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Where Are You Going, Electroanalysis?

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Abstract: A very general (and subjective) view is provided concerning the present state and possible development of electrochemical approaches to analysis. Both topics of interest are considered in the framework of the general character of contemporary science.

Keywords: Electroanalysis; Measuring techniques; Application fields; Present state; Prospects.

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Introduction

Having been invited to present his opinion on the present state of electroanalysis and on its possible development, the author briefly surveys this wide field. This is, of course, an individual insight and should serve as a basis for discussion.

First of all, it is necessary to place electroanalysis in the general framework of the present day's life. Analytical chemistry, including its parts based on electrochemistry, is a very wide scientific field, whose main feature is the concept of application. It widely applies to the principles of many scientific disciplines, primarily all the branches of chemistry, physics, mathematics and informatics and, in rapidly growing proportion, of molecular and cell biology. The use of its results is analogously extensive, from participation in basic scientific research, to generation of indispensable data for technologies, biomedicine, ecology, etc. etc. Therefore, analytical chemistry intensely reflects the present situation in science and technology, which is characterized by interpenetration of scientific fields, enhanced development at the borders of disciplines and by continuously growing demand for teamwork and good communication among the specialists. All this provides fantastic possibilities, but places very high demands on the actors. A more detailed treatment of these questions can be found, e.g., in ref. [1].

Electroanalytical chemistry has been very popular in our country, primarily due to the Heyrovský' s polarography. At present, our emphasis on electrochemistry and electroanalysis is somewhat decreasing, but still exceeds that in most other countries. Electrochemistry definitely offers many possibilities for solution of analytical problems and it depends on all of us, whether or not we recognize and use them. The following two sections of this text briefly summarize the present state and outline possible directions in further development.

Present State of Electroanalysis

Measuring Techniques

The principal measuring techniques have been the same for quite a long time. There are, of course, many improvements in the technical aspects of measurements, but these are due to wide application of computer technologies and informatics; the principles remaining the same. Modern instrumentation and data treatment are definitely improving most analytical parameters, such as the sensitivity of measurement and its reliability. On the other hand, they often cause that the experimenters tend to forget about the principles and a critical evaluation of the data obtained. It seems that the most important result of computer treatment of experimental data is the fact that many hardware operations can be replaced by software (a typical example: charging current compensation in polarography and voltammetry).

Faradaic measurements, involving various modifications of voltammetry and coulometry, are now the most common electroanalytical measuring technique/s, due to its/their versatility and rapid response. The importance of ion-selective potentiometry has somewhat decreased, primarily because of rather slow response of the respective sensors. However, the principal feature of the selectivity towards the target analyte is being transferred from potentiometry to voltammetric measurements. Classical low-frequency conductance measurements keep their importance in specialized applications. For the rebirth of impedance measurements, see below.

Working Electrodes

This is a very active field, because the working electrode character is a principal factor in determining the properties and applicability of electroanalytical measurements. Unfortunately, the extensive set of publications on various electrode materials is very variable in quality, because it is rather simple to change electrode a little and obtain the results whose contribution can be discussed and the resultant improvements recommended. Nevertheless, there are many highly useful reports on electrode materials and their modification.

When looking on the wide field of electrode materials, it becomes clear that a great majority of voltammetric / coulometric measurements could be carried out with the two electrode materials; namely, mercury and a kind of carbon. Metallic mercury has some disadvantages: it is liquid, which may cause difficulties in the instrumental design, and reportedly toxic, even if not very much (an example of hysterical panic: a TV shot in which policemen in full protective clothing approach a small bottle of mercury left exposed at a public place). Carbon materials — and, especially, carbon pastes — offer almost unlimited possibilities of use either in the pure form or chemically / biologically modified (for recent reviews, see e.g. refs. [2,3]). For use at more negative potentials, bismuth matrices can often effectively replace mercury [4].

The electrode materials are frequently modified in various means to enhance the measuring selectivity and sometimes also its sensitivity. The quality of this research is very diverse. The electrode surface or the whole bulk (e.g., with carbon pastes) is modified, e.g., with nanoparticles (“nano” is one of momentarily fashionable expressions), or with systems taken from molecular and cell biology. The results may be good, but they are always specialized to meet certain conditions and applications.

Microelectrodes are a very important subject. Small dimensions are generally required at present, in view of minimization of all the analytical instrumentation. However, from the electrochemical point of view, microelectrodes and their arrays have much more important properties, connected primarily with the mass transport conditions around the electrode(s). Therefore, microelectrode systems seem to be very useful and promising (see, e.g. ref. [5]).

Application Field

Electroanalytical meaurements are now primarily used for simple, inexpensive, and rapid determinations. In practical circles, they often cannot compete with simple absorption spectrometry. A few of classical ion-selective electrodes are generally used (glass pH electrodes, fluoride ISEs and a few others). There are some electrochemical sensors for field analyses and some detectors for continuous analyses. However, more attention is paid to combinations of electrochemical measurements with other analytical techniques.

Electrochemical measurements are gradually gaining a greater importance in detection for high-performance separations in condensed phases. The reasons for this are the simplicity of electrochemical systems, their easy miniaturization, the possibility of utilizing their inherent selectivity and, especially, sophisticated combinations of electrochemical measurements with spectrometric devices, including highly efficient mass spectrometers (see, e.g., ref. [6]). In such a connection, high-frequency impedimetry has also been revitalized (see, e.g., refs. [7,8]).

An Outlook to the Future

Electroanalytical measurements should be useful and successful in the future. The reasons for this assumption are manifold and can be summarized as follows:

A) Electrochemistry is a well-defined discipline and all the analytical applications benefit from a very substantial background;

B) Electrochemistry is inexpensive compared to spectroscopic and other measuring techniques;

C) Electrochemical cells are usually easy to miniaturize;

D) Electrochemical measurements are characterized by sensitively controlled selectivity;

E) Electrochemical measurements can readily be combined with spectroscopic ones at the same site and in the same time;

The features **A-E**) can also be used to predict the future:

a) Electrochemical principles will widely be used in designing single- and multi-use detectors, sensors, and continual monitoring units (see, e.g., ref. [9]);

b) Standard determinations of a great variety of substances will be simply and effectively carried out using electrochemical cells;

c) Simple, selective and sensitive electrochemical detection, possibly combined with spectro-scopy, will be used in high-performance separations of substances in condensed phases;

d) Special attention will probably be devoted to electrochemical detection for chip separations and analyses.

Conclusions

Electroanalytical measurements have a bright future, provided that their principal advantages are utilized. The pros mainly comprise the good theoretical background, a very broad spectrum of electrode materials and possibilities of modifying them in order to obtain the desired properties, wide applications to high-performance detection in condensed phases, especially in capillary and chip separation systems, the possibility of designing inexpensive electrodes and sensors — often, as disposable components —, or various detection and monitoring units.

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