Electrochemical parameters for quality control in liquid biofuels

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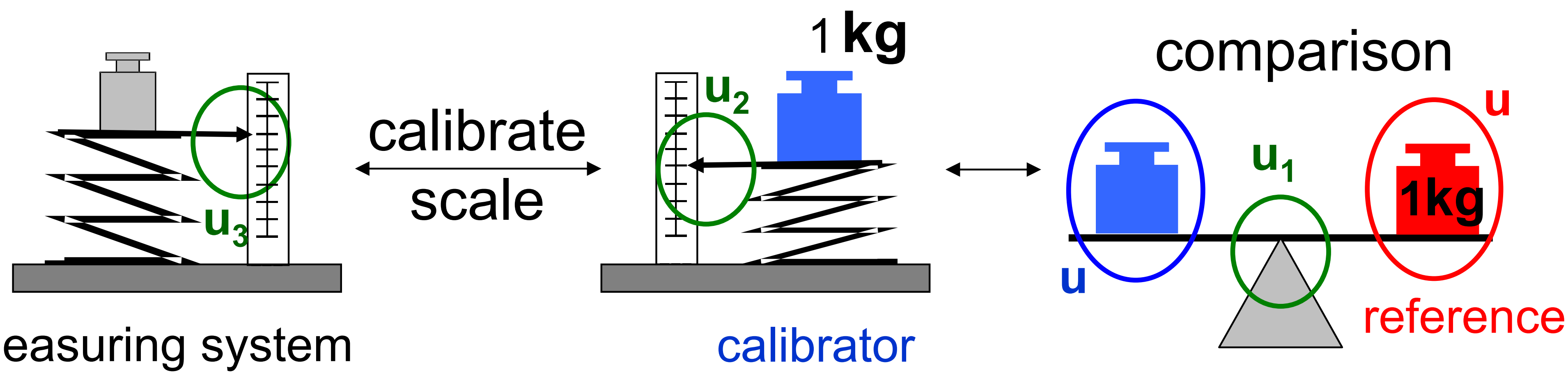
Overview

- Traceability –a central concept measurement
- Standards for Bioethanol - Electrochemical methods
- pH/pHe
- Limits of pH measurements in non aqueous solvents
- Electrolytic conductivity
- How to ensure traceability

Traceability – a central concept in measurement



$0.6 \pm\sqrt{(u^2 + u^2 + u_i^2 \ldots)}$ **kg**

confidence quantified by	**uncertainty of reference, calibrator, calibration/comparison, …**

Comparable results requires a calibration hierarchy linking the value measured in the sample to a common metrological reference,. if possible to the SI

Metrology in Chemistry - Electrochemical methods

Traceability concept has been well developed for measurement results in physics but not for the chemical field.

Problems in Chemical measurements

identity, the measurand - what I am measuring, anyway?

interferences, analyte response in matrix and in the measurement standard (calibrator)

inhomogeneity and instability of sample and calibrator

Metrology in Electrochemistry

pH
conductivity
analyte activity

are among the most frequently measured quantities - particular in on/in- line analysis

➡ low cost, direct, small size, user friendly

The advantage of electrochemical methods is the direct conversion of chemical parameters into electrical quantities

Modelling

Monitoring

Control

Risk Assessment

Environment
Health
Production
Trade

Examples for biofuel (bioethanol) pH and conductivity…

pH measurement in bioethanol - existing standards

pH as a measure to verify the absence of strong acids and alkali
- as indicator for risk of corrosion

ASTM D 6423-99 (> 70 (v/v) % ethanol)
defined method for pH of anhydrous ethanol - pHe 6.5 to 9.0 ((22 ± 2) °C)
pHe depends on the device and on the measurement conditions

DIN EN 15490 (5 (v/v) % ethanol ?)
determination of pHe 6.5 to 9.0 ((22 ± 2) °C)
LiCl in ethanol reference electrolyte, aqueous buffer solutions, poor reproducibility
method adopted from pH measurements in wine

ABNT NBR 10891
Hydrous ethanol (% water?) pH 6 -8 ((20 ± 2) °C)
aqueous buffer solution, defined stirring condition and mesurement time
reference electrolyte?

Limits of pH measurements in non aqueous solvents

pH is a measure of the **acidity of a aqueous solution**.

Other protic solvents also self-dissociate (autoprotolysis)

$H_2O \rightleftharpoons H_3O^+ + OH^-$

$2\ C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$

Results in different autoprotolysis constants: (at 25 °C)

water: $pK_W = 14.00$ ethanol: $pK_{(auto)} = 19.10$

The relative dielectric constant of water is 78.3 of ethanol 24.3

The range of the "pH scale":

in water 0 to14 and in **ethanol -4.2 to 19.1**

in ethanol pH = 9.8 is neutral (at 25 °C)

pH of ethanol - water mixtures

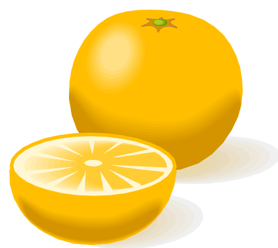
Addition of ethanol to aqueous solution :
decrease in the dielectric constant results in a alteration of the p*K*
and thus **in a shift of the acid-base equilibrium**

“Alcohol Error“: aqueous solution + 10 - 30 % ethanol ΔpH = 0.1-0.2
aqueous solution + 70 % ethanol ΔpH = 1.5
Result depends on the water content of the solvent

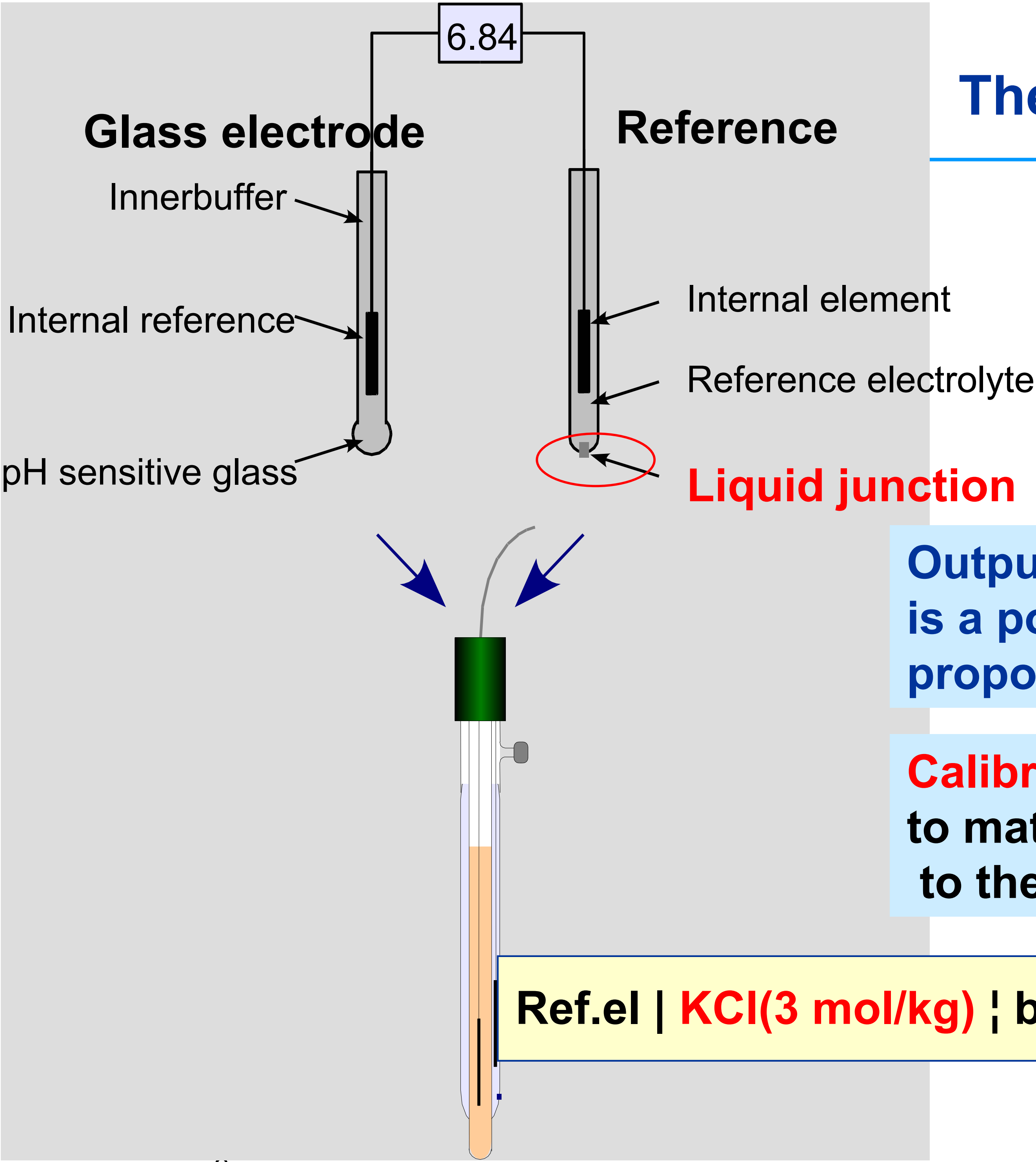
Each water- ethanol mixture need standard buffers of the same water content

Comparability of standard buffer specify the same pH but different water content can not be expected

compared to



The pH electrode



Output of pH electrodes is a potential difference proportional to the pH value

Calibration is required to match the pH meter to the electrode

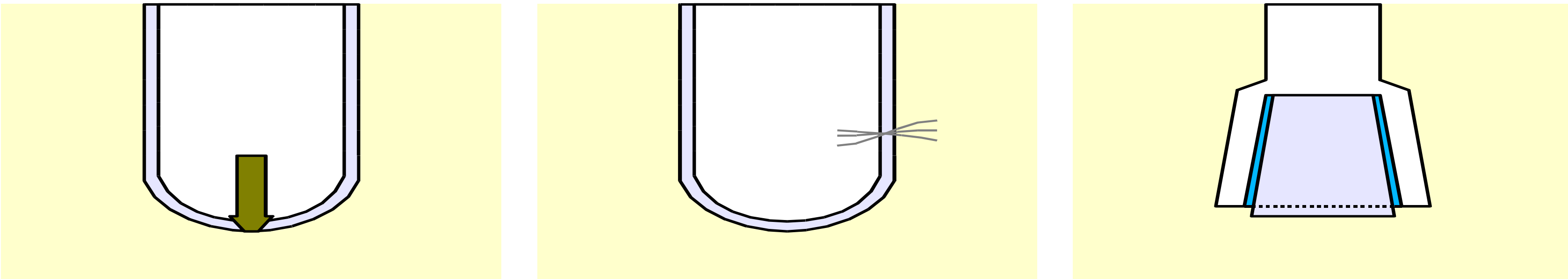
Ref.el | KCl(3 mol/kg) ¦ buffer, sample | glass el

The liquid junction potential

Any junction between two solutions of different composition generates a potential due to the different ion mobility: **liquid junction potential (E_j)** depends on

$$E = E_{\mathrm{glass}} - E_{\mathrm{ref}} + E_{\mathrm{j}}$$

- geometry of lj device (diaphragm)
- composition of reference electrolyte and buffer/sample
- flow condition



Residual liquid junction potential (rljp)
difference in E_j between standard buffer and sample
contributes to the uncertainty of the pH value (often largest contribution ≥ 5 mV)

pHe – a useful quantity?

**Due to the lack of buffer containing ethanol -
pH electrode is also calibrated using aqueous buffer solutions for pH measured in ethanol-water mixtures**

Uncertainty of pH increased due to **an additional unknown phase boundary potential** between aqueous and non aqueous solutions at the interface solution / reference electrolyte

“pHe” in ethanol is on a different scale
Certified buffer for mixed solvent doesn't exist
Calibration hierarchy is not established
“pH“ of ethanol-water mixtures indicated by a pH meter calibrated with aqueous buffer
“are subject to no simple interpretation“
What is the measurand pH, pHe, electrode potential (mV reading) ?

Conductivity of biofuels- existing standards

Conductivity as a measure of
ionic contaminants and risk of corrosion

Expected conductivity range in biofuel: 0.001 to 0.5 mS/m

DIN 51627-4 and ANP NBR 10547 related to ethanol fuel
maximal conductivity: 500 µS/m
DIN 51627-4: calibration solution max 10 mS/m (25 °C)
cell constant 0.1 cm^{-1} to 1 cm^{-1}
measurement temperature (25±0.1) °C

ASTM D-2624-95: related to aviation and distillate fuel (pS/m)
ASTM D1125: related to water (nS/m)

Traceability of electrolytic conductivity results

$$\kappa = \frac{1}{R} K$$

κ depends on concentration, charge and mobility of ions in solution

primary method

$$K = l/A$$

cell constant *K* traceable to SI via length measurements (supposes field homogeneity)

→ determine κ_{ref} of a reference solution by a traceable measurements of *R*

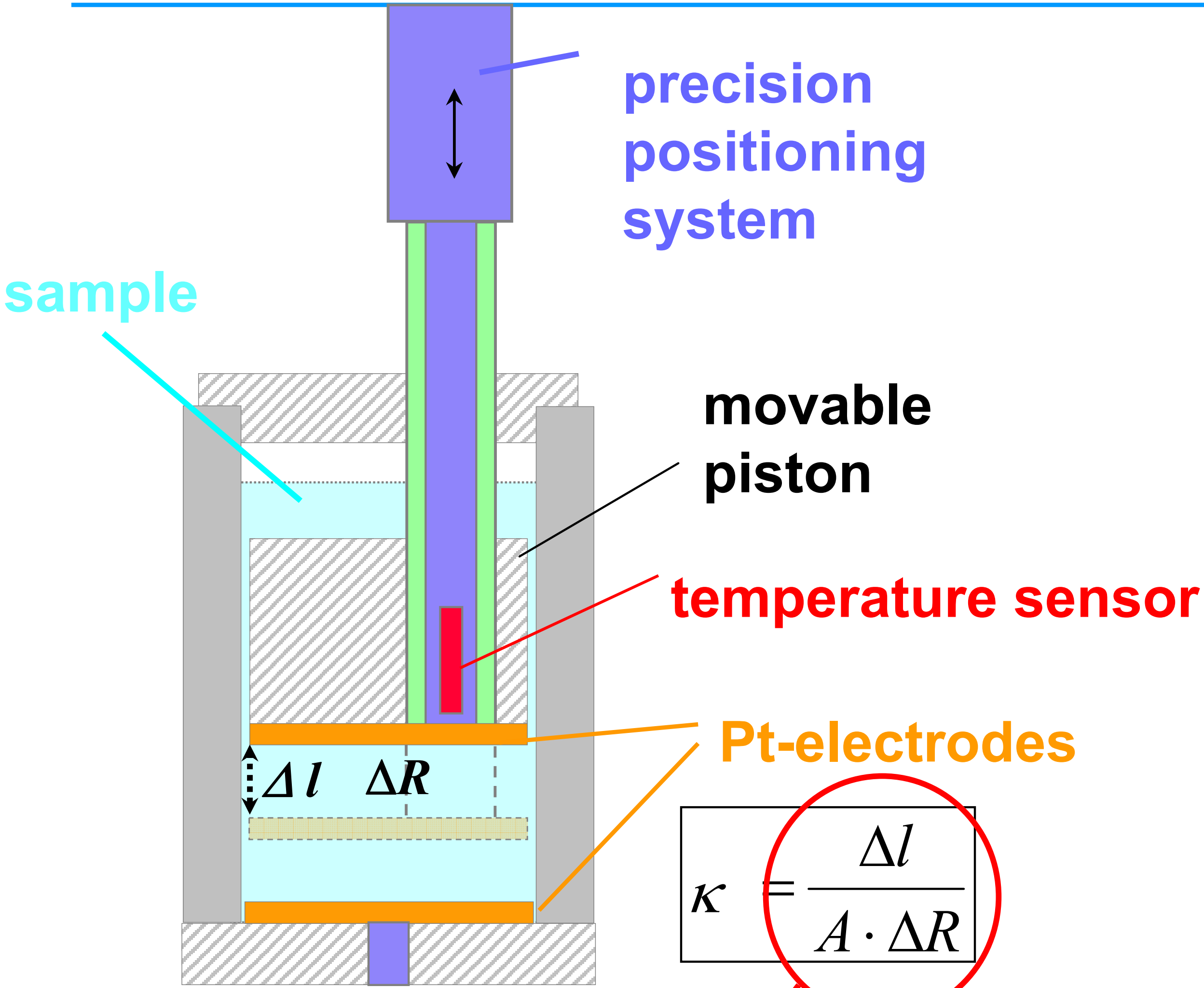
secondary method

$$K_{sec} = \kappa_{ref} \cdot R$$

determine K_{sec} of secondary cells of any geometry, using a reference solution of known κ_{ref} and a measurement of *R*

→ **traceable measurement of a sample of unknown conductivity**

Primary method for conductivity: PTB Cell (piston type)



$$\kappa = \frac{\Delta l}{A \cdot \Delta R}$$

results of measurements are traced back to SI units “meter” and “Ohm”

Conductivity at low ranges – metrological aspects

conductivity is a useful parameter for bioethanol – BUT:

Certified calibration standards traceable to the SI with stated uncertainty only exist > 10 mS/m

Standards with low conductivity possibly are not stable (CO_2!!)
Often conductivity is measured \`in-line\` and need in-line calibration in closed loop

CCQM-P83 for low conductivity values ~ 0.5 mS/m 2008/2009

Interaction of solution and electrodes strongly influences the conductivity measurement

Calibration using common KCl calibration solution is critical
Primary measurement method for biofuel has to be developed

How to ensure traceability of pH and conductivity measured in ethanol-water mixtures

Agreement on the measurand - what am I measuring, anyway?

Selection of a target uncertainty

Reference material and reference method development and testing

Selection and validation of a measurement procedure

Establishing a calibration hierarchy

Identification of all uncertainty components
(pH: uncertainty budget following example in DIN 19268)

Thank you for your attention !

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