

Traceability and calibration of reference pH buffer solutions

by P. Arquint & H. Bühler

The determination of pH is one of the most routine of all laboratory measurements, but one which can be of vital importance. The reliability of pH measurements depends on the use of appropriate reference solutions which unfortunately are frequently taken for granted and used with little appreciation of what is involved in their production. This article discusses the production and quality control processes that lie behind a commercially available range of buffers that qualify to be classed as certified reference materials (CRMs).

Any reference pH buffer must satisfy certain quality criteria, such as high stability, good protection against contamination, ease of use and a long shelf life. In addition to these indispensable basic properties, buffer solutions that are being used as Certified Reference Materials (CRMs) must also satisfy additional QC criteria. These include the existence of a fully-documented traceability scheme which clearly shows how the buffer relates to international primary reference materials, and in addition, errors or uncertainty associated with all steps in the complete chain of pH measurements must be quantified. These aspects are illustrated by reference to the production of the Hamilton Duracal Buffer family [Figure 1].



Figure 1. The Duracal family of buffers are classified as Certified Reference Materials. Covering the pH range from 1.09 to 12.00, they are supplied in containers that have a built-in "calibration compartment" to minimise the risk of contamination.

Determination of pH value

In the production of the Duracal buffers, the pH value is measured using a SinglePore glass pH electrode which features a free-flowing capillary liquid junction. This type of electrode exhibits minimal adsorption and memory effects which are problems that frequently occur with most commonly-used diaphragm electrodes. The pH

value of the buffer is determined using a two step procedure [Figure 2]. Firstly the slope of the calibration curve is calculated using two secondary standards (SS1 and SS2), chosen to bracket the pH value of the target. The unknown pH value of the target is then calculated using the slope and by measuring the difference in potential between the target and SS1.

Traceability

In the production of CRMs it is vital to ensure complete traceability through an unbroken chain of comparisons to a reference of the highest metrological quality, namely primary reference materials. Most manufacturers apply only a "top-down" approach to such traceability. In the production of the Duracal buffers, this is complemented by a "bottom-up" approach which results finally in a closed-loop or circular traceability system.

Top-down traceability

The top or primary level of this traceability scheme is a primary reference material such as those provided by the National Institute of Standards and Technology, USA (NIST) or the Physikalisch Technische Bundesanstalt, Germany (PTB). In the production of Duracal buffers, the secondary reference buffer solutions that are used are provided by the German centre for measurement and calibration, the Deutscher Kalibrierdienst (DKD), whose responsibility is to calibrate these secondary standards with respect to the primary standards. The DKD secondary reference material is then used to calibrate the Duracal CRM which is at the tertiary level of the hierarchy.

Bottom-up traceability

To ensure even higher reliability and accuracy, each production lot of Duracal buffers is sent to the DKD laboratory for external, independent and impartial verification against a secondary reference material (a different batch from that used in the top-down approach). As before, it is the responsibility of DKD to ensure that the secondary standard is calibrated against the

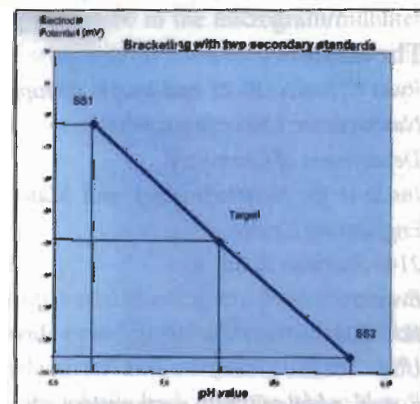


Figure 2. The two-step determination of target pH value (in this case pH 8.0).

primary standard. At this point the loop is closed: the NIST or PTB standard is both the starting and finishing point of the traceability/calibration process.

Determination of error/uncertainty

Traceability to national and international standards is only valid if in addition, the errors or uncertainties implicit in each stage of the overall measurement chain are quantified. To do this a "balance sheet" or "budget" of the individual error/uncertainties must be established.

At the heart of the measurement process is the calibration curve [Figure 2]. In the first step the slope of the calibration curve is calculated by dividing the difference in measured electrical potential of the two secondary standards, namely $E(SS1) - E(SS2)$, by the difference in pH values of these standards, $pH(SS1) - pH(SS2)$. There are four possible sources of error/uncertainty in this step. These are the measurement of the potential E , the pH value of the secondary standards, the measurement of temperature and finally the residual liquid junction potential (RLJP) in both standards [Table 1]. It can be seen that the individual contributions to the overall uncertainty are in general small. The biggest single source of error is that arising from the measurement of the electrical potential itself.

The second step calculates the pH of the buffer X from SS1 using the value of the slope. The sources of error involved in this step are the same as in the first step above, with the addition of the error associated with the slope, k , itself [Table 2]. Again, the absolute values of the error are small, and this time the RLJP contributes the largest source of uncertainty.

Conclusion

The design philosophy behind Duracal buffers is the production of a buffer solution with clear traceability to international standards and with a low error/uncertainty associated with the pH value. In addition, and more importantly, the uncertainty must be quantitated. The procedures used in the production process and the data generated show that these objectives have been attained. It should be noted, however, that the stability of the buffer solution over time and its intrinsic buffering capacity can frequently be more important on a practical level than the uncertainty associated with the buffer value, especially if this error is in itself small. The patented formulation of the Duracal buffers ensures such long-term stability.

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Source of Uncertainty	Estimate of x	Std Uncertainty	Sensitivity Coeff.	Uncert. Contribution
$E(SS1) - E(SS2)$	306mV	0.5mV	0.19 /pH	0.096 mV/pH
T (°K)	298.15°K	0.1°K	0.198 mV/°K	0.02 mV/pH
E(rljp)	0.2 mV	0.1 mV	0.19 /pH	0.02 mV/pH
$pH(SS1) - pH(SS2)$	5.17 pH	0.004 pH	11.4 mV/pH	0.048 mV/pH

Table 1. Quantification of errors in each step involved in the calculation of the slope of the calibration curve. The first column identifies the step, the second a typical measured value, the third column the associated error, and the fourth column shows the effect of this error on the calculation of the slope. The last column shows the final error/uncertainty contribution to the slope.

Source of Uncertainty	Estimate of x	Std Uncertainty	Sensitivity Coeff.	Uncertainty Contribution
$pH(SS1)$	4.01pH	0.003 H	1	0.003 pH
$E(X) - E(SS1)$	59mV	0.2mV	0.017mV/pH	0.0034 pH
T (°K)	298.15°K	0.1°K	0.001ph/°K	0.00001 pH
E(rljp)	0.6 mV	0.3 mV	0.017 pH/mV	0.0051 pH
k	59mV/pH	0.1mV/pH	0.0168 pH/mV	0.0017 pH

Table 2. Quantification of errors in each step involved in the calculation of the pH value from the calibration curve. The sources of error are as defined in Table 1 above, plus k the error associated with the slope itself. The final contribution of each step to the overall uncertainty is shown in column 5.

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