltammetric current and flow rate theoretically deduced by Levich for the domain $2000 < Re < 4000$:

$$i = k\,V^{7/8}\ . \tag{28}$$

and determined the value of the constant k in the equation.

Blaedel and Schieffer[59] reported examinations with a tubular electrode at which the turbulence was ensured by mechanical stirring. Due to this stirring, mass transfer increased. In the case of ω_s = 1500 to 2000 rpm of stirrer speed, they obtained the following relationship concerning the limiting current:

$$i_L \sim (\omega_s)^{1/2} C \tag{29}$$

For ω_s = 20 to 30 rpm;

$$i_L = (\omega_s)^{b}\,C\ (V_{lin})^{1/3} \tag{30}$$

where V_{lin} is the linear flow rate. Note that at high stirring rates, the limiting current is independent of the rate of linear flow. At the low stirring rates, the value of b is close to zero. In this latter case, the mass transfer depends only to a small extent on the speed of the stirring. The authors regard intermediate cases as transient periods between laminar and turbulent flows.

Bernstein and Vielstich[81] studied the kinetics of the electrodes using turbulent pipe flow and very thin working electrodes. The experiments were performed with coiled pipes. The platinum electrode had an inside diameter of 10 mm. The lengths of the electrodes were 2.5, 5.0, and 7.0 μm. The pipe also contained a reference and a counter electrode. The measurements were carried out at Re numbers of 5000 to 20,000. Since the length of the electrode was very small, probably one can hardly speak about a turbulent boundary layer being developed in the direction of the flow.

Ross and Wragg[82] studied the mass transfer equation concerning concentric annular electrodes, where the ratio of the annuli radii was 0.5. Following the procedure used by Linton and Sherwood[83] and Van Shaw et al.[84] to solve the differential equation describing convective diffusion, Ross and Wragg deduced the following relationship:

$$St = 0.276\ Sc^{-0.66}\ Re^{-0.42} \left(\frac{d_e}{L}\right)^{1/3} \qquad (31)$$

St, the Stanton number, is dimensionless with $St = j/CV$, $d_e = d_2 - d_1$, where d_2 and d_1 are the annulus diameters, and L is the length of the electrode. Equation 31 is in good agreement with experimental results. The experimental curve was only 7% lower than the theoretical one.

Dreesen et al.[85] also investigated mass transfer using a ring electrode. The length of the electrode was varied between 0.3 and 4 mm and was incorporated into the wall of a tube. For the regions of $2 \times 10^2 < Re < 2 \times 10^5$ and $600 < Pr < 36{,}000$, respectively, they obtained the following equations:

$$Sh \sim Re^{0.58 \pm 0.03}\ Sc^{0.33 \pm 0.015} \text{ for } 2 \times 10^3 < Re < 10^4 \qquad (32)$$

$$Sh \sim Re^{0.74 \pm 0.03}\ Sc^{0.33 \pm 0.01} \text{ for } Re > 2 \times 10^4 \qquad (33)$$

They found the critical value of Re number to be 2×10^3.

d. Spherical Electrode

For spherical electrodes, Bardin and Dikusar[65] obtained an equation similar to that for disk electrodes. The relationship mentioned earlier is valid for disk electrodes if $d_1/d_2 \leqslant 0.25$, while for spherical electrodes if $d_1/d_2 \leqslant 0.40$, where d_1 is the diameter of the electrode and d_2 is the diameter of the disk or sphere.

e. Rotating Disk Electrode

Rotating disk electrodes, due to their easily approachable surface, are of significant importance from the point of electrochemical examinations. According to Levich, if $Re \sim 10^4$, a turbulent boundary layer is formed on the rotating disk, and the following equation describes the mass transfer:

$$Sh = \text{constant}\ Re^{0.9}\ Sc^{0.25} \qquad (34)$$

Many authors[86,87] experimentally studied mass transfer on a rotating disk in turbulent flow. It was found that in the Re number region investigated by them ($Re < 10^6$) a laminar flow is being formed around the rotation axis, which contributes at least 10% of the Sh number. Ellison and Cornet[88] performed measurements with higher Re numbers. They observed the transition between laminar and turbulent flows at an Re number of 3.0×10^5 and indicated the beginning of the turbulent flow at an Re number of 8.9×10^5. They performed the examinations up to Re numbers of 1.18×10^7 in the region $34 < Sc < 1400$. By applying least squares analysis these authors obtained the following correlation for an average Sh number:

$$\overline{Sh} = 1.17 \times 10^{-2}\ Re^{0.896}\ Sc^{0.249} \qquad (35)$$

The relative standard error from curve-fitting is ±8%. In the transition range, the equation must be modified because laminar flow brings its own mass transfer term into existence.

The average experimental Sh number obtained by Ellison and Cornet is in good agreement with the result based on the theory of Deissler's "eddy diffusivity"[72]

$$\overline{Sh} = 1.12 \times 10^{-2}\ Re^{0.91}\ Sc^{0.25} \qquad (36)$$

and is similar to the Tien, Wasan, and Wilke's results deduced from friction analogy[89]

$$\overline{Sh} = 5.93 \times 10^{-3}\ Re^{0.91}\ Sc^{0.34} \qquad (37)$$

Mohr and Newman[90] investigated mass transfer to a rotating disk in transition flow range of $2 \times 10^5 < Re < 3 \times 10^5$. They obtained the resultant correlation for the average transfer rate:

$$\overline{Sh} = 0.89 \times 10^5\ Re^{-1/2}\ Sc^{1/3} + 9.7 \times 10^{-15}\ Re^3\ Sc^{1/3} \qquad (38)$$

f. Rotating Ring Electrode

At rotating ring electrodes, where the surface of the ring is perpendicular to the rotating axis, the mass transfer equations deduced for the turbulent region are of two different kinds. If we suppose that the turbulent diffusion coefficient increases with the third power of the distance from the electrode, the mass transfer will change with the one third power of the Sc number. If we accept that the turbulent diffusion coefficient is proportional to the fourth power of the distance, then the mass transfer depends on the one fourth power of the Sc number.

Hamann and co-workers[91] performing their examinations in the regions of $2.7 \times 10^5 < Re < 10^6$ and $500 < Sc < 2000$ derived the following relationship:

$$Sh = 1.77 \times 10^{-2}\ Re^{0.878}\ Sc^{0.34} \qquad (39)$$

which was justified by experimental results. In this way they also proved the correctness of the relationship

$$D_{turb} \sim y^3 \qquad (40)$$

The equation obtained by Ellison and Cornet[92] for a rotating ring electrode agreed with the equation deduced at a rotating disk electrode. Bagotskaya[71] has found the following relationship:

$$Sh \sim Re \qquad (41)$$

According to Kishinevskii and co-workers,[93-95] in the examinations of diffusion kinetics, the turbulent diffusion coefficient changes with the fourth power of the distance from surface. By performing their measurements with narrow and wide ring electrodes they found a good agreement between theoretical and empirical results. This is not in accordance with the results of Hamann[91] and others.[58] However the discrepancy between the two mathematical approaches is not too big, and is most apparent in the values of D_{turb} very near to the surface of the electrode.

Velichko[96] reported an experimental setup in which the effect exerted upon the mass transfer by a variation in electrode size can be studied. In the case of turbulent flow, in the equation

$$\mathrm{Sh} \sim \mathrm{Re}^{m} \qquad (42)$$

m = 0.9. By decreasing the dimensions of the electrode between 10.1 and 0.15 mm width, the value of m decreases from 0.89 to 0.56, which can be explained by incomplete formation of the diffusion boundary layer. It was experimentally found, in the case of an electrode of 0.15 mm width at an Re number of 4.18×10^5, the value of m increases to 0.9. It can be assumed that this discrepancy is due to the eccentricity of the ring and is commensurate with the ring width. In this way a periodic change in the concentration boundary layer occurs, which leads to a more intensive mass transfer. Additionally the presence of the so-called surfacial turbulence can have a role.

Deslouis and Keddam[97] observed the former relationship by examining, at a large Sc number ($\mathrm{Sc} \sim 3000$), the formation of the mass flux at a rotating ring electrode. In the case of a wide ring (4 to 37 mm), the experiments proved that the diffusion current depends on the 0.9th power of the Re number, while in the case of narrower rings (0.05 to 0.15 mm), due to the effect of radial convection the exponent of the Re number decreases to 0.6.

Daguenet[98] reported on the changes in the 0.9 exponent when the electrode surface is not smooth.

Dikusar[99] studied, by using a double ring electrode, the dependence of mass transfer on the rotation rate, the diffusion coefficient, and the viscosity. He accepted 2.7×10^5 as the value of Re_{cr}. Over this Re number, he found the mass transfer coefficient to be proportional to $\omega^{0.6}$. Their experiments proved that the inner ring does not exert any effect upon the mass transfer taking place on the outer ring, if the Re number is higher than 10^6.

g. Rotating Cylinder Electrode

Empirical correlations of currents to rotating cylinder electrodes generally use the Stanton number. For the case of a cell consisting of a rotating inner cylinder and a static outer cylinder, Gabe and Robinson[73] deduced a relationship based on the Prandtl-Karman three-zones structure. They assumed diffusion increased because of the turbulent pulsations and solved the Fick law for all three zones. They obtained exponents −0.333 and −0.666 for Re and Sc parameters.

Arvia[100] pointed out that turbulence can be attained at a lower rotation speed if the inner cylinder rotates.

Kishinevskii and co-workers[101] emphasized the advantageous property of the rotating cylinder electrode. On the side surface of the cylinder, a totally developed hydrodynamic boundary layer is formed. Due to this, it is very suitable for the study of diffusion conditions.

h. Rotating Hemispherical Electrode

Chin[102] studied, in the 910 and 6300 Sc number region, mass transfer to a rotating hemispherical electrode. Since the diameter of the electrode and the diameter of the rod to which the electrode was fixed were identical, the author did not need to account for collisions of opposite boundary layers at the end of the electrode. To establish the relationship concerning the mass transfer, he used the Chilton-Colburn equation[74] and got the following result:

$$Sh = 0.0198\ Re^{0.8}\ Sc^{0.33} \qquad (43)$$

To experimentally prove the validity of the equation, he performed examinations in the region of $5000 < Re < 100{,}000$ at four various Sc numbers. In the case of the mentioned geometrical arrangement, he found the transition between laminar and turbulent flow at $Re = 40{,}000$.

According to the regressive analysis of the data of turbulence, the experimentally obtained coefficient agreed within ±5% of the theoretically deduced value of 0.0198. The good agreement between the experimental and theoretical data of Chin proved that the Chilton-Colburn equation[74] can advantageously be applied for the description of turbulent mass transfer on rotating asymmetrical surfaces (e.g., conical bodies, paraboloids, etc.). In the case of a rod or rotating sphere of larger diameter than that of the electrode, the transition period appeared at $Re = 15{,}000$ while the exponent of the Re number and the value of the constant in the equation changed. In such cases a radial flow is being formed at the equator, which reduces the stability of the boundary layers being formed around the upper and lower hemispheres, and must always be taken into consideration.

i. Rough surfaces

Levich deduced a relationship for mass transfer occurring at a rough surface. He stated that in the case of laminar flow, the roughness promotes the formation of turbulence and the mixing of the liquid. In the case of a turbulent flow, in the vicinity of the surface the flow would be dampened and due to this, the diffusion current would be reduced. He did not experimentally prove his theoretical deduction.

Dawson and Trass[103] studied the mass transfer in a square duct with smooth and rough surfaces. To examine the effect of roughness, they applied six V-shaped grooves of 2 to 14 mm depth, perpendicular to the direction of flow. They carried out their measurements in the regions $3000 < Re < 120{,}000$ and $390 < Sc < 4600$, respectively. They obtained, for an Re number larger than 15,000, the following relationship:

$$\frac{St_{rough}}{St_{smooth}} = f(e^+, Sc) \qquad (44)$$

where f is the function of parameters being in parentheses, e^+ is the dimensionless roughness height, which is proportional to the height of roughness and the viscosity and the gravitational constant, and inversely proportional to the shear stress.

Based on their experimental results, they can distinguish three cases. In the "hydraulically smooth" region, where $e^+ < 3$, i.e., the roughness height is a little bit larger than the thickness of the diffusion boundary layer, roughness exerts little or no effect upon the rate of mass transfer. This shows that though the roughness penetrates into the viscous sublayer it is not capable of generating sufficient turbulence to disrupt the diffusion boundary layer. In the transition region, where $3 < e^+ < 25$, the roughness disrupts the viscous sublayer and the turbulence penetrates into the valleys between

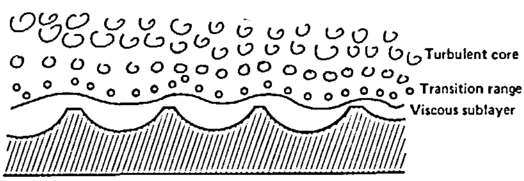

FIGURE 4. The structure of the boundary layer at rough surface. (From Dawson, D. A. and Trass, O., *Int. J. Heat Mass Transfer*, 15, 1317 (1972). With permission.)

the roughness elements, resulting in rapid increases in the rates of both momentum and mass transfer. As can be seen in Figure 4, the viscous sublayer is quite thin at the peaks, while in the valleys it is thicker. With an increasing Re number, the thickness of the viscous sublayer decreases to such an extent that at the peaks, turbulence is being formed that extends into the valleys. In the fully rough region, where $e^+ > 25$, the following relationship can be stated as derived by least squares fitting:

$$\frac{St_{rough}}{St_{smooth}} = 1.94 \times Sc^{0.09} \ (e^+)^{-0.1}$$

$$(\text{for } 25 \leq e^+ \leq 120) \qquad (45)$$

with a standard deviation of 3.3%. For cases of Re numbers less than 15,000, molecular properties are significant,[104] and the above relationship cannot be applied.

Daguenet and co-workers studied the effect of roughness on a rotating disk electrode. At first, they selected a small round surface element on a rotating disk of smooth surface,[105] for which they described the mass transfer equation. Thereafter, they chose a surface element in one of the cavities of an electrode with a uniformly rough surface.[106,107] The height of the roughness was significantly greater than the thickness of the diffusion boundary layer. They could not find any relationship between e/r_o and the Sh number; e/r_o is characteristic of the extent of roughness, where e is the height of roughness and r_o is the distance between the center of the small surface element and the center of the rotating disk. The measured changes were within the error of measurement. The examination was extended over the whole rotating disk electrode[108] and showed that with increasing the roughness, the relationship $i \sim \omega,^{0.9}$ valid for smooth surfaces, becomes $i \sim \omega.^{0.66}$

For local measurements on a rough rotating disk,[109] the following equations were obtained for the surfaces of the pyramids, the valleys, and the peaks (Figure 5):

$$Sh_{pyramid} \sim Sc^{1/3} \, Re_{r_o}^{\ 2/3} \qquad (46)$$

$$Sh_{valley} \sim Sc^{1/3} \, Re_{r_o}^{2/3} \qquad (47)$$

$$Sh_{peak} \sim Sc^{1/3} \, Re_{r_o}^{4/9} \qquad (48)$$

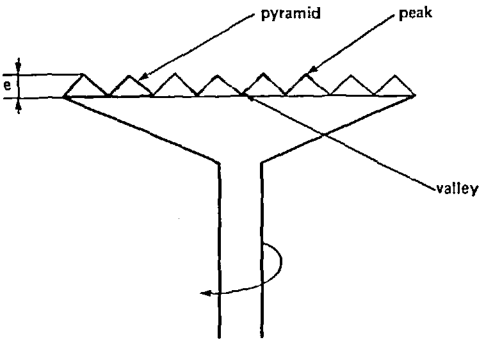

FIGURE 5. The rough surface of the rotating disk electrode applied by Daguenet and co-workers, *J. Chem. Phys.*, 7, 1102 (1973). With permission.

and for the whole surface of the disk:

$$Sh \sim Sc^{1/3}\ Re^{2/3} \qquad (49)$$

The equations prove that, from the point of mass transfer, not the peaks — but the valleys — have a determining role.

Meklati and Daguenet[110] examined the diffusion layer far from the attack-edge of the electrode and liquid, at a distance where the height of roughness is greater than the thickness of diffusion boundary layer. They stated that no diffusional region had been established.

j. Non-Newtonian Liquids

Barz and Vielstich[111] studied the modification of the mass transfer equation in the case of rotating ring and disk electrodes when non-Newtonian liquids were in turbulent flow. Increasing the concentration of polyoxyethylene, they observed that the exponent of the Re number approximates more and more the value for laminar flow 0.5. They explained this by assuming that the long chains of the molecules hinder microscopic fluctuations, due to the turbulence.

D. Hydrodynamic Voltammetry of Systems with Complicated Geometry or Complicated Hydrodynamic Conditions

A characteristic feature of research done earlier in hydrodynamic voltammetry was the elucidation of theoretical problems of an electrode system for a special practical task, as well as the application of the system. In some cases — even nowadays — application of a new detector system, improved for a special task, is followed by the theoretical treatment of the convective diffusion problem relating to the system.

On the other hand, a lot of papers deal with the theoretical problems of electrodes of very different geometry and under different electrochemical conditions. Matsuda's activity serves as a good example of the latter trend.

Matsuda[112] developed a uniform handling procedure. It describes the current-potential relationship valid for electrodes formed by bodies of revolution under conditions of convective diffusion (placed in a laminar parallel flow). A general term relating to the concentration distribution in the vicinity of the body of revolution is applied to bodies of different shapes.[114-120] Considering the rates of the electron transfer reaction and the rate of chemical reaction preceding or following the electron transfer processes, respectively, Matsuda described relationships for tubular -,[113] wedge-shaped,[114] cone-shaped,[115] spherical,[116] disk-,[118] and ring electrodes.[117]

Recently, Marchiano and Arvia's interest was attracted by systems involving natural convection.[121,122] As is well known, for a solution containing parts with different densities, natural convection occurs — the difference in density may be caused by either a temperature gradient or a concentration difference in the solution.

They fabricated a so-called thermal convective electrode,[121,122] and the convective diffusion problems of this electrode in question were investigated both theoretically and practically. The thermal convective electrode system consists of a vertical flat plate electrode dipping into a static solution. A temperature difference is produced between the electrode and the liquid. For the theoretical treatment of the problem, a hydrodynamic (Navier-Stokes) equation should be solved in which, in addition to the mass-transfer, the energy transfer also is taken into consideration. The relationship obtained, in the case of $\Delta T = 0$ (i.e., the temperature difference is equal to zero) transforms into the relationship valid for a flat plate electrode derived by Levich.

The validity of their relationships was experimentally proved by Marchiano and Arvia, and the current-potential equations holding for the electrode were also given. The authors are of the opinion that the electrode system is suitable for the investigations of kinetic problems, although in our view, the experiment carried on under nonisothermal conditions can be regarded only as a new variety of voltammetric measurements, and its extensive application in practice cannot be expected.

Newman also made some very important contributions concerning transport processes in electrolyte solutions.[123,124] He treated the problems of hydrodynamic voltammetry primarily in electrochemical aspects. He also studied the effect of migration appearing in electrolytes.[125,126]

He studied the conditions formed on the rotated disk electrode by considering the changes of parameters of transport processes inside the diffusion layer,[123] radial diffusion at the edges of the electrode,[127] and the mass transfer conditions existing on the rear of a cylinder placed into the flow parallel to its axis.[128]

1. Electrode Systems with Special Geometry

The rotated disk electrode was examined by Nagy and Horanyi[129,130] for the case of an inhomogeneous electrode surface.

Chin[131] studied an electrode of hemispherical shape. He drew the conclusion that it can be used advantageously instead of rotated disk electrode, especially if the electrode is made of metal and anodic dissolution is the subject of examination. With a similar view, Cobo, Marchiano, and Arvia[132] examined a rotated body as a working electrode, the active surface of which is a spherical segment. For this electrode, the equation for a rotated disk electrode derived by Levich[6] was found to be valid.

Rotated and vibrated wire electrodes[133-135] are widely used following amperometric and biamperometic titrations.

Gerdil[136] developed a rotated so-called GC-platinum electrode (the GC — usually having another meaning, here is the abbreviation of golf club!). According to the author, the electrode is exceptionally stable and has a well-defined geometry.

Different double electrode systems similar to the rotated ring-disk electrodes have been developed by researchers. The so-called dimicro electrode made by Kermiche-Aouanouk and Daguenet[137] consists of two microdisk electrodes on the radius of a rotated inert disk.

Gerischer et al.[138,139] were the first to apply electrode systems for kinetic investigations using two electrodes in a flow tube. Studying the effect of flow rate on the limiting current in the case of flat plate electrodes placed in the tube, they observed a $V^{1/3}$

dependence. (For flat plate electrodes a $V^{1/2}$ dependence was derived!) In our opinion, the explanation is that the hydrodynamic conditions in the tube didn't fulfill the assumption used in the derivation of equations valid for plate electrodes, namely the thickness of the boundary layer on the surface of the electrode was not negligible relative to the length and width of the plate. Thus, it was a tube electrode, rather than a flat plate.

The double electrode used by Kenkel and Bard[140] was similarly arranged. Two porous electrodes (see below) placed in a tube are suitable for carrying out electrochemical reactions occurring in two steps in addition to kinetic investigations.

Filinovsky et al.[141] and Dikusar[142] used a double-ring electrode for kinetic studies. Dikusar also proved his theoretical results with experiments. Several authors have studied the arrangement in which the electrode consists of a tube with a cylinder in it. Of these types several varieties are known, differing by which electrode is used as the working one, and whether convection is ensured by rotation of the tube or the cylinder.

Gabe and Robinson[143,144] and Arvia and Carrozza[145] studied the convective diffusion to a rotating cylindrical electrode in a fixed cylindrical cell.

2. *Measurements in Spectrochemical Cells*

Recently, to gain a better understanding of electrochemical processes, optical methods have shown increasingly wide application. These investigations include the study of (1) the state of the electrode surface, (2) electrochemical processes with *in situ* detection of intermediates, and (3) adsorption on the electrode surface, and so on.

According to Kuwana,[146] depending on the object and purpose of the investigation, the following methods are most frequently used: (1) normal transmission spectroscopy, (2) internal reflection spectroscopy, and (3) specular reflectance.

The detection and monitoring of the short-lived intermediates is facilitated by the use of optically transparent electrodes, (e.g., References 147 to 153).

Lately, some works were reported on measurements under various hydrodynamic conditions, too.[154-157]

Schwing, et al.[154] prepared a circulation cell suitable for optical and electroanalytical studies of the kinetics of fast reactions. In this arrangement, part of the electrolyte is recycled to the electrochemical cell after passing through the flow-through cuvette of a photometer.

Richards and Evans[155] fed a continuously produced component from a porous electrode to the sample cavity of a NMR spectrometer.

Albery et al.[156,157] introduced, under laminar flow conditions, a component produced on a tubular electrode to the sample cavity of an ESR spectrometer. They solved the convective diffusion equations for first and second order kinetics of radical formation, using a simulation technique.

3. *Porous Electrodes*

The application of electrolytic cells containing porous electrodes, as reported at first by Perskaya and Zaidenman,[158] only recently gained importance. The use of these porous electrodes, consisting of metal or carbon granules, are mainly proposed for organic synthetic processes and chromatographic purposes. They also can be used for construction of fuel cells.

Fujinaga,[159] Roe,[160] and Blaedel and Strohl,[161] for the chromatographic separation of various metals and isotopes, used columns filled with metal or graphite granules; detection was performed voltammetrically or coulometrically.

Sioda[162-168] proposed the use of porous platinum and graphite electrodes, mainly for carrying out continuous electrochemical reactions, e.g., for production of free radicals. Thus the cells developed by him can be considered as continuously working reactors.

Wroblowa[169,170] applied a cell containing a porous electrode, called a flow-through electrode, as a fuel cell.

Nowadays, the most important analytical application of the porous electrode is in liquid chromatography. Very sensitive detection can be achieved with porous electrode systems operating in the coulometric mode (e.g., References 171, 172).

The processes occurring on porous electrodes in flowing solutions have been treated theoretically by Gurevich and Bagotzky[173] and Sioda.[164] The difficulties in theoretically describing the porous electrodes are due to the complicated nature of the processes occurring in them. There are potential, concentration, and current gradients inside these electrodes. Moreover, concentration gradients exist for the starting materials and the reaction products, as well. The problem is treated by the authors as one-dimensional, which is an oversimplification.

Sioda[164] deduced an equation for the factor R that denotes the effectiveness of the electrolysis. Here, R is defined as the ratio of the concentration of the substance undergoing electrolysis vs. its initial concentration, c_o

$$R = \frac{i_L}{nF \cdot V\, c_o}$$

By assuming uniform flow-rate inside the electrode:

$$R = 1 - \exp\left(-ba^{1-\alpha} \times V^{\alpha-1} \times L\right) \qquad (50)$$

where V is the volumetric flow rate, α is the rate exponent, determined either experimentally or calculated from the convection diffusion equation, a is the cross sectional area of the porous electrode, $b = j \cdot s$, s is the factor of proportionality, and L is the length of the porous electrode.

The gold minigrid electrode applied by Blaedel and Boyer[174] is, to a certain extent, similar to the porous electrodes. By placing several gold minigrids, introduced by Murray[175] as an optically transparent electrode, in the flow, the authors aimed to design a very sensitive cell, by increasing the electrode surface. The equation for the limiting current obtained experimentally, has the following form:

$$i_L \alpha NV^{1/3}c \qquad (51)$$

where N is the number of the minigrids used, and V is the volumetric flow-rate. Wroblowa[176,177] deduced equations considering the radial and axial diffusion for these systems. Ateya[178] discussed the radial diffusion, and considered the entrance effects arising upon entry of the electrolyte into the electrode.

In the small-volume measuring cell applied by Blaedel, the significant increase of the electrode surface results in a different working mode of the detector cell than that of the classic voltammetric one, because in the case of six grids, 18% of the electroactive component passing through the cell is transformed.

When using the cells as a liquid chromatographic detector for increasing the sensitivity, the aim is often to achieve total conversion, and so the cells containing high surface-area electrodes, i.e., carbon cloth, platinum gauze, or platinum plug of rolled screenings, generally operate in the couometric mode.[171,172]

4. Magneto-Hydrodynamic Voltammetry

For the time being, the investigations concerning the effect of a magnetic field on the processes occurring in the electrolytic cell can be regarded only as matters of curiosity. According to Soviet[179] and Japanese[180,181] authors, the magnetic field affects the first and second order maxima and the migration and diffusion current. The effect is, in most cases, due to convection in the electrolytic cell, produced or influenced by the magnetic field. This so-called magneto-hydrodynamic effect was investigated by several authors.[182-187] According to Aogaki et al.[182-184] the convective diffusion can be controlled by an outer magnetic field.

5. Hydrodynamic Modulation

Bruckenstein et al.[188] examined several aspects of the hydrodynamically modulated rotating disk electrode. The design of these electrodes is the same as for the disk electrode, but the rotation speed of the disk can be changed according to selected programs. The speed of rotation can be varied in a linear, quadratic, or exponential fashion with time. It is also possible to perform square-wave or sinusoidal modulation of the rotation-speed function selected.

The use of the portion of the disk currents arising from modulation for information provides a lot of advantages, partly from an analytical point of view, partly for the investigation of the mechanism of the electrode system. By eliminating the effect of the charging current using a proper modulation, the analysis of solutions of low concentrations ($\sim 5 \times 10^{-8}$ M) can also be carried out.[189] At the same time, for theoretical considerations, it is important to obtain experimental results that are free of disturbing effects, such as surface reactions or currents partly connected with the charging of the double layer, partly originating from irreversible reactions of the supporting electrolyte.

6. Membrane- Covered Electrodes

An interesting group of working electrodes is that of membrane-covered electrodes. Various membrane types are used, depending on the information desired. The most important difference is whether the membrane is inert or active. In the first case, the membrane can serve for the protection of the indicator electrode, or selects the components arriving at the electrode, while in the second case a component incorporated into the membrane causes or catalyzes a chemical reaction, which helps to gain electrochemical information of the concentration of the electroinactive component. The best known representative of the first group is the oxygen sensor applied first by Clark,[190] while the second group contains the voltammetric enzyme electrodes.[191]

The structure of membrane-covered electrodes may be different depending on whether the electrode is a combined or a simple one. Membrane-covered mercury electrodes (and some of the enzyme electrodes) have a simple construction, while oxygen sensors and other types of gas-sensing electrodes in most cases contain the reference electrode, too.

The schematic design of the Clark electrode is given in Figure 6. The theoretical description of the functioning of the membrane-coated electrodes is a rather complicated task, even in the case of an inert coating layer. One approach by Lucero[192] treats the functioning of the membrane-coated polarographic gas electrodes on the basis of a physical model. The transport through the membrane, and the response time properties of the system are modeled by the combination of electrical circuit elements. Hersch[193] treated the galvanic cell oxygen sensors in the same way.

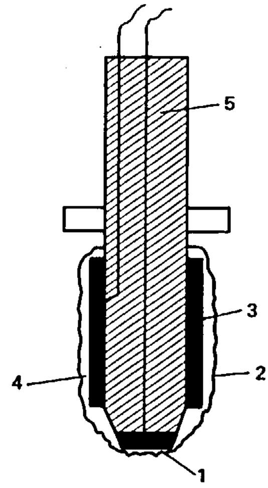

FIGURE 6. The schematic design of the Clark electrodes. (1) Platinum working electrode, (2) gas-permeable membrane, (3) silver reference electrode, (4) electrolyte jelly, and (5) electrode body made of insulating material.

Connected with their investigations with the galvanic cell oxygen sensor of Hersch,[193] Mancy et al.[194] studied the mass transport processes using membrane-coated working electrodes. It was assumed a uniformly stirred solution with a homogeneous concentration exists outside the membrane, while in the membrane phase itself, and between the membrane and the electrode, a diffusion process predominates. Describing the two-layer diffusion, a quantitative solution could be given only for particular cases. The solution for the steady-state current (i_∞) case gave a result in accordance with experience as well as deriving directly from Fick's laws:

$$i_\infty = nFA\,\frac{P_m}{b}\,c \qquad (52)$$

where P_m is the permeability of the membrane, and b is the thickness of the membrane.

The equation is valid only for the case when the diffusion through the membrane is rate determining. This assumption holds in the majority of the cases.

Schuler and Kreuzer[195] discussed the Clark electrode. They neglected any diffusion in the electrolyte layer between the membrane and the electrode surface, but the convective diffusion outside the membrane was considered. The current equation with this assumption is the following:

$$i = nF\,\frac{p_{O_2}}{\dfrac{\omega}{A \times P_m} + \dfrac{\epsilon}{A \times P_o}} \qquad (53)$$

where p_{O_2} is the partial pressure of oxygen, ω is the thickness of the membrane, ε is the diffusion boundary layer thickness outside the membrane, P_m is the permeation coefficient of the membrane, and P_o is the permeation coefficient of the medium. The thickness of the diffusion boundary layer was expressed by using the analogous equation found valid for heat transfer, which contains dimensionless quantities. It was concluded that the flow rate dependence of the current can be minimized by reducing the cathode diameter and/or by using a membrane of low permeation.

Though a large resistance — low permeation — of the membrane is disadvantageous in that it causes lower sensitivity and greater response time, in practice the most common feature is that the transport through the membrane is rate determining.

From the above, it follows that the main condition for good functioning of a membrane-covered electrode is a vigorous convection outside the electrode membrane.

For electrodes coated with active membranes, the situation is more complicated. Even assuming the most simple case, not only must the transport process inside the membrane be considered, but the catalyzed chemical reaction as well.

The mechanism of the function of the platinum electrode coated with a membrane containing glucose oxidase in an immobilized form has been described by Mell and Maloy[196] by digital simulation. Prior to the simulation, the authors made some preliminary experiments. They proved that with vigorous stirring of the solution, mainly the diffusion through the membrane and the chemical reaction in the membrane have to be considered.

Digital simulation was done by applying several boundary conditions customary in polarography. On the basis of these calculations, the steady-state behavior of the enzyme electrode was described. Accordingly, linear calibration curves are to be expected when using low substrate concentrations, regardless of the rate-controlling step (diffusion or chemical reaction). If the rate of the chemical reaction is high with respect to that of the diffusion, a straight line calibration curve is obtained for a wide concentration range.

III. PRACTICE OF HYDRODYNAMIC VOLTAMMETRY

A. Working Electrodes

The voltammetric method became a widely used analytical tool only with the application of the dropping mercury electrode. Various solid electrodes (mainly metals) were already in use before Heyrovsky's discovery, but they gained greater importance in analytical practice only recently, mainly in those cases where mercury electrodes cannot be employed. In hydrodynamic voltammetry, especially when using it in automated, continuous analyzers, mechanical impact-proofing of the electrode plays a very important role. Therefore, many attempts have been made to use solid electrodes. These types of working electrodes are undoubtedly superior in this respect to dropping mercury electrodes, but they are more troublesome from the electrochemical point of view.

In early investigations aimed at determining the concentration of components of a flowing solution, dropping mercury electrodes were used. In recent applications, the use of electrodes with a constant surface area is preferred. Recently, various solid electrodes (such as made from noble metals or graphite) are often applied as base or substrate electrodes, on which the active electrode surface is a mercury film.

Beside the classical dropping mercury electrode,[197-203] numerous other mercury electrodes were developed for the analysis of flowing solutions. The dropping mercury electrodes in today's cells operate mostly with a drop time control.[204,205] Besides the vertical arrangement there are also cells with horizontal[206-206] or inclined[209,210] electrodes. Strafelda and Dolezal[211] used a Smoler capillary.[212] Several authors applied rapidly dropping electrodes[205,206] and also mercury electrodes with constant surface area.[213-215]

Fleet et al.[216] discussed in detail the applicability of various working electrodes in flowing solutions, in connection with a special problem: the indirect complexometric determination of calcium and magnesium. The hanging mercury drop electrode and the mercury-coated platinum electrode are used as mercury electrodes. The hanging mercury drop electrode proved to be the best. The platinum electrode covered with mercury ensured a high sensitivity, but also showed a high residual current, probably owing to the difficulties of producing the film.

For inverse voltammetry with flow conditions, the mercury-covered graphite electrodes seem to be the most advantageous, compared to other mercury electrodes with a constant surface area.

The preparation and properties of mercury-covered graphite electrodes have been described by numerous authors.[217-222]

The solid electrodes most often applied in voltammetry can be divided into two groups: noble metal electrodes, and graphite and carbon electrodes. In addition to electrodes belonging to these groups, electrodes of different materials are known.

Of electrodes made of other materials, boron carbide[223] is worth mentioning, but as electrodes of similar hardness can also be prepared from glassy carbon, it is losing its importance. Platinum is a very widely used and investigated electrode material, which is applied in a great variety of forms such as a disk, wire, tube, etc. Its electrochemical properties are outstanding, its polarization range is very broad, mainly in the anodic direction, and the residual current is relatively low. The main difficulty with the application of platinum electrodes is caused by surface phenomena such as adsorption and chemisorption, and by the fact that platinum is not fully inert. In fact, it may be oxidized and a layer of platinum oxides formed on its surface. The phenomena connected with oxide formation and the possibility of its removal with reducing agents have been elucidated by several authors.[224-227]

Besides the oxide layer forming on the platinum electrode, the electrode function may be further influenced by other films that build up on the surface, in many cases due to various electrode processes.[228] As these films generally are insulators, they must be removed before use. For this purpose, cleaning with sulfuric and nitric acid is generally used.

With the anodic polarization of platinum electrodes, another problem arises. The magnitude of the problem depends on the value of the starting negative potential used, because the amount of hydrogen adsorbed on the surface of the electrode is dependent on this potential. In the course of anodic polarization the hydrogen is oxidized, causing an anodic current and thus distorting the voltammogram.

In using platinum electrodes, a common practice is to pretreat the electrodes before use. The pretreatment ensures that the properties of the electrodes are the same after each pretreatment.

There are a lot of publications dealing with the pretreating procedures. Bishop,[229] in reviewing the problem of the activation and inactivation of platinum electrodes, pointed out the faults of the methods often used. He listed common steps in the different procedures: several anodic and cathodic polarization cycles in pure sulfuric acid, a prolonged cathodic polarization, and removal of the adsorbed or dissolved hydrogen potentiostatically at a potential of 0.25 to 0.4 V.

The behavior of the gold electrode is similar to that of the platinum electrode, but is somewhat simpler, because neither oxygen nor hydrogen is soluble in gold. Gold is also oxidizable though to a lesser extent than platinum if the medium does not contain complexing agents. However, considering the fact that in chloride solutions the electrode reacts chemically with the medium at a potential of +0.6 V, its use is limited. Widespread application of the gold electrode is hindered also by problems connected with sealing of metallic gold to glass; therefore, the preparation of the gold electrode is more complicated than that of the platinum electrode.

As reported by Guilbault,[230] by melting noble metal powders with low-alkali glasses, electrodes with good surface and mechanical properties can be prepared.

The carbon and graphite electrodes used earlier for industrial purposes gained importance only later in analysis because the surface properties of carbon and graphite (mainly their porosity) made it difficult to obtain reproducible results.

Earlier, the porosity of the electrode surface was eliminated almost exclusively by various impregnation techniques. The best electrodes of today are made by technologies ensuring a suitable structure and low porosity of carbon or graphite without any additives. The first graphite electrodes for analytical use were prepared by impregnation with wax.[231-233] Application of various waxes was considered, and the properties of the electrodes were improved by varying the impregnation process.

The simplest procedure for preparing such electrodes by the impregnation of the suitable graphite rod, mostly of spectroscopic purity, is to heat it with melted wax (at 90 to 100°C) for 2 hr. After the electrode is cooled, the side of the rod is covered with an insulator, and the disk itself is activated mechanically by polishing. Gaylor et al.[231,232] used opal wax from E. I. du Pont de Nemours Co., or castor wax from the Baker Castor Oil Co.

According to Morris and Schempf,[233] the properties of the electrode can be considerably improved by impregnation in vacuum.

One of the most frequently used carbon electrodes is the carbon paste electrode developed by Adams.[235,236] They are prepared from graphite powder of spectral purity by mixing it with a so-called pasting agent, which is a liquid that does not mix with water. The main points for choosing the liquid are: small volatility, low solubility, and the absence of electroactive impurities. As such agents, bromine naphthalene, benzene, paraffin oil, bromophorm, and carbon tetrachloride were tested. In the carbon paste electrode developed by Adams, the graphite powder is mixed with Nujol®;* in the one of Farsang[237,238] with silicon oil. The pastes are generally packed in an electrode holder of Teflon® or other indifferent material. To ensure electric contact, mercury or a platinum contact is generally used. The measuring surface of the electrode is smoothed and renewed with a spatula or another smooth plate.[228] The residual current of the carbon paste electrodes is small and the potential range extends from about −1.1 V to +1.1 V, depending on the pH of the electrolyte used.

Lindquist[239] designed an electrode with a wide polarization range. He calls this electrode a carbon paste electrode, but in our opinion, it could also be called a wax impregnated one. The important feature of this electrode is its surprisingly good quality ensured by a vacuum treatment of the graphite (in 0.1 M H_2SO_4 1.7 V vs. SCE is reached). The graphite powder is treated in a vacuum of 10^{-2} mm Hg at 1000°C for 1 hr, then poured into a mixture of melted ceresine wax and paraffin oil, and mixed. After 30 min it is cooled; the product formed is ground and placed in the electrode holder and heated to 80°C in order to obtain a homogeneous paste. The surface is smoothed with a piano wire.

Lindquist also reports on the effect of pasting agents.[240] He made a comparative investigation with seven different pasting agents and three systems with different electrochemical properties (ferri-ferrocyanide, quinone-hydroquinone, and phenol). He studied the resistance of the paste, the effect of the temperature on the half peak po-

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* 3 g UPG powder (Ultra Carbon Corp., Bay City, Mich.) with 2 m*l* of Nujol®.[261]

TABLE 1

Anodic Polarization Range of Silicone Rubber Based Graphite Electrode in Different Supporting Electrolyte

Supporting electrolyte	Polarization range vs. S.C.E. (V) (i = 1 μA)
0.1 *M* KCl	+1.35
1.0 *M* KCl	+1.32
0.1 *M* Na_2SO_4	+1.25
1.0 *M* NH_4NO_3	+1.30
0.2 *M* CH_3COOH	+1.40
0.1 *M* HCl	+1.30
0.1 *M* H_2SO_4	+1.40
0.1 *M* $NaNO_3$	+0.65
0.1 *M* NaOH	+0.70
Britton-Robinson buffer pH 8.1	+1.20
Britton-Robinson buffer pH 4.5	+1.20
Michaelis phosphate buffer pH 7.0	+1.25

From Pungor, E. and Szepesváry, E., *Anal. Chim. Acta*, 51, 417 (1970). With permission.

tential, and the reproducibility of the measurements. In his opinion, it is difficult to draw definite conclusions from the investigation, because in some cases different pasting liquids result in the same behavior and with another compound different behavior. The selection of the ideal pasting liquid is also difficult. It seems that for application to different tasks, the preparation of different pastes may be advantageous. For example, use of the FIL paste (Fluorochemical Inert Liquid FC-43, British Drug Houses, Ltd.) yields well-developed voltammograms, but the potential range is narrow. For achieving a wide potential range, the author suggested the use of his own, earlier reported[239] electrode.

A graphite electrode of heterogeneous phase, the so-called silicone rubber-based graphite electrode was designed by Pungor et al.[241,242] This electrode is prepared by dispersing graphite powder of spectral purity in poly(siloxanediol) with subsequent cold curing. The limit of the anodic polarization of the electrode in various background electrolytes is shown in Table 1. The limit for cathodic polarization is about −0.4 to −0.5 V, even in oxygen-free solutions. The residual current in the above background electrolytes at 1.0 V does not exceed 0.2 μA, and with later developed microelectrodes[243] is even better.

The graphite electrode with a polyethylene base developed by Mascini and Liberti,[244] similar to the one with a silicon rubber base, contains the graphite dispersed in an inert matrix. The electrodes are prepared by melting the components together at an elevated temperature.

Recently, the most popular electrodes are, undoubtedly, the graphite electrodes of homogeneous phase, the pyrolytic graphite and the glassy carbon electrodes. These electrodes were introduced about 15 years ago, and they proved to be very suitable in analytical practice, due to their good mechanical and electrochemical properties.[245-248]

There are numerous unsolved problems concerning the various graphite electrodes. We have relatively little data on the cause of good or bad functioning of an electrode for a certain case. The work of Elving and Panzer[249] is worth mentioning on the better understanding of the functioning and behavior of electrodes. The authors studied the pyrolytic graphite and glassy carbon electrodes in aqueous and nonaqueous solutions. Their method of study was mainly cyclic voltammetry, but they investigated the problems of the surface renewal by microscopic studies, to relate the accumulated charge and the potential of the electrodes. The most important findings are their statements about the renewal of the electrode surface. They proved that the surface of pyrolytic graphite electrode cannot be renewed reproducibly by polishing it with SiC paper, because the new surface has a different specific surface area, due to its roughness. Upon creating a fully new surface, the reversibility of the system investigated decreased. Therefore, the authors suggest the use of this method only if absolutely necessary.

Upon polishing the glassy carbon electrode with a 600 mesh SiC paper, tiny cracks appeared, which resulted in a high residual current. For example, the residual current of an electrode so treated was 70 μA, while polishing the same electrode with Al_2O_3 of 0.5 mm grain size, the residual current was 0.5 μA. In most cases, the polishing is not necessary at all, because the electrodes can be cleaned satisfactorily in a mixture of sulfuric and nitric acids.

In the case of pyrolytic graphite and glassy carbon electrodes, the embedding of the electrode material in a suitable electrode body is often a problem. Elving and Panzer[249] suggested epoxy resins for this purpose. Levy and Farina[250] designed a glassy carbon electrode for investigations of electrochemical processes occurring in melts, using a special glass — having the same thermal expansion as the glassy carbon (GCS-4 borosilicate glass, General Electric Co.) — as electrode socket.

Voltammetric solid electrodes are often made by the users themselves, and numerous types are commercially available, too. Some of these are listed in Table 2.

The various components studied often react with the material of the electrode, thus resulting in electrode surfaces with new properties. This phenomenon, which causes much difficulty, might provide the stimulation for experiments concerning the application of electrodes with chemically modified surfaces. The results in this new field will presumably advance further progress mainly in solution of different analytical tasks, in electrosynthesis and energy conversion. Miller[251] reacted the carboxylic groups of oxidized graphite with optically active amino acids, thus making it possible to obtain electrode-reaction products of S and R configuration from optically inactive starting materials. Lane and Hubbard[252] used, for in vivo determination of catecholamines, a platinum electrode treated with iodide ions. Murray et al. [253,254] designed chemically modified stannic oxide and glassy carbon electrodes by using different organosilanes to produce electrode surfaces with various properties.

B. Reference and Auxiliary Electrodes

Reference electrodes of the second kind are most frequently used. In polarography, mercury electrodes of high surface area also play an important role.

The general requirements for reference electrodes should also be fulfilled when using conditions that may have mass transport that is not wholly diffusion controlled. In addition to this, the electrode should possess a sufficient mechanical strength. Voltammetric investigations in flowing solutions involve mostly prolonged, continuous, or intermittent operation of the measuring system. Thus, the fulfillment of the requirement that the potential of the reference electrode should not change causes many problems. The change in the potential of the reference electrode during prolonged stress especially causes problems if the current is measured at a constant potential and a two-electrode system is employed.

Measurements at a constant potential, i.e., under amperometric conditions, is very often used in the hydrodynamic voltammetry (see later).

Though the use of two-electrode cells is still justified by various circumstances, the three-electrode systems permitting potentiostatic measurements are gaining importance.

TABLE 2

Some Voltammetric Electrodes Available in the Market

Firm	Model	Electrode type
Metrohm	EA 268	
	EA 205	
	EA 263	Platinum electrodes
	EA 282/1	
	EA 280	
	EA 277	
	EA 278	
	EA 279-12	Gold electrodes
	EA 279-70	
	EA 276	Glassy carbon electrode
	EA 267	Carbon paste electrode
Beckman	188551	Electrode assembly with interchangeable electrode tips
	39084	Vitreous carbon
	39086	Platinum
	39087	Gold
	39088	Platinum wire
	39090	Palladium
	39091	Silver
PAR	9333	Glassy carbon electrode
	9319	Paraffin-impregnated graphite electrode
	9324	Spectroscopic grade graphite electrode
	9326	Carbon paste electrode
	9312	Platinum wire
Tacussel	CV 30	Rotating vitreous carbon electrode
	Au 30	Rotating gold electrode
	Pt 30	Rotating platinum electrode

In two-electrode cells, reference electrodes of the second kind are employed in certain cases in forms available commercially, but versions better suited for hydrodynamic conditions are also often encountered. One type is a so-called flowing reference electrode. An example is the redox reference electrode used by Novak,[255] which consists of a platinum plate immersed in a flowing solution with a constant concentration of Fe^{2+} and Fe^{3+} ions. There is no other information about the use of this electrode system. Widely used in practice are the flowing Ag/AgCl electrodes. In all cases these consist of silver covered with an AgCl layer, and of a flowing solution of constant chloride ion concentration. Blaedel et al. used general reference electrodes with separated compartments (the reference and indicator electrodes are separated by an ion-exchanger membrane, e.g., References 256, 257). In many other cases the silver electrodes covered with silver chloride are immersed directly into the solution to be investigated which contains chloride ions at a constant concentration (e.g., References 243, 258).

In cases where a third electrode is also used, the reference electrode is often placed into the effluent solution. It could be advantageous, because the classical electrodes of the second kind used in this case cause fewer changes in the hydrodynamic conditions. In some cases[259,260] this means that the reference electrode is placed directly after the unit containing the working electrode, or in other cases in the collector vessel for the effluent solutions (e.g., References 215, 260, 261). This is frequently the case with automatic analyzers and chromatographic detection.

Besides classical electrodes of the second kind, the use of the so-called pseudo-reference electrodes is widespread, too. They fulfill the main requirements for reference electrodes inasmuch as *their potential does not change during the measurement*. But this does not generally mean that the potential of the reference electrode is a well-defined, constant value, (e.g., Reference 262). The use of such pseudo-reference electrodes is mainly connected with the application of potentiostatic measurements, but they are also applied in two-electrode measuring cells.

Noble metals, primarily platinum electrodes, are most frequently used as auxuliary electrodes. Their design depends on the measuring cell and the working electrode. For example, if in a tubular measuring cell the cylinder with a smaller diameter in the middle of the tube is the working electrode, then the outer cylinder is the auxiliary electrode, and conversely.

As used by Stulik and Hora,[259] the working and auxiliary electrodes are tubes of the same construction. The same design is described by MacDonald and Duke.[262]

In the work of Johnson and Larochelle,[263] the platinum wire used as an auxiliary electrode is wound on the glass tube of the reference calomel electrode.

C. Measuring Cells Used in Hydrodynamic Voltammetry

The main requirements for voltammetric detector cells are the following:

- Low resistance
- Small dead volume
- High sensitivity
- Low noise level
- High stability

For voltammetric measurements the *low resistance* is an important requirement, especially if the measuring cell contains two electrodes. High resistance would distort the voltammetric curve through the high iR potential drop, and thus also the current measured on a selected potential.

In two-electrode measuring cells using conventional reference electrodes of the second kind, the resistance of the cell changes between several and a few hundred kilohms, depending on the nature of the ceramic plug of the salt bridge that separates the reference from the working electrode. (The value of the cell resistance is generally determined in a measuring cell filled with a supporting electrolyte often used.)

The importance of reducing the cell resistance diminishes when using potentiostatic control — that is, applying a controlled polarization potential. Under such conditions, the resistance of cells developed for voltammetric purposes does not cause any appreciable problem.

The value of the *dead volume* (hold-up) is connected with the response-time of the measuring cell. The aim is, of course, to design cells with a fast response and small inertia. To satisfy this requirement is in general equivalent to efforts to develop small volume measuring cells. We shall see, later on, that these requirements are also connected with achieving high sensitivity.

According to convention, the response time is defined as the time period required for the current to reach 90 to 95% of its new value characteristic for the new solution, provided that the current is measured at a constant potential. According to Blaedel,[262] the processes occurring in the detector cell, when one solution is replaced by another,

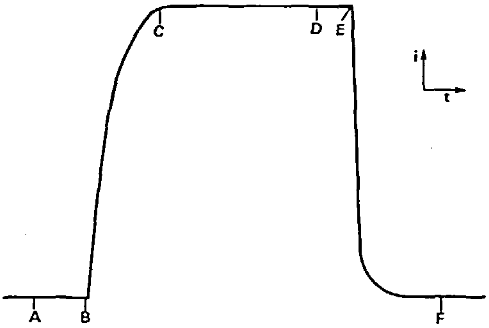

FIGURE 7. Cell response. (Reprinted with permission from Blaedel, W. N. and Strohl, J. H., *Anal. Chem.*, 33, 1631 (1961). Copyright by the American Chemical Society.) (A) Solution switched from the supporting electrolyte to solution containing electroactive component; (D) solution switched back to the supporting electrolyte. (A—B) and (D—E) are the dead regions; (B—C) and (E—F) are flushing regions.

can be subdivided into different steps (see Figure 7). Lund and Opheim studied the response properties of the automatic analyzer containing dropping mercury electrodes in a similar way.[265]

The dead volume of the measuring cell can be characterized by the volume of the solution flowing through the cell during the response time. In the case of a measuring system with good response properties, the response time is generally a few seconds, and the hold-up is below 1 m*l*.

Concerning the *sensitivity* of hydrodynamic voltammetric measuring cells, we can establish that the practical use of the method — mainly in the field of chromatography — is primarily due to the design of detector cells with suitable sensitivity. There are some fields where high sensitivity is not indispensable (e.g., in automatic analyzers). However, in numerous cases (beside the chromatography, already mentioned, in environmental analysis, biological, and clinical analysis) the general use of voltammetry is useful only by using detector cells of high sensitivity. The sensitivity of the voltammetric method can be increased in many ways. We intend to discuss mainly those that are connected with the cell design.

In the case of electrode processes with fast electron transport, the sensitivity of the method can be increased by increasing mass transport. Measuring cells with turbulent flow are made for this purpose. Of these, the wall jet electrode of Matsuda,[266] the similar detector cell developed by Pungor et al. (Figure 8),[267] and the cell containing a turbulent tubular electrode designed by Blaedel[268] are worth mentioning.

Another possibility for increasing the sensitivity of the cell is increasing the area of the electrode surface. This also can be carried out in different ways, e.g., with the detector cell containing gold minigrids developed by Blaedel and Boyer,[269] the cells containing various porous electrodes (Takata and Muto[270] use graphite cloth electrodes or platinum gauze electrodes; Johnson and Larochelle[271] use a platinum electrode packed with platinum wire).

For similar reasons thin-layer cells are also employed, where the solution to be investigated flows between two planar parallel plates.

In the cell developed by Kissinger and Adams[272] as a liquid chromatographic detector, the material of the working electrode is carbon paste. It is placed in the cavity of the block containing the liquid layer.

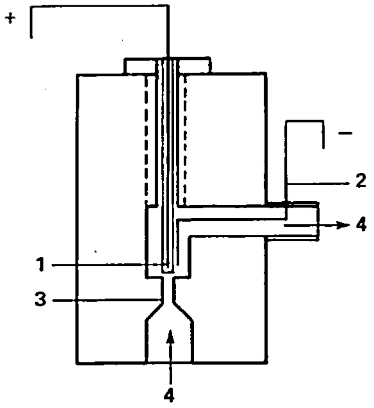

FIGURE 8. Construction of the cell used by Pungor and co-workers. (1) Working electrode, (2) reference electrode, (3) jet, and (4) direction of liquid flow.

Takata and Muto[270] designed a cell with a sandwich structure, in that the carbon cloth or platinum gauze electrodes have two active sides. These are surrounded on the two sides by two Ag/AgI auxiliary electrodes, and these are separated from the working electrode by an ion-exchange membrane.

By increasing the ratio of electrode surface to solution volume, more than the usually small fraction of the material is transformed in the measuring cell. Thus it is possible to use for quantification of the coulombs passing through the measuring system in a coulometric mode. In this fashion, chromatographic detector cells can electrolyze all of the component (e.g., References 270, 271, 273).

The *noise level* is, in general, influenced by whatever ensures the motion of the solution of the electrode. For example, the peristaltic pumps used for moving liquids cause a pulsating flow, thus inducing the oscillation of the measured current. To diminish this oscillation, damping electrically with RC-circuits generally used in polarography is applicable only with restrictions. With high damping the response properties of the system can worsen remarkably.

The use of various flow-buffer vessels for this purpose is restricted. Though several attempts have been made, (e.g., Reference 274) to eliminate the noise originating from the properties of the various pumps, a good solution for the problem has not thus far been found.

Another source of noise is the turbulence taking place in the voltammetric cells. For the case of cells of poorly defined hydrodynamic conditions, the undesirable turbulence could increase the noise. However, if well-defined hydrodynamic conditions are ensured in the measuring cells, the turbulence does not cause any problem with respect to noise.[275]

Problems connected with the *stability* of the measuring cells were already mentioned when discussing the working and reference electrodes. The main problem is the contamination of the working electrode surface. The continuous change in the potential of the reference electrode when using two-electrode measuring cells can also adversely affect the results.

The stability of the measuring cells with time can be expected for cells with simple construction. In these cases changes in the hydrodynamic conditions and mechanical damage are not expected.

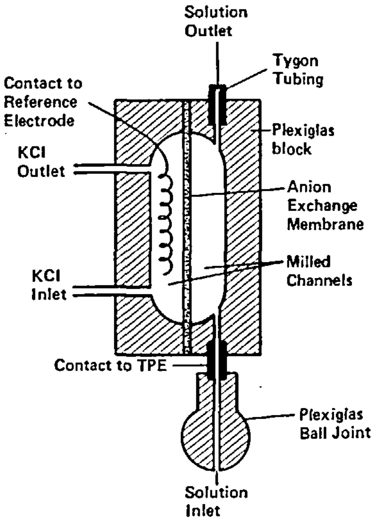

FIGURE 9. Flow-through measuring cell containing tubular electrode. (Reprinted with permission from Blaedel, W. J. and Klatt, L. N., *Anal. Chem.*, 38, 879 (1966). Copyright by the American Chemical Society.)

Cells for hydrodynamic voltammetric measurements of today are very numerous. Their classification with emphasis on individual types is, of necessity, arbitrary.

In flowing solutions, voltammetric investigations can be carried out under very favorable hydrodynamic conditions using detector cells that form a section of the flow tube. In certain cases part of the flow tube serves as the working electrode (tubular electrodes, see Figure 9). In others, the working (or possibly the reference) electrode is introduced into the flow-through cell, which is a part of the flow tube (Figure 10). The routine use of the latter cells is facilitated by the fact that the electrodes are easily interchangeable.[283]

In many cases one can conveniently use measuring cells assembled from two parts — or possibly from several parts. Examples are the thin-layer cells that are often made of Perspex® or other plastics containing engravings, holes or channels[270,272] (Figure 11). The volume of these cells is extremely small (few microliters), while the surface of the working electrodes can be relatively be very high.

As mentioned earlier (in the case of the three-electrode systems) the reference electrodes, which are more complicated and difficult to accommodate, are placed into the effluent solution widely separated from the working electrode (e.g., Reference 272).

Surveying the types of measuring cells applied today mainly for analytical purposes, one can say that though the ensuring of well-defined hydrodynamic conditions is considered, the study of the cells from a hydrodynamic point of view is generally not done. That is, the dependence of the current on the parameters of the cell of the flowing system is not investigated theoretically. In general, the objective is to develop a measuring cell with a possibly linear concentration response which meets the analytical requirements.

Few measuring cells for hydrodynamic voltammetry for analytical purposes are commercially available. Rotating disk and rotating ring disk electrodes are available, to-

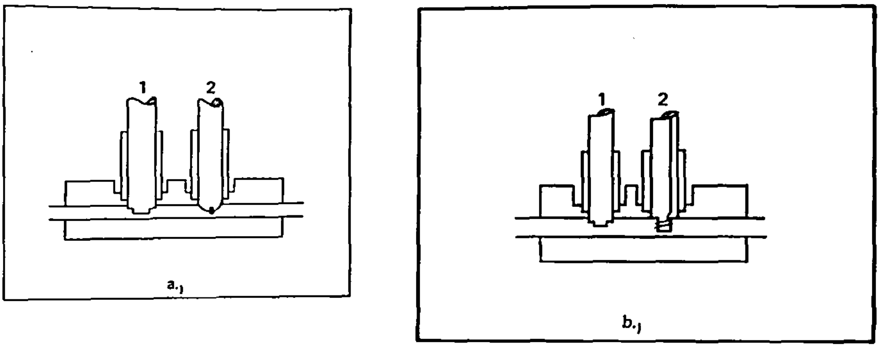

FIGURE 10. Flow-through measuring cell containing disk type silicone rubber based graphite electrode. (1) Working electrode; (2) reference electrode: (a) saturated calomel, (b) silver-silver chloride.

gether with mechanical units ensuring the rotation of the electrode at constant speed (e.g., References 276, 277).

Another commercially available unit (cell or electrode combination) serves for the measurement of dissolved oxygen (e.g., References 278 to 280).

As reported recently, chromatographic detector cells have now appeared on the market.[281, 282]

D. Practical Problems of Hydrodynamic Voltammetric Measurements

As with other analytical methods, problems such as sensitivity and selectivity arise in hydrodynamic voltammetry. However, due to the specificity of the method, special problems also occur, i.e., ensuring constant hydrodynamic conditions, etc.

In order to solve the problems, several approaches exist. One of them is the physical and chemical approach, the other one is the use of different techniques and electronics.

Later, problems connected with the practice of hydrodynamic voltammetry will be discussed according to the above considerations.

1. Concentration Determination

For analytical examinations, the signal is basis of concentration determination. That is, the limiting current can be determined either on the basis of the function of current intensity vs. polarization potential recorded in certain time intervals in a given potential range, or by measuring the current intensity at a fixed potential, which is in the limiting current range of the component to be examined.

In theoretical works, the limiting current functions are generally examined. However, quite a few works are known that discuss the theoretical deduction of the total current-potential curve holding for certain voltammetric measuring cells (e.g., Matsuda's papers[112-120]).

Mainly, the measurement of the limiting current is done in practice, although the recording of current potential curves with time has also been employed.[284-286]

It is to be noted that both the theoretically deduced current-potential functions and the limiting current equations assume steady-state conditions. In the case of current-potential recordings, it means that the relationships deduced theoretically agree with the data of the curve recorded point by point.

The agreement of experimental current-potential curves with the theoretical ones depends first of all on the ratio of the flow rate and the polarization rate. (According to Sharma and Dutt,[287] the current-potential curves recorded automatically and manually in turbulent flow are the same. However, the polarization rate is not given.) In

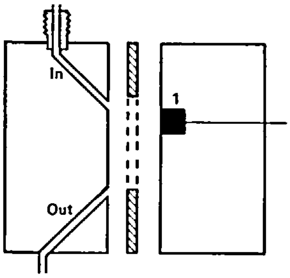

FIGURE 11. Flow-through thin-layer cell containing a carbon paste working electrode. (From Kissinger, P. T. et al., *Anal. Lett.*, 6, 465 (1973). With permission.) Reference and counter electrodes are in the overflowing solution.

practice, the current potential curves are, of course, recorded by automatic scanning techniques.

In choosing the appropriate measuring technique of recording current-potential curves or recording the current at constant potential, the character of the task to be solved must be considered. Obviously, if the concentration of a component is to be determined continuously, then preferably the limiting current-time curve should be recorded. If in the solution to be examined, qualitative changes may occur, then these, of course, can be followed by recording current-potential curves with time. Naturally, the choice of the method is influenced also by the fact that the latter procedure requires a more complicated instrument.

The relationship of current intensity vs. time at constant potential can be extremely easily transformed into a concentration-time correlation by the linear relationship existing betweeen the limiting current and concentration. When measuring the current intensity at constant potential, the conditions of a steady-state condition are realized. This implies numerous advantages (see later).

In hydrodynamic voltammetry the determination of concentration of solutions to be analyzed is carried out — in almost every case — by using calibration curves. The standard or analyte addition method is used only in special cases, e.g., in stripping voltammetry. The accuracy of measurements is influenced by about the same factors as in classical voltammetry, that is, graphical evaluation and stability.

2. *The Problem of Sensitivity*

To increase the sensitivity of the voltammetric method, different techniques — mainly AC measuring ones — were developed. These methods however are not commonly applied under convective diffusion conditions. In this relation, first of all, pulse voltammetry (normal and differential pulse) is considered. Such experiments are reported by MacDonald and Duke[288] and Stulik and Hora.[289]

The sensitivity of the voltammetric method is limited by the residual current, which is primarily the condenser current. However, for voltammetric examinations performed under convective diffusion conditions, the effect of the condenser current can be eliminated or significantly reduced, in the case of electrodes of constant surface area, without using any special technique, by measuring the current at constant potential.

The effect of the components of the residual current connected with different Faraday-type transitions can also be eliminated, since the steady-state condition ensures that the measurement is performed after the relaxation of the time-dependent electrode-surface reactions.

At the same time, the measurement of current at constant potential offers possibilities to compensate for the residual current. It can be performed either electrically or physicochemically by using a difference measuring technique. In the latter case, the difference between the current characteristic to the solution to be analyzed and a blank solution, respectively, is measured.

If it is considered that the current measured under convective diffusion conditions — due to the increase of the mass transport — may achieve a value higher than that of the diffusion current, then it is obvious that the current measured at constant potential and under convective diffusion conditions may result in a significant increase in sensitivity compared to classical voltammetry. In this sense, hydrodynamic voltammetry with the measurement of the current at constant potential (hydrodynamic amperometry) can be regarded as a highly sensitive voltammetric method. Consequently, the voltammetric measurements are best performed under hydrodynamic conditions in many cases, even if the task itself does not especially require it. That is why measurements made with a tubular electrode under hydrodynamic conditions are recommended by Mason et al.[290,291] and Sharma et al.[292] for the determination of the drug content of pharmaceuticals.

Blaedel and co-workers[293] reach a detection limit as low as 2×10^{-7} *M*, measuring the current at constant potential in flowing solution. Bruckenstein and co-workers[294] could determine concentrations in the 10^{-8} *M* range by using a rotating disk electrode.

The sensitivity can be further increased by improving the hydrodynamic conditions. When using appropriate thin layer cells (e.g., References 295, 296) and increased mass-transport via turbulent flow (e.g., References 297, 298), surprisingly high sensitivities were reached.

To utilize the advantages offered by measurements performed under convective diffusion conditions and at constant potential, a new, so-called injection measuring technique has been developed by Pungor et al.[299] In the course of the injection technique, the analysis of the sample solution of small volume is carried out in a flow-through analysis channel. The electrolyte or reagent chosen for the determination is passed through the analysis channel at a constant rate. At a certain point in the channel, a small volume (some 10 μl) of the sample to be examined is injected into the flowing solution. The flowing and injected solutions enter a mixer to homogenize the stream. The homogenized solution then reaches the voltammetric detector cell. The current from the detector cell (which measures the current at a constant potential) follows the concentration changes of the solution giving a peak-type current-time curve.

On the basis of a simple mathematical model, a relationship[299] between the characteristic data of the curve obtained (peak height, area under the peak) and the quantity of the injected electroactive component can be deduced. Considering the fact that hydrodynamic conditions are constant, and both the peak height and the area under the peak are proportional to the quantity of the electroactive component, the injection measuring technique is a reliable analytical method that is simple to apply in practice. The advantageous applicability of the method has been justified by a great number of experiments and the solving of analytical problems.[300,301,329]

In addition to the analysis of electroactive sample solutions, the method was found to be easily applicable in the following cases:

Analysis of electrochemically inactive sample solutions carried out by having

- the supporting electrolyte containing an electroactive reagent which reacts chemically with the component to be determined
- an electrochemically inactive reagent in the supporting electrolyte which, in the course of chemical reaction with the sample, produces an electroactive component

Periodic analysis of inactive streaming samples performed

- by injecting the electroactive reagent, which reacts chemically with the streaming solution
- by injecting the reagent, which is inactive itself, but leads to an electroactive product by reacting chemically with the streaming solution

It is easy to see that with different working electrodes, electrode potentials and medium applied to the measurement, the injection measuring technique becomes a widely applicable method.

These days, one of the important requirements of analytical methods is the capability to do rapid serial analysis of different samples having similar composition. This goal is most likely achieved by flow-through systems. Thus the injection measuring technique is a convenient and up-to-date method.

First of all, the reliability of analyses is increased significantly if the concentration determination is based on a titration equivalence point and not on a direct signal. In streaming solutions, titrations can be performed only with the help of an appropriate reagent addition program. The correct evaluation of the titration curves is the other main problem arising for titrations in streaming solutions.

Nagy et al.[302] developed the so-called triangle programmed titration technique for solving these problems. As it is clear from the above, this operation is also performed in a flow-through analysis channel. A reagent with a mass flow increasing and decreasing according to a triangle program is introduced into the sample solution at a given point of the analysis channel. The flow rate of the sample solution is constant. The solution flows into the detector cell placed in the channel behind the mixing unit. Consequently, the detector signal-time curve obtained is actually a titration curve. Strictly speaking, due to the triangle programmed reagent addition, two symmetrical titration curves are obtained.

One of the main advantages of the triangle programmed titration technique is that the evaluation is accomplished using the two equivalence points, instead of the starting point of the titration curve and the equivalence point. (As a matter of fact, the starting point can be determined only with uncertainty.) This ensures great reliability and accuracy. The time elapsed between the appearance of the two titration equivalence points serves as basis for the evaluation.[302,303] Another important advantage of the method is that the results are independent of the actual state of the working electrode. This means that a long term stability of the working electrode is not strictly required to obtain accurate results.

This method, which enables the application of electrolytic or volumetric reagent addition techniques[304,305] and different detector cells[303-305] is reliable, extremely extensively applied, and an easy-to-automate analytical method. It must be noted that highly accurate titrations can be carried out in various concentration ranges by varying the reagent addition program.

The above procedures — for flow-through systems — generally make the measurement too complicated.

3. The Problem of Selectivity

In order to improve the selectivity of the voltammetric method, the use of AC techniques is usually applied. For this purpose, experiments were also made under hydrodynamic conditions. Buchanan and Bacon[306] applied square-wave polarographic detection for the analysis of ion-exchanged solutions. The current was recorded periodically at the potentials corresponding to the peak currents of the four metals.

Lane and Hubbard[307] used the so-called differential double pulse voltammetric technique for determination of dopamine in the presence of ascorbic acid under in vivo conditions.

Blank[308] used detector cells containing two working electrodes for solving selectivity problems. The two electrodes were connected in two different circuits. Applying different electrode potentials, the determination of the concentrations of dopamine and norepinephrine become possible in the presence of each other.

Adams[309] found it also reasonable to use more than one electrode polarized to different potentials for determining concentrations of various catecholamines in the brain.

The application of a membrane coverage can also ensure selective determinations, especially in the case of gases.

The relatively poor selectivity, but very high sensitivity of the hydrodynamic voltammetric method explains the combination of the liquid chromatograph with voltammetric detection. This is one of the most dynamically developing analytical methods of today.

In practice, chromatography is generally applied combined with the above mentioned methods for further improving selectivity.

Square-wave polarography[306] and pulse-voltammetry[307] have been used in analysis of chromatographic eluates.

4. The Problem of Long-Term Stability

In the practice of continuous voltammetric measurements, the stability of the measuring system plays a key role. The most unstable part of the measuring system is generally the working electrode. In the case of the earlier predominantly applied dropping mercury electrode, the problems are mainly connected with the unfavorable mechanical resistivity of the electrode (clogging of the capillary, unsystematic dropping upon mechanical effects). These problems are eliminated partly by using capillary electrodes of great diameter and partly by employing mercury-electrodes of constant surface area.

Problems connected with the application of dropping mercury electrodes in an automatic analyzer system are discussed in detail by Lund and Opheim.[310,312]

Electrodes of constant surface area, mainly the solid ones, in general possess very favorable features from the point of view of mechanics. Usually the problems are the changing nature of the surface of these electrodes with time. As mentioned above, the change in the electrode surface is caused mainly by two facts. The first is changes in the surface phenomena occurring mainly at noble metal electrodes (hydrogen adsorption and solution, formation of oxide films, adsorption phenomena); the other is the so-called film formation in the course of the measurements. An insulating film on the electrode surface is formed when the product of the electrode reaction does not dissolve in the medium used.

According to the above, the functioning of the working electrodes requires, in both cases, pretreatment of the electrode surface. The surface pretreatment for the noble metal electrodes has been discussed already.

Under favorable conditions the pretreatment of the working electrode is only needed at the beginning of the measurement. To carry out the pretreatment under hydrodynamic conditions, one possibility is the design of such a measuring system that enables the alternative flow-through of the solutions for the surface pretreatment and the measuring solution. Another is to ensure the easy removal of the electrode from the measuring system for surface preparation.

The above procedures — for flow-through systems — generally make the measurement complicated.

In every case it is desirable to protect the working electrode. Methods developed to decrease the damage of the working electrode are also suitable for the regeneration of the working electrode.

Different ways are known to prevent the contamination of the electrode surface. One possibility is to cover the measuring surface of the electrode (Clark-type electrodes, membrane-covered mercury electrodes). Obviously, it solves only a part of the problem, as it protects the electrode mainly from the mechanical contaminants.

Another physical method for preventing contamination of the electrode and for regeneration of it was suggested by Blaedel.[293] He proposed to flow the sample and a blank solution having a similar composition alternatively through the measuring cell.

In order to reduce stress on the working electrode, Novak[313] suggested a method according to which the polarization potential is applied only periodically. The essence of the pulse polarographic technique is similar in that the electrode is polarized only for a short time.

We have to mention that the injection technique discussed earlier has an advantage in this respect too, as only the supporting electrolyte is flowing between the sample injections. During this interval, the conditioning of the electrodes is performed.

Koryta and co-workers[314,315] performed the periodical regeneration of an electrode electrochemically in the course of their investigations in biological systems. Cyclic voltammetric curves were recorded periodically, utilizing the fact that the polarization in the opposite direction to the original one, in many cases, results in an electrode condition similar to the starting one. The same solution was used by Kamlyuk and Kamlyuk[316] in the determination of oxygen solved in water.

For the periodical electrochemical regeneration of the electrode surface, a ring shaped analysis cell divided into segments was constructed by Turjan.[317] The working electrode was rotated centrically and passed through the region of the flowing liquid to be analyzed, then the region of the regenerating solutions (which was supplied by auxiliary electrodes removing the contamination) and finally the region of the wash water and that of the standard solution of known concentration, as well.

A method applying three part measuring cycles in order to avoid passivation of the indicator electrode is elaborated by Stulik and Hora.[289] For the measuring period of the cycle, they used an impulse-like polarization, and besides this, a cleaning and a relaxation period were applied. For cleaning, a suitable potential was used during which the metals investigated were removed from the platinum electrode, and during relaxation the measuring potential was applied. Current measurements were begun only after relaxation of the charging current.

In its present form, this method is suitable for solving special problems, only in cases when the potential used for cleaning does not influence the electrode process itself.

As described already at the discussion of working electrodes, the renewal of the surface of electrodes having a constant surface area presents many problems — even in that case when the electrode is not used for monitoring flowing or mixed solutions. Naturally, the difficulties for analysis of static solutions are increased under hydrodynamic conditions.

From the point of view of reproducible renewal of the electrode surface, the carbon paste and the glassy carbon electrodes possess the most favorable characteristics. In their case — with some skill — the electrode surface can be renewed with an error of some 1 to 2%. Surface renewal done in a mechanical way is difficult to do automatically in a flowing or mixed system. In this respect, attempts have been made.[318] However, a convenient solution of the problem has not been reached. In order to solve and eliminate surface phenomena problems, researchers choose or produce the best working electrodes from among those at their disposal. In many cases the occurrence of interfering electrode surface phenomena can be avoided by choosing proper conditions for the analysis. In addition to these, the majority of the detector cells made for analytical purposes are constructed in such a way that the periodical "maintenance" of their electrodes is possible by grinding or polishing of the electrode surface, putting fresh carbon paste into the electrode body, replacing the membrane and gel, respectively, in the case of membrane electrode (see O_2 measurement), exchange of the enzyme layer in the case of enzyme electrode, exchange of the reference electrode solution, etc., or the exchange of the electrode itself, if needed.

5. The Problem of Constant Hydrodynamic Conditions

On the basis described earlier, it is self-evident that the limiting current data obtained under convective diffusion conditions can be used for analytical purposes only if the measurements were carried out under well defined and constant — possibly known — hydrodynamic conditions. From among the hydrodynamic parameters, mainly the flow or mixing rate of the electrolyte and the moving speed of the electrode significantly affect the value of the current intensity.

Considering the effect of the flow rate, different ways can be chosen in the course of the measurements. Most frequently the flow rate and the moving speed of the electrode, respectively, are maintained strictly at constant values. At rotating and vibrating electrodes this can be achieved by accessories ensuring a constant rate. There is a large amount of electrode rotating equipment commercially available (e.g., Reference 319).

In early experiments, the constancy of the flow of the fluid to be examined under convective diffusion conditions was often accomplished hydrostatically, so the constant flow rate was provided by keeping the hydrostatic pressure at a constant value. The flow rate can be controlled by N_2 gas pressure.[320] Presently, the constant fluid flow rate is ensured mainly by different pumps, usually with peristaltic ones. Two problems should be pointed out regarding the fluid transport pumps. With peristaltic pumps, the flow rate depends generally on the stability of the characteristics of the transporting tubes. In the course of long-term continuous measurements, the stability of the flow rate of the transporting unit should be tested. A further problem originates from the character of the peristaltic pump, namely — owing to its construction — it cannot transport the liquid continuously with a constant speed, but with a more or less oscillating speed. This periodical change of the flow rate results in an oscillation in the current intensity flowing in the measuring system. In general, this oscillation can be neglected and signal evaluation is not disturbed. However, the interfering effect of this oscillation may reach a significant value when measuring very low concentrations. In high performance liquid chromatographic systems, the voltammetric detector cells serve for determining solutions of very low concentration ($\sim 10^{-8}$ *M*). In this case, the oscillation caused by the pumps is buffered by the chromatographic column. In other fields, where the task is also to determine solutions of very low concentrations, such as inverse voltammetric measurements the convective diffusion conditions are generally applied only in the course of deposition process, and here the above mentioned phenomenon of oscillation does not cause interference.

Some attempts to eliminate the effect of changes in the flow rate, are known too. Those kinds of procedures do not strictly belong to this discussion. An example is where the flow of the solution in the analysis channel is stopped and the analysis is carried out in a static solution. This is the stop-flow technique.

According to the ideas of Bowers and co-workers,[321] the working electrode used in a flowing solution should be coated with a membrane in order to eliminate the effect of the flow rate. For membrane-covered electrodes the measured signal is independent of the flow rate, provided the value of the flow rate is appropriately high, e.g., for oxygen electrodes the linear rate is suggested to be about 10 cm/sec. In our experiments performed with a membrane-covered mercury electrode[301] the signal measured became independent of the flow rate above the flow rate of 4 mℓ/min.

Strafelda[322] compensates for the effect of flow rate by rotating or vibrating the electrode at a high rate, so that the flow rate of the liquid examined is negligible in comparison. The results of Blaedel's[323] investigations using a turbulent tubular electrode are also similar. Namely, the flow rate of the solution streaming through the electrode does not play any role in the value of the current intensity. This is explained by supposing that suitable turbulence is produced in the tubular electrode.

In practice, if circumstances allow, it is expedient to perform the voltammetric measurements by keeping the flow rate at a constant value. However, in some cases this cannot be managed due to the nature of the task. To solve such a task (control of a continuous chemical process in tubular reactor) Pungor et al.[324] designed a signal transmitter that does not directly measure the current corresponding to the actual concentration, but the ratio of the convective diffusion current of the sample to that of an appropriate standard. The limiting current of the two components is measured at two different potentials alternatively.

From the knowledge of the flow rate and the limiting current equation holding for the given system, the concentration can be calculated from the current intensity measured. This method is, however, very seldom adapted.

6. The Problem of Dissolved Oxygen

The examinations of reactions, primarily reductions taking place at negative potentials and the concentration determinations from them, are complicated by dissolved oxygen — due to its electroactivity. The most frequently used way to remove the oxygen is to let inert gas bubble through the solution. Also for experiments carried out in streaming solutions a very frequent procedure is to bubble N_2 or some other inert gas through the solution prior to the solution entering the measuring system. In liquid chromatography the oxygen removal is done in the solvent and sample before the solvent enters the chromatographic column.[325] By changing the pressure of the N_2 or other gas, the flow rate can also be regulated.[320]

Several papers report on the problems occurring by oxygen release in automatic analysis. Fleet[326] determined calcium and magnesium in a Technicon Auto-Analyzer®. He used N_2 to deaerate the flowing solution. Because the anodic oxidization of EDTA and EGTA reagents takes place at a potential value about zero volts, this solution is convenient. The situation is more complicated when the analytical determination is to be performed in the negative potential range. Lento[327] used a time delay coil to saturate the solution with nitrogen. In this case the problem is that before washing, the sampling probe draws in air, and this can be seen on the recordings.

Silvestri[286] mixes the sample solution with a great amount of the oxygen-free background electrolyte; Cullen,[328] similarly to Lento, applies a mixing coil for the saturation of the liquid with nitrogen.

Lund and Opheim[310] discuss in detail the problem of deoxygenation. According to them, the methods of deoxygenation discussed above and used in the automatic analyzers solve only a part of the problems caused by the presence of dissolved oxygen.

Therefore, they designed a device for deoxygenation of the sample solutions before analysis. The unit for introducing nitrogen removes oxygen simultaneously from three samples. Considering however, that the sampling probe draws in air during the transportation of the sample, this system is also only successful when the pump is stopped during sample transportation. As opposed to the opinion of the authors, this cannot be considered the most favorable situation.

From the above, one can conclude that the problem of deoxygenation in polarographic analyses using automatic analyzers of the Technicon type is not solved satisfactorily at present.

7. *The Effect of Temperature*

The same aspects are valid for temperature effects in hydrodynamic voltammetry as for measurements under pure diffusion conditions. Among the parameters influencing the hydrodynamic properties of the system is the temperature-dependent kinematic viscosity. When the electrode process used for concentration determination is transport controlled, and is not coupled with chemical reactions, the change in the current due to the change in temperature is 1 to 2%/°C. Therefore, great attention should be paid to the constancy of temperature only in special cases. If the electrode process is coupled with a chemical reaction, the effect of the temperature may, of course, be greater. Thus measurements are to be carried out in thermostated solutions.

When determining the concentrations of gases dissolved in liquids, consideration of temperature effects is extremely important. The most often used such measurements are those for determining dissolved oxygen; the measuring sensors designed for this purpose perform temperature compensation.

IV. THE APPLICATION OF HYDRODYNAMIC VOLTAMMETRY

For the application of hydrodynamic voltammetry, an extremely large scale of possibilities is offered. However, only a small fraction of these possibilities has been realized in practice so far. However, we are witnessing the rapid extension of voltammetry in analytical practice. Although the flow-through voltammetric detector cells have already been known for chromatographic purposes for about 25 years, this method has become widely applied only in the last 5 years.

The voltammetric examinations carried out under convective diffusion conditions are used in numerous other fields beside chemical analysis. However, as previously mentioned, this paper deals mainly with electroanalytical aspects of hydrodynamic voltammetry. Thus the preparative electrochemical processes and studies concerning the anodic dissolution of metals are not treated here.

A. Investigation of the Kinetics of Electrode Processes

Both in extent and significance, the most important field of hydrodynamic voltammetry is undoubtedly the study of mechanism and kinetics of different electrochemical processes. For this purpose, until now the rotating disk electrode operating under very simple and well-defined hydrodynamic conditions has been universally used. When describing the limiting current equations holding for a rotated disk electrode, it has been noticed that the voltammetric curves obtained under different hydrodynamic conditions, for example at different electrode rotating rates, provide sufficient data to determine the rate of quasi-reversible and irreversible electrode processes, even in the case when the electrode process is combined with a chemical reaction. The relating information and the detailed description of their concrete employment can be found in the comprehensive works of Riddiford[330] and Adams.[331]

A more effective tool for the investigation of the electrode mechanism is the rotating ring disk electrode. For its application, however, more complicated and not commonly manufactured instruments are needed than is the case for rotated disk electrodes. This electrode system is, first of all, convenient for the investigation of electrode processes which are combined with chemical reactions. In the case of organic materials, the opportunity to detect intermediates of short lifetime is ensured by this electrode system. The anodic dissolution of metals and alloys, as well as different catalytic reactions can advantageously be studied by the rotating ring disk electrode. Detailed results achieved in this field are reported in the detailed work of Adams,[331] Riddiford,[330] and also in papers written by Bruckenstein et al. (e.g., References 332 to 335), and Nekrasov et al. (e.g., References 335 to 338).

For the investigation of different electrode processes, many other types of electrode species and measuring cells are used in addition to the above ones. To determine the rate of electron transfer processes, Jordan and Javick[339] used rotated and circulatory electrolysis cells, Marchiano and Arvia the so-called thermal free convection electrode,[340] while Blaedel[341] used a turbulent tubular electrode.

To solve tasks similar to those of rotated ring disk electrodes, different double electrodes have been developed by researchers as was discussed earlier.

B. Study of the Reaction Rate of Chemical Reactions

The hydrodynamic voltammetric method, in addition to the investigations of kinetics of electrode processes, is suitable to the determination of the rate of chemical processes. Until now this possibility has been employed only to study the rate of the enzyme catalyzed reactions, and through this to determine the activity of enzymes.

Blaedel and Olson[342] constructed an arrangement containing two tubular electrodes, convenient for differential voltammetric measurements. Smith and Olson[343-345] used them to study rates of processes catalyzed by monoamino-oxidase enzyme and that of processes catalyzed by lactate dehydrogenase and alcohol dehydrogenase enzyme.

A circulatory cell was designed by Landolt[346] to study rapid chemical reactions.

In another circulatory cell developed by Schwing et al.,[347] chemical reactions can be followed by voltammetric and photometric detection.

Cells containing different optically transparent electrodes make possible the study of processes involving spectrochemical and electrochemical changes.

Johnson and Resnick[348] prepared a rotated ring disk electrode in which the disk was made of an optically transparent material. Products arising due to the photolysis of benzophenon and potassium ferrioxalate were detected on the ring electrode.

C. Determination of Diffusion Coefficients

The hydrodynamic voltammetric measuring technique is also an appropriate method for the determination of the diffusion coefficients of different components. Current intensity data obtained at rotated disk electrodes most frequently provide the basis of determination of diffusion coefficients (e.g., References 349 to 351), but other electrode systems were also used for this purpose.[352,353]

Concerning the determination of the diffusion coefficient, it must be noticed that the rate of the electrode process may be highly influenced by the quality of the electrode (see Blaedel's publication[341]). Consequently the diffusion coefficient defined this way is also dependent on the electrode applied. This fact should be taken into account when using diffusion coefficients obtained with the voltammetric method.

A further example for the nonanalytical application of hydrodynamic voltammetry is the so-called electrochemical rotameter. Ranz[354] suggests the application of the well-defined correlation between the voltammetric current and the flow rate for the determination of unknown flow rates.

D. Amperometric Titrations

The first extended analytical application of voltammetric measurements performed under convective diffusion conditions can be regarded as amperometric titrations. Generally, rotated and vibrating electrodes, as well as stationary electrodes placed into a mixed solution are used in order to be able to follow titrations involving the consumption or excess of an electroactive component, and to detect the end point of the chemical reaction. Constant convection should be present to closely follow the titration process. Stock[355] gives a detailed report on measuring devices used and on titration processes performed with one- and two-polarized electrodes.

At amperometric titrations under the conditions of convective diffusion, the advantages of current intensity measurements performed at a constant working electrode potential prevail. Thus in amperometric titrations the advantages both of hydrodynamic voltammetry and titration measuring technique are present.

E. Methods Using Hydrodynamic Voltammetry to Increase Sensitivity of the Voltammetric Method

In order to improve the sensitivity of the voltammetric method, convective diffusion conditions are used not only for amperometric titrations, but in several other cases, too. Hydrodynamic voltammetry as a highly sensitive analytical method has already been treated earlier, so here the convective diffusion mass-transfer applied in stripping technique is surveyed. In inverse voltammetric analysis the concentration process is carried out under convective diffusion conditions produced in different ways. Štulikova and Vydra[356] determined mercury with a rotated disk electrode made of glassy carbon, while a mercury-coated glassy carbon rotated disk electrode was used for the inverse voltammetric determination of the lead content of a drinking water sample.

Clem[357-359] performs the concentration step of the anodic stripping voltammetric determination in a rotated cell. Heavy metals in the parts per million concentration range were determined by using different working electrodes, mercury, platinum, and wax-impregnated graphite. For inverse voltammetric purposes, a measuring system containing a tubular working electrode was developed by Lieberman and Zirino[360] and Seitz et al.[361] According to both works the metal ions to be determined, Zn and Tl in seawater, were concentrated on a mercury film coated graphite electrode. The current distribution on the tubular electrodes is not uniform along the tube length, thus the thickness of the mercury film deposited from the continuously flowing solution varies along the electrode length. The thickest part is in the entrance section. To form a uniformly thick mercury film, Mason and co-workers[361] formed the film in static solution.

Lieberman and Zirino[360] described a system in which a solution containing mercury ion, and one with the sample solution, were alternatively flowed through the cell. This ensured development of the mercury film.

Due to the varying current density along the tubular electrode, the deposition level of the metal in question is not continuous either. This results in a potential difference between the actual stripping peaks and the theoretical ones.

To avoid the problems originated from the tubular electrodes, Wang and Ariel[362] passed the solution to be analyzed through a flow-through cell onto the glassy carbon disk electrode. When the solution containing mercury was passed through the cell, the indicator electrode was polarized to a potential of −1.25 V. When passing the sample solution through the cell, a polarization potential equal to the deposition potential of the metal ion to be determined was applied. The flow of the sample solution was stopped and the stripping curves recorded after a short rest period.

F. Fields of Analytical Application

Strictly speaking, in the analytical application of hydrodynamic voltammetry, the following must be noticed. The demand for the determination of concentration of a component may arise in several ways. Frequently the task is to determine the concentration of a given constituent in a mixed or continuously flowing electrolyte. In this case, owing to the type of the task, the voltammetric measurement is to be made under convective diffusion conditions, e.g., analysis of solutions leaving a chromatographic column or a continuously operating reactor.

Sometimes it is also required that the concentration conditions of a system should be reported as a function of time. In these cases, continuous sampling and analysis can be realized by constructing a recirculation system or a by-pass circuit containing voltammetric cell.

In certain voltammetric concentration determinations the operation of the sensor necessitates convective diffusion conditions, e.g., membrane-coated indicator electrodes, enzyme electrodes.

The hydrodynamic voltammetric measuring technique — based on its advantages described above — can be applied in many cases for everyday analytical tasks, such as the analysis of sample solutions containing electroactive components and originating from different places.

It is commonly known that one of the most efficient ways for rapid serial analysis of samples of small volume and of more or less similar composition is the analysis in a flow-through channel. Thus in mechanized or automated analyzers containing a flow-through analysis channel with voltammetric detection, the analysis takes place under convective diffusion conditions.

1. Determination of Dissolved Oxygen and Other Gases

As regards the concrete applications of hydrodynamic voltammetry, first of all the determination of dissolved oxygen must be pointed out. Initially, for this purpose dropping mercury electrodes were used,[363,364] but since Clark has developed the membrane-covered oxygen sensor,[365] this method has lost considerable importance. The schematic design of Clark's electrode is shown in Figure 6. The working electrode is platinum and the reference electrode is silver-silver chloride. Reference electrodes of zinc,[366] lead,[367] and silver-silver oxide[369] were also used. Nowadays the most frequently used working electrode of the voltammetric oxygen sensitive sensor is made of gold, while the reference electrode is of silver.[367,370]

The oxygen sensitive sensors with a galvanic cell have become widespread in the analysis of surface waters, and especially in industrial practice. In these systems, the two electrodes form a galvanic cell with the basic electrolyte. The current streaming through the galvanic cell is proportional to the oxygen concentration of the electrolyte. Hersch[371] and Mancy et al.[372] developed a galvanic cell sensitive to oxygen that contained a silver cathode and lead anode. The electrolyte is 1 M KOH, which has good conductivity and produces a low residual current in the absence of oxygen. It also dissolves the lead hydroxide, thereby ensuring the cleanness of the anode.

From the above, it is obvious that for reliable operation of the oxygen sensor, during the measurement the electrode must be moved or convection should be produced in the medium examined.

The oxygen sensor gains application most often in the determination of the dissolved oxygen content of surface waters, boiler waters, and sewages,[372,373] in the rate determinations of oxygen uptake in biological systems,[372] and in measuring the oxygen content of different gases.[371,374,375]

A quite significant application of oxygen sensors is the determination of oxygen contained by different physiological fluids.[376-381]

In addition to oxygen, the concentrations of several other gases were determined in different media. Novak[382] measured the quantity of SO_2 and H_2S in an industrial atmosphere, being the first to apply graphite indicator electrode under convective diffusion conditions.

To determine the CO content of air, a measuring cell was developed by Novak,[383] while a membrane-coated platinum electrode containing sensor, similar to the oxygen sensor was constructed by Bay et al.[384] for the same goal.

Kuempel and Shults[385] designed a flow-through thin-layer cell including a mercury working electrode to measure the Cl_2 and SO_2 contents of air. In the course of their experiments, the concentrations of the previous components were monitored by recording the current in the cell at a constant rate of air flow and at constant potential, while in the determination of Cl_2, a method, similar to the "stripping" technique was used. Namely, the Cl_2 was concentrated on the mercury electrode in the form of Hg_2Cl_2, then the concentration of the sample examined was determined on the basis of the current-potential curves.

Kane and Young[374] elaborated on a new sensor for the purpose of process control analysis. A membrane-covered sensor was used for the determination of oxygen content in sewage; of oxygen content in a nitrogen blanket in a tank used for storing ethylene dichloride; and of chlorine content in a benzene-hydrogen chloride atmosphere. The working and reference electrodes of the cell were identical with that of Clark's; a platinum auxiliary electrode was also added. This kind of cell construction seemed to meet the requirements better than Clark's electrode.

For the determination of small Cl_2 concentrations, a membrane-free sensor was produced. A membrane-covered sensor does not show enough sensitivity to Cl_2 owing to the lower diffusion rate of Cl_2 through the membrane.

A method to determine the concentration of the chlorine water used in the chlorination of surface waters was developed by Nagy et al.[386,387] Because of the special circumstances of high chlorine concentration, electrolyte concentration not high enough, and a changing flow rate, continuous flow-through sampling and analysis were employed. The sampling area was separated from the analysis cell by a gas-permeable membrane. The concentration of Cl_2 diffusing from the flowing sample solution through the membrane into the flowing background electrolyte was followed continuously by a graphite working electrode.

2. *Determination of Different Metals*

One of the most important applications of voltammetry is the determination of concentrations of metal ions for samples of different origin. It is evident that these determinations, chiefly in industrial solutions, were found among the first applications of voltammetric examinations carried out in streaming solutions. So Bertram et al.[388] and Alkire et al.[389] determined the concentration of uranium, while Lewis and Overton[390] determined that of Bi and Cd; Lifsich[391] did that of Cu, Cd, Zn, and Pb. The application of the polarographic method to process control is hindered by several circumstances. Due to this it has not achieved wide-ranged application in the practice yet (e.g., Reference 392). Palei et al.[393] devised a mercury-coated platinum electrode for direct metal analysis to eliminate the problems of the dropping mercury electrode. The mercury film was renewed by automatically dipping the electrode into mercury.

A mercury drop electrode of constant surface area was applied by Fleet[394] for the indirect determination (through EDTA) of Ca and Mg. Štrafelda and Štastny[395] utilized the possibility of detecting EDTA by a dropping mercury electrode for the continuous determination of water hardness. The same task was solved by Pungor et al.[396] with a membrane-covered mercury electrode.

3. Determination of Organic Compounds

In another important application field of voltammetry, the determination of organic compounds, hydrodynamic voltammetry is thought to be an extremely promising method. It is increasingly applied in process control tasks and in automatic analyses, as well. For example, Holland and Benham[397] used automatic voltammetry for controlling the sewage of a plant producing nitroglycerine.

For the determination of different compounds important from the point of view of pharmaceutics or therapy, the graphite electrodes are often used advantageously. In some cases, these compounds are detected directly, in other cases, hydrodynamic voltammetry is combined with the chromatographic separation method.

The direct determination approach was attempted by several researchers with a Technicon® automatic analyzer, e.g., Cinci and Silvestri[398] performed the determination of the compound sulfenazone with a flow-through cell containing a dropping mercury electrode as the working electrode and AC polarography.

Chlordiazoepoxide and diazepoxide and the drug content of pharmaceuticals containing these compounds were determined by Lund and Opheim.[399] For the automatic determination of different drugs, MacDonald and Duke[400] constructed a flow-through detector cell containing a platinum electrode placed into the Technicon® system.

With the help of the injection measuring technique described earlier, Pungor et al.[387] determined the concentration of pharmaceutically important compounds (Table 3), and the drug content of different pharmaceutical preparations (Table 4). In the course of these examinations, the effect of other constituents in the tablet, in addition to the drug, also was investigated.[417,418]

Several papers published by Kissinger and co-workers[402,403] report on the liquid-chromatographic-voltammetric determination of pharmaceuticals. Epinephrine, norepinephrine, isoproterenol, L-DOPA, α-methyl-DOPA, phenylephrine, ascorbic acid, and acetaminophen contents of different productions were determined. The chromatographic separation preceding the voltammetric determination was, of course, necessary only in the case of multicomponent systems; however, in those cases when previous separation was not required, authors utilized the favorable analytical conditions offered by hydrodynamic voltammetry.

4. Determination of Dissolution Rate of Drugs from Pharmaceutical Preparations

Stimulated by problems arising in pharmacy, a method and a device have been developed to be able to follow the dissolution process of drugs from solid preparations.[387-404]

It is well known that the therapeutic effect of a pharmaceutical product can basically depend on the characteristic dissolution rate of its drug content. In addition to preparations with rapid drug dissolution, there are often tablets or capsules of slow dissolution. In the former case, the pharmaceutical product ensures a quick therapeutic effect, while in the latter a prolonged or retarded one.

Both the quality control of solid pharmaceutical products and the development of preparation technology of products with prolonged or retarded effect require the determination of the dissolution rate of drugs. The problem was solved under different experimental conditions;[405,406] researchers carried out examinations by different sampling and analytical methods.

According to one version of the measuring method and device[387-417] developed by us, the dissolution of the drug is followed by continuous sampling and voltammetric analysis. First of all, for the investigation of dissolution properties of drugs with prolonged or retarded effect, a method was devised[404] in the course of which (beside the continuous sampling and analysis) periodic sampling and automatic analysis with injection technique are possible.

TABLE 3

Determination of Several Compounds of Pharmaceutical Importance with the Help of the Injection Technique

Material tested	Supporting electrolyte
Hydroquinone	Phosphate buffer pH = 7.0
p-Phenylene diamine	0.1 M HCl
p-Toluidine	0.1 M HCl
p-Phenetidine	Phosphate buffer pH = 7.0
α-Naphthylamine	0.1 M KCl
Oxytetracycline	0.1 M KCl
Ascorbic acid	B-R buffer pH = 4.0
Pyrogallol	B-R buffer pH = 7.0
Adrenaline	B-R buffer pH = 3.61
Gallic acid	B-R buffer pH = 3.61
Isoprenaline	0.1 M KCl
α-Methyl-DOPA	0.1 M KCl
Chlorpromazine	0.1 M KCl; 0.01 M HCl
Diethazine	0.1 M KCl
Amidopyrine	0.1 M KCl
Uric acid	Phosphate buffer pH = 8.3
Adenine	Acetate buffer pH = 4.8
Guanine	Acetate buffer pH = 4.8
Xanthine	Phosphate buffer pH = 8.3
Hypoxanthine	Phosphate buffer pH = 8.3
Adenosine	Phosphate buffer pH = 8.3
Guanosine	Acetate buffer pH = 4.8
5′-GMP	Acetate buffer pH = 4.8
Morphine	4 N H_2SO_4
Ethylmorphine	4 N H_2SO_4
Papaverine	4 N H_2SO_4
Codeine	4 N H_2SO_4

From Pungor, E. et al., *Pure Appl. Chem.*, 44, 595 (1975). With permission.

TABLE 4

Determination of Drug Content of Some Pharmaceutical Preparation with the Help of the Injection Technique

Preparation	Drug	Firm
Hibernal pill	Chlorpromazine[a]	EGYT, Budapest
Amidazophen tablet	Amidopyrine[a]	Chinoin, Budapest
Pipolphen pill	Promethazine[a]	EGYT, Budapest
Tiscercin pill	Levomepromazine[a]	EGYT, Budapest
Scutamil pill	*N*-acetyl-*p*-aminophenol[a]	EGYT, Budapest
Chlorocid pill	Chloramphenicol[b]	EGYT, Budapest
Seduxen tablet	Diazepam[b]	Richter G., Budapest

[a] Working electrode: silicone rubber based graphite electrode

[b] Working electrode: flat surfaced membrane covered mercury electrode[396]

5. In Vivo Measurements

In order to become acquainted with the transport of drugs and biologically important compounds in the human organism, determination of these compounds in physiological fluids is extremely significant. Lately, this field has been extensively treated in literature. The majority of publications offers the liquid-chromatographic-voltammetric method for the occasional concentration determination in body fluids.[402,403,407-410] Koryta,[411] in his in vivo experiments, followed the concentration of ascorbic acid that was injected into a kidney ready for transplantation. By recording cyclic voltammetric curves it was possible to control the operation of the organ (kidney). The biogenic amine concentration in brain tissue was determined from time to time by Adams, also on the basis of cyclic voltammograms.[412-414]

As already mentioned, in many cases the oxygen concentration of different body fluids can be determined with the Clark electrode. Besides oxygen, few other components in blood have been determined in vivo. A flow-through cell containing a small graphite working electrode of ∿1 mm in diameter and a Ag/AgCl reference electrode was built into a artery or vein of narcotized experimental animals by Pungor et al.[387,415,416] This measuring system followed the entrance and distribution of ascorbic acid, amidopyrine, and prometazine in the bloodstream.

6. Chromatovoltammetry

The flow-through voltammetric measuring cells gained the widest analytical application in the field of chromatography. In 1952, Kemula[418] applied a dropping mercury electrode for chromatographic detection and called his method chromatopolarography. Thereafter many authors reported on their works in which a cell containing a dropping mercury electrode was connected to the chromatographic column. In this way different metals,[418-425] halides,[426] organic acids,[420] esters,[427] nitrophenols,[421] nitrotoluols,[428,429] nitropyridine derivatives,[430] naphthene isomers,[431] benzenes,[432] furasol and nitrofuraldoximes,[433] pyridine,[434] pesticides,[435,436] vitamins,[437] and amino acids via copper complexes[438,439] were determined.

Authors, in general, point out the high sensitivity of the method. Huber and coworkers[435] carried out the determination of a few nanograms of pesticide with the mentioned method. Besides, they emphasize that in many cases the selectivity of the chromatographic determination increases. Under fortunate conditions, the solvent can be selected in the way that it should serve as electrolyte to the polarographic measurement.

The chromatographic application of the rotating dropping mercury electrode is also known.[440] The authors showed that for the rotated dropping mercury electrode the limiting current is at least 10 to 15-fold greater than on the dropping mercury electrode. They used their cell for the gas-chromatographic determination of nitrobenzene and nitrophenol isomers.

In the 1960s, the development of solid electrodes, operating in the anodic polarization region, greatly contributed to the further development of the chromatopolarographic method and its wider application. The solid electrodes made possible the measurement of the oxidation or reduction current of numerous organic and biologically important compounds often occurring in chromatographic examinations. The new type of voltammetric measuring cells of minute dimensions, which could be commercially developed, with solid electrodes as well as the recently elaborated new voltammetric techniques (tensammetry, square wave, stripping voltammetry, etc.) led to the development of chromatographic detectors that are able to meet all the requirements of modern chromatography.

Carbon paste,[441] silicone rubber based graphite,[442] or glassy carbon[443] electrodes are most often used as working electrodes in the most frequently used cells.

Generally two fundamental types of cell construction are used. The one type is the thin-layer cell[441] developed by Kissinger and co-workers, in which a thin Teflon® spacer is placed between two plastic blocks. The hole in the Teflon® spacer forms a channel when the two plastic blocks are pressed together. The carbon paste measuring electrode of about 2 to 4 mm diameter is placed in the bore of the channel wall.

Kissinger and co-workers achieved very good results using amperometric detectors for the measurement of biogenic amines,[441] phenolic sympathetic amines,[444] as well as at the determination of ascorbic acid,[445,446] uric acid,[447,448] homovallin acid,[449] and homogentisic acid[450] in blood and urine samples, and of ascorbic acid in food[445] and uric acid in cereal products.[451] This technique is particularly sensitive, rapid, and inexpensive. One picogram of electrochemically active component could be detected. Satisfactory quantitation is achieved with minimum sample manipulation and without need for any chemical reagents.

Blank[452] reported also on the application of the thin-layer cell for determination of serotonin and dopamine in mouse brain tissue. The limit of detectability was 0.1 pmol.

A modified version of Kissinger's cell was developed by Blank,[453] who placed two measuring electrodes in the cell, and in this way attained the separation of compounds that overlap chromatographically, but have differing electrochemical formal potentials. His purpose was to analyze the normal, endogenous brain components, norepinephrine (NE) and dopamine (DA) and additionally, any spurious 6-OH-DA without lengthening the elution time. 6-OH-DA is not resolved from the other components of concern. Separation and quantitation of all components can, however, be easily effected by using two measuring electrodes. The first, lower potential electrode ($E_1 = +0.45$ V) only measures 6-OH-DA, while the second ($E_2 = +0.8$ V) responds to all species.

The other type of voltammetric cell is the so-called wall-jet electrode cell developed by Pungor and co-workers[442,454] and Fleet and Little,[443] for chromatographic purposes. In these cells the electrode of about 1.5 mm diameter is perpendicular to the direction of flow and the nozzle in the stream before the electrode establishes a jet flow. This type of cell was used for selective measurement of purine bases in the presence of pyrimidine bases,[442] amino acids, phenols, steroids, drugs, etc.[443]

Not only graphite electrodes are used for chromatographic purposes. A detector cell with a Pt working electrode was also developed for the gas-chromatographic determination of CO[455] based on the oxidation of CO at a constant potential to CO_2. Examinations were also carried out in connection with the development of mercury-plated platinum wire and porous-plug electrodes and their application to liquid chromatography.[456]

Generally, in the amperometric detector cells, direct current is measured at the fixed voltage value characteristic for the component. Systems containing two or three electrodes are used equally often.

Lately, papers have been published in which the authors reported on the advantageous application of the technique of differential pulse,[457] stripping voltammetry,[458] tensammetry,[459] and oscillopolarography.[460] Enhanced selectivity can be obtained when employing the differential pulse mode, and was illustrated for a test solution of *p*-aminophenol, 3,4 dihydroxyphenylalanine and sulfanilamide.[457] Detection of Se(IV) in the chromatographic effluent was carried out by anodic stripping voltammetry at a tubular Au electrode. SiO_2 disturbed the measurement.[458] The tensammetric detector has been applied to analysis in water of some industrial mixtures of surfactants of the polyethylene glycol monoalkyl ether type.[459] Concentrations in the order of 30 ppb could be detected. The importance of the tensammetric method is first that this detection allows the determination of aliphatic as well as of aromatic surfactants, whereas the generally used UV detector is only sensitive to aromatic surfactants. Secondly, tensammetric detection is specific for surface active compounds. Heptachlor, heptachlor epoxide, and hexachlorocyclohexane from plant material and soil were analyzed by oscillopolarography in the range of 1 to 20 ppb.[460] The different applications of voltammetric cells for chromatographic purpose are summarized in Table 5.

The extensive and successful research in the field of electroanalytical detectors, as well as the advantageous properties of these ones, justify their application in chromatography. Summing up, it can be stated that they possess a broad linear measuring range (10^5), their sensitivity is in most cases very high (limit of detectability: 10^{-12} . . . 10^{-9}g), and the volume of detector cells is very small (1 to 5 μl).

Specificity of detectors is an advantage for the performance of many analytical tasks. Many components possess similar chromatographic (but different electrochemical) properties than the component to be examined. Thus, they do not interfere with the detection.

Since the electrochemical detectors are not universal, their everyday application can be expected to be for specific instruments and as complementary detectors to universal ones for the solution of special and unique problems.

With electrochemical detectors it must be taken into consideration that the signal is sensitive to variations in the experimental conditions. These are usually changes taking place in the temperature of the cell and the flow rate of the liquid. Accordingly, the value of these parameters should be kept constant or a reference channel should be applied in the apparatus. For electroanalytical detectors one has to deal sooner with their contamination than, for example, is true for optical detectors. Another error source is that irreversible processes may take place on the surface of the sensors, which would lead to irreproducible results. However, in such cases the cleaning of the electrode surface or the eventual change of the electrode can easily and rapidly solve the problem.

As this review shows, the wide use of electrochemical detectors in chromatography underwent a significant acceleration in the past few years, and with their application the solution of many analytical problems is to be expected in the near future.

TABLE 5

Chromatovoltammetric Determination of Different Samples

Components	Characteristics of the separation	Detection technique	Quantitative characteristics of the determination	Ref.
Co, Cu, Ni, Mn	Dowex® 1-X10, HCl eluent	DC, DME	Amount of sample: 20 μg to 2 mg metal content 2—15%	419
Cd, Cu, Pb	Dowex® 50; 0.39 M HCl	DC, DME	Detection limit 10^{-4} M	420
Cd, Cu, Fe, Ni *p*-Nitrophenol, Cd	Glass packing; 0.5 M NaCl Glass packing; 0.5 M NaCl	DC, DME DC, silicone rubber based graphite	Detection limit 1.3×10^{-6} M Detection limit 1.9×10^{-8} M	421
Co, Ni	Wofatit® KPS3G; 0.1 M KCl	DC, DME	5-12 μg detectable	422
Pb, Cd	Dowex® 50; 1.05 N HNO_3	DC, DME	Amount of sample: 0.01 mmol	423
Cu, Cd, Pb in high purity Bi	Ion-exchange chromatography	DC, DME	Detection limits: 5.5×10^{-6}% Cu; 4.6×10^{-6}% Cd and 4.4×10^{-6}% Pb	424

TABLE 5 (continued)

Chromatovoltammetric Determination of Different Samples

Components	Characteristics of the separation	Detection technique	Quantitative characteristics of the determination	Ref.
Zn, Sn	Anion exchanger	DC, DME	Detection limit 1.3 × 10^{-5}%	425
I^-, Br^-, Cl^-, SCN^-	On hydrous zirconium oxyd; KNO_3	DC, DME	0.5—3 μmol sample	426
Thiophosphoric esters	Polyethylene powder; cyclohexane; 48% ethanol-acetate buffer	DC, DME	0.1—10 mg detectable	427
Nitrotoluenes	Ni(γ-picoline)$_4$ (SCN)$_2$	DC, DME	0.1—0.5 mg sample	428, 429
Nitropyridine derivatives	Reversed-phase or ion-exchange chromatography	DC, DME and Hg-plated Pt		430
Isomers of methyl methylnaphthenes	Ni(γ-picoline)$_4$(SCN)$_2$	DC, AC, DME	0.1—0.5 mg sample	431
Furasol and nitrofuraldoximes	Ni(γ-picoline)$_4$(SCN)$_2$	DC, DME	0.05—0.1 mg sample	432
Mononitroethylbenzenes	Co(γ-picoline)$_4$(SCN)$_2$ Ni(γ-picoline)$_4$(SCN)$_2$	DC, DME	0.05—0.3 mg sample	433
Pyridine	GC, Triton® X-305 on Chromosorb® W	DC, DME	Detection limit 7 × 10^{-8} g/mℓ	434
Pesticide (parathion, methyl parathion) and *p*-nitrophenol	Silanised diatomaceous earth coated with 2,2,4-trimethyl pentane, water-acetic acid-NaOH-KCl eluent	DC, DME	Few ng amounts detectable	435
Parathion, methyl parathion	Corasil C_{18} methanol-water KCl	DC, DME	0.01—10 μg detectable	436
Vitamin K_1	TLC hexane isopropanol	DC, DME	—	437
L-amino acids (forming Cu-complexes)	Dowex® 50-W-X8; buffer solution	DC, DME	Detection limit 5 μ*M*	438
Amino acids (forming Cu-complexes)	Zeo-Karb® 225 (X-8); buffer solution	DC, DME	Sensitivity is similar to that of the ninhydrin method	439
Nitrobenzene in aniline, nitrophenol isomers	GC	DC, RDME	Detection limit 1 ppm	440
Biogenic amines	Cation exchanger SCX; 0.1 *M* $HClO_4$	DC, carbon paste electrode	Detection limit 10 pg	441

TABLE 5 (continued)

Chromatovoltammetric Determination of Different Samples

Components	Characteristics of the separation	Detection technique	Quantitative characteristics of the determination	Ref.
Purine bases	Sephadex® G10; NaCl, Na$_2$HPO$_4$	DC, silicone rubber based graphite electrode	Detection limit 10^{-10} mol	442
Steroids (chlormadinone and estrone)	—	DC and pulse glassy carbon electrode	Detection limit 10^{-10}g	443
Amino acids	SCX column; methanol borate eluent			
Phenolic phenylethylamines	Pellicular cation exchanger; H$_2$SO$_4$ and Na$_2$SO$_4$	DC, carbon paste electrode	Detection limit 2 μg/m*l*	444
Ascorbic acid in foodstuffs, pharmaceutical and body fluids	Pellicular anion exchanger acetate buffer	DC, carbon paste electrode	Nanogram range	445
Uric and ascorbic acid, catecholamines, and related tyrosine metabolites in urine and serum	DC, carbon	paste electrode	Detection limit 1 pg	446
Serum uric acid	Pellicular anion exchanger	DC, carbon paste electrode	Detection limit ~1 pg	447, 448
Homovanillic acid in human urine	Pellicular anion exchanger; acetate, and citrate buffer	DC, carbon paste electrode and cyclic voltammetry	Detection limit 100 pg	449
Homogentistic acid in serum and urine	Pellicular anion exchanger; acetate buffer	DC, carbon paste electrode	Detection limit for serum: 1 μg/m*l*; and 1 μg/m*l* for urine	450
Uric acid in cereal products	Pellicular anion exchanger; acetate buffer	DC, carbon paste electrode	Detection limit 2 μg/g	451
Serotonin and dopamine in tissue	Strong cation exchanger citrate, acetate buffer	DC, carbon paste electrode	Detection limit 0.1 pmol	452
Norepinephrine and dopamine 6 hydroxy-dopamine	Pellicular strong cation exchange resin	DC, carbon paste electrode	Dynamic range 0.40 pmol to 48 nmol	453
Carbon monoxide	GC	DC, Pt electrode	ppm	455
Benzil and 1,4 naphthoquinone *p-Nitroaniline*	Reverse-phase chrom. 50:50 methanol-water containing 0.05 *M* LiClO$_4$	DC, Hg-plated Pt and porous plug electrode	Detection limit 14 × 10^{-10} mol	456

TABLE 5 (continued)

Chromatovoltammetric Determination of Different Samples

Components	Characteristics of the separation	Detection technique	Quantitative characteristics of the determination	Ref.
p-Aminophenol, 3,4-dihydroxyphenylalanine, sulfanilamide	Strong cation exchanger 0.05 M H_2SO_4 aqueous mobile phase	Pulse and differential pulse mode Carbon paste electrode	Detection limit 5 pg	457
Se(IV)	Strong cation exchanger; $HClO_4$ eluent	Anodic stripping voltammetry, tubular Au electrode	Detection limit 4 ppb	458
Some industrial mixtures of surfactants of the polyethylene glycol monoalkyl ether type	Chromosorb® G; 0.1 M Na_2SO_4, 0.03 M CH_3COONa, 0.16 M acetic acid	AC, DME tensammetric method	Detection limit 30 ppb	459
Heptachlor, heptachlorepoxide and hexachlorcyclohexane	TLC 0.05 M tetramethylammonium bromide in 10% ethanol	Oscillopolarography	Detection limit 1—20 ppb	460

V. CONCLUSION

In the last few years hydrodynamic voltammetry has become a very powerful tool in instrumental analysis. It means much more than the application of voltammetry under hydrodynamic conditions.

Much remains to be done in the theoretical solutions of mass transport processes. Besides deriving relationships for systems of simple geometry and simple voltammetric conditions, it can be expected that solutions for more complicated conditions will be needed.

The use of voltammetric techniques with flow-through cells opened a new chapter in voltammetry, especially for solid electrodes. The application of flow-through systems in voltammetry helped to overcome a lot of difficulties arising at the use of electrodes of constant surface area, and besides this it involves many special advantages. Thus hydrodynamic voltammetry has become a very applicable method that is used even when the measurement under hydrodynamic conditions does not follow from the character of the task to be solved.

It can be expected that further efforts will be made for developing indicator electrodes of better properties on one hand, while on the other, different measuring techniques will be applied to increase the capability of the voltammetric method.

GLOSSARY OF SYMBOLS

j	Mass flux
i_L	Limiting current
n	Number of electrons involved in the electrode reaction
F	Faraday constant
c	Concentration in the bulk of the solution

c_o	Concentration on the surface of the body (electrode)
D	Diffusion coeffient
δ and δ_d	Thickness of the diffusion layer
δ_h	Thickness of the hydrodynamic boundary layer
δ_o	Thickness of the viscous sublayer
V	Flow rate of solution
ω	Rotation speed of electrode
ν	Kinematic viscosity
A	Surface area (body, electrode)
ϱ	Density of the solution
y	Distance from the surface (perpendicular)
q	Rate of heat transfer
s	Specific heat
T	Absolute temperature
k	Thermal conductivity

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