Quality control of pH measurements considering activity and concentration scales:

UNCERTAINTY BUDGET OF PRIMARY AND SECONDARY APPARATUSES

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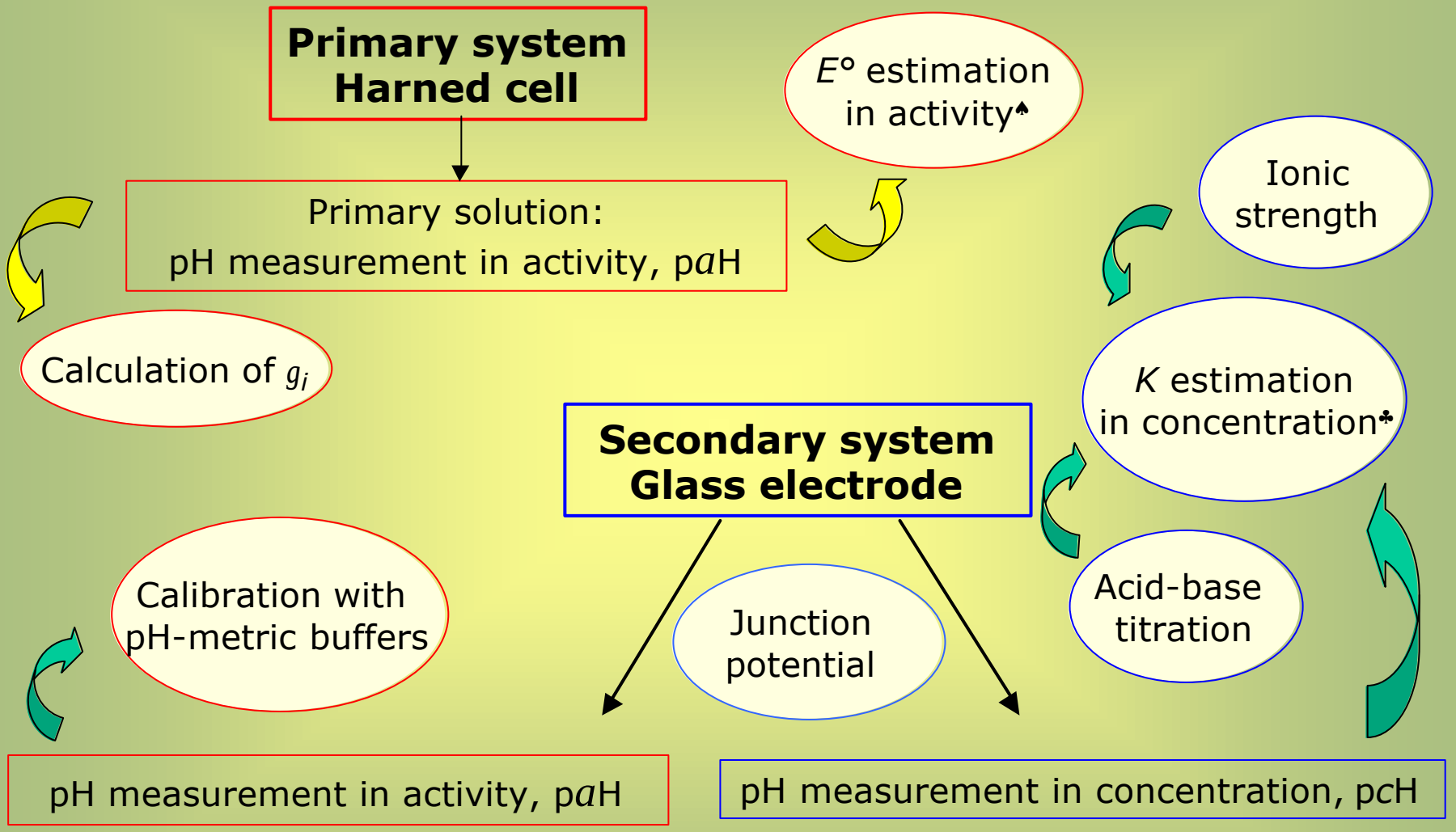
pH measurement scheme



♠ *E° = standard potential difference*
♣ *K = formal potential difference*

Junction potential

Glass electrodes operate according to the general equation (1):

$$E = K + s\,\mathrm{pc}H + E_J \qquad (1)$$

$$E_J = J_A[H^+] + J_B[OH^-] \qquad (2)$$

i) E the instrumental reading (e.m.f.),
ii) K the formal potential difference,
iii) s the Nernstian slope (59.16 mV at 25°C),
iv) J the parameter related to the junction potential (E_J) acting in the acidic (J_A) or in the basic (J_B) field.

The role of the junction potential is well known in the secondary pcH measurement, it depends on the ionic strength of the testing solution and is related also to the gap of overall ion concentration between internal and external solution with respect to the glass membrane.

$$E_J(I) = J_A[H^+] + J_B[OH^-]$$

Data from acid-base titration (V_{KOH} and E), at fixed I, in the range 1.5<pcH<3.5, are elaborated obtaining the contemporary refinement of C_{H+}, K, and J_A (range 11<pcH<12 for J_B).

I (M)	3.0	1.0	0.10	0.030
J_A (mV·mol^{-1}·l)	75	–20	–32	–55

The knowledge of J_A and J_B, obtained by the procedure in concentration, helps us in the uncertainty budget estimation for paH with buffers as well.

Two point calibration: practical slope and related uncertainty are affected by different contributions of $E_J(I)$. We were able to consider the quoted parameters assessing a reliable uncertainty budget.

Primary pH measurement of a phosphate buffer

p*a*H = 6.847

U (p*a*H) = 0.006 (k = 2)

*Secondary pH measurement in **activity** scale*

p*a*H = 6.85

U (p*a*H) = 0.02 (k = 2)

*Secondary pH measurement in **concentration** scale*

p*c*H = 6.80

U (p*c*H) = 0.02 (k = 2)