Voltammetry and polarography

- Sample preparation may sometimes be time-consuming relative to the usually short probe time.
- Interference from electrochemical signals of species other than those whose analysis is required
- Restricted anodic or cathodic ranges of some electrode materials
- Perfect renewal of electrode surface between analyses is not always feasible.
- Complexities in electrochemical or chemical behavior of required species in solution may prevent straightforward detection.

Electrometric titration

- Precision and accuracy are usually better when the titration determines a single analyte, although the successive titration of several analytes may be possible.
- Concentration and reaction speed must be high enough to permit rapid equilibration and to yield reproducible end points. Approximately 10^{-5} M may be taken as the lowest practical limit, although titration at lower concentrations is sometimes possible.

Potentiometric membrane electrodes

- Potential drift
- Interferences
- Often requires aqueous solutions

Capabilities and Related Techniques

Electrogravimetry

- *Estimated analysis time*: After sample preparation, electrolysis requires 15 min to well over an hour, depending on conditions.
- *Coulometric titrations:* Applicable for all volumetric reactions
- *Atomic absorption spectrophotometry:* Quantitative and qualitative determination of metal ions in the presence of other ions
- *X-ray fluorescence:* Qualitative and quantitative determination of elements

Controlled-potential coulometry

- *Estimated analysis time:* 5 to 30 min per measurement, after solution preparation
- Determination of major constituents, metals, and certain organics; study of electrochemical reactions. Suitable for determinations requiring greater selectivity than obtainable by constant-current techniques. Small-scale preparations
- Quantitative determination of metal ions
- *Controlled-potential electrolysis:* Can be used as a separation technique before other measurement techniques
- *Polarography and solid-electrode voltammetry:* These techniques measure electrolysis current-potential characteristics of solution samples, provide more global qualitative information on sample composition, and are more suitable for minor constituent and trace analysis but not as accurate or precise.

Voltammetry and polarography

- *Estimated analysis time*: 15 min to 3 h per sample, depending on sample-preparation time. In batch analysis, the probing of individual solutions for several components may require only minutes.
- *Coulometry:* Small amounts of reagents may be electrogenerated without the need for standardization and storage of dilute solutions. Analysis possible in same lower regions as voltammetry but without the same versatility of multielement analysis
- *Potentiometry:* The exceptional sensitivity of many ion-sensitive systems makes them widely and often simply used as direct probes and in titration methods. Some redox couples may be slow in establishing equilibrium at indicator electrodes.
- *Amperometry:* Offers more flexibility in selection of convenient solid electrode materials, because electrode history is less significant in titration techniques. May be used at low concentrations at which other titration methods are inaccurate (~10^{-4} mol/L), but cannot reach the low levels attained by voltammetry for direct analysis
- *Conductometry:* May not be used in the presence of high concentrations of electrolyte species other than that required
- *Classical wet chemistry:* Generally more accurate, but electrochemical methods offer better detection limits for trace analyses

Electrometric titration

- *Estimated analysis time:* At least several minutes after sample preparation
- *Catalytic techniques:* Determinations by effect of a substance upon the speed of a normally slow reaction. The effect can be monitored electrochemically, or electrochemical titration can be used to maintain constancy of the reacting system.
- *Stripping analysis:* Quantitative determination of analytes, usually metals in very dilute solutions
- *Electrographic analysis:* Qualitative or, at best, semiquantitative analysis of metallic samples

Potentiometric membrane electrodes

- *Estimated analysis time:* Several minutes per sample after dissolution or other sample preparation
- *Amperometric gas sensors:* Quantification of oxygen and hydrogen peroxide
- *Ultraviolet/visible spectroscopy:* Direct or indirect determination of cation, anion, gaseous, and molecular species
- *Ion chromatography:* Determination of cation and anion species concentrations
- *Atomic spectroscopies:* Quantification of sample elemental components
- *Voltammetry:* Quantification of cations, anions, and certain organics

ELECTROCHEMISTRY is a branch of physical chemistry that deals with the chemical changes produced by electricity and the production of electricity by chemical changes. The voltaic pile discovered by Volta in 1799 was the first electrochemical device, which lead to the production of batteries for reliable production of electrical current. Conversely, electricity can bring about chemical changes in a process known as electrolysis (meaning "electric-splitting"), whereby substances are separated by the application an electric current in an electrochemical cell. This process of chemical splitting was quickly discovered in 1800 by William Nicholson, who copied Volta's battery and observed the decomposition (electrolysis) of water into oxygen and hydrogen. Soon thereafter in 1839, Christian Schonbein and William Grove demonstrated the reverse reaction of a fuel cell, whereby an electric current is generated by the recombination of hydrogen and oxygen.

The process of electrolysis has a number of general uses in separating elements from naturally occurring sources. Applications are too numerous to list, but some examples include:

- Reduction of salts to yield pure metals
- Reduction of neutral organic molecules
- Production of oxygen for spacecraft and nuclear submarines via electrolysis of acidified water
- Production of pure hydrogen to serve as a fuel through electrolysis of acidified water (even possible with wind-power-generated electrolysis). Further uses include hydrocracking, reduction of unsaturated hydrocarbons, as well as a reactant in the Haber procedure for industrial ammonia synthesis.
- Isolation and purification of pure metals by reduction of the corresponding salts (aluminum, calcium, magnesium, sodium, potassium, copper)
- Industrial production of chlorine and chlorate ions
- Cleaning of metallic artifacts (coins, statues, and ancient weapons) (Ref 5, 6) and restoration of parts (Ref 7)
- Synthesis of polyfluorinated organic compounds (electrofluorination)
- Reduction of CO_2 to produce useful fuel hydrocarbons (methane, ethane, ethylene) (Ref 8)
- Growth of conductive crystals on an electrode (electrocrystallization) (Ref 9, 10)

Various electrochemical methods, based on the process of electrolysis, have been developed for chemical analysis. The oldest method is electrogravimetry or electrodeposition (Ref 11). Various electrochemical methods of chemical analysis also have been developed based on the measurement of an electrical signal generated by the process of electrolysis in an electrochemical cell. Electrochemical techniques are of three types: potentiometric, voltammetric (amperometric), and coulometric. Potentiometry is the most commonly used of the electrochemical techniques and involves the measurement of a potential (voltage) generated by a cell under essentially equilibrium conditions. Coulometry involves the determination of the weight of metal deposited or released at the cathode by measuring the electrical charge (electrical current over a determined time frame) produced by an electrochemical cell.

The basic foundation of these methods is Faraday's law(s) of electrolysis, which state that the amount of any substance deposited or liberated during electrolysis is proportional to the quantity of electric charge passed and to the equivalent weight of the substance. Faraday's law of electrolysis is involved in several electroanalytical techniques. The mathematical formulation is:

$$Q = n \times F \times N$$

where F is the Faraday constant (96,495 C/mol), and Q is the minimum number of coulombs (C) required to alter the charge of N moles of a given species by n units. The reaction may involve deposition (of silver, for example) on an electrode; dissolution from an attackable anode, such as of silver or tin; or alteration of the charge of a species in the solution, for example, $Fe^{3+} + e \rightarrow Fe^{2+}$. If the current is constant at I amperes and flows for t seconds, the number of moles, N, of the substance electrolyzed can be calculated by using Faraday's law:

$$N = \frac{1}{nF} \int_0^t I dt$$

Faraday's laws also can be summarized in terms of mass by the equation:

$$m = (Q/F) \times (M/z)$$

where m is the mass (in grams, g) of the isolated substance, Q is the total electric charge (in coulombs, C) passed used in the isolation of the mass at the electrode, M is the molar mass (g/mol) of the isolated substance, and z is the valence (charge) of the substance ions involved in the process (number of electrons transferred per ion). If the reaction proceeds with 100% current efficiency, the total electric charge (Q) is calculated from the integrated equation:

$$Q = \int_0^t I dt$$

This article describes various methods of electrochemical analysis. The oldest electroanalytical technique is electrogravimetry, where the element of interest is deposited electrolytically onto an electrode and weighed. A more common method is coulometry, which is comprised of several techniques that use an instrument known as a coulometer (or electric charge counter). Coulometers may be a chemical device (chemical coulometer) or an electronic device (integrator). In either case, coulometers can be used to determine the amount of an analyte by measuring the electrical current and time (i.e., total charge) required for complete oxidation or reduction of the analyte. Coulometers also are used in a technique known as voltammetry, where quantitative information about the analyte is obtained by measuring electrical current as a function of applied voltage. The methods of coulometry do not require weighing and allow for shorter analysis times. Coulometry is used in quantitative chemical analysis and the study of electrochemical mechanisms. Example applications of coulometry include:

- Measurement and determination of inorganic substances and metals of different oxidation state in the presence of each other (Ref 12)
- Examination of corroded materials (Ref 13)
- Determination of uranium and plutonium assays in nuclear fuel (Ref 14, 15)

Electrochemical Cells

The basic process of an electrochemical reaction requires an electrochemical cell comprised of two half cells with an electrode (cathode and anode) that are in a medium (electrolyte) that can conduct electricity. The term *anode* or *cathode* is applied to one or the other of the electrodes depending on whether the electrochemical reaction is an oxidation or a reduction reaction, regardless of the voltage potential between the electrodes. The oxidized species (O) of metal (M) occurs at a site when an atom dislodges from the solid and enters the environment (or solution) as a positive ion (or cation):

$$M \rightarrow M^{n+} + ne^- \quad \text{(Eq 1)}$$

This formation of a cation (M^{n+}) occurs with n number of electrons (with a charge of ne) remaining in the solid. A conducting medium (electrolyte) between the electrodes is necessary, because the oxidation reaction can only be sustained if the number of electrons (n) left over from the oxidized metal (O) can be consumed (reduced) at the cathode of the cell. Hence, the cathodic reaction is referred to as reduction. With stoichiometric coefficients (b and c) that depend on the chemical specie, the reduction reaction at the cathode is expressed as:

$$b \times \mathrm{O} + ne^- \rightarrow c \times \mathrm{R} \qquad \text{(Eq 2)}$$

where O denotes a soluble oxidant, and R is the reduced form of the oxidant that may or may not be a soluble species. It was decided in 1953 at the International Union of Pure and Applied Chemistry (IUPAC) meeting that the half-cell reactions should be conventionally written in the reduction direction (Eq 2).

Equilibrium Potential

Either the anodic (Eq 1) or the cathodic (Eq 2) reaction can control the overall rate of the reaction. The equilibrium potential, also called the reversible potential, is the electrode potential measured under zero current (rest potential) when the electrochemical equilibrium occurs. If the resistance between the electrodes of the galvanic cell is made very high, so that very little current flows, the extent of reaction being small enough not to change the activities of reactants and products, the potential difference between the two electrodes remains constant and is the maximum cell voltage, called the electromotive force of the cell.

The potential of an electrochemical cell under equilibrium conditions is defined as the Nernst equation:

$$U_0 = U^* + \frac{RT}{nF}\ \ln\left[\frac{a_\mathrm{O}^b}{a_\mathrm{R}^c}\right] = U^* - \frac{RT}{nF}\ \frac{c}{b}\ \ln\left[\frac{a_\mathrm{R}}{a_\mathrm{O}}\right] \qquad \text{(Eq 3)}$$

where U_0 is the equilibrium potential relative to a reference potential (U^*), and where a_O and a_R are the activities (concentrations) of the oxidized and reduced species. The reference potential (U^*) established by the IUPAC is based on a half cell with standard hydrogen electrode (SHE), where reaction is based on electron activity from hydrogen in an aqueous solution with reduction into hydrogen gas at 1 bar ($\mathrm{H}^+ + e^- \leftrightarrow \frac{1}{2}\,\mathrm{H_2[gas]}$). The equilibrium potential also can be expressed in terms of the chemical potential (or Gibbs free energy), which depends on the concentration (activity, a) and chemical formula of the species involved. At equilibrium, the change in Gibbs free energy (G) is balanced for oxidation (Ox) and reduction (Red):

$$-\frac{\Delta G_\mathrm{Red}}{nF} = +\frac{\Delta G_\mathrm{Ox}}{nF} \qquad \text{(Eq 4)}$$

With the SHE potential as a reference, the equilibrium potential expressed in terms of chemical potentials (μ) is:

$$U_0 = \frac{(b\mu_\mathrm{O} + n\mu_\mathrm{e} - c\mu_\mathrm{R})}{nF} \qquad \text{(Eq 5)}$$

where μ_e is the standard chemical potential or Gibbs free energy of an electron in the SHE half cell, where $\mu_\mathrm{e} = \mu\ (\mathrm{H_2,\ gas}) - \mu\ (\mathrm{H^+,\ aqueous})$.

Electrolytic Cells

The external circuit connection between the cathode and anode and the voltage/current relationship in an electrochemical cell determines whether the cell operates as a battery, an electrolytic cell, or perhaps as a fuel cell. Either the anodic reaction or the cathodic reaction can control the overall rate of the reaction, and electrochemical methods can drive the reactions away from the equilibrium potential. The relationship between current (I) and potential difference (ΔU, from equilibrium potential U_0) in a cell is described by the Tafel equation:

$$I = nFk\ \exp\left[\pm\alpha\ nF\frac{\Delta U}{RT}\right] \qquad \text{(Eq 6)}$$

where the plus sign under the exponent refers to an anodic reaction, a minus sign refers to a cathodic reaction, n is the number of electrons involved in the electrode reaction, and k is the rate constant for the electrode reaction. The α term is an exponential factor related to the specific electrochemical conditions. Even with the same reagents and process, the voltage-current behavior can be modified by changing things such as additives in the electrolyte or surface conditions of the electrode. The α term, also referred to as the transfer or symmetry coefficient, is generally taken to be 0.5.

At equilibrium, no measurable current flows, such that the rate of metal dissolution ($\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne^-$) results in an anodic current (I_A) that is equal to the cathodic current (I_C) from the rate of metal cation deposition ($\mathrm{M}^{n+} + ne^- \rightarrow \mathrm{M}$). Both reactions occur simultaneously, and at equilibrium they are balanced with an equal exchange of electrons back and forth. This inherent current at equilibrium is termed the exchange current (I_0), such that $I_0 = -I_\mathrm{C} = I_\mathrm{A}$.

The current-voltage relationship is not linear but changes exponentially with changes in the potential from the equilibrium point. As an example, Fig. 1 is an example of the current-voltage relationships for metal dissolution/deposition reactions. This curve follows the Butler-Volmer equation:

$$I = I_0\left\{\exp\left(\frac{\alpha F}{RT}\eta\right) - \exp(1-\alpha)\frac{F}{RT}\eta\right\} \qquad \text{(Eq 7)}$$

where I is the current, I_0 is the exchange current, F is the Faraday constant, R is the gas constant, T is the absolute temperature, and α is the transfer or symmetry coefficient. The term η is the overpotential (ΔU) defined by:

$$\eta = V - U_0 \qquad \text{(Eq 8)}$$

where V is the experimentally applied voltage, and U_0 is the equilibrium potential given by the Nernst equation. The overpotential is a measure of how far the reaction is from equilibrium.

Electrolysis leads to the separation and isolation of metals originally in a molten or a solution (ionic) mixture on an electrode by using a direct current and a voltage called the decomposition potential. In an electrolytic cell (Fig. 2), the anions (negative ions) go to the anode (positive electrode) and the cations (positive ions) go to the cathode (negative

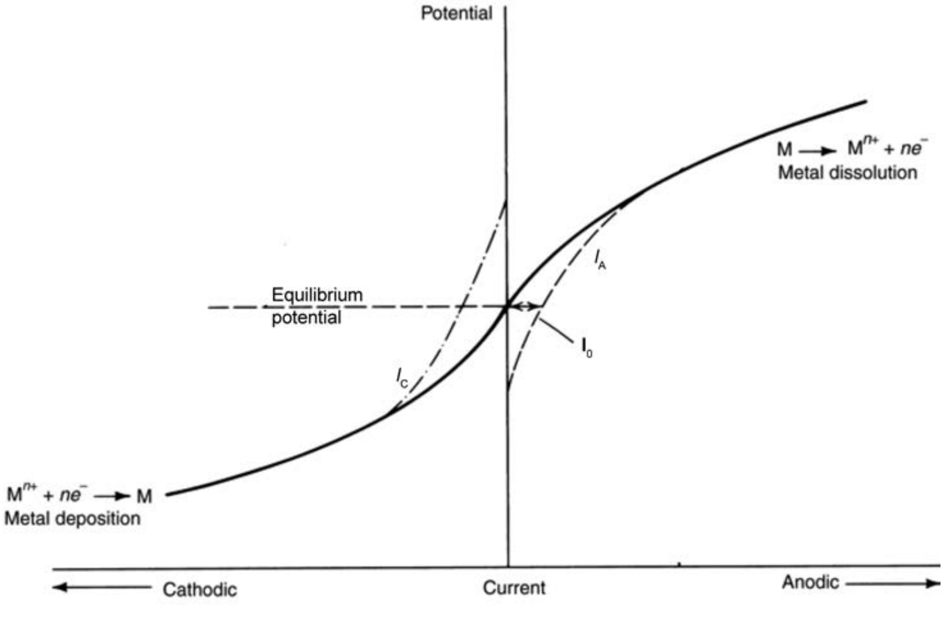

Fig. 1 Current-potential relationships for a metal dissolution or a deposition reaction in an electrochemical cell. The exchange current (I_0) at the equilibrium potential (U_0) has two components, $I_\mathrm{A} = -I_\mathrm{C}$, which results in zero net current at equilibrium. The solid line shows the measurable current; the dashed lines (I_C, I_A) show the partial dissolution/deposition currents.

electrode). So, for example, oxygen would go to the anode and iron would go to the cathode. The electrolyte serves as the source of the mobile ions that will eventually deposit the metal at the cathode. The electric circuit provides the energy for the ions to deposit due to electron transfer.

The electrolytic cell is fundamental in electrochemical analysis. The two classic types of cells used in the major techniques are the constant-current cell and the controlled-potential cell (Fig. 3). The difference between the two basic types of cells is the addition of a reference electrode in controlled-potential electrolysis (Fig. 3a, bottom). Both types of cells typically contain large platinum gauze electrodes (Fig. 3a) or a mercury cathode and a flat spiral wire anode (Fig. 3b). The mercury cathode has the advantages of a high hydrogen overpotential and the ability to form an amalgam with most metals. In both cases, efficient stirring is used to prevent concentration polarization.

In a constant-current (galvanostatic) cell, the total charge is defined as the product of the current and the exactly measured time of the reaction. In controlled-potential electrolysis, however, the current decreases exponentially in time as the analyte is consumed (Fig. 4). As the analyte is consumed during electrolysis, the current decays more or less exponentially toward zero, and the electrolysis is terminated when the current reaches a suitably low value, indicating complete electrolysis. In controlled-potential cells, where currents are changing continuously in time, it is convenient to use coulometers that measure charge that results from the oxidation or reduction of an analyte. Coulometers may be electrochemical devices based on the laws of Faraday or electronic charge integrators (see the section "Coulometry" in this article).

Determining the voltage of the cell necessary to achieve the required separation requires knowing the reactions that occur at each electrode and the potential of each electrode by using the Nernst equation. If the potential is made more positive than the equilibrium potential, then $I_A > |I_C|$ (i.e., the first exponential term in Eq 7 increases in value, and the second one decreases), and the metal dissolution reaction will proceed. Similarly, if E is made more negative than the equilibrium potential, $I_A > |I_C|$, then metal cation deposition proceeds. Over a short potential range, the two reactions oppose each other, but for sufficiently large overpotentials (η_A, anodic; or η_C, cathodic), one reaction occurs at a negligible rate; that is, one or the other of the exponential terms in the Butler-Volmer equation (Eq 7) becomes negligible.

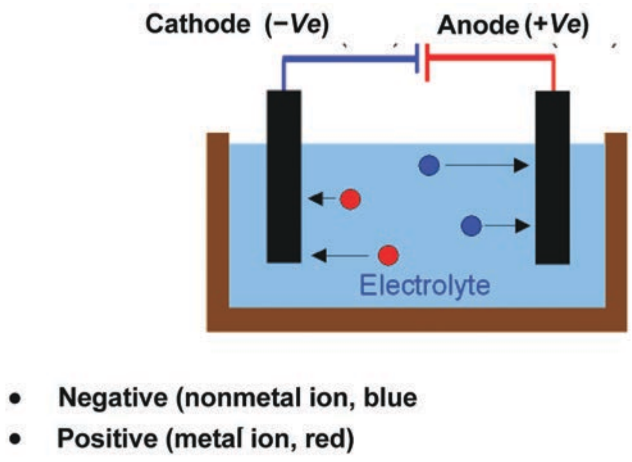

Fig. 2 A simple electrolysis setup. The electrodes (black bars) are often made out of graphite.

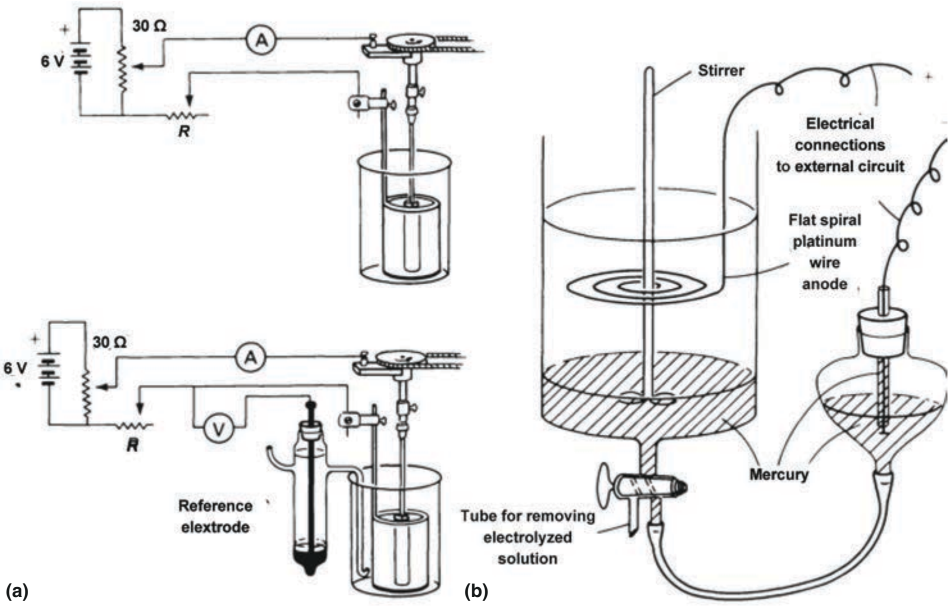

Fig. 3 Classical cell types. (a) Constant-current (top) and controlled-potential (bottom) cells. (b) Cell for constant-current electrolysis with mercury cathode. Source: Ref 16

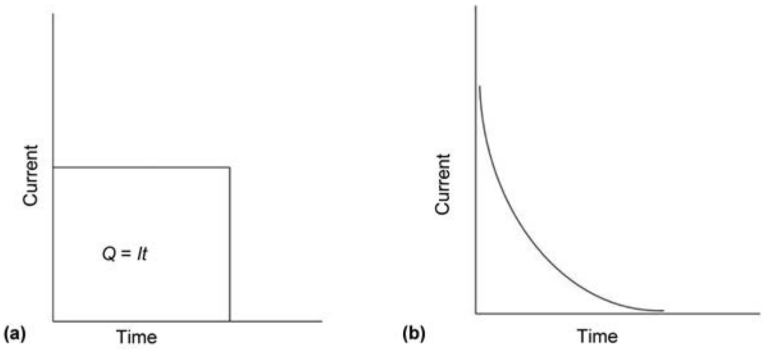

Fig. 4 Current-time curves of electrolytic cells with (a) constant-current circuit and (b) controlled-potential circuit

Controlled-Potential Electrolysis

In controlled-potential electrolysis (Fig. 3a, bottom), the cell includes the addition of a reference electrode, which acts as a sensor of the working-electrode potential. The three electrodes in the solution containing analyte are:

- The working electrode with a varying potential in time
- The reference (typically a calomel or Ag/AgCl) electrode that maintains constant potential
- The counterelectrode (mercury or platinum) that completes the circuit and conducts electrons from the signal source through the solution to the working electrode

The electrolysis current flows between the working electrode and the counterelectrode. The stable reference electrode of known potential (versus the SHE) acts as a sensor of the working-electrode potential. Typical reference electrodes are the types used for measuring pH, such as Hg-Hg_2Cl_2, KCl (sat'd) (the saturated calomel electrode, SCE); Ag-AgCl(s), KCl(sat'd); or Hg-Hg_2SO_4(s), K_2SO_4(sat'd). During electrolysis, the potentiostat compares the potential (voltage) between the working and reference electrodes with the desired control potential and minimizes this difference by controlling the voltage applied to the counterelectrode.

Selectivity in an analysis by controlled-potential coulometry is achieved by maintaining the working-electrode potential constant and by using the differences in the potentials at which different substances react. In aqueous acidic solutions, the available potential range (versus SCE) extends from approximately +1.2 to −0.1 V at platinum and from +0.1 to −1.0 V at mercury. The positive limit is established at platinum by the evolution of oxygen and at mercury by its dissolution; the negative limits are established by the evolution of hydrogen. In chloride media, the positive limit at platinum is lowered by the evolution of chlorine and at mercury by the formation of Hg_2Cl_2.

The standard potential of the reaction considered or, more specifically, the formal potential in the particular medium of the electrolysis determines the potential at which a substance is electroactive. Metal ion species having reactions that have positive formal reduction potentials, for example, Fe^{3+}, Ce^{4+}, and Au^{3+} in certain media, and which are therefore considered oxidizing agents, are electrolytically reduced at positive control potentials, usually at a platinum electrode. The ions of metals with negative or slightly positive formal potentials, for example, Cu^{2+}, Pb^{2+}, Ti^{4+}, and Zn^{2+}, are reduced at negative control potentials, usually at a mercury electrode.

When the rate of charge transfer in an electrolysis reaction is large compared to the rate of mass transport and there are no complicating side reactions, the extent of the electrolysis reaction as a function of potential can be expressed by a form of the Nernst equation. Such processes are generally known in electrochemistry as reversible. The exact form of the equation depends on the type of reaction considered. Table 1 summarizes the three most common types of reactions encountered in controlled-potential electrolysis, together with the relevant Nernst equations. Equation A in Table 1 (for a type I reaction) shows the logarithmic relationship between the working-electrode potential and the ratios of the concentrations of the oxidized and reduced species at equilibrium, that is, when the current is zero in the electrolysis.

Table 1 Types of reactions in controlled-potential electrolysis and applicable Nernst equations

Type of reaction(a)	Nernst equation(b)
I. Oxidized and reduced species soluble in solution	
M(m) + ne^- → M(m − n) Example: $Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E = E^{\circ\prime} + RT/nF \cdot \log \{[M(m)]/[M(m - n)]\}$ (Eq A)
II. Solid metal electrodeposition	
M(m) + me^- → M(s) Example: $Ag^+ + e^- \rightarrow Ag(s)$	$E = E^{\circ\prime} + RT/nF \cdot \log [M(m)]$ (Eq B)
III. Amalgam formation	
M(m) + me^- → M(Hg) Example: $Cu^{2+} + 2e^- \rightarrow Cu(Hg)$	$E = E^{\circ\prime} + RT/nF \cdot \log \{[M(m)]/[M(Hg)]\}$ (Eq C)

(a) m and n represent the number of electrons in the reaction or, in M(m), the oxidation state of the metal. (b) In the equations, E is the working-electrode potential, $E^{\circ\prime}$ is the reference potential of the reaction, R is the gas constant, T is the absolute temperature, and F is the Faraday constant. Brackets indicate concentrations of the oxidized and reduced species of the metal at equilibrium.

Figure 5 presents a graph of the extent of reaction versus potential for a type I electrolysis. This graph is similar to the current-potential curve for reversible processes in voltammetry and polarography (see the section "Voltammetry" in this article). At 25 °C (75 °F), the value of RT/nF is 59.2/n mV; thus, for the reduction of 99.9% of the M(m) in the solution, that is, for [M(m)]/[M(m − n)] to be 0.001 at equilibrium, the control potential E must be 3 × (59.2/n), or 177/n mV more negative than $E^{\circ\prime}$. Quantitative oxidations require E to be more positive than $E^{\circ\prime}$ by the same voltage.

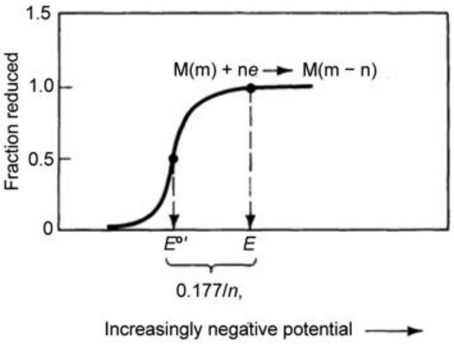

Fig. 5 Completeness of reaction as a function of potential for the reversible reduction of a metal ion species to another soluble species. E is the control potential required for 99.9% conversion of M (m) to M(m − n).

In reversible electrolytic processes, the electrolysis can be reversed by appropriate adjustment of the control potential. This technique is used in several procedures in coulometry. The first control potential is used to transform all the substance determined in the sample to one oxidation state. The potential is then changed to reverse the electrolysis. The current is integrated during the second electrolysis to measure the quantity of the substance present.

The Nernst equation may also be used to calculate the difference in formal potentials required for the complete separation of two species in the same sample solution or to calculate their mutual interference. For example, for two type I reactions, equal molar concentrations of the two species, and less than 0.1% interference, the minimum difference in formal potentials at 25 °C (75 °F) in millivolts must be:

$$E_1^{\circ\prime} - E_2^{\circ\prime} = \frac{177}{n_1} + \frac{177}{n_2} \qquad \text{(Eq 9)}$$

For a type II reaction—the electrodeposition of metal on a substrate of the same metal—the metal film is assumed (for greater than monolayer deposits) to have an activity of 1; thus, only the concentration of the solution species appears in Eq B in Table 1. Therefore, unlike type I reactions, the fraction of metal deposited is not independent of potential. A decreasing initial concentration of the metal requires an increasingly negative control potential to deposit a given fraction. Very low concentrations of metals and depositions on foreign substrates exhibit different characteristics.

Type III processes, in which the metal ion is reduced at a mercury electrode to form an amalgam, are generally reversible if the metal is soluble in mercury to the extent required by electrolysis. Otherwise, a metal film will form on the electrode, and the process will be similar to a type II reaction. Equation C in Table 1 for amalgam formation is similar to that for type I, except that the concentrations of M(m) and M in the logarithmic term are their concentrations in the solution and mercury, respectively. Because of their solubility in mercury, metals that participate in electrolytic amalgam formation, for example, copper, lead, indium, and thallium, have formal potentials for the reactions that are significantly more positive than those for the formation of the corresponding solid metal.

Many other electrolytic processes exhibit lower rates of charge transfer (termed irreversible or non-Nernstian) or involve chemical reactions, such as a follow-up reaction, coupled to the electron transfer. Many of the analytical methods of controlled-potential coulometry are based on such reactions; examples are the procedures for vanadium and uranium. Irreversible processes require a greater difference between the control potential and the $E^{\circ\prime}$ to effect rapid electrolysis, and, depending on the degree of irreversibility, a reverse electrolysis may not be feasible. In addition, separation factors for systems involving irreversible couples must be determined empirically.

Coulometry

Coulometers measure charge and can be used to determine the amount of an analyte involved in an oxidation or reduction reaction. In experiments with currents changing continuously in time (e.g., controlled-potential electrolysis), it is more convenient to use counters for the quantity of charge passed. The electrolysis current can be integrated by an electronic integrator (coulometer) or with an electrochemical coulometer. Electrochemical coulometers are based on the laws of Faraday. The basic components consist of an electrolytic cell and a chemical coulometer placed in series with a working electrode (Fig. 6). In operation of the cell, the electrolysis current flows between the working electrode and counterelectrode. The working electrode, where the desired reaction occurs, is usually a mercury pool or a platinum screen, although other inert materials have been used. The area of the working electrode is as large as possible, and the solution is vigorously stirred to maximize the rate of electrolysis. The counterelectrode is also an inert material, usually platinum. The volume of gas or mercury liberated, which is proportional to charge, is measured.

There are basically three types of coulometric techniques:

- *Potentiostatic coulometry:* (also known as controlled-potential coulometry) where the electric potential is held constant via a potentiostat
- *Coulometric titration:* (also known as amperostatic coulometry) where the current is kept constant via an amperostat or galvanostat
- *Voltammetry:* where quantitative information about the analyte is obtained by measuring electrical current as a function of applied voltage

The latter two methods are described in separate sections of this article.

Controlled-Potential Coulometry (Ref 1)

Controlled-potential coulometry is similar in applicability to the classical solution techniques of gravimetry and titrimetry. Like the classical methods, it is used primarily for major constituent analysis and is characterized by high precision and accuracy (typically 0.1%). Coulometry routinely requires only approximately 1 to 10 mg of analyte substance. This relatively small sample size is advantageous when the quantity of material available for analysis is small or must be limited because of its value, toxicity, or radioactivity. Controlled-potential coulometry is especially applicable to assays of alloys, compounds, and nonmetallic materials for the transition and heavier elements. Organic compounds and nonmetals—for example, halides and nitrogen-oxygen compounds—are also suitable for determination.

Accurate coulometry requires that electrolysis be performed as rapidly as possible by controlling the potential at a point where the rate of electrolysis is limited only by mass transport of the reacting species. For reversible processes, E is not far from the value shown in Fig. 5, which will also ensure complete electrolysis. When E is set at this value, the electrolysis current as a function of time is:

$$I = I_o \exp(-pt) \qquad \text{(Eq 10)}$$

where I_o is a constant (a theoretical initial current), and p is an overall rate constant of the electrolysis. These constants incorporate parameters that are determined by the mass transport characteristics of the cell and the diffusion coefficient of the species electrolyzed.

Figure 7 shows the current-time curves observed in the coulometric determinations of gold and silver. Because the current scale is logarithmic, the curves should theoretically be straight lines. These curves deviate slightly from Eq 10 at the beginning of electrolysis due to imperfect compensation of the solution resistance by the potentiostat and at the end of electrolysis because the current tends to level off at the background current.

Table 2 lists the metals for which accurate methods have been developed and the basic electrochemistry of the procedures. A double arrow in the reaction indicates that the method involves a multistep or reverse electrolysis. In reversible electrolytic processes, the electrolysis can be reversed by appropriate adjustment of the control potential. This technique is used in several procedures in coulometry (Table 2). The first control potential is used to transform all the substance determined in the sample to one oxidation state. The potential is then changed to reverse the electrolysis. The current is integrated during the second electrolysis to measure the quantity of the substance present.

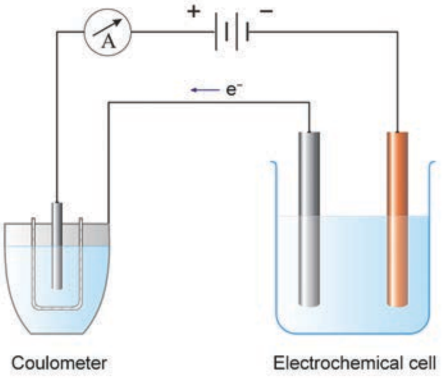

Fig. 6 The coulometer-electrochemical cell setup. Source: Ref 17

Determination of Gold

Because the quantities of metal available for analysis are usually small and high accuracy (0.1%) is frequently desired, the assay for gold in various materials is a useful example of the application of coulometry. The current-time curve for this electrolysis was discussed and shown in Fig. 7. If the sample contains none of the few interfering elements, such as iridium or ruthenium, the gold can usually be determined immediately after dissolution without further pretreatment. Each determination requires approximately 10 min. Aqua regia—3 parts hydrochloric acid (HCl) and 1 part nitric acid (HNO_3)—typically is used for the dissolution, and sulfamic acid (NH_2SO_3H) is included in the supporting electrolyte to remove the interfering nitrogen oxides and nitrite ion produced during the dissolution. If

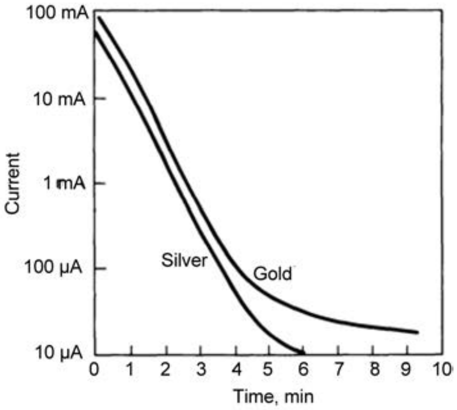

Fig. 7 Current-time curves for the reduction of Ag^+ to Ag(s) and Au^{3+} to Au(s) on a platinum electrode. Electrolysis conditions: silver, 0.1 M H_2SO_4, E = +0.16 V versus saturated calomel electrode (SCE); gold, 0.5 M HCl, E = +0.48 V versus SCE

Table 2 Examples of metals determined by controlled-potential coulometry

Metal	Working electrode	Overall reaction	Supporting electrolyte
Antimony	Hg	$Sb^{3+} \rightarrow Sb(Hg)$	0.4 M tartaric acid, 1 M HCl
Arsenic	Pt	$As^{3+} \rightarrow As^{5+}$	1 M H_2SO_4
Bismuth	Hg	$Bi^{3+} \rightarrow Bi(Hg)$	0.5 M tartrate, 0.2 M HCl
Cadmium	Hg	$Cd^{2+} \rightarrow Cd(Hg)$	1 M HCl
Chromium	Hg	$Cr^{3+} \rightleftarrows Cr^{2+}$	6 M HCl
	Au	$Cr^{6+} \rightarrow Cr^{3+}$	1 M H_2SO_4
Cobalt	Pt	$Co^{2+} \rightarrow Co^{3+}$	1,10-phenanthroline, acetic acid
Copper	Hg	$Cu^{2+} \rightarrow Cu(Hg)$	1 M H_2SO_4
Europium	Hg	$Eu^{3+} \rightleftarrows Eu^{2+}$	0.1 M HCl or $HClO_4$
Gold	Pt	$Au^{3+} \rightarrow Au(s)$	0.5 M HCl
Indium	Hg	$In^{3+} \rightarrow In(Hg)$	1 M KCl, 0.25 M HCl
Iridium	Pt	$Ir^{4+} \rightleftarrows Ir^{3+}$	0.5 M HCl
Iron	Pt	$Fe^{3+} \rightleftarrows Fe^{2+}$	0.5 M H_2SO_4
Lead	Hg	$Pb^{2+} \rightarrow Pb(Hg)$	1 M $HClO_4$
Manganese	Pt	$Mn^{2+} \rightarrow Mn^{3+}$	0.25 M $Na_4P_2O_7$
Mercury	Hg	$Hg^{2+} \rightarrow Hg(liq)$	1.5 M $HClO_4$
Molybdenum	Hg	$Mo^{6+} \rightarrow Mo^{5+}$	0.2 M $(NH_4)_2C_2O_4$, 1.3 M H_2SO_4
Neptunium	Pt	$Np^{6+} \rightleftarrows Np^{5+}$	1 M H_2SO_4
Nickel	Hg	$Ni^{2+} \rightarrow Ni(Hg)$	1 M pyridine, 0.5 M HCl
Palladium	Pt	$Pd^{2+} \rightleftarrows Pd^{4+}$	0.2 M NaN_3, 0.2 M Na_2HPO_4
Plutonium	Pt	$Pu^{4+} \rightleftarrows Pu^{3+}$	1 M $HClO_4$ or, to avoid iron interference, 5.5 M HCl, 0.015 M sulfamic acid, NaH_2PO_4
Rhodium	Hg	$Rh^{3+} \rightarrow Rh(Hg)$	0.2 M HCl
Ruthenium	Pt	$Ru^{4+} \rightarrow Ru^{3+}$	5 M HCl
Silver	Pt	$Ag^{+} \rightarrow Ag(s)$	0.1 M H_2SO_4
Technetium	Hg	$Tc^{7+} \rightarrow Tc^{3+}$	Acetate-tripolyphosphate
Thallium	Pt	$Tl^{+} \rightarrow Tl^{3+}$	1 M HCl
Tin	Hg	$Sn^{4+} \rightleftarrows Sn(Hg)$	3 M KBr, 0.2 M HBr
Titanium	Hg	$Ti^{4+} \rightarrow Ti^{3+}$	6–9 M H_2SO_4
Uranium	Hg	$U^{6+} \rightarrow U^{4+}$	0.5 M H_2SO_4
Vanadium	Pt	$V^{5+} \rightarrow V^{4+}$	1.5 M H_3PO_4
		$V^{4+} \rightarrow V^{5+}$	
Zinc	Hg	$Zn^{2+} \rightleftarrows Zn(Hg)$	1 M NH_4H citrate, 3 M NH_4OH

Source: Ref 1

large quantities of iron are present in the sample, phosphoric acid (H_3PO_4) can also be added to remove its interference.

Gold electroplating solutions that contain cyanide or sulfite ions and scrap materials containing organic compounds must be subjected to a more severe pretreatment before measurement of the gold. This typically involves a sulfuric acid-nitric acid (H_2SO_4-HNO_3) boildown or fuming with perchloric acid ($HClO_4$), which removes or destroys the complexing species and organics. This treatment precipitates most of the gold as the metal; it is then redissolved in aqua regia for coulometric measurement. After several determinations, the gold metal that has been deposited on the platinum electrode is stripped electrolytically by controlling the potential at +1.00 V in 2 M HCl.

Determination of Uranium

Uranium is another element that has been determined frequently in various sample types by controlled-potential coulometry. The adaptability of coulometry to automated and remote operation makes it useful for nuclear materials that contain uranium, plutonium, or both. Highly radioactive samples can be handled if there are no chemical interferences. Methods have been developed for separating the uranium from fission products in nuclear-reactor and waste samples before coulometric determination. A procedure is also available for coulometrically measuring the ratio of uranium oxidation states in uranium oxide fuels.

As indicated in Table 2, coulometric determination involves conversion of U^{6+} to U^{4+}. However, electrolysis proceeds in two steps. First, the U^{6+} is reduced directly at the electrode by the reaction:

$$U^{6+} + e^{-} \rightarrow U^{5+}$$

The U^{5+} then disproportionates:

$$2U^{5+} \rightarrow U^{6+} + U^{4+}$$

Thus, an exhaustive electrolysis results in the reduction of U^{6+} to U^{4+} and an overall two-electron change in valence.

The reduction is carried out at a mercury-pool electrode, usually in H_2SO_4 (also containing sulfamic acid if HNO_3 was used to dissolve the sample), at a control potential of −0.325 V versus SCE. A preliminary electrolysis performed at +0.075 V pre-reduces any oxides of mercury and substances such as Fe^{3+}, Cr^{6+}, and Pu^{4+} that would interfere in the subsequent uranium electrolysis. Copper, if present in the sample, can also be determined, because the reduction of uranium is irreversible at the mercury electrode. The Cu^{2+} and U^{6+} are reduced together at −0.325 V. The Cu(Hg) is then oxidized back to Cu^{2+} at +0.100 V. Integration of the current during the second electrolysis yields the amount of copper, and subtraction of this quantity of electricity from the total in the first electrolysis provides the amount of uranium.

Coulometric measurement requires approximately 30 min, including removal of oxygen from the solution (which also would be reduced at −0.325 V), pre-electrolysis, and uranium electrolysis. Because of the homogeneous disproportionation reaction, the uranium electrolysis is somewhat slower than most, and its electrolysis current-time curve differs slightly from that predicted by Eq 10 for simple reactions.

Electrogravimetry (Ref 2)

Electrogravimetry (also known as electrodeposition) is the oldest quantitative electrochemical procedure (Ref 11) described by Gibbs and may refer to:

- *Electroplating*: a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode
- *Electrophoretic deposition:* a term for a broad range of industrial processes that includes electrocoating, e-coating, cathodic electrodeposition, anodic electrodeposition, and electrophoretic coating, or electrophoretic painting
- *Underpotential deposition:* a phenomenon of electrodeposition of a species (typically reduction of a metal cation to a solid metal) at a potential less negative than the equilibrium (Nernst) potential for the reduction of this metal

Unlike most electrochemical techniques, the reaction in electrogravimetry often must be allowed to go to completion efficiently, prolonging analysis times. However, the technique is more accurate (0.1%) than controlled-potential coulometry (0.2 to 5%) or polarography (2%). Use of efficient stirring lessens analysis time. Overall analysis time depends on the technique used.

To achieve separation and complete deposition requires knowing the potential of each electrode by using the Nernst equation (Eq 3). For a cell reaction ($M^{n+} + ne^{-} \rightarrow M$) occurring at 25 °C (75 °F), the required potential (E) is:

$$E = E^{*} + \frac{0.0591}{n} \log \left[M^{+}\right] \qquad \text{(Eq 11)}$$

where E^* is the potential of the reference electrode. Therefore, the voltage becomes more negative by $0.0591/n$ V or $59/n$ mV for each tenfold decrease in concentration.

Electrogravimetry normally requires complete or nearly complete deposition. The electrode must be totally covered by the metal to ensure formation of a monolayer. If not, the activity of the solid metal cannot be considered to be unity, and Eq 11 will not hold. This presents problems in the deposition of small amounts of metal.

Potential for Separation

The applied potential (E_{APP}) for separation may be determined from the calculated (E_{CAL}, Eq 11). This result, coupled with knowledge of the IR drop and the overpotentials of the cathode and anode (η_C and η_A, respectively), yields:

$$E_{APP} = E_{CAL} + IR + \eta_C \text{ and } \eta_A \quad \text{(Eq 12)}$$

Application of an electromotive force (emf) to the cell initiates current flow and thus the desired reaction. The overpotential developed at an electrode usually results from the difference in concentration of the ions in the bulk solution and at the electrode surface and provides one source of resistance to current flow. For an anodic process exhibiting an overpotential effect, the applied emf must be more positive than the calculated potential; for a cathodic process with associated overpotential, it must be more negative than the calculated value. In a dilute solution, depletion in concentration near the electrode increases resistance (R), yielding a change (IR) in potential. This IR drop may lead to serious disadvantages in instrumental conditions, because it is not always constant and is sometimes unknown.

Such factors as the applied voltage, the electrode potential at the electrodes of interest, the current flowing, the amount of electricity used, and the nature of the deposit at the electrodes affect electrolysis of a solution. The deposition of copper on a platinum cathode best exemplifies the principles of electrogravimetry. The cell may be represented as:

$$\text{Pt, Cu} \rightarrow \text{Cu}^{2+}(0.100\ M)$$

$$\text{H}^{+}(1.000\ M) \rightarrow \text{O}_2(0.2\ \text{atm}), \text{Pt}$$

Using the Nernst equation (at 25 °C, or 75 °F) for the electrode oxidation reaction of Cu → $Cu^{2+} + 2e^-$:

$$E_{Cu} = 0.337 + \frac{0.0591}{2} \log\left[\text{Cu}^{2+}\right]$$

$$E_{Cu} = 0.337 + 0.0296 \log[0.100] = 0.307 \text{ V}$$

For the reduction electrode ($O_2 + 4H^+ 4e^- \rightarrow 2H_2O$):

$$E_{O_2} = 1.229 + \frac{0.0591}{4} \log\left[\frac{[\text{O}_2]\left[\text{H}^{+4}\right]}{|\text{H}_2\text{O}|}\right]$$

Because $|H_2O|$ concentration is approximately constant and $|O_2|$ partial pressure (p_{O_2}) is approximately 0.20 atm, then:

$$E_{O_2} = 1.229 + 0.0148 \log\left\{\left[\text{H}^{+4}\right] p_{O_2}\right\}$$

$$E_{O_2} = 1.229 + 0.0148 \log\left\{\left[1.000^4\right] 0.20\right\} \\ = 1.219 \text{ V}$$

Therefore, the cell potential for the reaction $2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$ is:

$$E_{cell} = E_{O_2} - E_{Cu} = 1.219 \text{ V} - 0.307 \text{ V} = 0.912 \text{ V}$$

To deposit copper metal, the reaction must be reversed by applying an external voltage at least equal to the cell potential together with the overpotentials and any IR drop. This value of voltage is the decomposition potential. The anodic overvoltage of oxygen in this cell may be taken as 0.40 V. The decomposition potentials vary with concentration, as does the IR drop; this must be considered. Current will flow only when:

$$E_{APP} = 0.912 \text{ V} + 0.40 \text{ V} + IR \text{ drop}$$

Therefore, E must be increased until it exceeds this sum to sustain electrolysis. The limiting current, proportional to concentration, decreases with concentration. In this case, the decomposition potential increases, and IR decreases.

A major problem is that voltages frequently must be maintained within close limits to ensure efficient separation of metals. Other factors affect separation. For example, the smoother the deposited metal, the higher the overpotential. In addition, increases in temperature affect the result. As temperature is raised, overpotential is decreased. In some cases, particularly in strong acid solution, overpotential may become pH dependent. Determination of a working potential may be difficult, and often a rough value is obtained by application of the Nernst equation (Eq 3 or 11) and modified by experiment.

Various parameters are occasionally advantageous in determination of the voltage conditions required by two metals to enable deposition of one in the presence of the other. The use of complexing agents may provide solutions with decomposition potentials very different from those in the noncomplexed state. This sometimes allows reversal of the order of deposition.

Physical Properties of Deposits

To ensure purity of the metal and quantitative deposition, electrolysis must exhibit the following characteristics. The ability of metals to adhere to the cathode is most important, because any loss from the cathode causes an error in the weight of the metal that cannot be accommodated. Smoother deposits generally adhere more favorably to the electrode. Therefore, effects that cause the metal deposit to be flaky or spongelike must be reduced or eliminated. The most common cause of this failing—the evolution of a gas coincident with metal deposition on the same electrode—must be prevented if possible by arranging electrolysis conditions.

The chemical nature of the medium may affect the smoothness of the deposit. For example, copper is deposited readily from a solution in nitric acid, but silver yields a better deposit when precipitated from the silver cyanide complex. In samples of cobalt, nickel, or copper containing chloride ions, the chloride ions must be removed to deposit the metals quantitatively (Ref 18).

Temperature increases hasten the rate of diffusion and thus the current density, which decreases deposition time. Hydrogen overpotential is also decreased; this may affect the degree of separation, particularly when metal complexes are involved.

The rate of flow of ions to an electrode is hastened by increasing their rate of movement in the solution. This is achieved by efficient stirring using a stirrer or a rotating or vibrating electrode (Ref 19). Again, the increased rate of diffusion decreases deposition time but lessens the concentration potential. This increases current density, which further decreases deposition time, as outlined previously.

Use of Incomplete Deposition

Small mass changes arising from electrolytic deposition may be monitored by using the piezoelectric effect. For example, in the determination of cadmium, metallic electrodes of a piezoelectric crystal are used as cathodes. The weight of cadmium deposited is related linearly to the fundamental frequency of the crystal; this is used to determine incomplete deposition of cadmium from a solution of 0.1 M $NaClO_4$. Analysis takes 15 min.

Methods and Instrumentation

The cell is fundamental to electrogravimetry equipment. The circuit requirements for electrogravimetry are a direct current source, a variable resistance, an ammeter for measuring current, and a voltmeter for voltage measurement. Direct current may be provided by batteries or a power supply that converts alternating current to direct current. Separation is normally carried out under conditions of constant current or constant or controlled voltage.

As noted, the two primary classical types of cells are constant-current and controlled-potential circuits (Fig. 3) with large platinum gauze electrodes or a mercury cathode and a flat spiral wire anode. In the case of the mercury cathode, solution may be removed without interfering with the electrolysis current. Thus, there is no oxidation of the elements deposited at the solution-amalgam interface. In the simple cell shown in Fig. 3(b), this may be accomplished by using the stop cock and siphon. The cell constant and specific resistance of the solution are low, allowing flow of a current of several amperes—normally sufficient to reduce all the solution components. This can be prevented by efficient stirring and by the heating effects of the current. New and modified cells and electrodes are available to improve precision or to be used at the microgram level.

Microelectrogravimetry is conducted easily in the following simply constructed cell using controlled potential (Ref 20). The cell contains a rapidly rotating helical platinum wire, 10 to 15 cm (4 to 6 in.) long and 0.05 cm (0.02 in.) in diameter. From 3 to 10 mg copper in copper foil have been recovered (99.5%) in 90 min by using this cell. Recovery from brass was lower (97.4 ± 0.8%). Lead and tin have also been deposited from brass. Cadmium was analyzed in micromolar concentration by using a piezoelectric electrode, as described earlier.

An electrolytic cell fitted with a mechanically homogenized system for decreasing concentration polarization yields dense, adhering, smooth, brilliant deposits that provide high-precision analysis of metallurgical samples and that may be used in quality control of metallurgical products. Use of vibrating electrodes improves the structure of the deposit and reduces the analysis time of electrogravimetry. Table 3 shows typical results. Table 4 lists results obtained by using internal electrolysis to deposit copper.

Table 3 Electrogravimetric determination of some metals by using vibrating electrodes

Metal	Mass, g	Relative error, %	Analysis time(a), min
Copper	0.1994	0.06	10
Lead	0.0972–0.6635	0.20	12
Bismuth	0.2013	0.05	15
Antimony	0.1022	0.11	14

(a) Note reduction in analysis time compared to that shown in Table 4. Source: Ref 2

Table 4 Determination of copper by using internal electrolysis

Mass, g	Relative error, %	Analysis time, min
0.02019	0.23	20
0.05029	0.90	35
0.10056	1.62	45

Source: Ref 2

Method Selection

Constant-current methods are the oldest in electrogravimetry. Continual increases in voltage maintain the constancy of current. Two problems arise in the separation of two ions in aqueous solution. First, the overpotential of hydrogen, if reached, causes deterioration in the smoothness of the deposit, with the effects considered earlier. Second, any second metal to be deposited must have a decomposition potential more negative than that of the hydrogen overpotential or the first deposited metal.

Considerable increases in voltage maintain analysis speed and ensure complete deposition. For example, when separating copper from other metals, such as zinc, copper is reduced to approximately $^1/_{100}$ of its concentration at 1.43 V. The current may be increased to give a final voltage of 2.2 V before hydrogen is evolved. For example, using 0.5 *M* sulfuric acid as the electrolyte, the hydrogen ion remains effectively constant while hydrogen is evolved. Codeposition will not occur if the metal from which copper is to be separated has a more negative potential than that for hydrogen.

Constant-Voltage Electrogravimetry

In the earlier example, hydrogen is not evolved below 2.2 V. Therefore, if electrolysis is conducted at a constant voltage from 1.43 to 2.2 V, copper may be deposited without hydrogen. However, the method, involving small currents and long separation times, is rarely used.

Internal Electrolysis

In this method, current is obtained from a secondary reaction usually consisting of attack of the anode by the electrolyte. The anode and cathode are connected directly to one another, creating a short-circuited galvanic cell (Fig. 8). Analysis of copper in the presence of lead necessitates use of the cell:

$$-\mathrm{Pb}\,\big|\,\mathrm{Pb}^{2+}\big|\,\big|\,\mathrm{Cu}^{2+}\big|\,\mathrm{Cu}+$$

where lead is the attackable anode. Energy is lost only by ohmic resistance, which controls the maximum current flowing through the cell:

$$IR = 0.22 + 0.0296\ \log\ \left[\mathrm{Cu}^{2+}\right]$$

for a 1 *M* Pb^{2+} solution at 25 °C (75 °F). Metal ions with decomposition potentials below -0.12 V, for example, silver and copper but not cadmium, may be deposited using this technique. To make I as large as possible, R must be kept as low as possible by using a high electrolyte concentration.

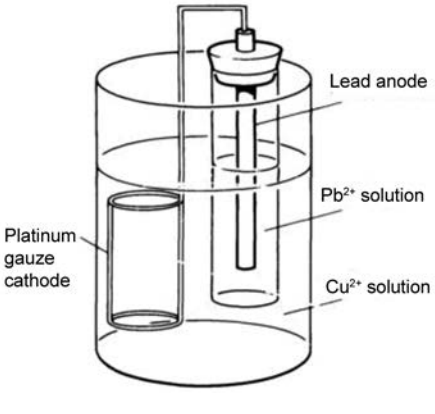

Fig. 8 Typical internal electrolysis cell

Electrolysis will take too long if large quantities of deposit are handled. In addition, the deposit becomes spongy, and metal ions may diffuse to the anode during prolonged electrolysis. Deposits are usually restricted to approximately 25 mg.

Considerations of High Precision and Automation

Advances in instrumentation and computer techniques have furthered high-precision analysis, automated techniques of analysis, and process on-line control. Electroanalytical probes are gaining acceptance in process control.

Metals may be separated using automated techniques. As an example, one such device consists of a stabilized operational amplifier that acts as a power potentiostat/galvanostat with voltages ≤10 V and a current ≤2 A. At the beginning of electrolysis, the apparatus maintains constant current until the working electrode reaches a preselected value of potential. This value is then constant throughout electrolysis. The apparatus was used to separate 0.1 g of Ag^+ from 0.3 g Cu^{2+} using platinum-rhodium working and auxiliary electrodes and a 1.0 *M* $\mathrm{Hg_2SO_4}$ solution as the reference electrode. The instrument may be used as a potentiostat for polarography as well as a voltage amplifier and current/voltage converter.

The anode may be selected not to affect the potential of the cell. In addition, dual anodes may be used to enlarge the surface area (Fig. 9) and may be protected from the electrolyte by a porous membrane. A platinum gauze electrode is placed between the cathode and anode, and the circuit is completed.

Types of Analysis

Quantitative Determination of Metal Ions

The separation and quantitative determination of metal ions from combinations of metals in alloys may be performed by using constant-

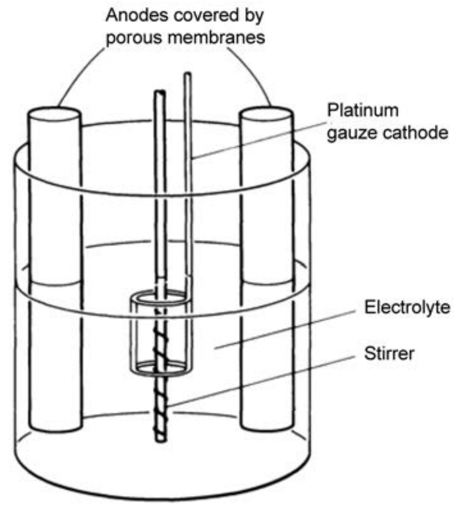

Fig. 9 Typical dual-anode cell

current electrolysis if there is sufficient difference between the decomposition potentials of the metals and other elements, such as hydrogen, being deposited on the cathode. Many elements are determined by using this method, such as Cu^{2+}, Cd^{2+}, Fe^{3+}, Sn^{2+}, and Zn^{2+}. Controlled-potential electrogravimetry may be used to determine many elements in the presence of others. Examples are copper in the presence of bismuth, cadmium, nickel, antimony, tin, or zinc and nickel in the presence of iron and zinc.

Removal of Interfering Ions

The mercury cathode is useful for removing ions that interfere with the metal of interest. Typical elements separated from those that interfere are aluminum, magnesium, titanium, and vanadium. These metals are high in the electromotive series of elements. Those much lower amalgamate with mercury and are separated before determination of those higher.

Effects of Complexation

When attempting to separate ions whose decomposition potentials are close, it is often appropriate to convert them to complexes having different potentials. A typical separation is that of bismuth and copper. When these are electrolyzed in sulfuric acid, the difference in potential is only 0.024 V. If the ions are then treated with a cyanide, the copper is reduced and complexes with cyanide:

$$Cu^{+} + 3(CN)^{-} \rightleftharpoons Cu(CN)_3^{2-}$$

The potential of this complex is much lower than before, providing a greater difference between the potentials than previously. In this case, copper is deposited quantitatively before the bismuth separates.

Internal Electrolysis

In this technique, analysis is restricted to small samples for which separation time is brief. A typical example is the deposition of silver using $Cu/CuSO_4$ as an anode. This may be accomplished in the presence of such elements as copper, iron, nickel, and zinc, which have higher deposition potentials. Another example is the selective deposition of traces of silver, cadmium, copper, and lead using several techniques. For example, an anode of $Cu/CuSO_4$ precipitates silver; an anode of $Pb/PbSO_4$ precipitates copper and silver; an anode of $Cd/CdSO_4$ precipitates lead, copper, and silver; and an anode of $Zn/ZnSO_4$ precipitates all four metals, which can then be analyzed by difference.

Use of Potential Buffers

If chlorocuprous ions are in solution, two competing reactions exist:

$$Cu^{+} + e^{-} \rightarrow Cu\ (\text{cathode})$$

$$Cu^{+} \rightarrow Cu^{2+} + e^{-}(\text{anode})$$

In the presence of sufficient hydrazine:

$$N_2H_5{}^{+} \rightarrow N_2 + 5H^{+} + 4e^{-}(0.17\ \text{V})$$

$$CuCl_3^{2-} \rightarrow Cu^{2+} + 3Cl^{-} + e^{-}(0.15\,\text{V})$$

Oxidation of hydrazine is preferred, and oxidation of Cu^{+} at the anode is suppressed, allowing only reduction at the cathode to occur. The action of hydrazine, termed a potential buffer, resembles that of a buffer when stabilizing pH.

Analysis of Oxidizable Species

Analysis of oxidizable species is carried out at the anode by increasing oxidation potential in a manner similar to the method of increasing reduction potential at the cathode. The effect of using attackable anodes in internal electrolysis has been noted. The discharge of ions is usually restricted to halide, hydroxyl, and sulfide ions. In the case of other ions, the hydroxyl ion from aqueous solutions is discharged as oxygen in preference. Decomposition potential in such cases depends mainly on the metal ions present.

Oxides of a metal may be deposited on the anode. In this case, the anode, of platinum gauze, has a larger surface area than the cathode. The situation is complicated by the tendency of the oxides to form hydrates. Suitable correction factors must be applied.

Applications

Estimation of Copper in a Copper-Manganese Alloy

Approximately 1 g of the alloy, which should contain 0 to 0.5 g Cu and 0.5 to 1.0 g Mn, was weighed accurately to 0.1 mg and dissolved in 25 mL of a solution of 5 parts sulfuric acid, 3 parts nitric acid, and 7 parts water. This mixture was heated until all the oxides of nitrogen had evolved, and the reddish color of nitrogen dioxide had disappeared. The solution was cooled, diluted to 150 mL with water, and placed in a tall form beaker with platinum gauze electrodes. The cathode was weighed accurately before use.

Manganese interferes with deposition of copper unless it is reduced from the Mn^{7+} state. This can be accomplished by using a solution of ascorbic acid or of the disodium salt of ethylene diamine tetraacetic acid (EDTA). Convenient strengths are 10 g in 10 mL water for ascorbic acid and 25 g in 50 mL water for the disodium salt of EDTA. In both cases, electrolysis takes approximately 1 h, but the currents applied should be different: 3 to 4 A in the presence of disodium EDTA and 4 to 6 A in the presence of ascorbic acid. These solutions must be added dropwise from a burette to remove the color of the Mn^{7+} salt as it forms.

The cathode was then removed from the cell, washed carefully with water, dried in an oven for approximately 30 min, and weighed. It was then returned to the oven for a further short period and reweighed. This procedure was repeated until a constant weight was achieved. The experiment was repeated a sufficient number of times to provide a suitable degree of precision.

Determination of Nickel in Samples Containing Chloride Ion

A sample containing approximately 0.3 g Ni was weighed to 0.1 mg in a 250 mL beaker; 4.1 mL concentrated sulfuric acid was added. A yellow precipitate formed with the evolution of hydrochloric acid fumes. The mixture was heated to near boiling on a hot plate until the solid precipitate changed through white to pale green. At this stage, all the chloride ions had been removed. The sides of the beaker were flamed continuously with a Bunsen burner or other means. The mixture was heated for another 5 min.

Next, 65 mL distilled water and 35 mL concentrated ammonia were added, and the solution was heated to approximately 70 °C (160 °F). Using a weighed net cathode and a platinum spiral anode, electrolysis was conducted at 70 to 80 °C (160 to 175 °F) with a current of approximately 2 A. Analysis required approximately 90 min. Dimethylglyoxime was added to a drop of the solution as a check that all the nickel had been removed from the solution. The electrodes were removed while the potential was applied, and the cathode was washed with water and then ethanol. It was dried in a current of air and then weighed. Table 5 shows typical results. Cobalt may be determined similarly.

Separation of Cadmium and Lead by Internal Electrolysis

Standard solutions of cadmium and lead were prepared as the nitrates. To a solution of each nitrate, a few drops of nitric acid were added to prevent hydrolysis, and the solution was diluted to 500 mL. The cadmium and lead were standardized by complexometric titration using EDTA. A solution containing approximately 1 to 3 mg of each of the lead and cadmium ions was prepared and placed in a tall form beaker. A solution of EDTA (the volume to contain approximately 500 mg EDTA) was added. The solution was diluted to 250 mL with distilled water, and the pH was adjusted to 2.5.

Table 5 Determination of Ni^{2+} in $NiCl_2$ solution

Solution, g	Nickel, g	mmol of nickel per gram of solution
2.3625	0.2657	1.9159
2.6052	0.2929	1.9153
2.6204	0.2983	1.9133
2.8191	0.3168	1.9144
2.4832	0.2792	1.9154
2.7186	0.3056	1.9150
2.3413	0.2632	1.9151
2.4821	0.2791	1.9156
2.4626	0.2767	1.9142
2.6911	0.3024	1.9143

Source: Ref 18

The combined electrode, previously weighed to 0.1 mg and consisting of a platinum gauze cathode and a bent zinc plate attached securely to it with copper wire, was added to the solution. Deposition of lead was complete in approximately 6 h. The electrode was removed from the bath and washed over the bath with a jet of distilled water. It was washed with ethanol, dried at 70 to 80 °C (160 to 175 °F), and weighed. The procedure was repeated for the deposition of cadmium, with the pH adjusted to 4.0. Electrolysis required approximately 12 h.

Voltammetry (Ref 3)

Voltammetry is a variation of controlled-potential coulometry, where information about the analyte is obtained by measuring current as a function of a variable applied potential. The basic circuit in voltammetry (Fig. 10) is similar to that of controlled-potential coulometry with three electrodes in the solution containing analyte. The electrolysis current flows between the working electrode and counterelectrode, and a stable reference electrode of known potential acts as a sensor of the working-electrode potential. Applied voltage is varied, depending on the position of the variable resistor.

Voltammetry involves measuring the current-voltage relationships when electroactive species in solution are subject to oxidation or reduction at electrodes under carefully controlled conditions. It involves probing a small region of a solution containing, for example, metal ions, by performing small-scale electrolysis between an indicator microelectrode and a reference electrode. A reference electrode, such as the saturated calomel electrode (SCE), is by definition nonpolarizable. That is, its potential remains the same regardless of the potential difference imposed between it and the indicator electrode. The latter is described as polarizable, because it faithfully adopts any potential imposed on it relative to the reference.

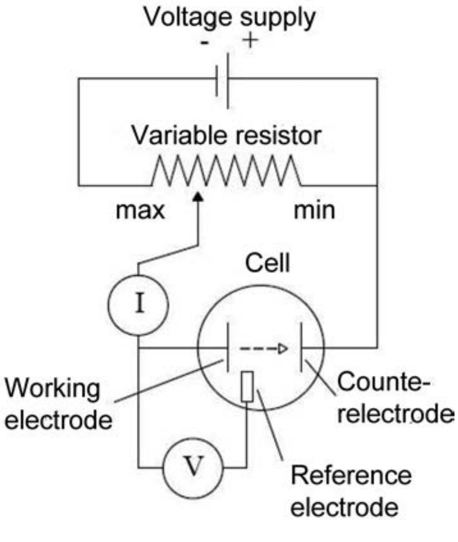

Fig. 10 Circuit of controlled-potential electrolysis cell for voltammetry

If the potential difference between indicator and reference electrode can be controlled accurately and varied uniformly, criteria which modern potentiostatic devices ensure, the corresponding currents that flow reflect the nature and concentration of oxidizable or reducible solutes in solution. Currents flow because of the exchange of electrons between the indicator electrode and electroactive solutes. The latter are frequently metal ions, and the electrode processes monitored are reductions. The indicator electrode then acts as a cathode.

Considerable care is necessary to ensure that electroreducible material reaches the indicator electrode only by natural diffusion. The other important mass-transfer processes, electrical migration and convection, are controlled rigorously; the former, an electric field effect, is related to the transport number of the metal ions and may be eliminated effectively by the presence of a large excess of a supporting, or base, electrolyte. The ionic components of this electrolyte (frequently potassium chloride) do not react with the indicator electrode at potentials at which the required species does, but the presence of the base electrolyte ensures that the transport number of the species whose analysis is required is reduced virtually to zero.

Convection effects may arise from stray vibrations and shock or even from temperature gradients within the solution. Thermostatic control and protection from any form of inadvertent stirring ensures that this interference is minimal. Under less common circumstances, controlled convection, particularly as rapidly rotated electrodes, is used to enhance current signals. For most circumstances, the current-voltage curves for metal ions in solution may be interpreted in terms of the interplay of the diffusion process, by which they arrive at the surface of the indicator electrode, and their reduction there when the applied potential has reached characteristic values.

The selection of indicator electrode material presents some problems. Prolonged accumulation of the products of reduction processes tends to alter the physical and electrochemical characteristics of solid microelectrodes. Mechanical or electrochemical removal of these depositions is not always satisfactory. That is, many solid electrodes develop an irreversible history if suitable precautions are not taken.

Electrodes

The most satisfactory microelectrode at applied potentials more negative than 0.0 V relative to the SCE is that based on mercury in the form of exactly reproducible drops issuing from the end of a capillary attached to a constant head reservoir. Voltammetry performed using the dropping mercury electrode (DME) is known as polarography.

The major limitation of using mercury as an electrode material is its restricted anodic range, which at best extends to +0.4 V versus SCE. This is not a disadvantage for metal analysis, although silver in many supporting electrolytes