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Review article

Amperometric sensing. A melting pot for material, electrochemical, and analytical sciences

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ABSTRACT

The critical review discusses the key points of the main blocks leading to the development and use of an amperometric sensing system. On the one side, most attention is paid to the electrode materials that may potentially induce impressive progresses in the performance of the device. On the other side, comparable room is given to the remaining parts constituting the sensing system as a whole, from tests in different solutions to problems arising from data processing. All these steps require care and knowledge of the manifold branches of science and technology that concur to realise and use the device at best. However, some of these aspects are too often underestimated, also due to the different scientific origin of researchers or analysts who are directly involved. The discussion is centred on both the virtues of amperometric sensing systems and on the limits they present. The last are especially evidenced, in order to induce full consciousness of the complexity and interdisciplinary features of this kind of analytical tools. Exemplificative literature dealing with the issues dealt with is cited and critically inserted in the frame of the overall picture.

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1. Introduction

An unprecedented variety of competencies concurs to the design and realisation of an effective amperometric sensor. Expertise is required in all steps of the physical development of the system and in the proper outline of measurement procedures; at varying the type of transduction of the device we met with differences, but also with surprising similarities.

Deep knowledge of the specific matrix of the sample to analyse is also mandatory. In particular, important areas in which amperometric sensors are advantageously applied are food authentication or processing, environmental monitoring, quality control in a number of productions, human health, and a wide number of industrial and natural sectors in which sensing brings added value with respect to laboratory analyses.

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Though the term 'sensing' is adopted to indicate systems consisting of probes and components that are different from one device to another, some notable common features may be evidenced. In addition to be small in dimension, in order to be even portable, sensors are required to *i*) perform measurements of short duration; *ii*) present meaningless deterioration of all components, especially of the sensitive element; *iii*) allow infrequent intervention of the operator, in order to be also suitable to work under remote-control; *iv*) require simple pre-treatment of the sample, possibly none at all. Additionally, they are typically low-cost devices.

All these characteristics render the sensing systems suitable to perform on-line or even in-line, i.e., *in situ*, measurements [1]. Sensors often allow continuous monitoring of an evolving or flowing system. Quite a different situation is found when considering more sophisticated laboratory instrumentation. Operations with similar facilities generally require pre-treatment of the sample, so that they are suitable only to perform at-line, or even off-line, analyses, requiring *a priori* definition of the sampling conditions and limiting the frequency of data collection.

Electrochemical, optical, and gravimetric sensors emerge as the most widespread and effective transduction systems. On the one side, amperometric sensors, at variance with the optical ones, may also work in opaque media. On the other side, the selectivity offered by optical techniques, operating in different regions of the electromagnetic radiation spectra, as well as also limitedly to a specific region at varying the wavelength, is much higher than that offered by the scale of potentials to apply to the electrode. In both cases, the measurement process does not alter significantly the composition of the sample, even after submitting it to a large number of measurements. However, the so-called 'history' of an electrode is well known to often constitute a serious obstacle in the obtainment of reliable and repeatable responses.

A number of electrode materials for amperometric sensing have become available to electroanalysts after being developed for different purposes than analysis, such as fuel cells or batteries, or preparative electrochemistry. Among the variety of materials proposed, wide room is occupied by biological recognition elements, possessing particularly high selectivity. Nevertheless, in this critical review we decided not to treat similar devices, which possess specific characteristics. It is, however, evident that many aspects discussed here also hold for biosensors.

Key performance indicators constitute the guide to best choice of the amperometric sensor: *i*) reversibility of the responses obtained on typically reversible redox couples, such as $[Fe(CN)_6]^{3-/2-}$, ferricenium ion/ferrocene (Fc^+/Fc) and derivatives, $[Ru(NH_3)_6]^{3+/2+}$, or others, which constitutes necessary condition for discarding the presence of resistances internal to the system or at the electrode|solution interface; *ii*) as low as possible fouling, in order to point to repeatability of the responses; iii) resolution of the individual responses, often gained by activation of electrocatalytic processes; *iv*) achievement of an as wide as possible potential window with respect to the oxidation or reduction potentials of the species of interest, which may be in turn once more pursued by activating electrocatalytic processes; v) selectivity of the responses, implying minimisation of the signals due to interfering species; *vi*) sensitivity; *vii*) Limit Of Detection (LOD) in respect to the target analytes. Moreover, the awareness of the goal to reach should be present since the beginning of the development or of the use of the sensor. This requires the definition of the scenario in which to operate, the execution of tests in standard solutions but also in the matrices of interest, and the outline of the procedure to follow in order to achieve best performance.

The depicted situation would lead to univocal correspondence between the analyte plus the matrix system and the sensor. Things are actually much less dramatic, and the same sensor is often suitable to solve different problems, eventually adapting the procedure to the specific purpose. A block diagram of the different steps toward the development of an effective sensor system is reported in Fig. 1.

The procedure starts from the analysis of the scenario in which the sensor will operate and is followed by a preliminary choice of the electrode material, i.e., of the sensing element. Electrochemical, spectroscopic, and microscopic characterisations of the material, complemented by electroanalytical tests on the analyte, furnish feedbacks to the best choice. The block 'device' in Fig. 1 is especially critical; we intend it to include, in addition to the engineering of the device as such, the hardware (potentiostat and waveform generator), and the software managing the experiment and acquiring and treating the signals. The expertise of the operator, probably more than in the case of sophisticated instrumentation, plays a basic role in properly planning and executing the measurement, as well as in dealing with the obtained responses and extracted data with highest efficiency. The expertise in electrochemical techniques [2,3] should be complemented by additional experimental and theoretical issues; working of a team may be often helpful or even necessary, especially as to the cited knowledge of the matrix.

The focus of this article is to emphasise the advantages of a multi-technique and multi-expertise approach to the development of a novel system, as well as of the integration of different competencies in using a sensing device properly. At the same time, limits to speculations imposed by the complexity of some of the new materials adopted, are suggested. Emphasis is also given to the

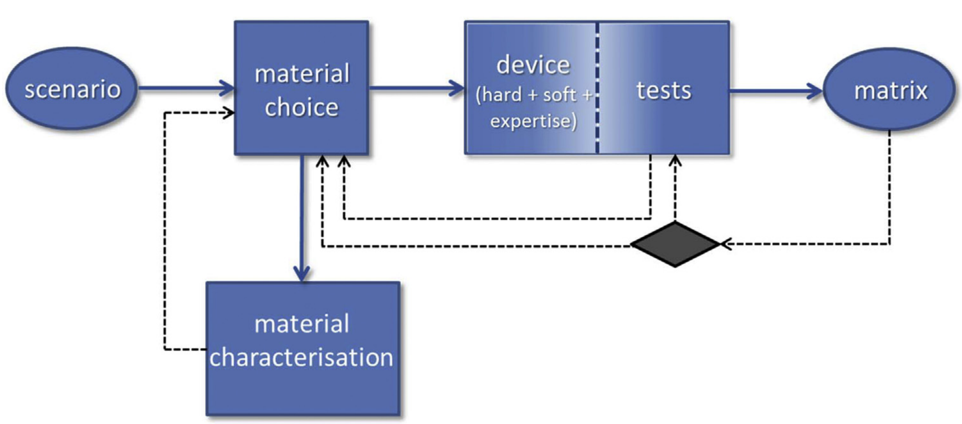

Fig. 1. Pipeline to effective amperometric sensing device. The broken lines indicate feedback of information, in the direction of the arrows. The diamond indicates a logical IF, i.e., a choice of the path to follow according to the results of tests on the matrix: going back to the material or only refining the procedure in test solutions.

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