Application Note AN-RA-006

有机溶中取SERS效的新策略

Enhancement of SERS features by electrochemical activation in nonaqueous media

The combination of electrochemistry (EC) and surface-enhanced Raman scattering (SERS) has received growing attention over the past several years due to the powerful features associated with the EC-SERS effect [1,2]. In particular, the electrochemical activation of metal electrodes allows the generation of SERS substrates which in turn enhance the Raman intensity in a single experiment.

Many electrochemical methods have been developed but are traditionally limited to aqueous media. Raman spectroelectrochemistry in organic solutions is an interesting alternative, but developing new EC-SERS procedures is still required.

This Application Note demonstrates that the electrochemical activation of gold and silver electrodes enables the detection of dyes and pesticides in organic media.

INSTRUMENTATION AND SOFTWARE

Measurements were performed using a SPELEC RAMAN instrument (785 nm laser), a Raman probe corresponding to the laser wavelength, and a Raman spectroelectrochemical cell for conventional electrodes (**Figure 1**).

Gold and silver working electrodes were used in combination with steel and Ag/AgCl counter and reference electrodes, respectively. The SPELEC RAMAN instrument was controlled with DropView SPELEC, a dedicated spectroelectrochemistry software that simultaneously acquires electrochemical and optical information. All hardware and software used for this study is compiled in **Table 1**.

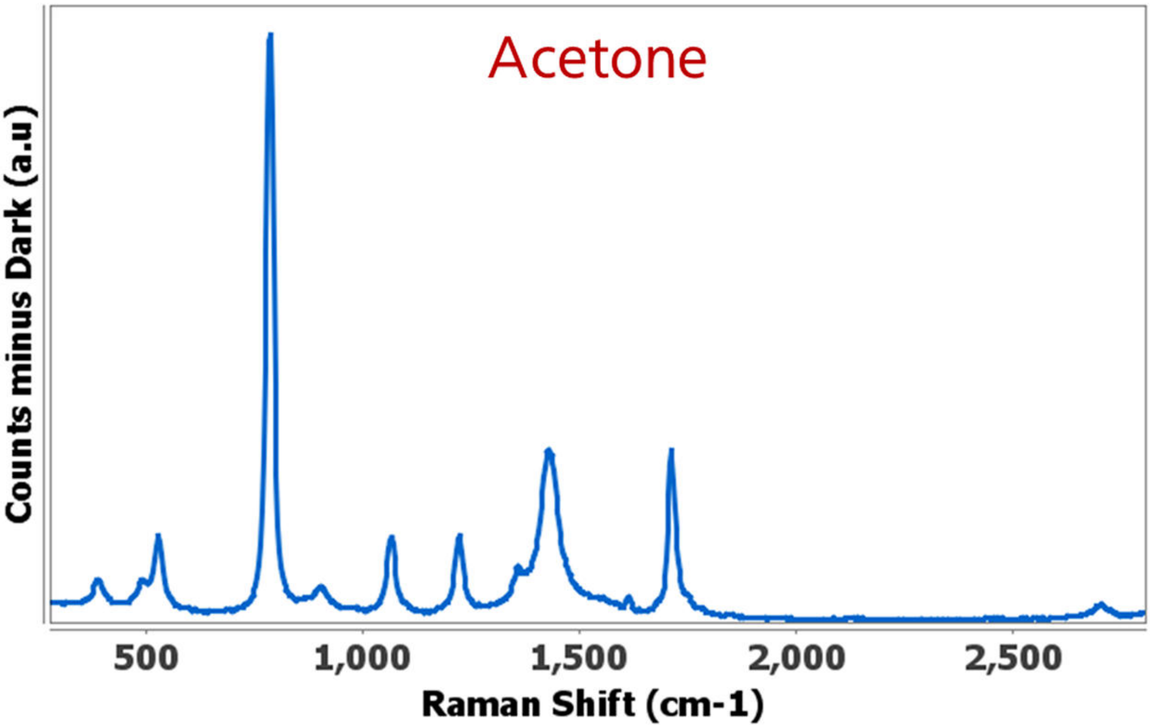
Figure 1. SPELEC RAMAN instrument and Raman probe used in combination with a Raman spectroelectrochemical cell for conventional electrodes.

Table 1. Hardware and software equipment overview

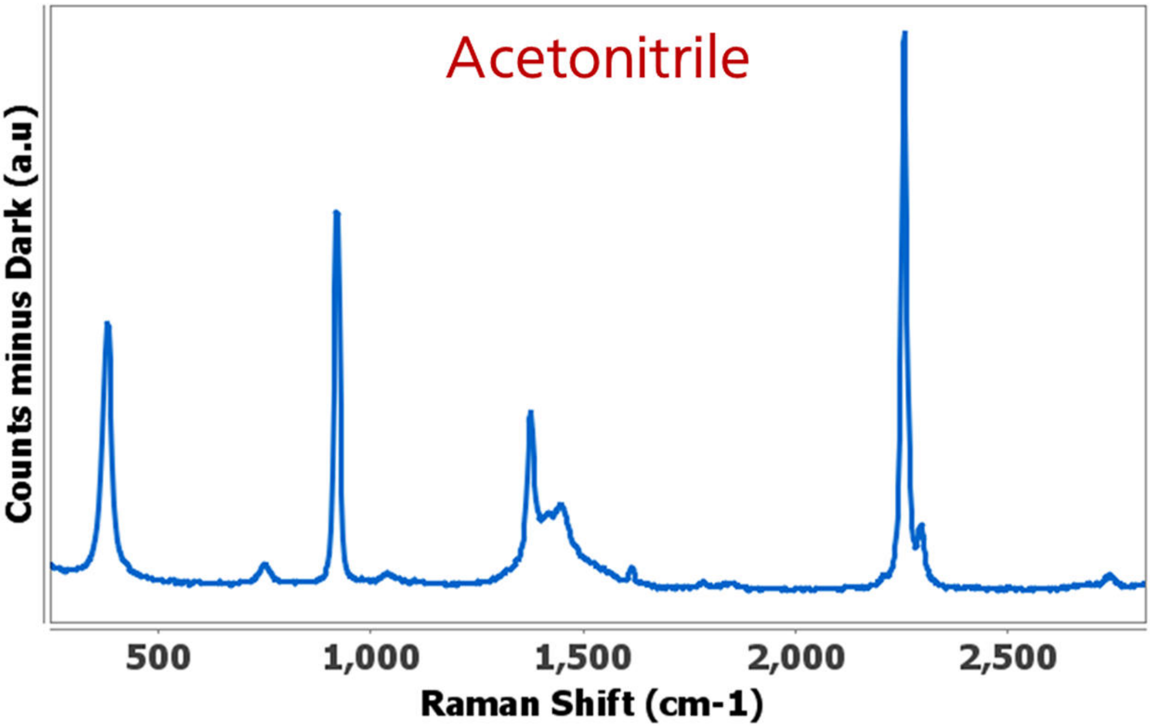
Equipment	Metrohm number
SPELEC RAMAN Instrument	SPELECRAMAN
Raman Probe	RAMANPROBE
Raman spectroelectrochemical cell for conventional electrodes	RAMANCELL-C
Gold electrode tip	6.09395.034
Silver electrode tip	6.09395.044
Separate steel electrode	6.0343.110
Ag/AgCl reference electrode	6.0728.120
DropView SPELEC Software	DropView SPELEC

APPLICATION: SERS EFFECT IN ORGANIC MEDIA

Organic solvents typically exhibit many Raman bands that could impair the analysis of the characteristic bands of the molecule of interest. **Figure 2** shows the Raman spectra from 12 different organic solvents. Medium selection is an important condition that must be considered for each application.


Acetone
Counts minus Dark (a.u)
500
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

a)


Acetonitrile
Counts minus Dark (a.u)
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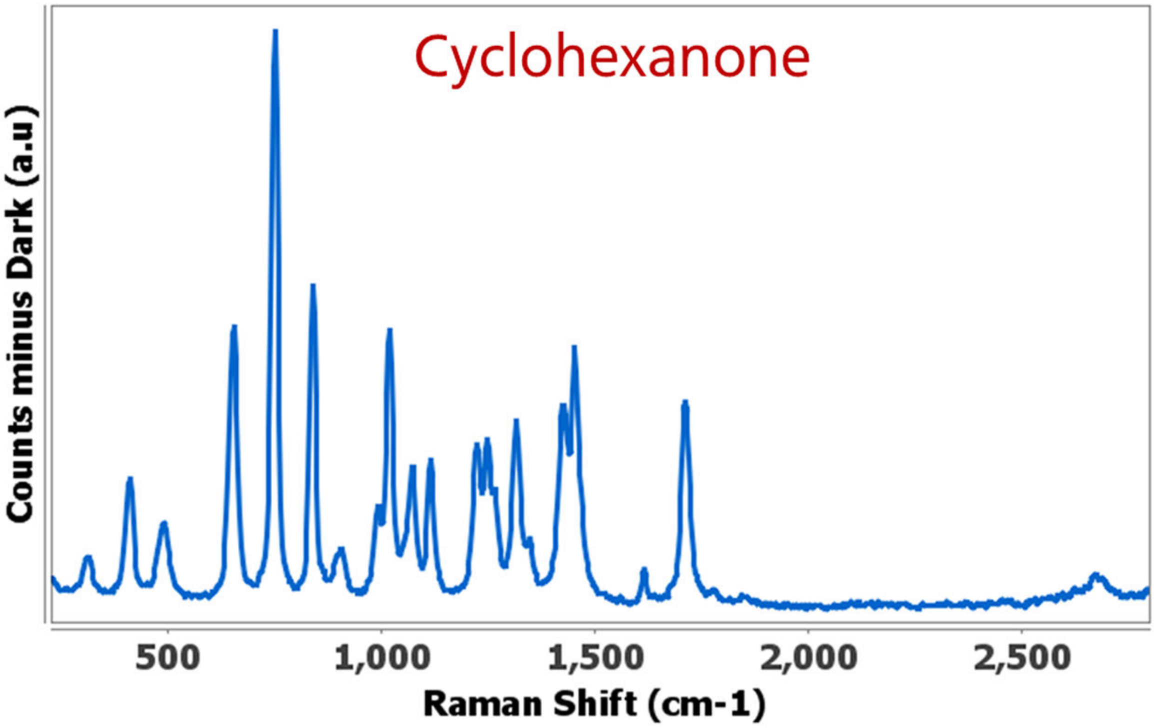
Raman Shift (cm-1)

b)


Cyclohexanone
Counts minus Dark (a.u)
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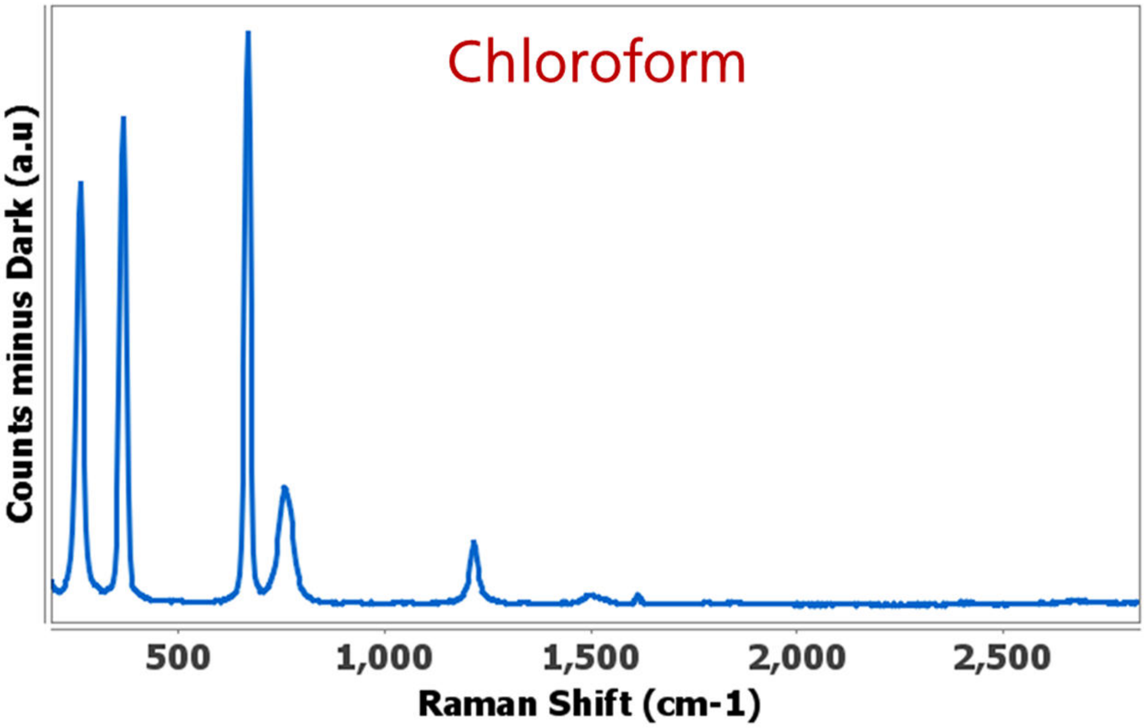
2,000
2,500
Raman Shift (cm-1)

c)


Chloroform
Counts minus Dark (a.u)
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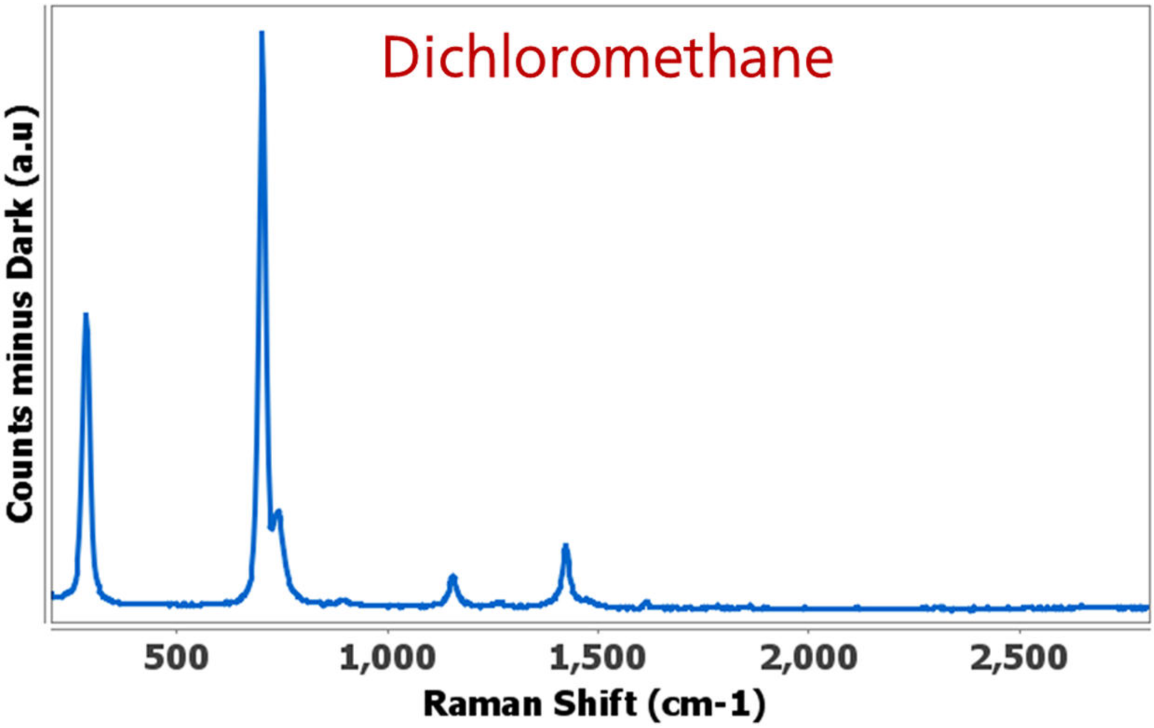
1,500
2,000
2,500
Raman Shift (cm-1)

d)


Dichloromethane
Counts minus Dark (a.u)
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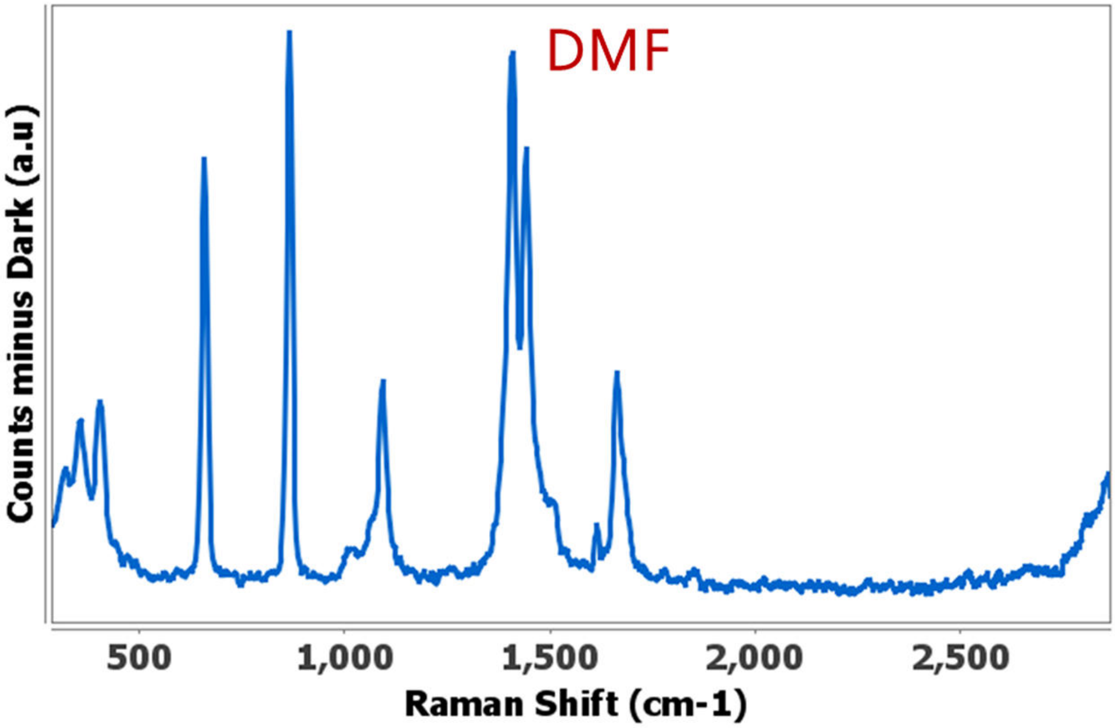
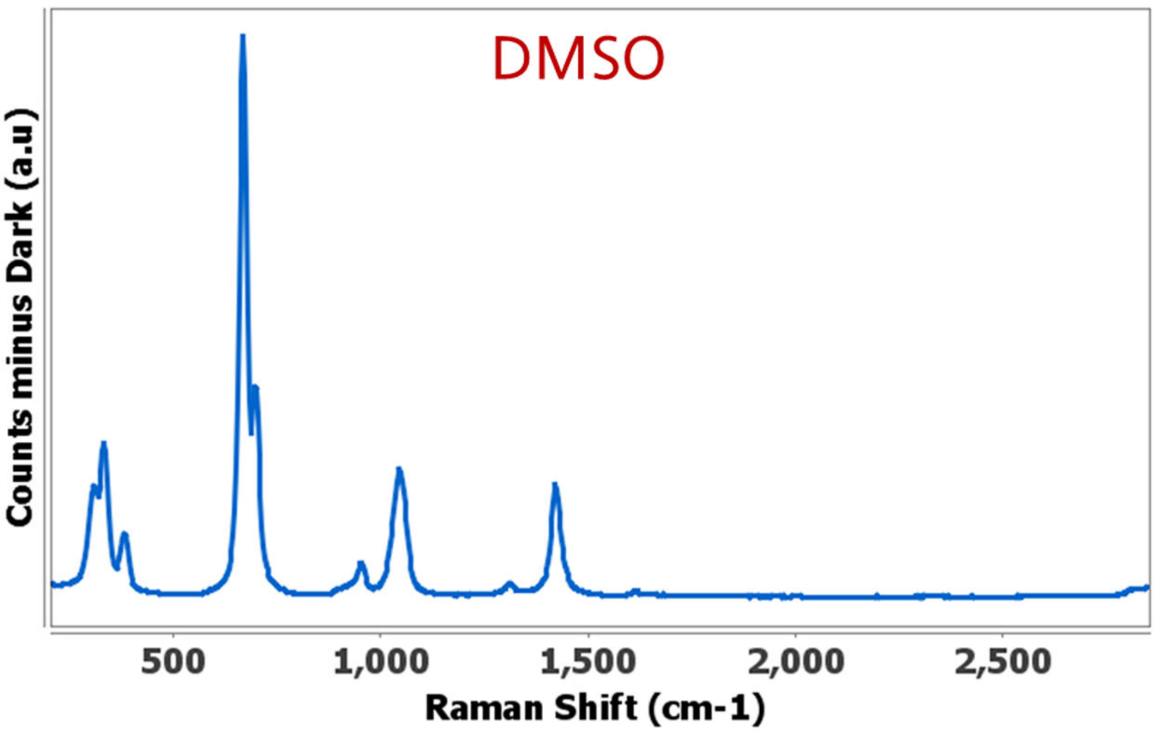
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

e)


DMF
Counts minus Dark (a.u)
500
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

f)


DMSO
Counts minus Dark (a.u)
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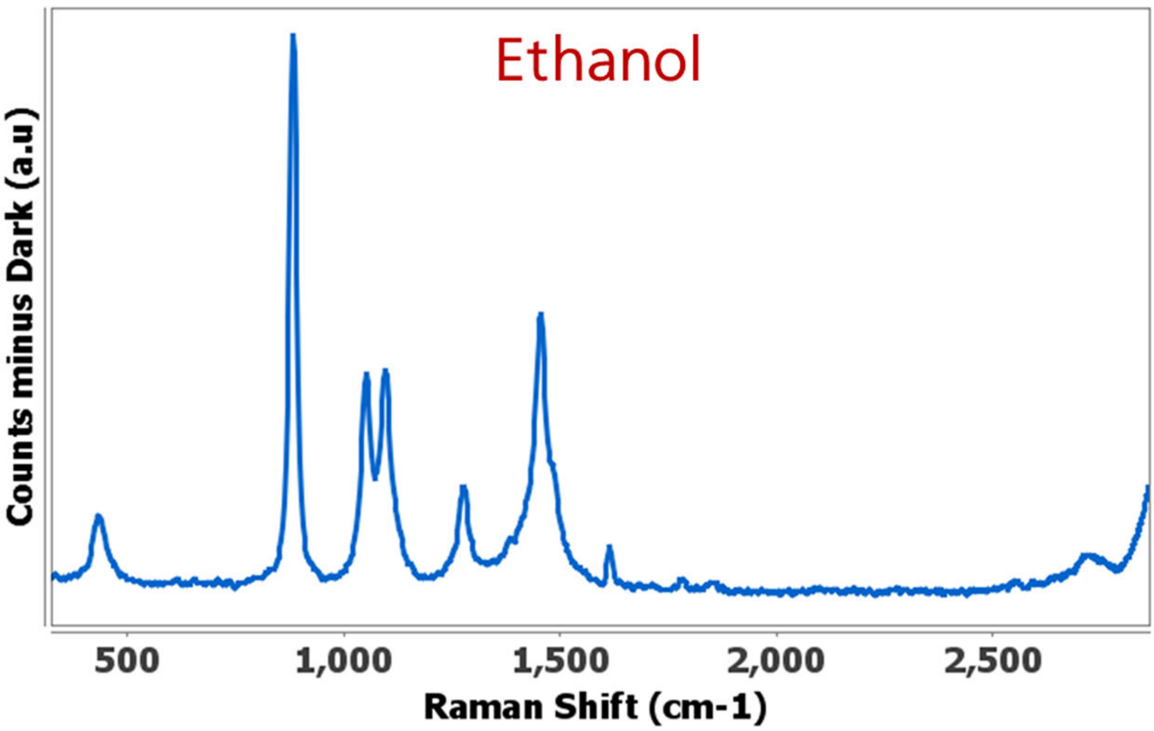
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

g)


Ethanol
Counts minus Dark (a.u)
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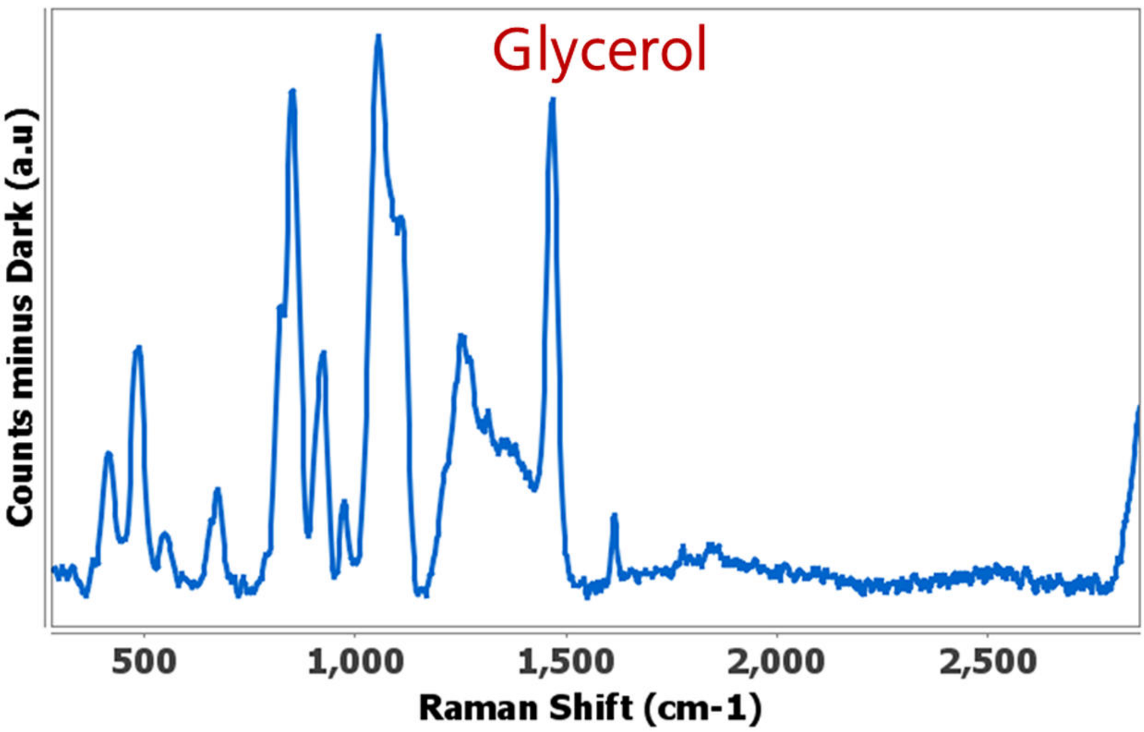
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

h)


Glycerol
Counts minus Dark (a.u)
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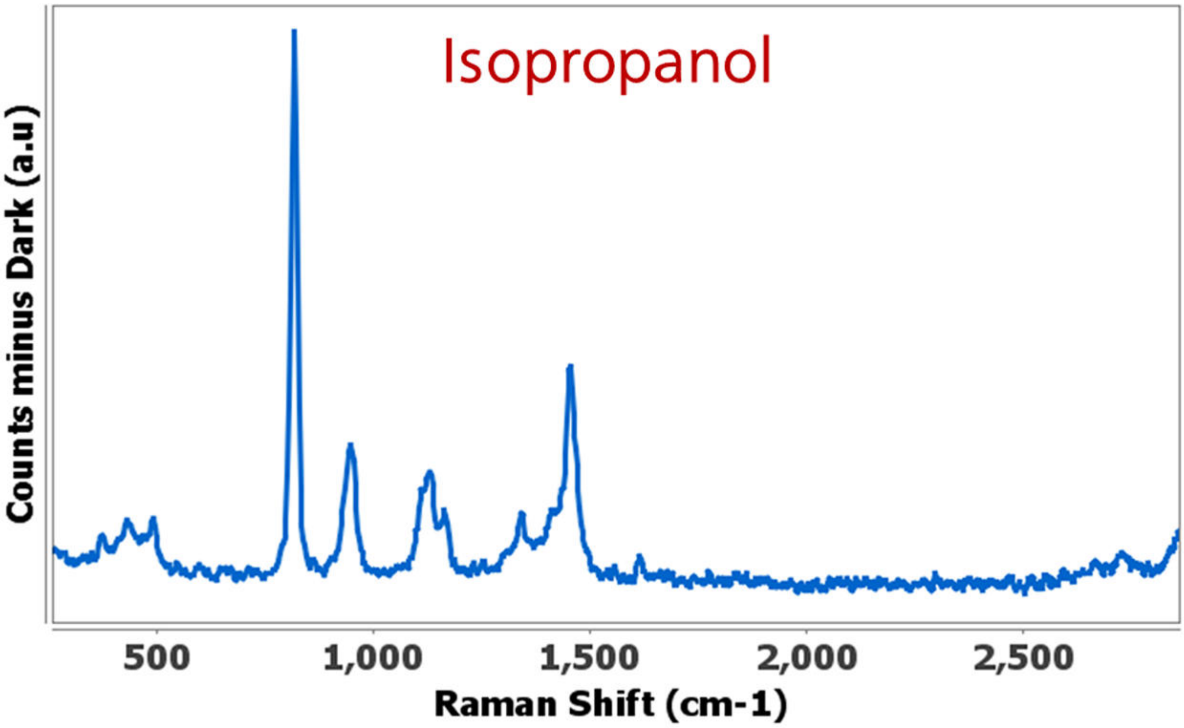
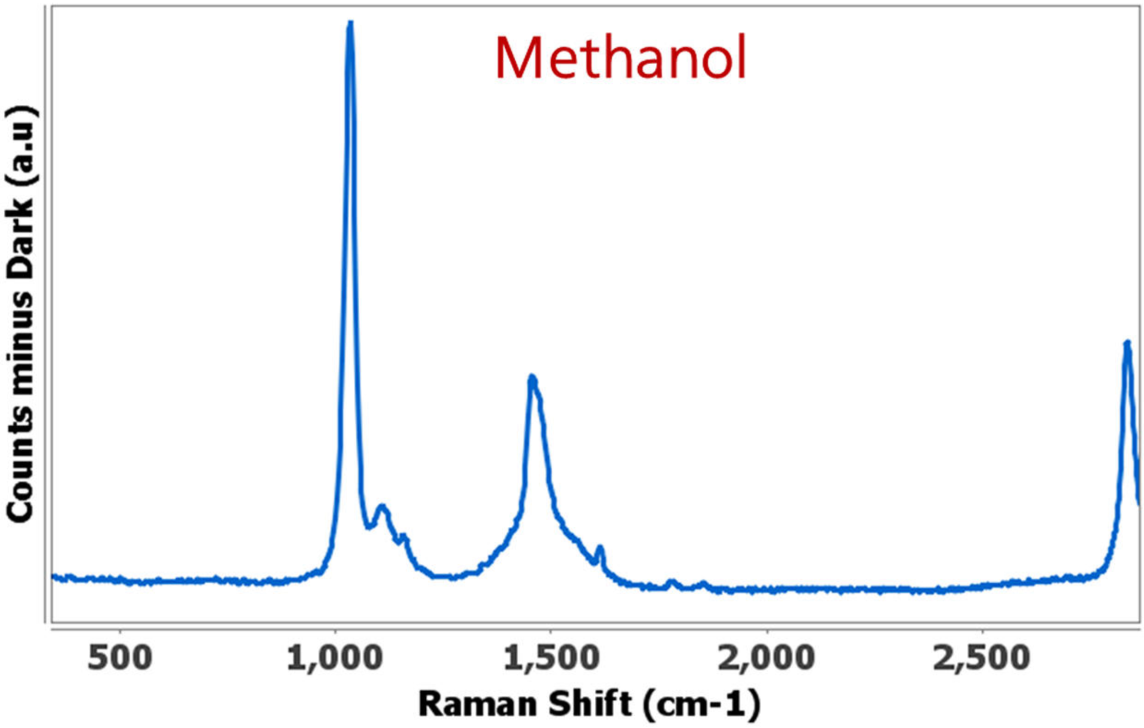
1,500
2,000
2,500
Raman Shift (cm-1)

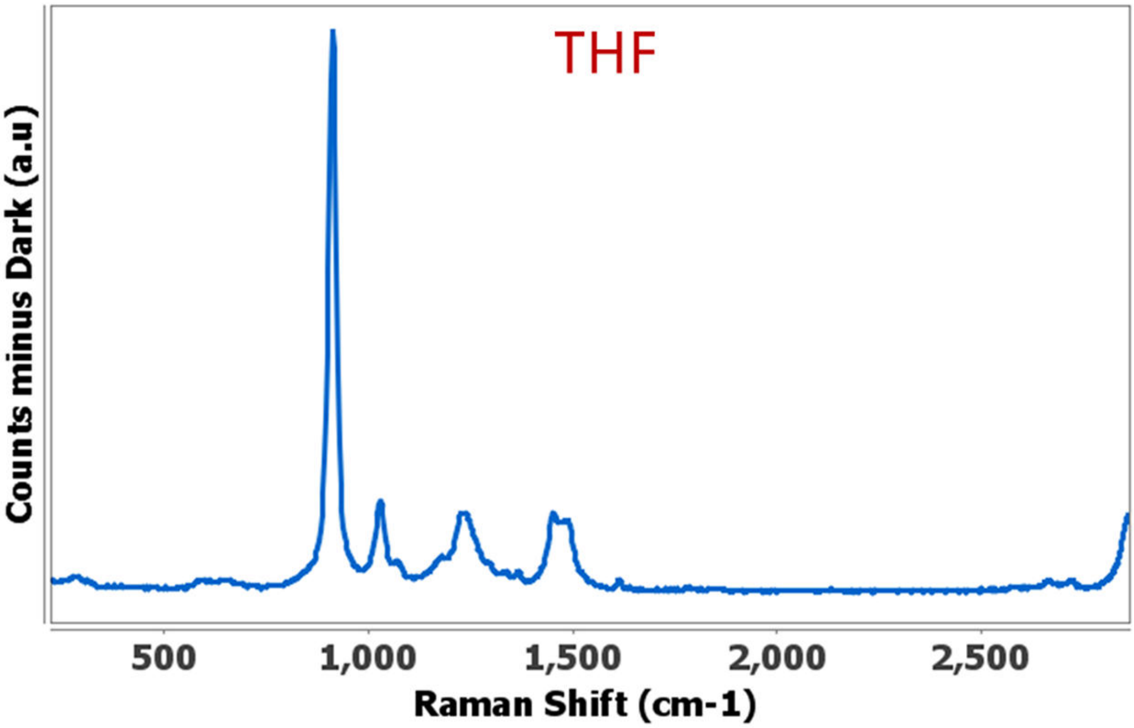
i)


Isopropanol
Counts minus Dark (a.u)
500
1,000
1,500
2,000
2,500
Raman Shift (cm-1)

j)



k)



l) Characteristic Raman spectra of (a) acetone, (b) acetonitrile, (c) cyclohexanone, (d) chloroform, (e) dichloromethane, (f) dimethylformamide (DMF), (g) dimethyl sulfoxide (DMSO), (h) ethanol, (i) glycerol, (j) isopropanol, (k) methanol, and (l) tetrahydrofuran (THF).

APPLICATION: SERS EFFECT IN ORGANIC MEDIA

Figure 2. Characteristic Raman spectra of a) acetone, b) acetonitrile, c) cyclohexanone, d) chloroform, e) dichloromethane, f) dimethylformamide (DMF), g) dimethyl sulfoxide (DMSO), h) ethanol, i) glycerol, j) isopropanol, k) methanol, and l) tetrahydrofuran (THF).

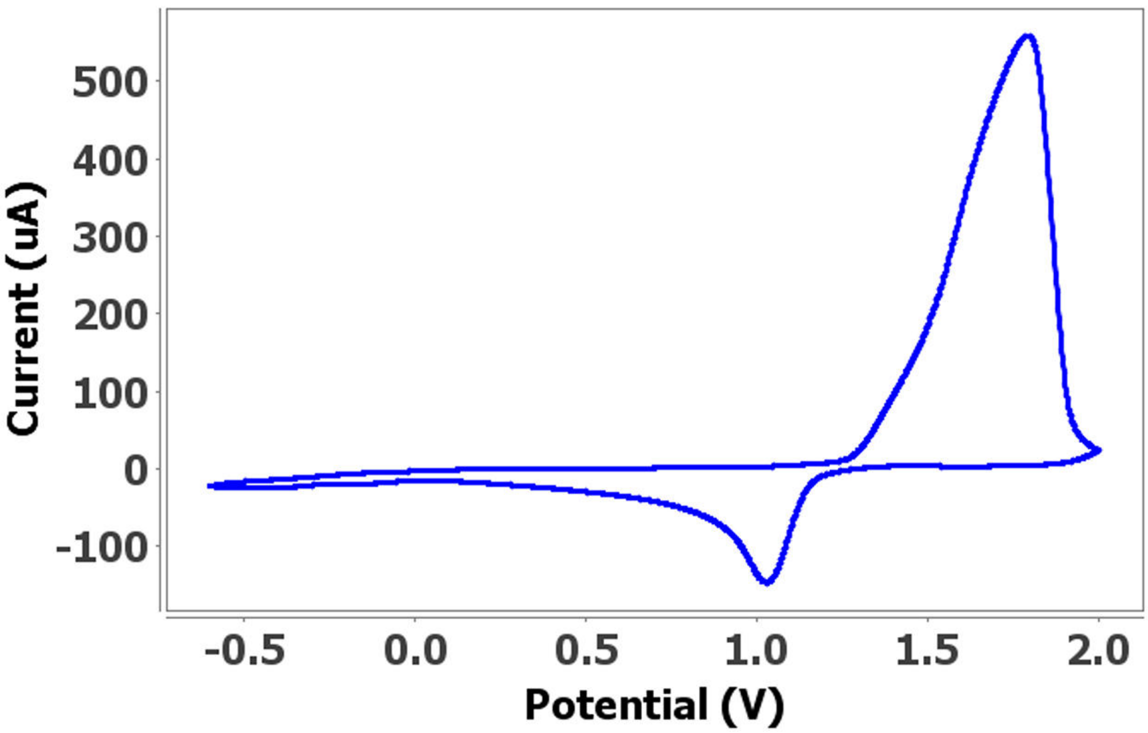
RESULTS: SERS EFFECT WITH A GOLD ELECTRODE

As a proof of concept, the detection of crystal violet (a dye widely used in Raman spectroscopy) is carried out in organic media with the Au electrode (**Table 1**). The electrochemical activation of this electrode consists of the initial oxidation of the gold surface followed by its subsequent reduction to generate metallic nanostructures with SERS properties during the cathodic scan.

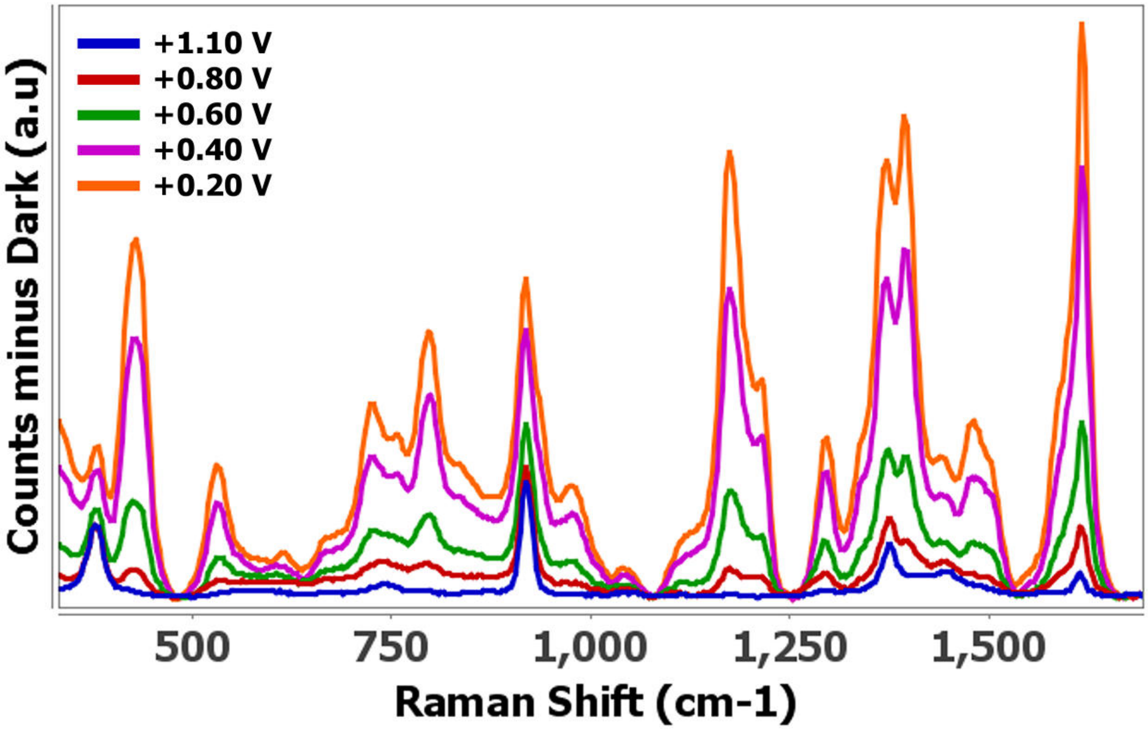
In order to achieve the highest enhancement factor, spectroelectrochemical detection of crystal violet was evaluated in different organic media. The best results were found by working in acetonitrile media with TBA (tetrabutylammonium hexafluorophosphate) as the supporting electrolyte. The potential was scanned from +0.70 V to +2.00 V and back to -0.60 V in the cathodic scan, returning to the initial potential (+0.70 V) at the end of the experiment. The cyclic voltammogram shown in **Figure 3a** was obtained in 0.1 mmol/L crystal violet and 0.1 mol/L TBA in acetonitrile using the described experimental conditions. **Figure 3a** shows the oxidation and reduction processes of the gold electrode at +1.80 V and +1.03 V, respectively.

Raman spectra were monitored concurrently during the electrochemical procedure. Although more than 50 spectra were recorded during the experiment, only a selection of them are plotted in **Figure 3b** to better visualize the optical signal evolution. Raman intensity increases during the cathodic scan, reaching its maximum value at +0.20 V. The characteristic Raman bands associated with the vibrational modes are perfectly well-defined.

The same experiment was carried out with varying concentrations of crystal violet. Analysis of the intensity associated with the Raman band at 1175 cm^{-1} enables the detection of 1 mol/L crystal violet, demonstrating the level of sensitivity achievable with this method.



a)



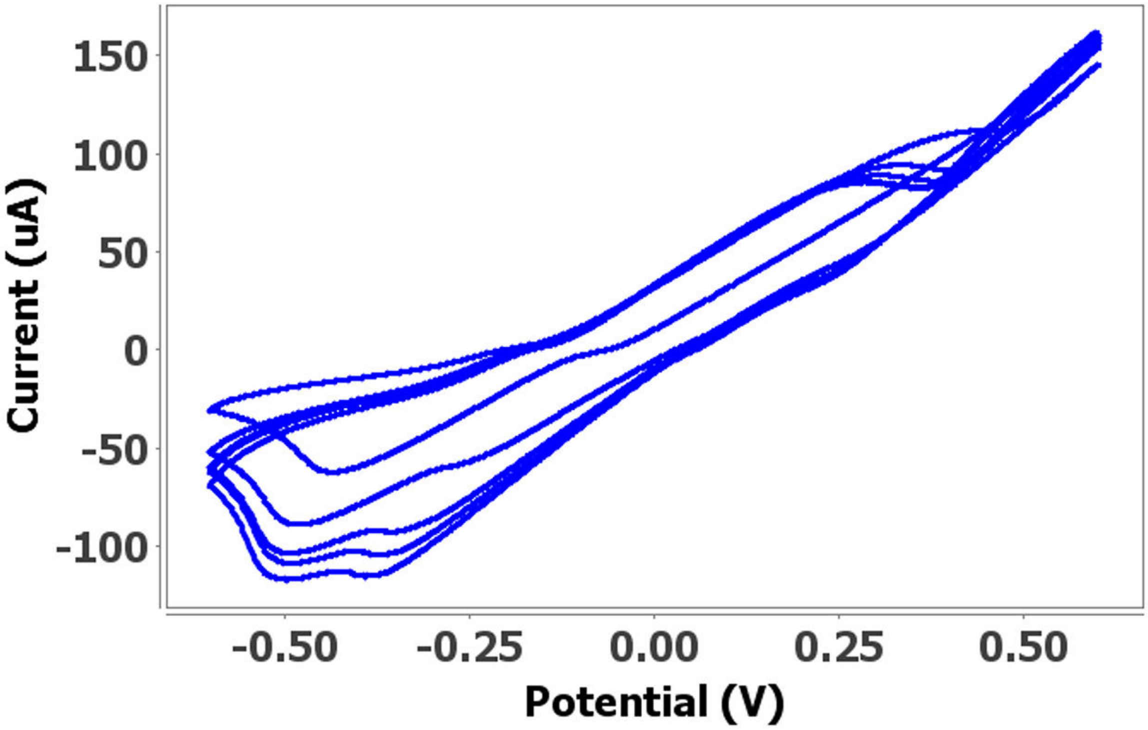
b) a) Cyclic voltammogram and b) evolution of Raman spectra at different potentials obtained in 0.1 mmol/L crystal violet and 0.1 mol/L TBA in acetonitrile while scanning the potential from +0.70 V to +2.00 V and back to +0.60 V. The integration time was 2000 ms.

Figure 3. a) Cyclic voltammogram and b) evolution of Raman spectra at different potentials obtained in 0.1 mmol/L crystal violet and 0.1 mol/L TBA in acetonitrile while scanning the potential from +0.70 V to +2.00 V and back to -0.60 V. The integration time was 2000 ms.

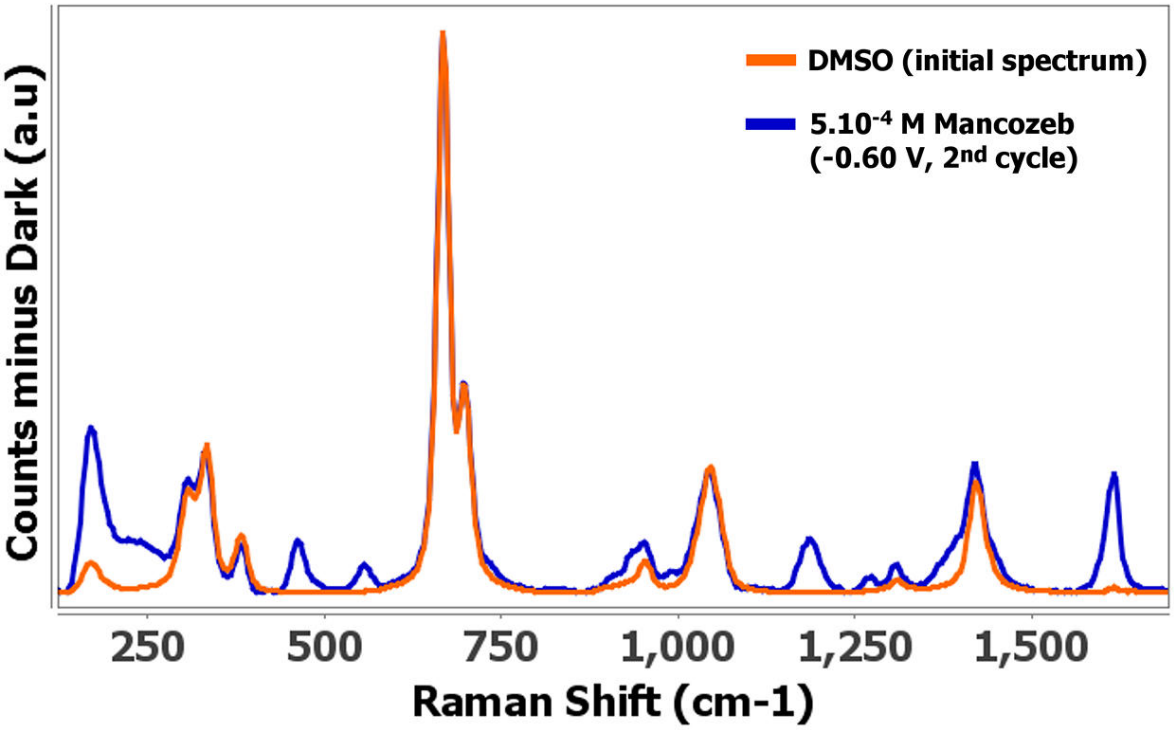
RESULTS: SERS EFFECT WITH A SILVER ELECTRODE

Like the previous example with gold, the electrochemical activation of silver electrode surfaces also produces an enhancement of Raman intensity. The spectroelectrochemical detection of mancozeb in an organic solvent was performed with the Ag electrode to prove this concept. Mancozeb is a fungicide which is insoluble in water. Previous solubility tests concluded that DMSO is one of the best solvents to ensure the solubility of this pesticide. Experimental conditions were optimized by working in 0.5 mmol/L mancozeb and 0.1 mol/L TBA in DMSO. In this case, the potential was scanned between +0.60 V and -0.60 V for five cycles (**Figure 4a**) since activation of the silver surface in this organic medium requires an initial cycle for pretreatment purposes.

Figure 4b shows that although several Raman bands are related to the DMSO solvent, characteristic signals of mancozeb centered at 240, 422, 463, 516, 560, 660, 912, 990, 1187, 1272, 1522 and 1615 cm^{-1} are also detected at -0.60 V (second cycle).



a)



b) a) Cyclic voltammogram and b) Raman spectra obtained in 0.5 mmol/L mancozeb and 0.1 mol/L TBA in DMSO while scanning the potential from +0.60 V to -0.60 V for five cycles. The integration time was 2000 ms.

Figure 4. a) Cyclic voltammogram and b) Raman spectra obtained in 0.5 mmol/L mancozeb and 0.1 mol/L TBA in DMSO while scanning the potential from +0.60 V to -0.60 V for five cycles. The integration time was 2000 ms.

Raman intensity of mancozeb was evaluated during the whole experiment and it remains constant from cycles 2 to 5. Therefore, only two cycles are required—the first to pretreat the surface, and the second to produce its SERS activation.

CONCLUSIONS

Some EC-SERS protocols are tedious, complex, and limited to aqueous solutions. Instrumental requirements can also complicate the improvement of electrochemical activation of metal electrodes. This study covered the detection of two different molecules (crystal violet and mancozeb) performed by Raman spectroelectrochemistry in organic solvents (acetonitrile and DMSO). Electrochemical activation, which consists of an initial oxidation followed by a reduction scan, allows the detection of 1 mol/L crystal violet. Of particular interest is the detection of mancozeb, a fungicide insoluble in water which requires organic media as, for instance, DMSO.

REFERENCES

1. González-Hernández, J.; Ott, C. E.; Arcos-Martínez, M. J.; et al. Rapid Determination of the ‘Legal Highs’ 4-MMC and 4-MEC by Spectroelectrochemistry: Simultaneous Cyclic Voltammetry and In Situ Surface-Enhanced Raman Spectroscopy. *Sensors* **2022**, *22* (1), 295. https://doi.org/10.3390/s22010295.
2. Ibánez, D.; González-García, M. B.; Hernández-Santos, D.; Fanjul-Bolado, P. Detection of Dithiocarbamate, Chloronicotinyl and Organophosphate Pesticides by Electrochemical Activation of SERS Features of Screen-Printed Electrodes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2021**, *248*, 119174. https://doi.org/10.1016/j.saa.2020.119174.

RELATED APPLICATION NOTES

AN-SEC-001 - Spectroelectrochemistry: an autovalidated analytical technique – Confirm results via two different routes in a single experiment

AN-SEC-002 - Gathering information from spectroelectrochemical experiments – Calculation of electrochemical parameters from data

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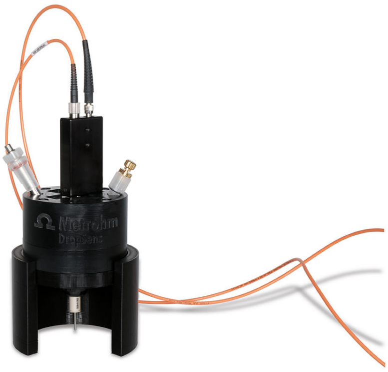
CONFIGURATION

785 nm

SPELECRAMAN 是一可行光化学拉曼量的器。SPELECRAMAN 将一个 3B 激光器 (785 nm ± 0.5)、一个双恒位/恒流和一个光(波范:787 - 1027 nm,拉曼位移:35 - 3000 cm^{-1})合在一个箱子中,并配有用的光化学件,可同步行光学和化学。

反射探用于激 785 nm 波(高 500 mW)。用于与网印刷 DropSens 拉曼流通池或任何拉曼装置一起工作。



拉曼光化学量 PEEK 的量池，其用于参比 RAMANPROBE 和瑞士万通。