



An overview of electrochemistry combined with mass spectrometry

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ARTICLE INFO

Keywords:

Electrochemical cell
Electrochemical reaction
Electrochemistry
Ionization
Liquid chromatography
Mass spectrometry
Metabolism
Microchip
Potentiostat
Protein cleavage

ABSTRACT

This is an overview of historical and technical aspects of the combination of electrochemistry with mass spectrometry. Some of the applications are highlighted. For a complete overview, the reader is referred to the other contributions in this Special Issue of *TrAC*.

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1. Introduction

There is increasing interest in the combined use of electrochemistry (EC) and mass spectrometry (MS) (EC-MS). EC can benefit from the identification and the quantitation of reaction products by means of a mass spectrometer (Fig. 1A). Studies of electrochemical reactions have been instrumental in the understanding of ion formation and unexpected redox reactions in electrospray ionization (ESI)-MS [1]. The history of combinations of EC and MS has been reviewed in detail [2].

For fundamentals of EC the reader is referred to books [3,4] and a thematic issue of *Chemical Reviews* [5]. MS makes use of a range of ionization methods, mass analyzers, sample-handling methods and couplings with chromatography [6,7]. It is impossible to equip

one mass spectrometer with all conceivable options and a choice has to be made to obtain the best possible information from EC.

Identification and quantitation of products of electrochemical reactions will help in the selection of the right conditions for scale-up for electrochemical synthesis [4] and in scale-down for miniaturizing EC on a chip [8,9]. MS can support the study of electrochemical reactions (e.g., by the detection of short-lived and unstable intermediates). However, electrochemical conversion of a sample can improve the response of a mass spectrometer in the detection of particular sample components [10,11] (Fig. 1B).

When EC produces a mixture of isomeric or isobaric molecules, one makes use of a separation method combined with MS [mostly liquid chromatography (LC)]. High-resolution MS and tandem MS are used to get more detailed insight into identification and quantitation of electrochemical-reaction products. LC as an intermediate between EC and MS (Fig. 1C) allows for nearly complete freedom of selection of reaction conditions in EC and ionization conditions in MS.

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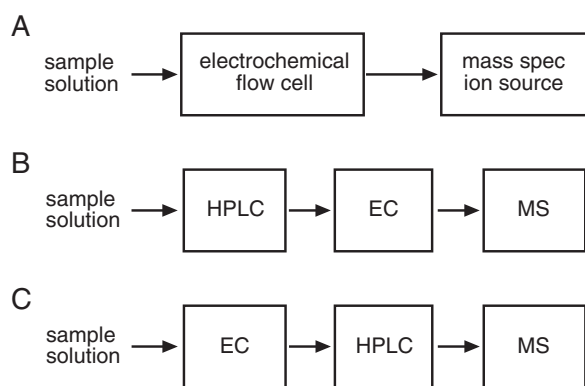


Fig. 1. Combinations of electrochemistry with mass spectrometry (MS). (A) Direct coupling; (B) Post-column reaction between high-performance liquid chromatography (HPLC) and mass spectrometer; and, (C) Electrochemistry prior to HPLC-MS.

Special cases of EC-MS are the inherent EC in ESI and the electrochemical reactions that take place in transfer lines due to high voltage applied to the sprayer for ESI [12,13].

The present overview highlights some of the fundamental and practical issues that arise when the instrumentation for EC is combined with MS.

2. Electrochemical cell

A simple electrochemical cell can be equipped with two electrodes, where the cathode supplies electrons for reduction and the anode removes electrons for oxidation. Much better control of reactions is obtained in a three-electrode cell, which is commonly used in EC-MS combinations (Fig. 2A). Electrochemical reactions at the working electrode (W) are controlled by the potential difference between W and the reference electrode (R). The current flowing through W is balanced by an identical current at the auxiliary electrode.

There is a variety of electrode configurations and materials. W can be a flat surface, a wire mesh, or a frit made of metal, glassy carbon, porous carbon, boron-doped diamond (BDD), to name a few [3,4]. Shape and material of the auxiliary electrode A can also vary. Rs can make use of well-defined standard potentials, as in Ag/AgCl or calomel, or can simply be metal wire pseudo-Rs that may be preferred for practical reasons.

Cells for bulk electrolysis can be assembled from glassware and individual electrodes [4]. The construction of low-volume flow-through cells is more refined. Thin-layer cells with flat electrodes

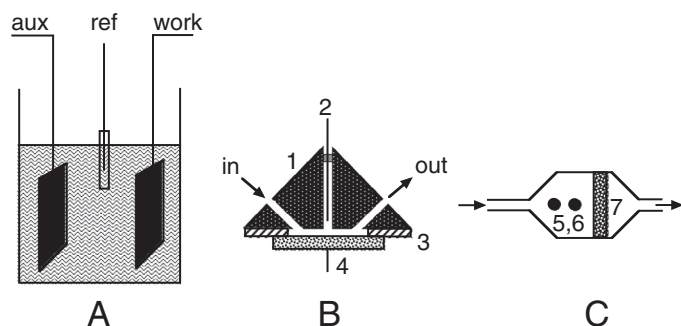


Fig. 2. (A) A general purpose electrochemical reactor; (B) Thin layer flow cell, 1: carbon loaded PTFE auxiliary electrode, 2: reference or pseudo-reference electrode, 3: spacer (e.g., 100- μm thick foil), 4: working electrode; and, (C) Coulometric flow cell, 5,6: Pd wire auxiliary and pseudo-reference electrodes; 7: porous carbon working electrode.

are popular because Ws can be removed, inspected and cleaned (Fig. 2B). Better conversion efficiency is possible at a larger W area and therefore porous flow-through electrodes are an attractive option (Fig. 2C). Such cells cannot be taken apart and W cannot be cleaned by polishing. Chemical cleaning is possible, but materials adsorbed to the inside of the frit may be difficult or impossible to remove.

Users who are not afraid of tampering with their mass spectrometer can consider placing an electrochemical cell inside the ion source if a short delay time between electrochemical reaction and MS detection is required [14,15]. Care should be taken to avoid exposure to high voltages, and it may be necessary to use an isolated, battery-powered potentiostat, or to use an isolation transformer between the mains and a potentiostat floating at high voltage.

For mass spectrometrists who want to start electrochemical experiments, there is a choice of manufacturers offering complete cells or components [16].

3. Potentiostats

Potentials delivered to the electrodes are generated by potentiostats that can be purchased off the shelf. Most potentiostats are computer controlled and can perform various electrochemical experiments. A simplified diagram is given in Fig. 3 [17]. Control voltage V_{in} for setting the cell potential is applied to amplifier A1. The current flowing through W is measured with amplifier A2 where $V_{out} = iR$. This cell current is in the low picoampere (pA) range in case of very sensitive electrochemical detection of low sample concentrations in LC. It is in the μA – mA range for electrochemical experiments on more concentrated samples in EC-MS, such as imitiation of drug metabolism, and it may be 1 mA up to several A in the case of larger batch cells for synthesis.

4. The auxiliary electrode

EC-MS experiments are aimed at identification of reaction products. Conditions for reactions at W are studied by varying electrode materials, cell potential, and composition of sample solution. Although most attention is paid to W, the charge-balancing reaction at the auxiliary electrode may affect the sample and complicate the interpretation of results obtained by the mass spectrometer.

Zettersten et al. observed reduction at the counter electrode of a product formed by oxidation at W. The reaction at the auxiliary electrode was prevented from taking place by a rearrangement of the position of the auxiliary electrode [18].

Nouri et al. observed direct electrochemical oxidation of lidocaine at the auxiliary electrode when they attempted to react the sample with electrogenerated reactive oxygen species (ROS) at W. This complication was overcome by the use of a two-compartment electrochemical cell [19].

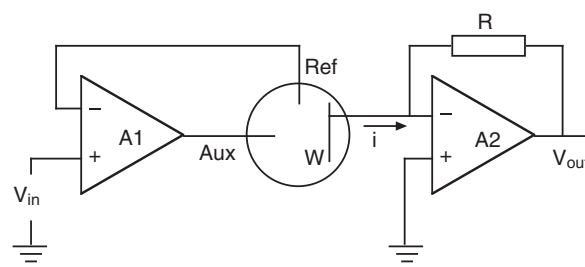


Fig. 3. A potentiostat.

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