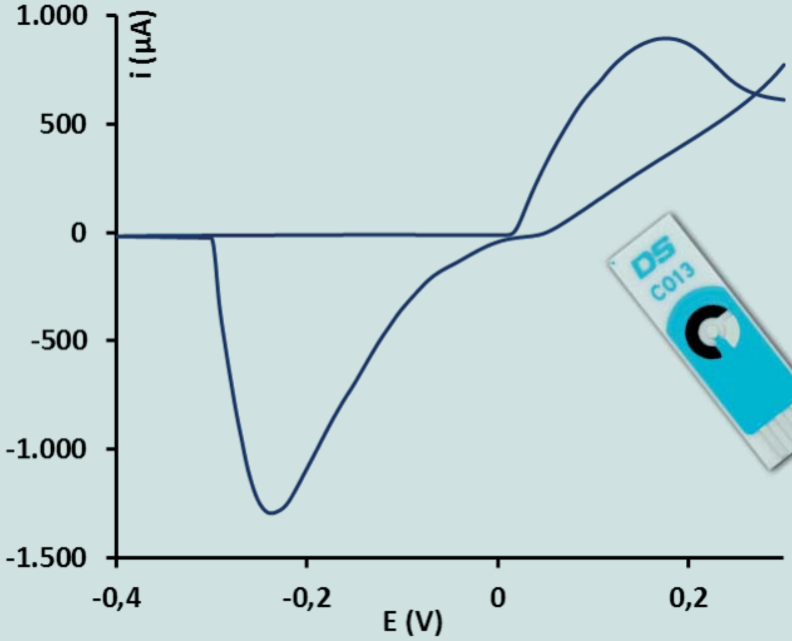
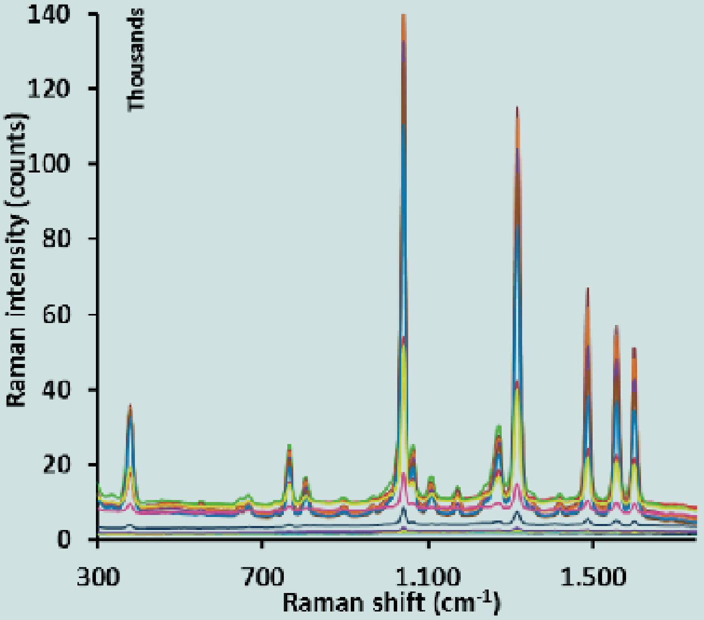
Metrohm White Paper

In situ SERS effect with screen-printed silver electrodes





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In this work, time resolved Raman spectroelectrochemistry measurements with screen printed electrodes are shown. The instrument used combines in a totally integrated box: a 785 nm laser source, a high resolution Raman spectrometer and a bipotentiostat/galvanostat. Experiments are controlled with an excellent spectroelectrochemical software which allows real time data collection and useful data treatment.

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Introduction

SPELEC RAMAN was coupled with a reflection Raman probe and a specific cell for **screen-printed electrodes**. An **in situ** surface-enhanced Raman spectroscopy (SERS) assay was carried out using screen-printed silver electrodes. The Tris(2-2'-bipyrdyl)dichlororuthenium(II) complex shows an intensive SERS effect after activation of the electrode surface by cyclic voltammetry. In situ dynamic SERS effect could be followed in real time by the SPELEC RAMAN instrument obtaining information on the electrode processes leading to high SERS signals. The sensitive detection of the ruthenium complex could be achieved in a simple and precise way using Raman spectroelectrochemistry, SPELEC RAMAN and cost-effective screen-printed silver electrodes.

Spelec Raman experimental setup. Compact Raman Spectroelectrochemistry

Consisting of Raman Spectrometer, 785 nm laser source, Bi-potentiostat/Galvanostat, Excellent spectroelectrochemical software, compact 25x24x11 cm box and portable weight about 2000 g.

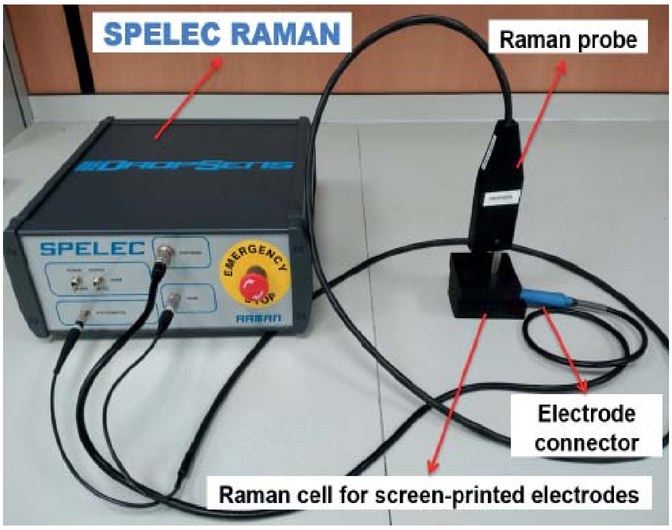

Figure 1. Fully integrated instrument for Raman spectroelectrochemistry

The Raman cell for SPEs (Figure 2) is built with black teflon material, with an innovative (magnets based) and easy to use open-close system. Focal distance has been optimised and the Raman probe is placed just on top of the working electrode surface.

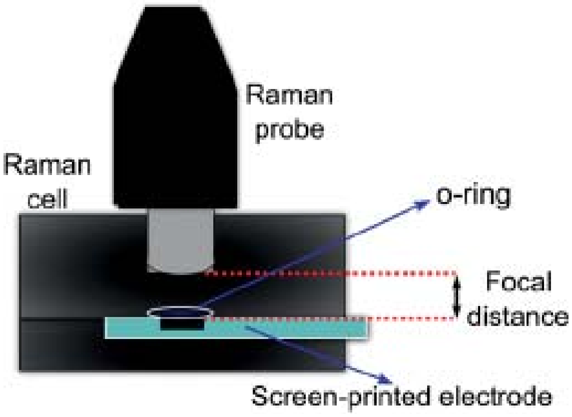

Figure 2. Raman cell for screen-printed electrodes

SPEs (ref. DRP-C013, Figure 3) used in this work consist of a flat ceramic strip on which a three electrode system comprising the electrochemical cell is screen-printed. The working silver electrode is circular with a diameter of 1.6 mm, and the device has also an auxiliary electrode made of carbon and a silver electrode which acts as a solid pseduoreference. All measurements were carried out at room temperature and using a solution of 60 µl.

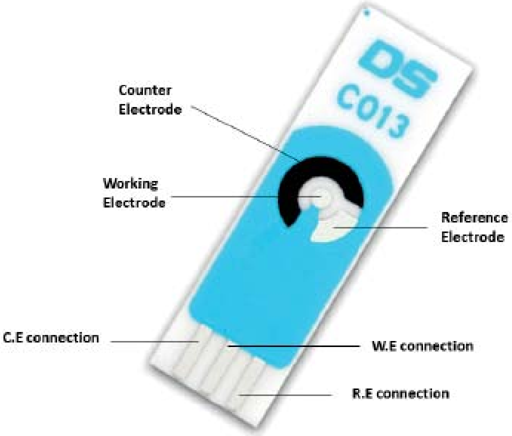

Figure 3. Silver screen-printed electrode

In situ dynamic SERS effect with screen-printed electrodes

In situ electrochemical activation of silver electrode surface for dynamic SERS effect was carried out in 0.1M KCl electrolyte solution by applying cyclic voltammetry between +0.3V and -0.4V at 0.05V/s in presence of the analyte molecule represented in Figure 4.

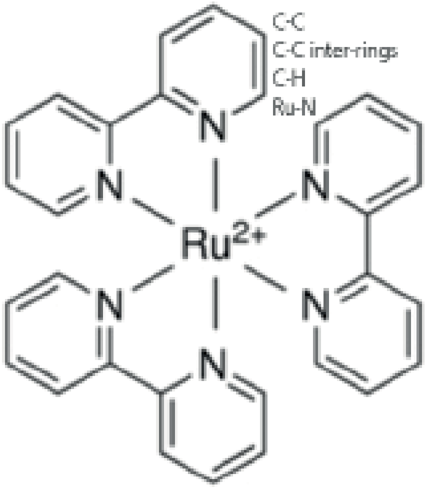

Figure 4. Molecular structure of Tris(2,2'-bipyridyl) dichlororuthenium(II)$[Ru(bpy)_3]^{2+}$

At initial potential the silver working electrode is oxidised to silver cation that in presence of chloride anions is deposited as AgCl. During the cathodic sweep it is reduced again to metallic silver obtaining a fresh nanostructured surface responsible of the SERS effect.

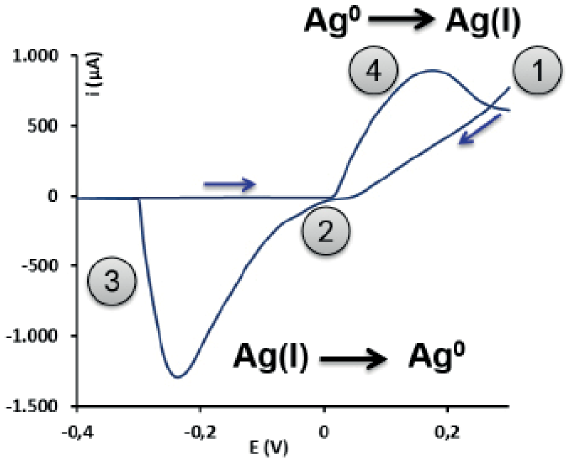

Figure 5. Cyclic voltammetry (CV) from +0.3 V to -0.4 V, 50 mV/s 40 µL of 2.5 µM $[Ru(bpy)_3]^{2+}$ in 0.1 M KCl

In the potential resolved spectra (Figure 6), it is demonstrated that there is no Raman signal at the beginning of the assay (1) for a concentration of Ru(bpy) $1 \cdot 10^{-6}$ M. During the cathodic sweep the Raman spectra can be obtained due to the SERS effect produced by the 'in situ' activated silver working electrode surface, with a maximum enhancement at a potential around -0.3V (3). In the backward scan the Raman signal decreases since the the silver electrodic surface is oxidised again.

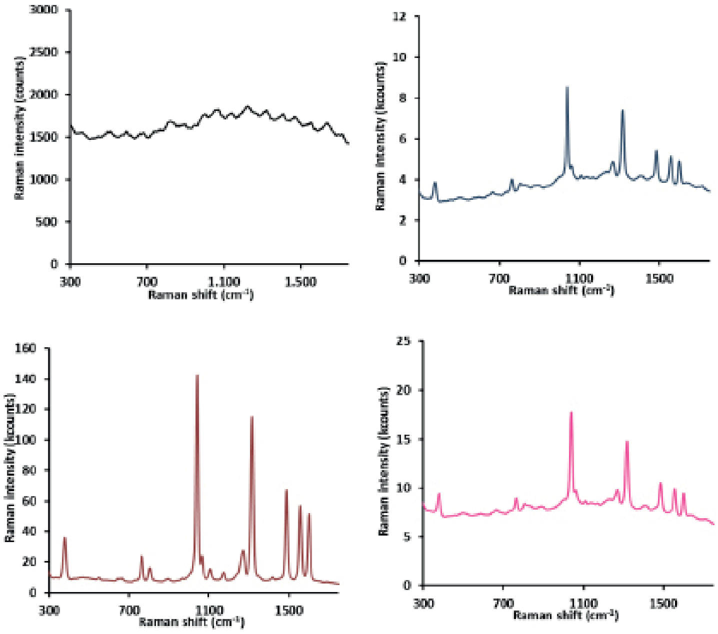

Figure 6. Potential-resolved spectra

Dynamic SERS effect followed by Spelec Raman

Therefore, it is demonstarted that the Raman espectra of ruthenium complex varied dynamically with the potentials applied during the voltammetry performed for the surface activation as illustrated previously. In the Figure 7 we can see in red colour the variation of the intensity on the Raman band at 1040 cm^{-1} with the potential with an integration time as low as 250 ms and using $5 \cdot 10^{-7}$M of ruthenium complex in the electrolyte solution.

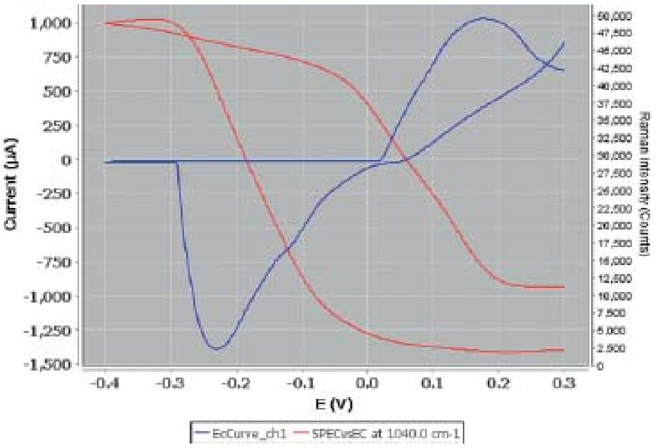

Figure 7. Dynamic correlation of Raman intensity at 1040 cm^{-1} with the electrochemical activation (red colour curve). Cyclic voltammogram (blue color).

$[Ru(bpy)^3]^{2+}$: 0.05 – 5 µM CV in 0.1 M KCl

The methodology can be used for quantitative analysis by recording the band intensity at 1040 cm^{-1} of the most intense spectrum at different concentrations of the analyte. A calibration plot is obtained with a linear range between $5 \cdot 10^{-8}$ and $5 \cdot 10^{-6}$M.

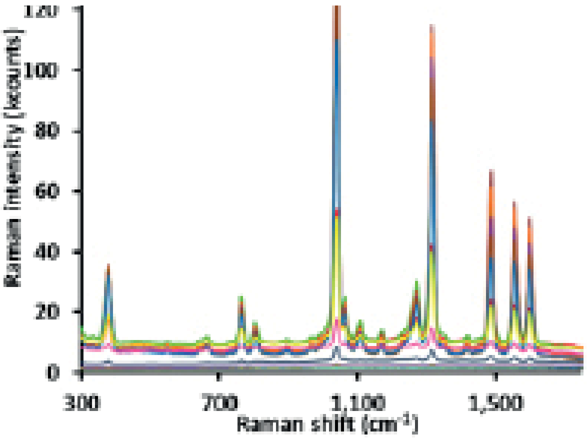

Figure 8. EC-SERS spectra corresponding to the calibration curve concentrations of the ruthenium complex

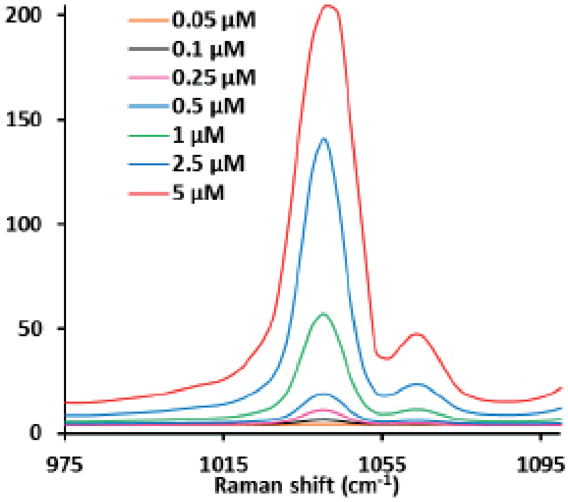

Figure 9. Peak intensity of band at 1040 cm^{-1} used for calibration purposes

Conclusions

- A compact instrument for real time Raman spectroelectrochemistry with simultaneous optical and electrochemical measurements has been developed.
- A specific cell for screen-printed electrodes provides straightforward and reproducible experiments with low-cost disposable electrodes.
- Silver screen-printed electrodes showed a great enhancement of Raman signals by in situ electrochemical SERS effect.
- In situ EC-SERS allows the high sensitive quantitative detection of $[Ru(bpy)_3]^{2+}$ with screen-printed electrodes.
- Metal screen-printed electrodes are promising, cost-effective SERS substrates.

References

[1] M.Fleischmann, P.J.hendra, A.J.McQuillan, Raman spectra of pyridine adsorbed at a silver electrode, Chem.Phys.Lett. 26 (1974) 163-166.

[2] B.Sharma, R.R,Frontiera, A.Henry, E.Ringe, R.P.Van Duyne, SERS:Materials, applications, and the future, Mater. Today 15 (2012) 16-25.

[3]L.Dunsch, Recent Advances in in situ multi-spectroelectrochemistry, J.Solid State Electrochem. 15 (2011) 1631-1646.

[4] C.Zong, C.J.Chen, M.Zhang, D.Y.Wu, B.Ren, Transient Electrochemical Surface Enhanced Raman Spectroscopy: a Millisecond time resolved study of an electrochemical redox process, JACS, 137 (2015) 11768-11774.

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