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# The Rise of Voltammetry[1]: From Polarography to the Scanning Electrochemical Microscope

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## Polarography

### *Dropping Mercury Electrode*

An excellent discussion of the work of Jaroslav Heyrovsky and the development of polarography is given by Zuman *(1).* Of critical importance in the invention of the polarographic technique was the fact that the electrochemical experiments were carried out using the dropping mercury electrode (DME). Mercury is unique among metal electrodes for several reasons. Because it is a liquid, its interface with the solution is atomically smooth and of well-defined area. Moreover it has a high overpotential for hydrogen evolution (i.e., the proton and water reduction reactions at mercury are slow compared, for example, to these reactions on platinum), so that it has a large range in the negative potential region in water where many reduction reactions can be studied. Finally, in the DME configuration, the surface is continually renewed, preventing contamination of the surface from solution impurities. Such contamination, even from low levels of impurities, can plague measurements with solid electrodes and lead to time-dependent and irreproducible behavior.

To understand why Heyrovsky began working with the DME in 1922, we have to go back a number of years (see the time line in Figure 1). In 1873, Gabriel Lippmann described experiments in which he measured the rise of mercury in a vertical capillary tube in contact with an aqueous solution (Figure 2A). The position of the mercury in the tube is determined by the surface tension of the interface. Lippmann showed that this position depended upon the potential applied across the interface, since the surface tension of mercury depends upon the charge at its surface. The surface tension is highest at the potential of zero charge, when there is no excess charge at the interface. When it is charged either positively or negatively from this position, the surface tension decreases, because the charged mercury atoms repel one another. The device, known as a Lippmann electrometer, could be used to measure small potential differences, but the main interest was in studies of the mercury–aqueous electrolyte interface and, in particular, for obtaining electrocapillary curves, which showed the change in surface tension as a function of potential.

These experiments were followed by experiments in which the mercury was allowed to drop out of a pulled cap-

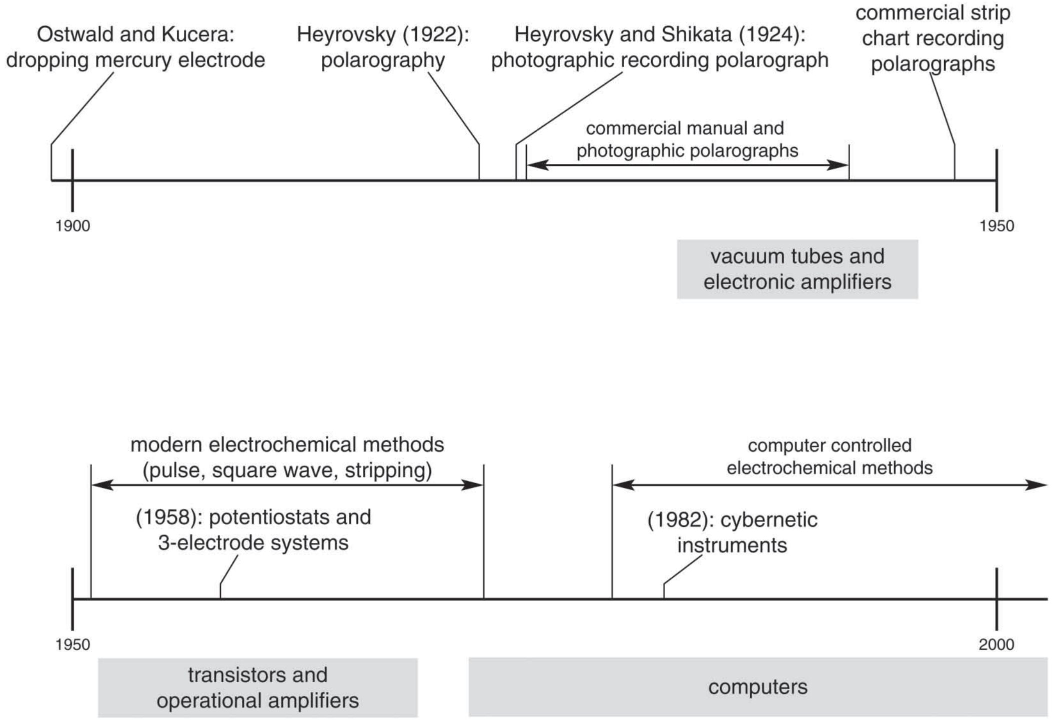


Figure 1. Time line for the development of voltammetry.

illary tube, for example by Ostwald, who measured with rapid (0.1 s per drop) outflows of mercury the potential difference between two dropping electrodes *(2).* Professor of experimental physics B. Kucera at the Czech University in Prague used a DME (Figure 2B) to obtain electrocapillary curves. Because the rate at which mercury falls from a small capillary and the size of the drop depends upon surface tension of mercury, Kucera established a technique of weighing the mercury drops falling from the DME and used these, rather than the Lippmann electrometer, to obtain electrocapillary curves. In fact there were discrepancies between measurements made by the two methods, which later were realized to result from adsorption of impurities at the mercury–electrolyte interface in the electrometer that changed the surface tension; these were less important at the continually renewed surface of the DME. Kucera introduced the DME to Heyrovsky and invited him in 1918 to join his laboratory and study these phenomena. For the next three years Heyrovsky continued these measurements, eventually using drop time measurements to replace the more tedious drop weight approach, and looked at the effect of solution components, such as metal ions, on the electrocapillary behavior.

### *Voltammetry*

The key experiments that marked the birth of voltammetry occurred in early 1922, when Heyrovsky began measuring the current flow, as well as the drop time, as a function of potential. The currents in such experiments were small, in the sub-microampere range, so that a very sensitive galvanometer was needed. At that time, galvanometers that used the deflection of a mirror and the observation of a reflected light beam (d'Arsonval galvanometers) were available and Heyrovsky procured one with a sensitivity of 4-mm deflection for 0.01 μA *(3).* On February 10, 1922 he obtained a current–potential ($i$–$E$) curve (along with an electrocapillary curve) with the DME in 1 M NaOH that had not been deaerated and recorded waves that showed reduction of oxygen and sodium ion at the mercury drops. The details of this experiment and those that followed are described by Zuman *(1).* The work was first described in a Czechoslovakian journal and at a Faraday Society meeting the next year *(3).*

These current–potential curves (later called polarograms, or, more generally, voltammograms) were obtained manually by applying a potential between the DME and a counter electrode (frequently a pool of mercury) and measuring the current with the galvanometer. Because the mercury drop grew from small (the capillary diameter) to large during the time period of several seconds and then fell off and was replaced by a new drop, the measured current oscillated during the measurement. Although the galvanometers used were fairly heavily damped, decreasing the magnitude of the current oscillation, it was still quite tedious to measure a complete curve with good potential resolution, because one had to watch the swinging light spot and average the high and low positions at every applied potential. However, in 1924 Heyrovsky with his coworker, Masuzo Shikata, built an instrument to record automatically the $i$–$E$ curve on a piece photographic paper held on a drum that turned with the change in applied potential and was illuminated through a slot by the light beam of the galvanometer (Figure 3) *(4).* After photographic development, the $i$–$E$ curve, with the small oscillations of the DME,

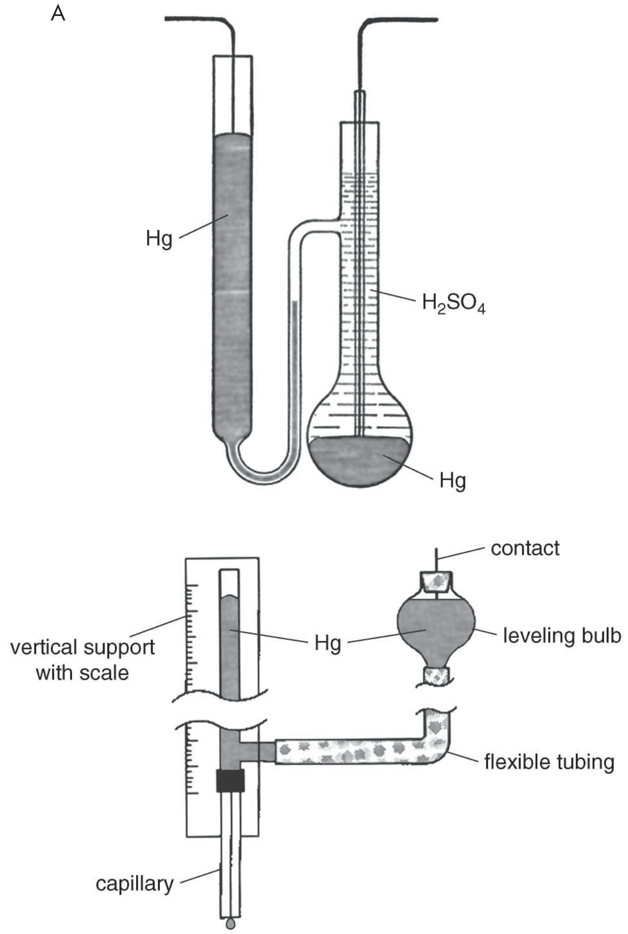


Figure 2. (A) Lippmann electrometer. (B) Dropping mercury electrode.

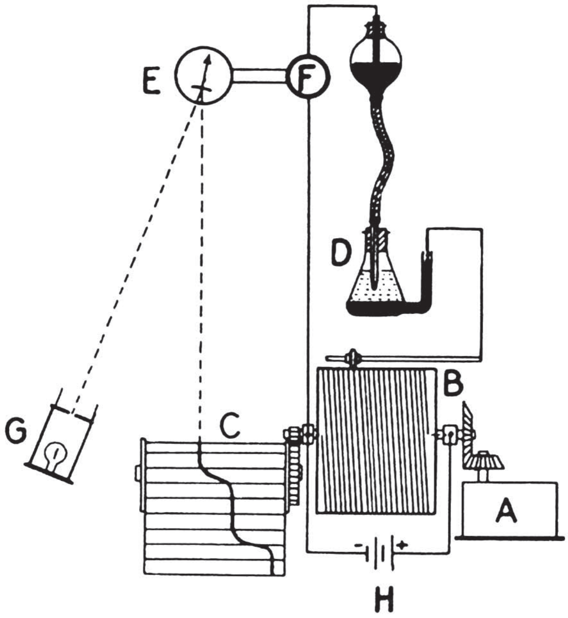
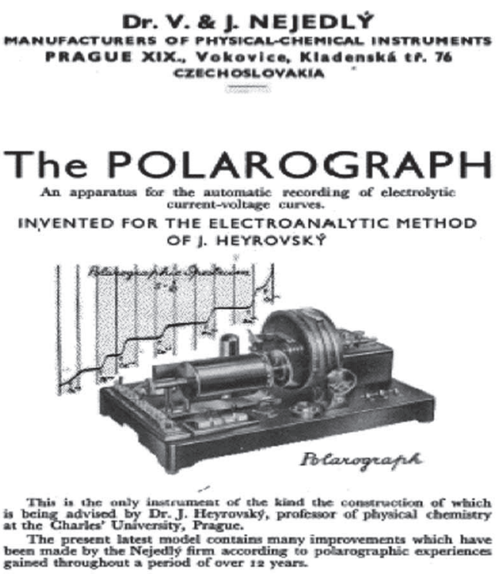


Figure 3. Heyrovsky–Shikata photographic recording polarograph *(4).*



Dr. V. & J. NEJEDLÝ
MANUFACTURERS OF PHYSICAL-CHEMICAL INSTRUMENTS
PRAGUE XIX., Vokovice, Kladenská tř. 76
CZECHOSLOVAKIA

The POLAROGRAPH
An apparatus for the automatic recording of electrolytic current-voltage curves.
INVENTED FOR THE ELECTROANALYTIC METHOD OF J. HEYROVSKÝ

This is the only instrument of the kind the construction of which is being advised by Dr. J. Heyrovský, professor of physical chemistry at the Charles' University, Prague.

The present latest model contains many improvements which have been made by the Nejedlý firm according to polarographic experiences gained throughout a period of over 12 years.

Figure 4. Commercial polarograph produced by V. and J. Nejedly, Prague, beginning in 1929.

Figure 5. Manual polarograph from E. H. Sargent & Company (model III).

Figure 6. Photographic recording polarograph from E. H. Sargent & Company (model XI).

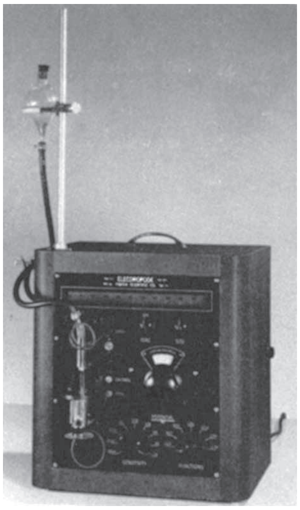


Figure 7. Manual polarographic instrument from Fisher Scientific Company, called the "Elecdropode".

was available. This instrument was probably the first automatic recording analytical instrument described, decades before electronic recorders were available. Although the authors did not patent the instrument, they obtained a copyright on the name they coined for the technique and the instrument: polarography and polarograph. Commercial instruments based on this design began being produced in Czechoslovakia by V. and J. Nejedly in 1929, and apparently by others elsewhere in Europe (Figure 4). A pamphlet from this company contains the following statement:

> Thus, the outlook seems justified that it should soon be impossible to enter any modern laboratory, either for routine work or for research, without finding one or more of these instruments. The successful applications of the polarographic methods have already had as a consequence a number of unauthorized imitations. As none of them is supervised by a scientific collaborator of the inventor, Dr. J. Heyrovsky, Professor of physical chemistry at Charles University, Prague, warning is hereby given against imitations and the unscientific and misleading pamphlets of other firms.

Heyrovsky visited the United States in 1933, including a stop at the University of Minnesota where he met the eminent analytical chemist, Isaac M. Kolthoff. This visit led to the start of research in polarography in the United States and publication of the monograph on polarography by Kolthoff and J. J. Lingane *(5)*. In terms of instrumentation, the onset of World War II in 1939 led to the United States becoming cutoff from Czechoslovakia, and the start of manufacture of these instruments in the United States. The name "Polarograph" was a registered trademark of E. H. Sargent & Company, who manufactured manual (model III) (Figure 5) and photographic (model XI) (Figure 6) versions. Other companies also produced these kinds of instruments, but because of copyright issues had to call them by other, rather imaginative, names, such as the "Elecdropode" (Fisher Scientific Company) (Figure 7) or the "Polarecord" (Metrohm, Ltd.). A

Figure 8. Polarographic instrument using a strip-chart recorder from Leeds & Northrup called the “Electrochemograph”.

listing of a number of commercial polarographic instruments is given by Meites *(6)*. The availability of the electronic strip chart recorder led to much more convenient instruments that no longer required photographic development, such as the Sargent model XXI Polarograph and the Leeds and Northrup Electrochemograph (Figure 8).

### *Later Developments*

During this period, up to about 1955, a number of variations of the basic polarographic method, for example, especially ones that promised higher sensitivity such as pulse and square wave polarography were described and commercial instruments by companies such as Mervyn Instruments and Southern Analytical Ltd., in England, were developed *(7)*. However these instruments were large and complicated, because this was still the vacuum tube electronics era, leading Meites to comment *(7)*.

> Unfortunately these instruments are necessarily very complex; they are, therefore, very expensive and in addition the time between successive breakdowns is too short to make the use of these techniques feasible as yet except in the very near proximity of a sophisticated instrument-maintenance group.

Moreover all of the polarographic instruments described above used a two-electrode configuration, comprising the DME and the counter electrode, which also served as the reference electrode. This arrangement is satisfactory with a small microelectrode, such as the DME, and with aqueous solutions with reasonable concentrations of ions. With this arrangement both the current and the solution resistance are small, so the applied voltage is close to the actual potential of the DME. However, with larger electrodes (i.e., with bigger currents) and many nonaqueous solvents (i.e., with higher resistance), the two-electrode arrangement is not satisfactory, and a three-electrode system, with separate reference and counter electrodes and powered by a potentiostat, is needed. Although potentiostats had been developed for controlled potential electrolysis experiments *(8),* including an electronic one by Hickling and later a commercially available one by Wenking, these had not yet been incorporated into voltammetric equipment. However the growing use of operational amplifiers, first in vacuum tube models and later based on transistors and ultimately integrated circuits, led to three-electrode potentio-static systems incorporating many different operation modes. The other major change that occurred was the availability, beginning in the late 1970s, of small personal computers. Although computers had been used in laboratory experiments in electrochemistry for a number of years, for example, using the venerable Digital Equipment PDP-8, commercial equipment did not become available until the smaller and more powerful PCs came on the scene *(9)*. These more recent advances will be discussed in other articles in this symposium.

## Scanning Electrochemical Microscopy

### *Ultramicroelectrodes*

The scanning electrochemical microscope (SECM) involves the use of a small tip (working electrode) that is scanned in close proximity to a surface. It allows high resolution chemical imaging of surfaces of all types and studies of fast heterogeneous and homogeneous reactions. Since the first reports on this instrument in 1989, it has become commercially available and is still undergoing development and finding new applications. A key component of the SECM is the tip, a so-called “ultramicroelectrode” (UME) (to distinguish it from the larger DME and related “microelectrodes”). Such electrodes, with tip diameters of the order of 25 μm (down to nm dimensions) also have a long history (Figure 9). William Hyde Wollaston was making small metal electrodes only shortly after voltaic

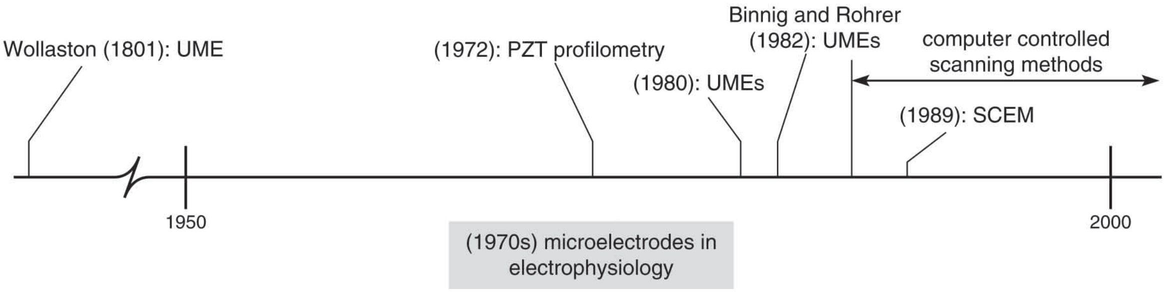


Figure 9. Time line for the development of ultramicroelectrodes and scanning electrochemical microscopy.

cells were discovered. In a typical example *(10)* he wrote this description of electrode fabrication:

> Having procured a small wire of fine gold, and given it as fine a point as I could, I inserted it into a capillary glass tube; and, after heating the tube, so as to make it adhere to the point and cover it in every part, I gradually ground it down, till, with a pocket lens, I could discern that the point of the gold was exposed.... The point exposed did not exceed (1/700)th of an inch in diameter. With another point, which I estimated at (1/1500)th... (Note these represent diameters of 36 and 17 μm, respectively).

Because it would have been exceedingly difficult to measure currents that would pass through such small electrodes in those times, one can only guess that Wollaston desired to get very high current densities with the feeble potential sources available, so he could visually detect chemical changes. Work on UMEs remained largely dormant until the early 1970s, when 50 to 200 μm diameter electrodes were applied to the detection of neurotransmitters in vivo, and in about 1980, when the advantages of such electrodes for studies in highly resistive media and at fast scan rates was realized *(11).*

### Scanning Probe Microscopy

At about the same time, there was interest in using very small electrodes (tips) for scanning surfaces in vacuum or air to obtain information about surface topography (profilometry). For example Young and coworkers at the National Bureau of Standards described the "Topografiner" that was capable of resolution of "30 Å perpendicular to the surface and 4000 Å in the plane of the surface" by controlling the motion of the tip with piezoelectric elements and measuring the electron tunneling or field emission current *(12).* This work culminated with the invention of the scanning tunneling microscope (STM) by Binnig and Rohrer that was capable of atomic resolution and resulted in the Nobel prize for this work *(13).* Our group became very interested in the STM after reading about this work and decided to build one to see whether it could be used to image surfaces under water, especially electrodes under potential control *(14).* We decided to build the instrument with digital control and data acquisition, rather than using the analog approach of earlier work, simply because this seemed easier for us, and we used an Apple II+ and an interface for this purpose. Although we did not attain atomic imaging in these first experiments, we did demonstrate the use of STM under water at an electrode surface. However, this study and continuing experiments with higher resolution STMs made us aware of the limitations of this technique for analytical and electrochemical investigations. One could not recognize isolated molecules adsorbed on surfaces immersed in solution, although the technique was very useful for looking at organized assemblies on surfaces. Moreover, it was not useful for nonconductive substrates, such as polymer layers, and did not provide a useful quantitative theory to estimate, for example, the distance of the tip from the surface or concentrations near the surface. We thus started thinking about a more electrochemical approach to scanning probe microscopy and eventually came up with the SECM technique.

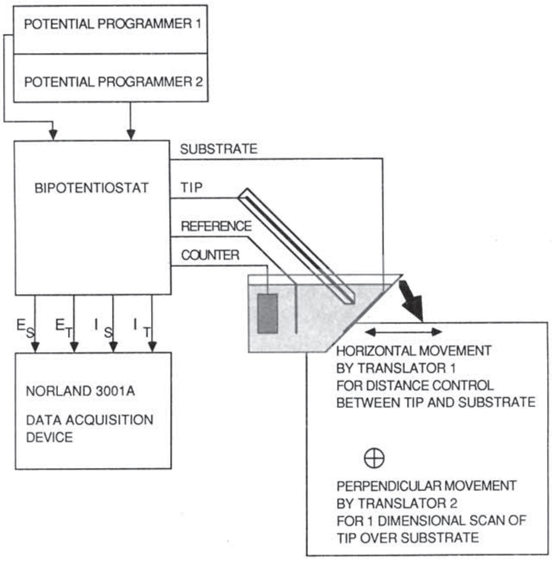


Figure 10. Block diagram of first scanning electrochemical microscope *(17)*.

### Scanning Electrochemical Microscopy

The idea of SECM was to use the scanning tip as an UME for some electroactive species (either the mediator in the solution or a species produced at the substrate interface) and somehow use this approach to interrogate a surface. A few electrochemical studies with UMEs near an electrode surface had been reported to study concentration profiles by studying electrochemical transients. For example, Engstrom and co-workers *(15),* manually positioned 10-μm C or 25-μm Pt electrodes near an electrode surface where electrolysis was carried out and used the potential step transients to find the concentrations at different distances from the surface and at different locations. We initially also first carried out transient experiments and considered, for example, using the time it takes for a tip generated species to diffuse to the substrate (the transit time) to measure the tip–substrate distance. However, when the tip was close to the surface, the application of a potential step at the tip induced a current in the substrate, because the tip and substrate were capacitively coupled. The time constant and size of this substrate capacitive signal would mask the desired faradaic signal at small distances where the transit time was very short. Moreover, having time as a variable complicated the collection and treatment of data. We then tried a steady-state approach.

In a collaborative experiment with Mark Wrighton and his group at MIT, we had carried out simulations of the electrochemistry at arrays of closely spaced electrodes (e.g., 2.3-μm wide electrodes spaced from 1.3 μm to longer distances) using one electrode as a generator and another as a collector *(16).* We saw that the currents quickly reached steady-state values under these conditions. Moreover, we saw that a neighboring (collector) electrode can cause feedback to the generating electrode. For example, in comparing the behavior seen at inter-

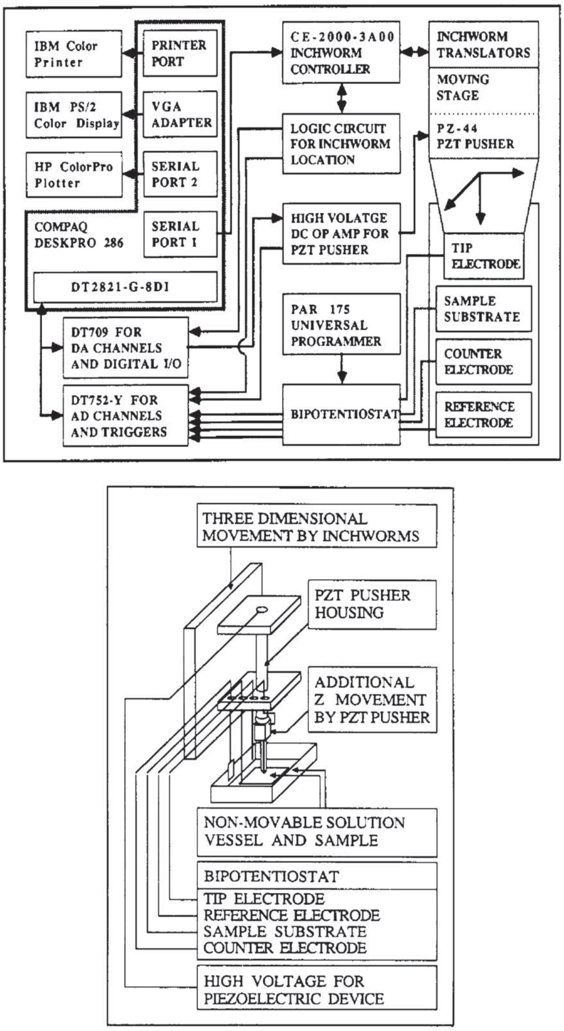


Figure 11. Block diagram of SECM that allowed 3D-imaging *(18).*

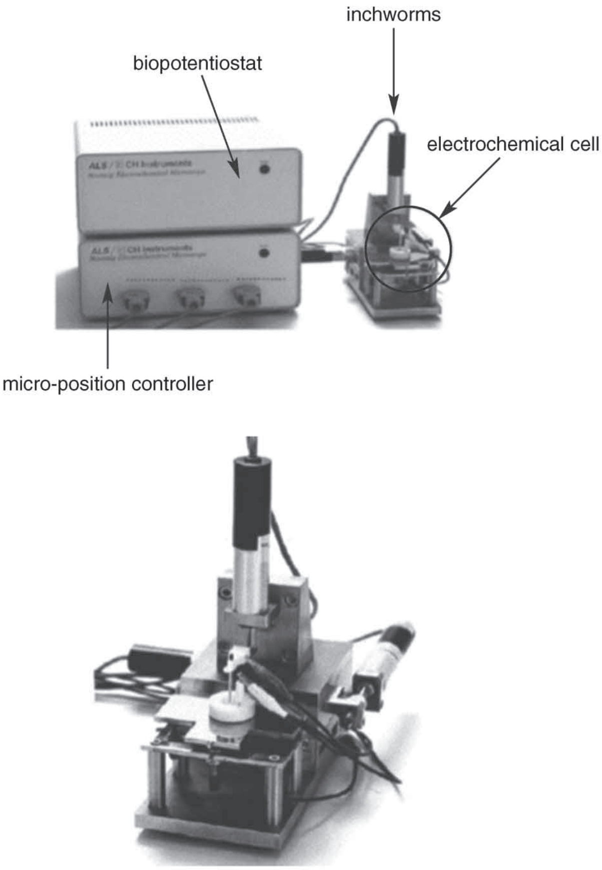


Figure 12. SECM produced by CH Instruments.

digitated electrodes to that at a rotating ring-disk electrode (RRDE), we wrote *(16)*:

> A phenomenon related to shielding but not possible at the RRDE is feedback. When the reduced species reaches the collector electrode, it is reoxidized to Ox that can diffuse back to the generator electrode. Thus, the collector electrodes act as a source and increase the flux of Ox to the generator. The effect of feedback was observed in the increased magnitude of the quasi-steady-state generator currents (see Table II).

The magnitude of this steady-state feedback was a function of the distance between the generator and collector electrodes, and increased as this spacing became smaller. We also realized that this approach might also be useful at insulators, because the UME tip current would be affected by blockage of the diffusion path to the tip and also by processes occurring on the insulator surface. Arrays of electrodes (and the related thin layer cells where two electrodes are held in close proximity in a face-to-face configuration) are not very convenient for these kinds of electrochemical studies because the distance between electrodes is fixed (and in the case of thin layer cells, it is difficult to make measurements free of resistance effects in the thin gap). However producing a similar configuration with a tip that could be scanned in three dimensions, allowing both a highly controlled variable distance between the electrodes and imaging possibilities, was more versatile, and we began experiments of this type.

Our first article on SECM *(17),* described the basic instrument and gave examples of two-dimensional imaging in the feedback mode (Figure 10). This was quickly followed by a more advanced instrument for true three-dimensional imaging and a quantitative theory for the feedback modes over conductors and insulators (Figure 11) *(18, 19).* Following these articles a number of other laboratories around the world began working in this field. A commercial SECM has been produced and marketed by CH Instruments (Austin, TX) since about 1997 (Figure 12).

Numerous applications of the SECM technique, for example, with biological systems, polymers, semiconductors, monolayers, and membranes, have been reported. It has been used to study corrosion, electrocatalysis, permeability, dissolution kinetics, living biological cells, and many other processes, and also to measure fast homogeneous kinetic reactions. It has also been used for fabrication, such as deposition and etching of metals at high resolution. A monograph on the SECM providing details of the technique and its application appeared in 2001 *(20).*

## Acknowledgments

This symposium celebrates the pioneers in the field of voltammetric instrumentation. Inevitably the advances are the results of the contributions of a great many people—many more than can be referenced in a single article. A few (but not all) of those from the United States who should be mentioned in connection with this are Paul Delahay, Don Smith, William Reinmuth, Robert Osteryoung, Charles N. Reilley, Fred Anson, and Irv Shain. I'm also indebted to the many students and post doctoral fellows in my laboratory who helped develop the SECM technique. Finally, I would like to acknowledge the continued support of the National Science Foundation (0451494) that was vital in the invention and development of SECM.

## Note

1. Voltammetry is a term coined in about 1940 by H. A. Laitinen and I. M. Kolthoff to describe measurements of current as a function of potential at small electrodes, but has grown to encompass many other types of electrochemical techniques. The name "polarography" was introduced in 1924 by M. Shikata and J. Heyrovsky and is now taken to mean voltammetry with the DME.

## Literature Cited

1. Zuman, P. Electrolysis with a Dropping Mercury Electrode: J. Heyrovsky's Contribution to Electrochemistry. *Crit. Rev. Anal. Chem.* **2001,** *31,* 281–289.
2. These and earlier experiments by Lippmann described in detail in Ostwald, W. *Electrochimie: Ihre Geschichte und Lehre;* Verlag: Leipzig, Germany, 1896; pp 1018–1042. English translation by the Smithsonian Institution Libraries Tranlation Program, now only available through the National Technical Information Service (NTIS), U.S. Department of Commerce, Technical Translation No. TT 74-52049/01/02: Ostwald, W. *Electrochemistry: History and Theory;* Date, N. P., Translator; Amerind Publishing Company: New Delhi, 1980.
3. Heyrovsky, J. *Trans. Faraday Soc.* **1924,** *19,* 692.
4. Heyrovsky, J.; Shikata, M. *Recl. Trav. Chim. Pays-Bas* **1925,** *44,* 496.
5. Kolthoff, I. M.; Lingane, J. J. *Polarography;* Interscience: New York, 1941; expanded to two volumes in 1952.
6. Meites, L. *Polarographic Techiques;* Wiley-Interscience: New York, 1955; pp 35–57.
7. Meites, L. *Polarographic Techiques;* Wiley-Interscience: New York, 1955; pp 577–592. See also: (a) Bond, A. M. *Modern Polarographic Methods in Analytical Chemistry;* Marcel Dekker: New York, 1980. (b) Schmidt, H.; von Stackelberg, M. *Modern Polarographic Methods;* Academic Press: New York, 1963.
8. Lingane, J. J. *Electroanalytical Chemistry;* Interscience: New York, 1958; pp 308–339.
9. He, P.; Avery, J. P.; Faulkner, L. R. *Anal. Chem.* **1982,** *54,* 1313A.
10. Wollaston, W. H. *Philos. Trans. R. Soc. London* **1801,** *91,* 427.
11. Wightman, R. M. *Anal. Chem.* **1981,** *53,* 1125A.
12. Young, R.; Ward, J.; Scire, F. *Rev. Sci. Instrum.* **1972,** *43,* 999.
13. Binnig, G.; Rohrer, H. *Helv. Phys. Acta* **1982,** *55,* 726.
14. Liu, H.-Y.; Fan, F.-R. F.; Lin C. W.; Bard, A. J. *J. Am. Chem. Soc.* **1986,** *108,* 3838.
15. Engstrom, R. C.; Weber, M.; Wunder, D. J.; Burgess, R.; Winquist, S. *Anal. Chem.* **1986,** *58,* 844.
16. Bard, A. J.; Crayston, J. A.; Kittlesen, G. P.; Varco Shea, T.; Wrighton, M. S. *Anal. Chem.* **1986,** *58,* 2321.
17. Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *Anal. Chem.* **1989,** *61,* 132.
18. Kwak, J.; Bard, A. J. *Anal. Chem.* **1989,** *61,* 1794.
19. Kwak, J.; Bard, A. J. *Anal. Chem.* **1989,** *61,* 1221.
20. Bard, A. J.; Mirkin, M. V. *Scanning Electrochemical Microscopy;* Marcel Dekker: New York, 2001.