



# Acidificação dos Oceanos

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11-10-2019

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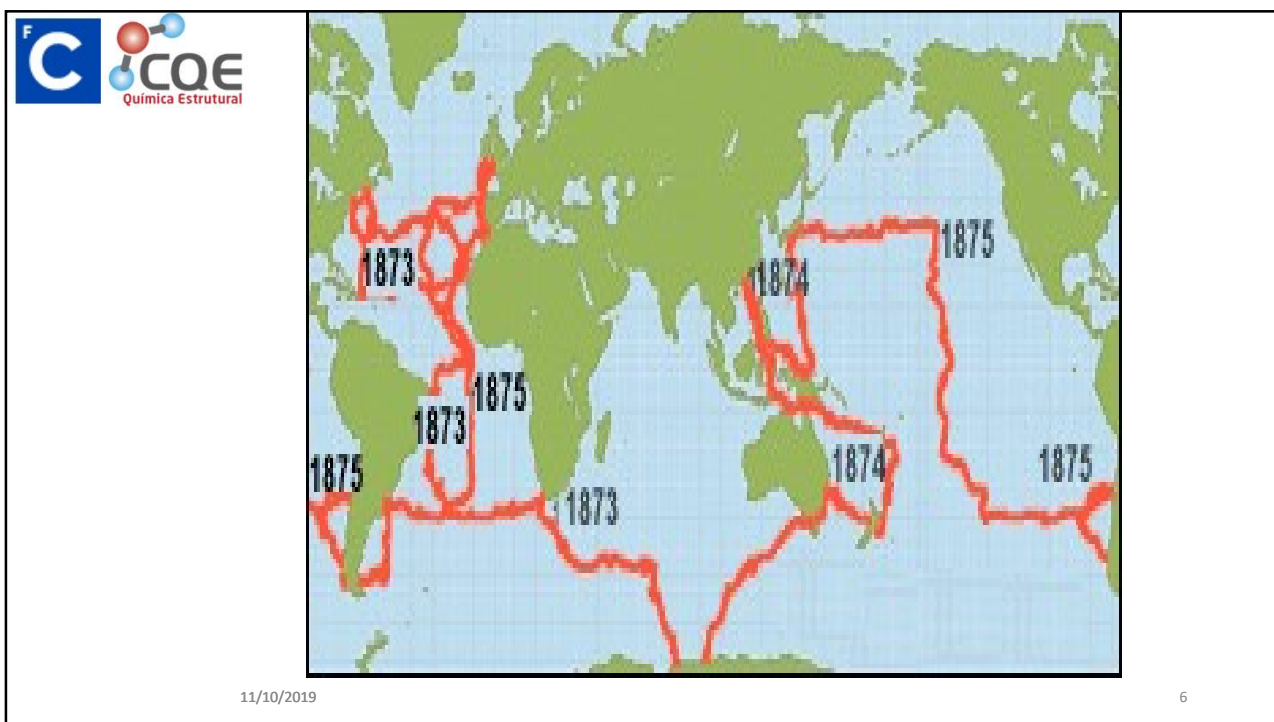
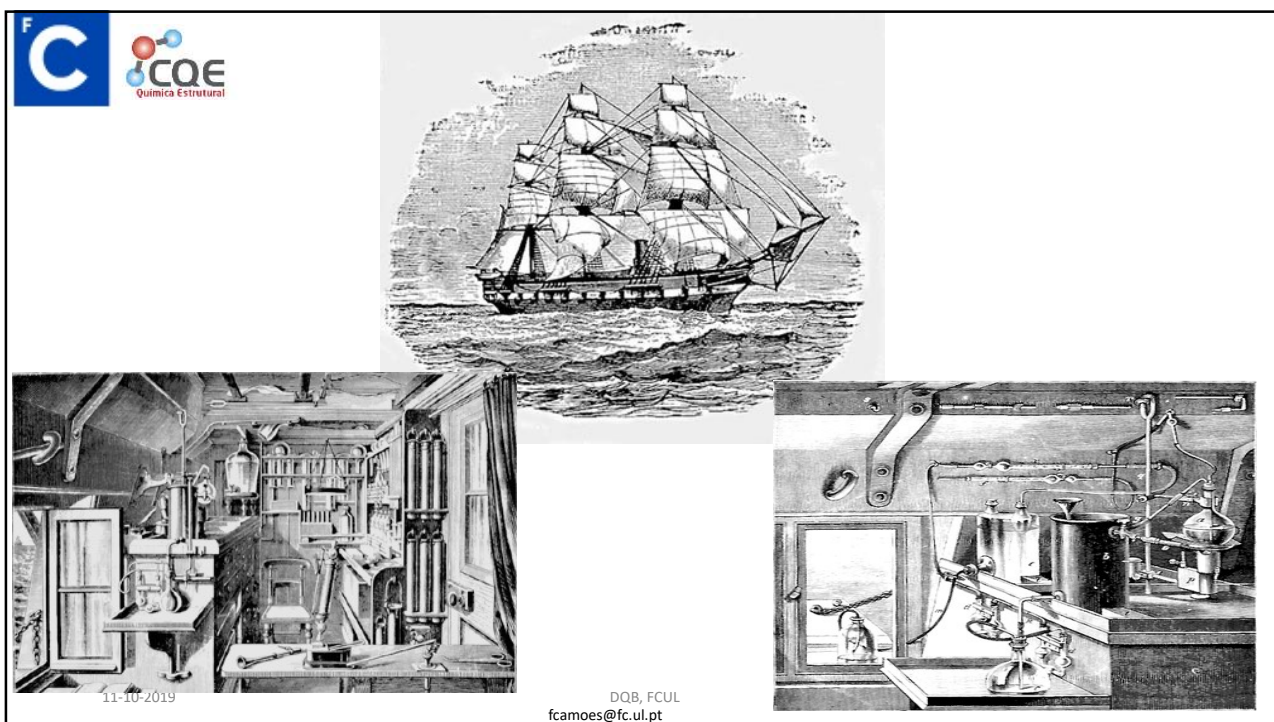
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8th of January 1873: Visit of the **King (???)**  
 to HMS *Challenger* on her inaugural visit to Lisbon.

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**Robert Boyle (1674)**  
published *Observations and Experiments on the Saltiness of the Sea*

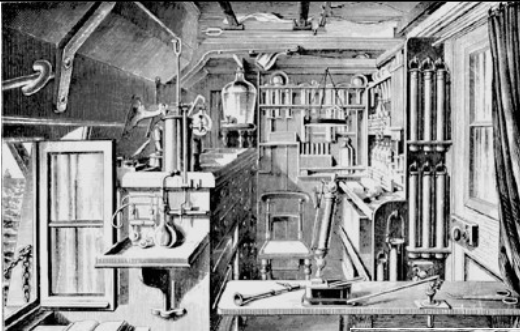
**George Forchammer (1865)**  
introduced the term *salinity, S*, for the total amount of dissolved salts in grams in one kilogram of seawater (g/kg, ‰).

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**Chemistry  
Laboratory-**  
**Salinity, carbonic acid and  
other chemical variables  
were measured.**

$\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightleftharpoons \text{AgCl} (\text{s})$   
 $\text{Ag}^+ (\text{aq}) + \text{Br}^- (\text{aq}) \rightleftharpoons \text{AgBr} (\text{s})$   
 $\text{Ag}^+ (\text{aq}) + \text{I}^- (\text{aq}) \rightleftharpoons \text{AgI} (\text{s})$

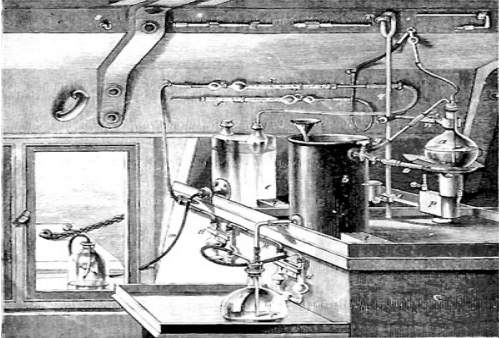
*M. Knudsen-S. Sørensen*

**Carbonic Acid Analysis**  
 Gas analysis began with an ingenious  
 boiling device shown here.  
 Evaporating gases could be trapped,  
 as was carbonic acid, which was  
 analyzed by chemical titration.

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$$



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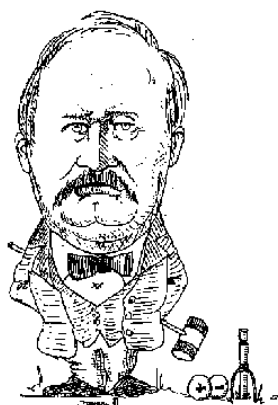
Portugal possui a 3<sup>a</sup> maior (1 727 408  $\text{km}^2$ ) zona económica exclusiva da UE (11%).

Estudos de extensão da plataforma continental irão atribuir a Portugal a jurisdição de novo território marítimo.



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**S. A. Arrhenius, Químico sueco (1859 –1927)**

*Teoria da Dissociação Electrolítica*

**Prémio Nobel da Química em 1903**

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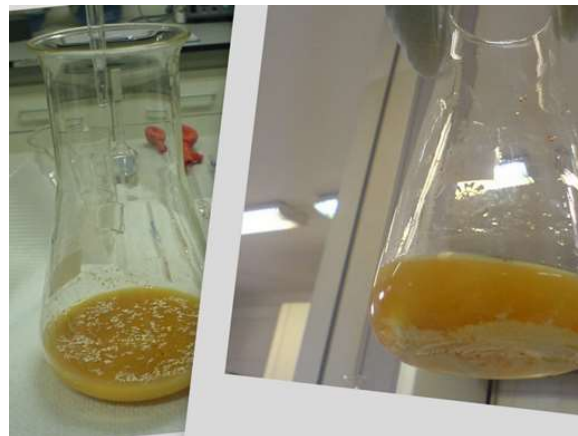
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- $\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightleftharpoons \text{AgCl} (\text{s})$
- $\text{Ag}^+ (\text{aq}) + \text{Br}^- (\text{aq}) \rightleftharpoons \text{AgBr} (\text{s})$
- $\text{Ag}^+ (\text{aq}) + \text{I}^- (\text{aq}) \rightleftharpoons \text{AgI} (\text{s})$

*M. Knudsen-S. Sorensen*  
(0.04 ppm 0.1-0.2 ppm)



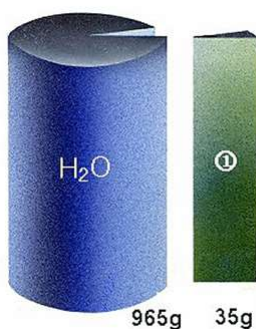
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## Salinidade



Componente	Composição mol kg <sup>-1</sup>
NaCl	0,4186
MgCl <sub>2</sub>	0,0596
Na <sub>2</sub> SO <sub>4</sub>	0,02856
KCl	0,01
CaCl <sub>2</sub>	0,005
....	...

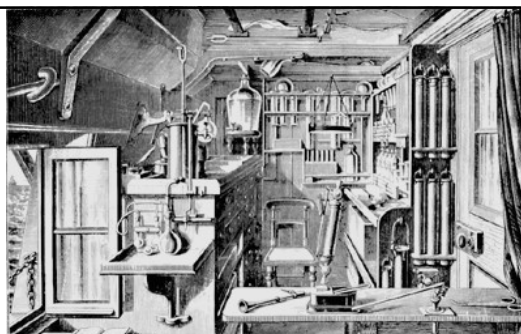


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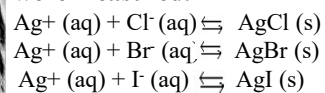
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**Chemistry  
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Salinity, carbonic acid and  
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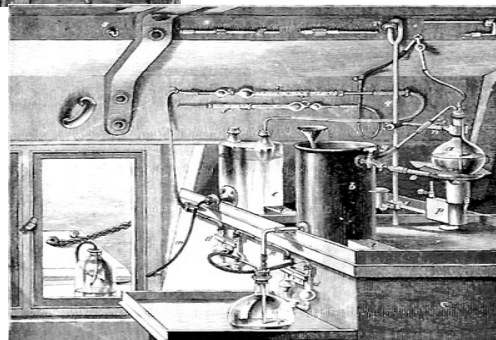
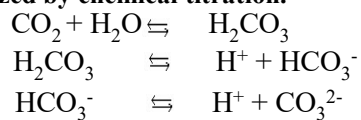


*M. Knudsen-S. Sørensen*

**Carbonic Acid Analysis**

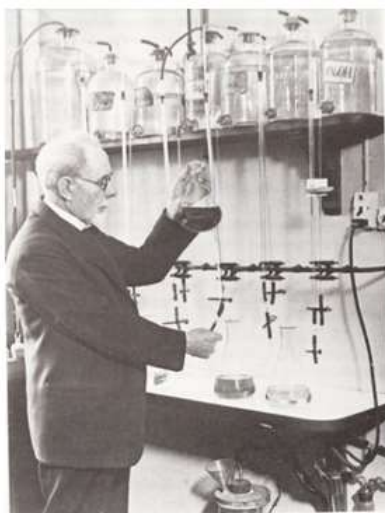
Gas analysis began with an ingenious  
boiling device shown here.

Evaporating gases could be trapped,  
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analyzed by chemical titration.



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**Søren P. L. Sørensen, Químico Dinamarquês (1868-1939)**

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**F CQEQ**  
Química Estrutural


**It started with beer**





**Carlsberg brewery Copenhagen 1909**



S.P.L. Sørensen proposed the name pH "Potentia Hydrogenii" as a measure of the Hydrogen ion concentration in aqueous solutions



$$\text{pH} = -\lg c_{\text{H}}$$


$$\text{pH} = -\lg a_{\text{H}}$$


pH is a measure of activity!

**A century of pH Measurements**  
MF Camões,  
Chemistry International, Vol 32, nº 2, March -April 2010, pages 3-7

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**F CQEQ**  
Química Estrutural

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**NATURAL E ANTROPOGÉNICO**

Maria Filomena Gomes Ferreira Crujo Camões



11/10/2019 file:///D:/Drive/Os%20meus%20documentos(OLD)/NATURAL%20E%20ANTROPOGÉNICO%202010.pdf



## Célula de Bjerrum

Pt, H<sub>2</sub> | Sol.(c<sub>H</sub>) || Ponte salina || 0.1 mol dm<sup>-3</sup> KCl | Hg<sub>2</sub>Cl<sub>2</sub> (s), Hg

$$\text{Lei empírica de Nernst } E_1 - E_2 = \frac{RT}{F} \ln \frac{(c_H)_2}{(c_H)_1}$$

M. F. Camões, A century of pH Measurement  
*Chemistry International*, 32, 2 (1910)

**pH measurement is often deceptively easy . . .**

**... pH measurement can also be exasperatingly difficult.**

G. Mattock, 1963

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## Parâmetros de Qualidade



### ✓ Condutividade

A condutividade eléctrica, K, de uma água permite avaliar o seu grau de mineralização e o valor prático da salinidade, dada a relação existente entre o teor em sais dissolvidos na água e a resistência, R, que ela oferece à passagem de corrente eléctrica.

↪ Determinada através de condutímetros e usando uma água do mar de referência

$$K = A / R$$

Método físico para medir a salinidade(1978), sendo esta, neste caso, uma grandeza adimensional.

### ✓ Acidez / pH

O pH da uma água representa uma medida da sua acidez, que pode ser traduzida pela actividade dos iões hidrogénio (a<sub>H</sub>) livres em soluções

$$\text{pH} = - \log (a_H)$$

↘ Influência no clima e reflexo dos processos de troca do dióxido de carbono.



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**FC**

**COE**  
Química Estrutural

Salinidade

H<sub>2</sub>O 965g

35g

Componente	Composição mol kg <sup>-1</sup>
NaCl	0,4186
MgCl <sub>2</sub>	0,0596
Na <sub>2</sub> SO <sub>4</sub>	0,02856
KCl	0,01
CaCl <sub>2</sub>	0,005
....	...

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is the saltiness or  
ed salt content of a body of water



1902- *absolut salinity*  
 $S = 0,03 + 1,805 (Cl)$

1969- UNESCO-  
 $S = 1,80655 (Cl)$

Salinity 35 ‰ = Clorinity 19,374 ‰

1978- PSU, electrical conductivity relative to  
a standard seawater

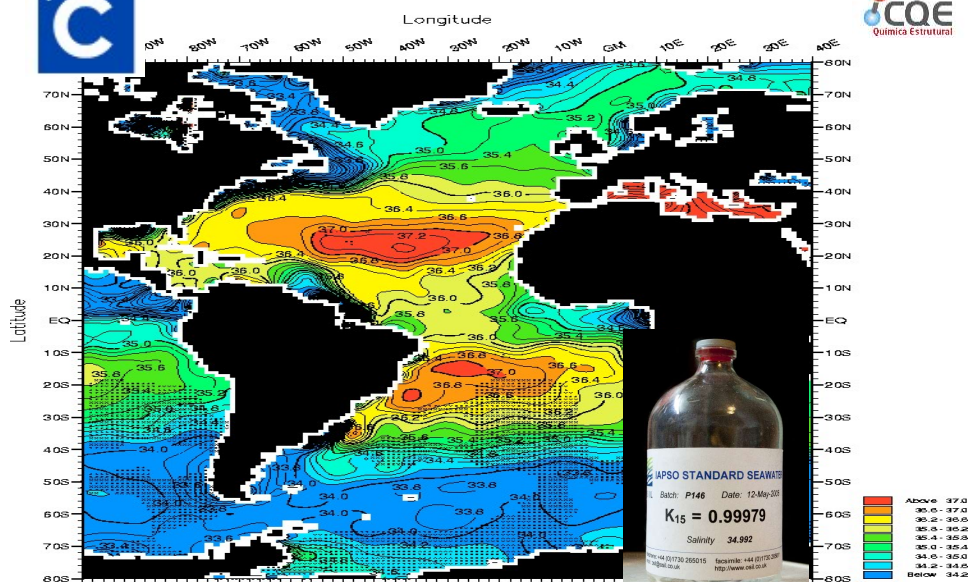


Fig. I2-1. April mean salinity (PSS) at the surface .  
Minimum Value= 0.00 Maximum Value= 42.22 Contour Interval: 0.20



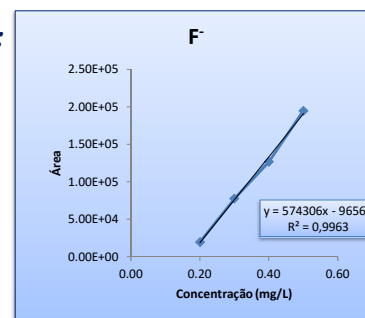
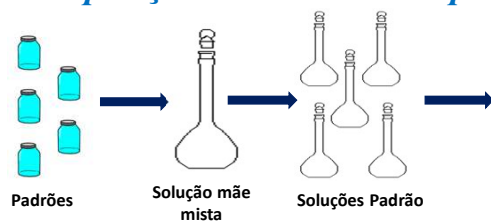
## Amostragem – Recolha de amostras

Mergulha-se a garrafa na água, tentando ao máximo evitar a entrada de ar.

Fecha-se bem para evitar a formação de bolhas de ar.

### Determinação dos Parâmetros de qualidade:

#### ✓ Composição iónica: Análise por CI



Determinação da composição iónica, catiões e aniões, em amostras previamente diluídas

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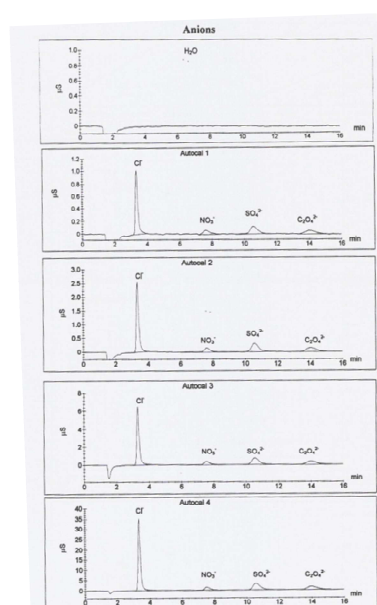



Figure A.1.8. Chromatograms of a calibration curve for anions, analysing Hi-Vol Whatman 41<sup>®</sup> filters.

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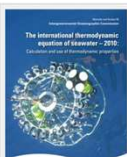


# TEOS-10

Thermodynamic Equation Of Seawater - 2010

### MENU

- Home
- Publications
- Software
- Educational resources
- JCS news
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### HOME


This site is the official source of information about the Thermodynamic Equation Of Seawater - 2010 (TEOS-10), and the way in which it should be used.

TEOS-10 is based on a Gibbs function formulation from which all thermodynamic properties of seawater (density, enthalpy, entropy sound speed, etc.) can be derived in a thermodynamically consistent manner. TEOS-10 was adopted by the Intergovernmental Oceanographic Commission at its 25th Assembly in June 2009 to replace EOS-80 as the official description of seawater and ice properties in marine science.

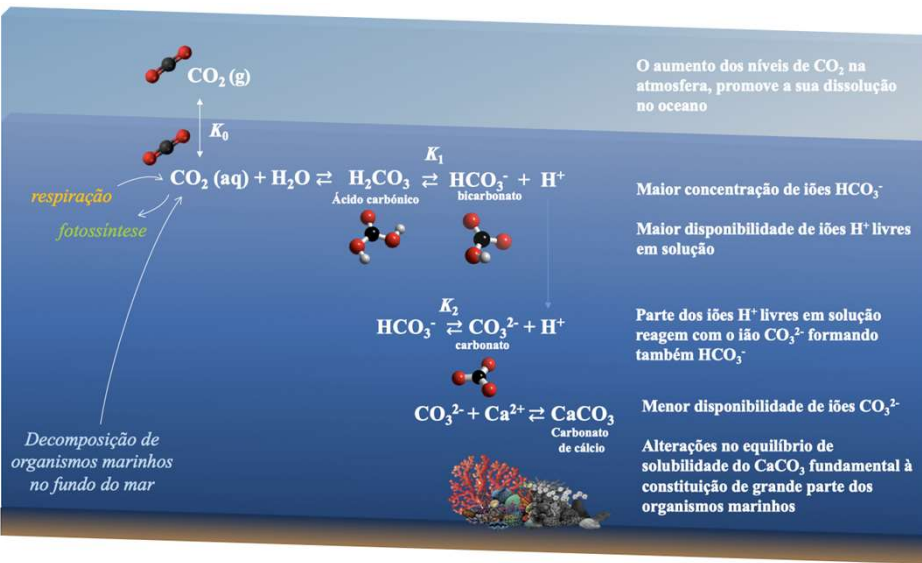
A significant change compared with past practice is that TEOS-10 uses Absolute Salinity  $S_A$  (mass fraction of salt in seawater) as opposed to Practical Salinity  $S_p$  (which is essentially a measure of the conductivity of seawater) to describe the salt content of seawater. Ocean salinities now have units of g/kg.

Absolute Salinity (g/kg) is an SI unit of concentration. The thermodynamic properties of seawater, such as density and enthalpy, are now correctly expressed as functions of Absolute Salinity rather than being functions of the conductivity of seawater. Spatial variations of the composition of

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## SISTEMA CARBONATO OCEÂNICO



respiração

fotossíntese

Decomposição de organismos marinhos no fundo do mar

O aumento dos níveis de  $\text{CO}_2$  na atmosfera, promove a sua dissolução no oceano

Maior concentração de íons  $\text{HCO}_3^-$

Maior disponibilidade de íons  $\text{H}^+$  livres em solução

Parte dos íons  $\text{H}^+$  livres em solução reagem com o íon  $\text{CO}_3^{2-}$  formando também  $\text{HCO}_3^-$

Menor disponibilidade de íons  $\text{CO}_3^{2-}$

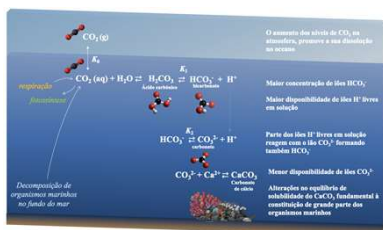
Alterações no equilíbrio de solubilidade do  $\text{CaCO}_3$  fundamental à constituição de grande parte dos organismos marinhos

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## Variáveis de Caracterização do Sistema Carbonato Oceânico

$$pH = -\lg\left(\frac{a_{H^+}}{a^0}\right)$$

$$pCO_2 = \frac{[CO_2]}{K_0}$$

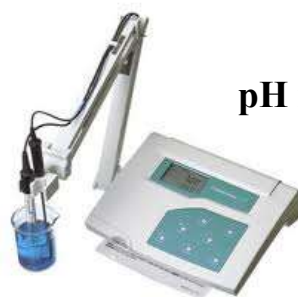
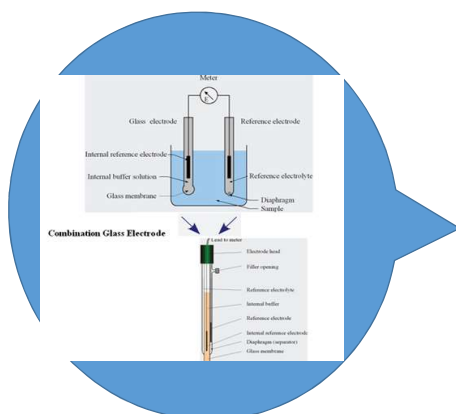


$$TA = [HCO_3^-] + 2 [CO_3^{2-}]$$

$$DIC = \sum CO_2 = [HCO_3^-] + [CO_3^{2-}] + [CO_2]$$

$$[CO_2] = [CO_2(aq)] + [H_2CO_3]$$

pH(X)



pH meter





## IUPAC Recommendations 2002

### Measurement of pH. Definition, standards, and procedures

By: Buck, RP (Buck, RP); Rondinini, S (Rondinini, S); Covington, AK (Covington, AK); Baucke, FGK (Baucke, FGK); Brett, CMA (Brett, CMA); Camoes, MF (Camoses, MF); Milton, MJT (Milton, MJT); Mussini, T (Mussini, T); Naumann, R (Naumann, R); Pratt, KW (Pratt, KW)

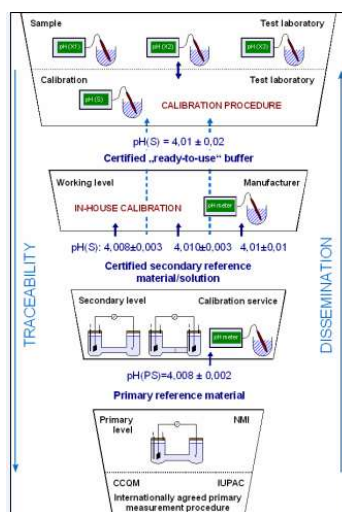
PURE AND APPLIED CHEMISTRY

Volume: 74 Issue: 11 Pages: 2169-2200

DOI: 10.1351/pac200274112169

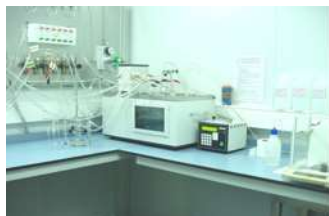
Published: NOV 2002

the uncertainties for the primary method, and for all subsequent measurements, permits the uncertainties for all procedures to be linked to the primary standards by an unbroken chain of comparisons. Thus, a rational choice can be made by the analyst of the appropriate procedure to achieve the target uncertainty of sample pH.

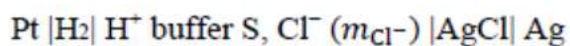




## PRIMARY MEASUREMENTS - PRIMARY STANDARDS



*Harned cell*



$$E = E^{\circ}_{\text{Ag,AgCl}} - \left( \frac{RT}{F} \ln 10 \right) \lg(a_{\text{H}^+} a_{\text{Cl}^-})$$

$$E = E^{\circ} - \frac{RT}{F} 2.303 \lg(m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-})$$



## ACIDITY FUNCTION

$$-\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-}) = \text{p}(a_{\text{H}^+} \gamma_{\text{Cl}^-}) = \frac{E - E^{\circ}}{\left[ \left( \frac{RT}{F} \right) \ln 10 \right]} + \lg(m_{\text{Cl}^-})$$

$$\text{p}(a_{\text{H}^+} \gamma_{\text{Cl}^-}) + \lg \gamma_{\text{Cl}^-} = -\lg a_{\text{H}^+} = \text{p}a_{\text{H}^+} = \text{pH}$$

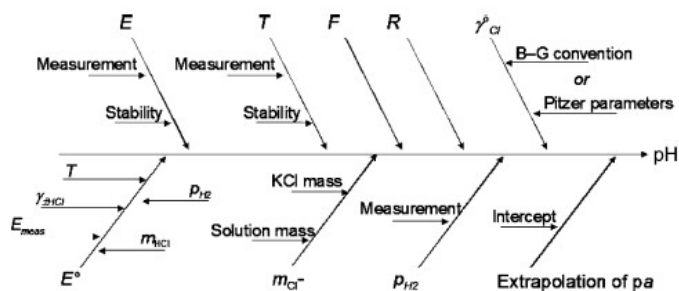
Debye-Hückel/Bates-Guggenheim ( $I \leq 0.1 \text{ mol kg}^{-1}$ ):

$$\lg(\gamma_{\text{Cl}^-})^{\circ} = \frac{-A\sqrt{I}}{1 + 1.5\sqrt{I}} \quad \dots \text{uncertainty of } 0.01 \text{ (95\% confidence interval) in pH associated with the Bates-Guggenheim....}$$



NBS pH Standards

Solution composition (molality)	pH(S) at 25 °C
<b>Primary Standards:*</b>	
potassium hydrogen tartrate (KHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> , sat'd. at 25 °C)	3.557
(KHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> , 0.01 m)	2.620
potassium dihydrogen citrate (KH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> , 0.05 m)	3.776
potassium hydrogen phthalate (KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub> , 0.05 m)	4.006
potassium dihydrogen phosphate/ disodium hydrogen phosphate (KH <sub>2</sub> PO <sub>4</sub> , 0.025 m + Na <sub>2</sub> HPO <sub>4</sub> , 0.025 m)	6.863
(KH <sub>2</sub> PO <sub>4</sub> , 0.0087 m + Na <sub>2</sub> HPO <sub>4</sub> , 0.0304 m)	7.410
sodium tetraborate decahydrate, (borax) (Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O, 0.01 m)	9.180
sodium bicarbonate/sodium carbonate (NaHCO <sub>3</sub> , 0.025 m + Na <sub>2</sub> CO <sub>3</sub> , 0.025 m)	10.010



Cause-effect diagram for pH Primary Measurement

$$E^0 = f(E, T, p_{H_2}, m_{HCl}, \Delta A_{g/AgCl})$$

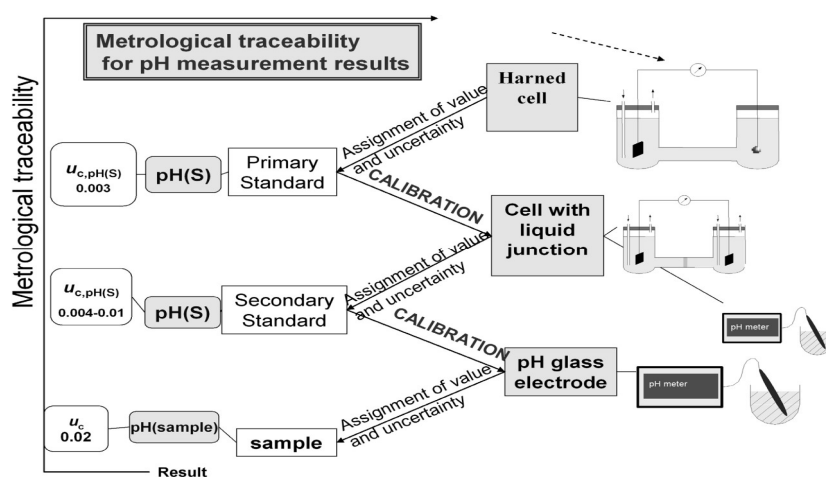
$$u_c = \sqrt{a_1^2 u_E^2 + a_2^2 u_T^2 + a_3^2 u_{p_{H_2}}^2 + a_4^2 u_{m_{HCl}}^2 + a_5^2 u_{\Delta A_{g/AgCl}}^2}$$


$a_1 = 1; a_2 = 0,00081; a_3 = 1.30E-07; a_4 = 5.14; a_5 = 1$


$$p(a_{H/Cl}) = f(E, E^0, T, p_{H_2}, m_{Cl^-}, \Delta A_{g/AgCl})$$

$$u_c = \sqrt{a_1^2 u_E^2 + a_2^2 u_{E^0}^2 + a_3^2 u_T^2 + a_4^2 u_{p_{H_2}}^2 + a_5^2 u_{m_{Cl^-}}^2 + a_6^2 u_{\Delta A_{g/AgCl}}^2}$$

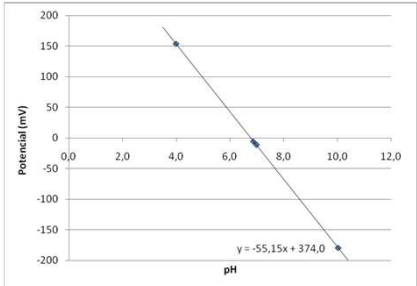
$a_1 = 16.9; a_2 = 16.9; a_3 = 0.031; a_4 = 2.20E-06; a_5 = 86.86; a_6 = 16.9$








$$E = E^0 + k \text{ pH}$$





**Certificado de Material de Referência**

**BUNICA 4.000.011**

**Preparação do MRC**  
O MRC (Material de Referência Certificado) consiste de uma solução preparada gravimetricamente a partir de um único componente de pureza conhecida, com o conteúdo exato de  $\text{H}^+$  definido a partir de medições com um método de referência primário em nível de grau A, e armazenado em frascos de polipropileno de alta qualidade devidamente caracterizados e certificados pelo IAPAC.

**Atividade e Interconformidade atitudinal na Certificação**  
A caracterização foi realizada no sistema primário de medição de pH (1), (2), (3) usando o método de pH calibrado pelo bufer.

**Reprodutibilidade Inter-laboratório**  
O valor certificado possui reprodutibilidade interlaboratório garantida através da caracterização do MRC realizada no sistema primário de medição de pH de laboratório.

**Finalidade de uso**  
O MRC tem sua utilização destinada à calibração de medidores de pH.

**Atividade e Interconformidade**  
A atividade do MRC é dada em termos de atividade de  $\text{H}^+$  em solução aquosa, sendo o valor certificado de pH 4.000.011 para um nível de atividade de aproximadamente 10%, baseado no método de medição de buferes de referência (1), (2), (3) com distribuição de buferes.

**Valor Certificado e Incerteza Expandida**  
O valor certificado de material de referência, a 25 °C ± 0,1 °C, com um intervalo de validade expandido, sendo a partir de medições primárias, realizadas em laboratório de referência, é de pH 4.000.011 para um nível de atividade de aproximadamente 10%, baseado no método de medição de buferes de referência (1), (2), (3) com distribuição de buferes.

**Prazo de Validade**  
O MRC permanece válido por 10 anos de medição de pH, em termos de medição de referência.  
O bufer deve ser armazenado à temperatura ambiente de referência até a data de validade de uso.


**Referências**  
(1) Bardsley, R. J., et al., Measurement of pH, Hydrogen, Hydroxyl, and Fluoride Ion Concentrations (1982), Pure Appl Chem, Vol. 54, No. 1, pp. 2109-2120, 1982.  
(2) IAPAC, "Activity of  $\text{H}^+$  and  $\text{OH}^-$  concentrations in primary pH measurement for the certification of standard solutions. Best. pract. appendix, Vol. 48, pp. 79-82, 1996.  
(3) IAPAC, "Activity of  $\text{H}^+$  and  $\text{OH}^-$  concentrations in primary pH measurement for the certification of standard solutions. Best. pract. appendix, Vol. 48, pp. 79-82, 1996.  
(4) Chen, J., et al., "Evaluation of the Accuracy of pH Measurements Using Standard Buffer Solutions", Metrologia, Vol. 48, pp. 79-82, 1996.


**Rastreabilidade Metroológica**  
O valor certificado possui rastreabilidade metroológica garantida através da caracterização do MRC realizada no sistema primário de medição de pH do Instituto.

**Finalidade de uso**  
O MRC tem sua utilização destinada à calibração de medidores de pH.

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Marine Chemistry xxx (2011) xxx-xxx

Contents lists available at ScienceDirect

**Marine Chemistry**

Journal homepage: [www.elsevier.com/locate/marchem](http://www.elsevier.com/locate/marchem)

**pH of seawater**

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**A B S T R A C T**

An important property of aqueous solutions is pH because it affects chemical and biochemical properties such as chemical reactions, equilibrium conditions, and biological toxicity. With the increasing uptake of fossil fuel CO<sub>2</sub> into the oceans, a decrease in pH is important to consider at this time. Unfortunately, many different methods for assessing pH have been used by different groups. The objectives of this review were to: (1) briefly examine the concept of pH as it was introduced and developed, up to the current scientific developments, assumptions, and recommendations; (2) critically assess the various approaches that different scientific groups have adopted for pH, balancing their preferences and arguments; (3) compare measuring vs. modeling pH; and (4) issue recommendations on an optimized approach or approaches for pH.

The main conclusions of this review are: (1) pH definitions and conventions are highly variable, which leads to highly variable estimates of pH. For example, for seawater at S<sub>w</sub> = 35.165 g/kg (sal), t = 25 °C, P = 1.0 atm, and

**pH = 0.002 desired accuracy** reflects the desire to measure changes in the CO<sub>2</sub> content of sea water that allow the increases due to the burning of fossil fuels to be observed. (determined using pH glass electrodes)

Modeling can, in principle, lead to pH estimates that are more accurate than measurements, which is illustrated with two Pitzer models for natural waters made up of the major components of seawater. But this principle still needs to be proven; (5) It is recommended that ocean scientists use the free concentration or activity of the proton to examine the effect of pH on processes in the oceans.

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**Metrology of Ocean Salinity and Acidity**  
**JRP 07e Ocean Metrology**

Ocean is the main regulator of the global climate system  
 Ocean is a sink for anthropogenic carbon dioxide  
 Salinity and temperature are driving forces for global ocean currents

**Impact**

- Long-term comparability of oceanographic data with appropriate uncertainties
- Converge in oceanographic monitoring programs
- Prerequisite for climate change research required for long-term prediction decisions
- Demanded by the European Marine Framework Directive (2002/43/EC)

**Objectives**

- Salinity, temperature, density, speed of sound, pH, composition, dissolved oxygen
- First time final trace of traceability
- Novel measurement capabilities with reduced uncertainties
- Improved standards

**Impact**

- Europe provides comparability of oceanographic data on Atlantic time scale
- European metrology institutes build up knowledge on ocean monitoring
- Metrological corridors established in oceanography
- Seawater data disseminated to oceanographic organizations and institutions worldwide

**Co-ordinator**  
PTB, Germany

**Principal partners**

- INMEL, Italy
- IPG, Portugal
- JRC (EMMA), EC
- LNEC, Portugal
- ETHZ, Finland
- MPIK, Hungary
- NPL, UK
- SML, Slovakia
- UT, Estonia

**Research Excellence Grant**  
University of Plymouth, UK

**Collaborators**

- SOCA
- MPRO
- MPWS
- OSL
- APAC
- OSCTRADES
- NET US, San Diego
- NET RECORD, UK, New York
- OSMA ITI, LAMAZ, Italy
- OSM, Ljubljana, Slovenia
- OSM ITI, COAST ITI, New York

**Budget 4.4 Mio €**

**State-of-the-art**

- Practical Salinity**  
Not traceable  
Long-term comparability not guaranteed
- Speed of sound**  
Existing data not sufficient for Equation of State
- pH**  
Analysis results  
Seawater composition not traceable  
Trace element species  
Poor knowledge
- Dissolved oxygen**  
Data depend on method

**Scientific work packages**

- WP1** Traceability of practical salinity based on primary standards  
Up to high pressure (100 MPa)  
88 PM
- WP2** Extended measurement range for thermodynamic properties of seawater  
Up to high pressure (100 MPa)  
97 PM
- WP3** Primary and reference methods for acidic and alkaline composition of seawater  
pH, trace, major elements  
RED + Trace elements  
103 PM
- WP4** Metrology of dissolved oxygen  
Oxidometric and coulometric methods with reduced uncertainties  
45 PM

**Impact**

- Traceability for Standard Seawater
- Transfer Standard for CTD sensor calibration
- Speed of sound data with reduced uncertainties  
Open access database and software
- Traceable results of pH, minor ions, nutrients, trace metals in seawater  
Practical Guides
- Traceable calibration of sensors with microfluidics  
Available by a factor of two  
Practical Guide

**EMRP**  
Cooperation with the European Metrology Programme  
Property of EURAMET



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B.V. Nemzer, A.G. Dickson / *Marine Chemistry* 96 (2005) 237–242

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**Solutions**

g each of buffer were  
 n in Table 1. All the salts  
 Cl, MgCl<sub>2</sub>, CaCl<sub>2</sub>) were  
 urified further by recryst-  
 gCl<sub>2</sub> and CaCl<sub>2</sub> were used  
 been assayed by titration  
 accuracy of better than  
 a stock solution prepared  
 and assayed coulometri-  
 etter than 0.02%. The Tris  
 1® (trihydroxyaminome-  
 Fisher Scientific Corpora-

Table 1  
 Nominal composition of equimolar (0.04 mol/kg-H<sub>2</sub>O Tris+0.04 mol/kg-H<sub>2</sub>O Tris-HCl) Tris buffer in synthetic seawater of salinity 35

Component	Concentration (mol/kg-H <sub>2</sub> O)	Concentration (mol/kg-soln)	Weight (g) in 1 kg solution <sup>a</sup>
NaCl	0.38762 <sup>b</sup>	0.37087	21.6884
Na <sub>2</sub> SO <sub>4</sub>	0.02927	0.02801	3.9808
KCl	0.01058	0.01012	0.7551
MgCl <sub>2</sub>	0.05474	0.05238	—
CaCl <sub>2</sub>	0.01075	0.01029	—
Tris	0.08000	0.07654	9.2748
HCl	0.04000	0.03827	—

<sup>a</sup> Weights in air at sea level (i.e., not corrected to mass). If a weight is not given, the component is added as the appropriate amount of a calibrated solution.

<sup>b</sup>  $m(\text{NaCl}) = 0.42762 - 0.04 \text{ mol/kg-H}_2\text{O}$ , i.e. replacing NaCl with HCl.

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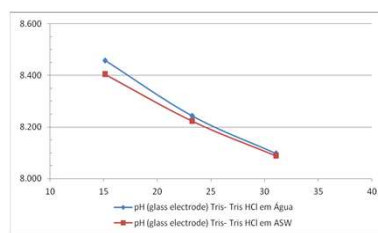
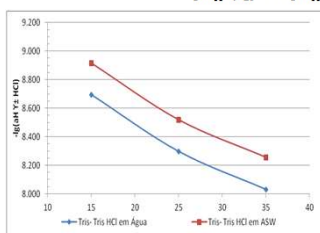
**Pt, H<sub>2</sub> | 0.04 equiv Tris-TrisHCl (PS) (ASW-NaCl,KCl,CaCl<sub>2</sub>,MgCl<sub>2</sub>,Na<sub>2</sub>SO<sub>4</sub>) | AgCl | Ag (compensated Cl)**

$$E = E^\circ - \frac{RT}{F} 2.303 [\lg(m_{H^+} \gamma_{H^+} \gamma_{Cl^-}) + \lg m_{Cl^-}]$$

$$p a_{H^+} \gamma_{Cl^-} = \frac{E - E^\circ}{\frac{RT}{F} 2.303} + \lg m_{Cl^-}$$

$$p a_{H^+} \gamma_{Cl^-} = p a_{H^+} - \lg \gamma_{Cl^-}$$

$$p m_{H^+} = p a_{H^+} + \lg \gamma_{H^+}$$



**Pt, H<sub>2</sub> | HCl, ASW (NaCl,KCl,CaCl<sub>2</sub>,MgCl<sub>2</sub>,Na<sub>2</sub>SO<sub>4</sub>) | AgCl | Ag**  
(*I*<sub>effective</sub> ≠ *I*<sub>formal</sub>)

$$E = E^\circ - \frac{RT}{F} 2.303 \lg(m_{H^+} m_{Cl^-} \gamma_{\pm}^2)$$

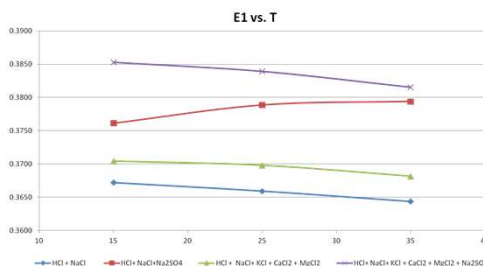
$$m_{H^+}$$

$$m_{H^+} + m_{HSO_4^-} = m_{HCl}$$

$$m_{HSO_4^-} + m_{SO_4^{2-}} = m_{Na_2SO_4}$$

$$K_a = \frac{m_{H^+} m_{SO_4^{2-}}}{m_{HSO_4^-}}$$

	HCl+NaCl+KCl+CaCl <sub>2</sub> +MgCl <sub>2</sub> +Na <sub>2</sub> SO <sub>4</sub>		
	15 °C	25 °C	35 °C
<i>m</i> H <sup>+</sup>	0,00585301	0,00494359	0,00416775
<i>m</i> HSO <sub>4</sub> <sup>-</sup>	0,0041803	0,00508972	0,00586556
<i>m</i> SO <sub>4</sub> <sup>2-</sup>	0,02506618	0,02415676	0,02338092
<i>K</i> <sub>a</sub>	0,03509617	0,0234632	0,01661321
<i>K</i> <sub>a,γ±</sub>	0,02582727	0,01713048	0,01201966





Pt | H<sub>2</sub> (g, 1 atm) | Tris+TrisHCl 0.04 equim, H<sub>2</sub>O/ASW | AgCl, Ag

$$E = E_{\text{Ag,AgCl}}^{\circ} - \left( \frac{RT}{F} \ln 10 \right) \lg (a_{\text{H}^+} a_{\text{Cl}^-})$$

$$E = E_{\text{Ag,AgCl}}^{\circ} - \left( \frac{RT}{F} \ln 10 \right) \lg (m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\pm}^2)$$

$$E = E_{\text{Ag,AgCl}}^{\circ} - \left( \frac{RT}{F} \ln 10 \right) [\lg m_{\text{Cl}^-} + 2 \lg (\gamma_{\pm})] - \left( \frac{RT}{F} \ln 10 \right) \lg m_{\text{H}^+}$$

$$E = E_{\text{Ag,AgCl}}^{\circ} - \left( \frac{RT}{F} \ln 10 \right) \lg (a_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-})$$

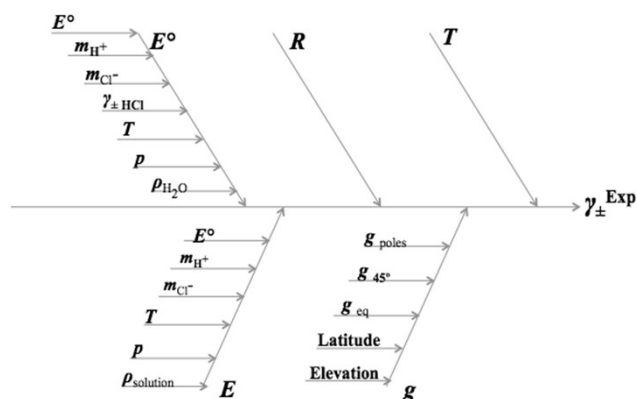
$$E = E_{\text{Ag,AgCl}}^{\circ} - \left( \frac{RT}{F} \ln 10 \right) [\lg m_{\text{H}^+} + \lg (a_{\text{H}^+} \gamma_{\text{Cl}^-})]$$

$p m_{\text{H}}$

\*  
EXPERIMENTALLY  
ASSESSED  
Pitzer

Pitzer

$p(a_{\text{H}} \gamma_{\text{Cl}})$







..... the IUPAC pH standard is only valid to  $I \leq 0.1$  m because of the limits of Eq. (12).

Potentially this approach could be extended to higher concentrations (e.g., seawater at  $I = 0.72$  m) by using the Pitzer equations for defining activity coefficients at higher concentrations:

$$\ln(\gamma_X) = z_X^2 F + \sum m_c (2B_{cX} + ZC_{cX}) + \sum m_a (2\Phi_{Xa} + \sum m_c \Psi_{cXa}) + \sum \sum m_c m_c \Psi_{ccX} + |z_X| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nX} + \sum \sum m_n m_c \zeta_{ncX} \quad (17)$$

where  $B$ ,  $C$ ,  $\Phi$ ,  $\Psi$ ,  $\lambda$  and  $\zeta$  are Pitzer-equation interaction parameters (Pitzer, 1991, 1995) among cations (c), anions(a), and neutral species(n),  $m_i$  is the molal concentration, and  $F$  and  $Z$  are equation functions . .....



$$\gamma_{\pm} = (\gamma_{H^+} \gamma_{Cl^-})^{1/2}$$

$\gamma_{Cl^-}$  (Pitzer)

$$\ln \gamma_{Cl^-} = z_{Cl^-}^2 F + \sum m_b [2B_{bc} + ZC_{bc}] + \sum m_a [2\Phi_{Ca} + \sum m_c \Psi_{cCa}]$$

$\gamma_{H^+}$  (Pitzer)

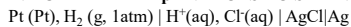
$$\ln \gamma_{H^+} = z_{H^+}^2 F + \sum m_b [2B_{ba} + ZC_{ba}] + \sum m_c [2\Phi_{Mc} + \sum m_a \Psi_{Ma}]$$

$\gamma_{\pm}$  (Pitzer)

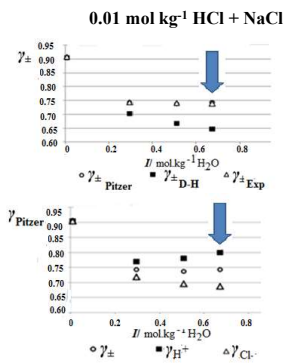
$$\ln \gamma_{MCl} = -z_M z_{Cl^-} |F + (v_m/v) \sum m_b [2B_{Ma} + ZC_{Ma} + 2(v_X/v_M) \Phi_{Xa}] + (v_X/v) \sum m_b [2B_{cX} + ZC_{cX} + 2(v_M/v_X) \Phi_{Mc}]$$



ASSIGNMENT OF PRIMARY pH VALUES TO SALINE WATERS



$$E = E_{Ag/AgCl}^0 - \left(\frac{RT}{F} \ln 10\right) \lg(a_{H^+} a_{Cl^-}) = E_{Ag/AgCl}^0 - \left(\frac{RT}{F} \ln 10\right) [\lg(m_{H^+} m_{Cl^-}) + \lg(\gamma_{H^+} \gamma_{Cl^-})]$$



Experimental:  $\gamma_{\pm}^2$

Pitzer:  $\gamma_{\pm}^2 = \gamma_{H^+} \gamma_{Cl^-}$

(25°C)	0.66 mol kg <sup>-1</sup> NaCl	(0.46 mol kg <sup>-1</sup> NaCl + 0.01 mol kg <sup>-1</sup> KCl + 0.01 mol kg <sup>-1</sup> CaCl <sub>2</sub> + 0.05 mol kg <sup>-1</sup> MgCl <sub>2</sub> )	(0.43 mol kg <sup>-1</sup> NaCl + 0.01 mol kg <sup>-1</sup> KCl + 0.01 mol kg <sup>-1</sup> CaCl <sub>2</sub> + 0.05 mol kg <sup>-1</sup> MgCl <sub>2</sub> + 0.029 mol kg <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> )
$\gamma_{\pm, \text{Exp}}$	0.737 ± 0.002	0.727 ± 0.003	ASW
$\gamma_{\pm, \text{Pitzer}}$	0.736	0.734	
$\gamma_{H^+} \gamma_{Cl^-}$			



Mean Gama for 0.01HCl&NaCl&Na2S04

Folha pronta para qualquer determinação de  $\gamma_{\pm}$  experimental a 25 °C

$\mu(E)$ (V)	$\mu(m_{H^+})$ (mol kg <sup>-1</sup> )	$\mu(m_{Cl^-})$ (mol kg <sup>-1</sup> )	$\mu(\gamma_{\pm})$ (at 25°C)	$\mu(T)$ (°C)	$\mu(P_{atm})$ (Pa)	$\mu(\rho_{sol})$ (kg m <sup>-3</sup> )	$\mu(E)$ (V)	$\mu(m_{H^+})$ (mol kg <sup>-1</sup> )	$\mu(m_{Cl^-})$ (mol kg <sup>-1</sup> )	$\mu(T)$ (°C)	$\mu(P_{atm})$ (Pa)	$\mu(\rho_{sol})$ (kg m <sup>-3</sup> )	$\mu(\gamma_{\pm})$ (at 25°C)	$\mu(\gamma_{\pm})$ (at 25°C)
0.466795	0.00943640	0.00943640	0.9042	25.00073501	101027.8361	101027.8361	0.466795	0.00943640	0.00943640	25.00073501	101027.8361	101027.8361	0.9042	0.9042

Determination of  $E_{meq}^*$  (V): 0.466795

Auxiliary calculations:  $E_{meq}^*$  (at T°): 0.467201

Determination of  $\gamma_{\pm}$  (at T°): 0.738789

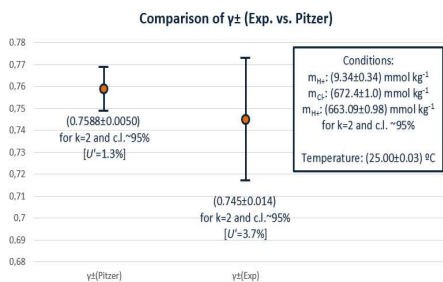
Calibration:  $\gamma_{\pm}^{\text{Exp}} = \text{EqH2SO4\_K2\_conc}(H)$



“...the evaluation of the uncertainty of the pH in complex seawater matrix (mathematical model, list of main sources, their evaluation and their propagation)...”

Comparison of  $\gamma_{\pm}$  estimated experimental and by Pitzer model

Measurement uncertainty: Kragten numerical method checked for function linearity

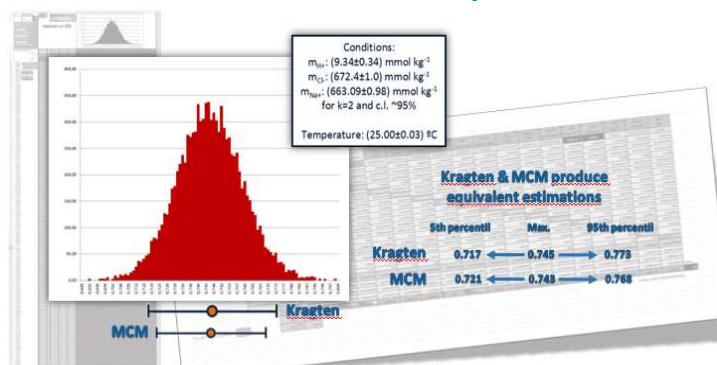


Measurement results are Metrologically compatible for 95% confidence level



Comparação de  $\gamma_{\pm}$  estimado experimentalmente u os métodos de Kragten ou simulação de Monte Carlo

MCM método com 10010 iterações





Accred Qual Assur  
DOI 10.1007/s00769-015-1163-y



GENERAL PAPER

## Compatibility of activity coefficients estimated experimentally and by Pitzer equations for the assessment of seawater pH

Bárbara Anes<sup>1</sup> · Ricardo J. N. Bettencourt da Silva<sup>1</sup> · Hugo F. P. Martins<sup>1</sup> ·  
Cristina S. Oliveira<sup>2</sup> · M. Filomena Camões<sup>1</sup>

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*water*

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Communication

### Traceability of pH to the Mole

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**Assessment of H<sup>+</sup> in complex aqueous solutions approaching seawater**

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Concentrations and activities  
Potentiometry  
Ion association  
Salinity  
Ion strength

**ABSTRACT**

pH measurements are used to assess both the free activity of aqueous solutions and the concentrations,  $m$ , of chemical species related to hydrogen ion, H<sup>+</sup>, through chemical equilibrium, provided that measurements in reference solutions with well known compositions are also carried out. Seawater is a highly complex electrolytic matrix of variable composition, rich in NaCl, where the determination of pH =  $-\lg a_{\text{H}^+}$  ( $a_{\text{H}^+} = m_{\text{H}^+} \gamma_{\text{H}^+}$ ) is the activity of the specified ion, H<sup>+</sup>, with the concentration  $m_{\text{H}^+}$  and activity coefficient  $\gamma_{\text{H}^+} = 1$  is an issue of controversy. Electrostaticity prevents measurement of individual ion activity coefficients, which are affected and depend on the other ions in presence, namely the counter ions. Nevertheless, mean activity coefficients,  $\gamma_{\pm}$ ,  $\gamma_{\pm}^{\text{H}^+}$ , in this case  $\gamma_{\pm} = \sqrt{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}}$ , can be experimentally assessed from the application of the Nernst equation to Harned cells (Pt|H<sub>2</sub>|a<sub>H</sub>|Ag|AgCl electrodes, without transference) in solutions of known  $m_{\text{NaCl}}$  and  $m_{\text{HCl}}$ . In this work measurements of electrical potential,  $E$ , were first taken in strategically planned solutions, ranging from 0.01 mol kg<sup>-1</sup> HCl to 0.01 mol kg<sup>-1</sup> NaCl, to 0.01 mol kg<sup>-1</sup> HCl + 0.01 mol kg<sup>-1</sup> NaCl + 0.01 mol kg<sup>-1</sup> MeCl<sub>2</sub>, of ionic strength,  $I = 0.07 \text{ mol kg}^{-1}$  at 15 °C, 25 °C and 35 °C with experimental pressure corrected to reference pressure of 1 atm. Mean activity coefficients were experimentally assessed with associated uncertainty. Further addition of sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, targeting artificial seawater (ASW), originates acid-base equilibria that affect the free hydrogen ion concentration,  $m_{\text{H}^+}$ . The changes introduced by the addition of sulfate in the measured Harned cell potential have been used to assess the free proton concentration and, based on the obtained results, to propose for the first time a procedure aiming to calculate values of bromide association constants with the corresponding uncertainty at 25 °C for both studied media. Further, the effective ionic strength of artificial seawater (ASW) was calculated and compared with the value obtained using the salinity based equation largely conveyed in the literature.

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Multiple seawater pH definitions yield a pH range >50x greater than 0.002 pH target uncertainty for climate studies.

pH scale	Definition of "pH"	Ionic Strength / mol kg <sup>-1</sup>	"pH" value
NIST SRMs	$-\log_{10} a(\text{H}^+)$	< 0.1	8.332
Free	$-\log_{10} c(\text{H}^+)$	0.4 – 0.9	8.195
Total	$-\log_{10} \Sigma [c(\text{H}^+) + c(\text{HSO}_4^-)]$	0.4 – 0.9	8.087
Seawater	$-\log_{10} \Sigma [c(\text{H}^+) + c(\text{HSO}_4^-) + c(\text{HF})]$	0.4 – 0.9	8.078

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## Certificate of Analysis

pH reference material (tris buffer in synthetic seawater)

Batch 10 (Bottled on August 3, 2011)

### Analysis Results

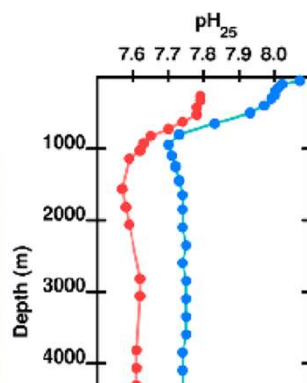
The pH

$$\text{pH} = -\log_{10} \left( \frac{[\text{H}^+]}{\text{mol kg-soln}^{-1}} \right)$$

was determined on the total hydrogen ion scale using a hydrogen / silver – silver chloride cell (DeValls & Dickson, 1998). Two separate samples were measured in triplicate, on two different dates

The pH estimated was  $8.0924 \pm 0.0004$  (6; 2)

The cited uncertainty represents the standard deviation. Figures in parentheses are the number of analyses made (total number of analyses; number of separate bottles)



- Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity. **Part 3: Seawater pH**, Dickson, A. G.; Camoes, M.F.; Spitzer, P.; Fiscaro, P.; Stoica, D.; Pawlowicz, R.; Feistel, R, *METROLOGIA*, 53, 1 (2016) R26-R39 DOI: 10.1088/0026-1394/53/1/R26
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- Filomena Camões, Bárbara Anes, Hugo Martins, Cristina Oliveira, Paola Fiscaro, Daniela Stoica, Petra Spitzer "Assessment of H<sup>+</sup> in complex aqueous solutions approaching seawater", *Journal of Electroanalytical Chemistry* 764 (2016) 88–92.
- MF. Camões, B. Anes "Traceability of pH to the mole", *Water* (2015), 7, 4247-4255; doi:10.3390/w7084247



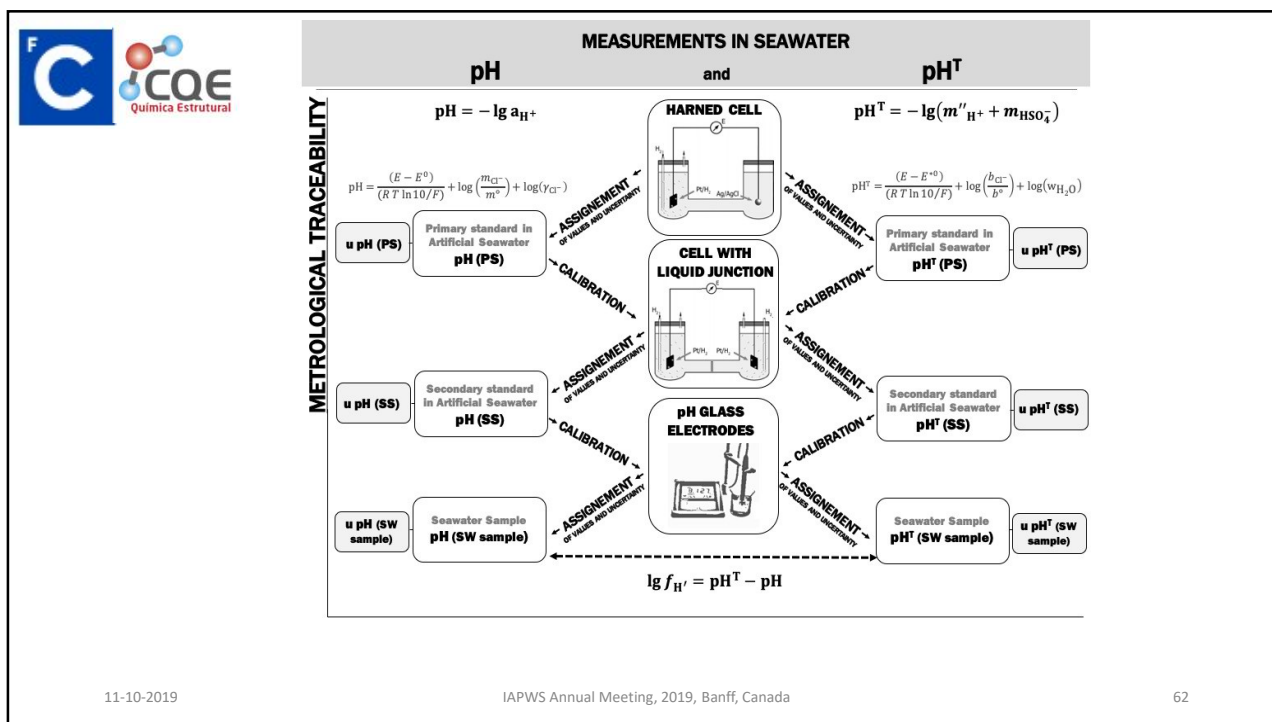
- **Uncertainty evaluation of alkalinity measurements on seawater samples**

Bárbara Anes; Ricardo J.N. Bettencourt da Silva; Cristina Oliveira; M. Filomena Camões, *Measurement* 129 (2018) 395-404, Doi: 10.1016/j.measurement.2018.07.042

- **Seawater pH measurements with a combination glass electrode and high ionic strength TRIS-TRIS HCl reference buffers - An uncertainty evaluation approach.** Anes, B (Anes, Barbara); da Silva, RJNB (Bettencourt da Silva, Ricardo J. N.); Oliveira, C (Oliveira, Cristina); Camoës, MF (Filomena Camoës, M.), *TALANTA*, 193 (2019) 118-22 DOI: 10.1016/j.talanta.2018.09.075.

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## Spectrophotometric measurements ( $\text{pH}^T$ ) → m-cresol indicator

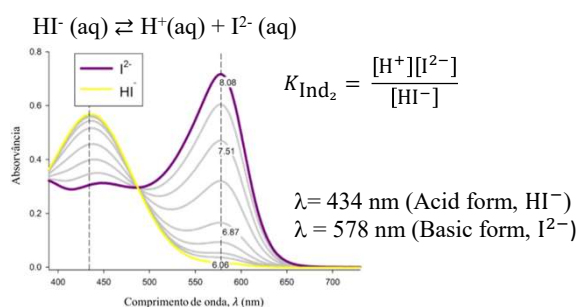
Andrew G Dickson (1993)



$$\text{pH}^T = -\lg (m_{\text{H}^+} + m_{\text{HSO}_4^-}) = -\lg [m_{\text{H}^+} (1 + \beta_{\text{HSO}_4^-} m_{\text{SO}_4^{2-}})]$$

kg of seawater

6 solutions of TRIS-TRIS HCl in ASW prepared independently in different laboratories (NMIs)



$$\text{pH}^T = pK_{\text{Ind}_2} + \lg \frac{[\text{I}^{2-}]}{[\text{HI}^-]}$$



	LNE	PTB
<b>pH</b> (primary method)	8.322	8.288
<b>pH<sub>T</sub></b> (spectrophotometric)	8.092	8.098

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## ISO 18191:2015(en) Water quality — Determination of $\text{pH}_t$ in sea water — Method using the indicator dye m-cresol purple

$$\text{pH}_t = -\lg [\text{H}^+]_t$$

The total hydrogen ion concentration

$$[\text{H}^+]_t = [\text{H}^+]_F (1 + S_T/K_S) \approx [\text{H}^+] + [\text{HSO}_4^-]$$

is expressed as moles per kilogram of sea water


The method is suitable for assaying oceanic levels of  $\text{pH}_t$  7.4 to 8.2 for normal sea water of practical salinity ranging from 20 to 40

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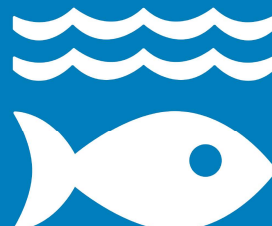
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# 14

## LIFE BELOW WATER



### SDG 14 TARGETS:

**14.1** By 2025, prevent and significantly reduce marine pollution of all kinds

**14.2** By 2020, sustainably manage and protect marine and coastal ecosystems to avoid significant adverse impacts



**14.3** Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels

**14.4:** By 2020, effectively regulate harvesting and end overfishing, illegal, unreported and unregulated fishing and destructive fishing practices


**14.5:** By 2020, conserve at least 10 per cent of coastal and marine areas

**14.6** By 2020, prohibit certain forms of fisheries subsidies which contribute to overcapacity and overfishing, eliminate subsidies that contribute to illegal, unreported and unregulated fishing

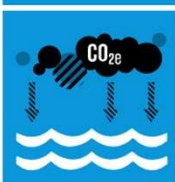
**14.7** By 2030, increase the economic benefits to Small Island developing States and least developed countries from the sustainable use of marine resources

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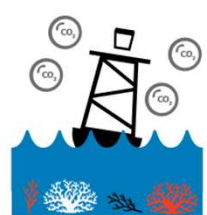
### TARGET 14.3



## REDUCE OCEAN ACIDIFICATION

Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels.

Open ocean sites show **current levels of acidity have increased by 26 per cent** since the start of the Industrial Revolution



4.3.1 “average marine acidity (pH) measured at an agreed suite of representative sampling stations”

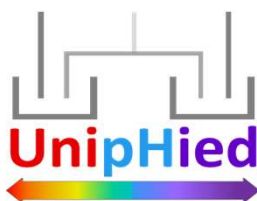
Methodology for measuring marine acidity recognized by United Nations

**A methodology to measure marine acidity will help keep track of national efforts to combat ocean acidification as countries fasten their pace to implement the UN Sustainable Development Goals.**

At the 51st IOC Executive Council meeting in July 2018, the IAEG-SDGs formally accepted a methodology for SDG indicator 14.3 as a Tier II indicator.

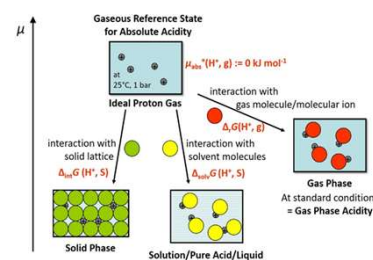
IOC-UNESCO developed the global framework for measuring and collecting data on marine pH with the support of the ocean acidification scientific community.

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## A unified pH scale for all solvents

### Meaning and assessment of pH in solvents other than water



Concept of a unified Brønsted acidity scale  $\text{pH}_{\text{abs}}$ , defined on the basis of the chemical potential of the proton,  $\mu(\text{H}^+)$

Values of  $\text{pHs} = -\lg(a_{\text{H}^+, \text{solv}})$  are related through the proton Gibbs free energy of transfer between solvents:

$$\mu = \delta G / \delta n = \mu^\circ + R T \ln a \quad \mu(\text{H}^+) = \mu^0(\text{H}^+) + R T \ln a(\text{H}^+) = \mu^0(\text{H}^+) - R T \ln 10 \times \text{pH}_5$$

$$\Delta G = -W_e = -n F E$$

Indicator electrode (Ind<sub>1</sub>) | Solution 1 (S<sub>1</sub>) | Bridge solution (B) | Solution 2 (S<sub>2</sub>) | Indicator electrode 2 (Ind<sub>2</sub>)

$$\Delta E = E(\text{Ind}_2) - E(\text{Ind}_1) = -\frac{RT \ln 10}{F} [\text{pH}(S_2) - \text{pH}(S_1)]$$

$$\Delta E = \Delta E_{\text{measured}} + \Delta E_j(\text{B}, S_1) - \Delta E_j(\text{B}, S_2)$$

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**Salinity** is the saltiness or dissolved salt content of a body of water

1902- *absolut salinity*  
 $S = 0,03 + 1,805 (Cl)$

1969- UNESCO-  
 $S = 1,80655 (Cl)$

Salinity 35 ‰ = Clorinity 19,374 ‰

1978- PSU, electrical conductivity relative to a standard seawater

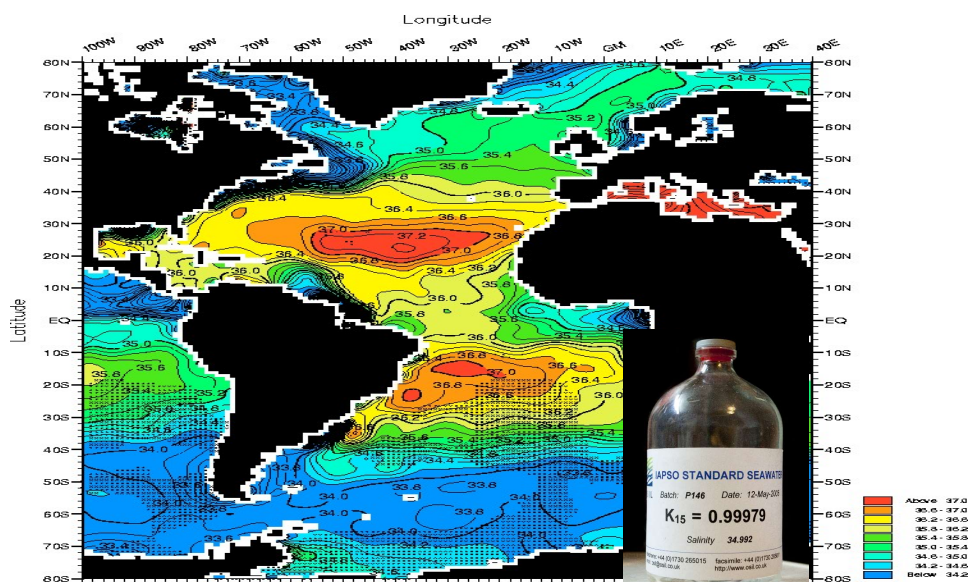


Fig. I2-1. April mean salinity (PSS) at the surface .  
 Minimum Value= 0.00 Maximum Value= 42.22 Contour Interval: 0.20



8th of January 1873: **King Luiz I** visited HMS *Challenger* on her inaugural visit to Lisbon. The first oceanographic ship was made by the order of **Queen Victoria** of Great Britain, under the strong recommendations of the Portuguese Scientist José Vicente Barbosa du Bocage. The *Challenger* was equipped with laboratories took on board six scientists who represent the dawn of the scientific disciplines Oceanographic Biology, Chemistry, Geology and Physics. It is most probable that **Prince Carlos**, 9 years old at the time, accompanied his father on the visit which may have triggered the Prince's passion for the Sea and a wealth of scientific developments.