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Vitae

Ray G. Clem is an analytical chemist employed by the University of California, Lawrence Berkeley Laboratory in the Nuclear Chemistry Division. His interests in the electroanalytical field include method development and applications, instrumentation development, and cell design. He has recently developed rotated cells for polarography, anodic stripping, and coulometry. He was co-inventor of the digital potentiostat. Present interests are the use of large digital computers for the analysis of polarographic and anodic stripping data.
WHAT HAPPENED TO POLAROGRAPHY

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"What happened to polarography?" was a question asked some time ago by Industrial Research. After a precocious beginning, having been invented by Dr. Jaroslav Heyrovsky over 50 years ago, it seemed to have disappeared. Like many other powerful but now common-place techniques like atomic-absorbance spectroscopy, it went into hibernation for a time because it was ahead of its time. Based upon Bunsen's now classical observations of the absorption of some sodium emission-lines by sodium vapor, it would have been possible to develop an AA spectrometer in the 1800's; however, the utility of his work had to await the development of a stable source of resonance lines in the 1950's. Development of modern polarography had to await the recent development of fast, stable, operational amplifiers.

That is not to say polarography was reported, buried, then finally rediscovered. It wasn't. Using polarographic instruments that were primitive by today's standards, Heyrovsky and his devoted colleagues did considerable research work. He was very alert to advances in instrumentation and was, for example, the first to use an oscilloscope for the study of fast electrode reactions employing sinusoidal current. For his invention of polarography and his subsequent pioneering efforts in the field, Heyrovsky was awarded the Nobel Prize in the 1950's. Major advances were also made in the field by Von...
Prior to the development of polarography, in a practical sense at least, the analyst had available only the laborious classical volumetric and gravimetric methods handed down from the previous two centuries. A sample constituent had to be present at the 1 mg level or greater to be determinable. With polarography, in one quantum jump, it became possible to determine sample constituents at the parts per million level—and with only a piece of glass capillary tubing, a galvanometer, a voltmeter, a calomel reference electrode, a battery-slide wire combination and a few pounds of mercury!

Polarography also came at a time when fast, sensitive photometric methods of comparable sensitivity were being developed. Since photometry is applicable to virtually every element on the period chart, and since photometry is simpler to instrument than is polarography, polarography was less widely used than it might otherwise have been.

The utility and desireability of the new polarography cannot be denied. It has reappeared in an all-electronic form and features direct sensitivity to the parts per billion level for many electroactive substances.

Its re-emergence is timely since it has the greatest sensitivity to environmentally important elements like lead and cadmium. It is being used in clinical work to determine lead in the blood of ghetto children. It is used in forensic work to determine drugs and arsenic in urine. In oceanography, polarography is employed to determine oxygen concentration profiles 1000 meters and more beneath the ocean surface. It is also used in industrial process
control--either on line or in the control lab. Polarography also plays a part in the measurement of concentration levels and in valence state determinations of uranium and plutonium in fused salt fuels employed in the molten salt reactor program. New uses are being added daily to the list of applications.

The study of fundamental electrode processes is moving ahead. Development of optically transparent thin metal electrodes permits the teaming of polarography and spectrophotometry to detect the measure species produced at the solution-electrode interface during electrolysis. ESCA is used to study the chemical changes produced by electrolysis on the surfaces of solid electrodes. Step potential experiments employing very fast potentiostats are giving a better picture of the mechanisms of electrode reactions. Ac polarographic studies are used to elucidate equilibrium kinetics. This store of fundamental data is growing rapidly.

Digital techniques are playing an increasingly important role in modern polarography. A third generation potentiostat called a digipotentiogator has been developed. It controls potential through digital injection or extraction of charge into or out of the cell. High speed digital computers are being used routinely to process digital data produced by this device.

Anatomy of the Polarographic Wave

Heyrovsky's dropping mercury electrode (DME) is the most widely used polarographic electrode. It consists simply of a vertically mounted glass capillary tube connected through a stand-pipe to a reservoir of mercury. In operation, a tiny drop of mercury appears at the capillary orifice, grows, then breaks from the mercury thread, only to be replaced by another drop. The DME is unique in that it has the property of periodic self-renewal. The drop period is highly reproducible.
In use, the DME has the most negative useful potential range of any electrode ever developed. Its positive potential utility, however, is limited by the anodic dissolution of the mercury. Other electrode materials such as Pt, Au, Al, graphite, tungsten, and silicon diodes are used in the positive, mercury-inaccessible, potential range. All electrodes employed in polarography are termed micro-electrodes because the amount of sample charged in oxidation state or removed through electrodeposition during the analysis is a very small percentage of the total sample.

A polarograph is an instrument used to scan the potential of the polarizable electrode versus a non-polarizable reference electrode and to record the resulting current data.

The cell containing the sample solution into which the electrodes dip, must be sparged of oxygen prior to the analysis if the scan is made at negative potentials. Unless oxygen is the substance determined, its presence constitutes an interference. Its removal is usually effected by bubbling nitrogen gas through the solution for 10-15 min. A recent LBL invention, a rotated cell for polarography permits the sparging of sample solutions within 75 sec or less.

Upon potential scanning the DME, very little current flows until a potential region is reached where the sample constituent can be reduced. At that point, the current increases abruptly to a new and higher level which then again becomes essentially parallel to the background current level. The current before the rise is called the background current (\(i_b\)). The current after the rise is called the diffusion current plateau. The extrapolated differences between the two levels is termed the diffusion current (\(i_d\)) and is directly related to the sample concentration. The potential on the polarographic wave mid-way between the two current levels is the half wave potential (\(E_{1/2}\)).
Electrooxidation waves are also possible. When these appear, the $i_d$ is less than $i_b$. All other reasoning is the same as that just discussed.

The diffusion plateau is so named, because the sole means of ion-transport to the electrode in the unstirred solutions employed for DME polarograph is diffusion. The current ceases to rise shortly after the $E_{1/2}$ potential is reached because the sample ions are being reduced as rapidly as they can diffuse up to the electrode. The diffusion or concentration gradient established during each drop period is destroyed when the drop falls. Thus each successive drop is born into a solution that is essentially the same as the bulk solution.

The current flowing at the DME consists of two components, and ratio of which varies in time during the life of each drop. One component comprises the background current and must be satisfied before the sample related current can appear. Isolation and recording of the latter component is the basis of modern polarography.

Examination of the wave reveals it is made up of periodic increases in current, followed by abrupt decreases in current. These periodic current changes are due to the growth and fall of the mercury drop. These drop oscillations become ever more pronounced as the electrode is scanned in either a positive or a negative direction from its open circuit or zero current potential value. The drop oscillations are due to the readjustment of the ratio of positive to negative ions in the immediate vicinity of the electrode under the influence of the externally applied potential. This imposed ion-movement is tantamount to charging a capacitor, thus this current is termed the capacitive current and comprises the background current component. Its magnitude depends upon the electrode surface area and upon the concentration of the indifferent salt added to the sample solution to make it highly conducting.
Since each mercury drop continually increases during its life, the area related capacitive current component is ever present. The time rate of change of drop area, however, decreases near the end of the drop life and in these last few moments before drop fall, the sample related component, called the faradic current is greatest. Every successful, modern, analog, polarographic technique makes use of this very important fact.

The Evolving Potentiostat

Modern polarographic instrumentation evolved from less elaborate, but electrically equivalent circuits. Every modern instrument has, as its heart, a potentiostat to control cell potential.

The first two-electrode, manual potentiostat applied the polarizing potential to the DME through the reference electrode and across the cell. This arrangement worked well when dealing with low current levels and highly conducting solutions, however, it had two major faults. If the cell current demand were too high, the reference electrode could also become polarized, resulting in a reference potential change and subsequently in damage to the reference. In poorly conducting solutions such as organic solvents, the resistance across the cell was included in the polarographic measurements resulting in severe iR distortion of the recorded wave.

To prevent damage to the reference electrode and to eliminate iR distortion, a three-electrode, manual potentiostat was developed. The DME-reference potential was measured with a high resistance voltmeter in a loop different from the power loop. Virtually, no current was drawn from the reference electrode. Inclusion of a third electrode permitted the maintenance
of any desired control potential between the DME and reference electrode with automatic compensation for the iR drop. This simple three-electrode circuit was the forerunner of the modern potentiostat.

The present-day analog potentiostat operates in the same manner as did the classical three-electrode potentiostat; however, it has several major advantages. It is extremely fast. An operation amplifier potentiostat can have a rise time on the order of microseconds when driving a resistive load. It can maintain a set control potential to within better than one millivolt for long periods of time. And, it loads the reference electrode only to the extent of picoamperes or less. Speed and accuracy of potential control become ever more important as the modern techniques become ever more sophisticated.

The Modern Polarographic Systems and Techniques

A modern polarographic instrument requires, in addition to the potentiostat, a system timer to synchronize data acquisition with the periodic fall of the drop. A delay and gate circuit to permit current sampling at the same point in time after drop fall, and finally, some means for potential scanning the desired potential range.

Modern techniques differ primarily in the way in which the cell potential is scanned. The methods presented are illustrative of the modern approach, are among the more widely used techniques for analysis, and are presented in order of increasing sensitivity. Two methods are commonly used to sense the instant of dropfall needed to start the delay and gate circuitry. One method senses the abrupt change in the drop capacitance, the other and more popular method employs an electromechanical "drop knocker" which hammers the capillary
at some adjustable rate to assure a constant and preselected drop time through physical dislodgement of the drop.

The delay and gate circuit permits current sampling at the most opportune time--just before drop fall.

Perhaps the simplest approach to the modern technique is Tast (German for "touch") polarography. The cell is continually polarized with a dc range and the current is sampled for 20–40 milliseconds before drop fall. The current information is stored on a memory capacitor prior to its presentation to a strip-chart recorder operated in a display and hold manner. After shorting the memory capacitor, the process is repeated for each succeeding drop until the scan is completed.

The recorded data, which appear as a histogram of current vs. voltage, are free of drop oscillations characteristic of classical polarography and the method sensitivity is improved with respect to classical methods by more than a factor of 100 to \( \approx 5 \times 10^{-7} \) M molar level.

Although this simple modification of the classical technique represents an improvement in sensitivity, it is not ideal because the drop capacitance is being charged through potential scanning during the current sampling interval. This charging component is included in the measurement.

If potential changing of the drop capacitance limits sensitivity, why not keep the cell potential constant during the current measuring interval? Pulse polarography does just that.

A succession of single potential-pulses of increasing height is applied to consecutive drops at a preselected time near the end of each drop life. The initial high capacitive current decays to a negligible value during the first
60 to 80% of the pulse duration. The faradaic current is sampled in the remaining time portion of the pulse interval.

Because the pulse is applied only once for perhaps 50 milliseconds to each drop, a diffusion gradient does not have a chance to develop. More faradaic current is thus available to measure than is available with Tast polarography. The only capacitive current included is that associated with the very small increase in drop area which occurs during the sampling period. The ratio of faradaic to capacitive current is therefore very favorable. Sensitivity to the $1 \times 10^{-8}$ M level has been reported.

The most sensitive analog technique is derivative pulse polarography. For scanning, a combination of pulse and Tast techniques is employed, but unlike either, it employs two current sampling intervals of equal time periods. The first sample period occurs just before the pulse application, the second sample period occurs at the end of the pulse. The current samples are stored on memory capacitors; the difference is displayed on a recorder operated in a display and hold manner. Differences in the two stored samples occur only in the region of the half-wave potential where the current is changing rapidly with the potential. The polarogram recorded in this way therefore is a peak shaped incremental derivative of the conventional dc polarogram. The peak height is directly related to the concentration and the potential peak location corresponds to the half-wave potential. Sensitivity to the $5 \times 10^{-9}$ M level has been reported.

Anodic stripping is a modification of classical polarography and thus is instrumentally much less complex than the techniques just discussed. Differential pulse techniques, however, have been used to advantage. A hanging
mercury drop, or better, a paraffin impregnated, mercury plated graphite electrode is used. Unlike DME polarography, the solution is efficiently stirred to increase the rate of mass transfer to the electrode and to make the diffusion layer as thin as possible. Only those elements such as Pb, Cd, Tl, In, Zn, Cu, and Bi which can be plated into the mercury then reversibly stripped out are amenable to this technique.

These elements are accumulated in the mercury phase to a concentration level much higher than they exist in the solution through prolonged deposition at a potential more negative than their half wave potentials. After a 5 to 10 min amalgam accumulation time, an anodic going dc ramp is effected. The elements held in the mercury phase must strip out when the cell potential is scanned through their half-wave potential values. The resulting polarogram consists of a series of anodic peaks. The peak heights are proportional to the concentrations and the peak locations are indicative of the elements present. Depending upon experimental conditions of electrode surface-area, volume of solution electrolyzed, stirring efficiency, and amalgam accumulation time, sensitivities on the order of $10^{-10}$ to $10^{-11}$ M levels are reached. For the elements amenable to this technique, this method has the highest sensitivity of any polarographic method yet devised. It rivals mass spectroscopy.

**Digital Polarography and Data Processing**

All the methods just mentioned, except anodic stripping analysis, employ signal measurement at the end of the drop life to optimize the signal current. It is impossible to independently measure the capacitive and faradaic currents with a single measurement.
Life is much simpler with digital equipment. In digital polarography, the cell current is converted to a digital pulse train with an analog to digital converter (ADC). The pulse rate is directly related to current. The ADC clock-rate defines the ultimate precision of the system. With a 1 MHz ADC, it is possible, in theory at least, to measure a 1 μA current signal to within one part in a million. A small computer or a pulse height analyzer operated in the multi-channel scaling mode is used for digital data storage.

The DME drop period is reproducible to within only a few 0.1% so a dual time base crystal oscillation capable of measuring a 1 sec period to within 1 ppm is used as a digital delay and gate unit. The unit is triggered by the fall of each drop, and simultaneously, the cell potential and memory location is advanced one potential increment and one data channel, respectively. Digital data are stored for 50% of the drop life in each data channel. Using digital expansion of the stored data, as little as \(5 \times 10^{-8}\) M material is detected.

If two digital scans, one of the supporting electrolytes alone and one of the supporting electrolytes plus sample, are stored in two memory locations and the first is subtracted from the second, the difference between the two is called a subtractive polarogram. It is possible to detect the reduction of an electroactive substance at the \(5 \times 10^{-9}\) M level. This improvement in sensitivity results because the background is normalized. A high count accumulation in each memory channel is necessary to accomplish this level of sensitivity and thus requires the use of a long drop time capillary.

The successful measurement of \(i_d\) depends on the validity of the assumption that the slope of the background current and the diffusion current plateau is constant. This is approximately so for high sample concentrations.
At ever lower concentrations, however, this assumption becomes ever less valid. Curve fitting to the background and diffusion plateau of a digitally recorded polarogram with a digital computer reveals the fit is better when using a second order polynomial. This technique is used routinely at LBL for processing polarographic data.

Similarly, a linear extrapolation of the current beneath an anodic stripping peak fails at very low sample concentrations. A computer program has been written at LBL which fits, by least squares minimization, up to a third order polynomial to extrapolate beneath the peak. Lead in water samples at the 4 ppb level has been determined this way with a precision of $\pm 0.25\%$.

**Digital Potentiostat**

Last year, a potentiostat was built for the first time at LBL which controls potential by the pulsed injection or extraction of charge into or out of the cell. Several advantages are gained by employing this new technique. Because the number of steps between detection and numerical output are less, considerable savings in weight, size, cost and power consumption are realized. Unlike the analog potentiostats used previously, the current source and potential sensing elements never operate simultaneously. For this reason the digital system is much more stable.

This instrument, also called a digipotentiogator, is presently being used to analyze water samples for lead and cadmium at the parts per billion level with anodic stripping as part of LBL's environmental effort. It is capable of a measuring precision of 0.01% and is housed in a box measuring $15 \times 3 \times 11$ cm. These features, plus its low cost and power requirements—
about 1 watt—make it eminently qualified for field use. It can also be used to digitize potentiometric and spectrophotometric data. Such data are in a suitable form for transmission from remote sampling stations to the laboratory facility by microwave relay or telephone line.

Industry should also find this device attractive in digital monitoring and in process control.
Figure Captions for Photographs

Photo 1. Digital Display of an Anodic Stripping Polarogram.

Lower trace: complete scan. Large peak at right is the mercury stripping peak.

Upper traces: digital expansion of portions of the lower trace showing from left to right the presence of 4 ppb Cd, 27 ppb Pb, and 10 ppb Cu, respectively.

Photo 2. The Bipolar Digipotentiogrator.


First wave is Pb, the second wave is Cd at the 67 and 66 ppb levels, respectively.

Photo 4. The author.
This image shows a diagram related to electrochemical processes, including reference, electrode, control, and potential components. It features various electrical and control elements such as reduction, differential comparator, spread potential, constant current source, rebalance, and digitizing logic. The diagram includes paths for reduction, oxidation, and digital output signals, with connections to constant current electron injectors and extractors. The labels and symbols indicate a complex system for handling control and potential adjustments in electrochemical applications.
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