

# Chapter 24. Coulometry

1) Electrogravimetry: sample soln.+ Pt전극(wire, gauze)

→ 직류전압 加 ┌ 일정전압법 (Constant applied cell potential)

| 일정전류법 (Constant electrolysis current)

└ 일정작업전극전위 (Constant working electrode potential)

→ 정량성분, 전해석출 → weighing

(금속의 순도, 합금성분의 정량에 利用)

2) Coulometry: sample soln. + 일정 전위의 전압 加 (전류효율100%)

→ 소요된 전기량 측정

# 1. Electrogravimetry

일정전위분해법 : 황산구리 용액에 Pt wire 및 Pt gauze (150cm<sup>2</sup>)전극을  
0.0220M Cu<sup>2+</sup> 200 ml + 1.00 M H<sup>+</sup> 용액에 담귀 (cell of 0.50 Ω)→

직류전압 加 → 전기분해

Cathode : Cu<sup>2+</sup> + 2e<sup>-</sup> → Cu 석출  $E^{\circ} = 0.34 \text{ V}$

Anode : 1/2O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> = H<sub>2</sub>O  $E^{\circ} = 1.23 \text{ V}$

→ 석출 전 후의 전극무게 측정 → 정량

Deposit 의 physical characteristic에 영향을 주는 요소:

① Current density ② Temp. ③ Complexing agent 의 존재

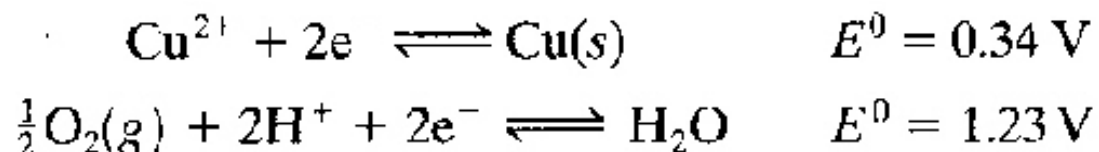
→ 실험적으로 결정

Electrolysis :  $E_{app} = E_C - E_a + \Pi_c + \Pi_a - IR$  (24-1)

## 24A-1 Current-Voltage relationships during an electrolysis.

- Initial Thermodynamic Potential of the cell

Standard potential data for the two half-reactions in the cell under consideration are



Using the method shown in Ex 22-6, the thermodynamic potential for this cell can be shown to be **-0.94 V** in **0.0220M Cu<sup>2+</sup> 200 ml + 1.00 M H<sup>+</sup> solution.**

When a potential of -2.5 V is applied to the cell,  $I_{\text{init}} = 1.5 \text{ A}$ . (See Fig.14-1a)

- Current changes during an electrolysis at constant applied potential;

$$I_t = I_0 e^{-kt}, \quad k = 25.8DA / V\delta$$

Typically,  $D = 10^{-5} \text{ cm}^2/\text{s}$ ,  $\delta = 2 \times 10^{-3} \text{ cm}$

Fig. 24-1 Changes in (a) current and (b) potentials  
during the electrolytic deposition of Cu(II) ion.  
A): Pb, B): Cd, C): Co

1-2. Constant current electrolysis :

By maintaining the current : 전해 동안 주기적 전압증가 要.

$$E_{app} = (E_a + \eta_a) - (E_c + \eta_c) + IR$$

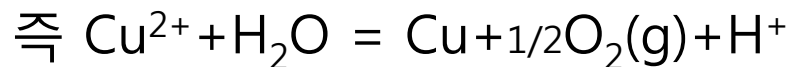
$$E_c = E^{\circ}_{Cu^{2+}, Cu} + 0.059/2 \log[Cu^{2+}]$$

ex) 0.01M  $Cu^{2+}$  99.9% 전해에 必要한 voltage

$$E_c = 0.34 + 0.059/2 * \log[10^{-2}] = 0.28 \text{ V}$$

전해 종료시  $E_c = 0.34 + 0.059/2 * \log[10^{-5}] = 0.19 \text{ V}$  (저하)

$\eta_a, \eta_c \rightarrow H^+$  의 accumulation  $\rightarrow$  depolarizer 첨가



Electrode reaction 의 속도에 의존 (Pt에서 거의 무시)

IR 강하  $\rightarrow$  이론적인 加 전압 값보다 약간 더 큰 전압 加

### 1-3. Controlled potential electrolysis (limited cathode potential electrolysis)

장치: ( working elec.의 전위  $\rightarrow$  reference에 대해 측정  
 $\rightarrow$  이론 값 만큼 전위 加  $\rightarrow$  )

Reference 전극에 대해 일정한 전위를 설정

$\rightarrow$  저항 조정  $\rightarrow$  working electrode의 전위가 일정하게  
조절

Fig 24-3. Apparatus for controlled-potential electrolysis.



적용 : 두 종류의 금속  $\rightarrow$  수소보다 양성, 전극전위 비슷  
 $\rightarrow$  분리 곤란(일정전류법)  
 $\leftarrow$  Controlled potential electrolysis 사용

전류  $I \rightarrow$  시간  $t$  에 대해 지수 함수적으로 감소

$$I = I_0 e^{-kt} \cdot \log I = -2.303kt + \log I_0$$

$$C_t/C_0 = i_t/i_0 = e^{-(DA/V\delta)t} = 10^{-0.43(DA/v\delta)t}$$

$v$  : 용액의 volume

$\delta$  : 확산 층의 두께

$$C_t/C_0 = e^{-kt} \quad k = mA/V$$

$m$  : mass transfer coefficient =  $D/\delta$

$$k = 25.8DA/(V\delta)$$

## 1-4. Mercury cathode electrolysis

음극: 백금대신 수은->전해

$M^{n+} + ne + Hg \rightarrow M(Hg) \rightarrow$  원소의 분리에 利用

ex)  $[Ag^+] = 10^{-6}M$ ,  $[Cu^{2+}] = 0.1M$  일 때

$$E_C = 0.08 + (-0.35) = 0.45V$$

$$E_C - \eta_C = 0.45 - 0.07 = 0.38(V)$$

구리  $E_C = 0.31V$ 이므로  $0.38V$  volt 에서  $Ag^+$ 을 정량적 석출 可能

## 1-5. Internal electrolysis

양극 : 석출금속보다 음의 단위를 가진 금속

음극: 백금

두 극 사이에 격막을 놓으면  $\rightarrow$  전지 형성  $\rightarrow$  내부전해법

## 24B An Introduction to coulometric methods of analysis

### Coulometry

→Analyte를 정량적으로 다른 산화상태로 변화시키는데 필요로 하는  
전기량

### 2. Controlled-potential coulometry

$$\int_0^t i dt = Q = nF(w/M)$$

(w : 산화 환원 물질의 무게 , M : formula weight, Q: charge quantity)

F ;  $964877 \pm 1.6 (\approx 96500)$  C/g 당량

Q를 측정 → w계산

## 24B-1 Units for Quantity of Electricity

The quantity of electricity or charge or charge is measured in units of coulombs(c).

$$Q = It \quad (24-3)$$

$$Q = \int_0^t i dt \quad (24-4)$$

$$n_A = \frac{Q}{nF} \quad (24-5)$$

## 24B-2 Type of Coulometric Methods

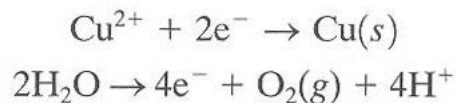
- ┌ Constant potential coulometry
- └ Constant current coulometry

### EXAMPLE 24-1

A constant current of 0.800 A was used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the mass of each product that was formed in 15.2 min, assuming that no other redox reactions occur.

#### Solution

The equivalent masses are determined from the two half-reactions



Thus, 1 mol of copper is equivalent to 2 mol of electrons and 1 mol of oxygen corresponds to 4 mol of electrons.

From Equation 24-3, we find

$$\begin{aligned}Q &= 0.800 \text{ A} \times 15.2 \text{ min} \times 60 \text{ s/min} \\ &= 729.6 \text{ A} \cdot \text{s} = 729.6 \text{ C}\end{aligned}$$

We can find the number of moles of Cu and O<sub>2</sub> from Equation 24-5:

$$\begin{aligned}n_{\text{Cu}} &= \frac{Q}{nF} = \frac{729.6 \text{ C}}{2 \text{ mol e}^{-} / \text{mol Cu} \times 96,485 \text{ C/mol e}^{-}} \\ &= 3.781 \times 10^{-3} \text{ mol Cu} \\ n_{\text{O}_2} &= \frac{Q}{nF} = \frac{729.6 \text{ C}}{4 \text{ mol e}^{-} / \text{mol O}_2 \times 96,485 \text{ C/mol e}^{-}} \\ &= 1.890 \times 10^{-3} \text{ mol O}_2\end{aligned}$$

The masses of Cu and O<sub>2</sub> are given by

$$\begin{aligned}m_{\text{Cu}} &= n_{\text{Cu}} M_{\text{Cu}} = 3.781 \times 10^{-3} \text{ mol Cu} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \\ &= 0.240 \text{ g Cu} \\ m_{\text{O}_2} &= n_{\text{O}_2} M_{\text{O}_2} = 1.890 \times 10^{-3} \text{ mol O}_2 \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \\ &= 0.0605 \text{ g O}_2\end{aligned}$$

## 2-1. Constant potential coulometry

$$Q = \int_0^t I dt = \int_0^t I_0 e^{-kt} dt = I_0(1 - 10^{-kt})/2.303k \approx I_0/2.303k$$

$I = I_0 e^{-kt}$ ,  $\log I = -2.303kt + \log I_0$  식에서  $I_0$ 와  $kt$ 를 구하여 Q값 계산

## 2-2. Constant current coulometry, (전기량 적정)

$I = \text{constant}$ 이므로  $Q = It$ 에서  $t$  측정하여 Q 계산

→정량물질의 선택적 전해가 어렵다.

→전해에 의해 생긴 제2 물질 →적정하여 정량

## 2-3. Coulometers

종류  $H_2$ ,  $O_2$  coulometer

Ag coulometer

$H_2$ ,  $N_2$  coulometer

Cu coulometer

$H_2$  coulometer

적산 coulometer

### 1. $H_2$ - $O_2$ coulometer

뷰렛모양의 전해용기에  $K_2SO_4$  용액을 담고 → Pt를 전극으로 하여

전기분해 → 발생 전  $H_2$ - $O_2$  의 부피 측정 (16.80ml/1mg)

## 2. Ag coulometer

Cathode : Pt crucible containing  $\text{AgNO}_3$  solution

Anode : Ag 전극

Pt+석출 전 Ag  $\rightarrow$  무게 측정  $\rightarrow$  Q계산

## 3. $\text{N}_2$ - $\text{H}_2$ coulometer

Hydrazine sulfate  $\rightarrow$  전기분해  $\rightarrow$  수소, 질소 발생  $\rightarrow$  gas 양 측정

$\rightarrow$  전기량 계산

## 4. 적정 전기량계

양극 : 은  $\text{KBr} + \text{K}_2\text{SO}_4$  용액  $\rightarrow$  전해

음극 : Pt



$\text{OH}^-$ 을 0.01  $\text{NHCl}$ 로 적정하여 구한다.





## 24C Controlled-potential coulometry

### 24C-1 Instrumentation

- Cells

Fig 24–5 illustrates two types of cells that are used for potentiostatic coulometry.

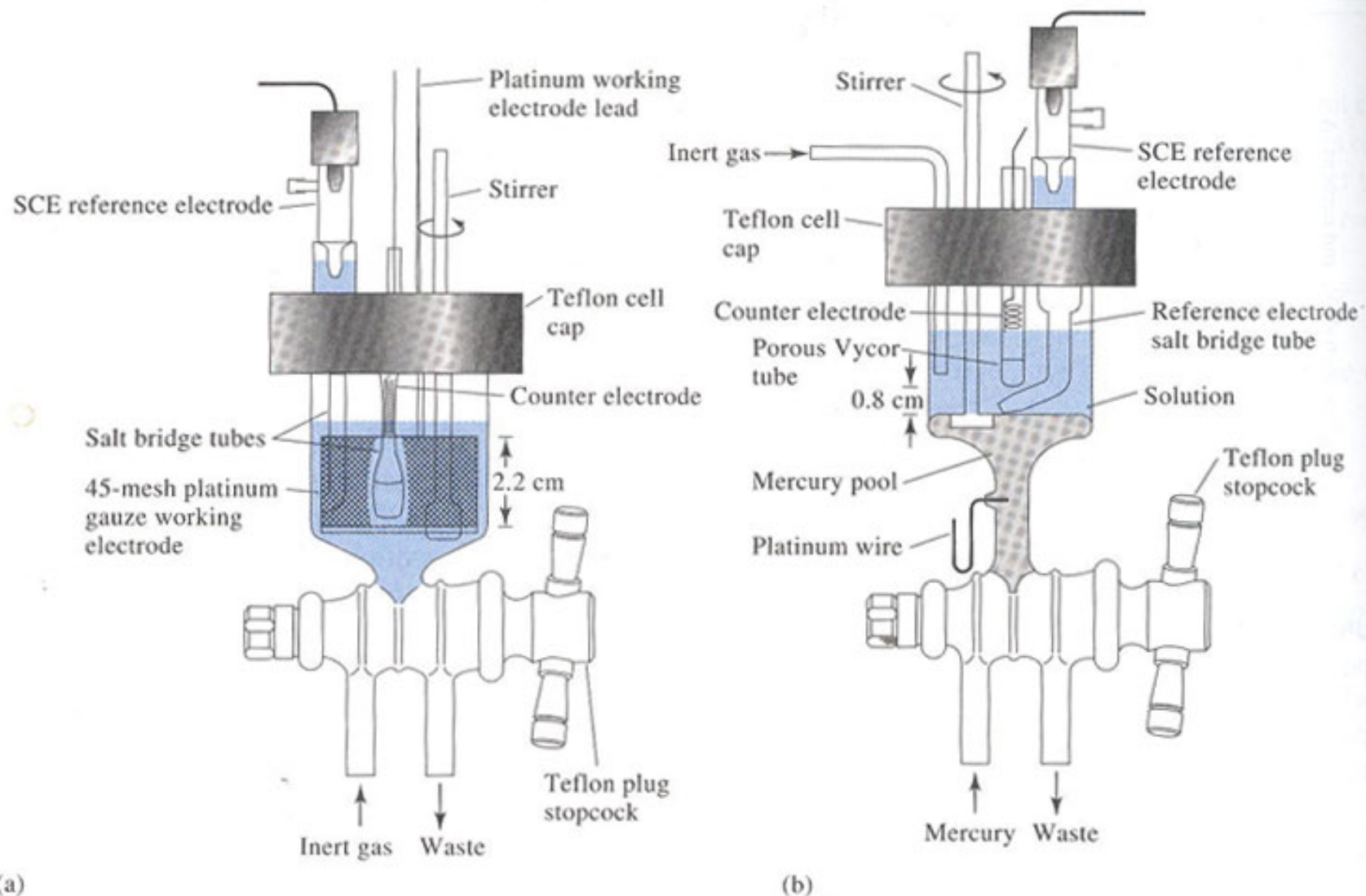
- Potentiostats

A potentiostat is an electronic device that maintains the potential of a working electrode at a constant level relative to a reference electrode.

Fig 24–6 is a schematic of an apparatus for controlled-potential coulometry, which contains a somewhat different type of potentiostat.

- Integrators

As shown in Section 3E–3, analog integrators can be constructed from operational amplifier circuits.

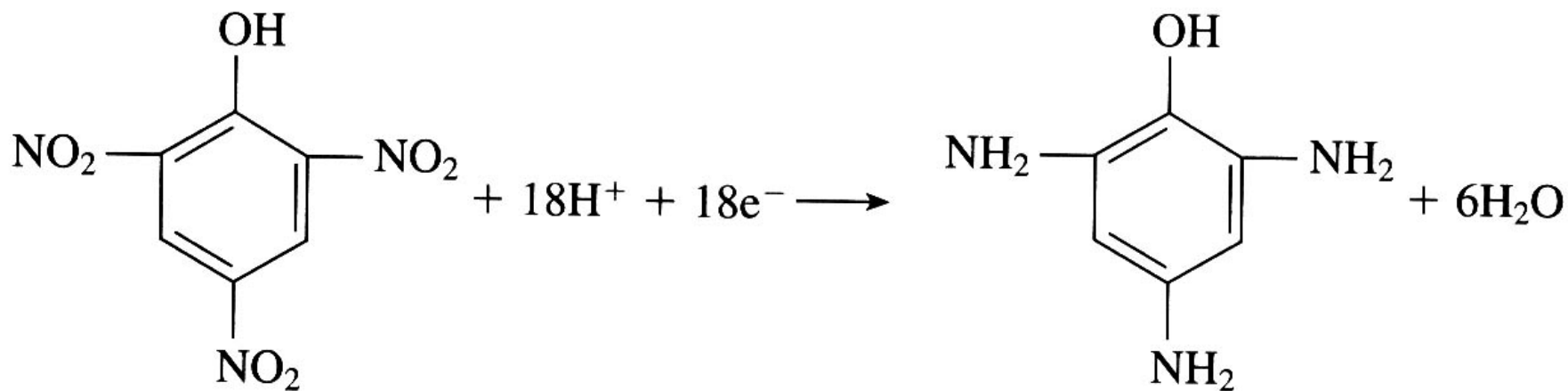


**FIGURE 24-5** Electrolysis cells for potentiostatic coulometry. Working electrode: (a) platinum gauze; (b) mercury pool. (Reprinted with permission from J. E. Harrar and C. L. Pomernacki, *Anal. Chem.*, 1973, 45, 57. Copyright 1973 American Chemical Society.)

Fig. 24-6 Schematic of a system for controlled-potential coulometry.

## 24C-2 Applications

Controlled-potential coulometric methods have been applied to more than fifty elements in inorganic compounds.



## 24D Coulometric titration

### 24D-1 Electrical Apparatus

Fig 24–7 is a conceptual diagram of a coulometric titration apparatus showing its main components.

Fig 24–8 is a photo of one of a number of automated coulometric titrators on the market. The instrument in Fig 24–8 is specifically designed for the Karl Fischer determination of water.

- Cells for coulometric Titrations

A typical coulometric titration cell is shown in Fig 24–9.

Note that the apparatus shown in Fig 24–10 provides either hydrogen or hydroxide ions depending on which arm is used.

Fig 24-7. Schematic of a manual coulometric titration apparatus.



**FIGURE 24-8** An automated coulometric titrator. All instrument functions are under control of an internal computer, and results of determinations appear on the LCD display. (Courtesy of Mettler-Toledo, Inc., Columbus, OH.)



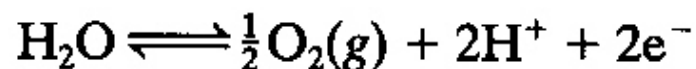
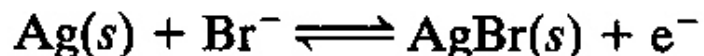
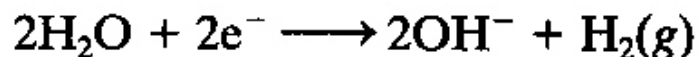
Fig 24-9 A typical coulometric titration cell.

Fig 24-10 A cell for external generation of acid and base.

## 24D-2 Applications of Coulometric Titrations

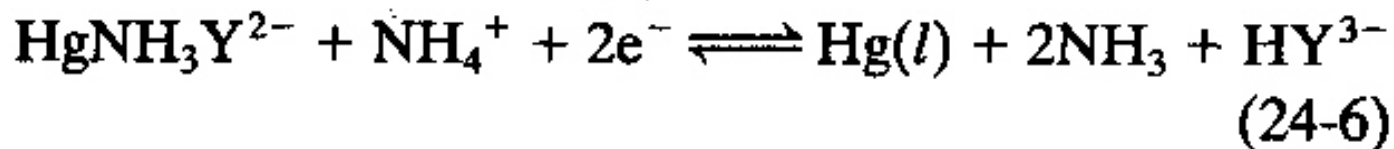
- Neutralization Titrations

Both weak and strong acids can be titrated with a high degree of accuracy using hydroxide ions generated at a cathode by the reaction.



- Precipitation and Complex-Formation Titrations

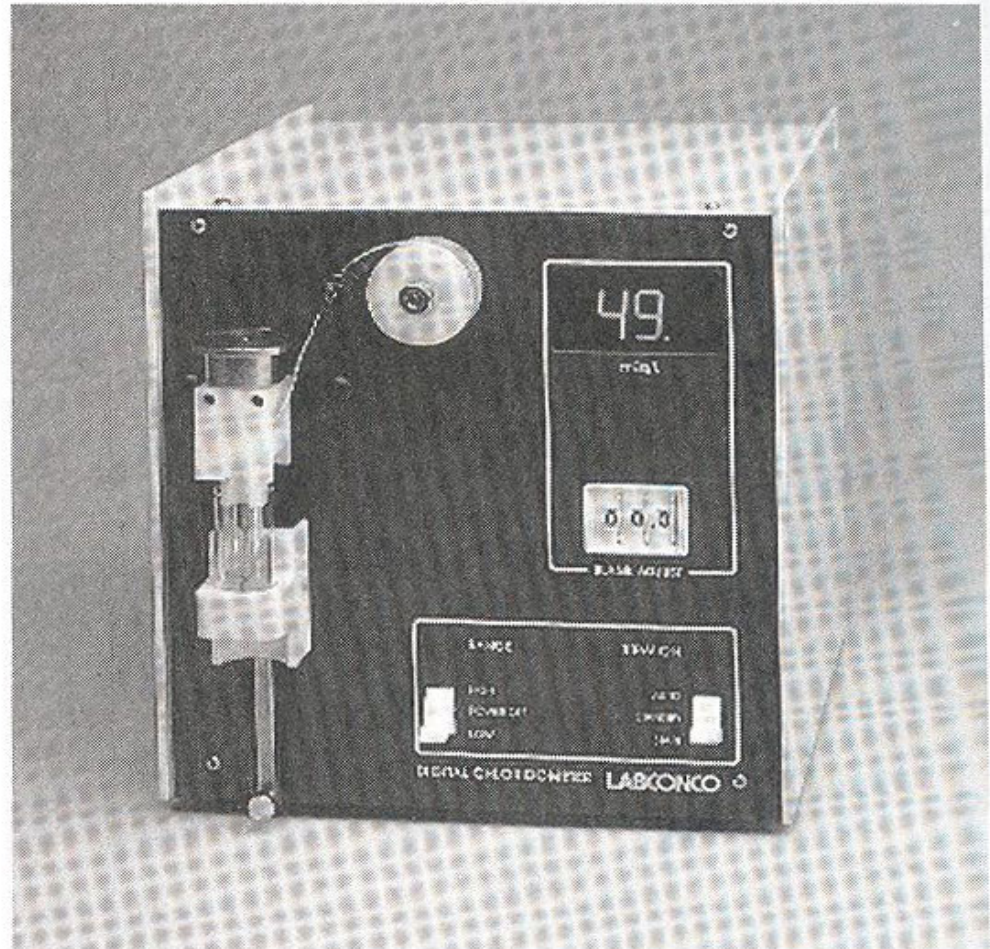
A variety of coulometric titrations involving anodically generated silver ions have been developed(see Table 24-1).



- Coulometric Titration of Chloride in Biological Fluids

The accepted reference method for determining chloride in blood serum, plasma, urine, sweat, and other body fluids is the coulometric titration procedure.

$$(n_{\text{Cl}^-})_u = t_u / t_s \times (n_{\text{Cl}^-})_s$$



**FIGURE 24-11** A commercial digital chloridometer. This coulometric titrator is designed to determine chloride ion in such clinical samples as serum, urine, and sweat. It is used in the diagnosis of cystic fibrosis. The chloridometer is also used in food and environmental laboratories. (Courtesy of Labconco Corp., Kansas City, MO.)

- Oxidation-Reduction Titrations

Table 24–2 indicates the variety of reagents that can be generated coulometrically and the analyses to which they then have been applied.

**TABLE 24-1** Summary of Coulometric Titrations Involving Neutralization, Precipitation, and Complex-Formation Reactions

Species Determined	Generator Electrode Reaction	Secondary Analytical Reaction
Acids	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- + \text{H}_2$	$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$
Bases	$\text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$	$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX}(s)$
Mercaptans (RSH)	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{RSH} \rightleftharpoons \text{AgSR}(s) + \text{H}^+$
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	$2\text{Hg} \rightleftharpoons \text{Hg}_2^{2+} + 2\text{e}^-$	$\text{Hg}_2^{2+} + 2\text{X}^- \rightleftharpoons \text{Hg}_2\text{X}_2(s)$
$\text{Zn}^{2+}$	$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	$3\text{Zn}^{2+} + 2\text{K}^+ + 2\text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2(s)$
$\text{Ca}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$	See Equation 24-6	$\text{HY}^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{CaY}^{2-} + \text{H}^+$ , etc.

- Comparison of Coulometric and Volumetric Titrations

There are several interesting analogies between coulometric and volumetric titration methods.

→ Titration error

- ① Variation in the current source of error
- ② Departure of the process from 100% current efficiency
- ③ Error in the measurement of current
- ④ Error in the measurement of time
- ⑤ Titration error due to the difference between the equivalence point & end point

정밀 : 0.01%

실험 및 이론:

1) Pt gauze를 nitric acid → rinsed-dried → weighing

2) Deposition :

$$E_{app} = (E_a + \eta_a) - (E_C + \eta_C) + iR$$

$$E_C = E^\circ_{Cu^{2+}} + 0.059/2 \log[Cu^{2+}]$$

@ 0.01M-Cu<sup>2+</sup> 99.9% 전해에 필요한 Voltage

$$E_C = 0.34 + 0.059/2 \log[10^{-2}] = 0.28V$$

$\eta_a$  : electrode reaction의 속도에 의존 → Pt에서는 거의 무시

$\eta_e$  : H<sup>+</sup>의 accumulation ← (depolarizer) (stirring)

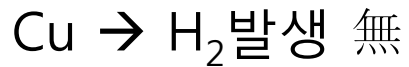
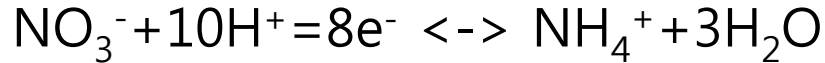
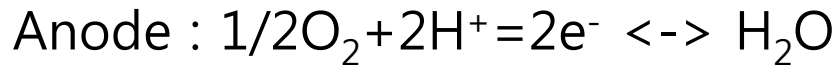


특정 이온만의 분리 → 다양한 기술 필요

\* IR 강하로 인해 이론적인 加 전압 값보다 약간 더 큰 전압은 加해야 한다.

H<sup>+</sup>의 방해감소 (depolarizer첨가) → H<sub>2</sub> gas발생(spongy식의 전착)

(Cu<sup>2+</sup>의 경우)





### 3-1. Electrolysis at controlled potential

Copper, ion 혼합물 정량 시

Working elec.의 전위 → reference에 대해 측정 → 이론값 만큼 加  
→ 보정해 주며 전압 加

### 3-2. Electrolytic separations

Easily reduced metals from small currents of less easily reduced material

### 3-3. Controlled-potential coulometry

Analyte → chemical state의 charge →  $q$ 를 측정 → phy. constant에 따라 양을 계산

$$w = QM/nF$$

$w$  : 산화, 환원전 물질의 무게

$F$  :  $96.4877 \pm 1.6$  coulomb/g

$M$  : 물질의 분자량

$Q$  : cell을 지나는 전하의 수

$$q = it \quad q = \int_t^o i dt$$

**TABLE 24-2** Summary of Coulometric Titrations  
Involving Oxidation-Reduction Reactions

Reagent	Generator Electrode Reaction	Substance Determined
Br <sub>2</sub>	$2\text{Br}^- \rightleftharpoons \text{Br}_2 + 2\text{e}^-$	As(III), Sb(III), U(IV), Ti(I), I <sup>-</sup> , SCN <sup>-</sup> , NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , NH <sub>2</sub> OH, phenol, aniline, mustard gas, mercaptans, 8-hydroxyquinoline, oleins
Cl <sub>2</sub>	$2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2\text{e}^-$	As(III), I <sup>-</sup> , styrene, fatty acids
I <sub>2</sub>	$2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$	As(III), Sb(III), S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , H <sub>2</sub> S, ascorbic acid
Ce <sup>4+</sup>	$\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + \text{e}^-$	Fe(II), Ti(III), U(IV), As(III), I <sup>-</sup> , Fe(CN) <sub>6</sub> <sup>4-</sup>
Mn <sup>3+</sup>	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + \text{e}^-$	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Fe(II), As(III)
Ag <sup>2+</sup>	$\text{Ag}^+ \rightleftharpoons \text{Ag}^{2+} + \text{e}^-$	Ce(III), V(IV), H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , As(III)
Fe <sup>2+</sup>	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	Cr(VI), Mn(VII), V(V), Ce(IV)
Ti <sup>3+</sup>	$\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	Fe(III), V(V), Ce(IV), U(VI)
CuCl <sub>3</sub> <sup>2-</sup>	$\text{Cu}^{2+} + 3\text{Cl}^- + \text{e}^- \rightleftharpoons \text{CuCl}_3^{2-}$	V(V), Cr(VI), IO <sub>3</sub> <sup>-</sup>
U <sup>4+</sup>	$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	Cr(VI), Ce(IV)