Activación electroquímica de plataformas de oro para la detección de pesticidas mediante espectroelectroquímica Raman

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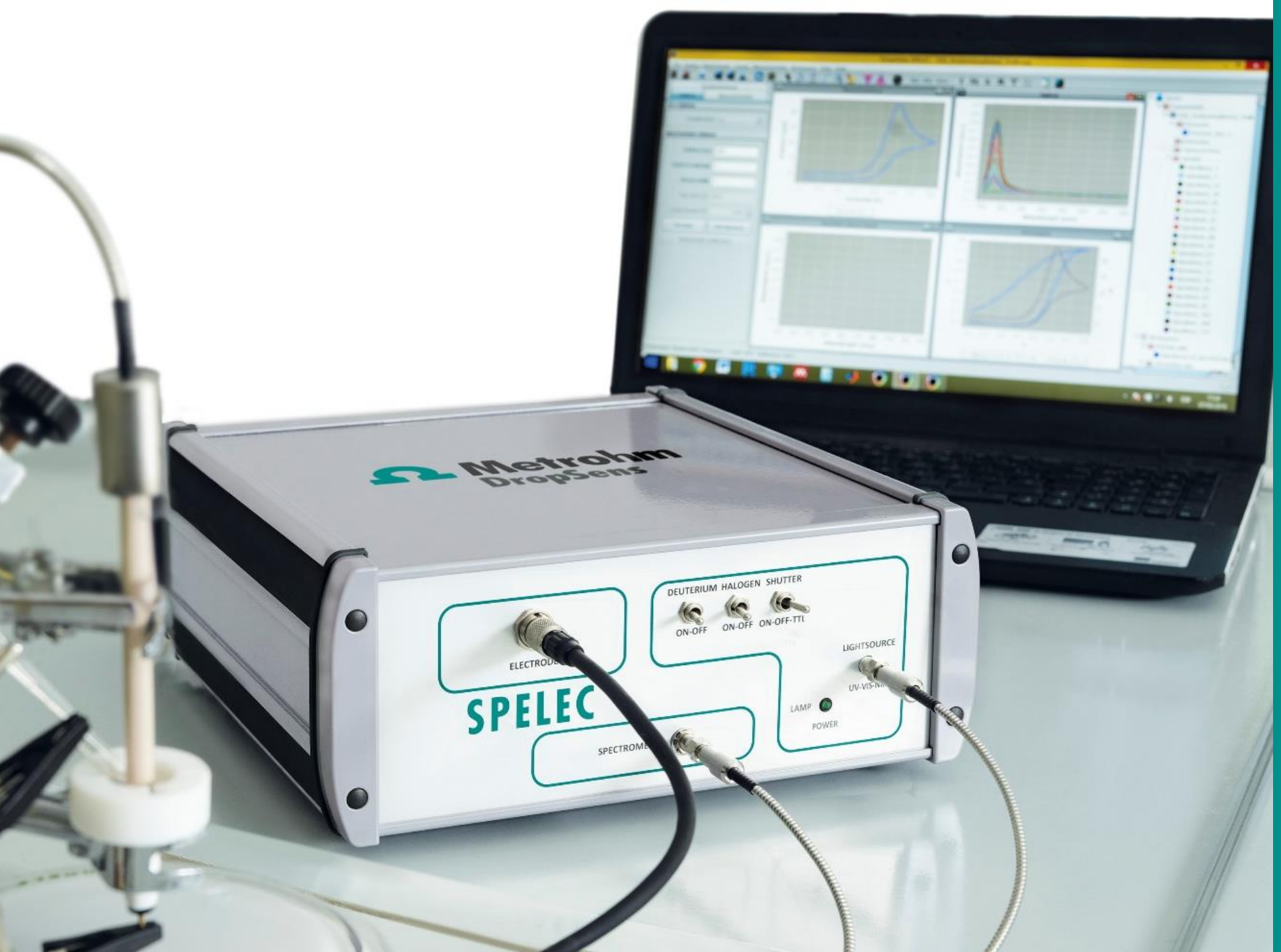

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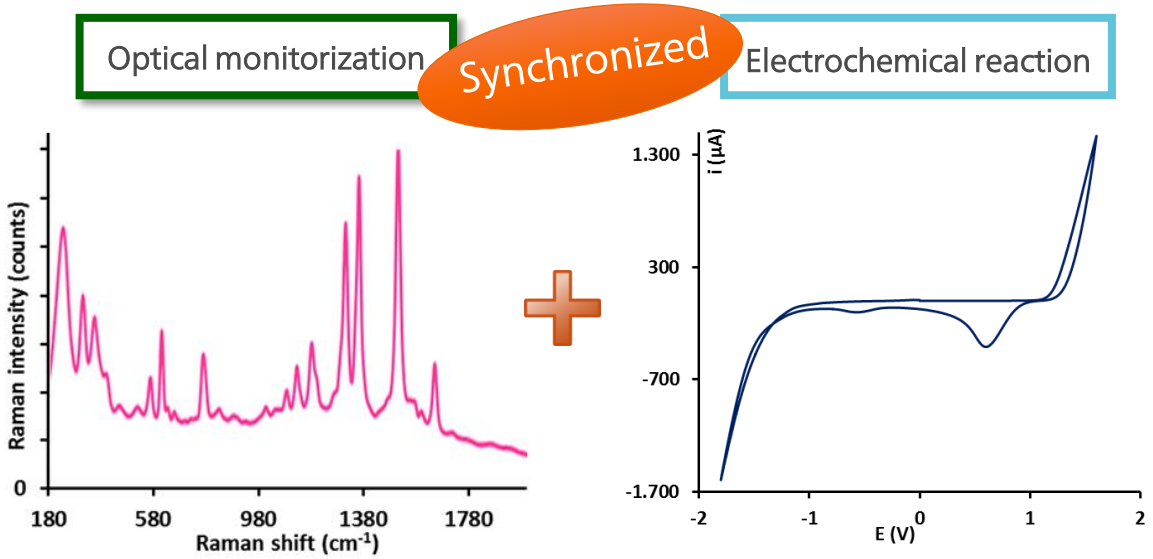
Introduction

Raman spectroelectrochemistry

Raman spectroscopy + Electrochemistry

RAMAN SPECTROELECTROCHEMISTRY



- Raman spectroelectrochemistry combines **the advantages of electrochemistry and Raman spectroscopy.**
- **Fingerprint** technique: optical **identification** of reaction intermediates, unstable species or product structures, during an electrochemical measurement.
- **Dynamic and complete analysis** of electron transfer processes and complex redox reactions.
- Study of **kinetics and mechanisms.**
- **Structural properties** of materials.
- Redox chemistry **of inorganic, organic and biological molecules.**
- …

Raman Spectroelectrochemistry: SERS effect

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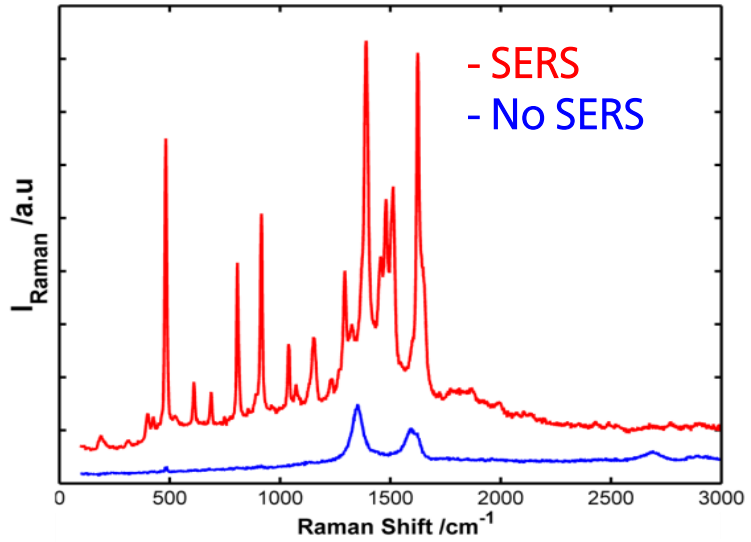
Surface-enhanced Raman scattering (SERS) effect consists of the **huge enhancement of the Raman intensity**.

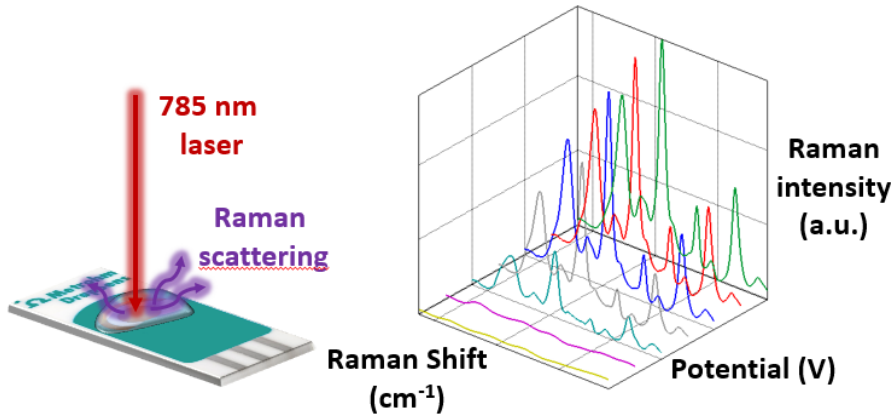


SERS band associated with the analyte are not observed (only two bands realted to the working electrode)

SERS band associated with the analyte are detected

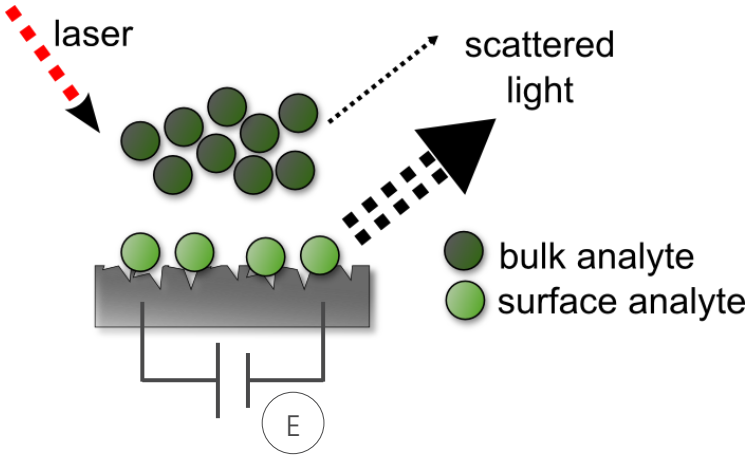
SERS effect due to presence of metal nanostructures

Activation of metallic screen-printed electrodes (SPEs) by electrochemical routes leads to the generation of reproducible structures with excellent SERS properties

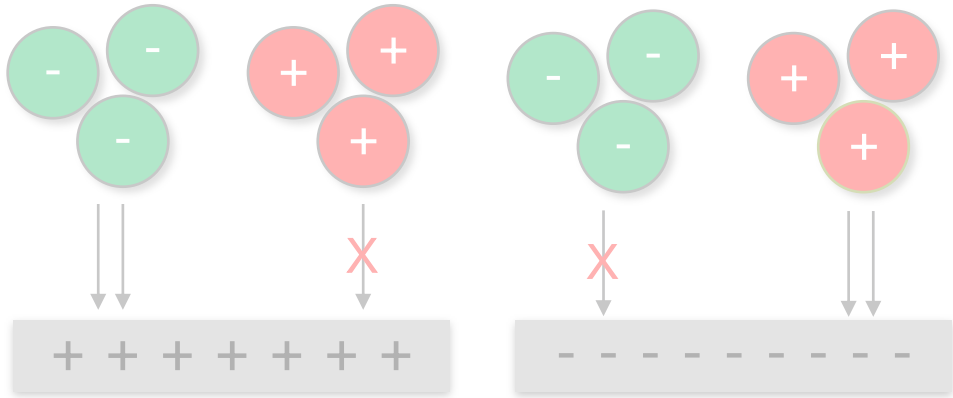


Raman Spectroelectrochemistry: EC-SERS effect

EC-SERS effect **enhanced or initiated by electrochemistry**.



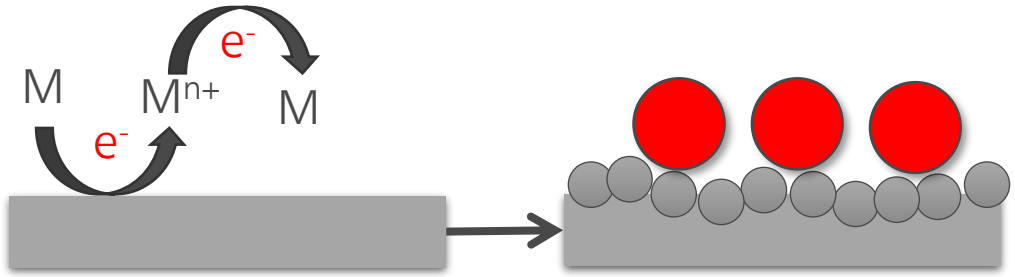
- Interaction of species with the surface can be potential-dependent



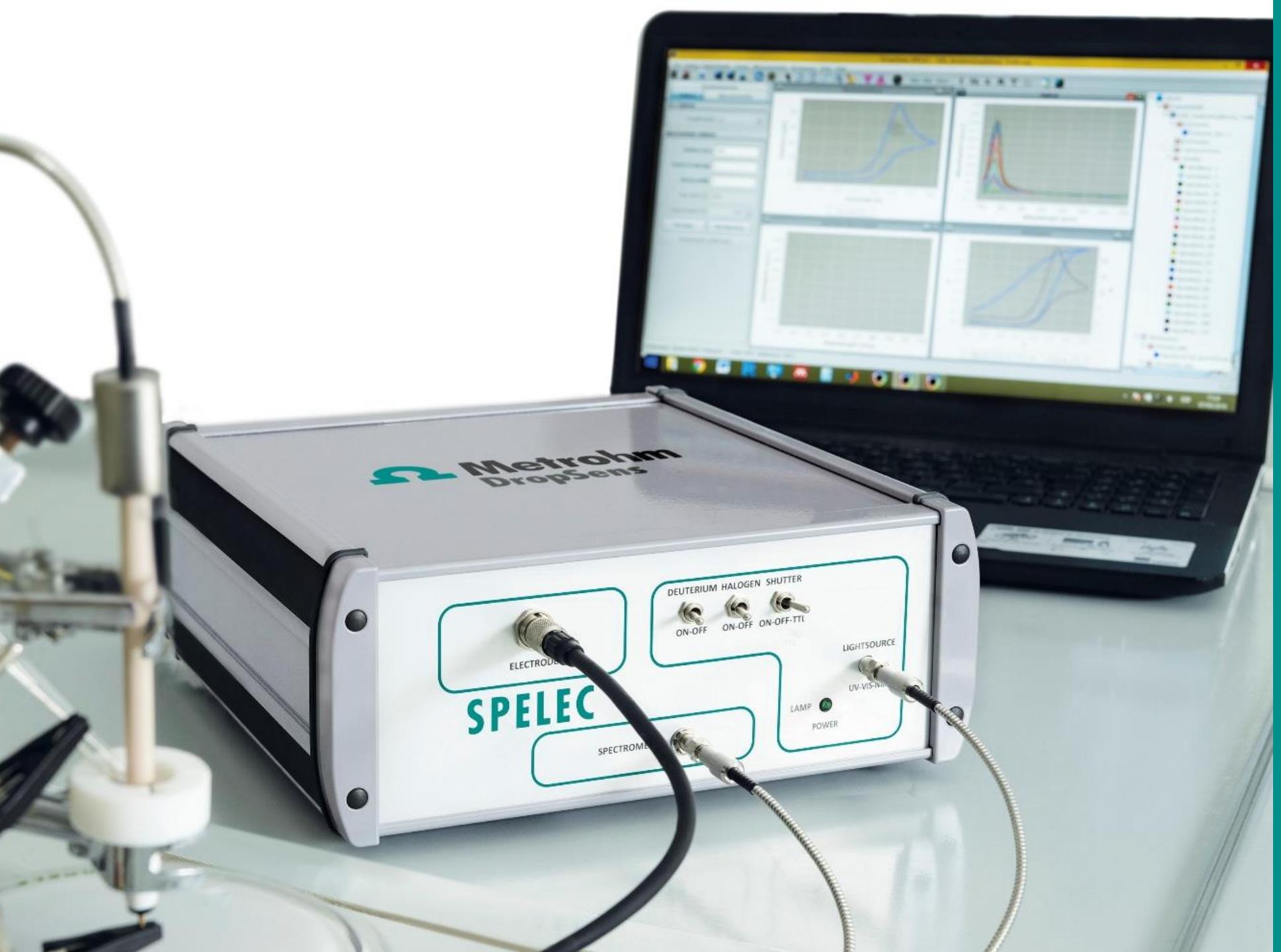
Increases analyte adsorption
Minimizes non-specific adsorption

- *In-situ* generation of fresh nanostructures in presence of the analyte

This work



Fresh nanofeatures: available for analyte interaction



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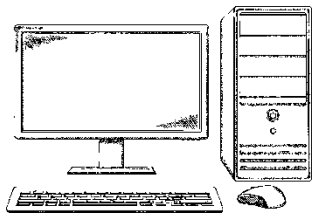
Set-up and instrument

Spectroelectrochemical setup
Detached set-up

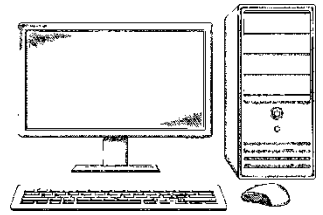


Spectroscopy software
Registration of spectroscopic data

Spectroscopic instrument

Spectroelectrochemical cell

Electrochemistry instrument



Electrochemistry software
Registration of electrochemical data

External software for data treatment and analysis

Articles

Projects

Conclusions

Reports

Protocols

Spectroelectrochemical setup
Fully integrated set-up

SPELEC software:
- Registration of optical & electrochemical data
- Data treatment and analysis

SPELEC instrument

Spectroelectrochemical cell

Conclusions

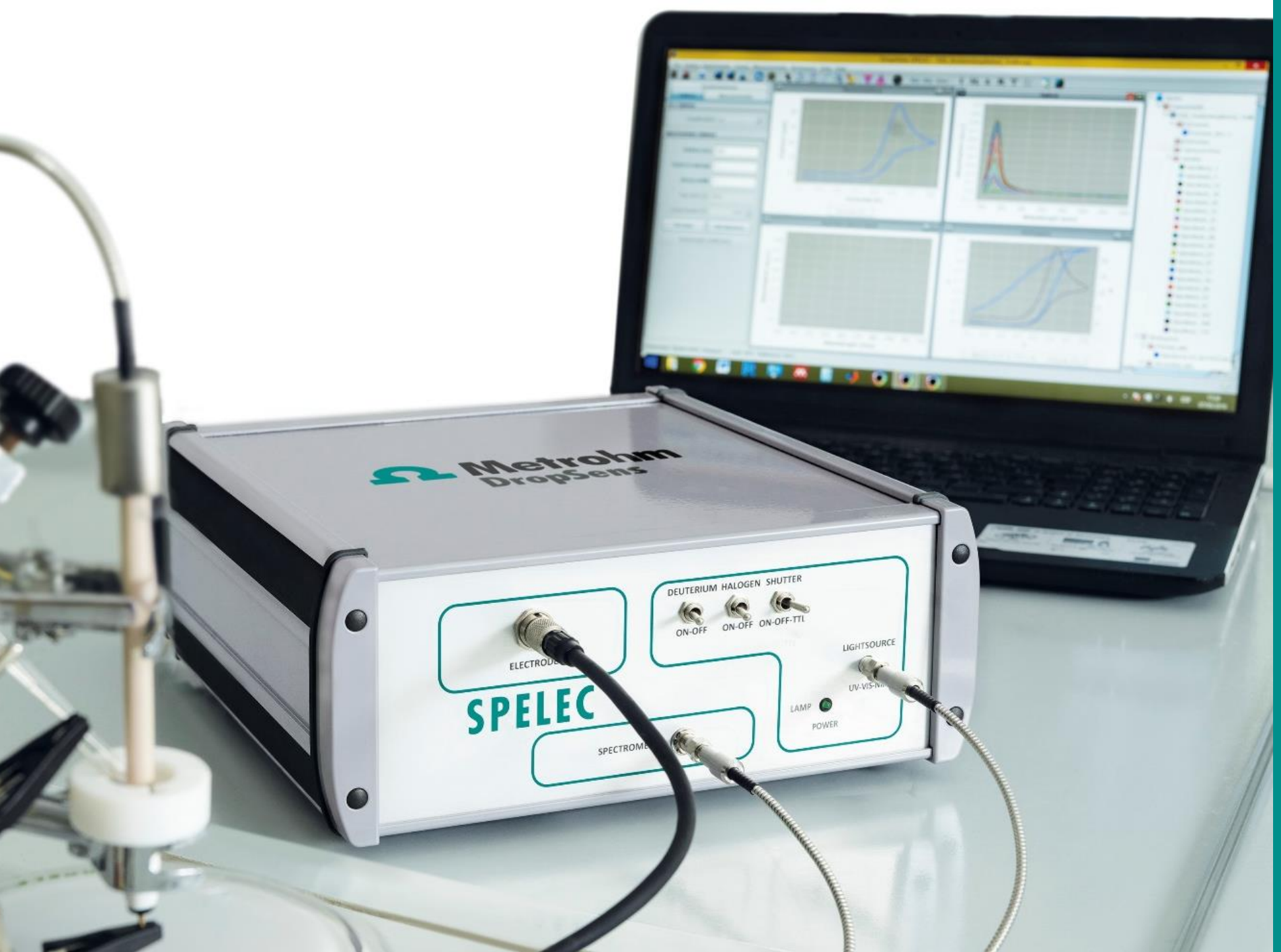
- Articles
- Reports
- Projects
- Protocols

Spectroelectrochemical instrument: SPELEC RAMAN

Metrohm DropSens

Fully integrated (SPELEC RAMAN) instrument for Raman spectroelectrochemistry

Main Specifications	
Laser Wavelength	785 nm
Laser optical power out	Up to 500 mW
Spectrometer Wavelength range	785 – 1010 nm
Spectrometer Resolution	< 4 cm^{-1}
Raman shift	0 – 2850 cm^{-1}
Potential range	± 4 V
Maximum measurable current	± 40 mA
Dimensions	25 x 24 x 11 cm (L x W x H)
Weight	3.95 Kg

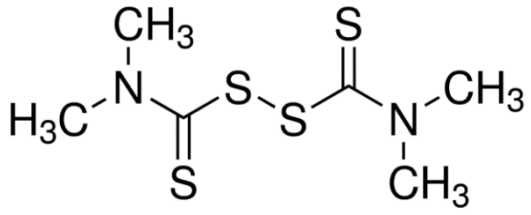

Metrohm
DropSens
DEUTERIUM HALOGEN SHUTTER
ON-OFF
ON-OFF
ON-OFF-TTL
LIGHTSOURCE
LAMP
POWER
SPELEC

Results

Results

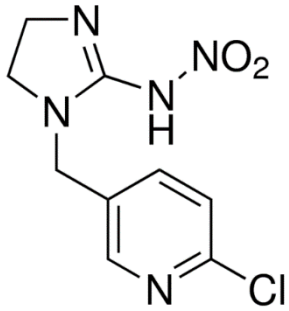
Detection of three different pesticides is analyzed:

Thiram:



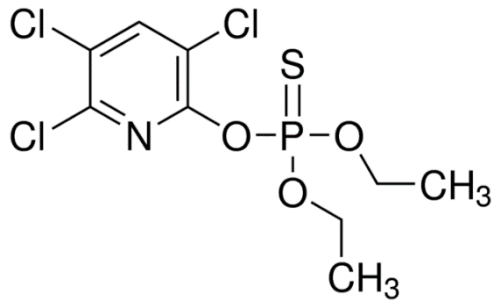
- **Dithiocarbamate** fungicide
- Control of fungal diseases
- Protection of fruits and vegetables

Imidacloprid



- **Chloronicotinyl** insecticide
- Control of pests (aphids, scale insects, whiteflies or leafhoppers)

Chlorpyrifos



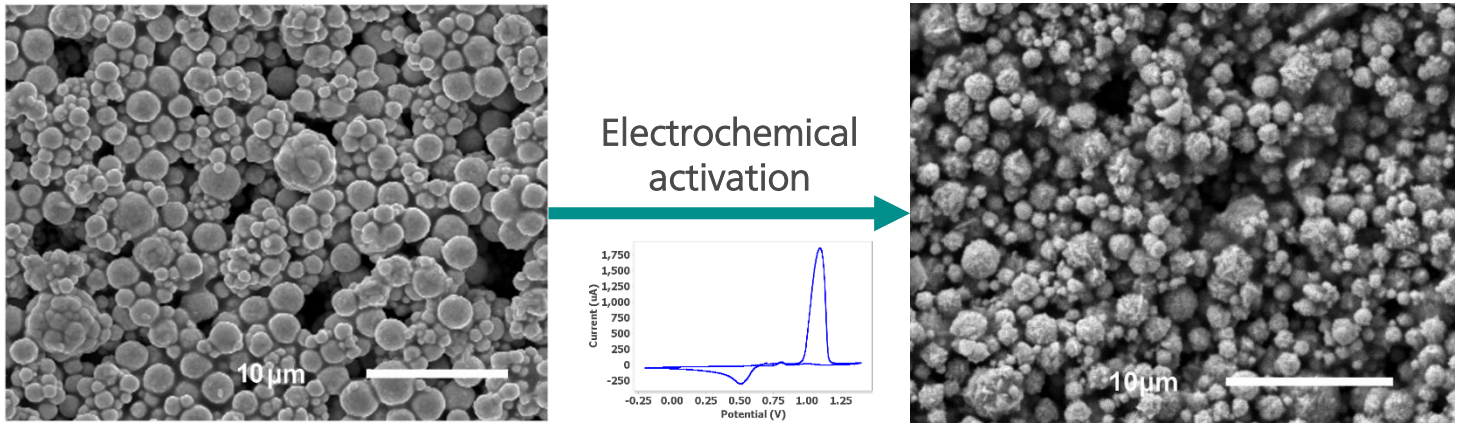
- **Organophosphate** insecticide
- Control of a variety of insect pests (mosquitoes, fire ants, cockroaches, horn flies, lice, fleas and turf)

Results

Thiram detection:

Initially, an EC-SERS methodology is applied. It consists of **two steps in a single experiment**:

1. Electrochemical activation of gold surface:
   - Gold screen-printed electrode (DRP-220BT)
   - HCl 0.1 M
   - Cyclic voltammetry: +0.70 V to +1.40 V and back to -0.20 V. Scan rate 0.05 V/s



AuNPs are deposited on the microstructures observed in the initial electrode

EC-SERS effect

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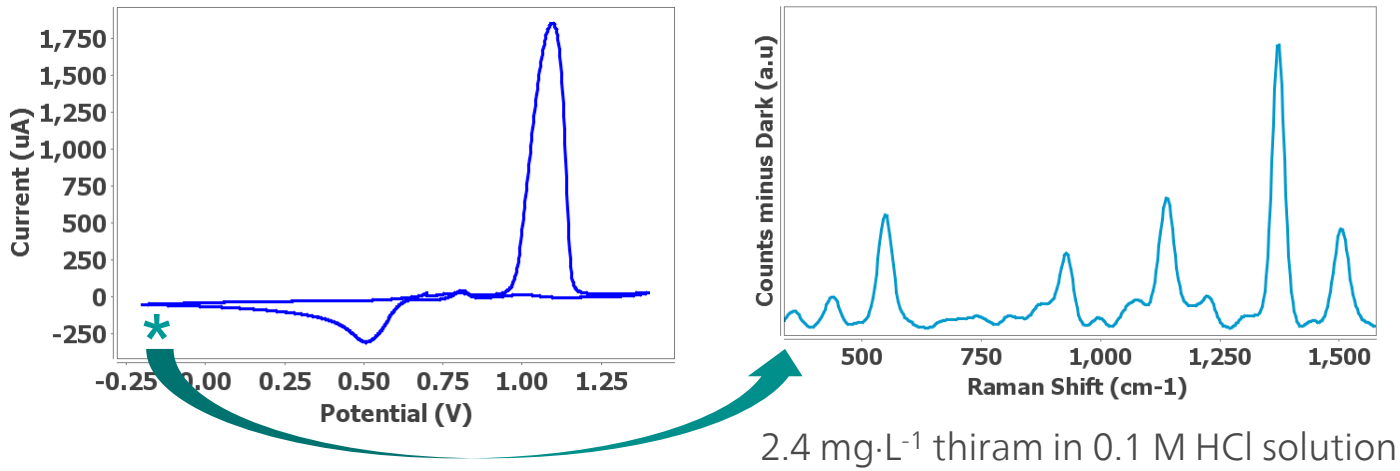
Results

Thiram detection:

Initially, an EC-SERS methodology is applied. It consist of **two steps in a single experiment**:

2. Thiram detection:
   - Integration time 2000 ms → 32 spectra during the whole experiment.



2.4 mg·L^{-1} thiram in 0.1 M HCl solution

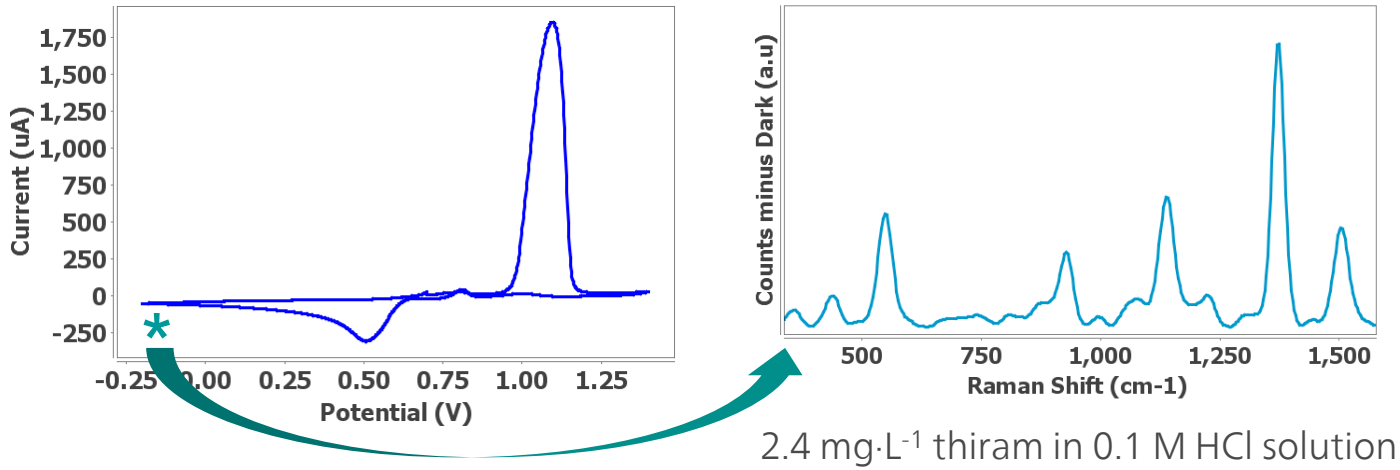
EC-SERS band (cm^{-1})	Assignment
349	S=CS deformation and CSS deformation
437	CH_3NC deformation
548	C=S stretching
863	CH_3N stretching
925	CH_3N stretching and C=S stretching
1075	C=S stretching
1138	CN stretching and CH_3 rocking
1380	CN stretching and CH_3 deformation
1435	CN stretching and CH_3 rocking
1507	CN stretching and CH_3 rocking

Results

Thiram detection:

Initially, an EC-SERS methodology is applied. It consist of **two steps in a single experiment**:

2. Thiram detection:
   - Integration time 2000 ms → 32 spectra during the whole experiment.



2.4 mg·L^{-1} thiram in 0.1 M HCl solution

- Detection limit: 0.240 mg·L^{-1} thiram
- ECM for Thiram in Water (US): 3 ug·L^{-1}
- Maximum Residue Limits (MRLs) EU: from 0.1 to 10 mg·L^{-1} depending on the food product

This methodology is not useful

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Results

Thiram detection:

A **new methodology** is developed. It consists of **three steps**:

1. **Preconcentration** of the 60 uL drop at **34 ºC for 15 min**:

   → Volume decreases to **25 uL** (HCl is concentrated until 0.24 M)

- Shorter times than 15 min do not concentrate enough the samples
- Longer times do not ensure the proper contact of the solution with WE, RE and CE.
- Higher temperature than 34 ºC does not allow the exhaustive control of the volume solution due to the fast evaporation of the drop.

Preconcentration plays an **essential role** in the detection of **low concentrations**

Results

Thiram detection:

A new methodology is developed. It consists of **three steps**:

1. **Preconcentration** of the 60 uL drop at **34 ºC for 15 min**
2. **Electrochemical activation** of gold surface:
   - Gold screen-printed electrode (DRP-220BT)
   - HCl 0.1 M
   - Cyclic voltammetry: +0.70 V to +1.40 V and back to -0.20 V.
3. **Thiram detection**

} Steps 2 and 3 in a single experiment

Total time: 16 min approximately
- 15 min preconcentration
- 64 s ≈ 1 min spectroelectrochemical detection

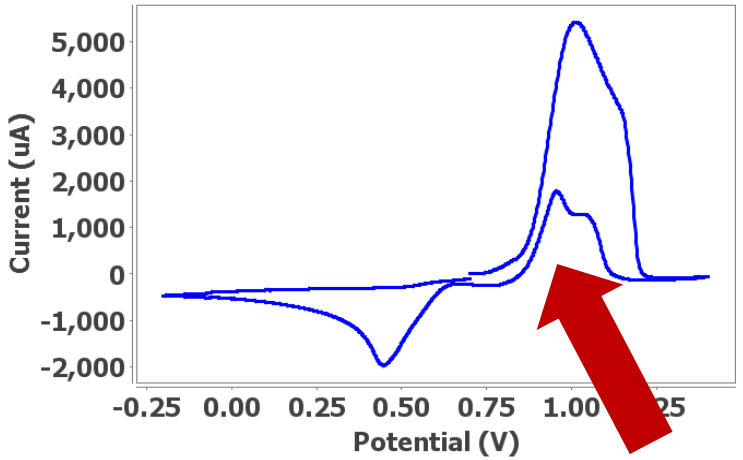
→ **Easy and quick protocol** instead of long and complex procedures of traditional methods

Results

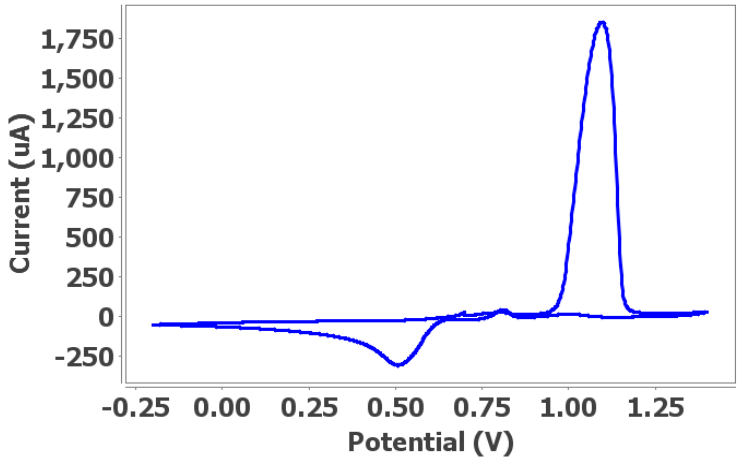
Thiram detection:

Spectroelectrochemical detection:

Preconcentration



Without preconcentration



Cyclic voltammogram obtained in 2.4 $mg \cdot L^{-1}$ thiram in 0.24 M HCl aqueous solution

Two new peaks are observed at +1.02 V and +0.95 V during the cathodic scan after the preconcentration of the sample

Voltametric profile suggests that these peaks are related to the desorption processes of gold halide ions and aurous and auric complexes generated in acid media.

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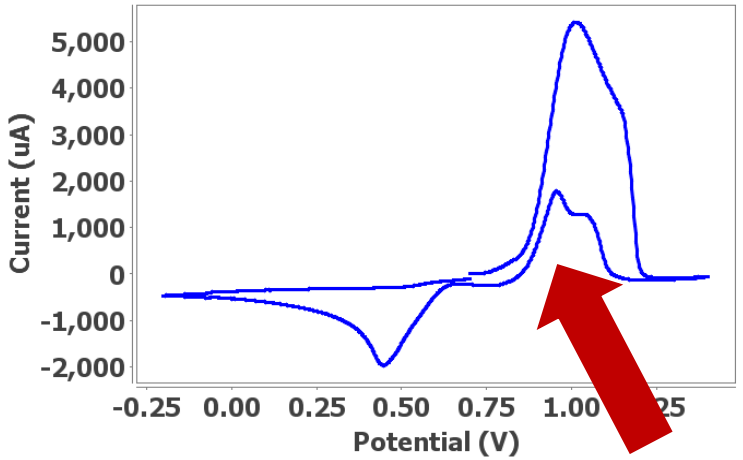
Results

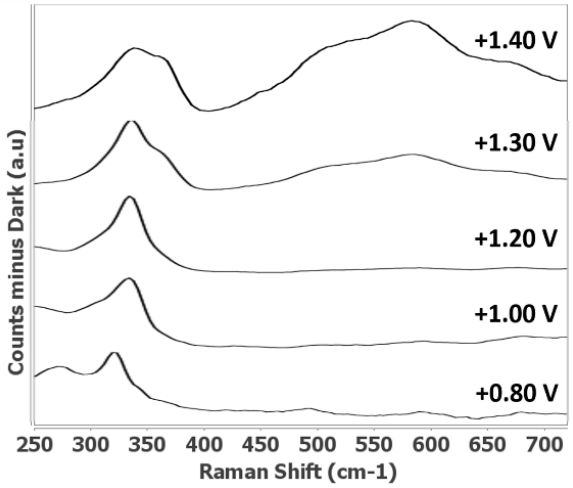
Thiram detection:

Spectroelectrochemical detection:

Preconcentration



Analysis of Raman spectra:



From +1.20 V to +1.40 V

- A new band is detected at 362 cm^{-1} associated with $AuCl_4^-$ adsorbed

At +0.80 V two bands are observed:

- At 270 cm^{-1} for $Au\text{-}Cl^-$ from the adsorbed Cl^-
- At 323 cm^{-1} related to $AuCl_2^-$ adsorbed

Up to +1.20 V:

- Band at 270 cm^{-1} disappears
- Band of $AuCl_2^-$ increases and is slightly shifted to 333 cm^{-1} due to the generation of different species.
- A new broad band at 570 cm^{-1} related to gold oxide appears

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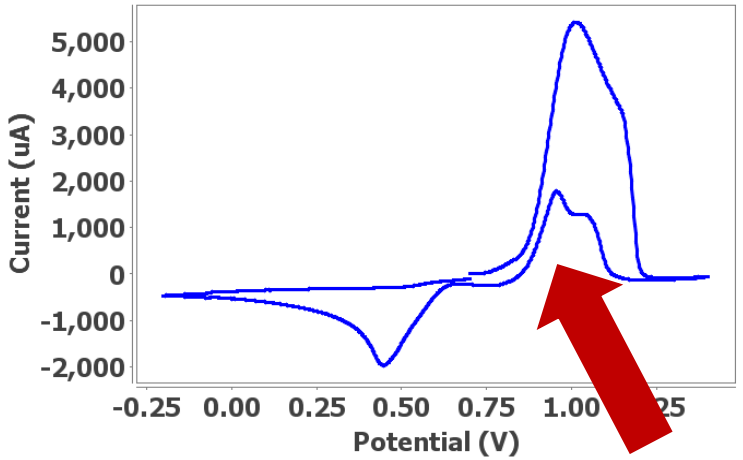
Results

Thiram detection:

Spectroelectrochemical detection:

Preconcentration

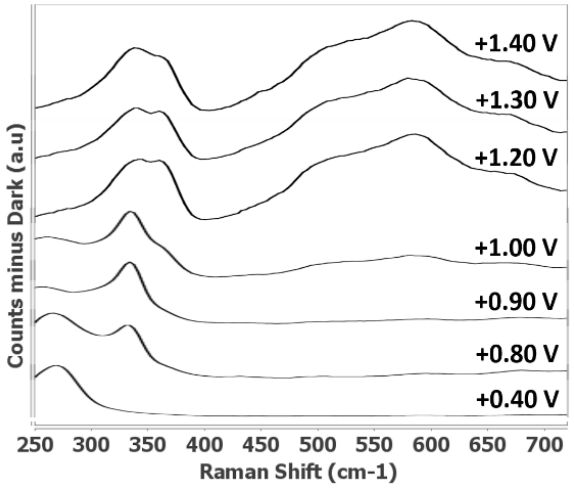


Analysis of Raman spectra:

At lower potential than +1.00 V:

- Bands at 333 cm^{-1} and 270 cm^{-1} increase
- Bands at 362 cm^{-1} and 570 cm^{-1} disappear.

Electrodissolution of gold in acid media

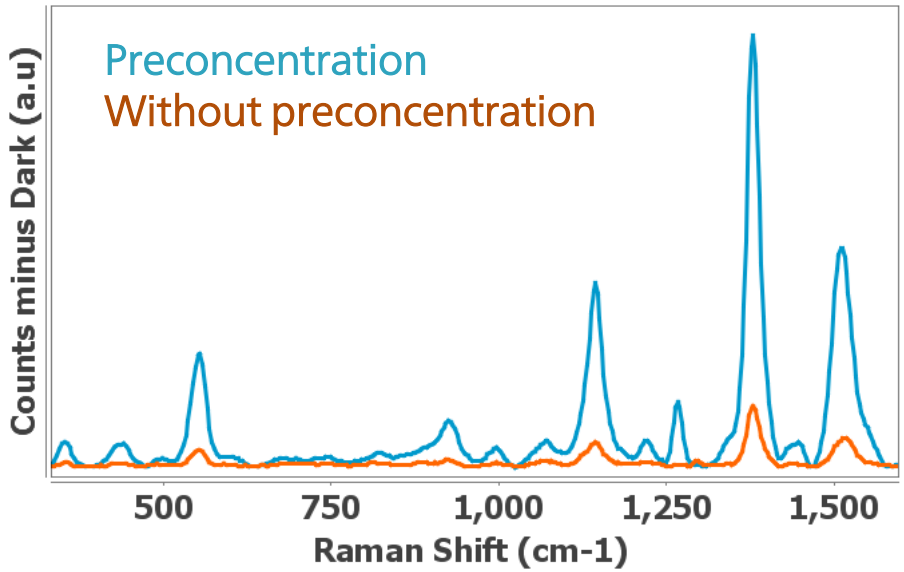


Spectrochim. Acta Part A, 2020, 340, 135975.

Results

Thiram detection:

Spectroelectrochemical detection:



Comparison demonstrates that preconcentration of the sample is crucial to enhance the Raman intensity.

Raman band at 1380 cm^{-1} offers the best features to detect lower thiram concentration due to its intensity is much higher than the other ones.

Preconcentration methodology allows the detection of 2.4 $\mu g \cdot L^{-1}$ thiram when an accurate adjustment of the baseline by polynomial fitting.

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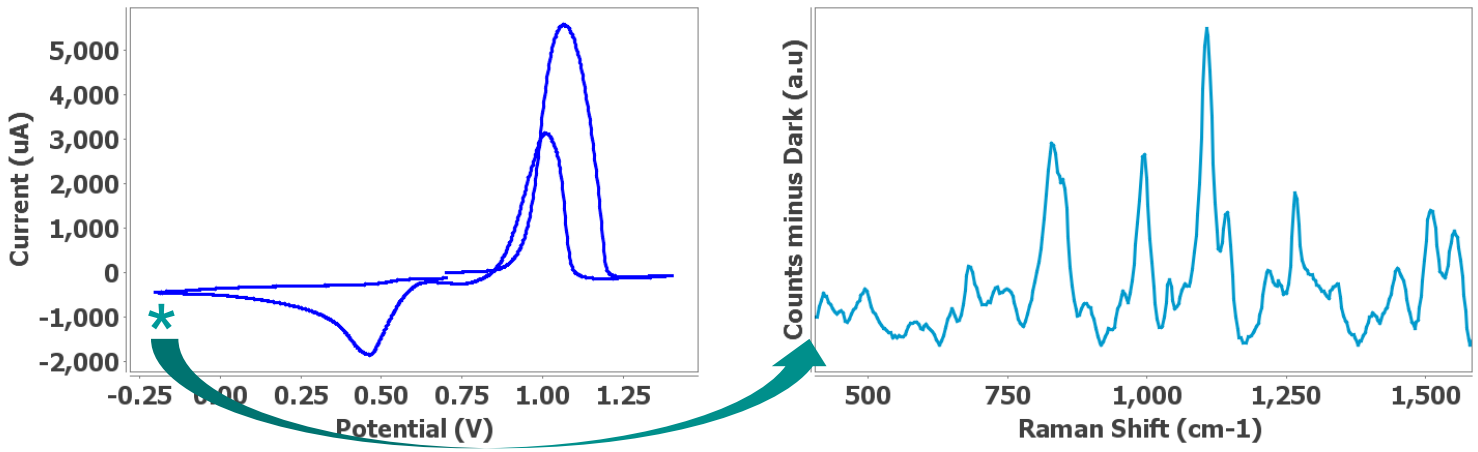
Results

The same methodology was followed to detect **imidacloprid:**



EC-SERS band (cm^{-1})	Assignment
829	CCC stretching
996	CCN and CCC bending
1107	CCC stretching and CH bending
1267	NN and stretching and CH wagging
1510	CCC and CH bending
1552	ONO stretching and CCC stretching

Analysis of band at **1107 cm^{-1}** allows the **detection of 25 $\mu g \cdot L^{-1}$**

<

ECM for Imidacloprid in Water (US) 50 $ug \cdot L^{-1}$
MRLs (EU) from 0.05 $mg \cdot L^{-1}$ depending on food

This procedure offers the **sensitivity** required.

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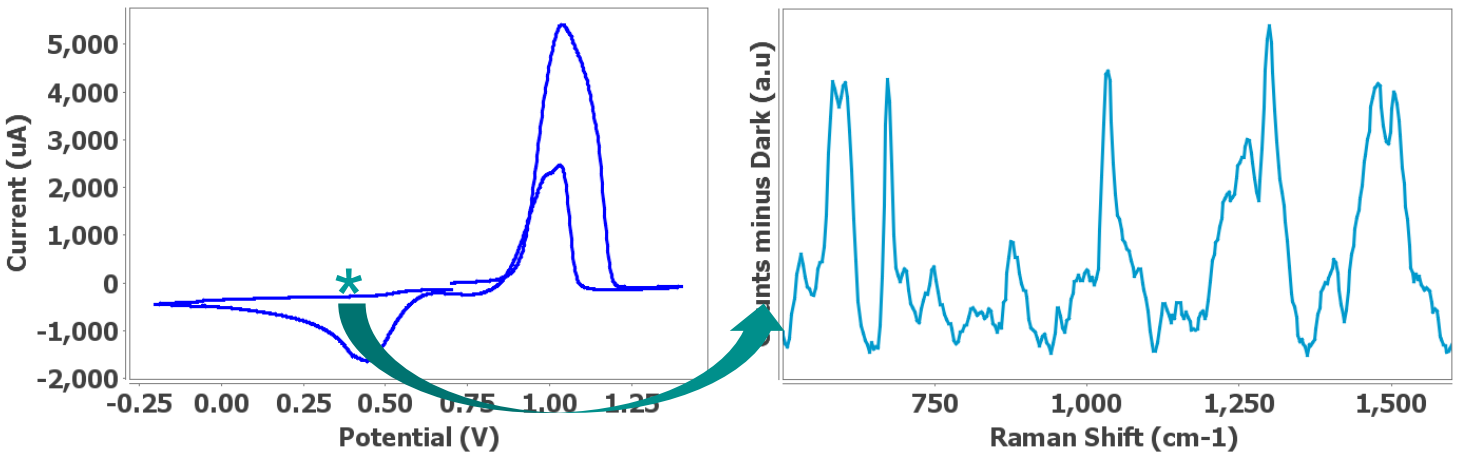
Results

The same methodology was followed to detect chlorpyrifos:



Analysis of Raman signal allows the detection of 3.5 mg·L^{-1}

EC-SERS band (cm^{-1})	Assignment
530	P-O stretching
583	P=S and C-Cl stretching
604	P=S and C-Cl stretching
674	C-Cl stretching
749	P-O-C stretching
876	P-O-C stretching
954	Cl-ring wagging
1034	P-O-C stretching
1129	ring breathing
1264	ring vibration and CH deformation
1300	ring vibration, CH deformation and CC stretching
1406	Cl-ring vibration, CN stretching and CH deformation
1478	ring vibration, C=C stretching and CH deformation
1504	ring vibration

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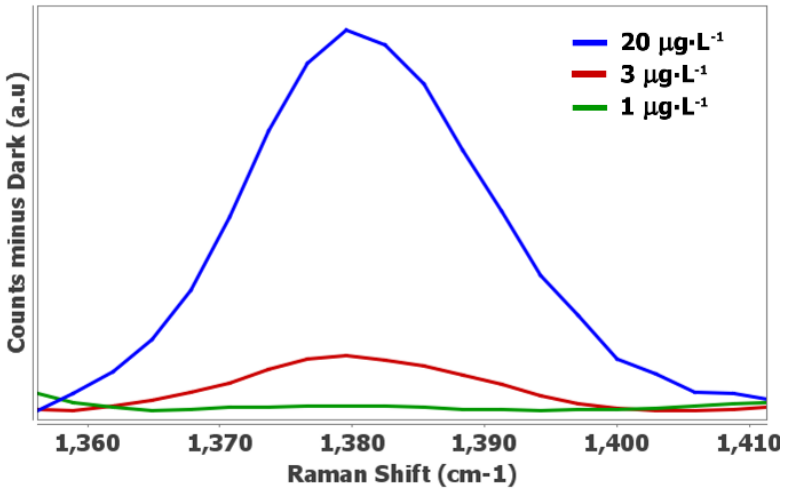
Results

Tap water analysis:

- As proof of concept, three different concentrations of thiram, 1, 3 and 20 µg·L^{-1} were prepared in 0.1 M HCl tab water solution.
- The same procedure (preconcentration and electrochemical activation) was followed:



- Analysis of band at 1380 cm^{-1} shows that **1 µg·L^{-1} thiram is not detected**. On the other hand, **3 and 20 µg·L^{-1} are easily detected.**

Agreement with the previous results (2.4 µg·L^{-1} minimum value detected).

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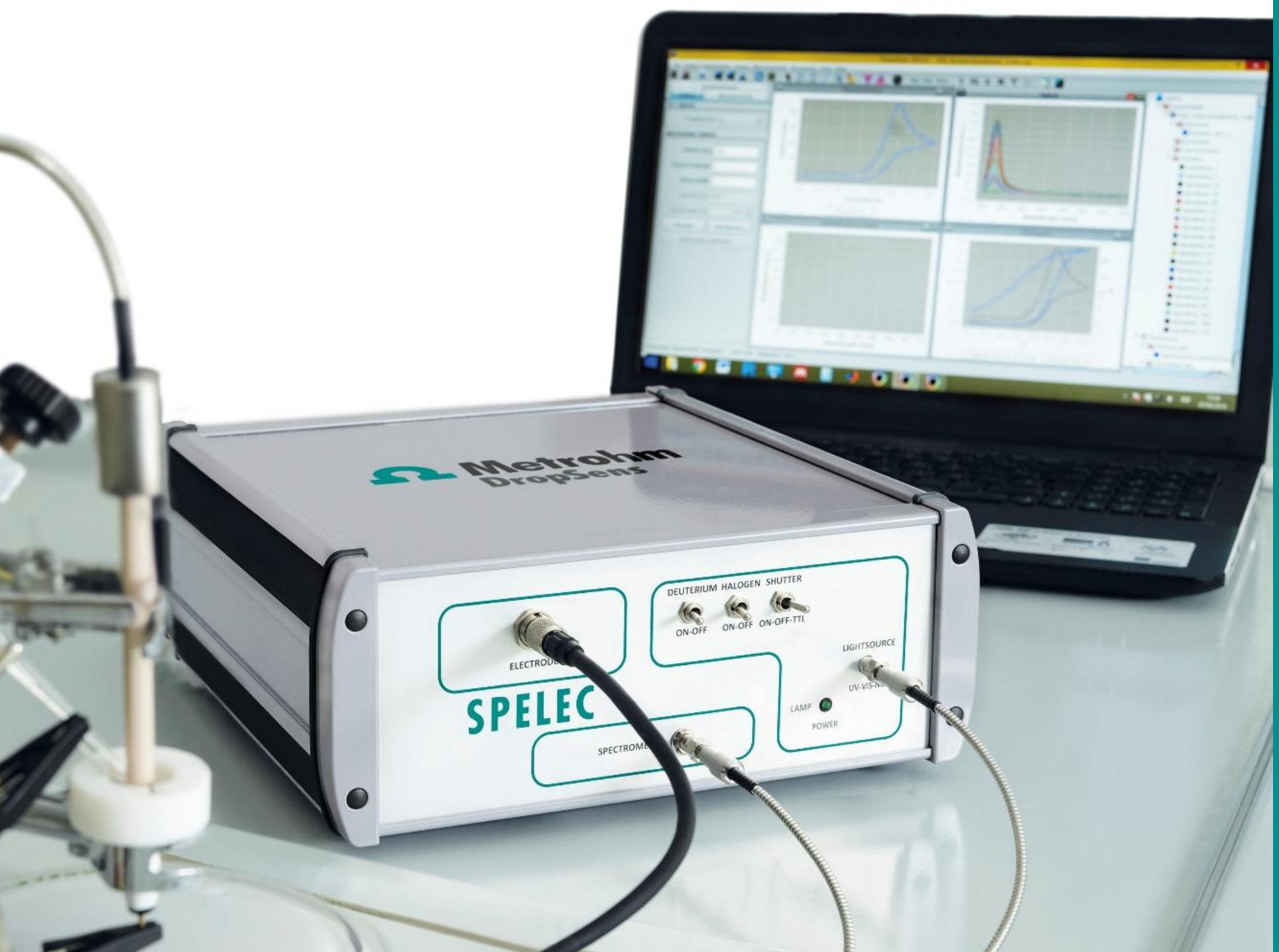

Final remarks

Final remarks

- ✓ Raman spectroelectrochemistry based on **EC-SERS effect** offers an **easy and quick procedure** for detection of pesticides. Complicated instrumentation, tedious pretreatment protocols or time-consuming measurement procedures used in other methods are avoided.
- ✓ EC-SERS procedure proposed in this work demonstrates that the **combination of preconcentration and the electrochemical activation of gold SPEs** allows the detection of **low concentration** of pesticides with **different chemical structure**.
- ✓ Sensitivity of this methodology is demonstrated since the detection of **2.4 $\mu g \cdot L^{-1}$ thiram and 25 $\mu g \cdot L^{-1}$ imidacloprid** is achieved.

https://www.youtube.com/watch?v=uUkhJGFzGAI

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Thank you for you attention!