Accreditation and Quality Assurance (2023) 28:95–100
https://doi.org/10.1007/s00769-022-01511-0

DISCUSSION FORUM

Quality- from adequacy to fitness for purpose

M. Filomena Camões[1]

Received: 20 January 2022 / Accepted: 22 May 2022 / Published online: 20 July 2022

Abstract
Scientific research and consequent progress, leads to the introduction of new concepts, new theories and new experimental methods and procedures. Their implementation, presentation and discussion, bring the associated need to choose and adopt the most appropriate terminology. The choice of the right words, definitions, or descriptions of all kinds, is far from being a minor task, demanding the best knowledge of the experts. As time goes by, this often requires revision and upgrading. In this work, Analytical Chemistry is the chosen scientific discipline, from where relevant examples are being taken and presented. Expression of acidity in terms of pH is addressed, covering a selection of developments where the author has been an active player along half a century, ranging from Chemistry to Metrology, hence involving expertise from both fields. Whilst much has been done, more is needed and continues to happen.

Keywords Concepts · Terms and procedures · pH · Calibration · Traceability · Measurand · UniphHied scale

Introduction

Analytical Chemistry is probably the most discussed branch of Chemistry in terms of namely, what it is, what and how to teach it. Being a problem-solving science overarching all material systems, it has deserved the attention of many scientists, searching for the perfect definition of this multidiscipline. The result has been a variety of proposals, each focusing some fundamental aspects, but none being sufficiently broad and complete. By the end of the xxth century a competition, "Analytical Chemistry- today's definition and interpretation", was promoted by the Federation of European Chemical Societies and, based on the winning contribution [1], a definition has been put forward: Analytical chemistry is a scientific discipline that develops and applies methods, instruments, and strategies to obtain information on the composition and nature of matter in space and time. Amazingly, the choice of the mere "a" alone rather than "the" has been far from straightforward ant it has only been agreed at the cost of many meetings, much time and travelling, loads of sound arguments by experts at National, European and International level, along several years. Later on, the awareness of the demand for quality statements led to the adoption by the Analytical Chemistry Division of IUPAC of an extended updated version: …., as well as on the value of these measurements, i.e., their uncertainty, validation, and/or traceability to fundamental standards [2]. These latter attributes pertain to the science of measurement and their application, being essential and among those that ensure the adequate quality of analytical results. A much more recent IUPAC recommendation [3] is again, simply "Scientific discipline that develops and applies strategies, instruments, and procedures to obtain information on the composition and nature of matter in space and time"; and managed to avoid the "a" of the original FECS definition!

Quality assurance and measurement matters in Analytical Chemistry were becoming acknowledged of importance at least equivalent to those in the physical and engineering domains. The imminence of the European market has greatly contributed to collaboration among countries in Europe focusing on Analytical Chemistry, with the formal establishment, in July 1989, of EURACHEM [4], a network of organizations having the objective of establishing a system for the international traceability of chemical measurements and the promotion of good quality practices. Between 1993 and 1995, Paul de Bièvre chaired EURACHEM, which three decades later continues to provide authoritative guidance within its expert working groups, publishing guides

---

✉ M. Filomena Camões
mfcamoes@fc.ul.pt

[1] Centro de Química Estrutural, Institute of Molecular Sciences, DQB-Faculdade de Ciências da Universidade de Lisboa, 1749-016 Campo Grande, Lisbon, Portugal

and supporting workshops to communicate good quality practices.

Developing a vocabulary that faithfully reflects the concepts is an art that requires deep scientific knowledge. Based on VIM 2, An International vocabulary of basic and general terms in metrology, published by BIPM (1993), basically addressing measurement in physics, a Joint Committee for Guides in Metrology (member organizations: BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML), fulfilled the need to adequately integrate measurements in chemistry, through the elaboration of VIM 3, International vocabulary of metrology — Basic and general concepts and associated terms [5]. Paul de Bièvre represented IUPAC to this Joint Committee and has been active contributor to this revision of the International Vocabulary of Metrology (1998–2008), after which he continued taking notes for a VIM 4 edition, in progress. At these later stages, having passed away in 2016, his contribution has remained via his writings [6], as well as through the memory of live discussions shared with the author along her 50-year journey of research in Analytical Chemistry. Probably the chemical kind-of-quantity most frequently considered, pH [7] is used to illustrate the progress jointly achieved in some key points of metrological nature.

Calibration Procedures

The PhD Thesis, Calibration Procedures for Glass Electrodes (1973), basis for the BS 2586:1976 Specification for Glass and Reference Electrodes for the Measurement of pH [8] dealing, in particular, with the development of reference pH buffer standards, based on organic bases free from alkaline ions, marked our entry to the multidisciplinary world of Analytical Chemistry [9]. With it came the opportunity to organize the IUPAC-Sponsored Conference "Harmonization of pH Scale Recommendations", Lisbon, Portugal (1980), which originated the IUPAC Recommendations (1984). The issue, at the time, was basically the recommendation of two calibration procedures, each supported and proposed by a different research group, either a single point calibration buffer solution, 0.05 mol kg^{-1} potassium hydrogen phthalate ($KHC_8H_4O_4$), with an assigned reference pH value (RVS) in association with the theoretical Nernst slope, or alternatively a multipoint calibration, two-point bracketing procedure, using two or more of the NBS (now NIST) pH buffer standards. The conclusion [10] was a compromise between both approaches which recognizes the advantages of accepting either of the procedures, as far as there is clear indication of which has been used. The quality of the manuscript, highly elucidative in chemical terms, was nevertheless insufficient to answer the needs of the emerging community of analytical chemists sensitive to Metrology in Chemistry (MiC) already concerned with quality issues, namely the levels of uncertainty associated with measurement results, which carries information about their validity for the intended use.

In 1998, the Consultative Committee for Amount of Substance (CCQM) decided to include the field of pH in its working program and key comparisons for this quantity started to be carried out, beginning with two phosphate buffer solutions.

A new task force within IUPAC, with the innovative input of metrologists, was set up and worked on the elaboration of a new recommendation. The definitions of a primary

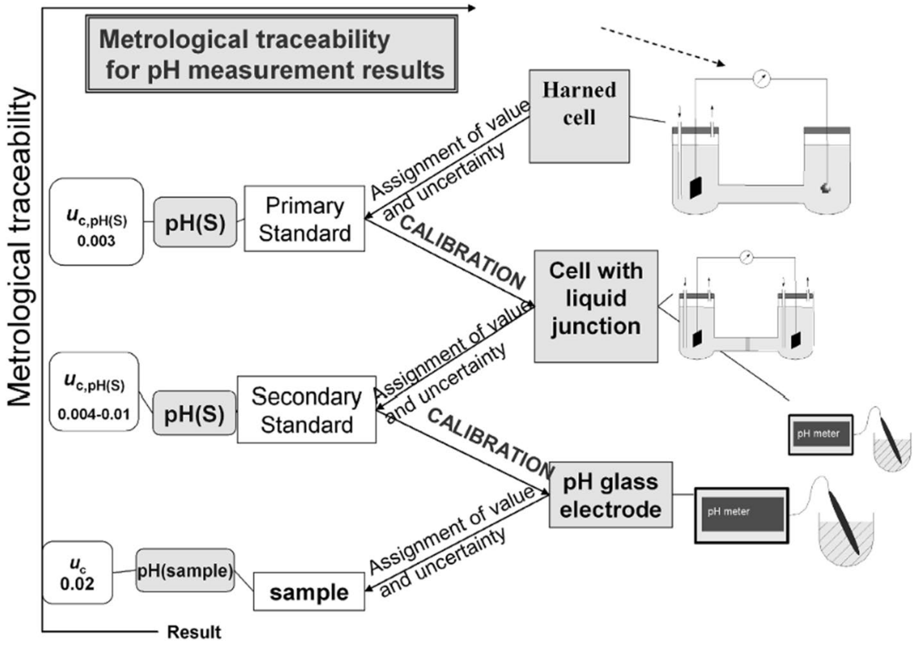

Fig. 1 Metrological traceability scheme for pH; u_c denotes expanded measurement uncertainties [12]

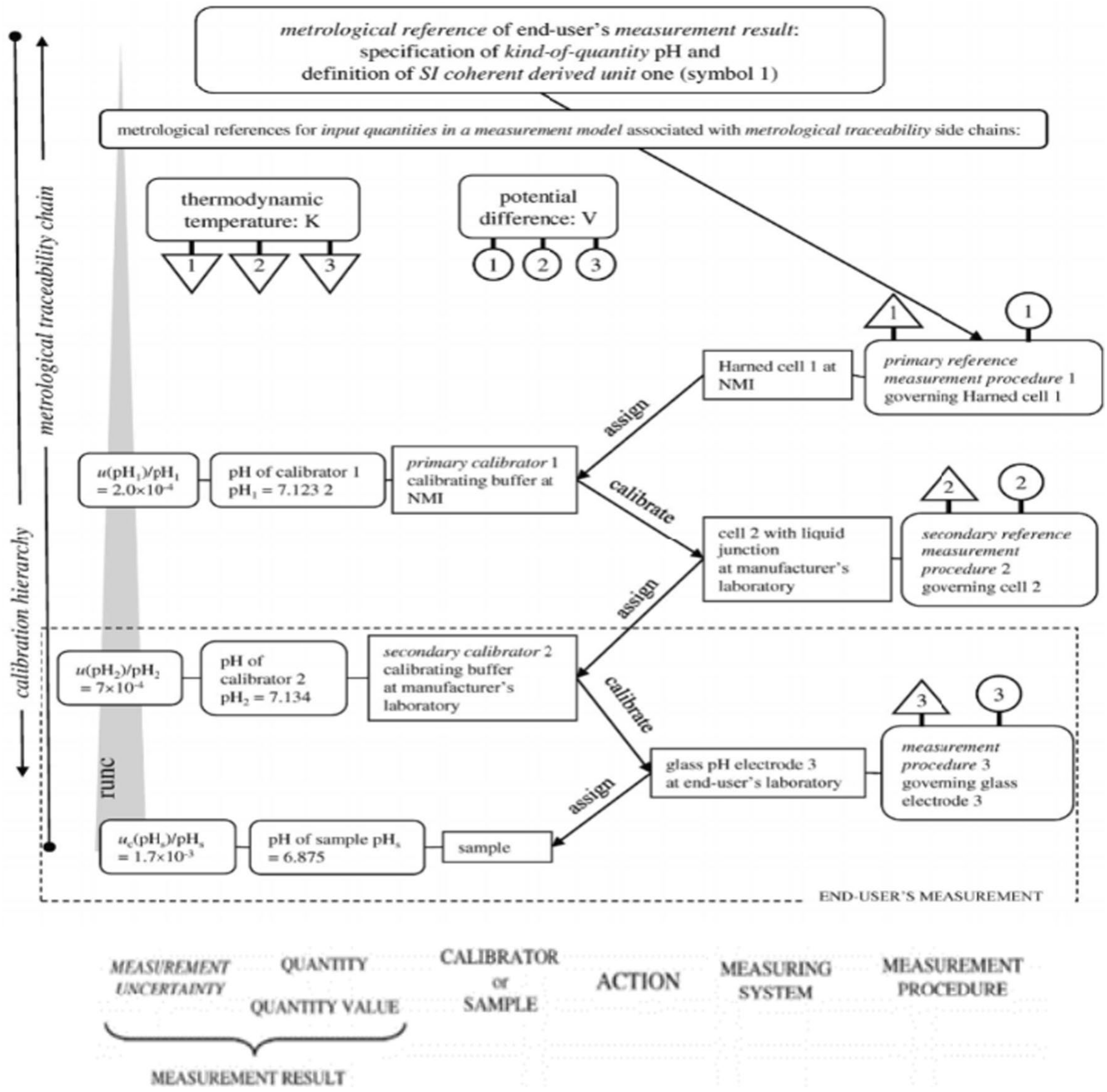

Fig. 2 Metrological traceability chain of a pH measurement result [13]

method and standards, secondary methods and standards for pH, with incorporation of the respective uncertainties in all subsequent measurements, permitted the derivation of an uncertainty budget with uncertainties for all procedures linked by an unbroken chain of comparisons [11]. This way, an informed choice can be made by the analyst, for adequacy to specified needs, aiming at a target uncertainty of the sample pH, Fig. 1.

After this pioneering work for pH aiming at formulating recommendations concerning traceability to higher references, thus establishing metrological traceability of a measurement result in chemistry, Paul de Bièvre promoted a broader IUPAC Project, addressing the design of similar informative traceability chains for a variety of examples of analytes and measurands. This led to the production of flow charts of generic calibration hierarchies illustrated with a variety of examples [13], Fig. 2.

Metrological Traceability

The establishment of traceability to the SI imposes the consideration of all uncertainty components, including those where there are limitations in the theory. If a convention is used without an estimate of its uncertainty, true traceability to the SI is not be established [14].The assignment of primary pH values, pH(S) to primary pH standards is based on potentiometric measurements, E/mV, of a cell known as the Harned cell (H^+ sensitive hydrogen gas electrode and Cl^- sensitive silver, silver chloride electrode, without transference) in association of calculations with the Nernst equation [15] and adoption of extra-thermodynamic assumptions concerning models of electrolyte solutions for calculation of mean or single activity coefficients, Fig. 3.

$\mathrm{Pt}|\mathrm{H}_2|\mathrm{H}^+\mathrm{buffer\ S,\ Cl}^-(m\mathrm{cl}^-)|\mathrm{AgCl}|\mathrm{Ag}$

$$E = E^0_{\mathrm{Ag,\ AgCl}^-}(R\,T\,F\ln 10)\,\mathrm{lg}\left(\mathrm{a_H} + \mathrm{a_{Cl^-}}\right)$$

Since pH = − lg $a_{\mathrm{H}=}$ − lg ($\gamma_\mathrm{H}.m_\mathrm{H}$), with a standing for activity, m/mol kg^{-1} for molality and γ for activity coefficient, assignment of pH values to standards transports an uncertainty associated with the electrolyte solutions model adopted for the calculation of activity coefficients, with subsequent projection on further measurements. In the case of low ionic strength aqueous solutions ($I < 0.1$ mol kg^{-1}), the Debye-Hückel model with the Bates–Guggenheim convention for the ion-size parameter of chloride ions is recommended. This contributes with an uncertainty component estimated to be ± 0.01 which must be included in the uncertainty of measured pH values, without which pH values are not traceable to the SI [16]. Similar approach to define high order reference buffer standards with assigned pH(S) values is being explored for higher ionic strengths, namely seawater ($I \approx 0.7$ mol kg^{-1}), in which case the Pitzer model, which considers not only electrostatic effects among species in solution, but also specific interactions is deserving preference [17].

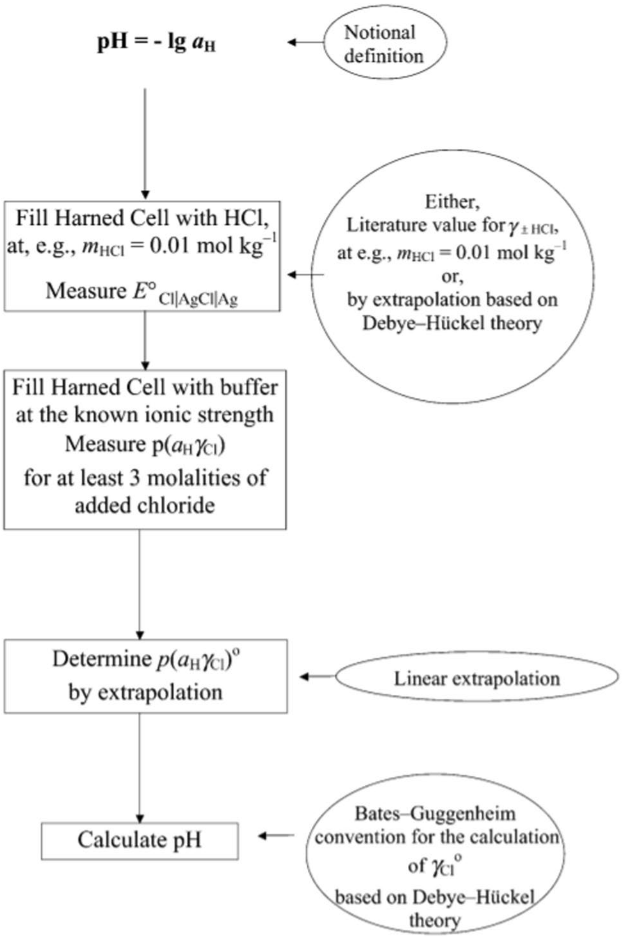

Fig. 3 Schematic representation of the Primary method for the assignment of Primary pH values to Primary pH buffer standards [11]

Measurand and Comparability

Seawater is a complex aqueous solution, containing a great diversity of chemical species, among which the hydrogen ion, H$^+$, is of special relevance upon chemical and biochemical reactions, hence on speciation of the elements. The uptake of atmospheric fossil fuel CO$_2$ promotes acidification, which is currently of great concern. These important issues support the need for measuring seawater pH.

The fact that there are different methods for assessing pH, e.g., potentiometric and spectrophotometric [16], used by different groups which, accordingly, tend to use the term “pH” with different meanings, hence different measurands according to their preferences, bring additional sources of uncertainty not yet clarified. Although it is widely recommended that ocean scientists use the free concentration or activity of the proton to examine the effect of pH on processes in the oceans, this is far from being the case. Unambiguous definition of the measurand is a starting point to establish the traceability for either quantity progressing to assign reference values. Establishing metrological traceability is a prerequisite to assess comparability of measurement results [17]. Only comparable things can be compared.

Once a satisfactory recommendation for measurement of pH of dilute aqueous solutions has been accepted, the next big question became seawater pH [18]. The absence of a recommended buffer system in a seawater background, led to breaking the principle that a calibrant solution must be as similar as possible to the sample to be assessed. In an undesired alternative, calibration of measuring setups with the available dilute reference buffers became a relatively common practice. This introduces an additional uncertainty to the sample pH measurement value [19], unwanted for the sake of fitness for the purpose of use of seawater pH values. A Tris-TrisHCl buffer system prepared in a seawater matrix [20] is of ample use as a reference, although it has not been formally acknowledged yet as such [21].

Acidity of aqueous solutions, expressed and assessed in terms of pH, is a vastly implemented and settled concept, despite the still standing issues undergoing further research briefly illustrated above. Definition of pH in solvents, S, other than water, H$_2$O, can be notionally established in similar terms, pH$_\mathrm{S}$ = − lg $a_{\mathrm{H+,S}}$ = − lg ($m_{\mathrm{H+,S}}\ \gamma_{\mathrm{H+,S}}$). In every solution, the activity of the solvated proton is linked to its concentration in that solvent. The standard state is concentration-based (1 mol kg^{-1} H$^+$), but the same concentration of protons in different solvents has different activities, hence different ability to influence processes. $\mathrm{pH_S}$ values within the same solvent can be compared to each other, but $\mathrm{pH_S}$ values between different solvents cannot. The same pH in different solvents refers to different acidity. Some standards have been recommended for $\mathrm{pH_S}$ scales with S consisting of a few organic solvents and some of their mixtures with water. However, these standards relate to measurements only within one solvent and do not cover measurements between different solvents, what would be necessary to establish an intersolvental pH scale.

Unified pH scale

The need for a unified pH scale arises from the impossibility to correlate the individual $\mathrm{pH_S}$ scales without further knowledge of the considered acid–base systems. A unified pH scale of absolute values, $\mathrm{pH_{abs}}$, enables the comparison of acidities in different solvents. The concept of a unified pH scale of absolute pH values, $\mathrm{pH_{abs}} = -\lg a_{\mathrm{abs,H+}}$, based on the chemical potential of H$^+$ (protochemical potential) in an independent standard state, proton gas at 1 bar and 25 °C: $\mu_{abs}(H^+,\mathrm{solv}) = 0$ kJ mol^{-1}, has been advanced, Eq. (1), aiming at defining and comparing acidity in any medium [22]

$$\mathrm{pH_{abs}} = \frac{\mu_{\mathrm{abs}}\left(\mathrm{H^+,solv}\right)}{-RTln(10)} \tag{1}$$

Since putting it into practical use is not experimentally feasible, it is favorable to define $\mathrm{pH_{abs}^{H_2O}}$, Eq.(2), which can be considered as the intersolvental continuation of the aqueous . pH scale, shifted by a constant value, thus aligning $\mathrm{pH_{abs}}$ values with the conventional pH values of the aqueous pH scale Eq. (2).

$$\mathrm{pH_{abs}^{H_2O}} = \mathrm{pH_{abs}} + \frac{\Delta G_{solv}\left(H^+,H_2\mathrm{O}\right)}{RTln(10)} \tag{2}$$

Through the Gibbs energy of transfer from water to solvent S,$\mathrm{pH_{abs}^{H_2O}}$ value serves as a thermodynamically well-defined link between the acidity in water and the acidity in any other medium.

The potentiometric method, linking the potential, *E*, of a chosen cell to the activity of a chemical species via the Nernst equation, is ideal for the measurement of $\mathrm{pH_{abs}^{H_2O}}$. Using water as an anchor solvent, unified acidities are measured via comparisons of $\mathrm{pH_{abs}^{H_2O}}$ values of two solutions, one in aqueous medium and the other one in the solvent under concern, thus obtaining $\Delta\ \mathrm{pH_{abs}^{H_2O}}$ values between the two solutions. When one of the solutions is a standard solution (e.g., an IUPAC standard pH buffer) with a known $\mathrm{pH_{abs}^{H_2O}}$ value, then the $\mathrm{pH_{abs}^{H_2O}}$ pH value of the second one can be easily obtained.

The use of the unified pH concept, $\mathrm{pH_{abs}^{H_2O}}$, which allows interpreting and comparison of the acidity of different types of solutions, requires reliable and objective determination. The technique used for such measurements is differential potentiometry, measuring directly the potential between two glass electrodes immersed in the two solutions that are under comparison [23]. $\mathrm{pH_{abs}^{H_2O}}$ can be determined by a single differential potentiometry measurement referenced to an aqueous reference buffer or by a ladder of differential potentiometric measurements that allows minimization of inconsistencies of various determinations [24].

Most appropriately the performance of the unified approach was investigated for saline waters [25]. In the context of seawater pH measurement, the ability to observe trends is most important. Metrological aspects are particularly important when attempting to discriminate between different sources of medium variability and to detect small changes between experimental results for discovering long-term trends or spatial variations. Despite the progress achieved in improving the quality of measured pH values, accurate potentiometric pH measurements in seawater still remain a challenge for science, particularly when aiming at assessing and quantifying ocean acidification in terms of long-term anthropogenically driven changes.

> Distant lighthouses...
>
> We're going far away, and the bright light begins to flash less brightly.
>
> Fernando Pessoa, 30 April 1926.

Acknowledgements The author wishes to acknowledge the Portuguese funding institution Fundação para a Ciência e a Tecnologia-FCT, for supporting her research, namely through project FCT (UIDB/00100/2020 and UIDP/00100/2020).

References

1. Cammann K (1992) Analytical chemistry—today's definition and interpretation. Fresenius J Anal Chem 343:812–813. https://doi.org/10.1007/BF00328560
2. https://iupac.org/who-we-are/divisions/division-details/?body_code=500
3. Hibbert DB, Korte E-H, Örnemark U (2021) Metrological and quality concepts in analytical chemistry (IUPAC recommendations 2021). Pure Appl Chem 93(9):997–1048. https://doi.org/10.1515/pac-2019-0819
4. https://www.eurachem.org/
5. International Vocabulary of Metrology (2008) 3rd edition, Bureau International des Poids et Mesures, Sèvres, France. www.bipm.org/en/publications/guides/vim.html

6. Williams A, de Bievre P (2014) Eurachem's 25th anniversary: two members' perspective. Accred Qual Assur 19:55–57. https://doi.org/10.1007/s00769-014-1040-0
7. Camões MF (2009) The quality of pH measurements 100 years after its definition. Accred Qual Assur 14:521–523. https://doi.org/10.1007/s00769-009-0573-0
8. Filomena M, Camões GFC, Covington AK (1974) New procedure for calibrating glass electrodes. Anal Chem 46:1547
9. Covington AK, Butikofer HP, Filomena Camões M, Ferrae MIA, Rebelo MJF (1985) Procedures for testing pH responsive glass electrodes at 25, 65 and 85ºC and determination of alkaline errors up to 1 mol dm^{-3} Na^{+}, K^{+}, Li+. Pure Appl Chem 57:887
10. Covington AK, Bates RG, Durst RA (1985) Definition of pH scales, standard reference values, measurement of pH and related terminology. Pure Appl Chem 57:531. https://doi.org/10.1515/iupac.57.0006
11. Buck RP, Rondinini S, Covington AK, Baucke FGK, Brett CMA, Camoes MF, Milton MJT, Mussini T, Naumann R, Pratt KW, Spitzer P, Wilson GS (2002) Measurement of pH Definition, standards, and procedures (IUPAC Recommendations 2002). Pure Appl Chem 74:2169. https://doi.org/10.1351/pac200274112169
12. Spitzer P, Seitz S (2010) Metrological traceability chain for pH measurement results. J Metrol Soc India 25(3):191–196. https://doi.org/10.1007/s12647-010-0019-5
13. Paul DB, René D, Aleš F, Hibbert DB (2011) Metrological traceability of measurement results in chemistry: concepts and implementation (IUPAC technical report). Pure Appl Chem 83(10):1873–1935. https://doi.org/10.1351/PAC-REP-07-09-39
14. Paul De Bièvre, H Gunzler (2005) Traceability in chemical measurement. In: (ed) by Paul De Bièvre (Kasterlee, Belgium) and Helmut Günzler (Weinheim, Germany). Springer: Berlin, Heidelberg, New York
15. Pingarrón JM, Labuda J, Barek J, Brett CMA, Camões MF, Miroslav Fojta D, Hibbert B (2019) Terminology of electrochemical methods of analysis (IUPAC recommendations 2019). Pure Appl Chem 92(4):641–694. https://doi.org/10.1515/pac-2018-0109
16. Camões MF, Anes B (2015) Traceability of pH to the mole. Water 7:4247–4255. https://doi.org/10.3390/w7084247
17. Anes B, Ricardo JN, da Silva B, Martins HFP, Oliveira CS, Filomena Camões M (2015) Compatibility of activity coefficients estimated experimentally and by pitzer equations for the assessment of seawater pH. Accredit Qual Assur 21(1–7):2015. https://doi.org/10.1007/s00769-015-1163-y
18. Marion GM, Millero FJ, Camões MF, Spitzer P, Feistel R, Chen C-TA (2011) pH of seawater. Mar Chem 126:89–96
19. Dickson AG, Camões MF, Spitzer P, Fisicaro P, Stoica D, Pawlowicz R, Feistel R (2015) Metrological challenges for measurements of key climatological observables. Part 3: seawater pH. Metrologia 53:R26–R39
20. Bárbara A, da Silva B, Ricardo JN, Cristina O, Filomena CM (2019) Seawater pH measurements with a combination glass electrode and high ionic strength TRIS-TRIS HCl reference buffers – an uncertainty evaluation approach. Talanta 193:118–122. https://doi.org/10.1016/j.talanta.2018.09.075
21. Stoica D, Anes BV, Fisicaro P, Camões MF (2021) Feasibility of multifunction calibration of H^{+}-responsive glass electrodes in seawater (IUPAC technical report). Pure Appl Chem 93(12):1487–1497. https://doi.org/10.1515/pac-2020-0202
22. Radtke V, Stoica D, Leito I, Camões MF, Krossing I, Bárbara A, Roziková M et al (2021) A unified pH scale for all solvents: part I - intention and reasoning (IUPAC technical report). Pure Appl Chem 93(9):049–1060. https://doi.org/10.1515/pac-2019-0504
23. Heering D, Stoica F, Camões B, Anes D, Nagy ZN, Szilágyi R, Quendera L, Ribeiro F, Bastkowski RB et al (2020) Symmetric potentiometric cells for the measurement of unified pH values. Symmetry 12:1150. https://doi.org/10.3390/sym12071150
24. da Silva RJN, Bettencourt SJ, Bárbara A, Agnes H, Ivo L, Teemu N, Daniela S et al (2021) Evaluation and validation of detailed and simplified models of the uncertainty of unified measurements in aqueous solutions. Anal Chim Acta 1182:338923. https://doi.org/10.1016/j.aca.2021.338923
25. Lainela S, Leito I, Heering A, Capitaine G, Anes B, Camões F, Stoica D (2021) Toward unified pH of saline solutions. Water 13(18):2522. https://doi.org/10.3390/w13182522