

Ion-selective electrodes in real-life applications: Can we reduce or even eliminate the need for calibration?

Matrafured 2008





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What is wrong with calibration?



Autonomous, deployable sensing devices become very complicated and costly







Can we evaluate the functionality (damaged, fouled, components leached out – "good" or "bad") of the sensors using a simple electric signal?

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Cosofret W., Lindner E., Buck R. P., *Electroanalysis*; **1993, 5, 725**





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Physical damage







100 k 50 k 0

500 k

1 M

1.5 M

Zre (ohms)

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2 M

2.5 M





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Biofouling



🖹 Tyndall













Liquid- and solid-contact ISEs in soil analysis

- Highly polluted soil (Pb, Cd, Cu, As, Zn)
- Three metal extraction procedures (aqua regia, 0.43 M acetic acid, 1e-3M HNO₃)
- Data correlated with AAS



Liquid- and solid-contact ISEs in soil analysis



log a

Bakker E., Pretsch.; Trends Anal. Chem.; 2005; 3, 199



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 $LOD_{IUPAK}^{Pb,AA} = 6.3 \times 10^{-6} M$ (130mg / kg)

 $\log Pb^{SC,AA} = 2.6 \times 10^{-5} M$ (540mg / kg)

 $\log Pb^{AAS,AA} = 8.7 \times 10^{-6} M$ (180mg / kg)

Important to use the whole response curve but direct evaluation of unknown concentration or standard addition is a lose-lose situation





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Anal. Chem. 2002, 74, 4027-4036

Rational Design of Potentiometric Trace Level Ion Sensors. A Ag⁺-Selective Electrode with a 100 ppt Detection Limit

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- 1) Error related with all parameters determined experimentally (R_T, K^{pot},
- D_{org}, D_{aq}, δ_{org}, δ_{aq}, [IL+]')
 Solid contact electrodes?

Understand factors dictating LOD in solid contact electrodes Models to predict the response

 $x = [\mathrm{IL}_n^{z_I^+}]' \frac{Z_I}{R_-}$



Liquid- and solid-contact ISEs in soil analysis





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Bakker E., Pretsch.; Trends Anal. Chem.; 2005; 3, 199

 $E = a + b \log([Pb^{2+}] + c)$

$$\log Pb^{SC,AA} = 1.1 \times 10^{-5} M$$

$$(228mg / kg) \qquad \text{university college dublin}$$

$$Multiple Multiple Mul$$





Limitations of the Current Methods of Calibration

UCD

DCL

Detection limits have arbitrary cut-offs

 Significant bias in IUPAC estimates near LOD





Multiple ISEs are used in a simplistic manner

 Only point estimates of concentrations are obtained for unknown samples, which imply a level of certainty that is not achieved



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Bayesian Approach to Calibration

- Bayesian statistical analyses are based on the concept of *prior* knowledge or beliefs being combined with data to form updated (or *posterior*) probability beliefs.
- In a calibration context:

Given a set of observed calibration data and model assumptions, we can estimate the calibration parameters and the concentrations of unknown samples (and their distributions).

 Bayesian approaches are easily implemented using open-source software (OpenBUGS), which can be called from more familiar software, such as MATLAB







Advantages of Bayesian Calibration



- However, the Bayesian approach provides an estimate of the uncertainty in the concentrations of unknown solutions.
- There is no arbitrary LOD. Estimates are merely more or less accurate, depending on measured emf.
- Multiple ISEs are easily incorporated





Bayesian

point estimates



Single ISE Approach

Liquid contact ISEs were used to measure [Pb²⁺].

Bayesian analysis used to find the calibration interval.

- Concentrations were determined at two points (345mV,375 mV).
- Results:
 - No fixed LOD, but estimate becomes increasingly less accurate at smaller concentrations
 - Asymmetric calibration intervals, especially near "LOD"
 - Size of the calibration interval depends on: individual ISE, number of calibration points, measured emf







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Integrate Multiple ISEs



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- Calibration model extended to include multiple ISEs
- The responses of three ISEs integrated to calculate a single calibration interval.



Calibration intervals from all methods compared for a theoretical solution of log(Pb²⁺) = 7.1



Tightest Calibration Intervals Obtained with Multiple ISEs



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Theoretical solution, $log(Pb^{2+}) = 7.1$

	log{Pb ²⁺ (mol L ⁻¹)}	(95% Cl)	
Single ISE, #1	-6.9	(-7.5, -6.4)	
Single ISE, #2	-6.9	(-7.2,-6.7)	
Single ISE, #3	-7.3	(-7.7,-6.1)	
Multiple ISEs	-7.1	(-7.4,-6.9)	
Non-linear least squares	-7.1	(-9.5,-4.7)	
IUPAC	-6.6	(-6.9,-6.3)	





Conclusions



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- Relatively simple electric signal can be used to evaluate the functionality of electrode (to encourage/discourage further use/calibration of ISEs)
- Bayesian analysis used
 - to find calibration interval,
 - to estimate the uncertainty in the concentration of unknown solution,
 - has no arbitrary LOD,
 - simultaneously incorporates all ISEs (not simple averaging)
- Has the time come to reconsider the definition of current IUPAC detection limit?





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