

電気化学

垣内 隆

8. クーロメトリー

クーロメトリー (Coulometry)

電気量を測る

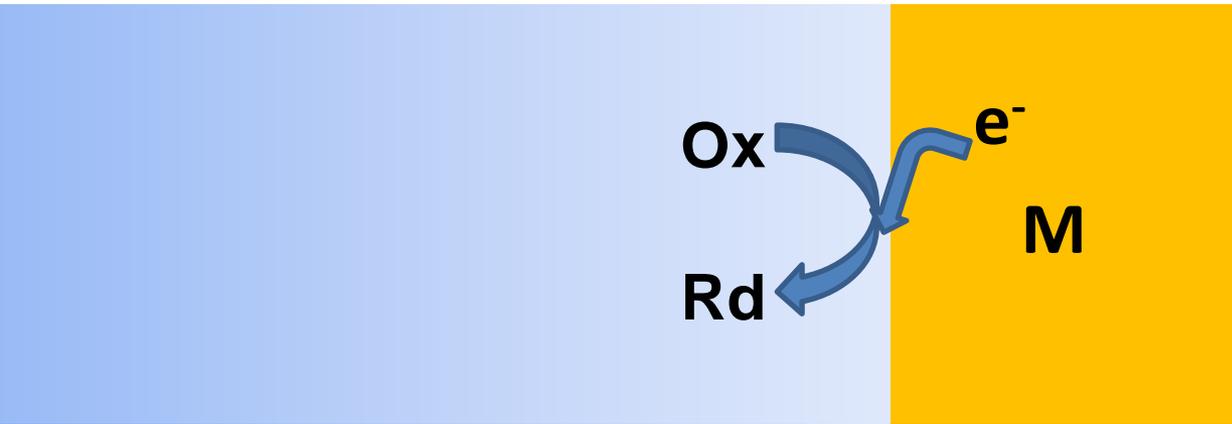
Electric charge

Quantity of electricity

電気量 = 電流 × 時間

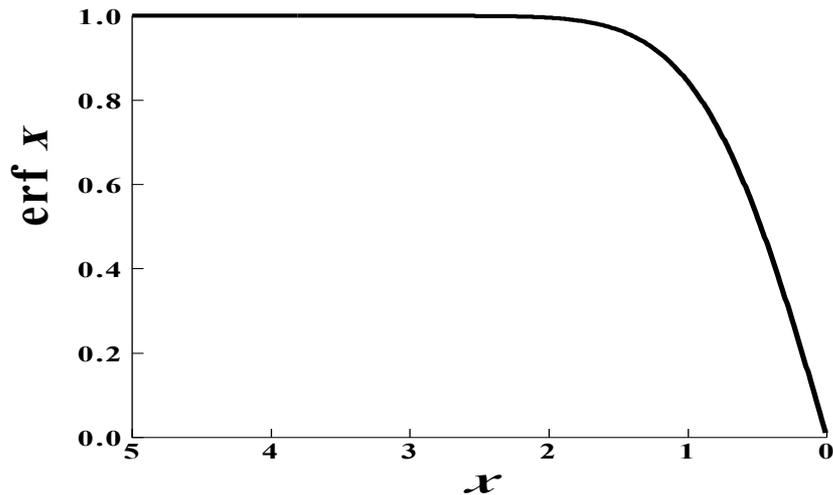
$$Q = \int i dt$$

一次元半無限拡散の場合



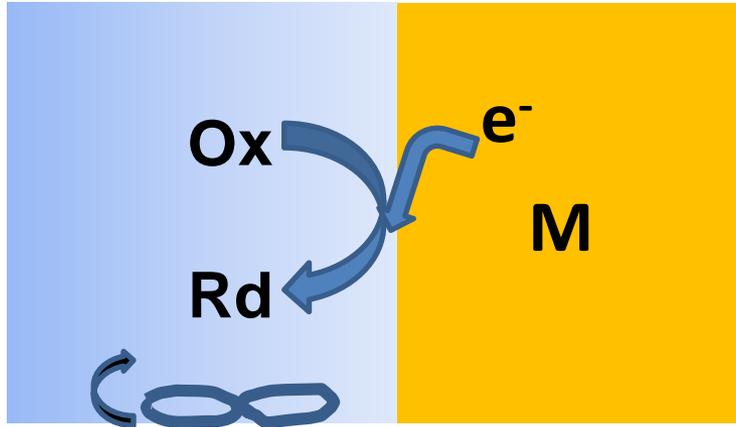
1. 大きな電極
例: 直径 1 mm の円板
2. 十分量の支持電解質
例: 100倍の濃度
3. そっとしておく

電極表面に到達した Ox はただちに還元される時、Ox 濃度プロファイルは

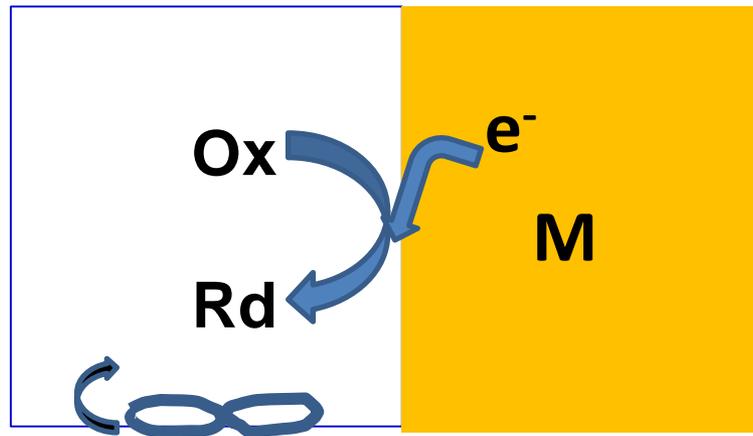


拡散方程式 (Fick の第二法則) を解いて





ややこしい



Ox の量を知るのが
目的なら溶液中のOx
を全て還元してしまっ
たら良いのでは？！



溶液中の Ox を全て還元するのに要した電気量を Q とすると

Ox の物質量は

$$m = \frac{Q}{nF} \quad (\text{単位は mol})$$

Faraday

(Michael Faraday, [1791年9月22日](#) - [1867年8月25日](#))



$Q = 1 \text{ mC}$, $n = 1$ なら

$$m = \frac{1 \times 10^{-3}}{96485} = 1.0364 \times 10^{-8} \text{ mol}$$

試料溶液が50 mLであったなら、 Ox の濃度は

$$2.0728 \times 10^{-7} \text{ mol dm}^{-3} = 0.20728 \text{ } \mu\text{mol dm}^{-3}$$

かなり低濃度

したがってクーロメトリーは高感度

クーロメトリーの特徴

高感度

容易に測定できる

$$1 \text{ mC} = 1 \times 10^{-3} \text{ C} = 1 \text{ mA} \times 1 \text{ s} = 1 \mu\text{A} \times 1000 \text{ s}$$

ただし、



反応はこれのみ、でない

「これのみ」を実現するには

1. 溶液中には目的のRedox種のみ

一定の電流を流せばよい： 測定が簡単（機器が単純）

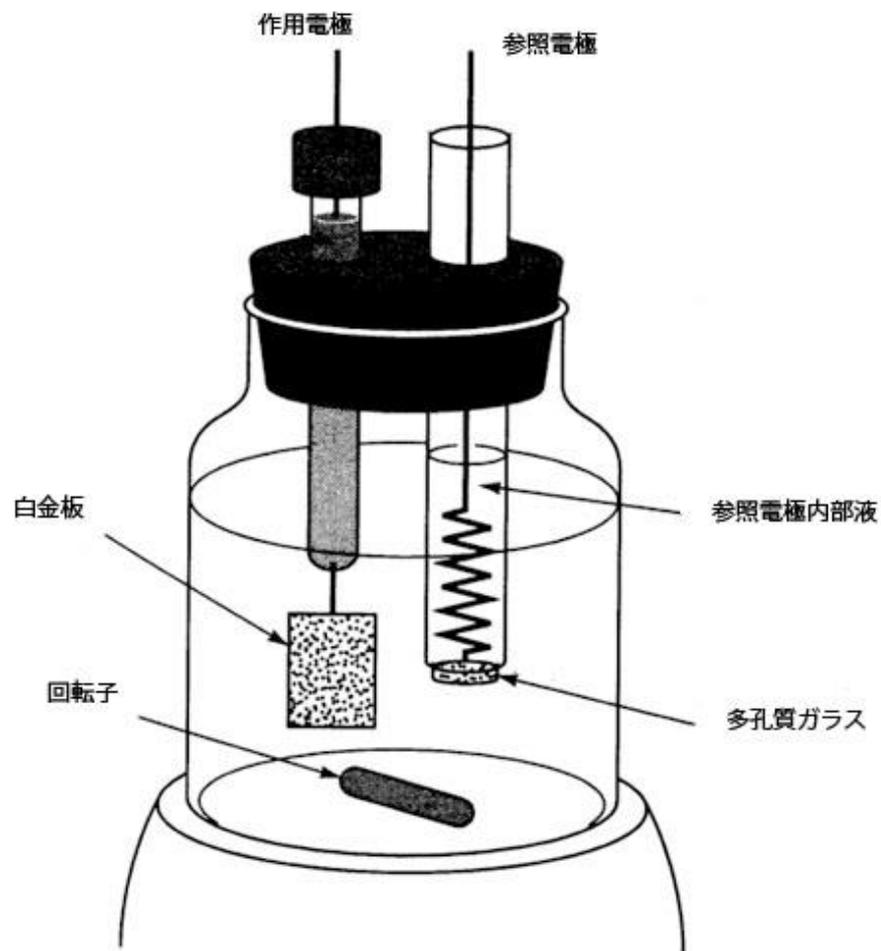
定電流クーロメトリー

2. 溶液中には複数のRedox種が存在

電圧（電極電位）を、目的のredox のみが起きる値に設定

定電位クーロメトリー

標準電極電位付近より正の（還元）あるいは負の（酸化） E^0 を持つ物質が共存すると、使えない



溶液中の全ての酸化体
(還元体)を電解してし
まう



これは、結構、たいへん

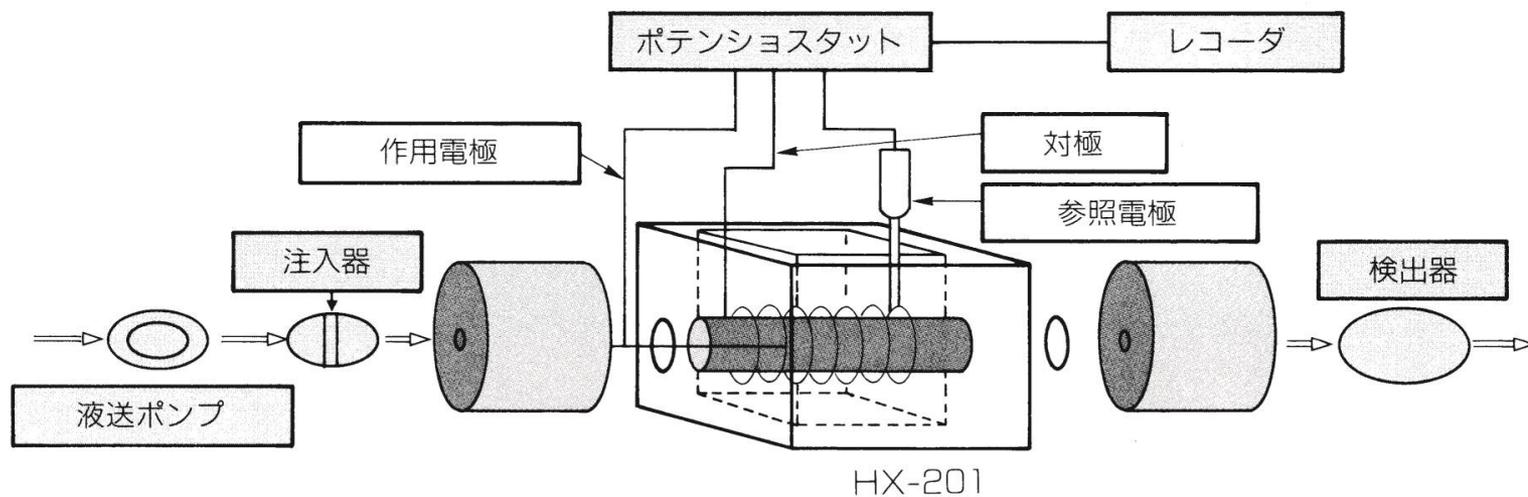
時間がかかる

「すべて電解してしまう」のバリエーション

発想の転換

フロークーロメトリー (Flow coulometry)

【HX-201 構成図】



HX-201 & HX-301



	HX-201	HX-301
容量	カラム型(2mℓ)	カラム型(1mℓ)
構成	作用極	バイコールガラス管／カーボン繊維
	対極	白金線(Φ0.3×300)
	参照電極	HX-R5

本カラムフロー電解セルは、京都大学 藤永太一郎博士他が開発された技術に基づいております。

カラムを二つ、つなぐ

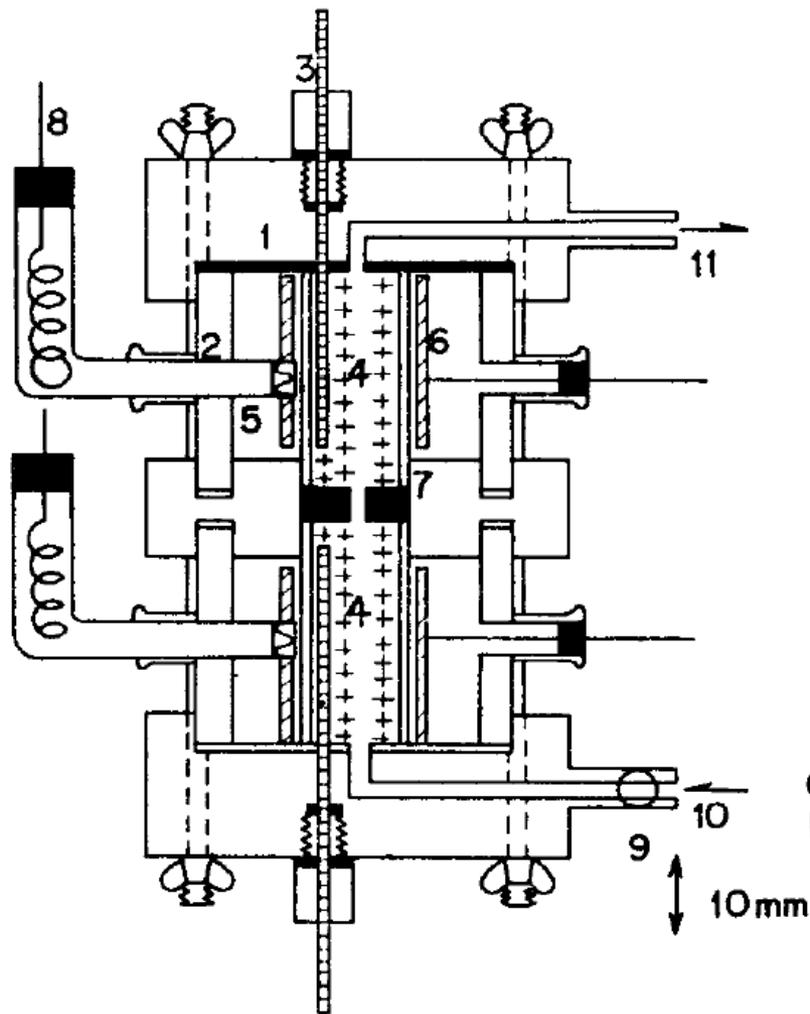


FIG. 1.—Electrolytic cell.

- (1) Teflon
- (2) Glass cylinder
- (3) Glassy carbon lead
- (4) Glassy carbon grains (working electrode)
- (5) Saturated KCl solution
- (6) Glassy carbon cylinder (counter electrode)
- (7) Porcelain cylinder
- (8) Ag-AgCl reference electrode
- (9) Sample inlet
- (10) Supporting electrolyte inlet
- (11) Supporting electrolyte outlet
- Silicone rubber.

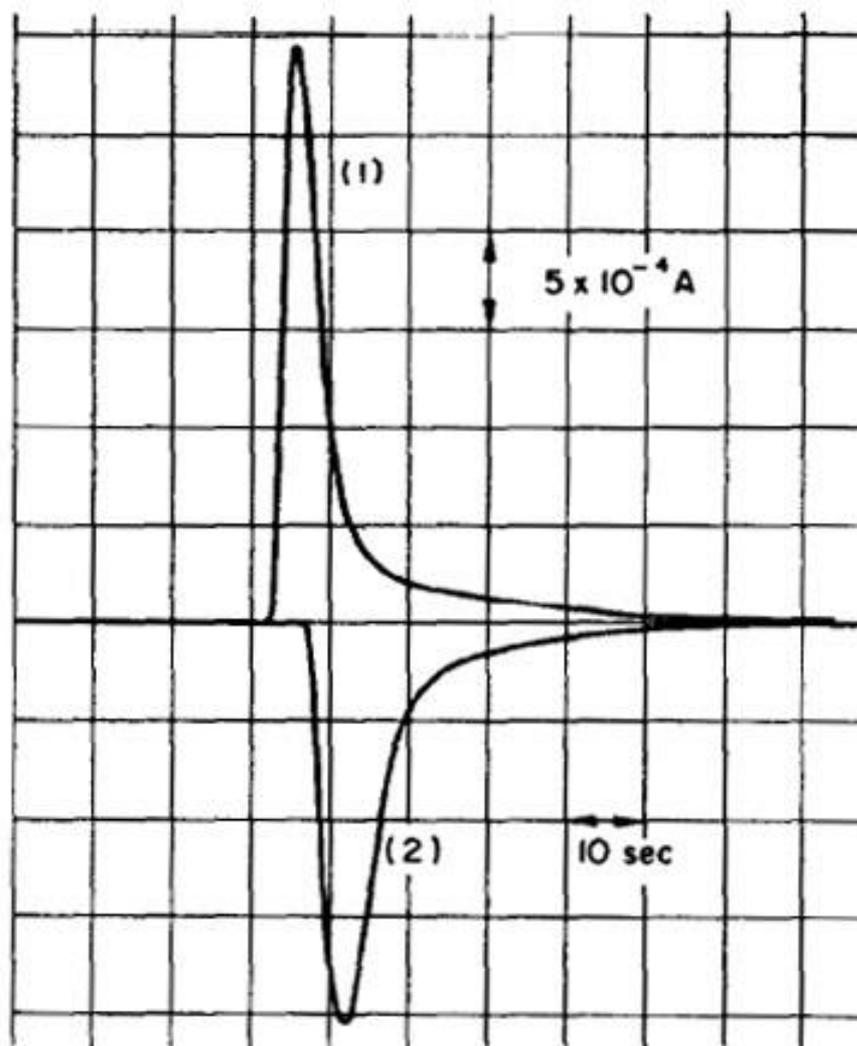


FIG. 3a.—Current-time curve recorded with $10 \mu\text{l}$ of $2.0 \times 10^{-3} \text{ M Fe(III)}$.
Electrolyte: $0.5 \text{ M H}_2\text{SO}_4$.
Flow-rate: 5 ml/min .

電氣量—電位曲線

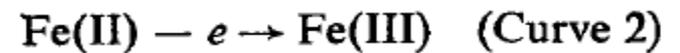
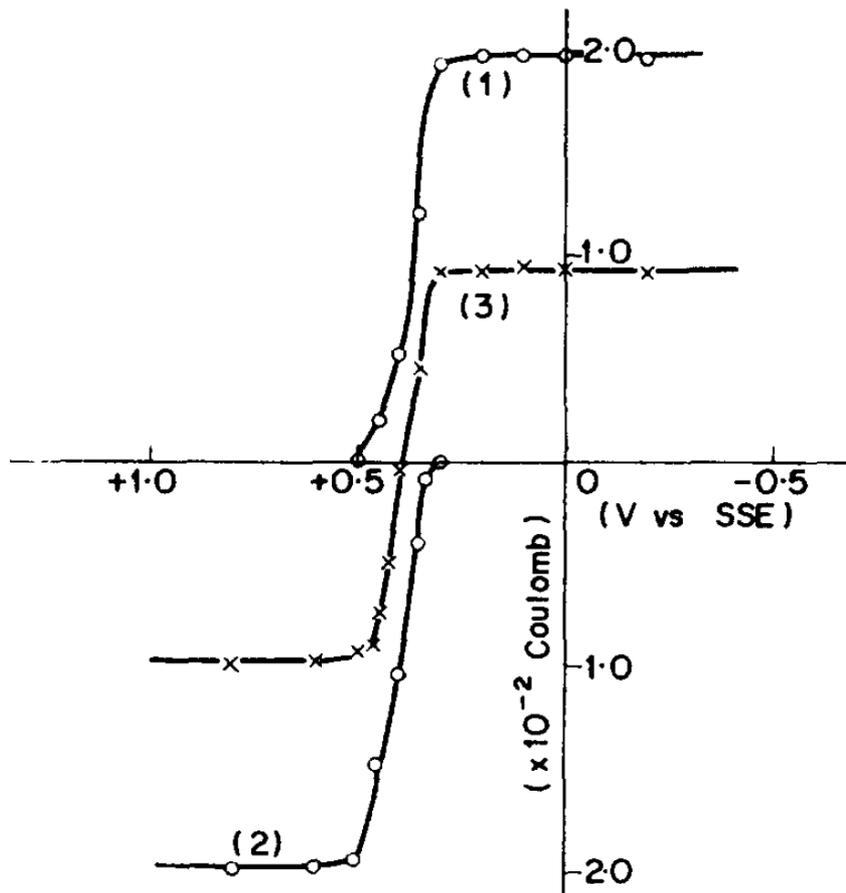


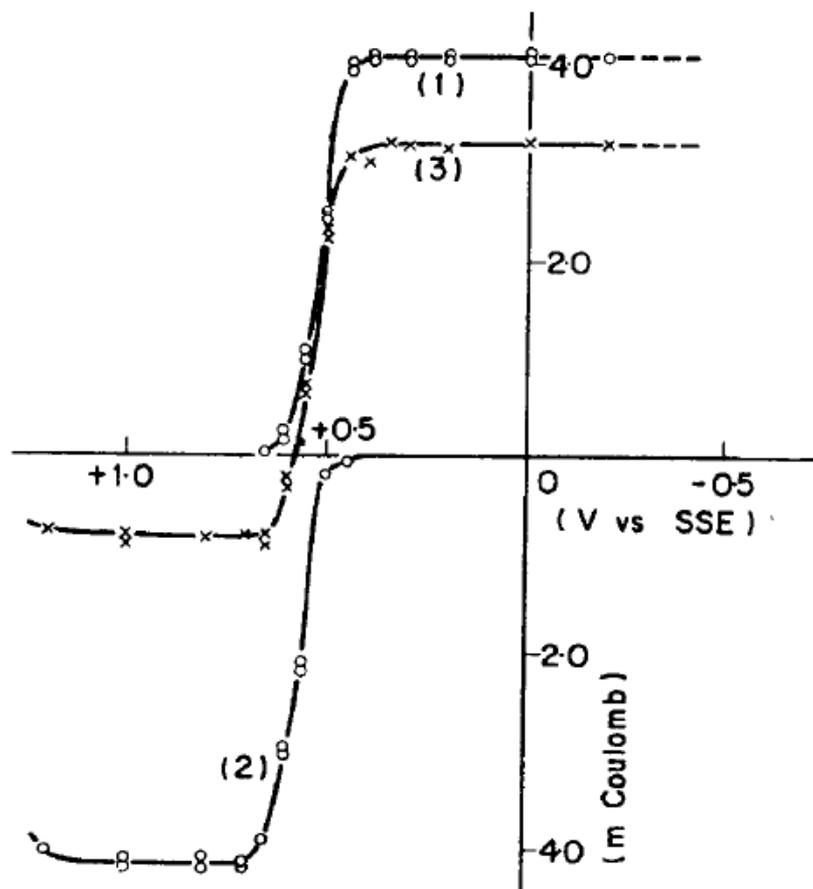
FIG. 2.—Coulomb-potential curves of iron.

Sample: (1) 2×10^{-7} mole Fe^{3+} , (2) 2×10^{-7} mole Fe^{2+} , (3) 0.94×10^{-7} mole Fe^{3+} ,
 1.06×10^{-7} mole Fe^{2+} .

Electrolyte: $0.5M \text{H}_2\text{SO}_4$.

Flow-rate: 5 ml/min.

電氣量—電位曲線



$$E_1 = +0.75\text{V}$$



$$E_2 = +0.10\text{V}$$

FIG. 5.—Coulomb-potential curves of plutonium.

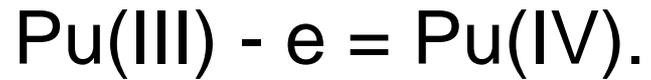
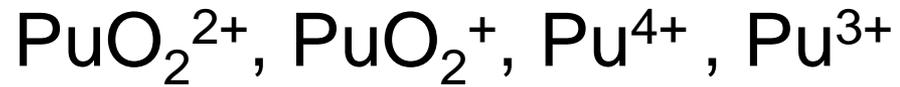
Sample: 4.18×10^{-8} mole Pu.

Electrolyte: $0.5M \text{H}_2\text{SO}_4$.

(1) $\text{Pu(IV)} + e = \text{Pu(III)}$.

(2) $\text{Pu(III)} - e = \text{Pu(IV)}$.

(3) Mixture of Pu(III) and Pu(IV).



Pu (isotopic composition; ^{239}Pu 91.3, ^{240}Pu 7.81, ^{241}Pu 0.85, and ^{242}Pu 0.04 atom %) was dissolved in 0.5M sulphuric acid



TABLE I.—DETERMINATION OF PLUTONIUM

Pu taken	<i>mmole</i> taken	Coulombs, calculated	Coulombs, found	Pu found, %
1.03 mg/ml 50 μ l	215	2.08×10^{-2}	2.04×10^{-2}	98.1
			2.07	99.5
			2.06	99.0
			2.01	96.7
			2.04	98.1
515 μ g/ml 50 μ l	108	1.04×10^{-2}	1.05×10^{-2}	100.9
			1.03	99.0
			1.03	99.0
			1.04	99.6
			1.05	100.9
51.5 μ g/ml 50 μ l	10.8	1.04×10^{-3}	1.07×10^{-3}	102.8
			1.04	99.6
			1.05	100.9
			1.03	98.9
			1.05	100.9
10.3 μ g/ml 50 μ l	2.2	2.08×10^{-4}	2.20×10^{-4}	105.9
			2.07	99.6
			2.02	97.1
			2.15	103.5
			2.05	98.5
5.0 μ g/ml 20 μ l	0.42	4.02×10^{-5}	3.97×10^{-5}	98.7
			3.94	98.0
			4.07	101.1
			3.93	97.8
			3.92	97.5

Potentials; first column +0.35 V *vs.* SSE, second column +0.75 V *vs.* SSE.
 Electrolyte; 0.5M H₂SO₄.
 Flow-rate; 5 ml/min.

我が国のプルトニウム管理状況

平成24年9月11日
内閣府
原子力政策担当室

(2) 海外に保管中の分離プルトニウム量(注1)

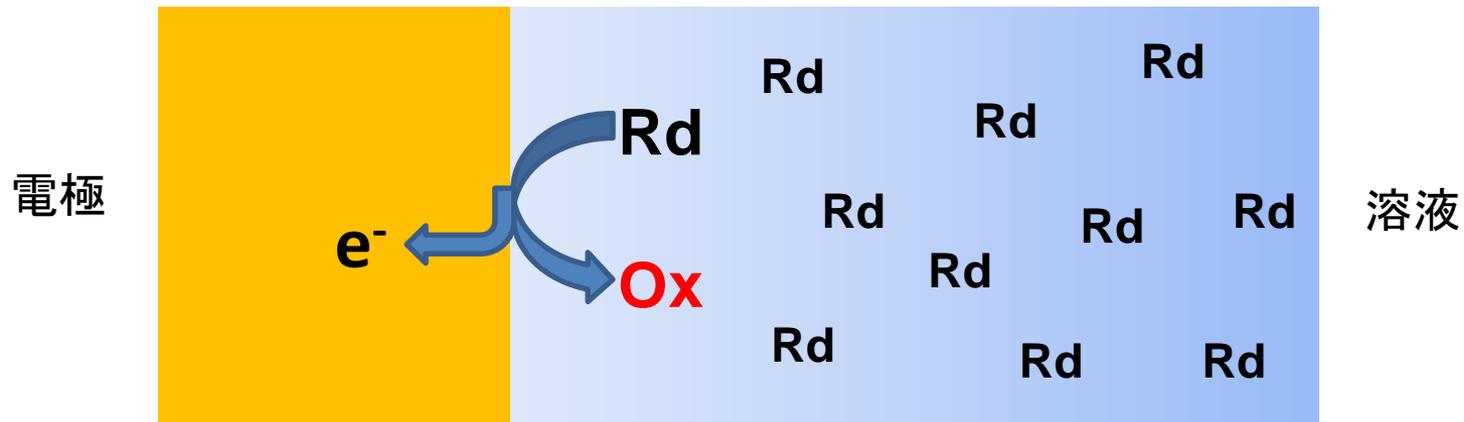
(基本的に海外でMOX燃料に加工して我が国の軽水炉で利用予定)

保管国	分離プルトニウム量	
		うち、核分裂性プルトニウム量
英国での回収分	17,028 (17,055)	11,616 (11,643)
仏国での回収分	17,931 (17,970)	11,692 (11,730)
合計	34,959 (35,025)	23,308 (23,373)

電量滴定法

Coulometric titration

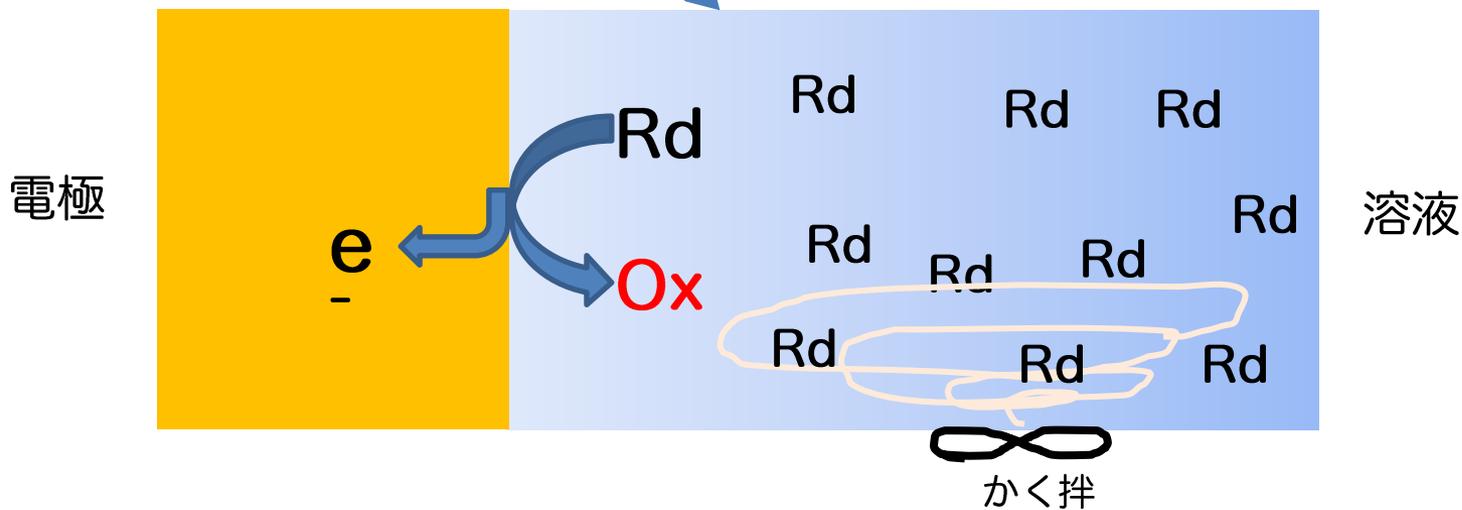
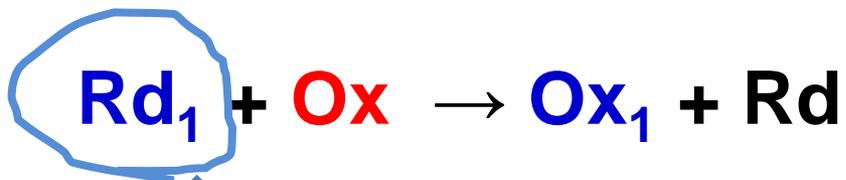
クーロメトリーの重要な応用



Ox は、流した電流分だけしか出来ない



Ox を高い精度で定量的に作り出すことが出来る

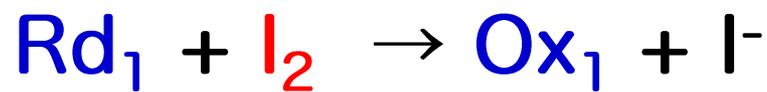
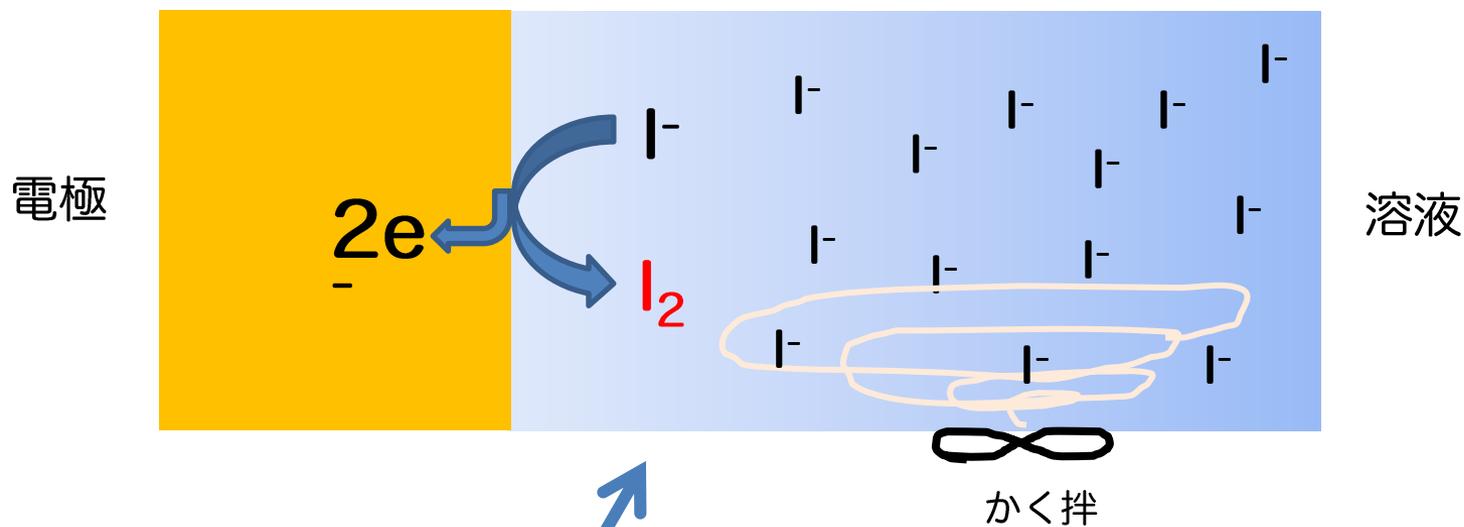


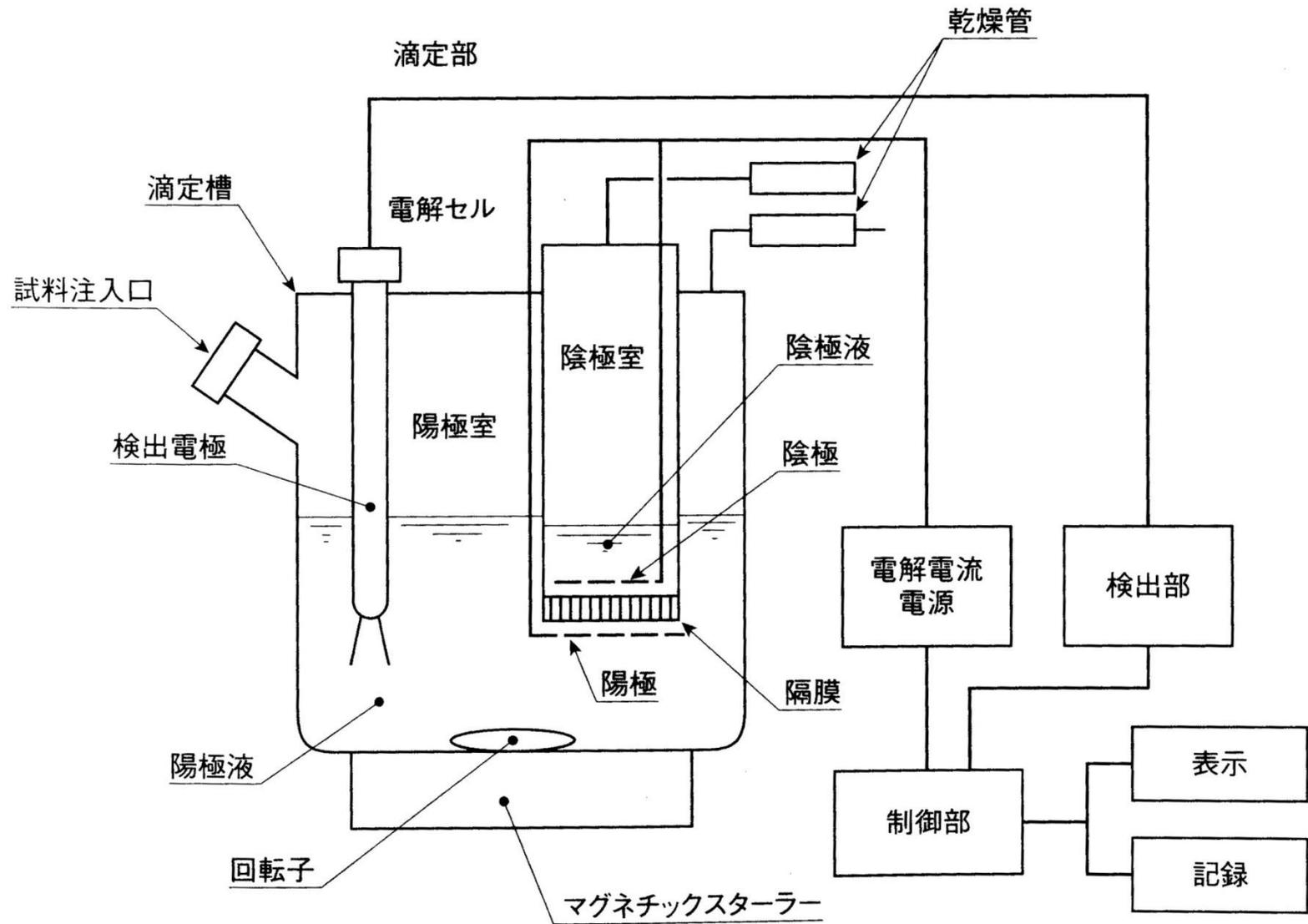
$$\text{Ox の消費量} = \text{使われた電気量} = \text{Rd}_1 \text{ の存在量}$$

正確にわかる



$$E_0 = 0.54 \text{ V}$$





K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

ROH : メタノール



Methoxy-2-propanol
2-(2-ethoxyethoxy)ethanol
など

B : ピリジン



Imidazole
Diethanolamine
など

ビュレットに入れ、滴定



電量滴定

カールフィッシャー	数 ppm ~ 100 %
比色法	0.1 ~ 数 %
IR	0.01 ~ 数 %
ガスクロマトグラフィー	数 ppm ~ 数 %
電気抵抗	0.3 ~ 数 %
比誘電率	1 ~ 数 %

表 1: 種々の水分測定法の測定範囲

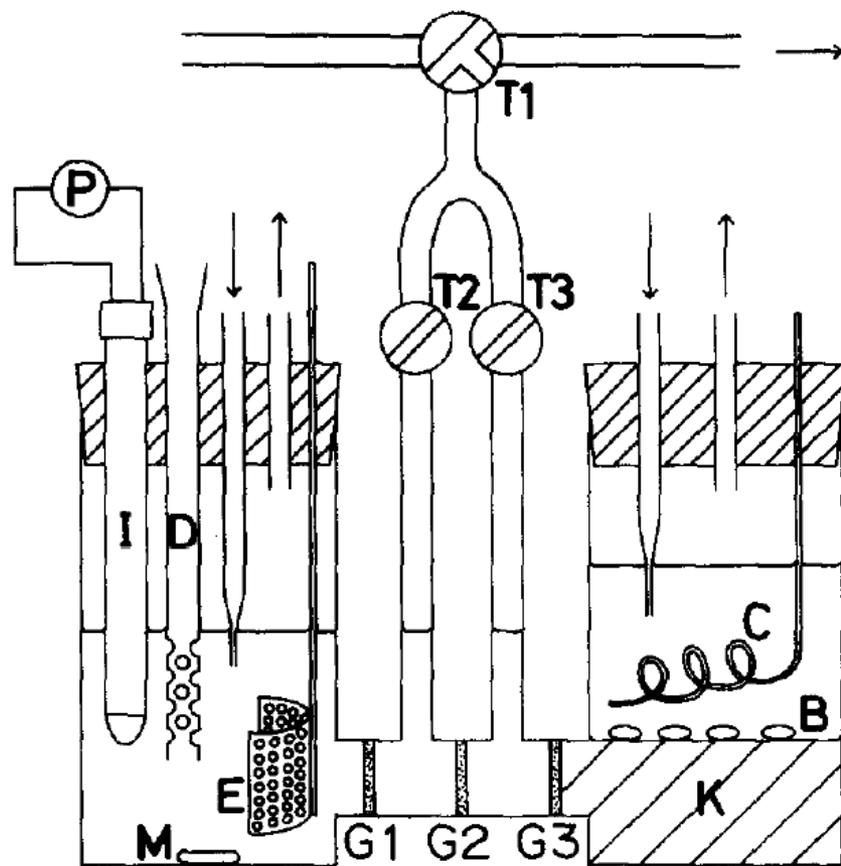
カールフィッシャー法は、水分含量測定の公定法である。

1. 日本工業規格（J I S）
2. 日本薬局方第13改正 一般試験法 27. 水分試験法
3. 第4版食品添加物公定書解説書 一般試験法 12. 水分定量法
4. 石油学会規格
5. 日本L P ガス協会規格
6. 日本農林規格（J A S）
7. 国際規格（I S O : International Organization for Standardization）
8. その他（A S T M : American Society for Testing Materials; B S : British Standard ; D I N : Deutsches Institut für Normung の定める Industrie Normen ）

もっとも精密な酸塩基滴定



もっとも正確な濃度の決定法



Sulfamic acid 水溶液の正確な
滴定

“The precision and accuracy
obtained were 0.01 %.”

A. Hioki, A. Kokubun, M. Kubota,
Analyst, **119**, 1879- 1882 (1994).

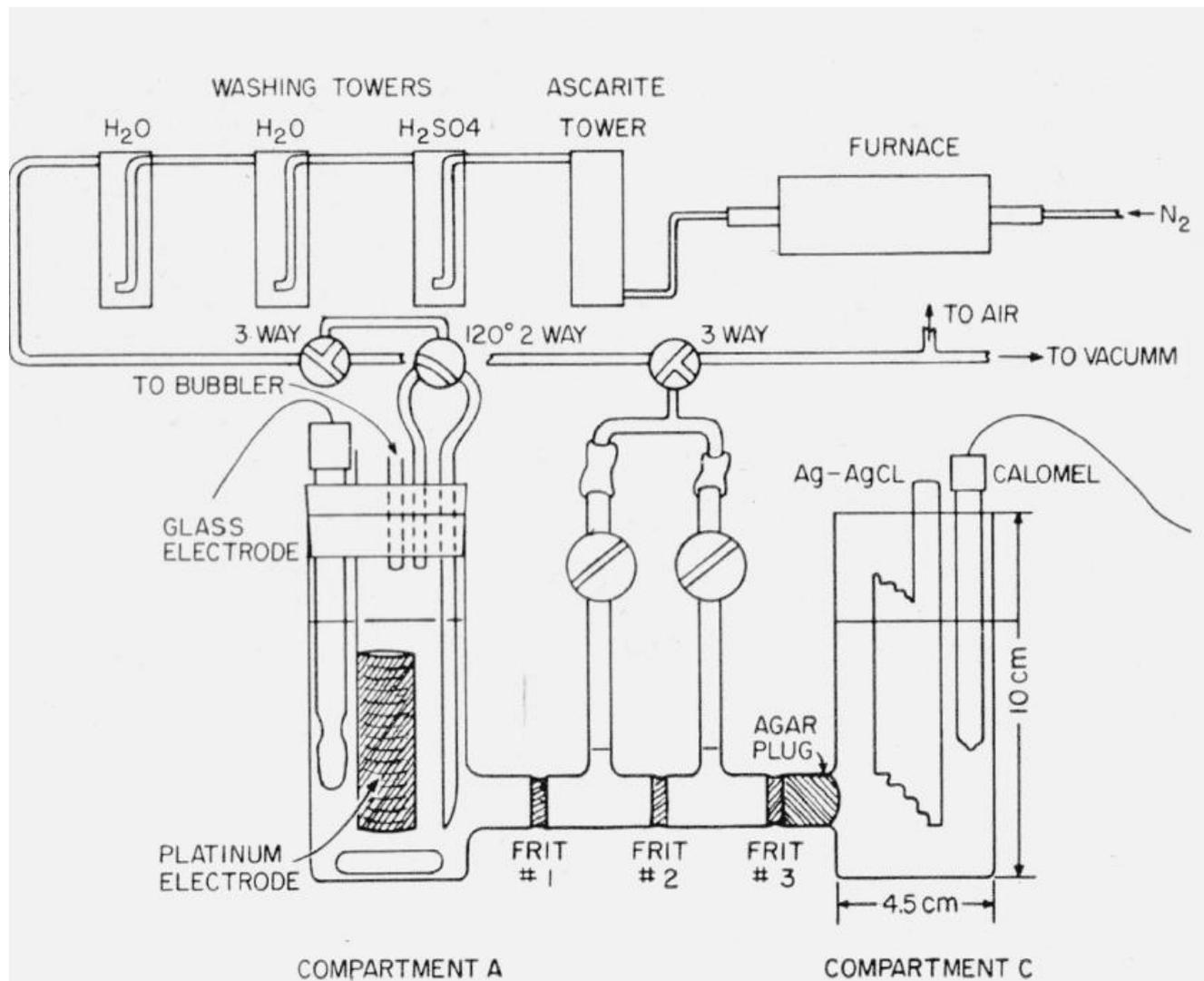


FIGURE 2. *Coulometric cell and associated apparatus.*

もっと別のアイデアは？

カーボンフェルト

内山俊一
(埼玉工業大学 学長)

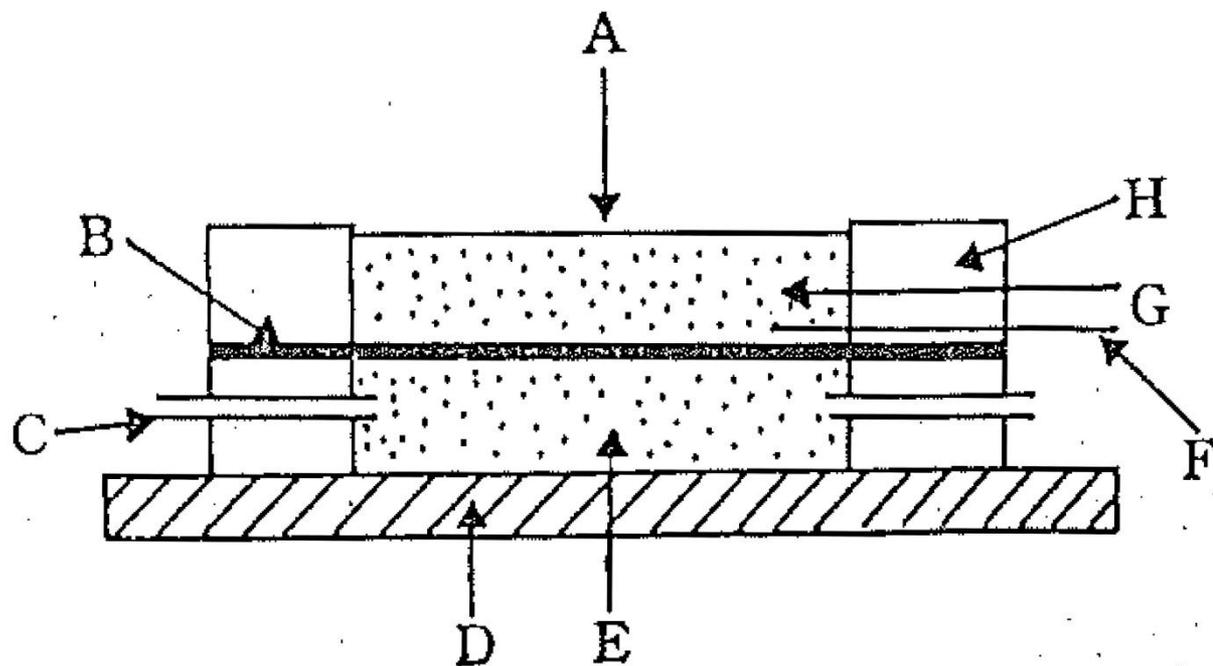


図 4-2 迅速クーロメトリックセル断面図の例。
 A : 試料添加, B : ナフイオン膜, C : 対極液交換用
 テフロンチューブ, D : カーボン板, E : 対極室用カ
 ーボンフェルト, F : 白金リード線, G : 電解質を含
 んだカーボンフェルト電極, H : アクリル板 (文献 24
 より改変).

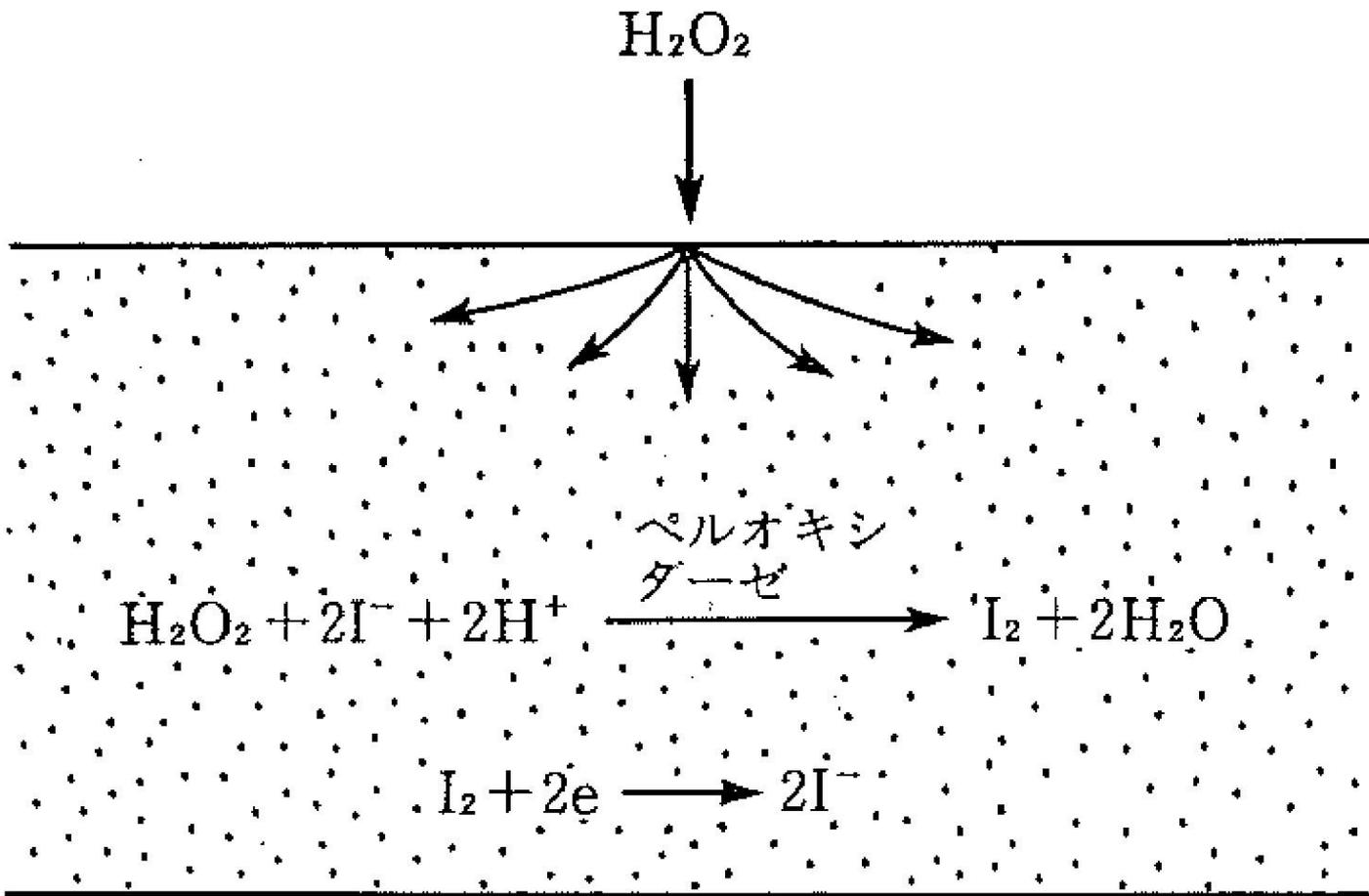
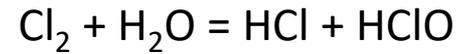
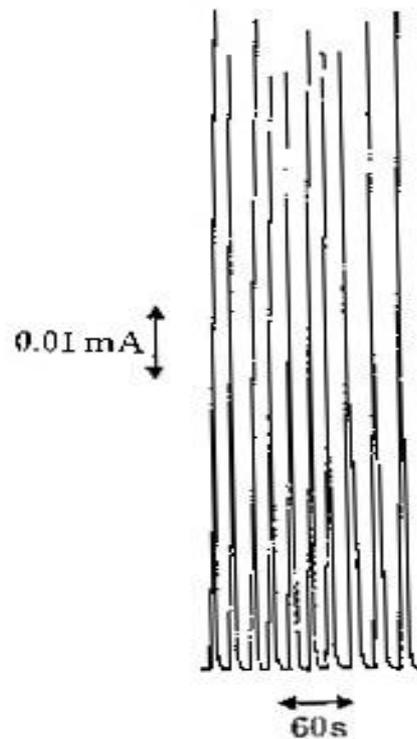


図 4-3 過酸化水素測定時に作用電極内で生じる反応.

バイオセンサーへの展開



$$K = 1.56 \times 10^{-4}$$

次亜塩素酸イオンと水道水中の残留塩素の測定結果

試料	電気量 (μC)	クーロメトリー			オルトトリジン法
		相対標準偏差 (%)	濃度 (ppm)	電解時間 (秒)	濃度 (ppm)
次亜塩素酸イオン	98.0	1.6	0.72	15	0.7
残留塩素					
A	85.3	2.2	0.63	16	0.6
B	53.8	1.8	0.35	15	0.3
C	83.3	1.5	0.61	15	0.6

15 回測定の平均値.

電気分析化学：電気化学の基礎

最近の特徴

電気化学の分析化学への応用

電気分析化学の大きな特徴として

1. 小型化できる
微量
2. 安価
使い捨て

Electrochemistry in Diabetes Management

ADAM HELLER*

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BEN FELDMAN

Abbott Diabetes Care, 1360 South Loop Road, Alameda, California 94502

RECEIVED ON JULY 12, 2009

CONSPICUOUS

Diabetes devastates lives and burdens society. Hypoglycemic (low glucose) episodes cause black-outs, and severe ones are life-threatening. Periods of hyperglycemia (high glucose) cause circulatory disease, stroke, amputations, blindness, kidney failure and nerve degeneration. In this Account, we describe the founding of TheraSense, now a major part of Abbott Diabetes Care, and the development of two products that have improved the lives of people with diabetes. The first, a virtually painless microcoulometer (300 nL volume), the FreeStyle blood glucose monitoring system, was approved by the FDA and became available in 2000. In 2009, this system was used in more than one billion blood assays. The second, the enzyme-wiring based, subcutaneously-implanted FreeStyle Navigator continuous glucose monitoring system, was approved by the FDA and became available in the United States in 2008.





FreeStyle



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FreeStyle Lite Blood Glucose Monitoring System

Small and discreet. FreeStyle Lite.



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Write a review

Overview

Features

Resources

Now it's easy to manage your diabetes on-the-go. The small, discreet FreeStyle Lite system offers big advantages. There's no coding needed and this meter requires the smallest blood sample size.¹ Plus, it has a convenient backlight and test strip port light, so you can test anytime.



FAQs



Owner's Guide



Where to Buy



click and drag to view features



FreeStyle Lite Blood Glucose Monitoring System >



For In Vitro Diagnostic Use



FreeStyle Freedom Lite Blood Glucose Monitoring System >



For In Vitro Diagnostic Use



FreeStyle Lite Blood Glucose Test Strips >



For In Vitro Diagnostic Use



FreeStyle InsuLinx Blood Glucose Monitoring System >



For In Vitro Diagnostic Use



FreeStyle InsuLinx Blood Glucose Test Strips >



For In Vitro Diagnostic Use



FreeStyle Precision Insulin Syringes >





FREESTYLE FREEDOM LITE BLOOD GLUCOSE MONITORING KIT RETAIL

Quantity (1 MIS EA)
 Order # 99073070914
 Mfg # 70914
 Mfg Name ABBOTT DIA
 HCPCS Cd E0607 - Blood glucose monitor home

Compare to Other Glucose Meters

BLN Preferred

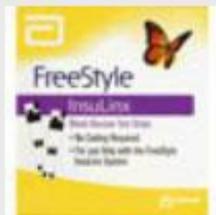
Over-the-Counter

Qty	Retail	You Pay
1 MIS	\$27.75	\$19.43

Login for Best Price

Info

Add to Cart



FREESTYLE INSULINX BLOODGLUCOSE TEST STRIPS, 100/B, RETAIL

Quantity (1 TES EA)
 Order # 99073071227
 Mfg # 71227
 Mfg Name ABBOTT DIA
 HCPCS Cd A4253 - Blood glucose/reagent strips

BLN Preferred

Over-the-Counter

Qty	Retail	You Pay
1 TES	\$295.32	\$206.72

Login for Best Price

Info

Add to Cart

着用できるセンサー (Wearable sensors)

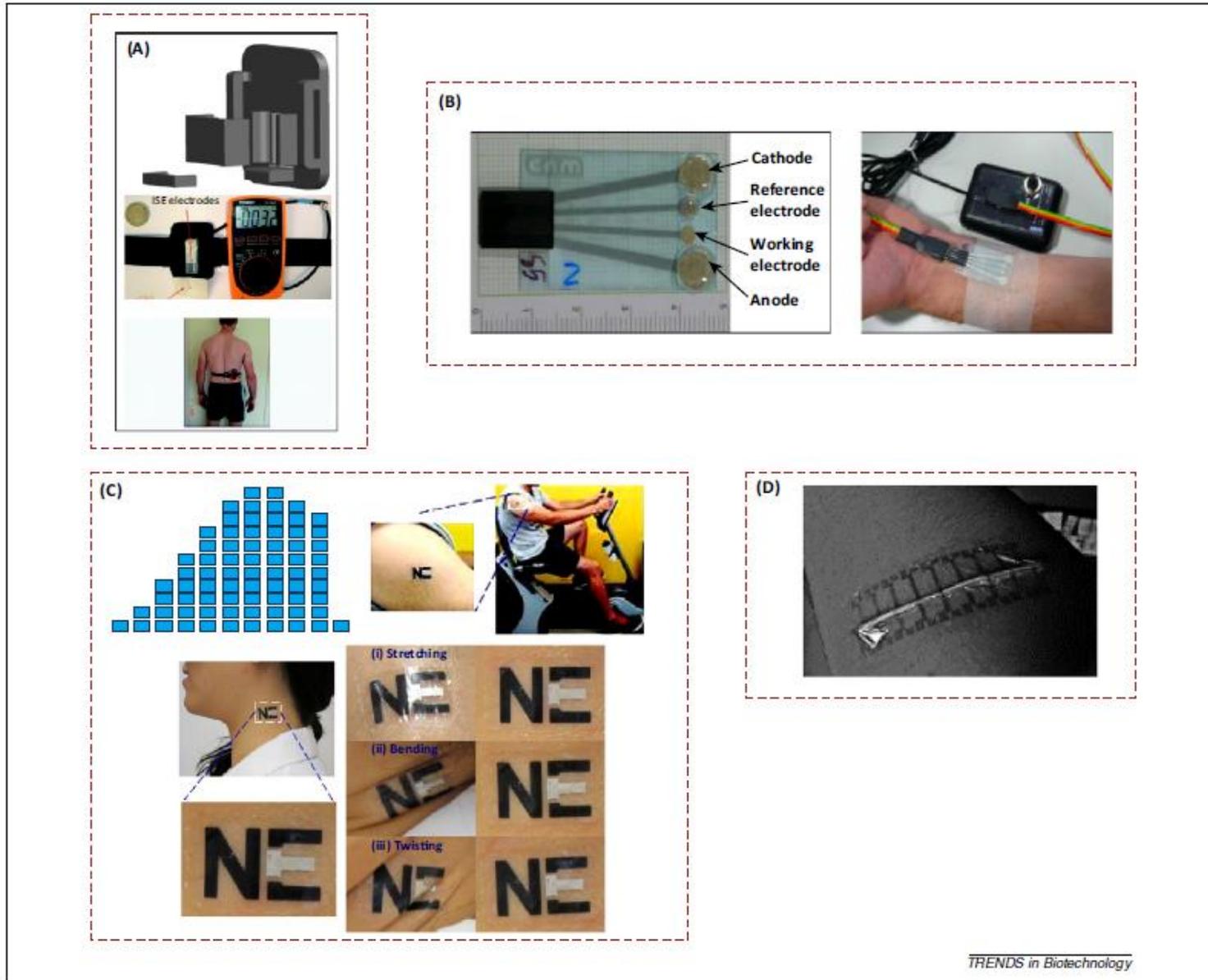


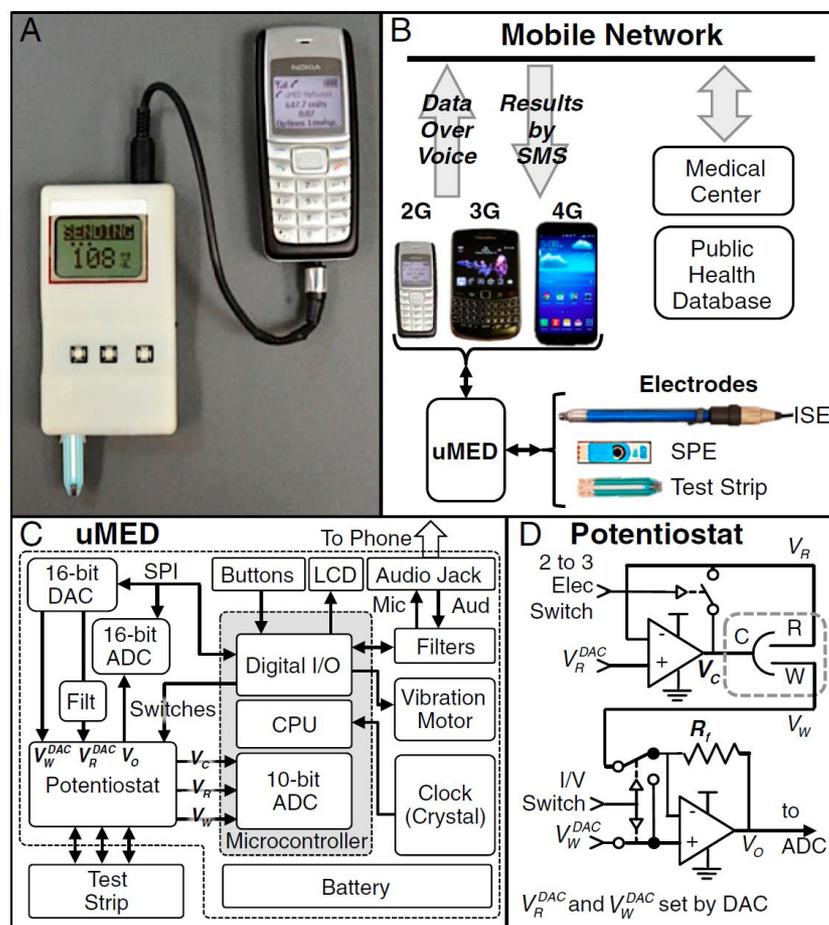
Figure 3. Sweat-based electrochemical sensors. (A) A wearable potentiometric sodium sensor worn by a subject [43]. (B) A flexible plastic-based sweat chloride sensor system consisting of the ion-selective electrodes for chloride sensing and iontophoretic electrodes for initiating chemically induced sweating [45]. (C) A participant on the stationary cycle wearing a lactate tattoo biosensor and the exercise intensity mode followed during continuous on-body lactate monitoring study. The tattoo sensor is resilient against repeated strains when applied to the neck of a subject [50]. (D) A skin patch-based electrochemical organic transistor for continuous lactate monitoring in human sweat [54].

TRENDS in Biotechnology

Universal mobile electrochemical detector designed for use in resource-limited applications

Alex Nemiroski^a, Dionysios C. Christodouleas^a, Jonathan W. Hennek^a, Ashok A. Kumar^b, E. Jane Maxwell^a, Maria Teresa Fernández-Abedul^c, and George M. Whitesides^{a,d,e,1}

^aDepartment of Chemistry and Chemical Biology, ^bSchool of Engineering and Applied Sciences, ^dWyss Institute for Biologically Inspired Engineering, and ^eThe Kavli Institute for Bionano Science, Harvard University, Cambridge, MA 02138; and ^cDepartamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Asturias, Spain



low-cost (~US\$ 25)

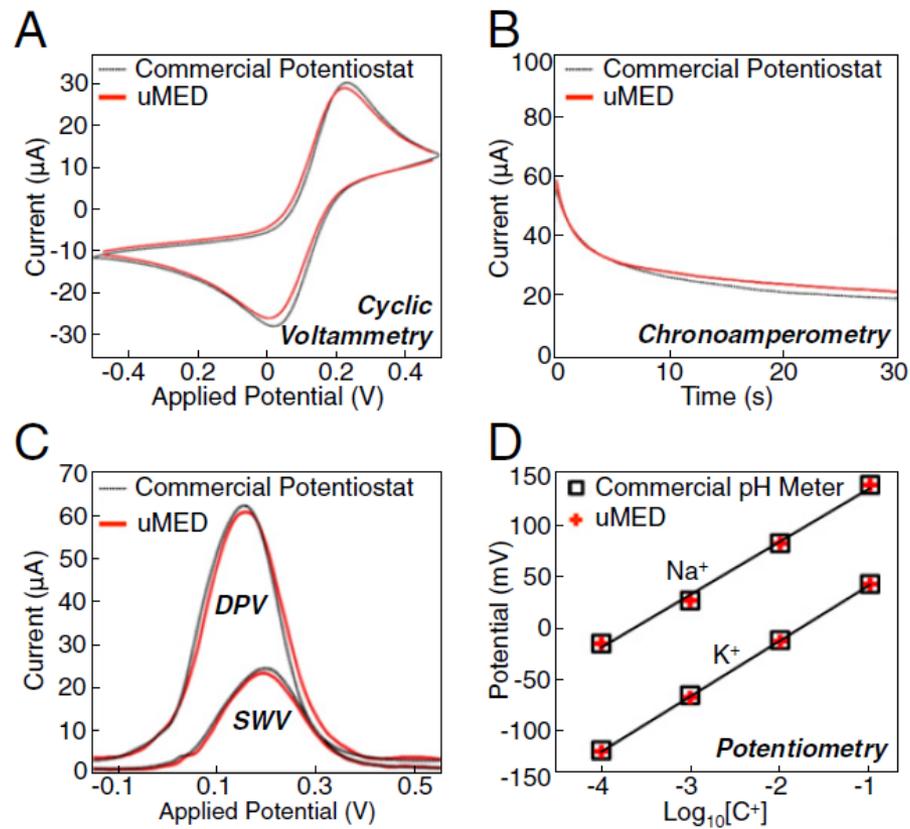
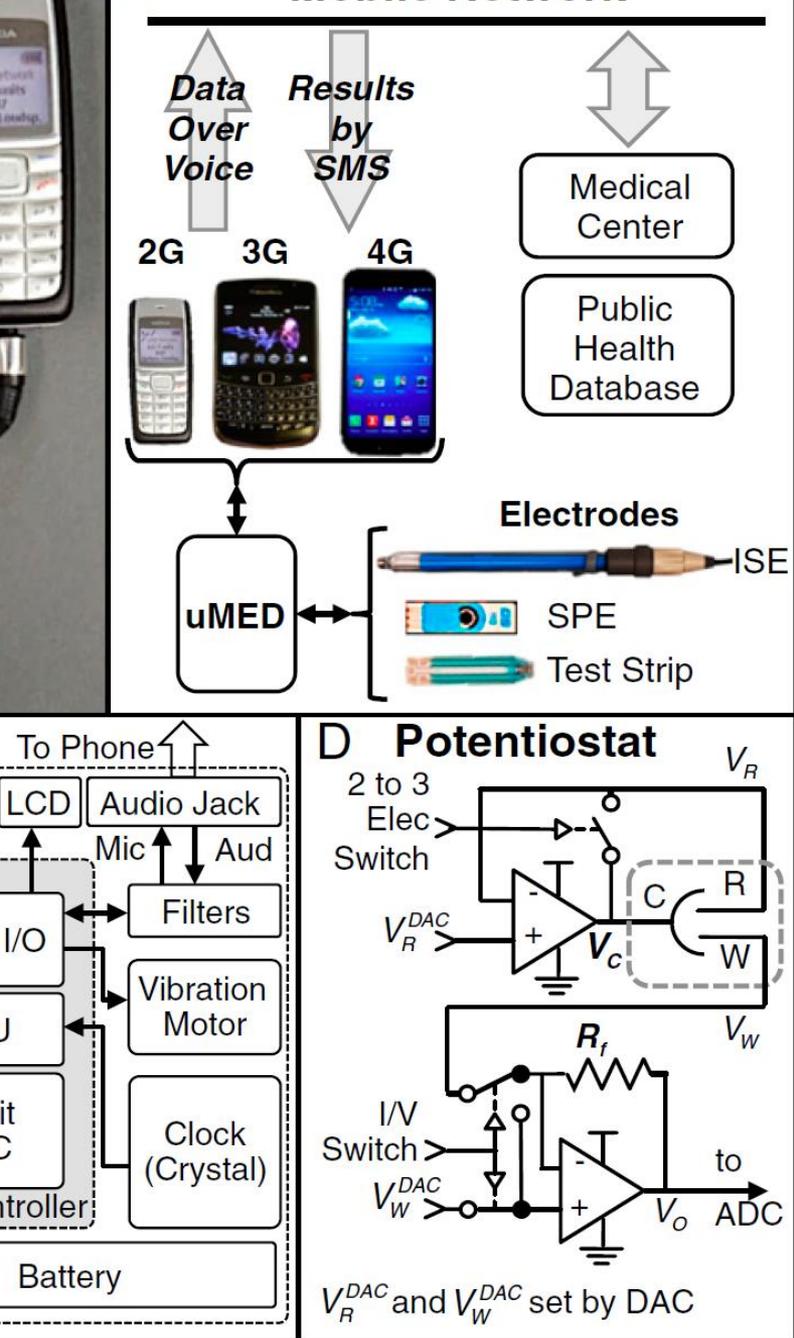


Fig. 2. (A) A cyclic voltammogram of 2.5 mM ferricyanide/ferrocyanide in 0.1 M KCl. (B) The measured current versus time for chronoamperometric detection of 1 mM ferrocyanide in 0.1 M KCl. (C) Differential pulse and square wave voltammograms of 1 mM 1-naphthol in 100 mM Tris, 100 mM NaCl. (D) Detection of $[\text{K}^+]$ and $[\text{Na}^+]$ with potentiometry in an ionic strength adjuster.

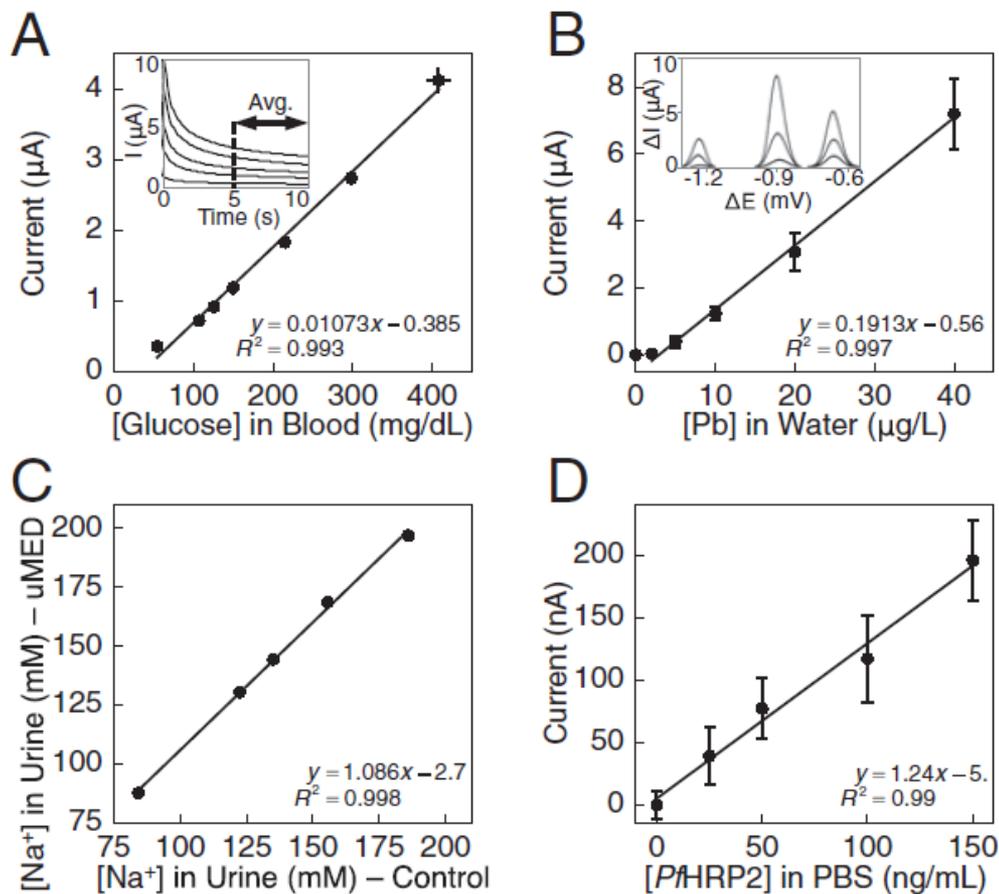


Fig. 3. (A) A calibration plot for [glucose] in assayed samples of human blood measured by chronoamperometry. (A, *Inset*) Transient current for five representative concentrations of glucose (107, 150, 215, 298, and 408 mg/dL). (B) A calibration plot for [Pb] measured by SWASV. (B, *Inset*) Square wave voltammograms for Zn, Cd, and Pb (left to right) at three concentrations (5, 10, and 20 $\mu\text{g/L}$). We performed an independent baseline correction on each peak. (C) Potentiometric measurement of [Na⁺] in assayed samples of human urine. (D) A calibration plot for [PfHRP2] in PBS (1 \times) measured by chronoamperometry. All error bars indicate SE ($n = 7$).