



Tutorial

A tutorial on the application of ion-selective electrode potentiometry: An analytical method with unique qualities, unexplored opportunities and potential pitfalls; Tutorial



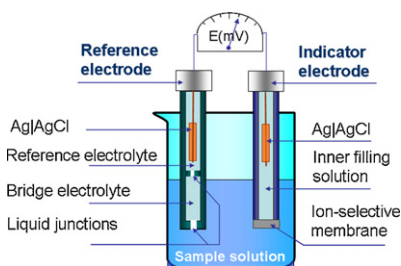
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HIGHLIGHTS

- ▶ Electrochemical cells for potentiometric measurement.
- ▶ Characterization of potentiometric electrodes.
- ▶ Measurement of ion activities and concentrations with potentiometric electrodes.
- ▶ Analysis of real samples: The role of the selectivity coefficient.
- ▶ Methods to evaluate the agreement between two methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Ion-selective potentiometry enjoys practical utility as a simple analytical technique to measure ionic constituents in complex samples. Advances in the field have improved the selectivity and decreased the detection limit of ion-selective electrodes (ISEs) by orders of magnitude such that trace analysis in micro and nanomolar concentrations is now possible with potentiometric sensors. This tutorial reviews the fundamental principles of ion-selective potentiometry, describes the practical considerations involved in the use of these sensors to measure real samples, and discusses the statistical evaluation of experimental results compared with alternative analytical techniques.

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1. Introduction

During the time we wrote this tutorial on ion-selective electrodes (ISEs), we received a letter from a colleague in which we were asked about commercial instruments that utilize the recent discoveries in the field of ISEs for monitoring sub-nanomolar lead ion concentrations in environmental samples. He approached us because he came across our paper in which we reported picomolar detection limits with lead ion-selective membranes [1]. We had to inform him that, as far as we know, no such instrument exists. We felt somewhat uncomfortable and embarrassed to give this information because the last 15 years of potentiometry was all about “the new wave of ion-selective electrodes” [2] with spectacular selectivities and previously unimaginable detection limits [2–8]. However, the focus of these papers was on the understanding of the underlining chemical principles of the ISE responses and on the elimination of experimental biases inherently related to their response mechanism. Consequently, the majority of these papers, including ours [1], were feasibility studies and only a very few were aimed for documenting the unique benefits of potentiometric ion-analysis through practical examples [9] with adequate error analysis, statistical support or proper comparison to an existing method. This is in sharp contrast to what occurred following the discovery of the first non-glass based ISEs in the late sixties [10–13], when the need for better methods to solve important practical problems (e.g., the measurement of ion concentrations in whole blood or fluoride in drinking water) was the driving force of the developments. At that time, the new ISEs were utilized to satisfy real needs that would be very difficult or impossible to fulfill with the existing analytical methods, e.g., analysis of the blood samples of astronauts during space flights. Consequently, simultaneous to their appearance, the new ISE-based methods were analyzed in detail for their precision and accuracy [14].

Compared to the meticulous examination of the analytical results with the new ISEs in the early years, it appears that during the last 15 years of development, when the selectivities and the detection limits of potentiometric sensors have been improved by many orders of magnitudes, we have forgotten that to have broad acceptance, new discoveries must satisfy real demands. Although it is very exciting to measure ionic concentrations at the

parts-per-trillion level (10^{-10} M), the need exists to demonstrate that these spectacular detection limits can be achieved in real samples and that the new method has obvious advantages over the old ones, a task typically done in method comparison studies. At the end of this tutorial we give a quick guide about the approaches for evaluating the performance characteristics of a new method and the appropriate statistical tools for assessing agreement between a new and an existing method that measures the same quantity.

The feasibility of trace level measurements with potentiometric ISEs has been demonstrated and the results have been summarized in excellent reviews and book chapters [4,6–8,15–19]. However most of these reviews were written for experts without detailed information on the methodology or validation of the novel ISEs. Consequently, to find practical information on ISE-based methods, one has to consult books [20–25] and IUPAC documents [26] from up to forty years ago. Therefore, in this tutorial, the emphasis will be on the sources of potential errors [21] and challenges of direct potentiometry and ways to address them. We hope that, by discussing these difficulties, those who are new to the field and “only” consider using potentiometry as an analytical method can understand how to translate these improvements in technology for solving real problems. If we can reach this goal we will not hesitate how to answer the question of Karl Camman “Ion-selective potentiometry: an analysts dream or nightmare?” [27].

2. Ion-selective potentiometry

2.1. Electrochemical cells for potentiometric measurement

The history of ion-selective potentiometry can be traced back to the studies of Walter Nernst on the acidity of aqueous solutions with a hydrogen gas sensor [28]. However, the discovery of the pH sensitive glasses by Max Cremer [29] and recording acid base titration curves with glass electrodes by Fritz Haber [30] about a century ago are the real landmarks of a new era in potentiometry. The first papers describing the use of glass electrodes in combination with commercial pH meters were published about 20 years later. The next “revolutionary” period in potentiometry started in the sixties [10–13] when new ISEs were reported at a rate that was best characterized with titles like the “Electrode of the Month” [31].

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