

Application Note AN_RA-010

利用丝网印刷电极进行 SERS 农药检测

Electrochemical enhancement of Raman intensity for easy detection of thiram and imidacloprid pesticides

The amplification of Raman signals via the electrochemical surface-enhanced Raman scattering (EC-SERS) effect provides an innovative approach to overcome the traditional sensitivity challenge of Raman spectroscopy. Moreover, the electrochemical activation of metallic screen-printed electrodes (SPEs) allows the generation of nanostructures with remarkable SERS performance.

This study uses an EC-SERS method designed for the detection of different pesticides considering gold SPEs as SERS platforms and incorporating a crucial preconcentration stage at the outset. The described setup avoids complex instrumentation, lengthy pretreatment protocols, or other time-consuming procedures commonly required by traditional pesticide detection methods.

INSTRUMENTATION AND SOFTWARE

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

Gold screen-printed electrodes (SPEs, 220BT) were used as the SERS substrate thanks to their electrochemical activation.

The SPELEC RAMAN was controlled with DropView SPELEC, a dedicated software that provides spectroelectrochemical information and includes tools to perform an adequate treatment and analysis of the collected data. 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 screen-printed electrodes.

Table 1. Hardware and software equipment overview.

Equipment	Article number
Instrument	SPELECRAMAN
Probe	RAMANPROBE
Raman spectroelectrochemical cell for SPEs	RAMANCELL
Gold SPE	220BT
Connection cable for SPEs	CAST
Software	DropView SPELEC

EC-SERS DETECTION OF THIRAM AND IMIDACLOPRID

Thiram (PESTANAL®, Sigma-Aldrich), imidacloprid (PESTANAL®, Sigma-Aldrich), ethanol (Merck) and hydrochloric acid (HCl, 25%, Merck) were used as received. All chemicals were analytical grade. Aqueous solutions were prepared using ultrapure water (Direct-QTM 5 system, Millipore).

According to the solubility of each pesticide in aqueous media, initial solutions are prepared as follows: 240 mg/L thiram in ethanol/0.1 mol/L HCl (50%/50%) and 255 mg/L imidacloprid in 0.1 mol/L HCl. Lower concentration solutions are prepared by dilution only using 0.1 mol/L HCl aqueous solution.

Before performing the spectroelectrochemical detection of the selected pesticides, a preconcentration step is implemented. Here, a 60 µL drop of the sample solution is placed onto the SPE, ensuring full coverage of the working, reference, and counter electrodes. Then, the SPE with the drop is placed on a preheated laboratory hot plate set to 34 ° C. Over a 15-minute period, the drop volume is reduced from 60 µL to 25 µL, concentrating HCl from 0.1 mol/L to 0.24 mol/L. The preconcentration is essential for low-concentration detection. Once this step is completed, the SPE is positioned in the Raman cell where the laser is focused onto the working electrode surface for spectroelectrochemical analysis.

The second stage of the procedure combines the electrochemical activation of the gold surface with pesticide detection in a single experiment. The potential is scanned from +0.70 V to +1.40 V and then back to -0.20 V at a scan rate of 0.05 V/s, using a solution containing the pesticide and 0.24 mol/L HCl. This procedure generates gold nanoparticles which are then used to enhance the Raman signal.

Figure 2 displays the cyclic voltammogram and the characteristic SERS spectrum of thiram obtained from analyzing 2.4 mg/L thiram in a 0.1 mol/L HCl solution. Although the Raman spectra are continuously recorded during the experiment, only the most intense spectrum is shown in Figure 2b.

The band centered at 1380 cm1 provides the most favorable characteristics for detecting lower thiram concentrations, as its intensity is significantly higher than that of other bands. Using the preconcentration and EC-SERS procedures described above, thiram detection was achieved at concentrations as low as 12 µg/L. Furthermore, with precise baseline adjustment through polynomial fitting, thiram detection was achieved even at 2.4 µg/L.

The methodology proposed enables the detection of this pesticide at concentrations lower than the maximum residue limits of thiram (0.1 mg/L) of the European Union [1].

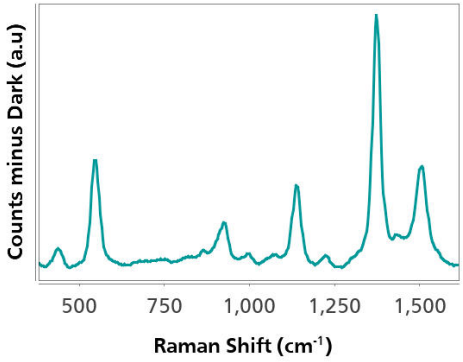
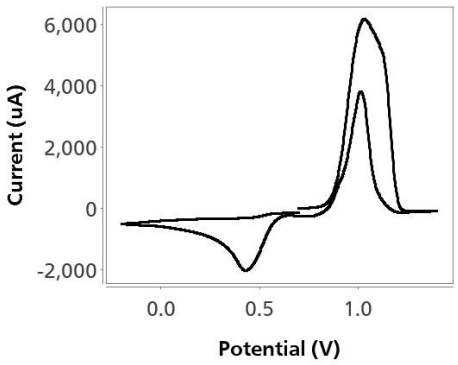


Figure 2. a) Cyclic voltammogram and b) characteristic SERS spectrum obtained of 2.4 mg/L thiram in an aqueous solution of HCl after a preconcentration step.

Imidacloprid was also detected following the same procedure (Figure 3). The analysis of the Raman band located at 1107 cm1 obtained after the initial preconcentration and subsequent EC-SERS measurement reveals notable results. As anticipated, the intensity of this band diminishes with decreasing concentrations—25 µg/L being the minimum detectable concentration using the proposed methodology. Considering that the European Union establishes maximum residue limits for imidacloprid from 0.05 to 10 mg/L [1], this procedure demonstrates the required sensitivity to comply with regulatory standards.



EC-SERS DETECTION OF THIRAM IN TAP WATER

Three different concentrations of thiram (1, 3, and 20 µg/L) were prepared in a 0.1 mol/L HCl tap water solution. As previously demonstrated, the Raman band at 1380 cm1 is particularly useful for thiram detection due to its significantly higher intensity compared to other Raman bands.

Based on the previous findings, the EC-SERS method enables the detection of thiram concentrations above 2.4 µg/L. Thus, the 3 µg/L and 20 µg/L concentrations are easily detectable. However, the 1 µg/L thiram concentration is not detected since Raman intensity at 1380 cm1 is essentially zero.

CONCLUSION

The EC-SERS procedure used in this study demonstrates how the electrochemical activation of gold screen-printed electrodes enables the detection of low concentrations of pesticides with different chemical structures.
The sensitivity of this method shows notable results in the analysis of Raman bands at 1380 cm1 for thiram and 1107 cm1 for imidacloprid, which allow the detection of 2.4 µg/L thiram and 25 µg/L imidacloprid. The approach was also applied to tap water samples, yielding promising results that demonstrate its potential.
Hence, Raman spectroelectrochemistry based on the EC-SERS effect offers users the quick, straightforward, and efficient detection of pesticides, opening doors to new applications in environmental monitoring and food safety.

REFERENCES

1. European Commission. *EU Pesticides Database*. https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en (accessed 2025-06-26).

RELATED APPLICATION NOTES

AN-RA-006 New strategies for obtaining the SERS effect in organic solvents

AN-RA-007 Enhancement of Raman intensity for the detection of fentanyl

AN-RA-008 Easy detection of enzymes with the electrochemical-SERS effect

AN-RA-009 Comparison of SPELEC RAMAN and standard Raman microscopes

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