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COULOMETRY PRESENT

Ray G. Clem

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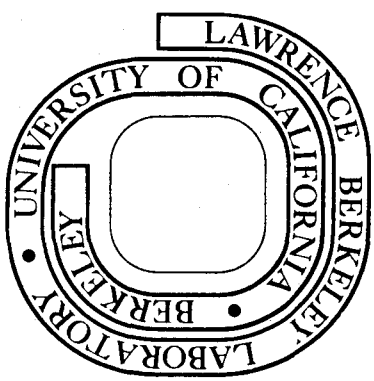

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COULOMETRY PRESENT*

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May 1973

Most modern-day techniques had their beginnings in the previous century. Coulometry is no exception. The discovery of the special relation which exists among such dissimilar quantities as equivalent weights, electrical current, and time, which forms the basis of coulometry, seems as incongruous and unlikely as the meeting of the men responsible for it.

Sir Humphery Davy, an English gentleman-scientist, discoverer of elements, and member of the Royal Academy, had need for a laboratory assistant--someone to help set up experiments, tend and operate the retort, and do other menial chores. The young man who eagerly applied for this position was an apprenticed book-binder who had developed an intense interest in science by reading the books he bound. His name was Michael Faraday.

Given the proper environment, Faraday's interest grew and matured to finally encompass the whole of science or "natural philosophy" as he called it. He had but one flaw in his education, however. He was no mathematician. Others who could formulate his prose into consise mathematical statements were the ones given credit for his scientific insights. Maxwells's celebrated light equations are, for example, a mathematical formulation of one of Faraday's ideas.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

A meticulous experimenter, Faraday is today remembered primarily for the work he could bring to completion in his laboratory. One such effort lead to the formualtion of the law of electrolysis and the estimation of a constant, both of which bear his name.

Faraday's Law states that the total quantity of chemical change produced at the electrodes of a cell is directly related to the quantity of electricity in coulombs passed.

The quantity of electricity required to produce one gram-equivalent weight of electrochemical change is 96,487 coulombs and is equal to one Faraday (F). His measurement of this constant in 1833 was within a few percent of the presently accepted value.

In the intervening 140 years, the law has been verified by the electro-reduction and -oxidation of metals, organic compounds, and gases in aqueous and non-aqueous solutions and in molten-salt baths, as well as in solid electrolytes.

Ninteenth century genius that he was, Faraday could not have foreseen the myriad developments and applications that would spring from his electro-chemical observations.

In the space effort, fuel-cells and batteries developed for man's voyage to the moon were designed based upon Faraday's Law.

Coulometric efficiency studies are made in the laboratory prior to building industrial facilities that produce aluminum by electrolysis, electrorefine copper, and produce caustic and chlorine by use of a mercury cell.

In the medical field, coulometry is being used to elucidate the chemistry of blood clotting. The recent discovery that the passage of a small

current across the broken ends of bones speeds healing is being studied employing coulometry.

The applications of coulometry in analytical chemistry are many and varied. Each year, ever greater amounts of plutonium and fissile uranium are being produced in the burgeoning nuclear reactor industry. So much, in fact, that these elements are now items of commerce. This requires close agreement between buyer and seller. Coulometric methods are the analytical techniques of choice. Uranium and plutonium methods are being automated to accomodate the large number of samples the International Safeguards and Controls Commission must analyze to inventory these fissile materials and thus prevent diversion.

The list of coulometric applications is growing daily.

Coulometry, discussed here, and polarography, presented in the January issue of IR, both are electroanalytical techniques involving electrolysis; they differ by the degree of electrolysis permitted and in the manner in which data are processed and presented.

Polarography therefore might be viewed as a coulometric process. The amount of material electrolyzed during the analysis, however, is a very small percentage of the total sample. For this reason, polarography is termed a "relative" technique. Calibration standards prepared on a weight basis are required to quantify the sample concentration through the comparison of diffusion-current heights.

In contrast, coulometry involves the measurement of coulombs: the product of two absolutely defined quantities--the ampere and the second. Coulometric analysis, unlike polarography, requires the exhaustive electrolysis of the sample solution. The sample weight then is determined directly through the current-time integral using Faraday's Law. Reference to weighed standards, therefore, is not required.

For this reason, coulometry is termed an "absolute" method. In this, it stands apart in utility and applicability, unique among all other wet analytical techniques.

Instrumentalists recognize two ways of performing coulometric analysis--by the passage of a constant current through the cell or by the application of a controlled potential to the cell. Only the latter is directly selective of the electrochemical reactions that take place in the cell. This will become apparent in the following exposition.

Coulometry is an enigma. Although it forms the basis of the field of electrochemistry and predates Heyrovsky's invention of polarography by 89 years, its first application for chemical analysis came only a scant 35 years ago through the efforts of Szelbelledy and Somorgi (1).

Their development, constant-current coulometry, is simple in principle and in instrumental requirements. It is an extension of classical volumetric techniques in which a chemical titrant, generated on the passage of a constant current through the cell, reacts with the sample in the bulk of the solution. An electrical switch serves as the buret stopcock. The bulk of the work in this field was done in a flurry of activity in the 1950's and early 1960's. As a result of these efforts, constant current methods exist for the generation of virtually every imaginable titrant.

To perform constant-current coulometry, several requirements must be satisfied. We will first consider instrumentation, electrodes, and cells; then examine the underlying principles of the method.

The instrumentation required consists of a galvanostat to force a constant current through the cell and a clock/scaler to measure the electrogeneration time.

A galvanostat may simply be a high gain, high current operational amplifier with the two-electrode coulometry cell placed in its feedback loop. Constant current flowing through the amplifier's input resistor, from a precision constant current source, causes a current of equal magnitude but of opposite polarity to flow through the cell to the summing point of the amplifier. The ability of the device to maintain a constant current through the cell's resistance is limited only by the amplifier's voltage compliance range.

The timer/scaler employed can be a simple, inexpensive device using as its time-base the 60 Hz line frequency to drive a clock or an electromechanical accumulating scaler. Alternatively, it can be a complex all-electronic device consisting of a thermostated crystal oscillator and an electronic accumulating scaler capable of measuring a 1-sec interval within better than one part in a million (2).

The combined precision of some galvanostat-timer/scalers approaches the 0.001% level.

The two-electrode cell consists of a container to hold the solution titrated, a working electrode at which the titrant is generated, and an isolated auxilary electrode. A gas dispersion tube is included if it is necessary to sparge oxygen from the cell.

Electrode materials used for titrant generation at positive potentials are generally gold or platinum. These are selected for their inertness to anodization and for their low background-current characteristics. The high hydrogen overvoltage characteristics of mercury makes it unique for titrant generation at negative potentials. All three materials are termed "passive" because they serve simply as a substrate for electron transfer.

Electrodes of silver metal, silver-silver halide, and mercury amalgams are termed "active". Silver ion is electrogenerated by anodization of silver metal. The halides, Cl^-, Br^-, and I^-, can be liberated by constant current reduction of the appropriate silver-silver halide electrode. Titrations for chelates with metal ions are effected by anodization of the appropriate mercury amalgam.

The surface area of the working electrodes is generally between 1- and 10-cm^2 and depends directly upon the magnitude of the generating current employed.

The auxilary electrode, which is not involved in the generation of the titrant, can be made of virtually any chemically inert conductor. Graphite, tantalum, niobium, as well as platinum or gold are commonly used.

The primary consideration in constant current methodology is that the electrogeneration efficiency for production of the titrant be 100%. Total efficiency, as we shall see, is never achieved, but it can be approached very closely as a limit.

Generation efficiency near 100% is assured by maintaining a high concentration of the substance called the "titrant precursor", from which the titrant is generated, by employing efficient stirring, and by not exceeding the limiting current density of the chemical system.

To see how these factors are interrelated, let's examine the effect increasing current has on cell potential as measured against a reference electrode in a well stirred potassium iodide solution contained in a coulometry cell. This salt serves as a precursor for the generation of iodine, an important titrant in classical titrimetry.

The scan is divided into three potential regions of interest. In the prewave region, a small change in applied current results in a large change in cell potential. In the half-wave region of the iodide wave, however, the cell potential changes very little for a large increase in current. The iodine serves as a strong potential buffer in this region. It functions, therefore, as a chemical means of controlling cell potential. In the current limiting region of the wave, the potential again changes greatly for small further increases in applied current. The wave height is directly related to the precursor concentration. The final current rise results from the electrolysis of water to generate oxygen.

Replacement of the electroactive potassium iodide with electroinactive sodium sulfate permits the evaluation of the background current at various potential values and thus the current efficiency of the iodine titration system at any given current level.

For example, at a total current level of 100 mA, if the background current is 10 μA, the generation efficiency is 99.99%. If the sample titrated also undergoes a direct reaction at the electrode, the overall efficiency is > 99.99%.

Obviously, as the applied current level approaches the background level, the generation efficiency approaches 0%.

If a constant current greater than the limiting current of the iodide wave is employed, oxygen in addition to iodine is produced. The generation efficiency for iodine is reduced by the amount of the oxygen produced, as well as by the background current level at that potential.

Since the current which does not produce the titrant appears as a titration "blank", it is clearly advantageous to select a current level such

that the blank can be ignored. The highest current employed is generally 90% of the limiting current of the precursor wave. This selection makes allowance for any momentary fluctuations in the stirring efficiency.

Efficient stirring assures effective transport of the titrant precursor to the electrode. The ultimate height of the iodide wave at any given concentration is determined by the stirring efficiency. Employing conventional means of stirring (e.g., magnetic stirring) the limiting current density is near 0.5 $mA/cm^2/meq$.

In the foregoing, scant mention was made of the sample species. Since the molar ratio of percursor to sample is generally made large ($\geqslant$ 10:1) by design, the sample substance carries very little of the total current. If, however, the precursor were absent, the sample might initially carry essentially all the current depending upon the level of the constant current. But in time, since the sample is reacting at the working electrode, its current would fall below the imposed constant current level. The cell potential, now unbuffered by the sample, would rapidly drift to the limiting potential of the solvent system. The current efficiency would then fall substantially below 100%. Consequently, the titration would be ruined. For this reason, the primary titration of the sample with constant current is not attempted.

So far we have directed all our attention to the anode reaction and patently ignored the cathode reaction. In our example, iodine liberated at the anode is reduced to iodide at the cathode. If a sample were present it too could be caught in an endless redox cycle. A ferrocyanide sample, for example, would be oxidized at the anode only to be reduced at the cathode. It would be quite impossible to determine a titration end point in such a system.

The electrode not involved in the electrogeneration of titrant, therefore, must be isolated to prevent secondary electrolysis. This is easily accomplished by placing the two electrodes in physically separate compartments electrically connected through a low leakage salt-bridge. Such bridges have been made from fritted glass, porous ceramic or glass, and ion exchange membranes. A bridge developed at Lawrence Berkeley Laboratory (LBL) is a fritted glass tube containing a fumed-silica gel of the precursor or supporting and is quite satisfactory for this purpose (3).

Virtually any technique used for end point detection in classical titrimetry can be used for constant-current coulometric titrations. These include chemical indicators, spectrophotometry, potentiometry, and amperometry.

Coulometric titrations find their greatest use in the sample range from a few micrograms to a few milligrams. Nanogram quantities can be titrated if special care is taken to miniaturize the cell and if highly sensitive endpoint detection equipment is available.

When one considers the scope and range of samples covered by the constant-current methodology and the simplicity of the instrumentation required, it is amazing that classical titrimetry is still more widely used than coulometry.

The precision attainable with constant-current coulometry is quite often comparable with the time-consuming, classical, weight-volumetric techniques. An accuracy approaching 0.01% is easily reached under ordinary laboratory conditions. A precision approaching 0.001% is attained by the National Bureau of Standards in its analysis of some reference materials.

For general analytical work, the time required per titration does not exceed 3-5 min. The technique is highly amenable to automation (4). Several

sample aliquots can be titrated in the same precursor solution before it becomes too dilute to function properly.

Almost any titrant used in inorganic analysis can be generated from the appropriate titrant precursor--at the flick of a switch. These include such common titrants as Fe^{2+}, I_2, ferri- and ferrocyanide, Ce^{4+}, OH^- and H^+.

Uncommon titrants such as Cr^{2+}, Ag^{2+}, Cu^+, Cl_2, Ti^{3+}, U^{5+}, and Br_2, which would be difficult or impossible to prepare and store in formal solution because of their high redox strength or instability, are also facilely generated. Chelometric titrations are also possible through the electroreduction of the Hg-EDTA complex.

Although constant-current titrations are elegantly simple, they have the same fault as classical titrations. Neither are highly specific. All too often this necessitates a laborious chemical separation of the desired sample constituent prior to the analysis.

If only it were possible to dwell at a factitious potential and thus not be forced to rely on the buffer potential of the titrant precursor, much greater selectivity would result. The sample could then be oxidized or reduced directly at the electrode. No chemical intermediate--the titrant--would be necessary. And there would be no need for an end point detection system.

Just as the granting of Alice in Wonderland's wishes sometimes compounded her problems, so it was with controlled-potential coulometry as we shall soon see.

The dawn of controlled-potential coulometry came with the invention of the potentiostat by Hickling in 1942. By 1945, James J. Lingane, a pioneer in the field, had demonstrated the great analytical utility of the technique. He

found that upon imposing a potential on the limiting current plateau of the sample species, the cell current decayed exponentially with time to an essentially constant background current level (5). A plot of the logarithm of the cell current vs. time yielded a straight line, thus proving that the current-time relationship was a simple first-order exponential function.

The slope of the log i-t plot, k, was called the electrolysis rate constant and was characteristic of the electroactive medium and the cell employed. Thus he found that k was directly related to the stirring efficiency, working electrode surface area, and the diffusion coefficient of the sample, but inversely related to the volume of the solution electrolyzed.

Since the magnitude of k affects the time required to make an analysis, it has become a figure of merit in cell design.

By now the reader is probably pondering: if the i-t relation is exponential, complete electrolysis is really achieved only at infinity. How does one make practical use of this fact in chemical analysis?

It is generally agreed that an electrolysis is complete and can be terminated when the cell current has decayed to $\leq 0.1\%$ of its initial value. The sample species is 99.9% electrolyzed at this final current value. This basis for termination is used primarily in the analysis of large samples.

For small samples, knowing the value of k, the time required to electrolyze the sample to 99.9% completion is calculated and the electrolysis is terminated at this point.

A blank electrolysis on the supporting electrolyte for the same period required to do the actual titration permits the correction of the sample current for the continuous background current.

Obviously since the quantity of electricity in controlled-potential coulometry is not a linear function in time as in constant-current coulometry, a more sophisticated means of integrating the quantity of coulombs consumed in the electrolysis was required.

Various electrochemical and electromechanical integrators were offered, but met with only moderate success. These integration techniques invariably failed at low sample concentration levels.

The practical development of the field awaited Glenn Booman's introduction of a potentiostat and current integrator based on operational amplifiers in 1957 (6). Accurate integration made possible the controlled-potential determination of semi-micro quantities of material. This development also permitted miniaturization of the cell. The analysis time per sample was reduced from one to two hours to about 30 min because efficient stirring was easier to effect in a small cell.

The much greater accuracy attainable with Booman's integrator gave question to the origin of positive errors approaching 1% and more under various conditions of sample concentration level and control potential.

Precise and accurate results were obtained for single element samples having a redox potential near 0.0 V vs. SCE, however, the results were generally high for elements oxidized or reduced near the anodic or cathodic limiting reaction of the solvent. Similar discordant results were obtained for two element samples having relatively close redox potentials, if the second element determined were irreversible. The result for the first element electrolyzed was generally high. The result for the second element was usually low. The magnitude of the error was a function of the sample concentration.

A partial explanation for the problem was given by Booman after mapping the potential gradients across his cell. In some regions the potential was less than the nominal control potential. This was expected. In other regions of the cell, the control potential was exceeded! This was surprising and disturbing.

The first truly definitive study of potential gradients in controlled-potential electrolysis cells was made in 1966 by Jackson Harrar with the assistance of Irving Shain at the Lawrence Livermore Laboratory (LLL) (7). Employing cells with compartmented electrodes and exaggerated geometry, they clearly demonstrated that the positive potential gradient existed, and further, that the magnitude of the gradient was a function of the current density and the spatial relation of the reference electrode with respect to the working and auxiliary electrodes. A general conclusion of these workers was that the reference electrode should be placed close to the working electrode on the line of minimum distance between it and the auxiliary electrode. This is the basis upon which all present-day coulometry cells are designed. Satisfying this criterion for dc potential control also results in maximum stability in the potential-cell control system (8).

Although viable coulometric cells and instrumentation had been developed, the 20 to 30 min required to sparge the cell and do an electrolysis often seemed to be an inordinately long time. A method requiring such a time expenditure was not likely to gain wide acceptance.

After some initial experimentation with conventional pool-type cells developed by Lingane in the 1940's, the workers at LBL decided that a new concept in cell design was needed to increase the rate constant, k.

Mark Twain once said that anyone can be successful--all that's required is confidence and ignorance. We were marked for success, for in our confidence, had we been cognizant of all the electrical and mechanical difficulties awaiting us in the development of the rotated cells, we might not have made the effort.

The first rotated cell that was developed employed mercury as the working electrode (9). The sample and mercury were aliquoted into a plastic cylinder closed at the bottom and partially opened at the top. The cylinder, mounted on the end of a motor shaft, was rotated at 1800 rpm. The mercury, owing to its greater density, was held against the wall of the cylinder. The less-dense sample solution was held in a thin-film on top of the mercury. The solution was contacted and stirred with a stationary, coaxial probe that contained the auxiliary and reference electrodes.

The most outstanding feature of this cell was its rapid sparging behavior. The cell solution could be sparged of oxygen in as little as 20 sec. This capability alone permitted the reduction of the analysis time to between 10 and 15 min. The electrolysis rate constant for this new cell was equal to any previously reported. Recent improvements at LBL have reduced the analysis time by a factor of 3.

The rotated platinum cell developed next was analogous to the mercury cell, but the cylinder was now constructed of platinum and lined with platinum gauze to increase the electrode surface area (10). In addition to rapid sparging behavior, the cell exhibited the highest electrolysis rate constants of any cell previously devised. With this cell it was possible to make an analysis within 3 to 5 min total analysis time.

These cells, in conjunction with the modularized, digital, electroanalytical system developed at LBL (2), enabled the routine analysis of sample constituents

at the ≤ 1-mg level with a precision approaching 0.01%. This degree of precision was realized through the development of a new technique termed "digital normalization" to evaluate the background current.

While viewing an electronic logrithmetic display of the digitally recorded data, a constant number of counts are subtracted from each data channel until all the data points in the decay curve fall on a straight line. The summation of the counts subtracted is equal to the background current contribution. The ability to treat each titration on an individual basis in this manner greatly increases the precision of the results.

This technique also solves the long-standing problem of analyzing certain nuclear materials by coulometry. Alpha-emitters produce electroactive radiolosis products such as hydrogen peroxide, chlorine, and other species at a constant rate in the sample solution. The magnitude of the background current, therefore, is a function of the concentration of the radioactive material. Evaluation of this background was no easy task. The background current measured for the supporting electrolyte alone was obviously different from that obtained in the presence of the activity. Digital normalization permits the determination of the total background on a routine basis -- again with high precision.

A recently developed computer program which fits the electrolysis current as the sum of two exponential equations yields results precise to within a few percent at ≤ 1-μg level.

Controlled-potential methods exist for a great many inorganic and organic compounds. The number is not as great as it might be because of the enormous amount of time required to develop methods. Hopefully, the development of the highly-efficient rotated cells will spark the wider interest the field deserves.

Perhaps the last under-developed electroanalytical technique in the field is voltage scanning coulometry pioneered by F. A. Scott, R. M. Peekema, and R. E. Connally (11), and by R. C. Propst (12). Controlled-potential coulometry was a giant step forward in terms of selectivity over constant-current methods, but a formal potential separation of more than 100 mV is required between electroactive sample constituents. Greater resolution than this is often required and would be afforded by the invention of a practical scanning coulometer.

Such an instrument would increment potential by sensing current demand. In potential regions in which there is no sample current, the instrument would scan rapidly. In potential ranges in which the sample could be reduced, the instrument would increment the control potential only after the sample in that increment was exhaustively electrolyzed.

If the digital data produced on each potential step were stored in adjacent memory channels, a series of peaks for each sample constituent would be recorded. The integral of each peak corresponds to the total amount of material in that peak. Overlapping sample peaks are easily deconvoluted with a digital computer. Some preliminary data at LBL indicate sensitivity to about the 10 ppb level using this technique.

The scanning coulometer would combine the advantages of resolution obtained with polarography with the absolute nature of the coulometric method.

The basis upon which a practical scanning coulometer could be built would involve sensing the negative potential gradient which exists on current demand in the rotated cell 180° from the coaxial reference-salt bridge probe.

The time required to make a coulometric scan would not exceed 10 to 15 min if rotated cells having very high electrolysis rate constants are used.

Industry should seriously consider the rotated cell concept. Electrosynthesis is seldom attempted on a commercial scale unless the product is of high value. Conventional coulometry cells do not readily lend themselves to continuous processing. Optimizing the cell geometry by placing the auxiliary and working electrodes close together compromises the mixing efficiency at the working electrode/solution interface. The electrolysis rate constant then suffers. On the other hand, wide spacing of electrodes to permit adequate mixing exacts a geometrical i^2R efficiency loss. This is of particular concern in highly resistive solutions used in organic electrosynthesis.

In contrast, the rotated cell concept lends itself to continuous processing with a very small electrical efficiency loss. Consider. An industrial rotated cell would consist of a concentric arrangement of cells or compartments. Each cell would be controlled by its potentiostat which would supply power to the cell through the attached, stationary coaxial probe. The feedstock would continuously pass into the first cell, overflow into the next and so on until it is collected as the finished product in an concave toroid at the upper edge of the last cell. The i^2R loss in such an arrangement would be minimal since the working electrode and auxiliary electrode distances need not be greater than a few millimeters, and since the rotating wall of feedstock is very efficiently stirred on contacting the stationary coaxial probe, the electrolysis rate constant would be quite favorable.

One need only solve a series of partial differential equations relating the flow rate, cell volumes, number of compartments and the electrolysis rate constant to determine the optimum operating conditions.

LITERATURE CITED

(1) L. Szebelledy and Z. Somorgi, Z. Anal. Chem., 112, 313, 323, 332, 385, 391, 395, 400 (1938).

(2) R. G. Clem and W. W. Goldsworthy, Anal. Chem., 43, 918 (1971).

(3) R. G. Clem, F. Jakob, and D. Anderberg, Anal. Chem., 43, 292 (1971).

(4) F. Jakob and R. G. Clem, MPI Appl. Notes, 6, 9 (1971).

(5) J. J. Lingane, J. Am. Chem. Soc., 67, 1916 (1945).

(6) G. L. Booman, Anal. Chem., 29, 213 (1957).

(7) J. E. Harrar and I. Shain, ibid., 38, 1148 (1966).

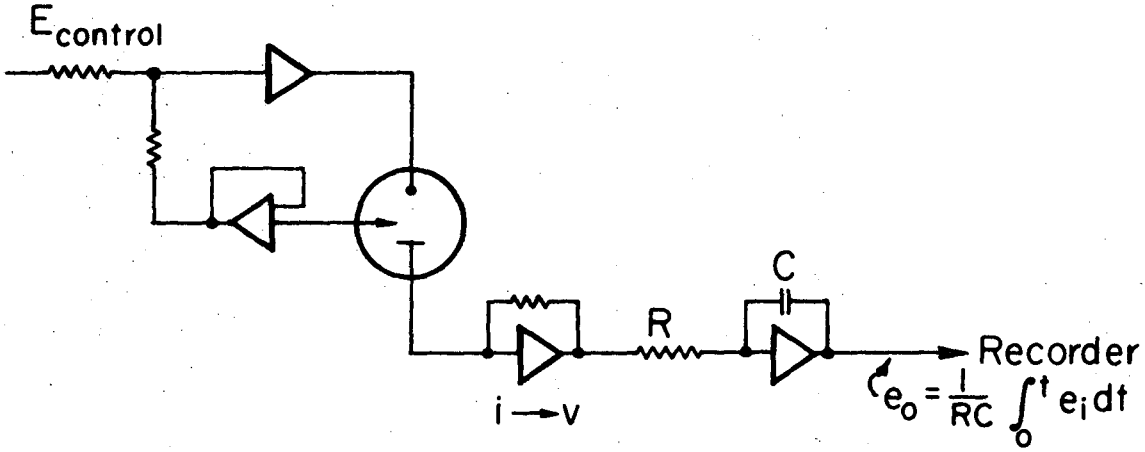
(8) J. E. Harrar and C. L. Pomernacki, Anal. Chem., 45, 57 (1973).

(9) R. G. Clem, F. Jakob, D. H. Anderberg, and L. D. Ornelas, ibid., 43, 1398 (1971).

(10) R. G. Clem, ibid., p. 1853.

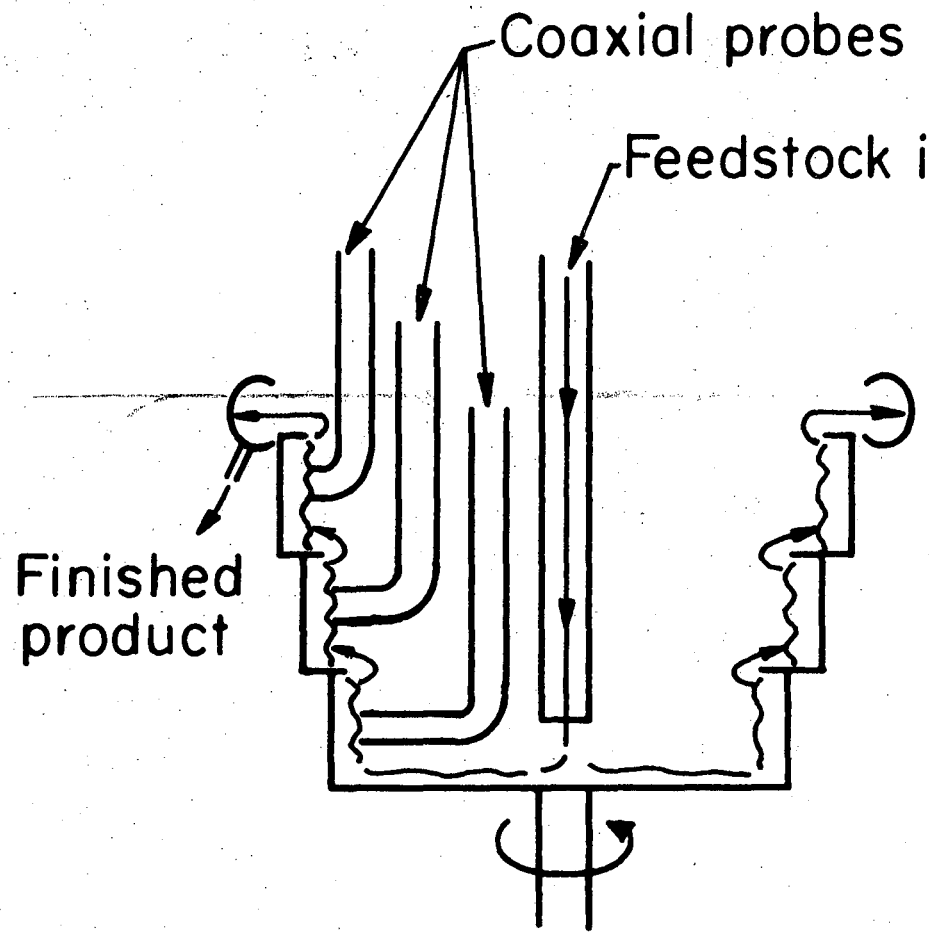
(11) F. A. Scott, R. M. Peekema, and R. E. Connally, ibid., 33, 1024 (1961).

(12) R. C. Propst, ibid., 35, 958 (1963).



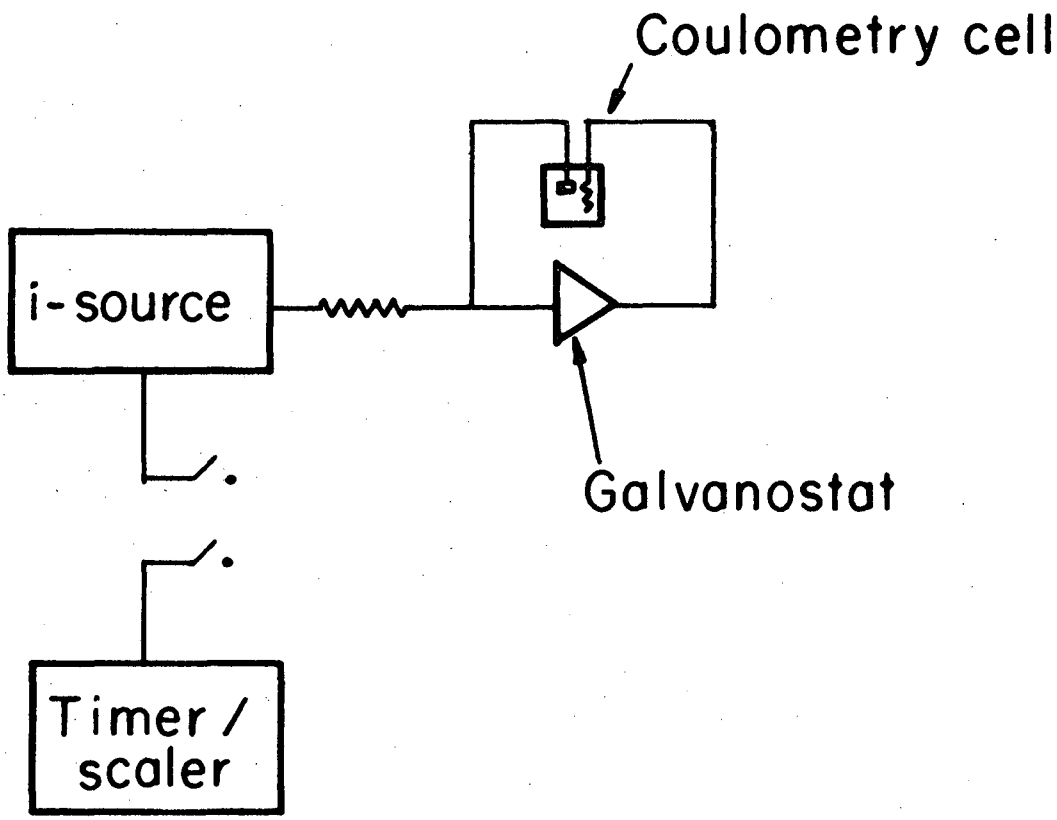
Potentiostat - integator

XBL 735 - 2910



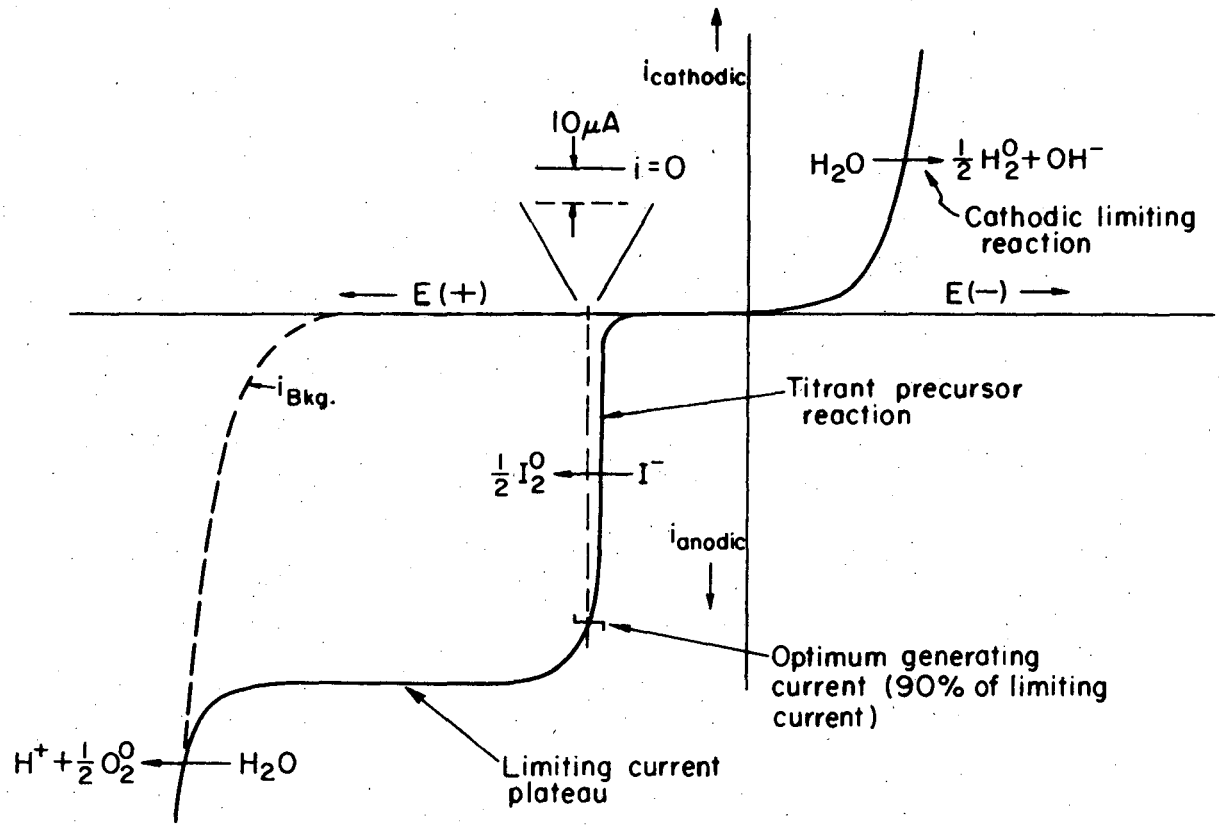
Multicompartmented rotated cell for continuous processing

XBL735-2911

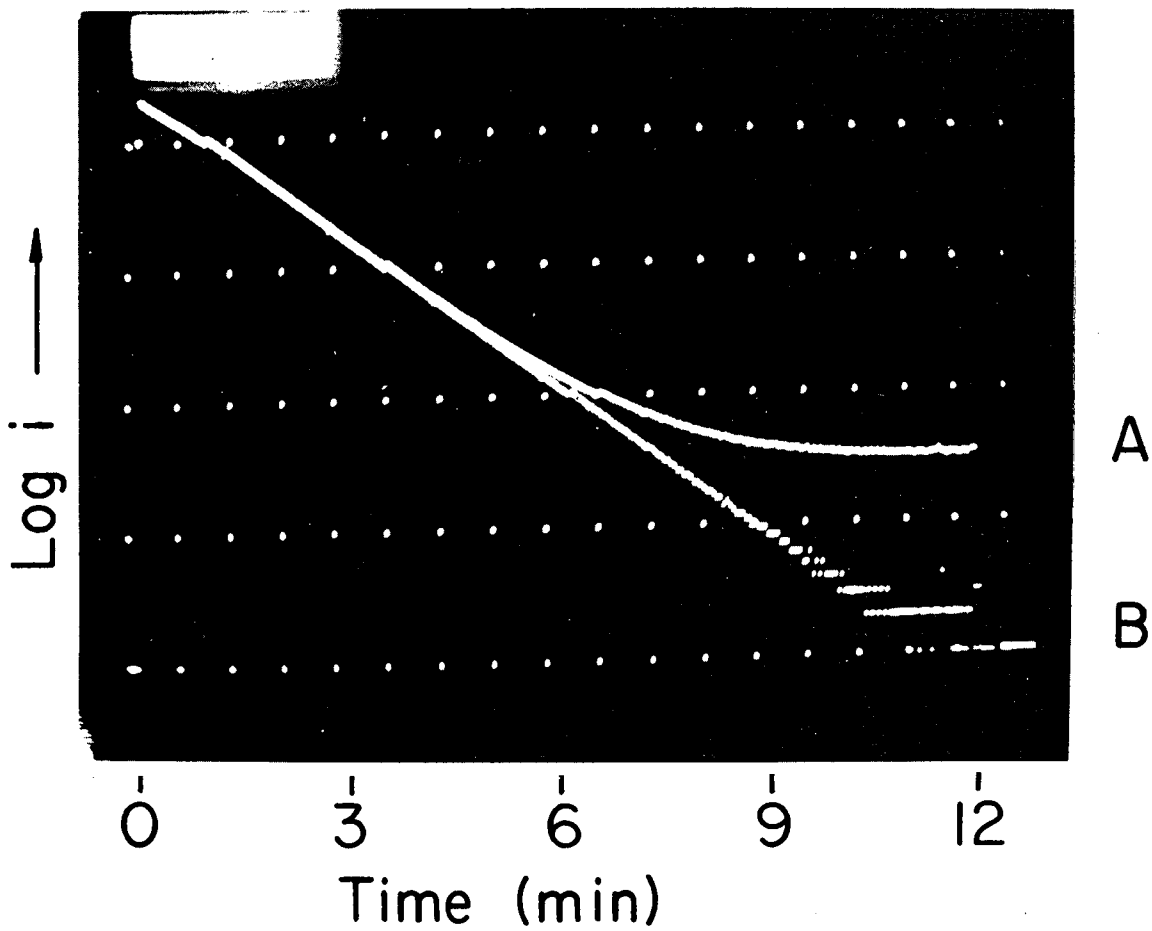


Galvanostat - timer/scaler

XBL735-2912


$i_{cathodic}$
10μA
i = 0
$H_2O \rightarrow \frac{1}{2} H_2^0 + OH^-$
Cathodic limiting reaction
E(+)
E(−)
$i_{Bkg.}$
Titrant precursor reaction
$\frac{1}{2} I_2^0 \leftarrow I^-$
i_{anodic}
Optimum generating current (90% of limiting current)
$H^+ + \frac{1}{2} O_2^0 \leftarrow H_2O$
Limiting current plateau

XBL735-2909



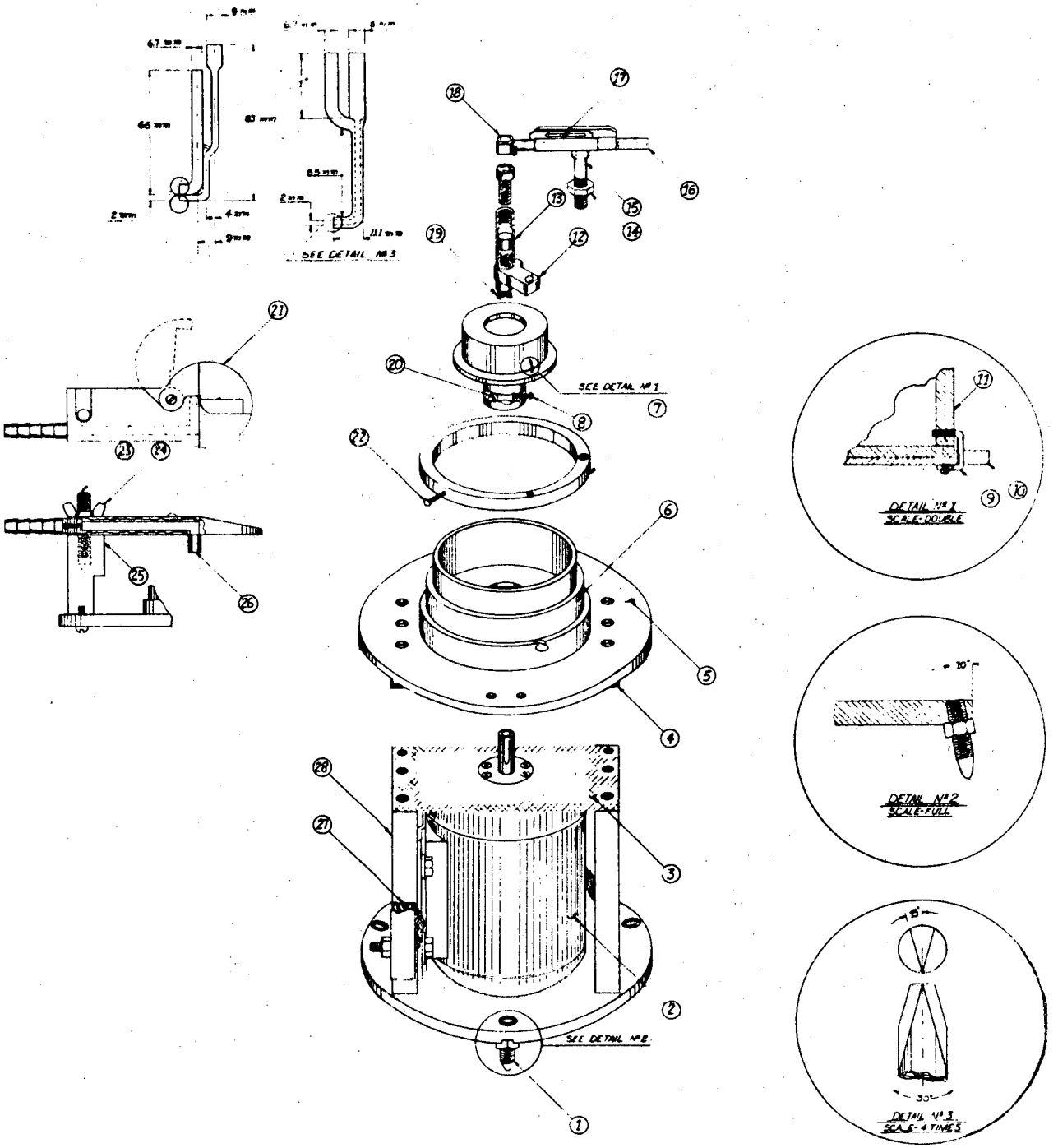
XBB 711-145

Normalization of a controlled-potential electrolysis of uranium.

A. Raw data 569.8 μg U^{6+} found

B. Normalized data: 561.6 μg U^{6+} found.

Uranium present: 561.8 μg.


SEE DETAIL Nº3
SEE DETAIL Nº1
SEE DETAIL Nº2
DETAIL Nº1
SCALE: DOUBLE
DETAIL Nº2
SCALE: FULL
DETAIL Nº3
SCALE: 4 TIMES

XBL 711-40

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