

Electrochemical Sensor Research at the Laboratoire d'Electrochimie of the EPFL

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Abstract. This review presents some recent developments in the field of electroanalytical sensors. We first explain the working principle of electrochemistry at the interface between two immiscible electrolyte solutions (ITIES), illustrated by the example of copper transferring through a water/1,2-dichloroethane interface when the ionophore 1,4,7,10-tetrathiacyclododecane is present in the organic phase. The obtained results show that assisted ion-transfer reactions take place with both Cu^{I} and Cu^{II} , but that the interfacial process is complicated by the fact that Cu^{I} disproportionates in water and that Cu^{II} can be reduced in the organic phase.

Based on the same experimental methodology, a new type of amperometric detector for non-redox ions has been developed using a composite polymer membrane supporting a gellified organic phase that can incorporate an ionophore such as valinomycin. We report here the use of a (*o*-nitrophenyl octyl ether)-(poly(vinyl chloride) (NPOE-PVC) gel micro-interface as a detector for cations and anions in ion-exchange chromatography. The main advantage of this approach is that selectivity and sensitivity can be tailored by the choice of the ionophore and by the polarisation potential.

This ion detector has also been incorporated in a miniaturised total-analysis system (μ -TAS) fabricated in a polymer sheet by UV-laser photoablation. This microfabrication technique is used for the prototyping of a disposable capillary-electrophoresis microsystem comprising on-chip injector, separation column and electrochemical detector. This system is further used with built-in carbon-ink electrodes for the detection of electroactive species. These microsystems are now under development for immuno-sensor applications.

1. Introduction

Electrochemistry, which celebrates this year the bicentenary of *Volta's* pioneering work, plays an important role in separation methods such as electrophoresis or electro dialysis and can be used for the detection of analytes by potentiometry as, *e.g.*, in ion-selective electrodes and potentiometric titrations, by conductimetry and by amperometry, *e.g.*, polarography and enzyme electrodes. The main advantages of the electrochemical techniques are their sensitivity, their selectivity, their low cost, as well as the variety of configurations and materials that can be employed.

To complement the range of available electroanalytical methods, new types of electrochemical transducers have recently emerged, incorporating micro-electrodes or biphasic systems. In the challenging development of miniaturised total-analysis systems (μ -TAS), the electrochemical sensors are likely to have a bright future, because the sensitivity of detection is often a key issue when working with very small amounts of sample.

These systems, alternative to conventional electrochemistry, have been the object of recent studies at the Laboratoire d'Electrochimie of the EPFL, and the present article gives an overview of some advances achieved in analytical electrochemistry. We focus here on the methodology at liquid/liquid interfaces and on the incorporation of electrochemical sensors in μ -TAS in order to show the properties, the capacities, as well as the applications and the stakes of such techniques. Although this choice is not exhaustive, it will inform about some new trends in the development of electrochemical sensors.

2. Material and Method

2.1. Liquid/Liquid Interfaces

Cyclic-voltammetry studies of ion transfer across the Interface between Two Immiscible Electrolyte Solutions (ITIES) were carried out using a four-electrode configuration as shown in *Fig. 1*. The interface is polarised by means of two reference electrodes (RE), and the current

is collected *via* two platinum counter-electrodes (CE). The interface is positioned between two luggin capillaries in order to minimise the electrical resistance between the two reference electrodes (commonly called IR drop) [1]. By using an extra-thermodynamic assumption, it is possible to relate the applied potential difference E to the *Galvani* potential difference $\Delta\phi$ between the aqueous and the organic phase. The difference between ion-transfer voltammetry and classical redox voltammetry on a solid electrode is the relationship between the potential and

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the concentrations of the species involved in the electrochemical reaction. If, in the latter case, these quantities are linked by the well-known *Nernst* equation

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{ox}}{a_{red}} \right) \quad (1)$$

in the former, we have an analogous equation between the *Galvani* potential difference and the concentrations of the transferring ion in the adjacent phases

$$\Delta_o^w \phi = \Delta_o^w \phi_i^0 + \frac{RT}{zF} \ln \left(\frac{a_i^o}{a_i^w} \right) \quad (2)$$

where $\Delta_o^w \phi_i^0$ is the standard transfer-potential of the ion, defined as the standard *Gibbs* energy of transfer expressed in a voltage scale:

$$\Delta_o^w \phi_i^0 = \frac{\Delta G_{tr,i}^{o,w \rightarrow o}}{zF} = \frac{(\mu_i^{o,0} - \mu_i^{w,0})}{zF} \quad (3)$$

The reason why ion-transfer reactions can be studied by voltammetry comes from the fact that the reactions are mass-transfer limited, and that, consequently, all the electroanalytical methodology can be transposed directly.

The electrochemical extraction of copper ions, assisted by 1,4,7,10-tetrathia-cyclododecane (TTCD), was studied using *Cell 1* where the organic phase was 1,2-dichloroethane (1,2-DCE) and where the supporting electrolytes were LiCl and bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) for the aqueous and the organic phase, respectively.

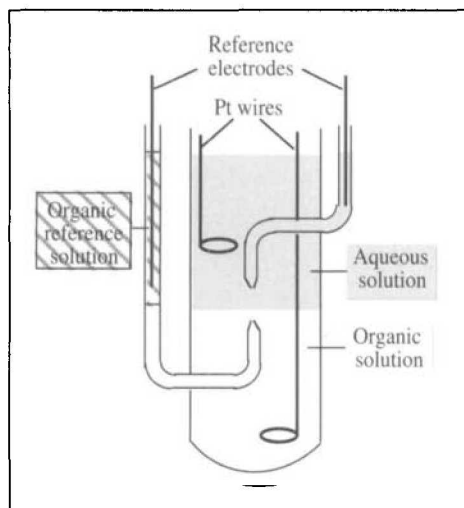
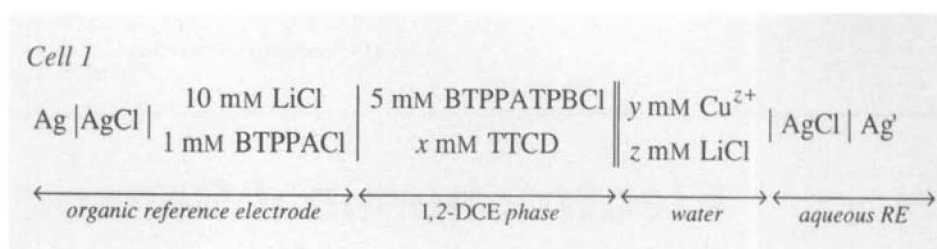


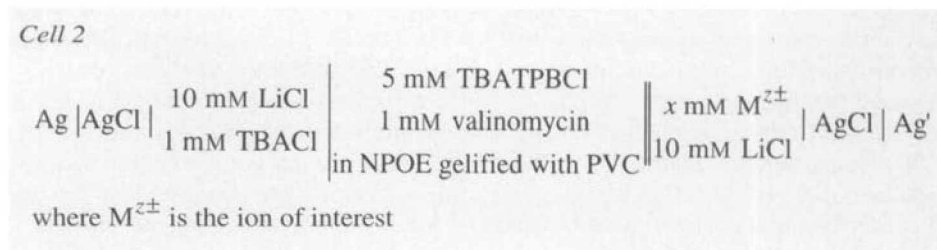
Fig. 1. Design of the electrochemical cell used for cyclic-voltammetry measurements at large ITIES



The internal cross-section of the interface was 1.13 cm², and the cell was kept at room temperature (23 ± 2°) and pH 6 for all experiments. All measured half-wave potentials were referred to the absolute *Galvani*-potential scale by adding an internal standard to the cell for each experiment (tetramethylammonium chloride (TMAcI), for which $\Delta_o^w \phi_{\text{TMA}}^0$ is equal to 160 mV [2]).

2.2. Liquid/Gel Microinterfaces

The polymer composite membranes were manufactured using an excimer laser in order to drill microholes of 10 μm diameter into a 23 μm thick polyethylene terephthalate (PET) membrane [3]. The organic-phase gel was prepared by dissolving 2.8% w/w poly(vinyl chloride) (PVC) in *o*-nitrophenyloctylether (NPOE) solution of 10 mM tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl), which was then cast onto the membrane (see [4][5] for further details). As shown in *Fig. 2*, the microfabricated membranes were tested in a flow-channel configuration to detect ammonium, sodium and potassium separately. Different concentrations of these ions were injected into a flow of 5 mM tartaric acid (pH 2.5) using an automated sampler (10 ml injection) (*Metrohm AG, CH*). Valinomycin was used to facilitate the transfer of these ions, and the electrochemical cell used can be described as follows (*Cell 2*):



Chrono-amperometry and pulse amperometry were performed using a computer-controlled potentiostat (*Sycopel Scientific Ltd., UK* and *Tacussel Pol 150 T, F*) from which the data were acquired using a *Windows*-based software. All the experiments were carried out at room temperature. This gel membrane detector was also incorporated in the miniaturised analytical devices described below.

2.3. Miniaturised Analytical Systems

The microfabrication of polymers such as PET was achieved by UV-laser photoablation [6] which is an alternative to the commonly used etching methods developed for silicon technology such as photolithography (see [7] for a review on the microfabrication processes). The dimensions of the produced micro-channels are: 1 to 20 cm long, 30 to 200 μm wide, and 15 to 60 μm deep. Reservoirs were opened by firing sufficient pulses to pierce the whole polymer sheet. The structures were then washed with water and ethanol, and sealed by lamination of a 35-μm thick polyethylene/polyethylene terephthalate (PE/PET) sheet.

Microfluidics is ensured either by capillary flow, syringe pumping, or by electroosmotic flow. As deduced from AFM, SEM and confocal *Raman* microscopy studies [6][8], photoablated polymer-microchannels are charged enough to allow the generation of an electroosmotic flow when exposed to high voltage (50 to 500 V/cm). A pH-dependence study of the electroosmotic-flow velocity showed that it correlates with the deprotonation of the aliphatic carboxylic-acid residues on the surface of the microchannels [6].

Carbon electrodes were incorporated as follows [9]: a microchannel is drilled, washed, filled with an excess of conductive carbon ink and cured at 70° for 2 h. Then, a thin layer of photoresist (1 mm) was spin-

coated and cured. As a last step, the main channel was laser-machined from the opposite side of the device in such a way that the bottom of the channel reached the carbon ink. The structure was finally sealed by lamination, through which an array of microholes was pierced at 1 mm before the electrodes in order to decouple the current from the mass flow. The resulting device is schematically shown in *Fig. 3*.

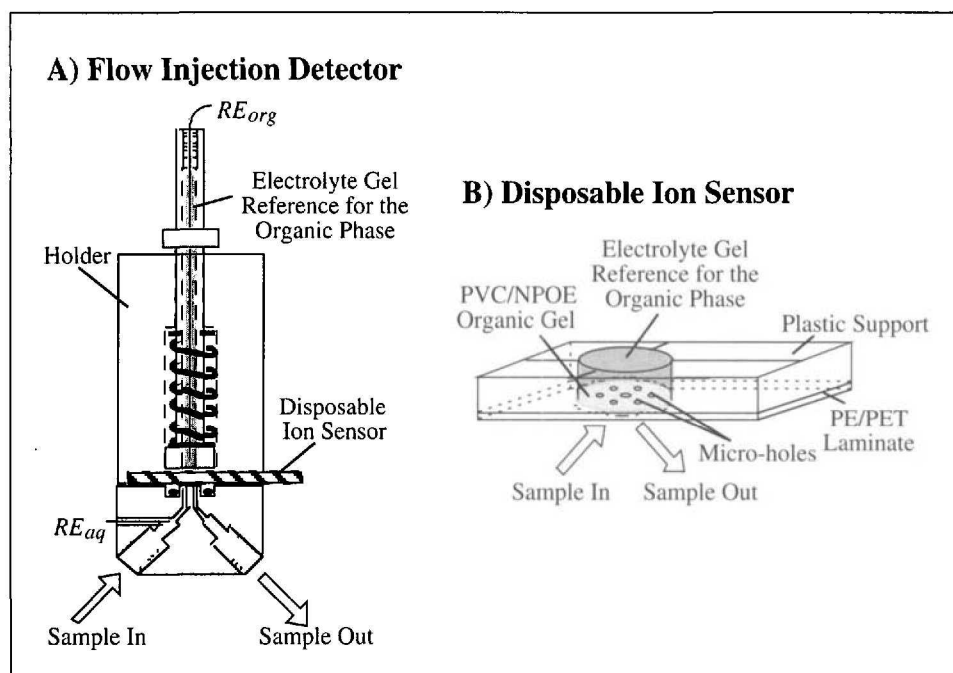


Fig. 2. A) Simplified diagram of the set-up for flow experiments. B) Scheme of the PVC-NPOE electrolytic gel supported in a microhole array.

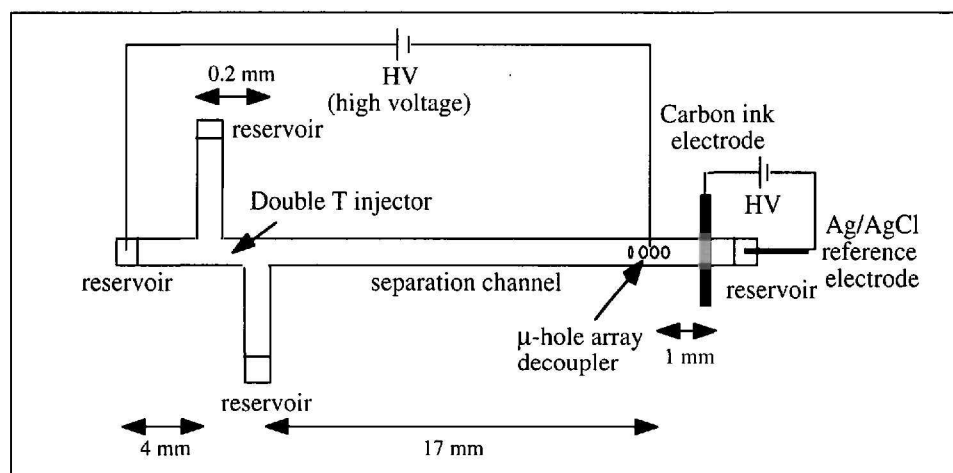


Fig. 3. Schematic drawing of a disposable photoablated polymer microchip comprising on-line injection, separation, and electrochemical detection

Amperometric detection was performed in three-electrode mode with a AEW2-Potentiostat (Sycopel Scientific, UK). Two carbon electrodes were incorporated within the microchannel and served as working and counter electrodes. An Ag/AgCl reference electrode was placed in the reservoir drop outside the channel.

3. Results and Discussion

3.1. Liquid/Liquid Interfaces as Ion Transducers

Since it has been demonstrated that the ITIES was polarisable in the same way as the metal/electrolyte-solution interface, the ITIES has become a topic of great interest due to its significance in solvent extraction and phase-transfer catalysis; understanding the ITIES is also important for

the analysis of the *in vivo* behaviour of lipophilic drugs, and for mimicking biological membranes [10–12]. Key points in this field are a better understanding of the mechanism of ion transfer through an interface, as well as the search for practical applications, essentially with an analytical scope.

3.1.1. Facilitated Ion-Transfer Reaction

As metal ions are strongly hydrated, their *Gibbs* energy of transfer is high. Consequently, they transfer at more positive potentials than ions, such as Li^+ commonly used as supporting electrolyte, limiting the potential window. Nevertheless, their transfer may become observable when they form a complex with an ionophore dissolved either in the organic or in the water phase [13]. Indeed, the *Gibbs* ener-

gy of the ion transfer is then lowered by the presence of the ligand, and the signal of the interfacial ion-crossing is visible within the available potential range.

This mechanism, called assisted ion-transfer, can occur through three different reaction pathways, namely [14]: Transfer by Interfacial Complexation/Decomplexation (TIC/TID), Transfer followed by Organic Complexation (TOC), and Aqueous Complexation followed by Transfer (ACT). If hydrophobic ligands are used, most of the transfer reactions follow the TIC/TID mechanism for which methodologies were developed to determine the ion-to-ligand stoichiometry (m) and the association constant of the complex formed in the organic phase [15–17]. In the case of a ligand excess, with respect to the metal concentration, the half-wave potential for the complex formation, $\Delta_o^w \phi_{1/2}(\text{ML}_m^{z+})$, depends on that for the simple transfer of the free metal ion, $\Delta_o^w \phi_{1/2}(\text{M}^{z+})$, on the bulk ligand concentration, c_L^o , and on the overall association constant of the complex, β_j^o :

$$\Delta_o^w \phi_{1/2}(\text{ML}_m^{z+}) = \Delta_o^w \phi_{1/2}(\text{M}^{z+}) - \frac{RT}{zF} \ln \left(1 + \sum_{j=1}^m \beta_j^o (c_L^o)^j \right) \quad (4)$$

with:

$$\beta_j^o = c_{\text{ML}_j^{z+}}^o / c_{\text{M}^{z+}}^o (c_L^o)^j \quad (5)$$

Assuming that β_m^o is larger than the association constant for each sub-stoichiometric species ($\beta_j^o < \beta_m^o$, $j < m$), Eqn. 4 simplifies to:

$$\Delta_o^w \phi_{1/2}(\text{ML}_m^{z+}) = \Delta_o^w \phi_{1/2}(\text{M}^{z+}) - \frac{RT}{zF} \ln \beta_m^o - \frac{mRT}{zF} \ln c_L^o \quad (6)$$

This relationship shows that the variation of the half-wave potential plotted as a function of $\log c_L^o$ gives the ion-to-ligand stoichiometry (m -value deduced from the slope) as well as the organic association constant (β_m^o deduced from the intercept).

3.1.2. Extraction of Metal Ions

As an example of metal extraction, we present here the transfer characteristics of copper at the polarised water/1,2-dichloroethane interface [18]. The ligand used to facilitate the ion crossing was 1,4,7,10-tetrathiacyclododecane (TTCD), which is a macrocyclic ring containing four sulfur atoms and which readily dissolves in the

apolar phase. The transfer mechanism was analysed by cyclic voltammetry using *Cell 1*.

Whatever the species initially present in the aqueous phase (*i.e.*, Cu^{2+} or Cu^+), the same voltammetric response was observed (a typical example is given in *Fig. 4*). The obtained potential window was limited by the transfer of chloride (on the left) and by that of Li^+ (on the right) from water to the oil phase. Furthermore, a reversible wave appeared on the left-hand side of the voltammogram and a non-reversible forward wave was visible at the right limit of the potential window. These two responses indicate that, regardless of the initial oxidation state of copper, both ionic species are present in the experimental conditions employed. When Cu^+ is preliminarily dissolved in the aqueous phase, both voltammetric waves are observed during the first cycle, suggesting that, first, Cu^{2+} ions are formed by disproportionation of Cu^+ in water, and then, that both Cu^+ and Cu^{2+} can transfer by formation of a complex with TTCD. In the case of Cu^{2+} , the voltammetric wave A is the only feature during the first forward cycle, while wave B appears during the reverse cycle. Then, the generation of Cu^+ (wave B) from Cu^{2+} ions seems to occur by homogeneous reduction of the Cu^{2+} complex by the anion TPBCl^- in the organic phase.

In order to confirm the homogeneous reduction of the $[\text{Cu}(\text{TTCD})_m]^{2+}$ complex in the organic phase by the supporting electrolyte anion, TPBCl^- was replaced

by a less reducing anion, namely tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($\text{TPB}(\text{CF}_3)_2$). The resulting voltammogram showed that the forward wave A became reversible and that no reversible wave B appeared near the left limit of the potential window. This behaviour proves that the non-reversible wave was effectively due to the assisted transfer of Cu^{2+} which was then reduced in the organic phase to form Cu^+ , transferring in turn assisted by TTCD.

The determination of the stoichiometry m and the overall association constant β_m^o of the $[\text{Cu}(\text{TTCD})_m]^+$ complex was achieved under the following conditions: Cu^+Cl^- concentration was 0.2 mM and the ligand was present in excess. Then, from *Eqn. 6*, the plot of $\Delta\phi_{1/2}^w(\text{ML}_m^z)$ vs. $\log c_L^o$ led to a 1:1 stoichiometry (in accordance with literature data [19–21]) and to a corresponding association constant of $\log \beta_1^o = 8.5$. These parameters could not be calculated for the $[\text{Cu}(\text{TTCD})_m]^{2+}$ complex because of the non-reversibility of the assisted transfer.

The above results show that cyclic voltammetry at the ITIES provides precious informations about the mechanism of ion transfer with complex formation, and demonstrate that such interfaces can be used as transducers for heavy-metal ions. This understanding of ion-transfer reactions across ITIES has opened out new routes where this interface can be used for analytical purposes, and an example of application is presented in the next section.

3.2. Micro-Composite Membranes for Amperometric Detectors

Because of the difficulty in the handling of liquids, which prevents the manufacturing of easy-to-use analytical devices, a lot of work has been devoted to the gelification of one of the phases (usually the organic phase) following the methodology used to produce polymer membranes in ion-selective electrodes [22–25]. Our group has recently developed a composite polymer membrane comprising a thin inert polymer layer which is micro-perforated and covered by a PVC-NPOE electrolyte gel [4][5][26][27]. These membranes afford the amperometric detection of ions by classical electrochemical methodology and have been named 'ionodes'.

3.2.1. On-Line Amperometric Detection for Monovalent Cations

As the half-wave potential of transfer depends on the affinity between the metal and the ionophore, it varies with the nature of the ligand. Similarly, when a series of ions have sufficiently different association constants with a given ligand, their transfer behaviour allows to identify them. This property has been used to develop a sensor able to discriminate ammonium against sodium and potassium.

As schematically illustrated in *Fig. 2*, the gel-membrane detector has been designed as a disposable device that can be easily incorporated into a flow cell. Such a detector has been employed in both conventional cation- and anion-exchange ion chromatography (IC), and miniaturised capillary electrophoresis (see *Section III.3.2*). For example, the detector comprising an ionophore such as valinomycin can improve the selectivity and replace the drawback of conductimetric detection in conventional IC. Indeed, the detection of ammonium ions is important in both medical and environmental fields; and the detection of ammonium in an excess of sodium has proved to be a difficult task in ion chromatography when using conductimetric detectors. In our case, the research was focused on the selective detection of ammonium in an excess of sodium.

Fig. 5a shows amperograms obtained for various concentrations of Na^+ , NH_4^+ and K^+ , in the presence of 10 mM valinomycin in the gel membrane [5]. The signals obtained from a conductimetric detection are shown in *Fig. 5b* over the same concentration range. It can be seen that the selectivity of the membrane is much larger for ammonium than for sodium. The reason is the different association constants of these ions with valinomycin, namely 12.0 for Na^+ , 14.6 for NH_4^+ and 16.0 for

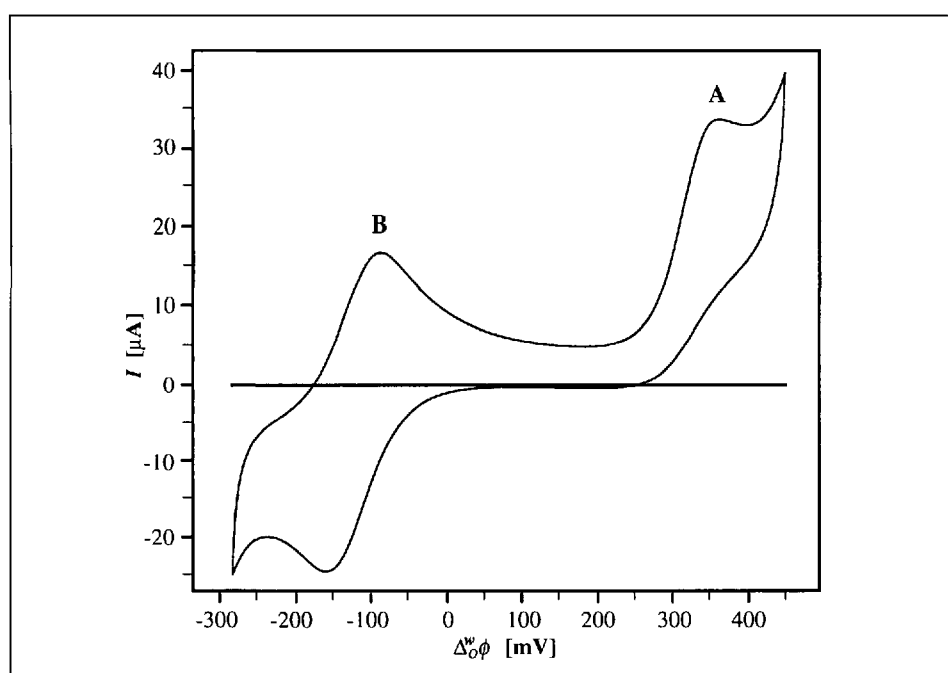


Fig. 4. Cyclic voltammogram obtained at a scan rate of 50 mV s^{-1} for the transfer of copper assisted by TTCD using *Cell 1* with $x = 8 \text{ mM}$, $y = 0.2 \text{ mM}$ and $z = 6 \text{ mM}$. The mark A shows the maximum forward-peak current corresponding to the $\text{Cu}^{2+}/\text{TTCD}$ complex, while peak B stands for the generation of Cu^+ .

K^+ [27]. Furthermore, low ppm levels of ammonium ion can be effectively detected in the presence of a 200-fold excess of Na^+ (see Fig. 5a A). Thus, the introduction of an ion-selective ionophore in the gel membrane increases substantially the selectivity of the detection. This methodology can of course be extended to detect other ions, provided appropriate ionophores are chosen.

3.2.2. On-Line Amperometric Detection for Anions

The micro-gel membrane has also been employed for the detection of anions, and Fig. 6 shows a typical pulse amperogram obtained with Cl^- , F^- , Br^- , NO_3^- and SO_4^{2-} . In this case, we cannot dope the membrane with ionophores, and we have to rely on the different Gibbs energies of transfer to differentiate the anions.

3.3. Microfluidic Devices for Biosensor Design

Often, reaction or separation time can be reduced by the miniaturisation of the device. A microfabrication facility has been developed with the photoablation of commercially available polymers [3]. The laser is used like a pen to 'draw' capillaries between 30 to 200 μm in width and 40 μm in depth. The channels are then closed with a low-temperature lamination process. This very flexible method allows the development of a complex network of microchannels that can be filled by capillary flow. It has been shown [6][8] that, depending on the laser-fabrication conditions, the surface can be either hydrophilic (then exhibiting a fast capillary flow) or hydrophobic (then exhibiting a very slow capillary flow).

3.3.1. Electrophoresis Micro-Devices with Integrated Carbon-Ink Detector

A special effort has been made for the integration of electrochemical detectors in the microchannels [9]. Different designs of carbon-paste electrodes have been developed for the applications listed below. The most interesting point of the electro-

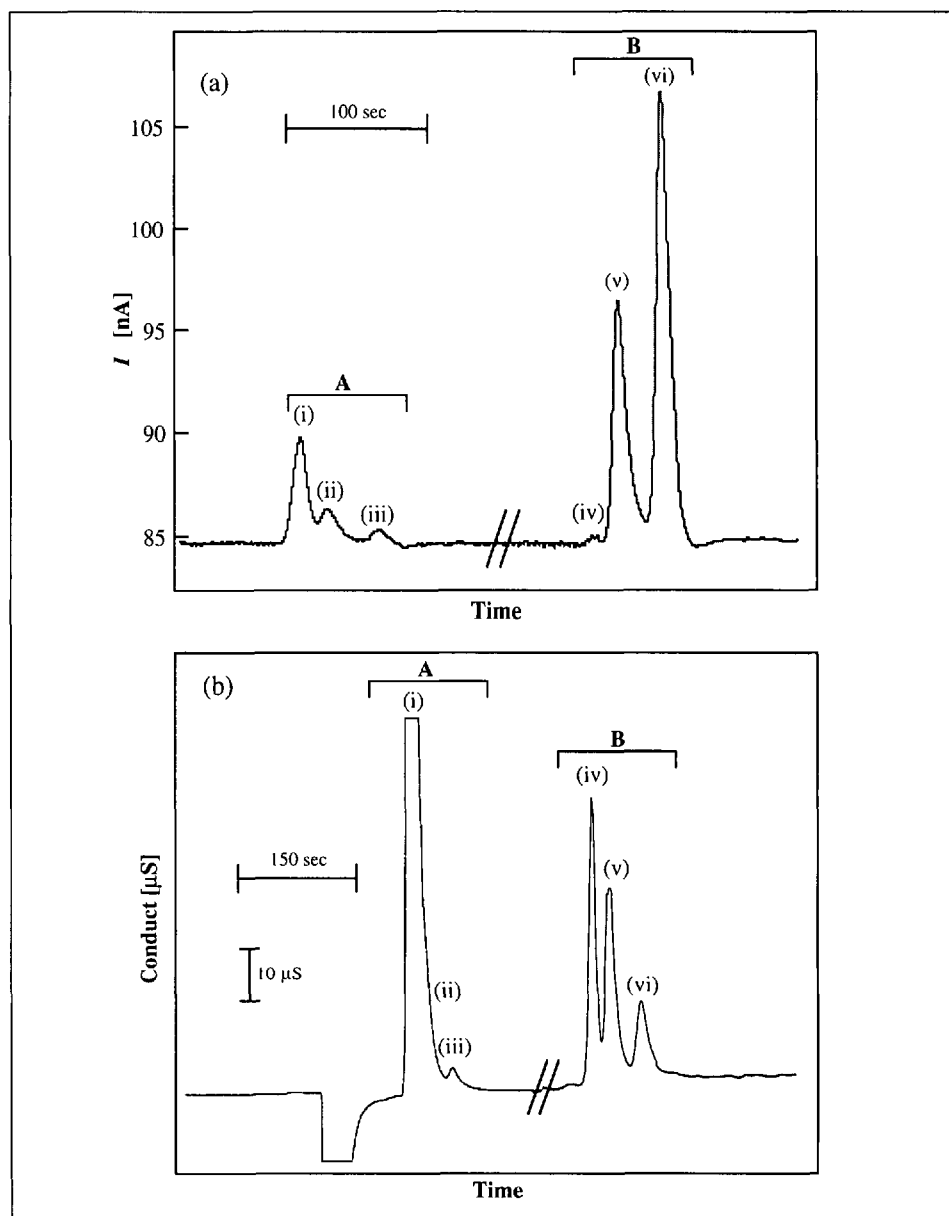
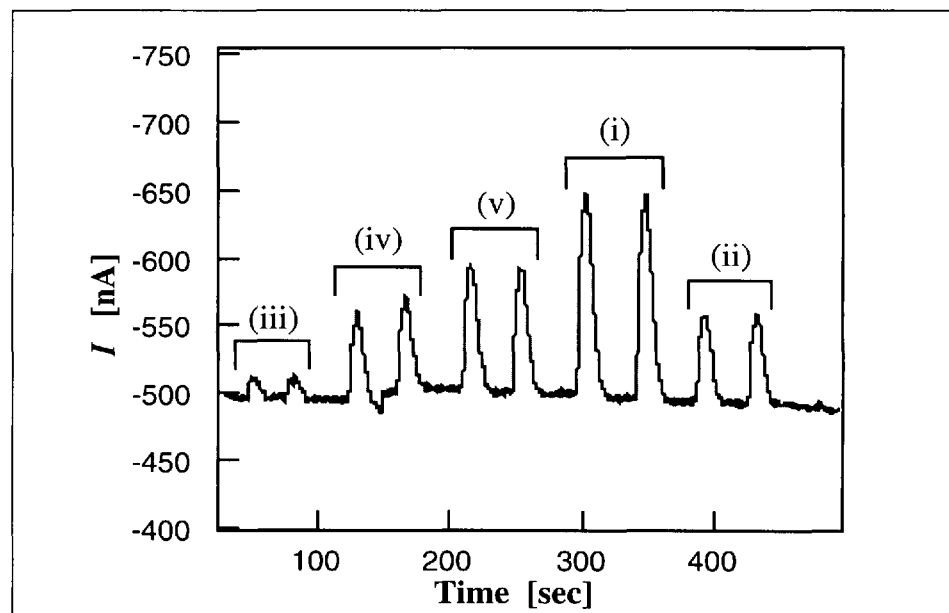


Fig. 5. (a) Pulse-amperograms recorded for monovalent cations facilitated by 10 mM valinomycin using the micro-gel membrane. (b) Chromatogram obtained for the monovalent cations based on a conductimetric detector. The concentrations of the standard solutions are A): i) 100 ppm Na^+ , ii) 0.5 ppm NH_4^+ and iii) 0.5 ppm K^+ , and B): iv) 5 ppm Na^+ , v) 5 ppm NH_4^+ and vi) 5 ppm K^+ . Flow rate is $0.85 \text{ ml}\cdot\text{min}^{-1}$ and 5 mM tartaric acid is used as an eluent.

Fig. 6. Pulse-amperograms recorded for the detection of anions without anion-exchange column and using the PVC-NPOE gel membrane. Initial and final pulse potentials are 200 mV and -400 mV, respectively, and the flow rate is $0.8 \text{ ml}\cdot\text{min}^{-1}$. The detected ions are: i) F^- , ii) Cl^- , iii) Br^- , iv) NO_3^- , and v) SO_4^{2-} . Each anion concentration is 100 ppm (mixture of 5 mM phthalic acid, 2% acetonitrile and sodium hydroxide (pH 4.5) is used as an eluent).



chemical detector is its flexibility that allows to address every single channel with a detector. Furthermore, the sensitivity of an electrochemical detector is weakly affected by the decrease of the volume, because it is an interfacial technique. The behaviour of the microelectrodes in these small volumes has been simulated using a commercial finite-element software, *Flux Expert*[®], which operates on Unix workstations [9].

A network of capillaries has then been fabricated to permit fast and repetitive electrophoresis on a microchip. This device is composed of a double-T injector (injection of 120 pl), a separation column of 1.9 cm, an electrical decoupler and an electrochemical detector (see Fig. 3). The importance of the decoupler is to allow the application of high voltage in the separation channel and electrochemical detection at the same time. This decoupler is the key feature of the device, because two electrical circuits placed at 1 mm from each other have to work independently. Its goal is to decouple the flux of mass towards the detector from the current that goes to the high-voltage cathode. Several separation, of electroactive molecules, e.g., polyphenols, have already been achieved with this device [9], and work is now in progress to improve the sensitivity of detection.

3.3.2. Composite Polymer-Membrane Detectors for Micro-Capillary Electrophoresis

On the other hand, an amperometric detector for non-redox ions, such as TMA⁺ or TEA⁺ has been integrated in the above-mentioned devices. The special purpose of this work was to use the electrochemical methodology of a polarised liquid/liquid interface. The current measured is proportional to the concentration of the transferring ions from the aqueous phase (in the capillary) to the organic phase (a thin PVC-NPOE-gel layer placed on an array of microholes at the end of the separation column). The fabrication method is the same as above (see [4]), apart from the micro-hole array on the channel that was filled with the organic polymer gel to form the liquid/liquid interfaces.

Preliminary experiments showed that it is possible to obtain an on-line column detection under high-voltage conditions. Concerning the coupling between capillary electrophoresis and electrochemical detection, improvements of the decoupling system are in progress to achieve a better sensitivity for these devices.

4. Conclusion

The presentation of the electrochemical methodology at the ITIES has shown that such interfaces can be used as ion transducers. This has been illustrated by the detection of copper ions that can transfer across the ITIES by formation of a complex with an ionophore dissolved in the organic phase. Similar assisted ion-transfer reactions have been performed with ammonium at a water/PVC-NPOE gel micro-interface, thereby allowing the development of new types of sensors that we called 'ionodes'.

Furthermore, μ -TAS have been manufactured by UV-laser photoablation, and electrochemical sensors have been integrated in these devices. Conductive carbon ink (working and counter electrodes) has been placed at the bottom of the microchannels, and the three-electrode mode has been shown to be very efficient for the minimisation of the IR drop. This configuration has also the advantage of being sensitive to the whole cross-section of the channel and should allow the total detection of a plug coming to the electrodes.

Also, the electrodes can be positioned very precisely which is of substantial importance for a sensitive and fast analysis. Moreover, a system has been found to decouple the mass and the current flow at the end of a separation column, which allowed us to develop a single-use capillary-electrophoresis system comprising an on-chip injector, a separation column, and an electrochemical detector. This decoupling system was further used to test a gelified liquid/liquid detector incorporated in a microcapillary-electrophoresis system. The preliminary results obtained with these sensors are very encouraging for the future development of precise and sensitive analytical systems.

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