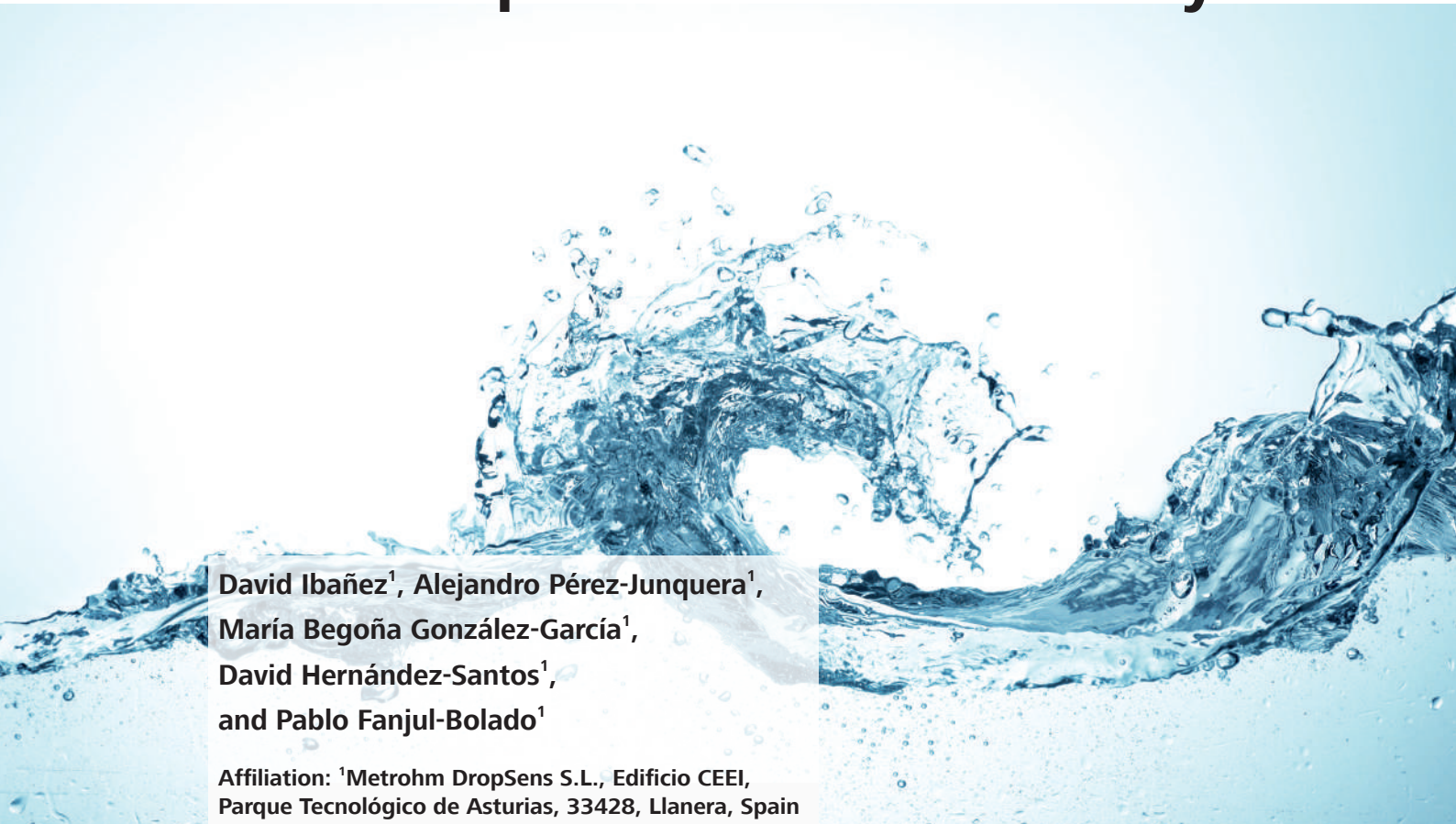


Overcoming the aqueous limitation for NIR Spectroelectrochemistry



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NIR spectroscopy has been traditionally limited due to the water absorption in this spectral range. In this way, the well-known water restriction has limited the development of new applications for NIR spectroelectrochemistry. In this work, several interesting alternatives are proposed in order to minimize or even to remove the aqueous contribution in this spectral range.

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Introduction

Over the last decades, near infrared (NIR) spectroscopy has received growing attention due to the industrial applications in which this technique is successfully employed. Traditionally, this spectroscopic technique has been limited due to the water absorption in this spectral range, and for this reason the combination of electrochemistry and NIR spectroscopy has been rarely used. However, a thin layer configuration for aqueous solutions minimizes water contribution in the NIR range and moreover, ionic liquids such as «green» solvents remove this contribution. These new procedures offer new possibilities for NIR spectroelectrochemistry applications [1].

In this work, the study of the redox behaviour of tetramethylbenzidine (TMB) by NIR spectroelectrochemistry has been performed following different procedures that allow the water absorption limitation to be overcome.

Instrumentation

The powerful and fully-integrated instrument for NIR Spectroelectrochemistry, SPELEC NIR, was used. This instrument combines the electrochemical equipment (bipotentiostat/galvanostat) and the spectroscopic equipment (light source and detector) in a unique box. SPELEC NIR is used in combination with a bifurcated reflection probe (DRP-RPROBE-VISNIR) (Figure 1).

This instrument is controlled by Dropview SPELEC, a dedicated software which allows performance of real-time spectroelectrochemical measurements and provides completely synchronized electrochemical and optical data.

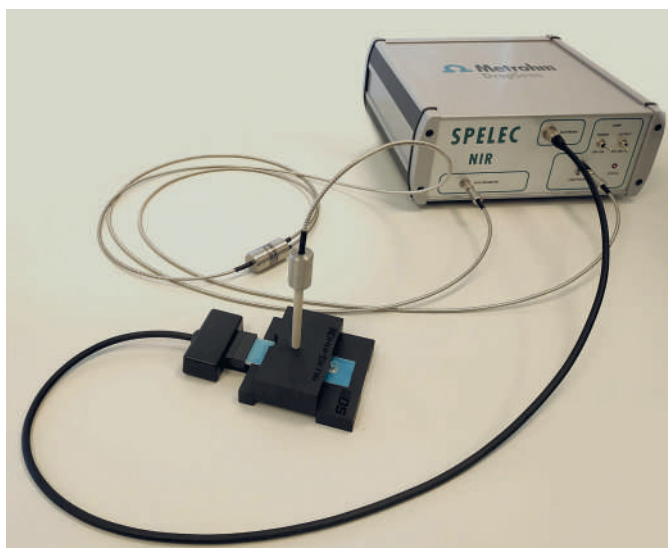


Figure 1. Setup for NIR spectroelectrochemistry

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Screen-Printed Electrodes, otherwise known as SPEs (DRP-110, DRP-220AT and DRP-TLFCL110-CIR) used in this work consist of a flat ceramic strip on which a three electrode system comprising the electrochemical cell is screen-printed. The carbon or gold working electrode is circular with a diameter of 4.0 mm, a silver electrode is used as a pseudo-reference electrode, and a carbon electrode acts as the counter electrode.

SPEs integrated in one channel flow-cell (DRP-TLFCL110-CIR, Figure 2a) have a transparent cover that defines a thin layer channel (100 μm) over the electrochemical cell. A holder (DRP-TLFCL-HOLDER) for a robust setup was used with DRP-TLFCL110-CIR electrodes (Figure 2b). DRP-110 electrodes were used in a near-normal reflection configuration in a reflection cell (DRP-REFLECELL).

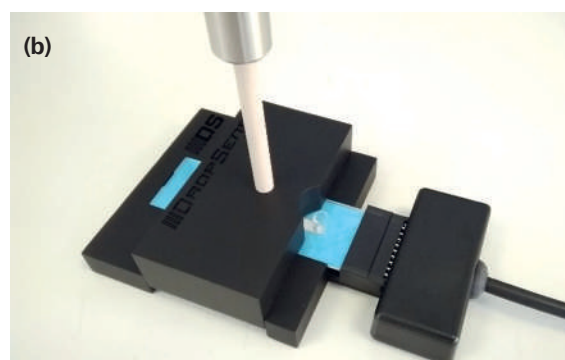
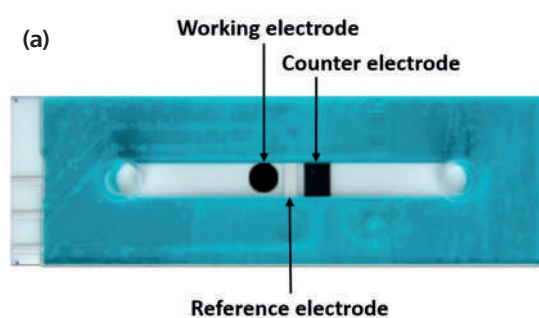
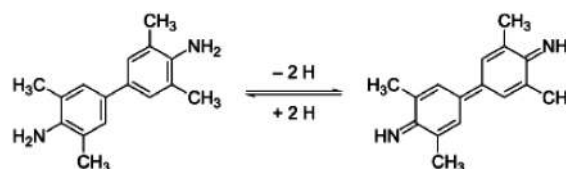


Figure 2. (a) DRP-TLFCL110-CIR. (b) DRP-TLFCL-HOLDER

Methods

Electrochemical oxidation of tetramethylbenzidine (TMB) was analyzed by linear sweep voltammetry with 10 mM TMB in HCl aqueous solution or in ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate). NIR spectra were simultaneously recorded alongside the electrochemical signal, obtaining information of the electrode surface during the whole experiment.



Reaction 1. Redox process of TMB

Results

In-situ dynamic NIR spectroelectrochemistry in aqueous solution

Oxidation of 5 mM TMB in 0.1 M HCl solution was carried out by scanning the potential from 0.00 V to +0.70 V (Figure 3a). As the spectra show (Figure 3b), NIR bands are not distinguished because the absorption of water is very high, and it

overlaps all other signals. Around 1450 nm, and from 1850 nm and beyond, only noise is observed due to water absorption obscuring the amount of light which arrives at the detector.

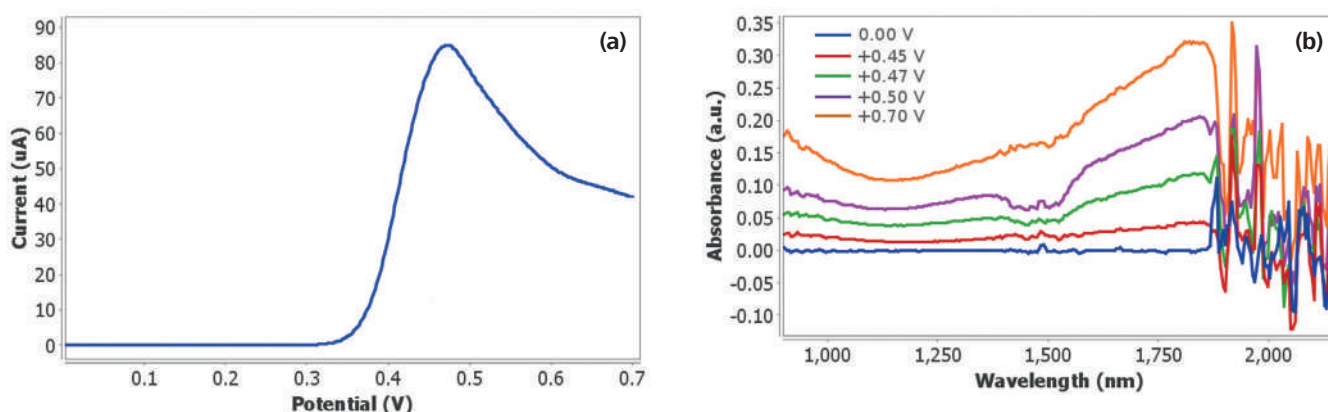


Figure 3. (a) Linear sweep voltammogram obtained by scanning the potential from 0.00 V to +0.70 V and (b) NIR spectra simultaneously obtained in 5 mM TMB in 0.1 M HCl aqueous solution using DRP-110 electrodes.

In-situ dynamic NIR spectroelectrochemistry in organic solution

Figure 4 displays the spectroelectrochemical information obtained when the electrochemical oxidation of TMB was performed in an organic solution. The electrochemical response (Figure 4a) displays the anodic peak associated with the oxida-

tion of TMB. On the other hand, the NIR spectra (Figure 4b) only show a part of a band which is centered at the visible range, at wavelengths below 900 nm.

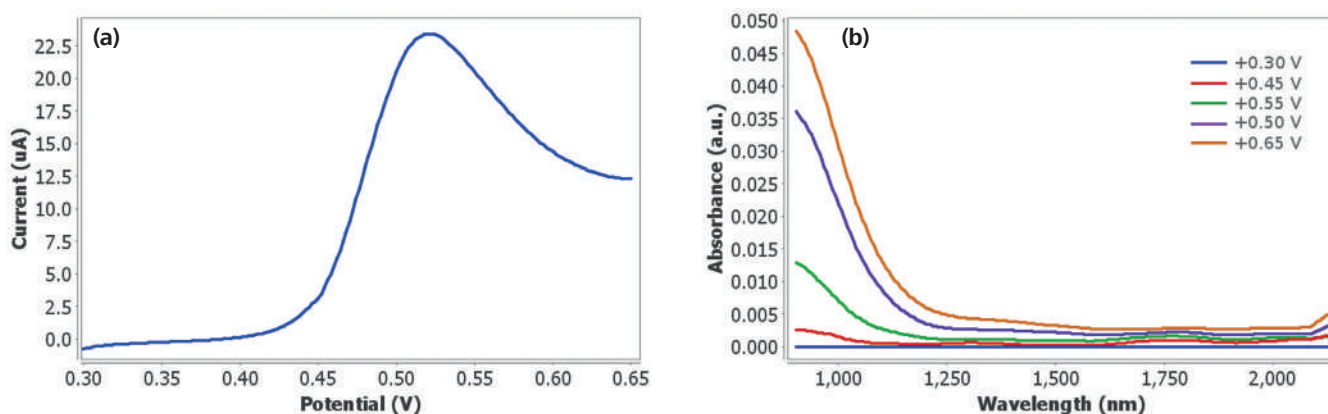


Figure 4. (a) Linear sweep voltammogram obtained by scanning the potential from +0.30 V to +0.65 V and (b) NIR spectra simultaneously obtained in 5 mM TMB in 0.1 M tetrabutylammonium in acetonitrile using DRP-220AT electrodes.

In-situ dynamic NIR spectroelectrochemistry in thin-film aqueous solutions

An interesting way to overcome the water limitation is by using the Metrohm Dropsens SPE integrated in a single channel flow-cell (DRP-TLFCL110-CIR) (Figure 2a). These electrodes display one thin channel that allows only minimal absorption of water. Figure 5 shows the results obtained with TMB in an aqueous solution using DRP-TLFCL110-CIR electrodes.

As shown in Figure 5b, the band at 1330 nm shows an increase in absorbance with the oxidation of TMB. Furthermore, NIR spectra are slightly limited at 1450 nm and even more so at 1950 nm, the wavelengths at which water shows the highest absorption.

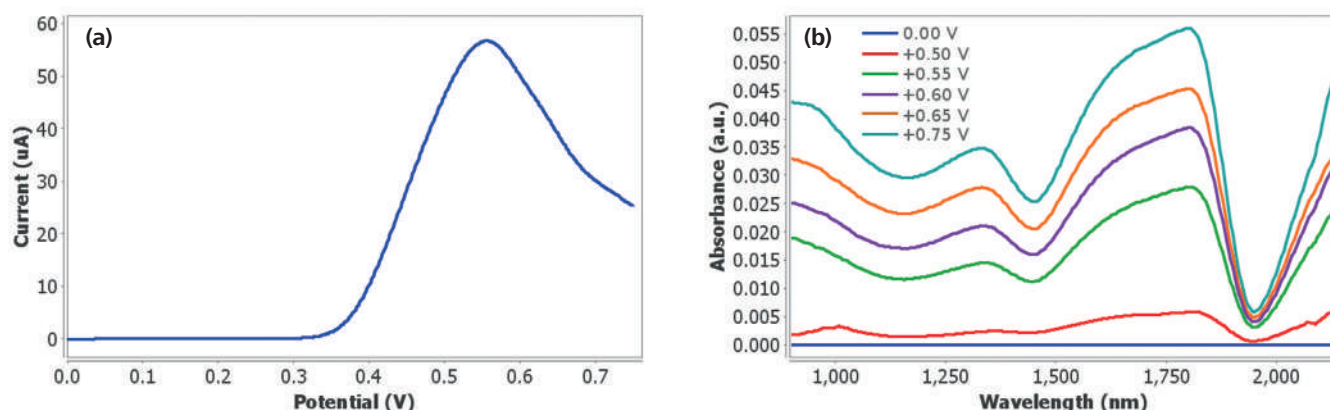


Figure 5. (a) Linear sweep voltammogram obtained by scanning the potential from 0.00 V to +0.75 V and (b) NIR spectra simultaneously obtained in 5 mM TMB in 0.1 M HCl aqueous solution in thin layer configuration (TLFCL110-CIR electrodes).

In-situ dynamic NIR spectroelectrochemistry in ionic liquids

One of the most useful procedures consists of studying the electrochemical oxidation of TMB in ionic liquid solutions. Ionic liquids are environmentally friendly solvents and show excellent properties such as a wide potential window, good conductivity, and high thermal stability [2–4]. Figure 6 demonstrates the good electrochemical response as well as the

improved NIR signal. In this case, NIR spectra are not limited by water and the complete NIR range is obtained. Figure 6b shows how the NIR band at 1300 nm increases as TMB is oxidized.

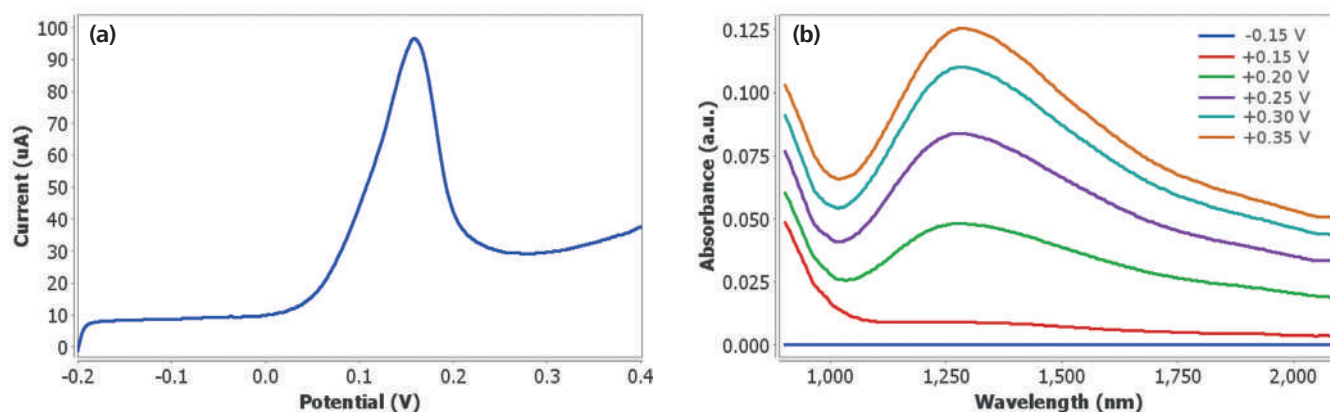


Figure 6. (a) Linear sweep voltammogram obtained by scanning the potential from -0.20 V to +0.40 V and (b) NIR spectra simultaneously obtained in 10 mM TMB in 1-butyl-3-methylimidazolium tetrafluoroborate using DRP-110 electrodes.

Conclusions

- A compact instrument for real-time NIR spectroelectrochemistry with simultaneous electrochemical and optical measurements has been developed.
- NIR spectroelectrochemistry provides information of a different nature (electrochemical and spectroscopic) about the various processes that take place on the electrode surface, allowing a better understanding of the analyzed system.
- Screen-Printed Electrodes integrated in a single channel flow-cell minimize the water contribution and NIR spectra are only slightly limited at the wavelengths of 1450 nm and 1950 nm.
- A dedicated cell for thin layer electrodes provides reproducible experiments with low-cost disposable electrodes.
- Ionic liquids are an interesting alternative to aqueous solutions; they avoid the challenge of water absorbance and provide NIR spectra without limitations.

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