

The quality of pH measurements 100 years after its definition

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Abstract Analytical chemistry is a scientific discipline based on the search of qualitative and quantitative information embodied in unknown samples which are representative of targeted systems. A. Lavoisier measured masses, S. Arrhenius discovered ions, namely hydrogen ions, S. Sørensen introduced pH and the chemical community has been dealing abundantly with them, first in the frame of classical analysis and later by means of instrumental methods of analysis responsible for large amount of data. Although statistical treatment of measurement results became part of the procedures, it took a few decades of thinking and globalization of the economy to realize that more was needed for the sake of evidence of quality; and this was found in the bases of the science of measurement and on the metrological approach. At the dawn of the twenty-first century, the most measured chemical parameter, pH, set the example of such hierarchical targeting of measurement results fit for a certain purpose, which is worth noticing particularly because 100 years have elapsed since its first definition and initial recommendation of the measurement procedure.

Keywords Analytical chemistry · Quality · Metrology · pH · Centenary

Cogito, ergo sum/I think therefore I am
René Descartes, 1637

In the course of time, there have always been findings and issues of a certain nature that triggered and supported

developments of great significance in one or several other scientific areas. This is the case of the inbreeding of a quality conscience into analytical chemistry.

Analytical chemistry is different from the other chemical sciences because of the perspective that, while the latter deal with studying the properties of known material systems, e.g. the boiling point of water or the ionization constant of acetic acid, in analytical chemistry one searches for relevant physical and chemical signals in order to reach qualitative and quantitative information embodied in unknown samples assumed representative of targeted systems, e.g. electrical conductivity of seawater samples as source of data on the salinity of the oceans. Despite the fact that Mankind has been there for millions of years with so much effort put on assessing the composition of matter, it is astonishing that it is only two centuries since A. Lavoisier started reasoning about the mass measurements and a century since Arrhenius [1] shocked his fellow scientists with his electrolytic dissociation theory, even before J. J. Thomson (1898) discovered the electron. It is hard to understand nowadays on how material systems and chemical transformations could be discussed and explained not knowing that there are ions and, in particular, hydrogen ions. Acknowledging this fact, a few years later, Sørensen [2, 3], for mere practical reasons of algebraic nature, defined pH as the negative decadic logarithm of hydrogen-ion concentration which, expressed in terms of a power of ten, is equal to its negative exponent. Simple as Sørensen's definition and measurement proposal may have looked for single and near to ideal aqueous solutions, it proved to be capable of turning into an exasperatingly difficult task when dealing with more complex media, where fundamental science on pH is still ongoing further development, e.g. in the environmental and health sectors [4, 5].

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It was the dawn of half a century of developments in chemical analysis based solely on the direct evaluation of physical and chemical manifestations. Names such as King [6], Vogel et al. [7] are examples of authors of books that became chemical bibles for those who were lucky enough to have lived that historical period.

In the second half of the twentieth century with the discovery of semi conductors and the development of electronic circuits with current amplifiers, a new age began during which chemical analysis turned classical analysis and the trend was set for the search and development of new and further sophisticated instrumental methods of analysis aiming at measuring analytical signals, more and better. Among those, potentiometric measurements associated with ion-selective electrodes indicators of various ionic species in aqueous solution, with glass electrodes selective to hydrogen ions at the top of the list, play an unquestionably useful role. Undoubtedly, it was an important step forward; at the same time it started the dark age of the black box approach, during which people got used to push some buttons to get some unquestioned measurement result, believing that they were doing analytical chemistry. Several times one could hear the statement from some illuminated minds that “analytical chemistry is nothing else other than instrumental methods of analysis”. Those who said it did not mean it as a compliment, but rather as a reducing argument trying to minimize analytical chemistry to the mere technical level of routinely performing chemical analyses. It was sad and hard to be taken by those who saw the superior beauty of a more exact science which requires a maximum intellectuality. Knowledge often takes time to settle and seed and it took a few decades for the analytical community to realize that all those data lacked evidence of their quality, hence demanding and imposing validation of results in a systematic and harmonized way.

Although statistical analysis has long been an assumed issue, later revisited and rejuvenated through Chemometrics, it was still looked upon as an isolated chapter, only for some, not systematically and universally dealt with by the analytical chemists.

In this particular year, 2009, when we celebrate one hundred years of Sørensen’s definition of pH, it is curious to realize how pH and Student’s *t* test, a tool of the trade, which has also celebrated a century, are linked ... through beer! In fact, Student’s *t* test was developed by a young English chemist, William Sealy Gosset (1877–1937), working at Guinness breweries in Ireland, who, after spending the academic year 1906/1907 with the famous statistician Karl Pearson, studying the practical problem of selecting the best variety of barley for beer making, from experiments in only four farms, published “The probable

error of a mean” in *Biometrika* 1908. For commercial reasons, Gosset published under the name of Student. The best variety of barley for the Irish soils was found, at the time, to be the *Danish Archer*. Danish was also Søren Peter Lauritz Sørensen (1868–1939), who recognized the importance of hydrogen-ion concentration, and pH—the most measured chemical parameter—on enzymatic activity, while he was the Director of the Department of Chemistry (1901–1938) of the Danish *Carlsberg* brewer.

It was the economic and legal perspective related with globalization, that came along with increased trade, exchange of goods and need for clear and reliable labels and analysis bulletins claiming compliance with requirements, that made mutual recognition of measurement results into a fundamental pre-requisite that promoted an integrated approach. There is no analytical result without an associated expression of its quality. The application of metrological principles in physics was resuscitated and gave rise to a new scientific discipline, that of the use of metrological principles in chemical measurement, Measurement Science in Chemistry, including the chemical operations such as mass transfer, or complex methodologies which go much beyond the simple measurements of mass and length.

An example which made recent history is that of the measurement of pH—definition, standards and procedures [8]. An issue that for years divided the scientific community was that of calibration of pH meters; research groups on one side of Atlantic Ocean adopted and defended the one-point calibration with 0.05 mol kg⁻¹ KHPthalate, the reference value standard, RVS, while others recommended the two point, or even multipoint calibration with two or more of the seven recommended NIST (ex-NBS) buffers. In a compromising attitude between the two schools, an IUPAC recommendation paper [9] presented both approaches as acceptable alternatives, with the only requirement that in delivering results, an indication should be given about which methodology had been adopted. With time this was considered a non-valid position from a professional union whose scope encompasses recommendations. Analysts claimed that to achieve equivalence of results, they required detailed instructions, not alternatives left to their own discretion and not knowing their equivalence. Voices became stronger and action had to be taken. A pH working party representing both tendencies and pertaining expertise was set up some time before the year 2000 and revision of the 1984–1985 recommendations [9] was undertaken. After the unanimous conclusion that it was a very good paper from the point of view of physical chemistry, there was also the general agreement that terms which had been used in just a colloquial manner, had in the meantime, acquired a specific meaning in the terminology proper to metrology in chemistry. Although this was new to several of the WP

members, it was agreed after some brain storming, that this would be the driving force for the development of the WP task and target measurement uncertainties for each hierarchical level of performance became the keyword. Guiding values were calculated and published, enhancing the fact that fitness for the intended use is the basis of the choice of level of performance characteristics and that primary measurement procedures with lowest possible measurement uncertainties, are not always the best option and sometimes, not even appropriate. The traceability of pH values was established all the way up to the mole, of course with a couple of extra-thermodynamic assumptions on the way, wherever it was necessary due to the abstract character of the definition.

The rest of the story is the 2002 IUPAC paper [8] and the inspiration that it gave to the implementation of a quality oriented approach of analytical processes and to the development of a template [10], that is, intended to systematize and encompass all possible chemicals measurements.

And a century later, we keep thinking now on pH measurements in some specific systems and on setting up the respective traceability chains as it is the case of, e.g. clinical and seawater measurements.

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