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Potentiometric Biosensors: Concept and Analytical Applications-An Editorial

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Editorial

Potentiometric assays rely on recording the potential/pH variation, and these determinations are applicable in food, clinical or environmental analysis. The analytical signal is due to the concentration variation of an ionic species.

Potentiometric measurements are applied to the determination of many organic and inorganic species (sugars, urea, antibiotics, neurotransmitters, pesticides, but also ammonia, carbon dioxide and many ionic species).

Potentiometric biosensors are developed by combining a biorecognition element (essentially an enzyme) with a transducer that senses the variation in protons (or other ions) amount, the recorded analytical signal being logarithmically correlated with the analyte concentration.

The present Editorial deals with the presentation of several types of sensors based on different transducers and biorecognition elements.

The simplest transducer in the development of potentiometric biosensors is the glass pH electrode. Glucose oxidase immobilization was achieved using cellophane [1], nylon [1-6] or nitrocellulose [5,7] membranes that are subsequently fixed on the sensitive bulb of the pH electrode that senses the pH diminution, as a result of the biocatalytical reaction occurring in the enzyme layer (glucose oxidation by glucose oxidase). Such potentiometric enzyme sensors possess a linear range of 10^{-4} to 5×10^{-2} M, allowing for glucose assay in fruit juices [4].

Glucose oxidase has been also coupled with other signal transducers for potentiometric purposes: the enzyme has been entrapped in a polypyrrole film by electro-polymerization on a Pt electrode, resulting in a potentiometric glucose biosensor [8].

Ion selective electrodes other than the pH glass electrode, such as the fluoride electrode, were also used in the development of potentiometric sensors. Glucose, maltose or lactate can be determined relying on the reaction of 4-fluoroaniline with H_2O_2 generated by the corresponding substrate oxidases. The fluoride anions resulted from the peroxidase-catalyzed reaction of fluoroaniline with hydrogen peroxide that involves cleavage of the C-F bond, are potentiometrically detected with the specific fluoride electrode. The analytical signal represented by the recorded voltage difference depends linearily on the logarithm of the analyte concentration within the range 0.1–1 mM [9].

Amygdalin can be assessed with a potentiometric biosensor using as transducer a cyanide anion selective electrode [10].

Enzymes such as glucose oxidase, lipase or acetylcholinesterase, were also immobilized on the sensitive membranes of ion-selective field effect transistors, resulting in the determination of glucose, triglycerides and pesticides respectively [11-13].

The development of potentiometric biosensors can also involve gas-sensitive electrodes (such as for carbon dioxide and ammonia resulted from enzyme reactions), as in the case of urea determination [14]. Gas–sensitive electrodes as transducers are obtained on the basis of a pH glass electrode and an electrolyte layer that is maintained close to the sensitive bulb by a gas-permeable membrane [15].

Increasingly complex electrode modification resulted in excellent analytical parameters:

Hypoxanthine assessment in fish meat was performed using a potentiometric enzyme electrode relying on xanthine oxidase and ferrocene carboxylic acid entrapment in a polypyrrole film that was obtained by applying galvanostatic technique. The linear range of analytical response of the developed enzyme sensor was 5–20 μM [16].

The immobilization of acetylcholinesterase on an antimony disk electrode by intermolecular cross-linkage of the enzyme and bovine serum albumin, using glutaraldehyde vapor, resulted in a potentiometric sensor enabling the assay of trichlorfon with fast response, given the ability of the organophosphorous pesticide to inhibit AChE [17].

A solid-state electrode consisting in a conducting resin (graphite/epoxy) and polyvinyl chloride matrix and responding to ammonium ions was used as transducer in urea assay [18].

Another type of urea biosensor consists of a glass-sealed metal microelectrode coated with a polyethylenimine film. Physical adsorption and subsequent reticulation with diluted aqueous glutaraldehyde solution for urease immobilization, resulted in enhanced analytical performances meaning short response times (15–30 s), a dynamic range with sigmoidal response versus urea for a concentration range 1×10−2.5 to 1×10−1.5 M and a lifetime of 4 weeks [19].

Urease immobilization on a modified fullerene nanomaterial and subsequent deposition on a screen-printed electrode that contained a poly (n-butyl acrylate) membrane entrapped with a hydrogen ionophore, resulted in a novel biosensor. The linearity of the biosensor was comprised between 2.31×10^{-3} M and 8.28×10^{-5} M. The sensitivity of the biosensor was very close to the theoretical Nernstian slope: 59.67 ± 0.91 mV/decade. Tests performed on cations commonly present in urine samples such as Na+, K+, Ca^{2+}, Mg^{2+} and NH^{4+} showed that these ionic species did not interfere with the urea analytical signal. The results obtained in real urine samples range between 17 and 19 mM, the difference between the results of UV-Vis

standard spectrometry and those obtained with the potentiometric biosensor being smaller than 5% [20].

The analytical parameters and methods' validation confirm the viability of the developed potentiometric sensors, for the assessment of various key biomolecules.

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