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Invited critical review

Ion Selective Electrodes (ISEs) and interferences—A review

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ABSTRACT

Ion Selective Electrodes (ISEs) are used to measure some of the most critical analytes on clinical laboratory and point-of-care analysers. These analytes which include Na^+, K^+, Cl^-, Ca^{2+}, Mg^{2+} and Li^+ are used for rapid patient care decisions. Although the electrodes are very selective, they are not free of interferences. It is important for laboratories to have an understanding of the type and extent of interferences in order to avoid incorrect clinical decisions and treatment.

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1. Introduction

Electrochemistry is the measurement of an electrical signal generated by a chemical system in an electrochemical cell. Electrochemical

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techniques are of 3 types: potentiometric, voltametric (amperometric) and coulometric. Potentiometry is the most commonly used of the electrochemical techniques and involves the measurement of a potential (voltage) generated by a cell under essentially equilibrium conditions [1]. We shall restrict our comments to ISEs that measure the activity of Na^+, K^+, Cl^-, Ca^{2+}, Mg^{2+} and Li^+ in biological fluids.

ISE methods can be classified as either indirect or direct. With indirect ISE methods the sample is diluted with diluent in ratios of ~1:20 to 1:34, depending on the analytical system. These are confined to laboratory general chemistry analysers. They are standardised using normal concentration of solids (lipids and proteins), 7% or 0.07 kg/L of the total plasma or serum volume (mass concentration of water 0.93 kg/L). Direct ISE methods are directly exposed to the undiluted sample and measure the activity or the physiologically relevant fraction of the ion of interest unaffected by solids concentration change. These are used with point-of-care systems and some laboratory analysers including the Ortho-Clinical Diagnostic and Roche Integra systems.

The ability to provide sensitive, reliable and inexpensive measurements of these clinically important analytes on small sample volumes in a variety of sample types within a very short time frame has made ISEs essential components in clinical laboratory analysers, blood gas analysers and increasingly, point-of-care analysers. There have been previous reviews of ISEs but none have examined the reported interferences in the clinical environment. The first part of the review examines interferences due to specific agents or substances. In the second part interferences with specific ISEs are reviewed.

For theoretical aspects on design and operations of ISEs we suggest readers refer to Clinical Chemistry text books or the excellent publication by Hirst and Stevens [2].

2. Definition of interference

Interference occurs when a substance or process leads to a false result in a measurement technique [3]. There are many sources of interference in clinical assays including sample type (blood, serum, plasma), sample content (drugs, metabolites, herbal products etc), sample collection, site of collection (capillary, venous arterial, IV contaminated), and sample treatment and storage. It is critical to understand the impact of interference in routine assays if that interference can lead to inappropriate interpretation and subsequent misdiagnosis.

The selectivity coefficient of an electrode defines the ability of the ISE to distinguish the ion of interest from interfering ions. The selectivity coefficients were established and first published in 1976 [4] and updated in 2000 [5].

3. Interference by specific agents or substances

3.1. Catheter and cannula carryover

Interferences from catheters and cannulas occur because of contamination of the device by intravenous fluids. Thus these require flushing before collecting samples for analysis. There is good published data recommending discard volumes but this is dependent to a degree on the type of catheter or cannula, the fluid being infused and the patient age. One study of arterial lines used in neonates infused with heparinised saline showed at least 1.6 mL of blood was needed to be withdrawn from the line prior to taking a sample for analysis [6]. In adult patients, the volume of discard blood can be dependent on the type of fluid being infused. For example, with glucose saline infusion only 3 mL of blood was required to be discarded for accurate K^+ measurement [7], whereas arterial catheters that had been used with sodium citrate infusions displayed Ca^{2+} interference even after discarding 9 mL of blood [8]. The most common volume discarded from catheters or cannulas in adult patients is 5 mL. Contamination of samples from inadequately flushed catheters or cannulas can affect analytes other than electrolytes. Samples from catheters containing very high concentrations of sodium heparin have yielded falsely lowered Na^+ values on the Ektachem 750 analyser (Ortho-Clinical Diagnostics, Rochester, NY, USA) which uses a direct ISE system [9].

One of the most frequently encountered interferences is from contamination with IV fluids containing Na^+, K^+, Cl^-, Ca^{2+}, and Mg^{2+}. Other less common or unusual interferences may originate from drug infusions e.g. ticarcillin contains high concentration of sodium [10], blood lines, dialysis lines etc. The mechanism of interference is either additive or through binding by the compounds contained in the fluids.

3.2. Surfactants

Interferences in ISE measurement systems can be introduced via surfactants from various sources. Malinowska and Meyerhoff found the addition of two nonionic surfactants Brij 35 and Triton X-100 which may be present in calibrating, rinsing and quality control solutions, can alter membrane behaviour [11]. While there was minimal effect on valinomycin based K^+ ISEs, the Ca^{2+} ISE using ETH129 and ETH 1001 ionophores showed decreased selectivity over K^+ by nearly one order of magnitude with Triton X-100. The effect on Na^+ depended on the ionophore, the surfactant and the surfactant concentration used; Triton X-100 decreased the selectivity significantly more than the addition of Brij 35 by changing the ion selectivity of the membrane. The error is likely to arise if membranes are exposed to these solutions for extended periods due to malfunctioning wash processes or exposed to third party quality solutions containing surfactants.

The interference by benzalkonium surfactant with Na^+ and K^+ ISEs is well documented in the literature [12–15]. Benzalkonium-heparin bonded or coated catheters are commonly used as intravascular-access devices in critical-care medicine to prevent thrombi from forming, and decrease the incidence of infections. False elevation of K^+ has been observed to be more common in analysers using indirect measurement, possibly because the surfactant interacts with the K^+ valinomycin membrane temporarily to alter the membrane's surface properties. In contrast, interference with the single Na^+ system was attributed to a particular Na^+ ionophore which interacts with the benzalkonium. This substance has also been reported to positively interfere with Na^+ and Ca^{2+} measurements on the IL GEM Premier 3000 (Instrumentation Laboratory, Lexington, MA, USA) [16].

An unusual interference has been reported in capillary samples contaminated with benzalkonium containing antiseptic hand cleaning agents. The Na^+ values were >150 mmol/L on the Bayer Rapidpoint 400 (Bayer (now Siemens Healthcare) Diagnostics, Medfield, MA, USA), but were unaffected on the Roche DP Modular (Roche Diagnostics, Mannheim, Germany) [15]. The source of the interference was the “alcohol rub” antiseptic agent (Microshield Antibacterial Hand Gel implemented as an extra precaution during the SARS outbreak) [15]. In laboratory experiments with 6 hand cleaning agents the most pronounced interference was on the Bayer Rapidpoint 400 and Rapidlab 865 (Bayer (now Siemens Healthcare) Diagnostics, Medfield, MA, USA), and the least was on the i-Stat analyser (i-Stat, Abbott Diagnostics, Abbott Park, IL, USA). In fact samples spiked with Microshield Antibacterial Hand Gel caused the most significant increase compared with other similar products [15].

3.3. Sample matrix

The sample matrix can significantly affect the ISE response. Deposition of protein can change the physical nature of the ISE membrane, causing at least a delay in the sensor response, or in the worst case, the sensor fails if the membrane is completely coated, resulting in non-Nernstian behaviour [17]. Deposits of proteins on the

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