



## Review

## Enhancing ion-selective polymeric membrane electrodes by instrumental control

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## ABSTRACT

This review aims to highlight a recent important direction to place ion-selective electrodes based on polymeric sensing materials under dynamic electrochemistry control. This allows one to design sensors with a range of improved characteristics. This review also showcases developments to achieve calibration-free ion-sensing strategies by using thin layer coulometry at ion-selective membranes. Finally, strategies to fabricate electrochemically-addressable ion-selective thin membrane layers are discussed, especially in view of realizing stripping ion-transfer voltammetric sensors.

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## 1. Introduction

For a long time, the field of ion-selective electrodes has been associated with a zero current potentiometric readout principle [1–3]. In the absence of current, one performs the simplest electrochemical measurement. The observed potential is in ideal cases directly related to the activity of the ion of interest. For this reason, potentiometry is often thought to provide thermodynamic information (i.e. ion activities) about a sample. But recent research has revealed that this is not always the case and that dynamic processes can also play an important role in zero current potentiometric measurements.

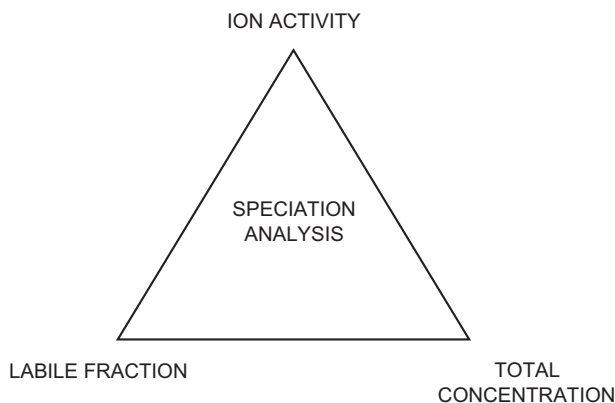
Selective chemical receptors and materials have been developed [3] to make polymeric membrane electrodes valuable tools in a variety of applications, especially in clinical diagnostics, where they are one of the key success stories of electrochemical-sensor technology [4,5]. They are also attractive in other fields, such as process control and environmental monitoring [6].

Binding affinities and dynamics in biological and environmental samples can complicate the ion speciation in solution and one may distinguish between the ion activity, the free ion concentration, labile complexes, inert complexes (see Fig. 1) and species adsorbed onto colloidal materials [7]. Quantifying these different species is important for understanding the dynamics and the toxicology of natural samples, but a full analysis is not always straightforward and often requires a multitude of orthogonal analytical techniques.

Today, total concentrations can be assessed by atomic spectrometric methods, such as inductively-coupled plasma mass

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**Fig. 1.** The speciation of ions is of key importance for understanding bioavailability and reactivity in natural and biomedical environments. Free ions can be assessed by potentiometric techniques, while dynamic electrochemical techniques, the topic of this review, may help quantify the labile ion fraction. Total concentrations can be detected by atomic spectrometric techniques or by chemical-modification steps followed by electrochemical detection.

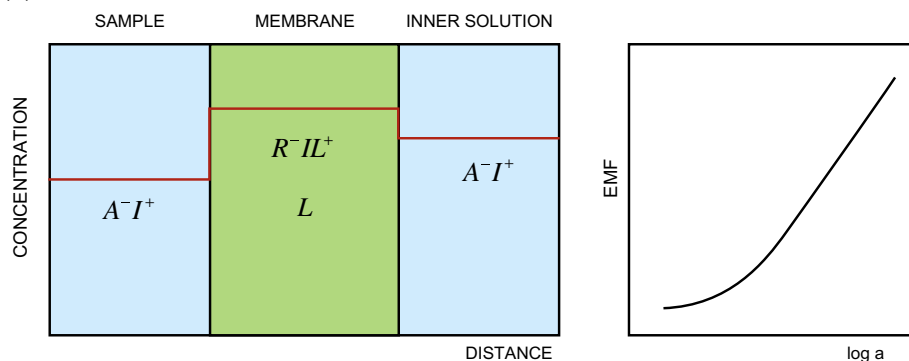
spectrometry (ICP-MS) or inductively-coupled plasma optical emission spectrometry (ICP-OES). Dynamic electrochemistry gives ready information on the labile fraction of the dissolved species, since inert complexes cannot be directly oxidized or reduced at

the electrode surface. Electrochemistry can also be used to assess total concentrations, in which case the sample is chemically treated to transform inaccessible species into labile complexes that can be detected. *In-situ* speciation analysis can be performed by submersible probes containing the required fluid-handling and electrochemical-detection protocols [8]. These approaches have been mainly established for the detection of redox-active substances, such as transition metals, and there is an important need to expand the palette of species that can be observed by electrochemical methodology. Ion-selective membranes operated by dynamic electrochemistry protocols may help introduce additional methodologies for speciation analysis in a variety of applications [9].

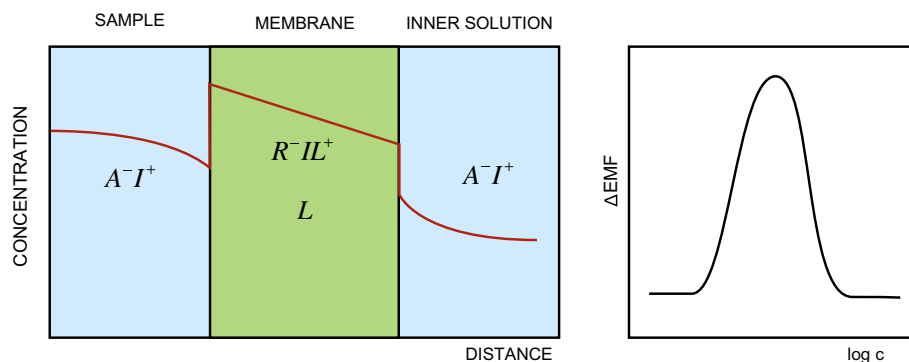
The advances described here were triggered by realizing the importance of ion fluxes with polymeric membrane ion-selective electrodes [10]. Their control and diminution resulted in an important improvement of the limits of detection (LODs) achievable with potentiometry down to ultra-trace levels [11]. Dynamic electrochemistry had been used by numerous researchers as a diagnostic tool to characterize ion-selective membranes [12,13], but its use as a readout protocol was stimulated by a great body of work in the area of physical electrochemistry at the interface of two immiscible electrolyte solutions (ITIES) [14–16].

This review is written primarily for the analytical chemist, who has some basic familiarity with the workings of polymeric membrane-based ion-selective electrodes.

#### (A) ZERO CURRENT POTENTIOMETRY



#### (B) DYNAMIC POTENTIOMETRY (STEPTRODES)



**Fig. 2.** (A) Potentiometry is classically understood as a technique where concentration changes near the interface can be neglected and the potential across the membrane is directly related to the ion activity in solution according to the Nernst Equation. Left: Concentration gradients across the membrane that contains a cation-exchanger,  $R^-$ , and a lipophilic ion receptor (ionophore),  $L$ , which can form stable but kinetically labile complexes of the type  $IL^+$  with the cationic analyte  $I^+$ . Right: a typical calibration curve gives the electromotive force that is linearly dependent on the logarithm of the ion activity in solution. This dependence diminishes near the limit of detection (LOD) as shown. (B) In dynamic potentiometry, an asymmetric extent of ion-exchange on either side of the membrane results in a counterdiffusion process between the analyte ion and a competing ion of the same charge sign. This results in ion fluxes that may give concentrations at the membrane surface that dramatically differ from those in the sample bulk. With the steptrodes concept shown, two membranes are measured against each other where this ion flux is slightly different, giving a very sensitive peak-shaped response around a critical concentration at which the spontaneous ion flux results in significant depletion of the analyte at the membrane surface, resulting in a large potential change [20].

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