電気化学

垣内　隆

5. ポテンショメトリー （つづき）

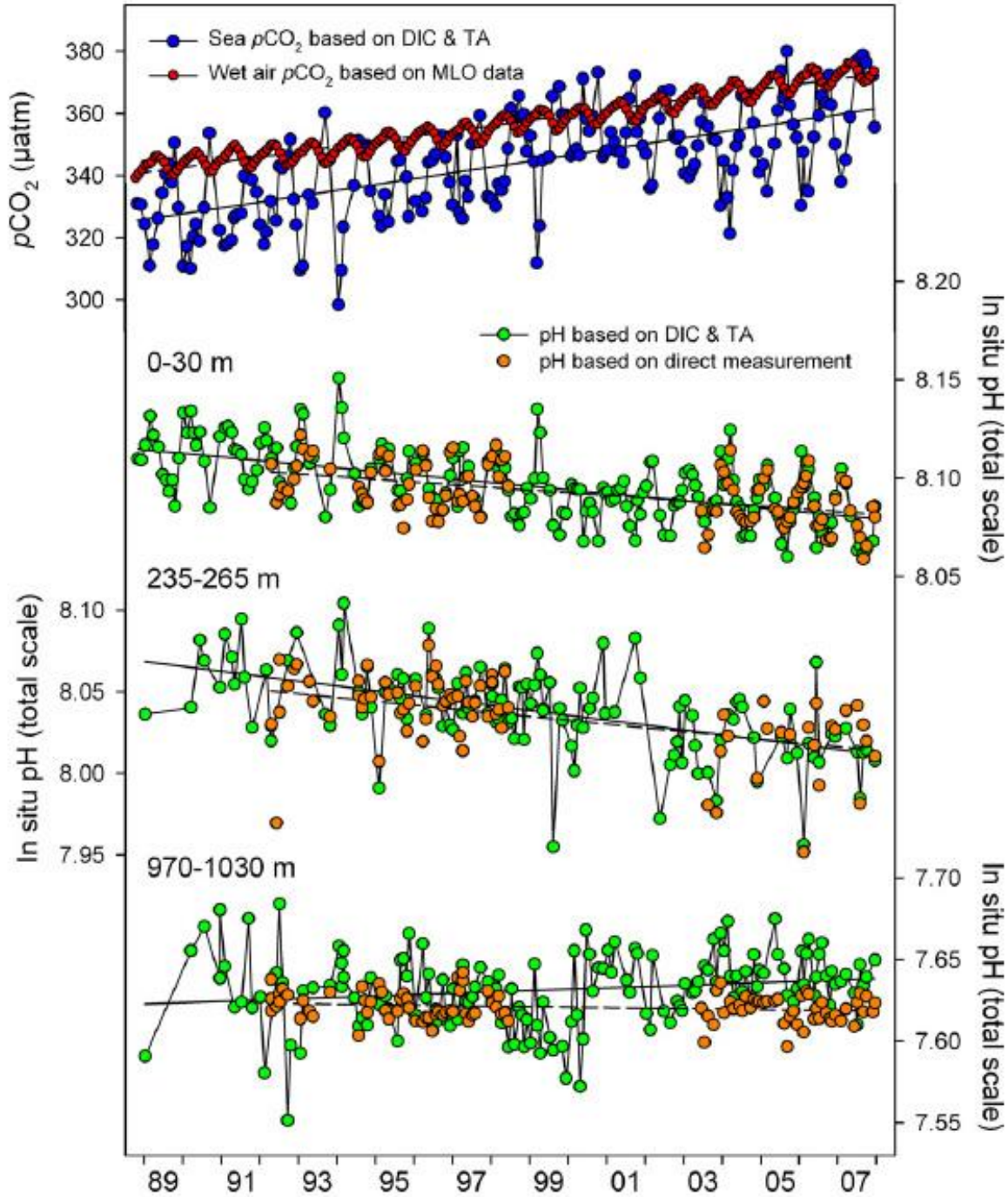
ガラス電極による pH 測定

膜電位差（相界面電位差）を利用するポテンショメトリー

- ガラス電極を用いる pH 測定法
- イオン選択性電極

実用的に広く用いられている

海水の pH



Time-series of mean carbonic acid system measurements within selected depth layers at Station ALOHA, 1988–2007. (First image) Partial pressure of CO2 in seawater calculated from DIC and TA (blue symbols) and in water-saturated air at in situ seawater temperature (red symbols). Linear regressions of the sea and air *p*CO2 values are represented by solid and dashed lines, respectively. (Second, third, and fourth images) In situ pH, based on direct measurements (orange symbols) or as calculated from DIC and TA (green symbols), in the surface layer and within layers centered at 250 and 1000 m. Linear regressions of the calculated and measured pH values are represented by solid and dashed lines, respectively.

J. E. Dore, R. Lukas, D. W. Sadler, M. J. Church, D. M. Karl, Proc. Natl. Acad. Sci, **106**, 12235-12240 (2009).

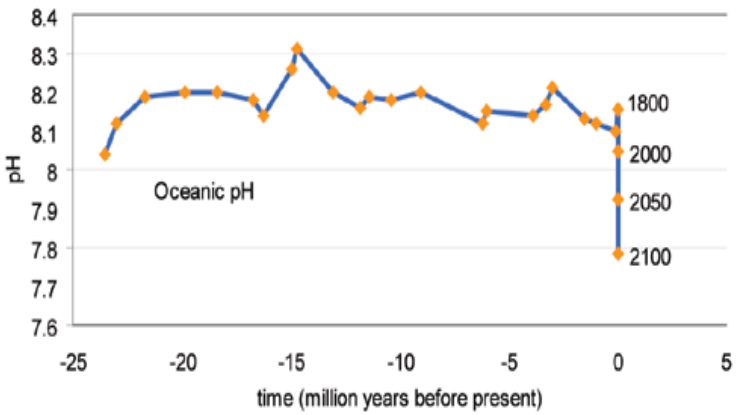
Dissolved inorganic carbon (DIC)
Total alkalinity (TA)

United Nations Conference on Sustainable Development, RIO+20
20 Jun 2012 - 22 Jun 2012
Rio de Janeiro, Brazil

RIO+20

Outcome of the Conference

The future we want



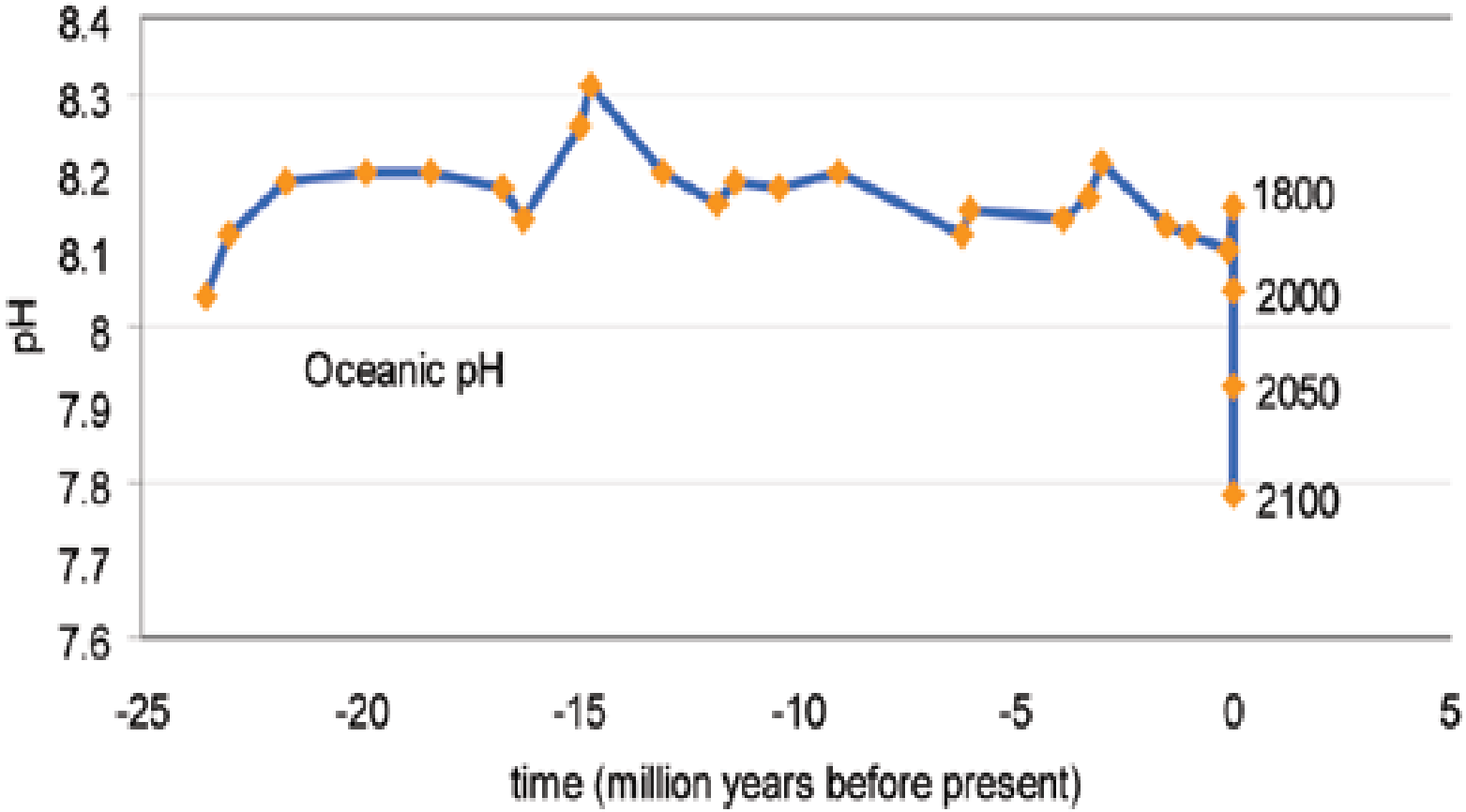
166. We call for support to **initiatives that address ocean acidification** and the impacts of climate change on marine and coastal ecosystems and resources. In this regard, we reiterate the need to work collectively to prevent further ocean acidification, as well as enhance the resilience of marine ecosystems and of the communities whose livelihoods depend on them, and to **support marine scientific research, monitoring and observation of ocean acidification** and particularly vulnerable ecosystems, including through enhanced international cooperation in this regard.

http://www.ocean-acidification.net/FAQacidity.html

What is ocean acidification? What is causing it?

The ocean absorbs approximately 1/3rd of the CO2 emitted to the atmosphere from the burning of fossil fuels (1). However, this valuable service comes at a steep ecological cost - the acidification of the ocean. As CO2 dissolves in seawater, the pH of the water decreases, which is called "acidification".

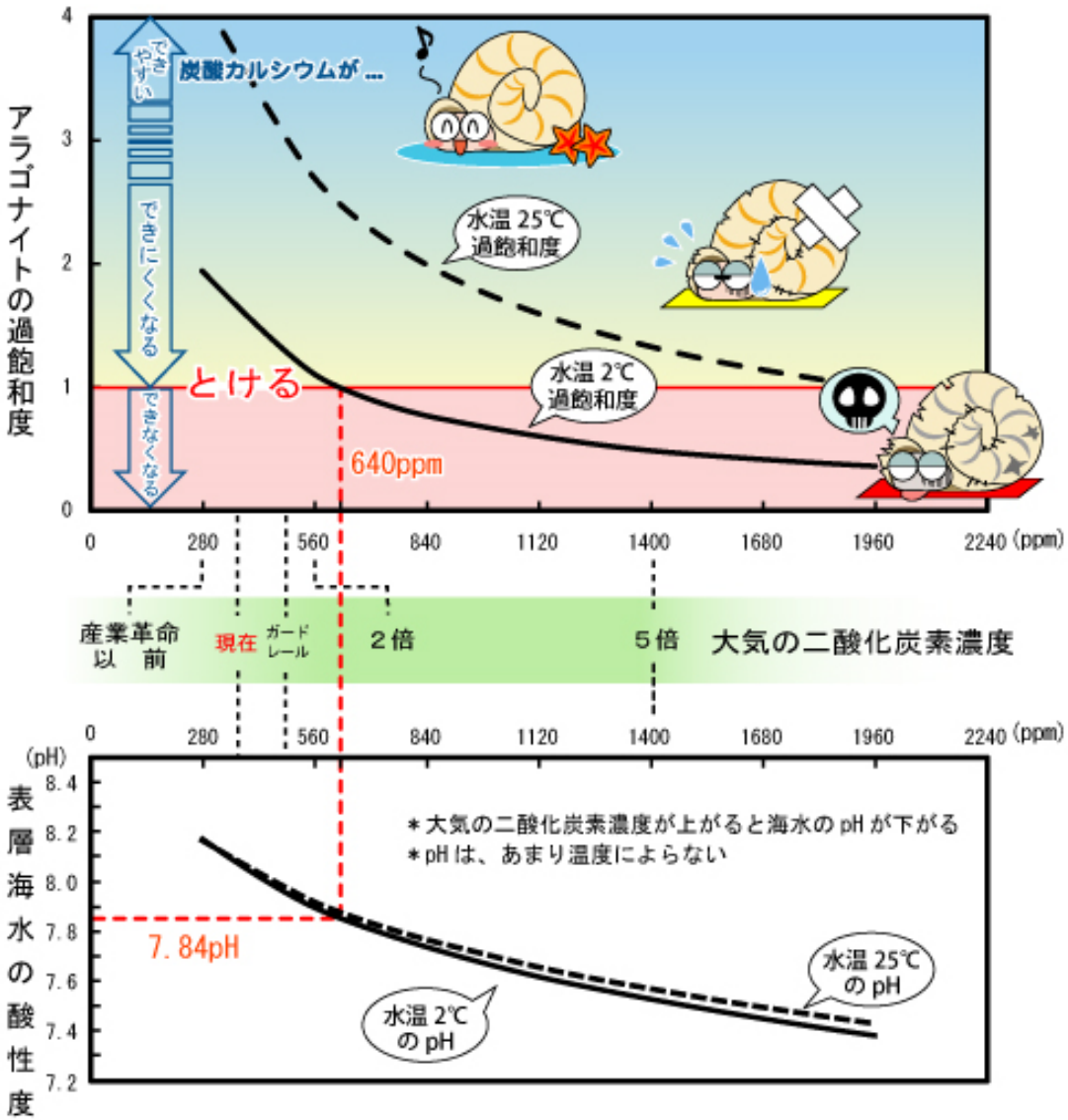
Since the beginning of the industrial revolution, ocean pH has dropped globally by approximately 0.1 pH units.



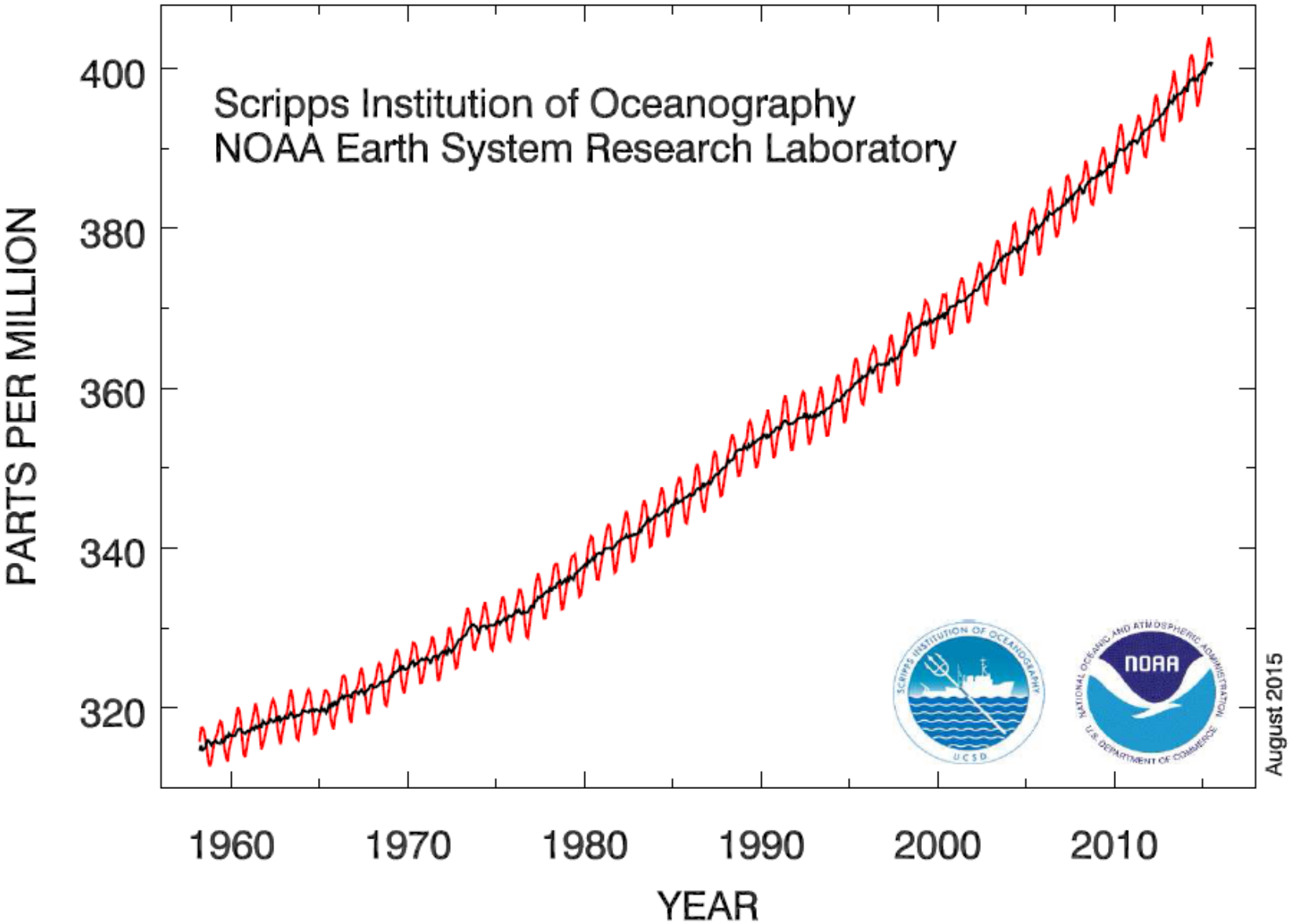
http://www.cger.nies.go.jp/ja/library/qa/6/6-1/qa_6-1-j.html

地球環境研究センター
副センター長
野尻 幸宏

図1　大気CO_2濃度が高くなるとアラゴナイト（あられ石型$CaCO_3$）ができなくなる？



ハワイ島　マウナ・ロア山頂の炭酸ガス濃度の経年変化



ハワイ島　マウナ・ロア山頂の炭酸ガス濃度の経年変化（黒線は年平均、赤線は季節変動も含めた変化）
データの出所 Scripps Institute of Oceanography/ NOAA Earth System Research Laboratory

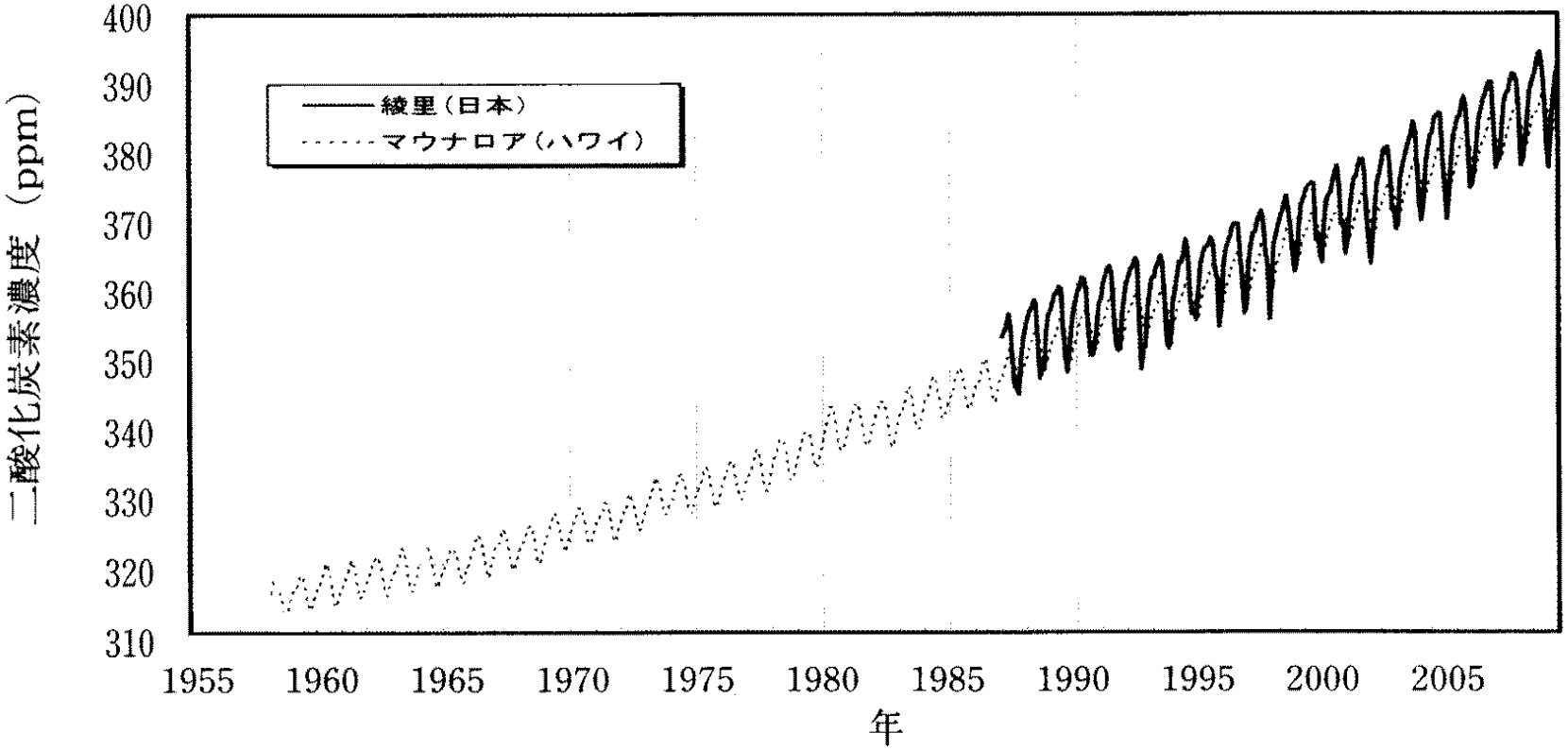


図２　日本およびマウナロア（ハワイ）の大気中二酸化炭素濃度

日本の大気環境観測所*(綾里(りょうり))，マウナロア（ハワイ）の二酸化炭素（CO_2）の月平均濃度（ppm）の変化.

世界気象機関（WMO）温室効果ガス世界資料センター（WDCGG）および米国二酸化炭素情報解析センターによる.

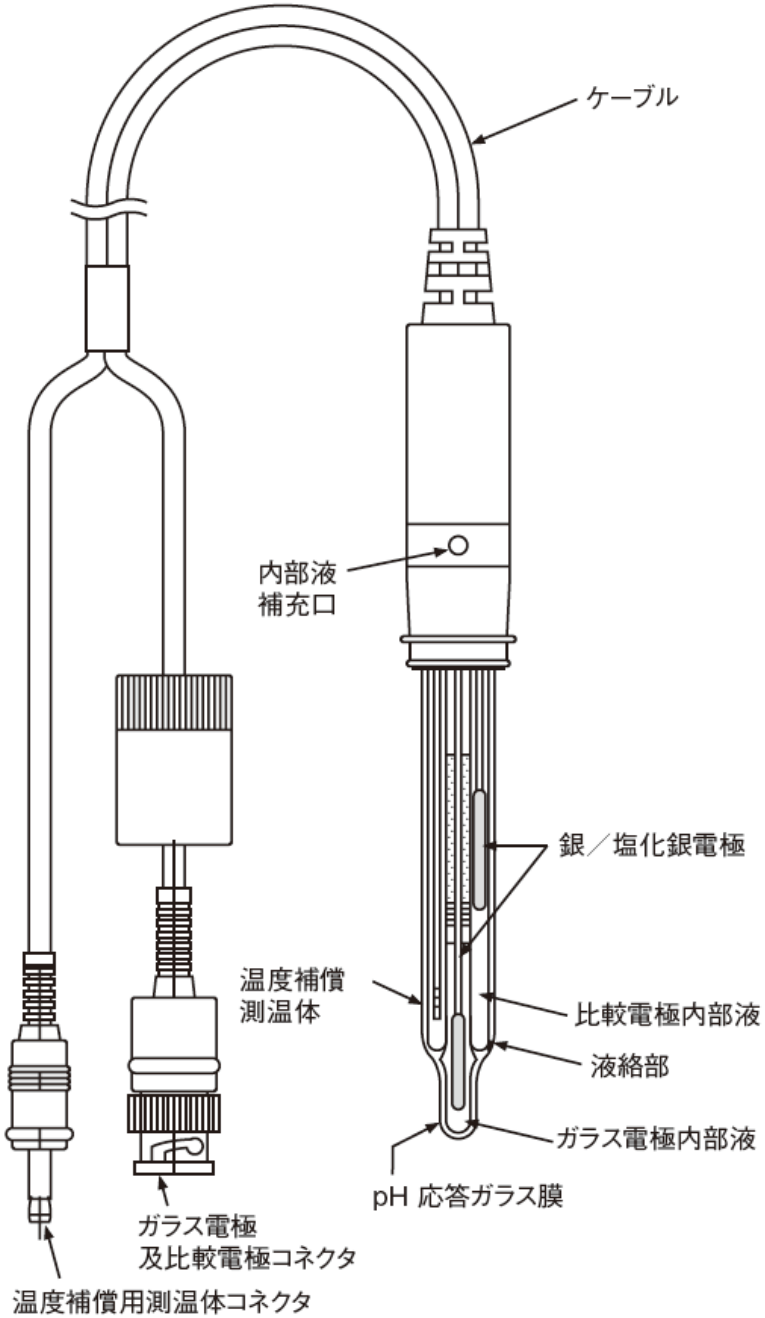
H23･24年 環境年表、国立天文台編

＊岩手県大船渡市三陸町綾里

ガラス電極を用いるpH 測定

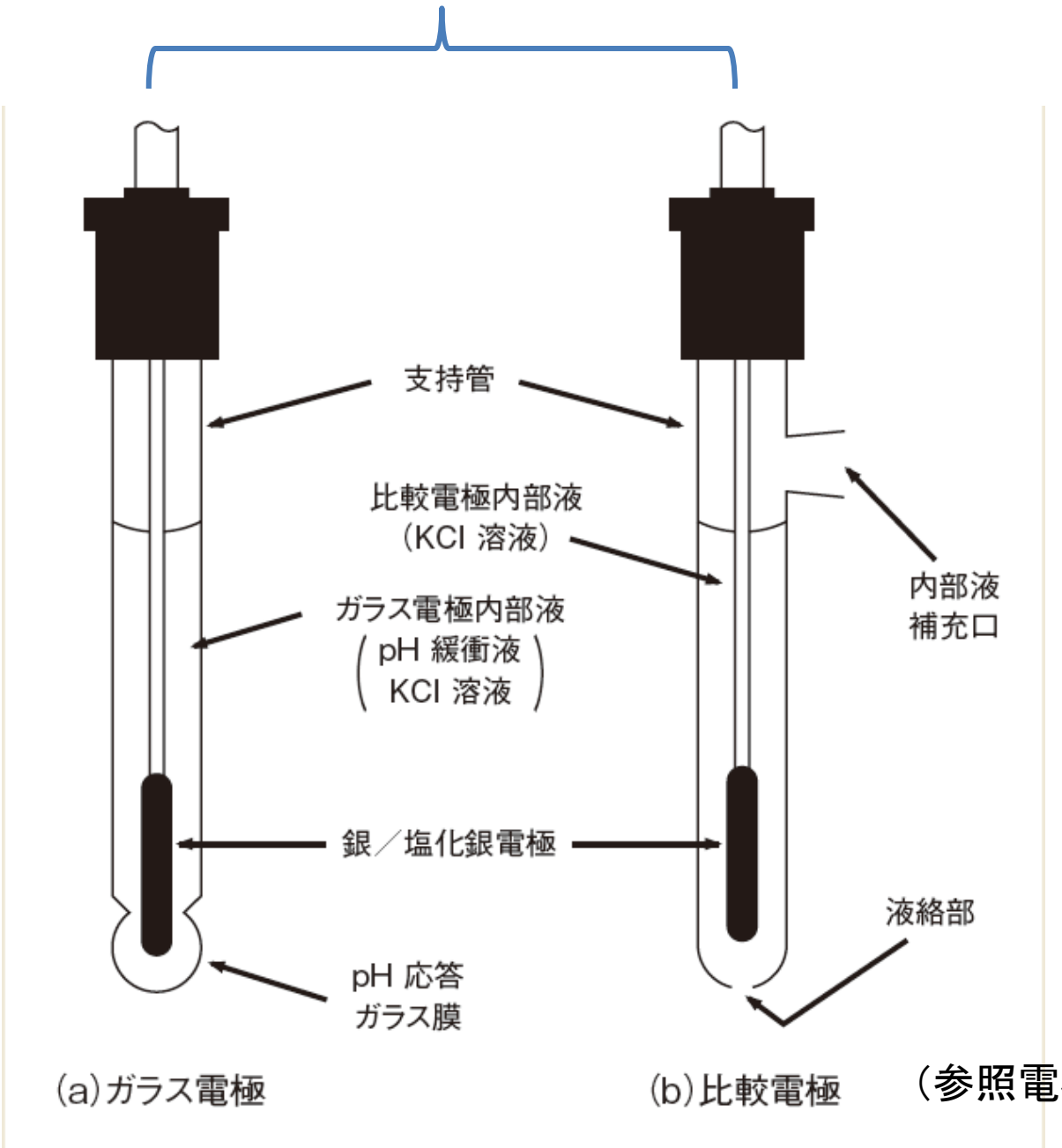
ガラス電極を用いるpH測定の仕組み？

複合型pH測定用ガラス電極



実は、電極2本が合体

ポテンショメトリー



（参照電極）

まず、pH 標準液を用いてpH　メーターを較正する

たいていの機器は

較正　（Calibration）

が必要。

ものさし
電子天秤
温度計
速度計
etc

JCSS市販**pH標準液**の種類及び規格

計量標準供給制度（JCSS)

種　類	pH及び規格（25℃）	
	第１種	第２種
しゅう酸塩pH標準液	1.679±0.005	1.68±0.015
フタル酸塩pH標準液	4.008±0.005	4.01±0.015
中性りん酸塩pH標準液	6.865±0.005	6.86±0.015
りん酸塩pH標準液	7.413±0.005	7.41±0.015
ほう酸塩pH標準液	―	9.18±0.015
炭酸塩pH標準液	―	10.01±0.015

注1）第１種pH標準液とは、登録事業者が値付けしたpH標準液のロットについて、指定校正機関が濃度信頼性試験を実施したとき、測定pH値が表の規格欄に掲げる第１種のpH値及び規格のもの。ただし、現在は、ほう酸塩及び炭酸塩の第１種pH標準液は販売されていません。
注2）第２種pH標準液とは、登録事業者が値付けしたpH標準液のロットについて、指定校正機関が濃度信頼性試験を実施したとき、測定pH値が表の規格欄に掲げる第２種のpH値及び規格のもの。

そもそも pH とは？

中性	ーーーーーー	pH = 7
酸性	ーーーーーー	pH < 7
酸性	ーーーーーー	pH > 7

もちろん 水の場合

$$K_{\mathrm{W}} = a_{\mathrm{H}^+} a_{\mathrm{OH}^-}$$

$$\mathrm{p}K_{\mathrm{W}} = -\log_{10} K_{\mathrm{W}}$$

T / °C	$\mathrm{p}K_{\mathrm{W}}$
0	14.95
25	13.99
50	13.26
75	12.70
100	12.25

水素イオン濃度（活量）は、条件によって 何桁も変わる

対数をとると良い

1909 年に セレンセン（S. L. P. Sørensen）は、たとえばペプシンという酵素による加水分解反応では 1 x 10^{-5} ~ 1 x 10^{-6} mol dm^{-3} 程度の低濃度の H^+ が反応に大きく影響することから、濃度そのものより、その濃度を 10 のべき乗で表したときの指数を使って濃度を表記することを提案

$$\mathrm{pH} = -\log_{10} c_{\mathrm{H}^+}$$

しかし、15年後に変更して

$$\boxed{\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+}}$$

IUPAC（国際純粋応用化学連合）2002 勧奨

$$\boxed{\mathrm{pH} = -\log a_{\mathrm{H}^+}}$$

a_{H^+} is not thermodynamically measureable!

単独イオンの活量 ••••••••• 熱力学的には測定できない . . .

直接、証明できない仮定が必要

$$\mathrm{pH} = -\log_{10} c_{\mathrm{H}^+}$$

から 15年後に

$$\boxed{\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+}}$$

に変更したのは

水素電極やガラス電極の電位測定（ポテンショメトリー）から
（非熱力学的に）測定されるのは、活量だから。

という事は、電池そのものが非熱力学的ということ？

そのとおり

電池は、右と左を分ける必要があるので、非熱力学的な装置。

ということは, 電気化学の根幹が非熱力学的であるということ。

近似的に、熱力学の関係式が使えることもある、と考えるべき。

pH 標準液の pH はどうして決めたのか？

種　類	pH及び規格（25℃）	
	第１種	第２種
しゅう酸塩pH標準液	1.679±0.005	1.68±0.015
フタル酸塩pH標準液	4.008±0.005	4.01±0.015
中性りん酸塩pH標準液	6.865±0.005	6.86±0.015
りん酸塩pH標準液	7.413±0.005	7.41±0.015
ほう酸塩pH標準液	―	9.18±0.015
炭酸塩pH標準液	―	10.01±0.015

非熱力学的仮定はどこに？　どの程度信頼できるの？

IUPAC(2002) のpH測定法は、二段階

1. pH 標準液の値付け

いわゆる液絡がない いわゆるHarned 電池を使ってpH緩衝液のpHをできるだけ精確に値付けする

Bates-Guggenheim 近似

2. 実際の測定

ガラス電極とKCl 塩橋（濃厚KCl水溶液）からなる電池を用いて

i) 電池にpH 標準緩衝液を入れて機器(電池）を校正

ii) 電池の溶液を試料溶液に入れ替えて、そのpHを相対的に決定

KCl 塩橋｜試料溶液間の液間電位差が一定
ガラス電極の応答（Nernst応答）が一定

1. pH 標準液の値付け

通称 Harned cell (so-called)

$$\mathrm{Pt \mid H_2, HCl \mid AgCl \mid Ag \mid Pt'}$$

"Cells without transference"
「液絡のない電池 」と言われる*

$$a_{\mathrm{HCl}} = a_{\mathrm{H^+}} a_{\mathrm{Cl^-}}$$

を測定

pH values of pH standard solutions

$$\mathrm{Pt \mid H_2, Buffer\ soln, KCl \mid AgCl \mid Ag \mid Pt'}$$

$$a_{\mathrm{HCl}} = a_{\mathrm{H^+}} a_{\mathrm{Cl^-}}$$

を測定

*本当は、液絡は、必ず、ある！
Liquid junction is hidden in Harned cell.

Pt | H_2, HCl | AgCl| Ag | Pt'

この電池の端子間電圧（電池電圧） E の表現は？

1. 電池の端子間電圧（電池電圧） は、左基準： 右 − 左 + 液間電位差

2. 右側の電極の電極電位
Nernst-Luther-Lewis 式

$$E^{\mathrm{R}} = E^{0}_{\mathrm{AgCl|Ag}} - \frac{RT}{F}\ln a_{\mathrm{Cl^-}}$$

左側の電極の電極電位
Nernst-Luther-Lewis 式

$$E^{\mathrm{L}} = \underbrace{E^{0}_{\mathrm{H^+|(1/2)H_2}}}_{\equiv 0} + \frac{RT}{F}\ln a_{\mathrm{H^+}}$$

液間電位差 $\Delta\phi_{\mathrm{LJP}} \simeq 0$

したがって

$$E = \underbrace{E^{0}_{\mathrm{AgCl|Ag}}}_{0.2224\ \mathrm{V\ at\ 25\ °C}} - \frac{RT}{F}\ln a_{\mathrm{H^+}} a_{\mathrm{Cl^-}}$$

$$Pt \mid H_2, HCl \mid AgCl \mid Ag \mid Pt'$$

$$\frac{1}{2}H_2 + AgCl \rightleftarrows H^+ + Ag$$

$$E = E^{\ominus}_{AgCl|Ag} - \frac{RT}{F} \ln a_{H^+} a_{Cl^-}$$

0.2224 V at 25 °C

$$\Delta G^{\ominus}_r = -0.2224 \times 96485 = -21.46 \text{ kJ mol}^{-1} \text{ at } 25\ ^\circ\text{C}$$

$$\boxed{\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag}$$

液間電位差は本当にないのか？

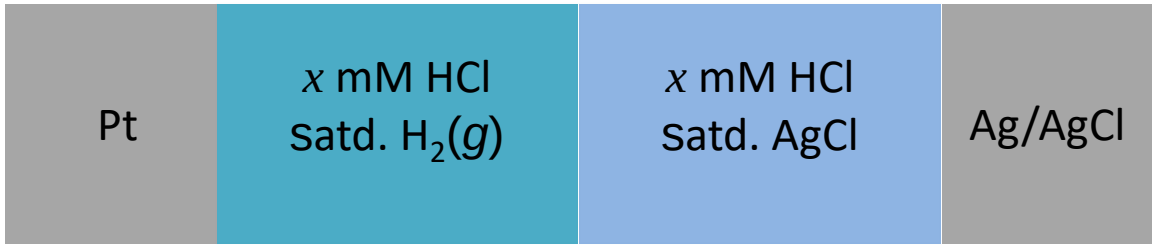
It is important to note that the difference between cells with and without liquid junctions is one of degree and not of kind. Thus the familiar cell:

$$(Pt);\ H_2,\ HCl,\ AgCl\ (s);\ Ag$$

really contains two (or more) solutions, and should, strictly, be represented as follows:

$$(Pt);\ H_2,\ HCl\ (satd.\ with\ H_2) : HCl\ (satd.\ with\ AgCl),\ AgCl\ (s);\ Ag$$

D. A. MacInnes, “The Principles of Electrochemistry,” Dover (1931, 1961), p.246.



$$AgCl + \tfrac{1}{2}H_2 = Ag + Cl^- + H^+$$

$\Delta G < 0$

$$\mathrm{Pt|\ H_2}(g),\ \underbrace{\text{Buffer soln}}_{\text{pH 緩衝液}},\ \mathrm{KCl(aq.)\ |\ AgCl|\ Ag}$$

Cl- は測定上必要だが、たいていの Buffer には含まれていないので、KClを添加。

$$E = E^0 - \frac{RT}{F}\ln \underbrace{a_{\mathrm{H^+}}\, a_{\mathrm{Cl^-}}}_{a_{\mathrm{HCl}}} = E^0 - \frac{RT}{F}\ln \underbrace{a_{\mathrm{H^+}}}_{\text{pH}}\, m_{\mathrm{Cl^-}}\, \gamma_{\mathrm{Cl^-}}$$

?

pH 緩衝液のイオン強度は 0.05 ~ 0.1 mol kg^{-1} 程度

［良い緩衝能を得るために必要］

その緩衝液中の γ_{Cl^-} ？

Bates-Guggenheim convention

$$\log_{10}\gamma_{Cl^-} = -\frac{A_m\sqrt{I}}{1+1.5\sqrt{I}}$$

$$I = \frac{1}{2}\sum_i (z_i)^2 m_i$$

イオン強度

cf.

$$\log_{10}\gamma_i = -(z_i)^2\frac{A_m\sqrt{I}}{1+B_m a\sqrt{I}}$$

Debye-Hückel 式（1923）

$$E = E^0 - \frac{RT}{F} \ln a_{H^+} m_{Cl^-} \gamma_{Cl^-}$$ を変形すると

$$-\ln a_{H^+} = -\ln(10)\log_{10} a_{H^+} = \ln(10)\mathrm{pH} = \frac{F}{RT}(E - E^0) + \ln m_{Cl^-} + \ln \gamma_{Cl^-}$$

?

$$\mathrm{pH} \propto \frac{1}{\ln(10)} \frac{F}{RT}(E - E^0)$$

1/59.16 mV

1 pH 単位 ⟺ 59.16 mV（25 ℃）

I ・・・ イオン強度

$$I^{(c)} = \frac{1}{2}\sum_{i} z_{\mathrm{i}}^{2} c_{\mathrm{i}}$$

$$I^{(m)} = \frac{1}{2}\sum_{i} z_{\mathrm{i}}^{2} m_{\mathrm{i}}$$

１:１ の完全解離した電解質水溶液では、その塩の濃度と同じ

電解質水溶液の場合

T	$A^{(c)}$	$A^{(m)}$
°C	$\mathrm{mol}^{-1/2}\ \mathrm{dm}^{3/2}$	$10^9\ \mathrm{mol}^{-1/2}\ \mathrm{kg}^{1/2}$
5	0.4939	0.4939
15	0.5016	0.5014
25	0.5106	0.5098
35	0.5206	0.5190
45	0.5316	0.5202

$$A^{(m)} = A^{(c)}(\rho_0)^{1/2}$$

水の密度（g/cm^3）

Harned 電池＋Bates-Guggenheim規約で決められたpH 第一次標準液のｐH値

Table 2 Typical values of pH(PS) for primary standards at 0–50 °C (see Section 6.2).

	Primary standards (PS)	Temp./°C 0	5	10	15	20	25	30	35	37	40	50
酒石酸水素カリウム	Sat. potassium hydrogen tartrate (at 25 °C)						3.557	3.552	3.549	3.548	3.547	3.549
クエン酸二水素カリウム	0.05 mol kg^{-1} potassium dihydrogen citrate	3.863	3.840	3.820	3.802	3.788	3.776	3.766	3.759	3.756	3.754	3.749
フタル酸水素カリウム	0.05 mol kg^{-1} potassium hydrogen phthalate	4.000	3.998	3.997	3.998	4.000	4.005	4.011	4.018	4.022	4.027	4.050
リン酸二水素ナトリウム＋リン酸水素カリウム	0.025 mol kg^{-1} disodium hydrogen phosphate + 0.025 mol kg^{-1} potassium dihydrogen phosphate	6.984	6.951	6.923	6.900	6.881	6.865	6.853	6.844	6.841	6.838	6.833
	0.03043 mol kg^{-1} disodium hydrogen phosphate + 0.008695 mol kg^{-1} potassium dihydrogen phosphate	7.534	7.500	7.472	7.448	7.429	7.413	7.400	7.389	7.386	7.380	7.367
テトラホウ酸二ナトリウム	0.01 mol kg^{-1} disodium tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102	9.088	9.068	9.011
炭酸水素ナトリウム＋炭酸ナトリウム	0.025 mol kg^{-1} sodium hydrogen carbonate + 0.025 mol kg^{-1} sodium carbonate	10.317	10.245	10.179	10.118	10.062	10.012	9.966	9.926	9.910	9.889	9.828

Pure Appl. Chem., Vol. 74, No. 11, pp. 2169–2200, 2002

pH標準液の値と較正操作の不確かさの目標値 （IUPAC2002)

Table 4 Summary of recommended target uncertainties.

	U(pH) (For coverage factor 2)	Comments
PRIMARY STANDARDS		
Uncertainty of PS measured (by an NMI) with Harned Cell I	0.004	
Repeatability of PS measured (by an NMI) with Harned Cell I	0.0015	
Reproducibility of measurements in comparisons with Harned Cell I	0.003	EUROMET comparisons
Typical variations between batches of PS buffers	0.003	
SECONDARY STANDARDS		
Value of SS compared with same PS material with Cell III	0.004	increase in uncertainty is negligible relative to PS used
Value of SS measured in Harned Cell I	0.01	e.g., biological buffers
Value of SS labeled against different PS with Cell II or IV	0.015	
Value of SS (not compatible with Pt | H_2) measured with Cell V	0.02	example based on phthalate
ELECTRODE CALIBRATION		
Multipoint (5-point) calibration	0.01–0.03	
Calibration (2-point) by bracketing	0.02–0.03	
Calibration (1-point), ΔpH = 3 and assumed slope	0.3	

Note: None of the above include the uncertainty associated with the Bates–Guggenheim convention so the results cannot be considered to be traceable to SI (see Section 5.2).

$$\log \gamma_{Cl^-} = -A \frac{\sqrt{I}}{1 + 1.5\sqrt{I}}$$

の近似に由来する不確かさ 0.01 (95% confidence interval) in pH

もし、液間電位差が無視出来るほど小さいか、試料溶液組成に依存しなければ
作用電極が 水素イオンの活量に応答する場合は、

$$E - E^\circ = \frac{RT}{F} \ln a_{\mathrm{H}^+} = \ln(10)\frac{RT}{F} \log a_{\mathrm{H}^+} = -\ln(10)\frac{RT}{F}\mathrm{pH}$$

59.2mV (25 ℃)

$$\mathrm{pH} = -\frac{1}{\ln(10)}\frac{F}{RT}(E - E^\circ)$$

参照電極｜pH標準液との間の液間電位差と
参照電極｜試料溶液との間の液間電位差が等しければ
それぞれの溶液の 端子間電圧 E_{std} と E_{spl} より

$$\mathrm{pH}_{\mathrm{spl}} = \mathrm{pH}_{\mathrm{std}} - \frac{1}{\ln(10)}\frac{F}{RT}\left(E_{\mathrm{spl}} - E_{\mathrm{std}}\right)$$

２点較正の場合は？

標準液 pH_1 の電位が E_{std1} ➡ $$\mathrm{pH}_{\mathrm{std1}} = -f\left(E_{\mathrm{std1}} - E^{\circ}\right)$$

標準液 pH_2 の電位が E_{std2} ➡ $$\mathrm{pH}_{\mathrm{std2}} = -f\left(E_{\mathrm{std2}} - E^{\circ}\right)$$

試料液 電位が E_{spl} ➡ $$\mathrm{pH}_{\mathrm{spl}} = -f\left(E_{\mathrm{spl}} - E^{\circ}\right)$$

Unknown は $\mathrm{pH}_{\mathrm{spl}}, f, E^{\circ}$

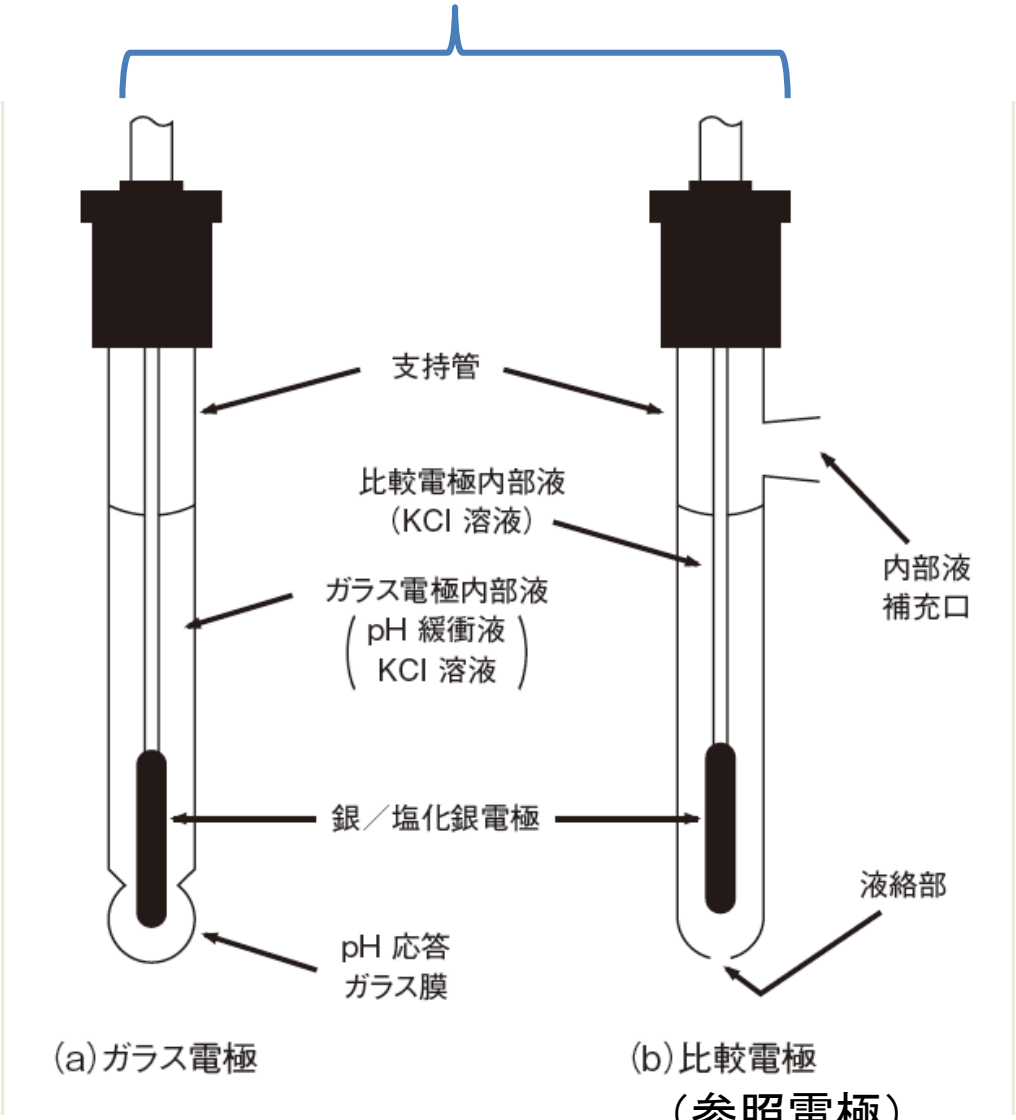
これを解くと？

現在では、実際のpH 測定には、水素電極ではなく、ほとんどもっぱら ガラス電極

１．水素電極　扱いが（やや）面倒

２．　試料溶液に酸化還元性の物質が入っていると、pH測定を妨害

ポテンショメトリー

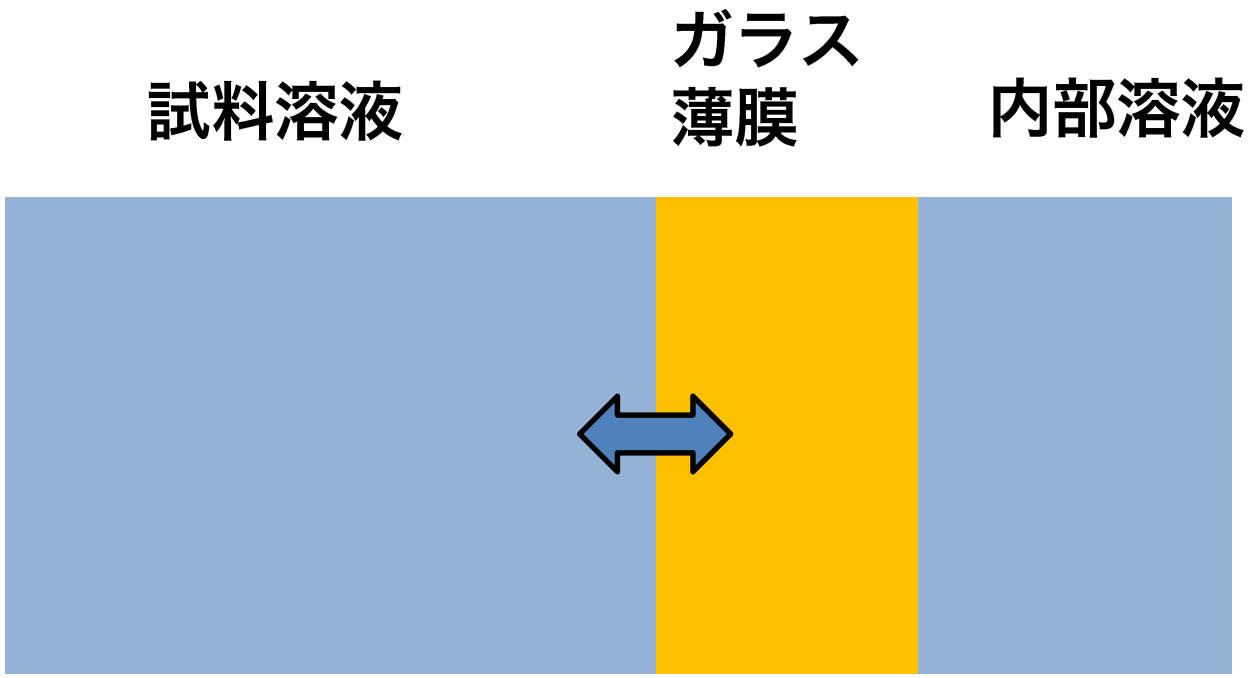


（参照電極）

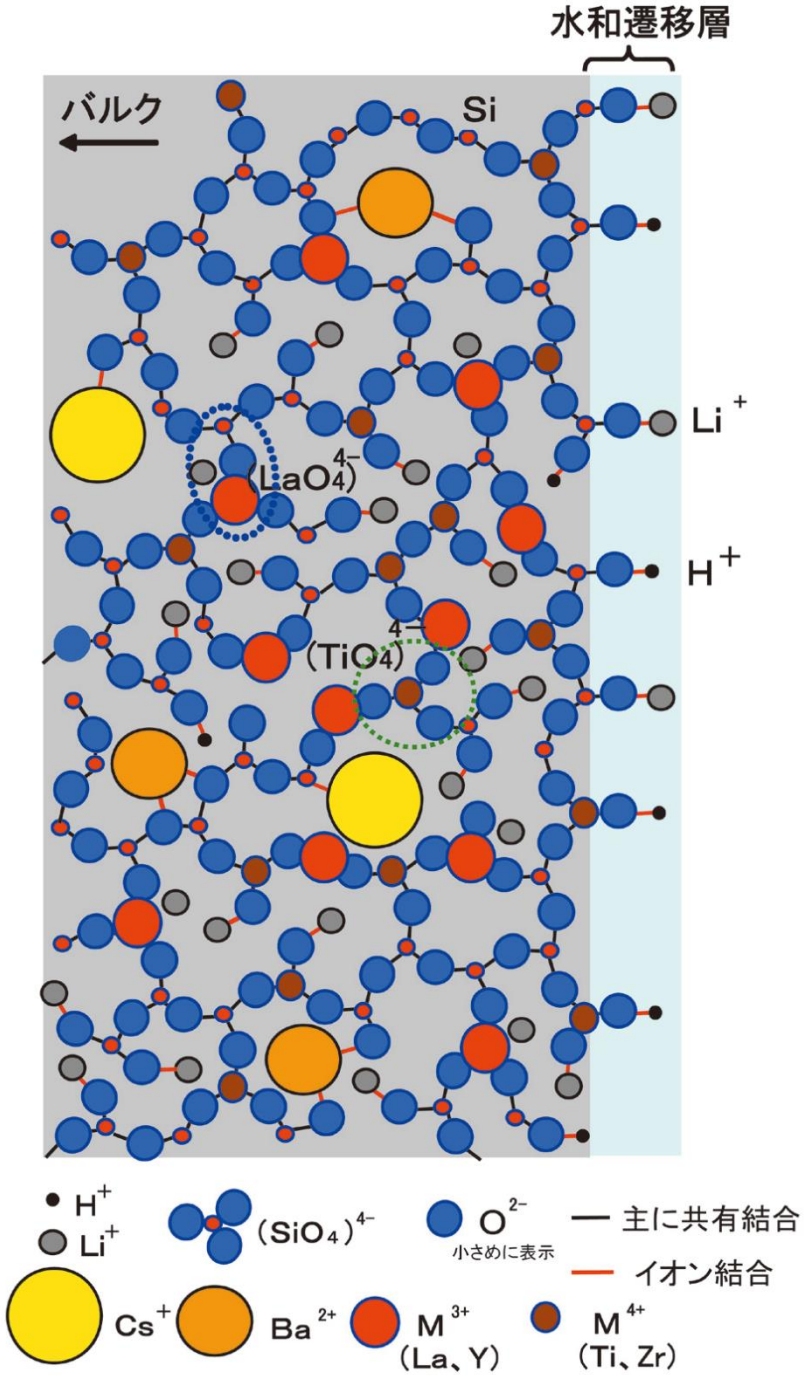
疑問

ガラス電極の pH 応答性

参照電極の液間電位差



H^+ がガラス薄膜に分配することによる相間電位差



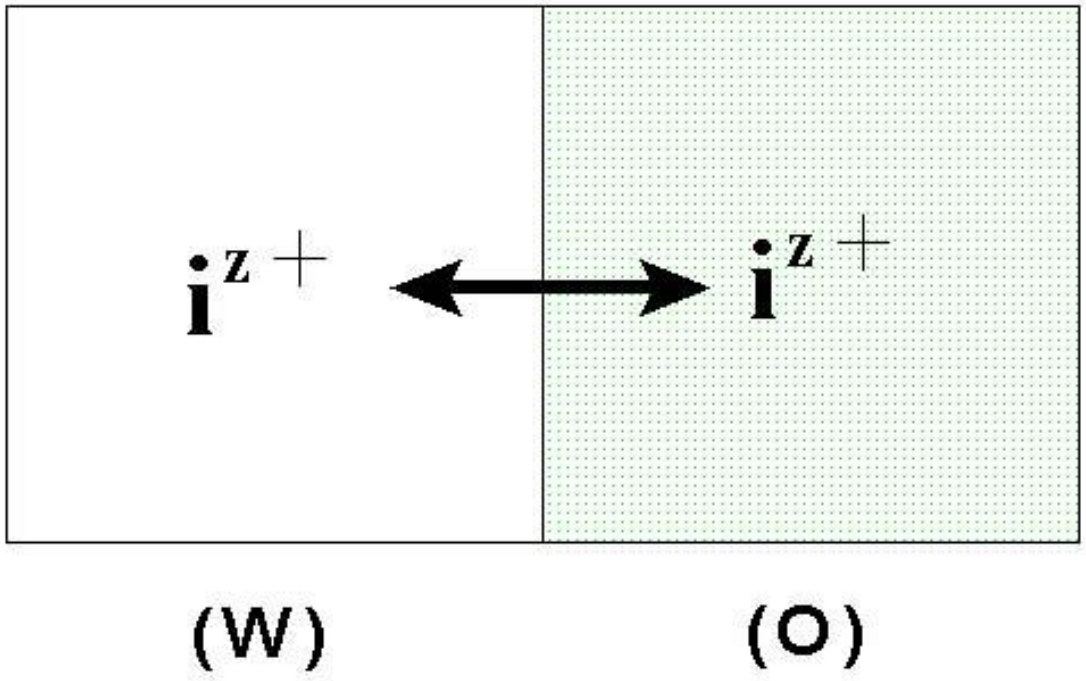
大川　浩美、セラミックス　43（2008）No. 12

pH のポテンショメトリーでは，酸化還元反応による電位発生（電位差）ではなく，イオンの２つの相間での分配によって生じる相間電位差（Phase-boundary potential）の変化を用いる.

そのほかのイオン選択性電極でも、同様の手法

酸化還元に関する Nernst 式と同様の式が，相間電位差について成り立つことを理解すること.

イオン i が隣接する二つの相 W と O へ
分配することを考える.



分配平衡の条件は

$$\tilde{\mu}_{\mathrm{i}}^{\mathrm{W}} = \tilde{\mu}_{\mathrm{i}}^{\mathrm{O}}$$

化学jポテンシャルの電気的な寄与を別に書くと

$$\tilde{\mu}_{\mathrm{i}}^{\alpha} = \mu_{\mathrm{i}}^{\mathrm{chem},\alpha} + \mu_{\mathrm{i}}^{\mathrm{el},\alpha}$$

すなわち

$$\tilde{\mu}_{\mathrm{i}}^{\alpha} = \mu_{\mathrm{i}}^{\alpha,\ominus} + RT \ln a_{\mathrm{i}}^{\alpha} + z_{\mathrm{i}} F \phi^{\alpha}$$

これを上の平衡条件に代入すると

$$\Delta_{\mathrm{O}}^{\mathrm{W}} \phi = \frac{\mu^{\mathrm{O},\ominus} - \mu^{\mathrm{W},\ominus}}{z_{\mathrm{i}} F} + \frac{RT}{z_{\mathrm{i}} F} \ln \frac{a^{\mathrm{O}}}{a^{\mathrm{W}}}$$

$$\Delta_{\mathrm{O}}^{\mathrm{W}} \phi = \phi^{\mathrm{W}} - \phi^{\mathrm{O}}$$

相間電位差（Phase-boundary potential）

$$\mu^{\mathrm{W},\ominus} - \mu^{\mathrm{O},\ominus} = \Delta G_{\mathrm{i}}^{\mathrm{O}\to\mathrm{W},\ominus}$$

イオンi のW 相とO 相の間の移行の Gibbs エネルギー変化

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_{\mathrm{i}}^{\ominus} = -\frac{\Delta G_{\mathrm{i}}^{\mathrm{O}\to\mathrm{W},\ominus}}{z_{\mathrm{i}}F}$$

と置くと,

$$\boxed{\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi_{\mathrm{i}}^{\ominus} + \frac{RT}{z_{\mathrm{i}}F}\ln\frac{a_{\mathrm{i}}^{\mathrm{O}}}{a_{\mathrm{i}}^{\mathrm{W}}}}$$

この表現は, 酸化還元反応についての Nernst と全く同じ形
これもまた Nernst によって提案された

W. Nernst, "Die elektromotorische Wirksamkeit der Ionen," *Z. phys. Chem.*, **8** (1891) 129; W. Nernst, "Über die Löslichkeit von Mischkrystallen," *Z. phys. Chem.*, **9** (1892) 137.

$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_{\mathrm{i}}^{\ominus}$ は，**標準イオン移動電位**と呼ばれ，酸化還元反応における標準電極電位に対応する物理量である．

その値は，イオンの二つの相を構成する溶媒に対する相対的な親和性を表し，溶媒とイオンによって決まる．

水と有機溶媒の２相系では、イオンの親水性・疎水性

ガラス膜では、シラノール基の解離とイオン交換

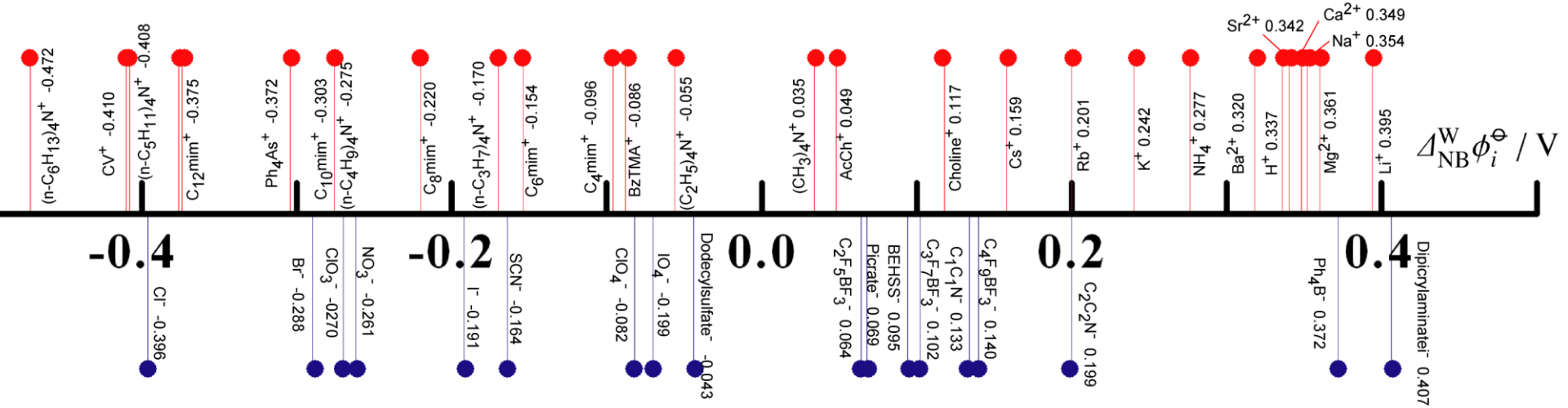
水／ニトロベンゼン(NB)および水／1，2ジクロルエタン(DCE)2相系の標準イオン移動電位 at 25 ºC

@ Cation	$\Delta_O^W\phi_i^\ominus$ / V NB	DCE
Li^+	0.39_8	0.49_3
Na^+	0.35_5	0.49_0
H^+	0.33_7	
NH_4^+	0.28_4	
K^+	0.24_1	0.49_9
Rb^+	0.20_1	0.44_5
Cs^+	0.15_9	0.36_4
Choline	0.11_7	
Acetylcholine	0.05_2	
$(CH_3)_4N^+$	0.03_7	0.18_2
$(C_2H_5)_4N^+$	-0.06_3	0.04_4
$(n\text{-}C_3H_7)_4N^+$	-0.16_0	-0.09_1
$(n\text{-}C_4H_9)_4N^+$	-0.27_0	-0.22_5
$(n\text{-}C_5H_{11})_4N^+$		-0.36_0
$(C_6H_5)_4As^+$	-0.37_2	-0.36_4
$(n\text{-}C_6H_{13})_4N^+$	-0.47_2	-0.49_4
Mg^{2+}	0.37_0	
Ca^{2+}	0.35_4	
Sr^{2+}	0.34_8	
Ba^{2+}	0.32_8	

@ Anion	$\Delta_O^W\phi_i^\ominus$ / V NB	DCE
Cl^-	-0.39_5	-0.48_1
Br^-	-0.33_5	-0.40_8
NO_3^-	-0.27_0	
I^-	-0.19_5	-0.27_3
SCN^-	-0.16_1	
ClO_4^-	-0.09_1	-0.17_8
BF_4^-	-0.10_3	
2,4-Dinitrophenolate	-0.04_3	
Dodecylsulfate	-0.10_3	
PF_6^-	0.01_2	
Picrate	0.04_7	
$(C_6H_5)_4B^-$	0.37_2	0.36_4

イオンの疎水性尺度

Nitrobenzene-W ２相間の標準イオン移動電位



ガラス薄膜の pH（酸濃度）応答性を初めて示した

Max　Cremer

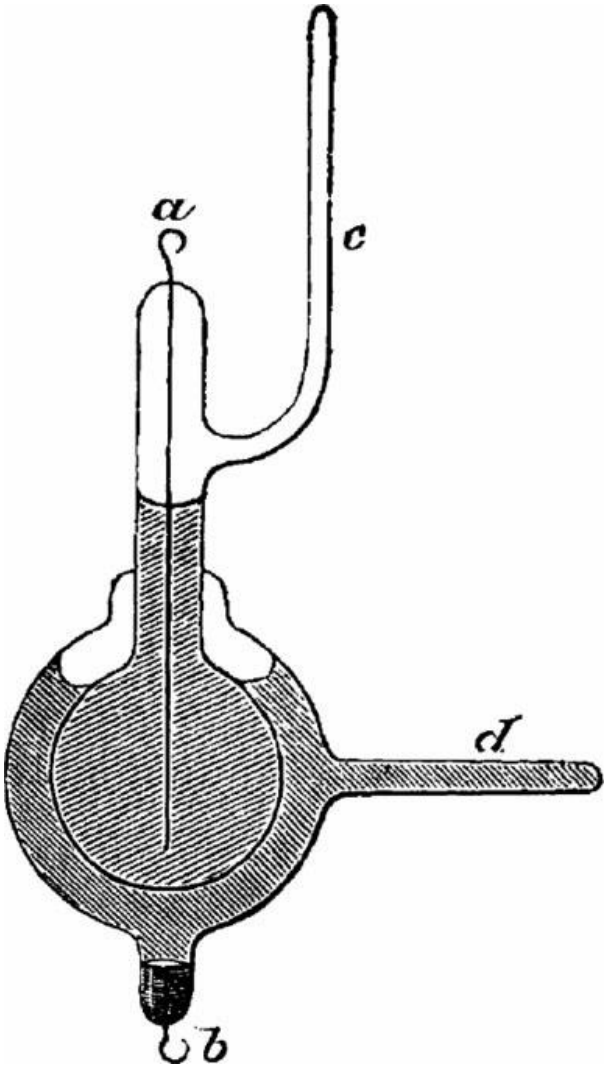
Z. Biol., **47**, 562 (1906).

生理学者　「生体膜との類比」

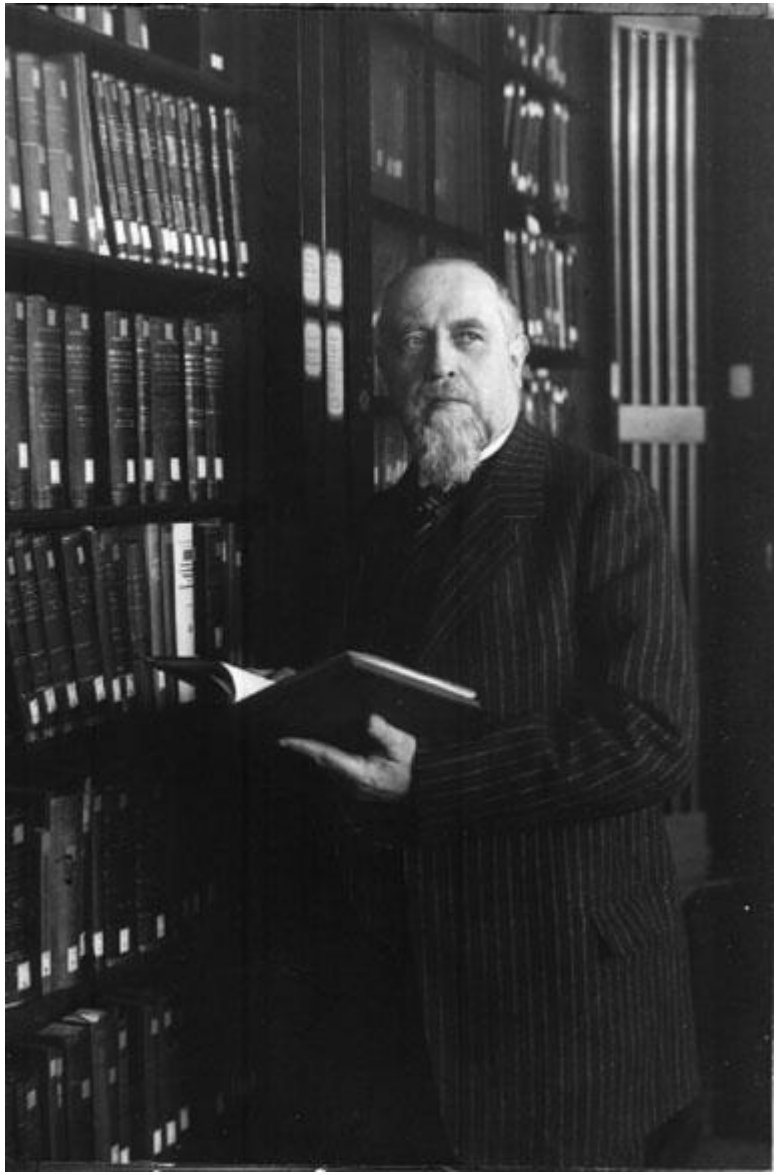
先行する知見

１．ガラスは誘電体ではない（ライデン瓶には不向き）

２．Helmholtz（の部下 Giesen）の実験
（ダニエル電池、素焼きの板の代わりにガラス薄膜）



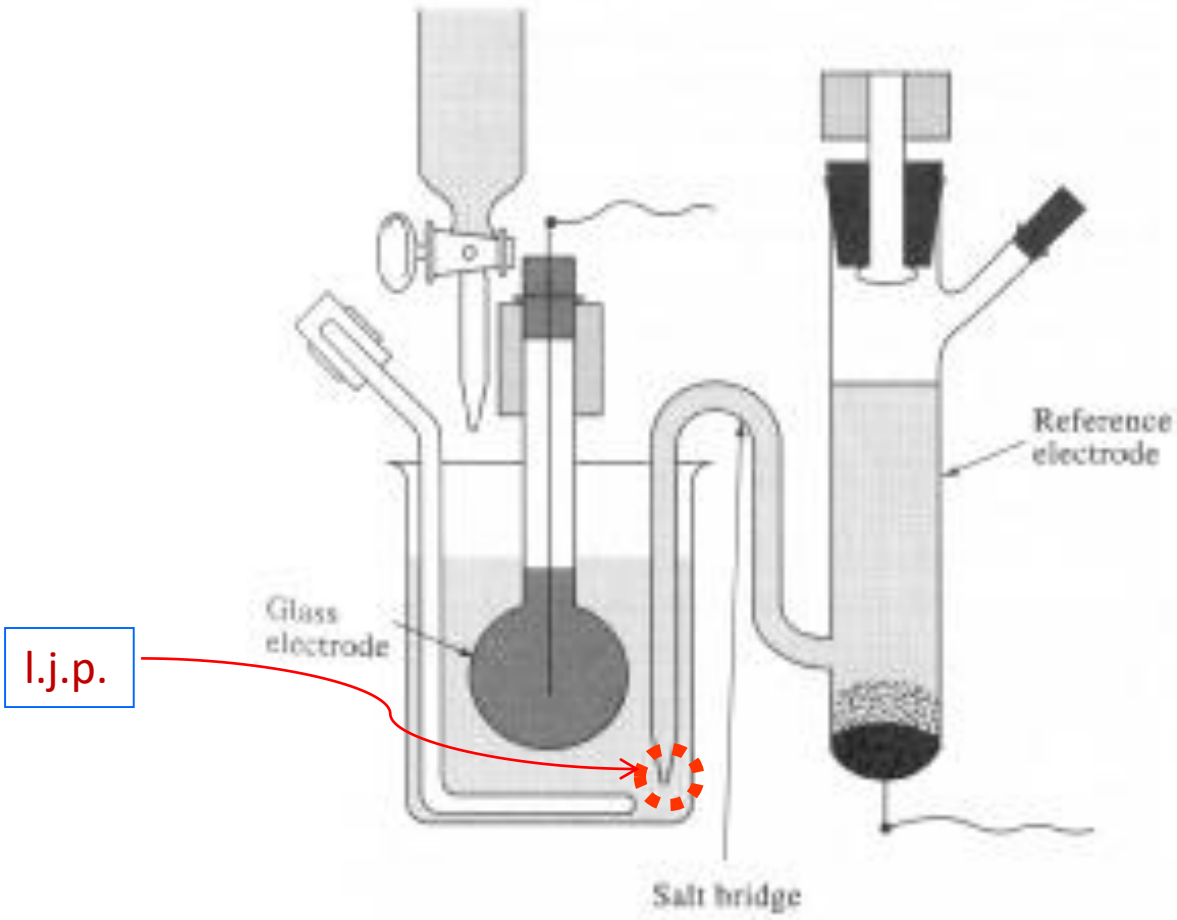
Giese-Helmholtz のセル



Max Cremer

F. Scholz, J. Solid State Electrochem., 15, 5-14 (2011).

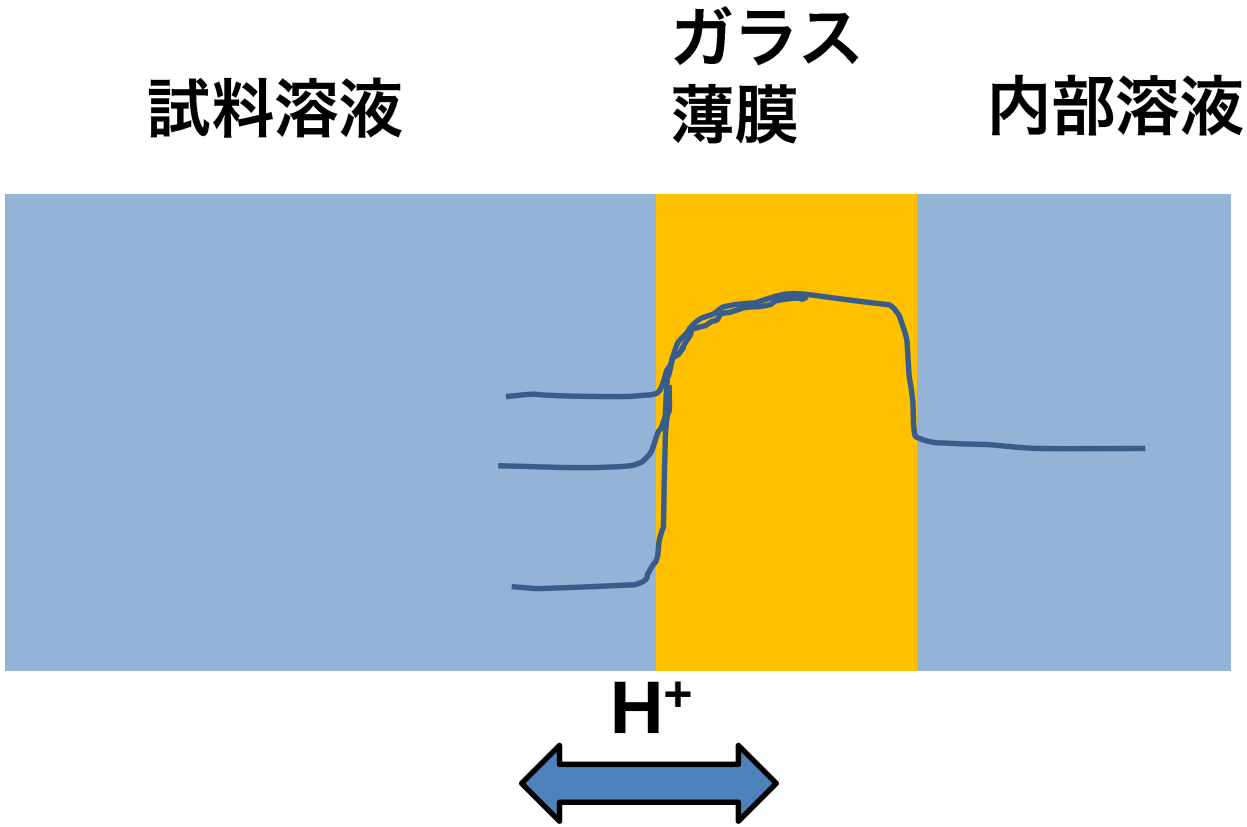
Potentiometric determination of pH with a glass electrode



F. Haber and Z. Klemensiewicz, *Z. phys. Chem.*, 67, 385 (1909).

F. Scholz, J. Solid State Electrochem., 15, 5-14 (2011).

F. Scholz, J. Solid State Electrochem., 15, 5-14 (2011).



H^+ のガラス薄膜｜溶液間分配による相間電位差

The Early History of the Development of the Glass Electrode for pH Measurements

Malcolm Dole

J. Chem. Educ., 57, 134 -134 (1980).

I came to Karlsruhe in November 1908 . . . . I was then 22. Haber proposed to me to explore the glass electrode, the interest for this topic having been suggested to him by the earlier work of Cremer. They tried already in Karlsruhe some experiments before I came, but without success. I have been handed over the respective apparatus, consisting of a piece of broken glass—cylinder about 3 mm thick, with a tin-foil sticked around. I saw at once that such an element could never work, being short-circuited all over the moist glass surface. Although I didn't know at this stage that glass-balloons have been used by Cremer (and previously by Giese), I blew the thin bulb which remains until today the classical form of the glass electrode. I also

installed a quadrant electrometer with the use of which I was well acquainted. With this arrangement I got at once positive results, especially as I discovered at the very beginning the aid of steaming and soaking the glass, quite independently, of course. I applied steaming at first as a method of cleaning, being in this case reluctant to use either chromic acid or organic liquids. I also learned in these first days the need of avoiding drying out of the glass-bulb and the superiority of soft over hard glass. Finally, I chose the kind of diagram for plotting the bilogarythmic curve as the most adequate way of presentation. When Haber went to see me in the laboratory after few days, I was able to show him a very good curve in HCl-KOH, with an efficiency of about 0.5 V. He would not believe first that it was possible to get these results in such a short time and I had to let him look in the reading telescope that he could plot the points by himself. The experiment proceeded smoothly, so he gave himself an outbreak of enthusiasm, leaped, embraced and praised me in his cheerful manner. [The "efficiency" figure of 0.5 V given by Klemensiewicz probably means the total voltage change in going from the acid to alkaline solution.]

ガラス電極の歴史

J Solid State Electrochem (2011) 15:47–65
DOI 10.1007/s10008-010-1105-x

REVIEW

The centenary of glass electrode: from Max Cremer to F. G. K. Baucke

Anatolii A. Belyustin

pH 測定用ガラス膜組成の最適化

Table 1 The glasses for pH-GEs

Marking	Composition	Author, year [reference]
Sodium silicate glasses (wt.%)		
Low-melting Thuringia soft glass	Na_2O–CaO–SiO_2 + add.	M Cremer, 1906 [2]
		F Haber et al. 1907, 1909 [3, 15]
		H Freundlich, P Rona, 1920 [16]
No 793A, Sheffield	Na_2O–CaO–SiO_2 + add.	WS Hughes, 1922 [18]
"Hughes's glass"	$20Na_2O$–$8CaO$–$72SiO_2$	WS Hughes, 1928 [23]
"MacInnes & Dole glass," Corning 015	$22Na_2O$–$6CaO$–$72SiO_2$	DA MacInnes, M Dole, 1929, 1930 [24, 25]
Lithium silicate glasses (mol.%)		
LiCa	18_1Li_2O–9_6CaO–72_3SiO_2	SI Sokolov, AG Passinskii, 1932 [26]
LiBa	$26Li_2O$–$3._6BaO$–$70._4SiO_2$	GP Avseevich, 1938–1948 [27, 28]
LiMg	$26._5Li_2O$–$12._3MgO$–$61._2SiO_2$	
LiCa	$25Li_2O$–$7CaO$–$68SiO_2$	HH Cary, WP Baxter, 1949 [29]
	Li_2O–Cs_2O–La_2O_3–SiO_2	GA Perley,1948, 1949 [30, 31]
Present day glasses for pH-GEs	21–33 Li_2O, 2–4 Cs_2O, 3–5 La_2O_3 (Nd_2O_3, Er_2O_3), 2–4% CaO (BaO)–SiO_2 (till 100%)	All world manufacturers

ガラス電極は、pH すなわち水素イオンの活量（単独イオン活量）を、そこそこ、正確に測定できる

百年以上、使い続けてきた

普通、±0.1 pH 単位ぐらいはいける

場合によっては、もう少し正確

しかし、0.01 以下は難しい

雨水、河川水、ボイラーの冷却水など、低イオン強度の試料は、 + 0.05 ないし +0.1 ずれてしまう（実際よりアルカリ側に見える）

塩橋の問題

$$
\begin{aligned}
E &= E^{0\prime} + \frac{RT}{F} \ln a_{\mathrm{H}^+}^{\mathrm{W}} \\
&= E^{0\prime} + \frac{RT}{F} \ln(10) \log_{10} a_{\mathrm{H}^+}^{\mathrm{W}} \\
&= E^{0\prime} - \underbrace{\ln(10) \frac{RT}{F}}_{\text{59.16 mV at 25 °C}} \mathrm{pH}
\end{aligned}
$$

ΔpH	ΔE /mV	
1	59.16	
0.1	5.916	
0.01	0.5916	
0.001	0.05916	
0.0001	0.005916	5.9 μV

ガラス電極は、pH すなわち水素イオンの活量（単独イオン活量）を、そこそこ、正確に測定できる

百年以上、使い続けてきた

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ΔpH = 0.1 は些細なこと?

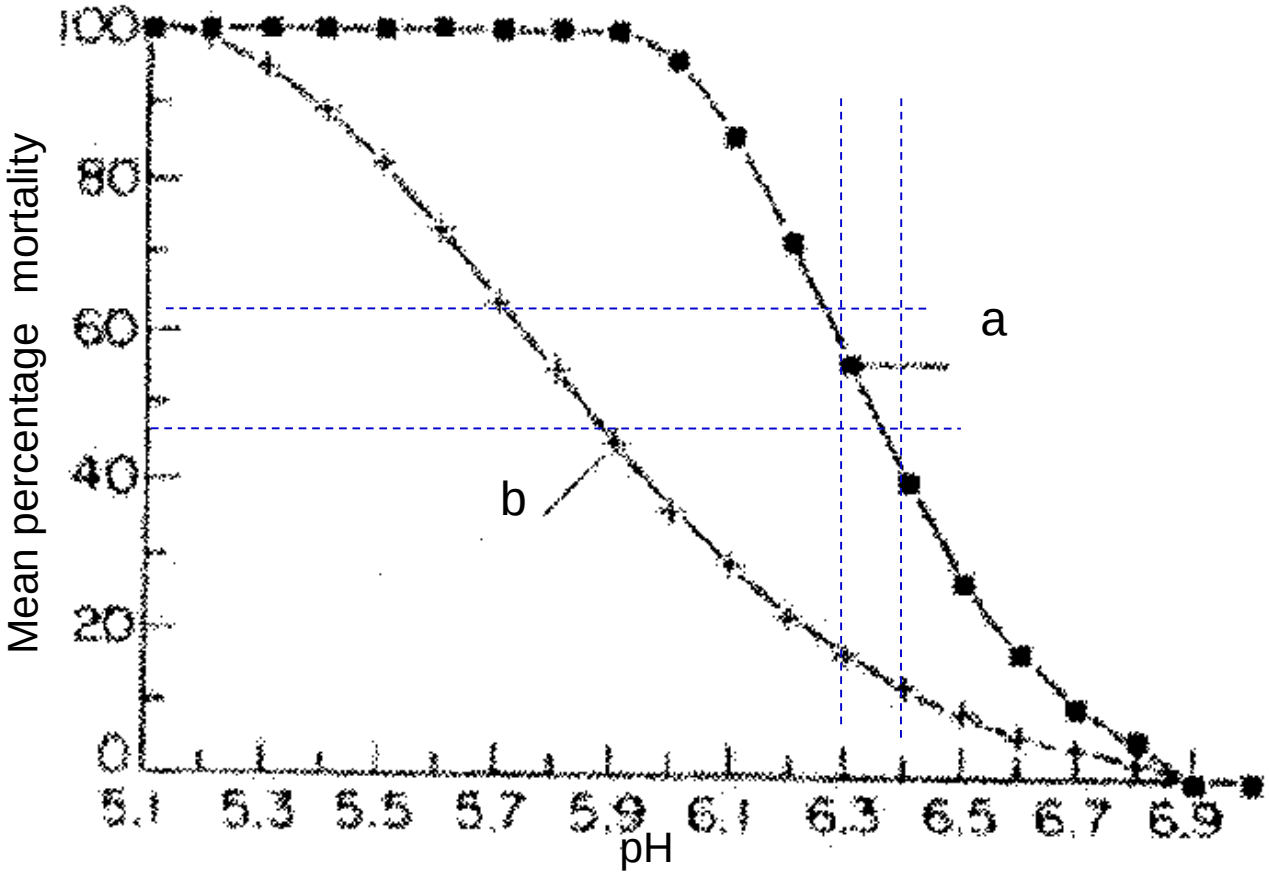
$$\Delta a_{H^+}/a_{H^+} \approx -\ln 10 \times \Delta\mathrm{pH} + (1/2)(\ln 10)^2 \times (\Delta\mathrm{pH})^2$$

pH の+ 0.1 と - 0.1 の変化は

a_{H+} 値が -20.4 % と25.7 % 変化することに相当する1

cf. pH of blood: 7.40 ±0.05

米国淡水魚２種の致死率のpH 依存性



Mortality of two hypothetical fish species in relation to pH. Curves are based on data for (a) *Pimephales promelas* Rafinesque (fathead minnow) and (b) *Stizostedion vitrrenum*.(walleye)

R. Hoenicke, M. A. Stapanian, L. J. Arent, R. C. Metcalf, *Freshwater Biol*., 25, 261-278 (1991).

雨水など

（低イオン強度水溶液　$I < 0.001$ mol dm^{-3}）

海水など

（高イオン強度水溶液　$I > 0.1$ mol dm^{-3}）

pH の正確な測定　（< 0.005 ）は、困難（不可能）

pH の正確な測定　（< 0.05）は、容易でない

3 mV

海水のイオン強度は、もっと高い
High ionic strength of seawater
I = 0.1 (S = 5) ～ 0.93 (S = 45)

模擬海水の一例

Table 1
Composition of buffer solution in synthetic sea water of salinity 35[a]

Component	mol kg^{-1} H_2O
NaCl	$0.42764 - m$
Na_2SO_4	0.02927
KCl	0.01058
$MgCl_2$	0.05474
$CaCl_2$	0.01075
HCl	m
'tris'	$2m$

[a] The concentrations m_S of the various components of a synthetic sea water with salinity S, are calculated:

$$m_S = \frac{m_{35} \times I_S}{I_{35}} \text{ where } I_S = \frac{19.919S}{1000 - 1.00198S}.$$

For NaCl, $m_{35} = 0.42764$ mol kg^{-1} H_2O. Note that the buffer concentration m is chosen independent of the salinity.

T. A. DelValls and A. G. Dickson, Deep-Sea Res. Part I-Oceanogr. Res. Pap., 45, 1541-1554 (1998)

海水では、

1. BG近似が使えない

Bates-Guggenheim approximation is not applicable.

2. KClSB は、うまく働かない

KClSB does not effectively cancel out LJP.

pH の値付けも、実際の測定も、IUPAC2002 のやり方が使えない

$$\mathrm{pH} = -\log a_{\mathrm{H}^+}$$

Pure Appl. Chem., Vol. 74, No. 11, pp. 2169–2200, 2002.
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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

MEASUREMENT OF pH.
DEFINITION, STANDARDS, AND PROCEDURES

(IUPAC Recommendations 2002)

Working Party on pH
R. P. BUCK (CHAIRMAN)[1], S. RONDININI (SECRETARY)[2,‡], A. K. COVINGTON (EDITOR)[3], F. G. K. BAUCKE[4], C. M. A. BRETT[5], M. F. CAMÕES[6], M. J. T. MILTON[7], T. MUSSINI[8], R. NAUMANN[9], K. W. PRATT[10], P. SPITZER[11], AND G. S. WILSON[12]

の枠組は、海水には使えない!

Two-step procedures

海洋科学における pH の定義は、定かではない

“According to Dickson (1984): ‘*The field of pH scales and the study of proton transfer reactions in seawater is one of the most confused areas of marine chemistry*.’ Twenty-seven years later, it still remains confusing, both to insiders and outsiders.”

Marine Chemistry 126 (2011) 89–96

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Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

pH of seawater

G.M. Marion [a,*], F.J. Millero [b], M.F. Camões [c], P. Spitzer [d], R. Feistel [e], C.-T.A. Chen [f]

[a] Desert Research Institute, 2215 Raggio Parkway, Reno, NV, 89512, USA
[b] Rosenstiel School, University of Miami, Miami, FL, USA
[c] University of Lisbon, Lisbon, Portugal
[d] Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
[e] Leibniz-Institut für Ostseeforschung, Warnemünde, Germany
[f] National Sun Yat-Sen University, Taiwan, ROC

海水のpH － ４つの定義が併存している

$$pH_F = -\log([H^+]/m^0)$$

$$pH = -\log(a_{H+}) = -\log(m_{H+}\gamma_{H+}/m^0)$$

$$pH_T = -\log(([H^+] + [HSO_4^-])/m^0)$$

$$pH_{SWS} = -\log(([H^+] + [HSO_4^-] + [HF])/m^0)$$

G. M. Marion, F. J. Millero, M. F. Camoes, P. Spitzer, R. Feistel, C. T. A. Chen, *Mar. Chem.*, **126**, 89-96 (2011).

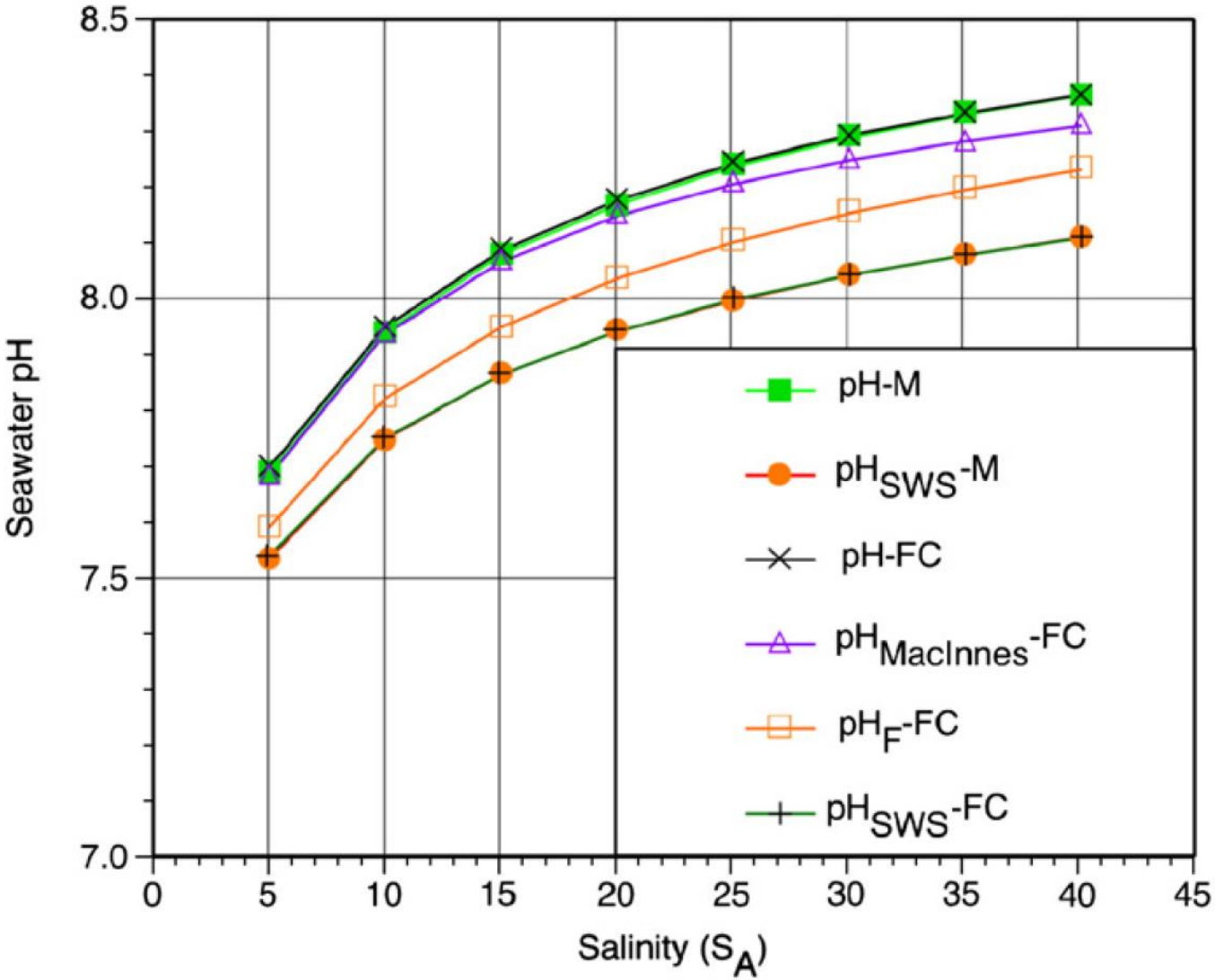


Fig. 2. Model-calculated pH values for seawater (molal concentrations, m) based on the FREZCHEM model (FC) compared to the Miami model (M). T=25 ºC, CO_2=3.33E-4 atm.

G. M. Marion, F. J. Millero, M. F. Camoes, P. Spitzer, R. Feistel, C. T. A. Chen, *Mar. Chem.*, **126**, 89-96 (2011).

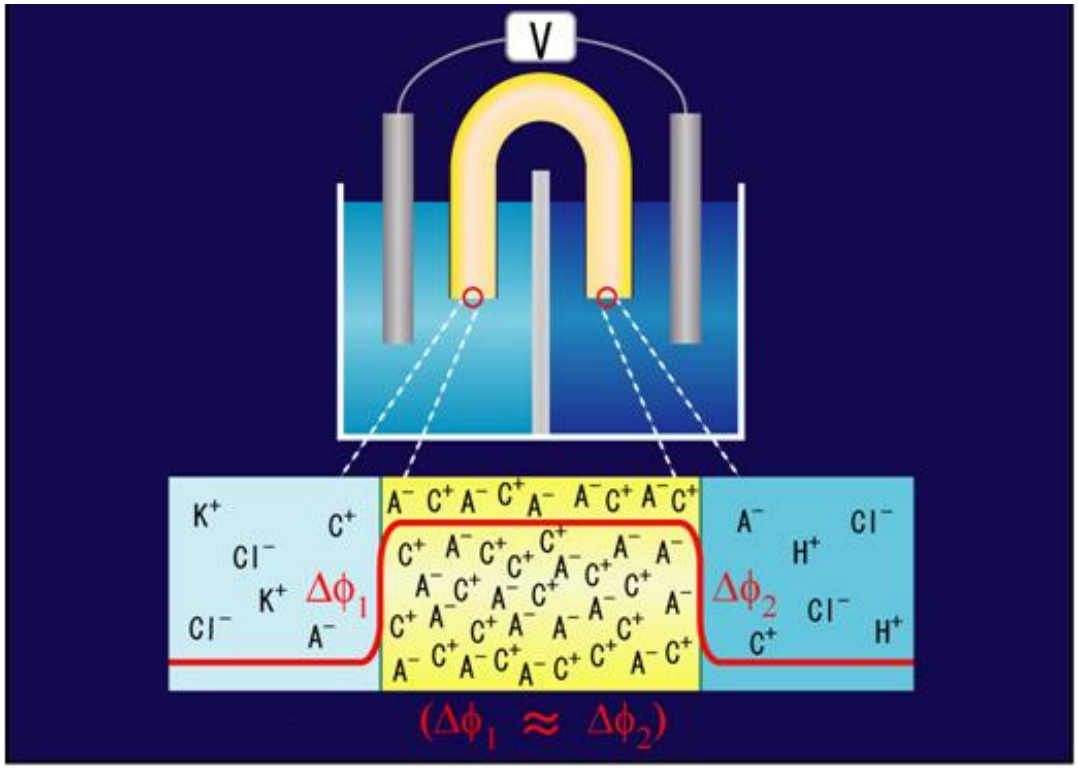
正確な pH 測定ができない最大の原因は、ガラス電極ではなく

参照電極側の液間電位差がゼロでないこと、また、それが変動すること、

KCｌが試料に流入することにより試料のイオン強度を変えてしまうこと

である。

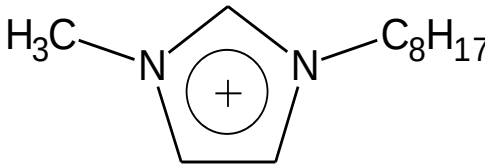
イオン液体塩橋

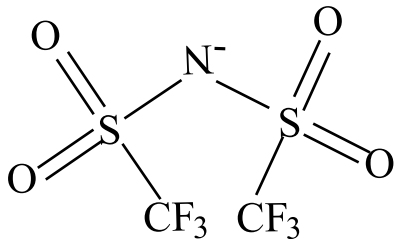


T. Kakiuchi, N. Tsujioka, S. Kurita, and Y. Iwami, *Electrochem. Commun.*, 5, 159-164 (2003).

T. Kakiuchi and T. Yoshimatsu, *Bull. Chem. Soc. Jpn.*, 79, 1017-1024 (2006).

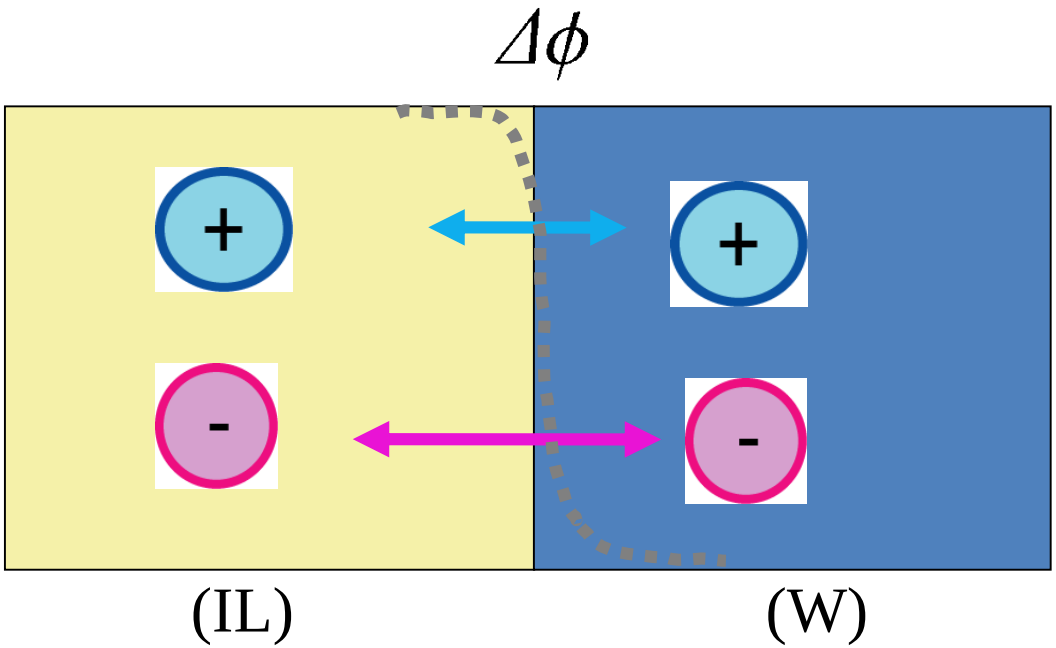
ほどほどに疎水性のイオン液体





$[C_8mim^+][C_1C_1N^-]$

IL-W ２相系



水との相互溶解度（25℃）

0.96 mM IL in W
0.9 wt% W in IL

$$\Delta\phi = -\frac{1}{2F}\left(\Delta G_{R^+}^{IL\to W,0} - \Delta G_{A^-}^{IL\to W,0}\right)$$

T. Kakiuchi, N. Tsujioka, S. Kurita, and Y. Iwami, *Electrochem. Commun.*, 5, 159-164 (2003).

昔ながらの塩橋

satd. KCl (aq.) --------- 動的
時間依存
拡散電位差

新しい塩橋

Ionic liquid --------- 熱力学的
時間に依存しない
分配電位差

- 試料の組成変化が少ない
- メンテナンスの労が激減
- 低イオン強度水溶液に対して安定で信頼できる液間電位差

An innovation since Tower (1896) !

Pt	H_2, 500μmol dm^{-3} H_2SO_4	$P_{444}CCOCC_2C_2N$	X μmol dm^{-3} H_2SO_4, H_2	Pt

X = 20～200μM

Table 3 Experimental and calculated pH value of 20 - 200 μmol dm^{-3} H_2SO_4 [81].

$c_{H_2SO_4}$	$m_{H_2SO_4}$	c_{H^+}	γ_{H^+}	pH_{cal}	pH_{ex}	pH_{ex}-pH_{cal}
μmol dm^{-3}	μmol kg^{-1}	μmol kg^{-1}				
20	20.06	40.04	0.9910	4.401	4.410 ± 0.021*	0.009
50	50.15	99.85	0.9860	4.007	4.008 ± 0.018*	0.001
100	100.30	198.87	0.9804	3.710	3.713 ± 0.026*	0.003
150	150.45	297.12	0.9762	3.538	3.543 ± 0.020*	0.005
200	200.59	394.67	0.9727	3.416	3.421 ± 0.029*	0.005

* 95 % confidence interval

M. Shibata, H. Sakaida, T. Kakiuchi, *Anal. Chem.*, **83**, 164-168 (2011).

Table 4. Effects of Diffusion Potential and Change in Ionic Strength Due to Dissolution of $TBMOEPC_2C_2N$ on Experimental pH Values

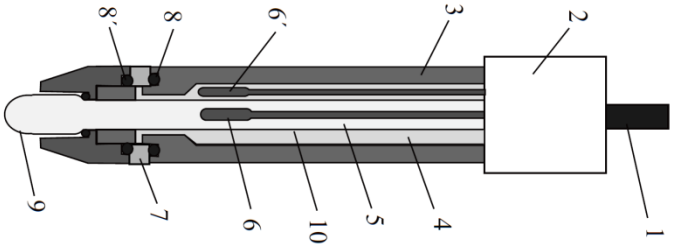
concn of $H_2SO_4/\mu mol\ dm^{-3}$	pH''''_{ex}	$pH''''_{ex} - pH'_{cal}$
20	4.408	0.002
50	4.007	−0.003
100	3.713	0.001
150	3.544	0.004
200	3.421	0.003

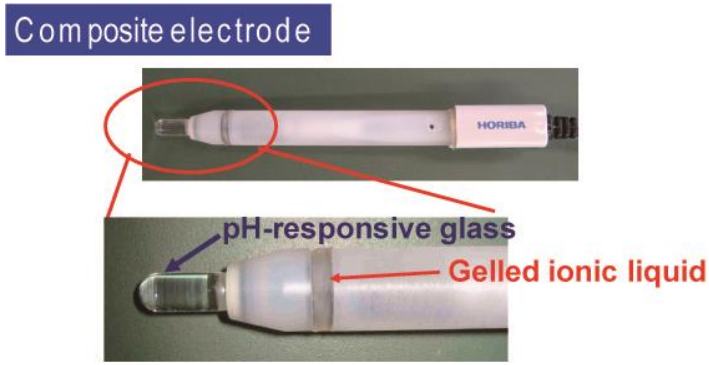
M. Shibata, H. Sakaida, T. Kakiuchi, *Anal. Chem.*, **83**, 164-168 (2011).

Determination of diluted sulfuric acid solutions with a glass combination electrode equipped with a gelled ILSB

Ag/AgCl	0.1 M KCl Satd. with TBMOEP][C_2C_2N	Gelled [TBMOEP][C_2C_2N]	x μM H_2SO_4	Glass electrode

Calibration of glass electrode with citrate and phosphate pH standard buffer solutions





M. Shibata, M. Kato, Y. Iwamoto, S. Nomura, T. Kakiuchi, submitted for publication.

Table 2: Effect of the diffusion potential and the change in the ionic strength due to the dissolution of $TBMOEPC_2C_2N$ on experimental pH values.

Molarity of H_2SO_4 / μmol dm^{-3}	ϕ^{W}_{diff} / mV	pH'_{cal}	pH'_{ex}	pH'_{ex}-pH_{cal}	pH_{ex}-pH'_{cal}	pH'_{ex}-pH'_{cal}
20	-0.199	4.406	4.430	0.029	0.027	0.024
50	-0.086	4.010	4.028	0.021	0.020	0.018
100	-0.041	3.712	3.718	0.008	0.006	0.006
150	-0.024	3.540	3.543	0.005	0.004	0.003
200	-0.016	3.418	3.421	0.005	0.003	0.003

M. Shibata, M. Kato, Y. Iwamoto, S. Nomura, T. Kakiuchi, submitted for publication.

HORIBA Scientific

ラクア
LAQUA

卓上型 pH・水質分析計

HORIBA

CODE:GZ0000273592
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Ionic Liquid Type pH Electrode
9600-10D Instruction Manual

Thank you for purchasing a HORIBA pH electrode.
This electrode does not cause the dissolution of KCl into a sample by adopting the ionic liquid type of a reference electrode. As a result, as compared with the conventional types of HORIBA pH electrodes, this electrode is excellent in the accuracy, reproducibility and stability in measuring any sample of low conductivity. Moreover, it is also optimal for pH measurement of any sample that reacts with KCl. This electrode can be used to connect to a pH meter (D-10, D-20, D-50, F-10, F-20, F-50, and F-70 series). Read this manual carefully, before using the electrode.

About this electrode

Life

This electrode contains ionic liquid (Tributyl (2-methoxyethyl) phosphonium bis (pentafluoroethanesulfonyl) amide) in the gel liquid junction of the reference electrode. When the gel liquid junction is immersed in an aqueous solution, an ionic liquid is solved into the aqueous solution (Solubility: 200 μmol/L). When the amount of an ionic liquid in gel reaches below a constant amount, an electrode reaches the end of its useful life. As a rule of thumb, a useful life is approximately one year for the use of two hours a day. The timing of replacing electrodes is any time when a calibration error occurs.

Re-verification of the Measurement Act after purchasing

For verification of the Measurement Act, a judgment about the results of a re-verification is severer than a judgment about the results of the check of an electrode during calibration with a pH meter. When a re-verification is performed after purchase, check whether linearity meets the verification standards in accordance with " Appendix 1. Procedure for linearity inspection " (page 4). If linearity does not meet the verification standards, clean an electrode in accordance with " Cleansing of electrode " (page 3). If linearity does not meet the verification standards even after the cleaning, replace the electrode with the new one because the electrode has reached the end of life.

Samples affecting measurements

- Organic solvents cause the deterioration of the gel liquid junction of a reference electrode. Avoid the cleaning in organic solvents and the pH measurement of organic solvents.
- Measurement error may be caused by a surface active agent or a heavy metal ion because of the properties of an ionic liquid type reference electrode. The degree of measurement error depends on the type and concentration of a surface active agent or a heavy metal ion. For reference about surface active agents, the table below shows a relationship between the concentrations of sodium dodecyl sulphate (SDS) and measurement errors in the case where SDS is contained in a sample.

Concentration of sodium dodecyl sulphate (mmol/L)	Measurement error (pH)
0.069	-0.01
0.69	-0.12
6.9	-0.86

As an example of reference about heavy metal ions, the table below shows a relationship between the concentrations of copper ions and measurement errors in the case that copper ions are contained in a sample.

Cu ion concentration (mmol/L)	Measurement error (pH)
1	0.04
10	0.34
100	0.41

Color variations of gel liquid junction

- After an electrode is immersed in a sample at a temperature higher than room temperature, the gel of the liquid junction might become cloudy when returning to room temperature. This is no problem with performance.
- When a colorful sample (coffee and soy sauce, etc.) is measured, the gel of the liquid junction might become colored. This is no problem with performance.
- If an electrode is stored at a high temperature for a long time, the gel liquid junction might discolor in brown. This is no problem with performance.

Sample after measurement

Although an ionic liquid is not a poisonoum substance, dispose of a used sample after measurement. Moreover, phosphorus and fluorine are contained in ionic liquid. They are designated as restricted substances under the Water Quality Pollution Control Act and Sewerage Service Act. A sample after ordinary pH measurement does not exceed the effluent standards. A sample (1 L) after an electrode has been immersed for at least 50 days might exceed a restricted value. When disposing of such sample, follow the related laws and/or regulations of your country.

Caution on use

Safety precaution

⚠ CAUTION

Glass fragments
Glass fragments can cause injury.
The outer tube and tip of the electrode are made from glass.
Be careful not to break them.

Points of concern

- A measured sample or measurement for a long time may cause the risk of the sensor members being dissolved. When food samples are measured, do not use the measured samples for an eating purpose. In the case of skin contact with a used sample, flush the sample with water, soap or detergent for skin.
- Do not shock the electrode.
- Do not measure chapped or cracked electrode. Replace such electrode with a new one.
- Do not allow the connector to come in contact with water or unclean hands. If not, accurate measurement cannot be performed.
- If the responsive glass membrane or liquid junction is very dirty and cannot be washed clean using ion exchange water, cleanse it depending on dirt condition. (Refer to " Maintenance " (page 3).)

HORIBA,Ltd.
2 Miyanohigashi, Kisshoin Minami-ku, Kyoto 601-8510 Japan
http://www.horiba.com

For any questions regarding this product, please contact your local agency, or inquire from the HORIBA website.
(http://global.horiba.com/contact_e/index.htm)

ILSB付き複合ガラス電極を用いる雨水のpH 測定の論文

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Notes

Application of a pH Electrode Incorporating an Ionic Liquid Salt Bridge to the Measurement of Rainwater Samples

Yota KUDO,* Manabu SHIBATA, Satoshi NOMURA,**† and Nobuaki OGAWA***

**Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegata Gakuencho, Akita 010–8502, Japan*
***HORIBA, Ltd., 2 Miyanohigashi, Kisshoin, Minami, Kyoto 601–8510, Japan*

ILSB付きガラス電極とKClSB付きガラス電極のpH 応答の時間変化

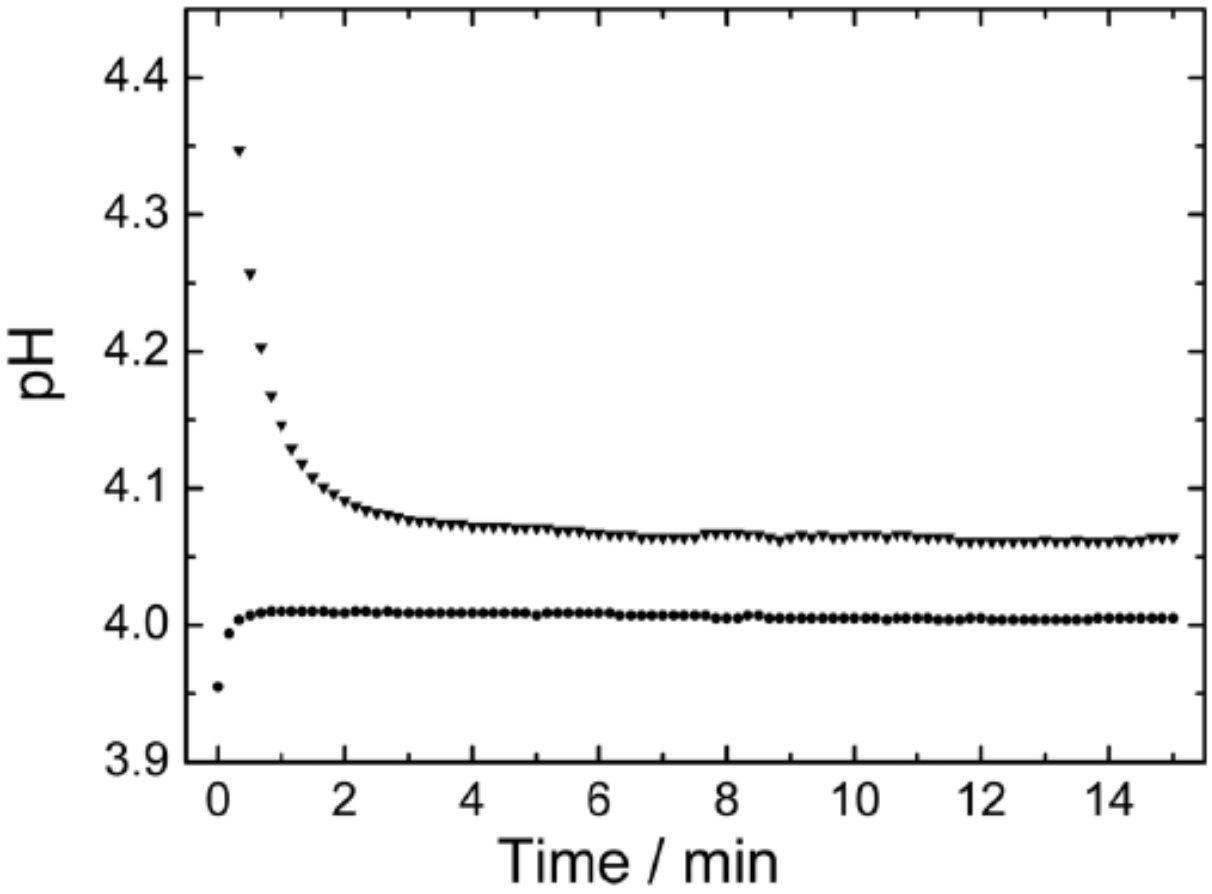

Fig. 1 Typical electrode response curves obtained in a 50 μmol dm^{-3} H_2SO_4 solution. (●) IL-E, (▼) KCl-E.

Y. Kudo, M. Shibata, S. Nomura, N. Ogawa, *Anal. Sci.*, **33**, 739-742 (2017)

pH測定複合ガラス電極を希薄硫酸水溶液に浸したときの電導率変化

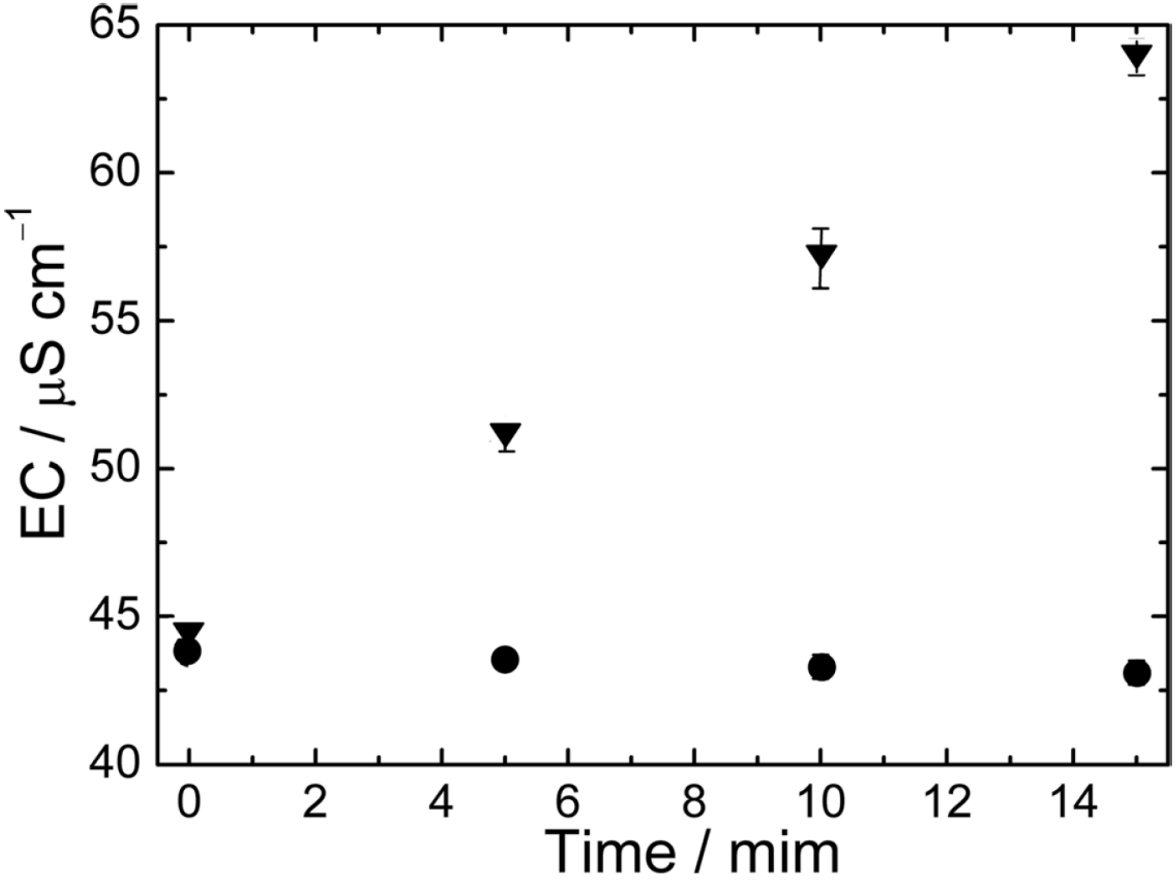

Fig. 3 The change of EC in a 50 μmol dm^{-3} H_2SO_4 solution during pH measurement. (●) IL-E, (▼) KCl-E.

Y. Kudo, M. Shibata, S. Nomura, N. Ogawa, *Anal. Sci.*, **33**, 739-742 (2017)

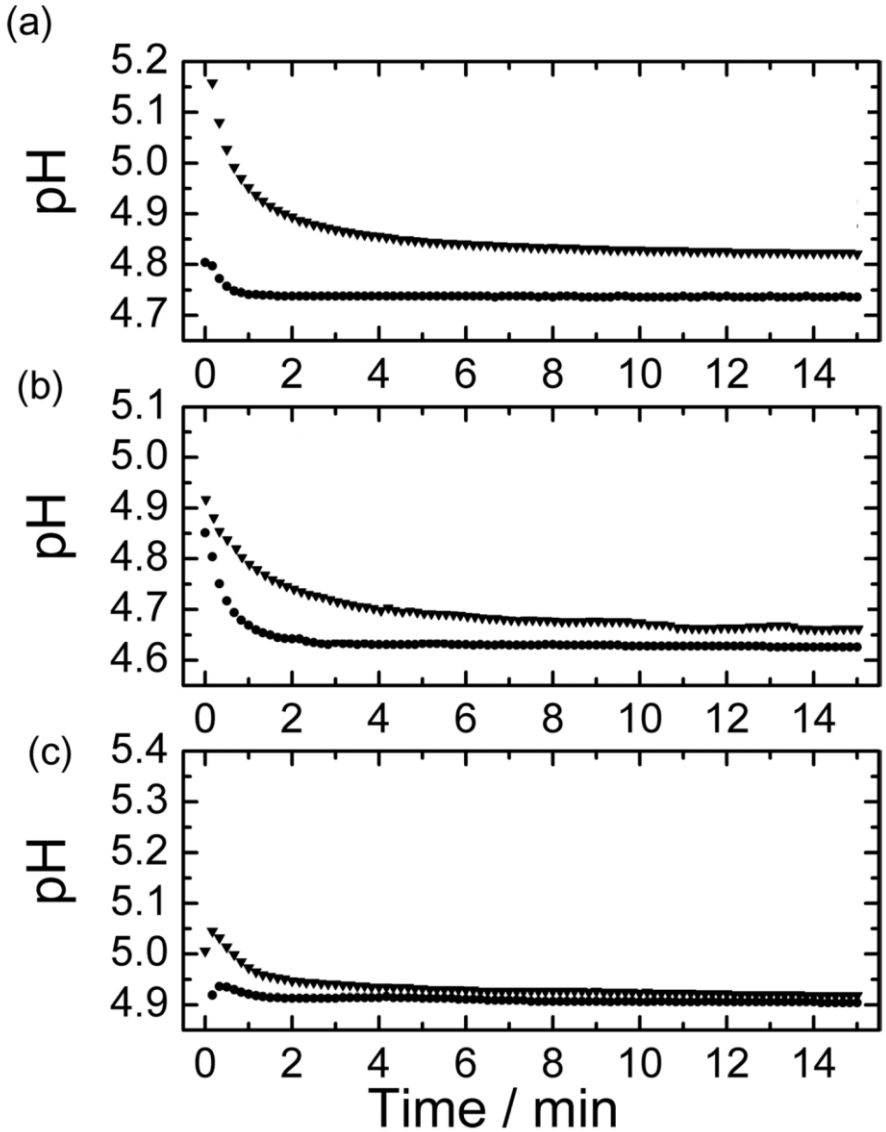

Fig. 4 Typical electrode response curves obtained in real rainwater samples. (●) IL-E, (▼) KCl-E. (a) Sample No. 2 (ionic strength: 45 μmol dm^{-3}), (b) sample No. 4 (ionic strength: 356 μmol dm^{-3}), (c) sample No. 6 (ionic strength: 748 μmol dm^{-3}).

Y. Kudo, M. Shibata, S. Nomura, N. Ogawa, *Anal. Sci.*, **33**, 739-742 (2017)