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Advancements in Analytical Techniques for Rapid Identification of Gunshot Residue and Low Explosives through Electrochemical Detection and Surface-Enhanced Raman Spectroscopy

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ABSTRACT

This research focuses on developing two analytical methods for forensic investigations using electrochemical detection and surface-enhanced Raman spectroscopy. For electrochemical analysis, screen-printed carbon electrodes are used to detect metals and nitrate/nitrite compounds commonly found in gunshot residue. Gold electrodeposition and copper modification enhance sensitivity and catalytic activity, respectively. Additionally, a screen-printed gold electrode modified with gold nanoparticles enables surface-enhanced Raman spectroscopy, requiring only a single drop of sample solution. Testing includes various compounds relevant to forensic identification, with Origin software used for data analysis. These techniques provide rapid and precise onsite examination of gunshot residue and low explosives, eliminating the need for benchtop instruments. Overall, these advancements enhance forensic inquiries and contribute to the ongoing progress of forensic science, aiding law enforcement agencies worldwide in seeking justice.

Electrochemical detection

Electrode preparation

- For Au-SPCE, a SPCE was modified in 10 mM **$HAuCl_4$** at -0.3 V for 180 s.
- For Cu/Au-SPCE, the Au-SPCE was further modified in 0.1 M **$CuSO_4$** using CVs (-1 to 0 V).

Electrochemical measurement

- For metals, Au-SPCE dipped in 30 mL of 0.1 M acetate buffer pH 4.5. **SWASV** applied at -1.5 V for 2 min and scanned -1.5 to 0.0 V
- For nitrate/nitrite, **LSV** done using Cu/Au-SPCE; scanned from -0.1 to -1.4 V in 0.1 M Na_2SO_4 and 1.2 mM KCl electrolyte

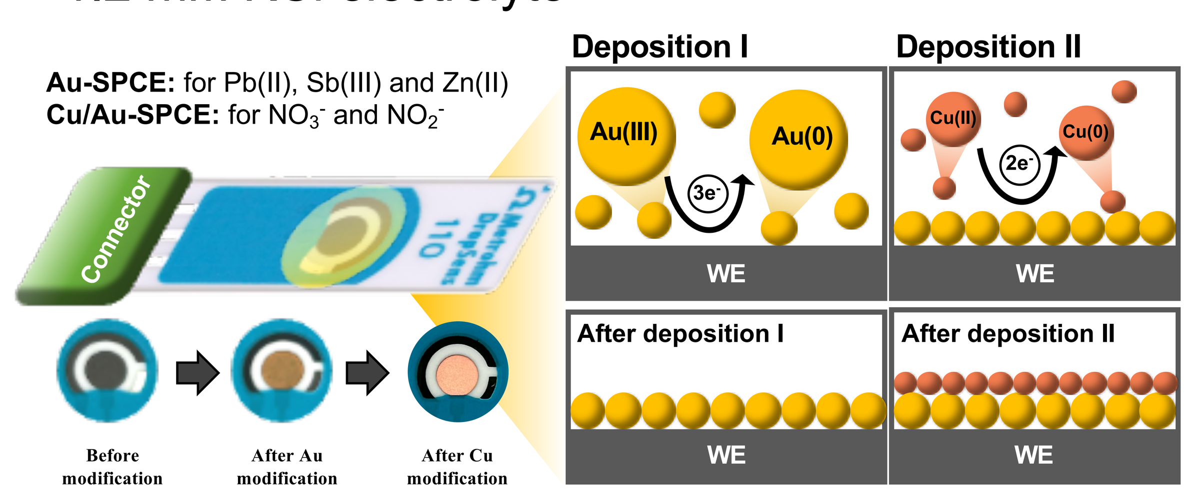

Fig. 1. Electrodeposition of Au(III) and Cu(II) on a SPCE

Calibration of Pb/Sb/Zn

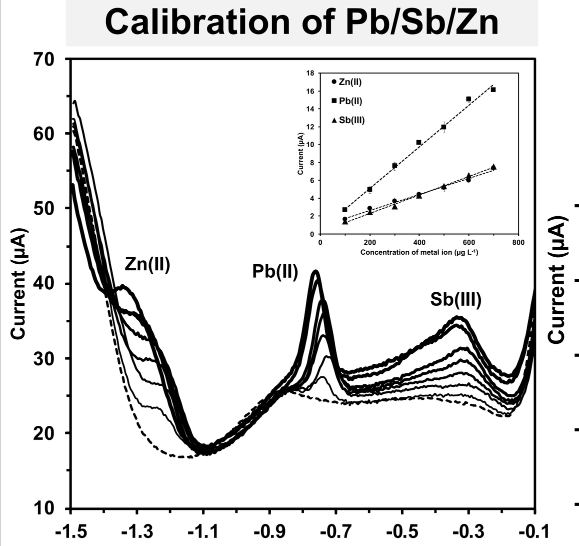

Fig. 2. SWASV detection of Zn, Pb, and Sb standards using the Au-SPCE and calibration.

Calibration of NO_3^-/NO_2^-

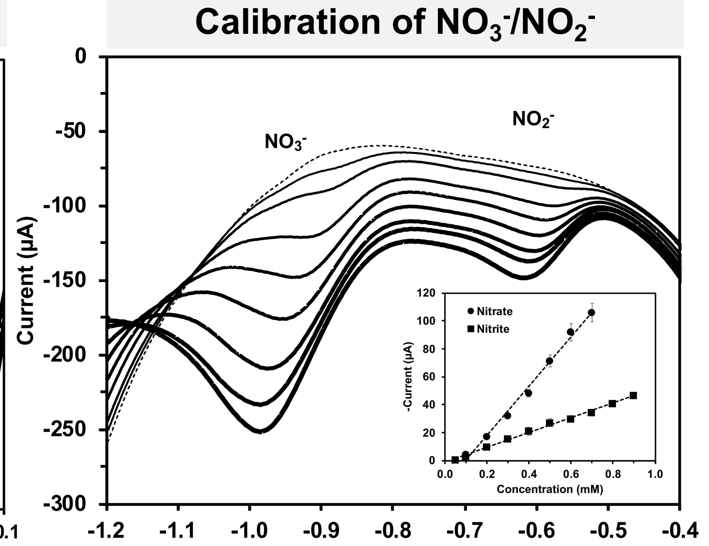

Fig. 3. Detection of nitrate/nitrite under LSV using the Cu/Au-SPCE and calibration.

Table 1. Sample analysis of spent cartridges (set I-II) and relevant surfaces (set III-IV) through monitoring Pb and Sb contents found in the selected samples using Au-SPCE under SWASV.

Sample	Found concentration (µg L^{-1})	
	Pb(II)	Sb(III)
Set I: 9 mm Luger spent cartridge		
Sample 1	361 ± 17	550 ± 27
Sample 2	172 ± 8	393 ± 12
Sample 3	276 ± 6	514 ± 17
Set II: 38 Special Ammo spent cartridge		
Sample 4	149 ± 9	470 ± 43
Sample 5	93 ± 11	233 ± 51
Sample 6	77 ± 15	365 ± 38
Set III: Surface of bullet recovery tank*		
Sample 7	726 ± 10	250 ± 33
Sample 8	845 ± 28	458 ± 26
Sample 9	2,074 ± 21	571 ± 25
Set IV: Surface of bullet recovery tank shield*		
Sample 10	1,089 ± 20	439 ± 13
Sample 11	568 ± 24	848 ± 18
Sample 12	1,311 ± 16	659 ± 13

Table 2. Sample analysis of low explosives including black powder (S1-S3) and smokeless gunpowder (S4-S6) through determination of nitrate and nitrite levels in both unburned and burned forms of samples using Cu/Au-SPCE under LSV.

Sample	$[NO_3^-]$ found (mM)		$[NO_2^-]$ found (mM)	
	Unburned	Burned	Unburned	Burned
S1: GOEX Black rifle powder	499.2 ± 6.4	n.d.	34.7 ± 1.0	52.5 ± 6.7
S2: American pioneer powder FFFG	289.4 ± 6.5	87.7 ± 2.1	34.3 ± 0.8	48.7 ± 4.8
S3: HODGDON Pyrodex	226.8 ± 6.0	n.d.	23.6 ± 1.2	34.5 ± 2.6
S4: HODGDON RETUMBO® rifle powder	n/a	41.2 ± 2.3	n/a	39.1 ± 1.8
S5: HODGDON H4831SC® rifle powder	n/a	82.2 ± 0.7	n/a	81.4 ± 1.4
S6: HODGDON H1000® rifle powder	n/a	89.8 ± 3.1	n/a	87.5 ± 1.5

*n.d. represents not detectable
**n/a represents not applicable

Conclusion

- The two electrodes were successfully developed using gold and copper for surface enhancement.
- The developed sensors were applied for analyzing lead, antimony, zinc, nitrate, and nitrite in GSR and low explosives.
- This developed electrochemical system offers simple and rapid examinations of forensic evidence found at a crime scene.

Reference

1. Snelling, W.O., and C. G Storm, The Analysis of Black Powder and Dynamite. 1913: Washington, Govt. print. off.
2. Yasir Abir, A., et al., Cu-electrodeposited gold electrode for the sensitive electrokinetic investigations of nitrate reduction and detection of the nitrate ion in acidic medium. Results in Chemistry, 2023. 5: p. 100702.

Surface-Enhanced Raman Spectroscopy (SERS)

SERS material preparation

- For Au-SPGE, a SPGE (DropSens, Switzerland) was modified in 0.01 M **$HAuCl_4$** at -0.3 V for 180 s.

Portable SERS instrument

- The FirstDefender RMX Handheld Chemical Identification (Thermo Fisher Scientific, USA) with 785 nm laser was employed for this study.

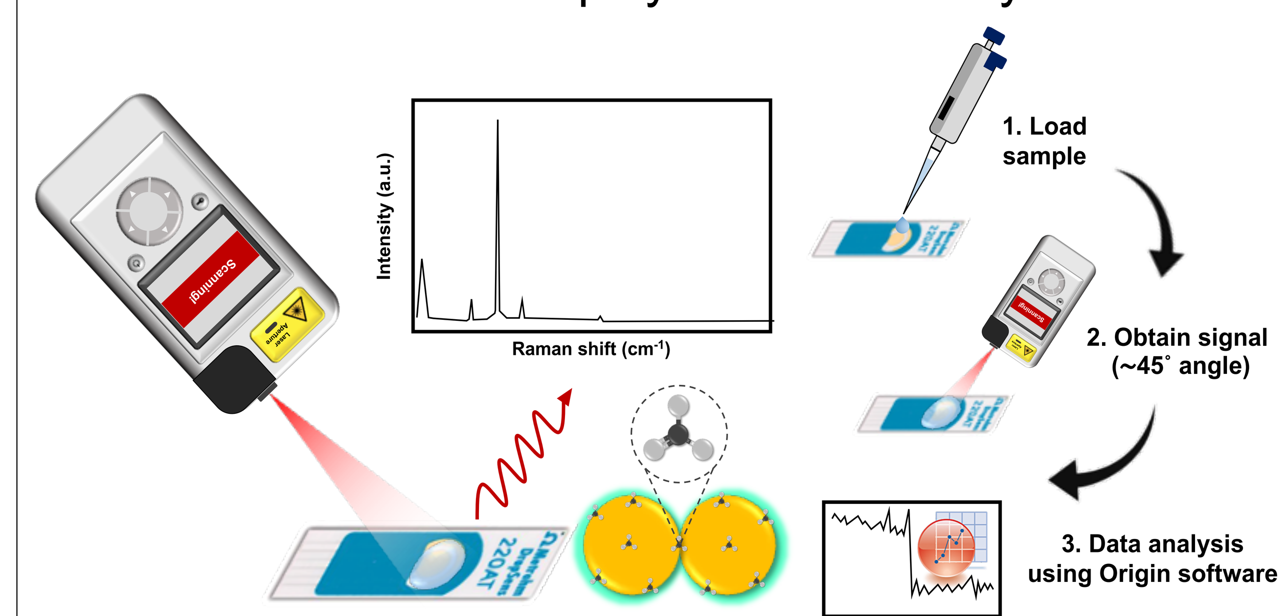

Fig. 4. Operating procedure for SERS detection using a Au-SPGE integrated with a portable SERS instrument.

Effect of deposition time of gold on KNO_3 detection

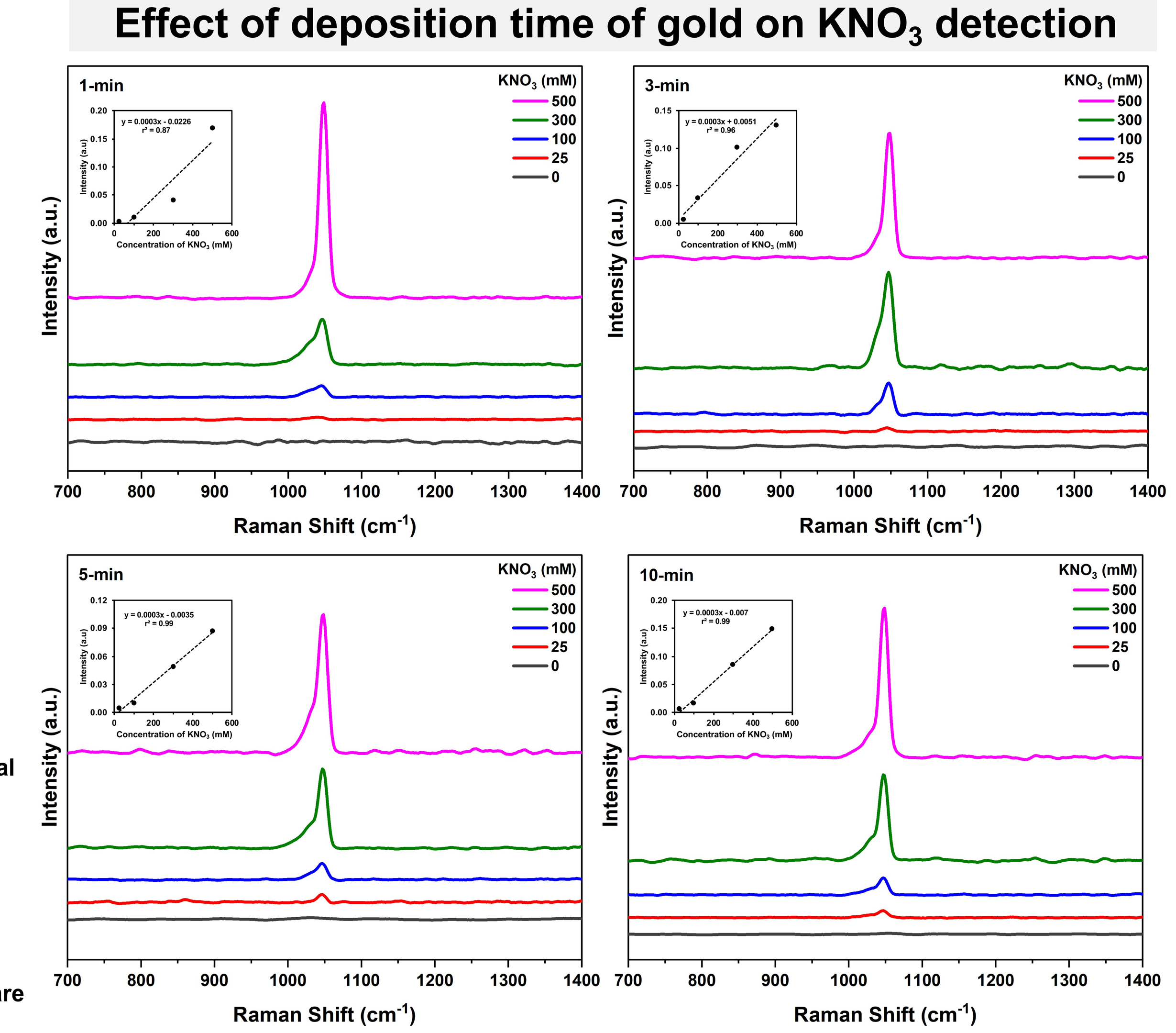

Fig. 5. SERS spectra with their calibrations obtained from detection of KNO_3 in a concentration range of 0-500 mM at varying deposition times (1 to 10 min) of Au nanostructures on SPGEs *via* electrodeposition.

Identifying $KClO_4/C_6H_5COONa$

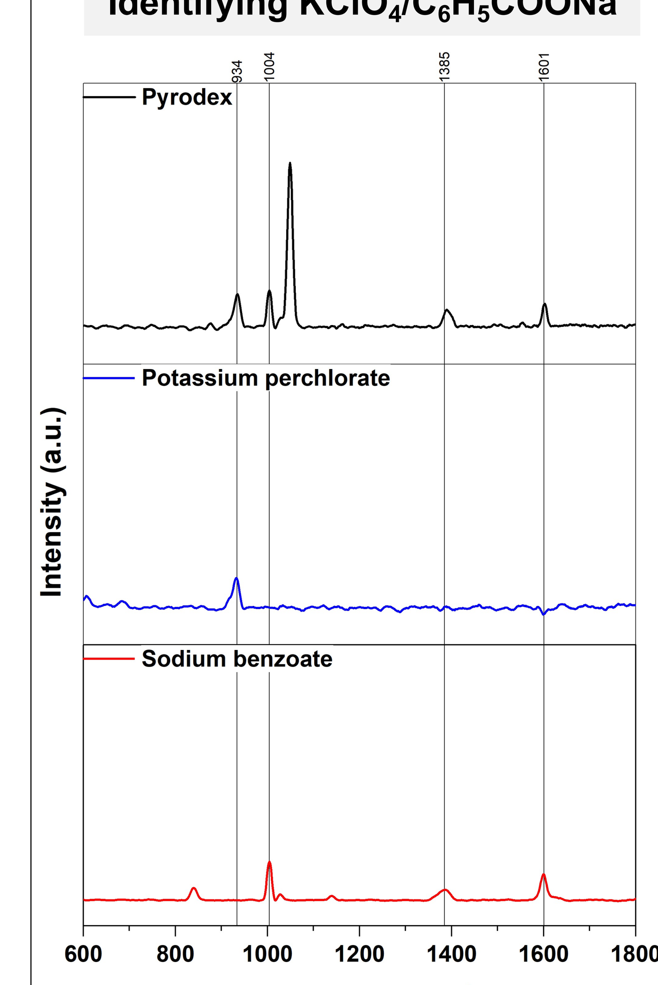

Fig. 6. SERS detection of Pyrodex gunpowder compared to $KClO_4$ and C_6H_5COONa standards using the SPGE with gold deposited.

Identifying DPA/its derivatives

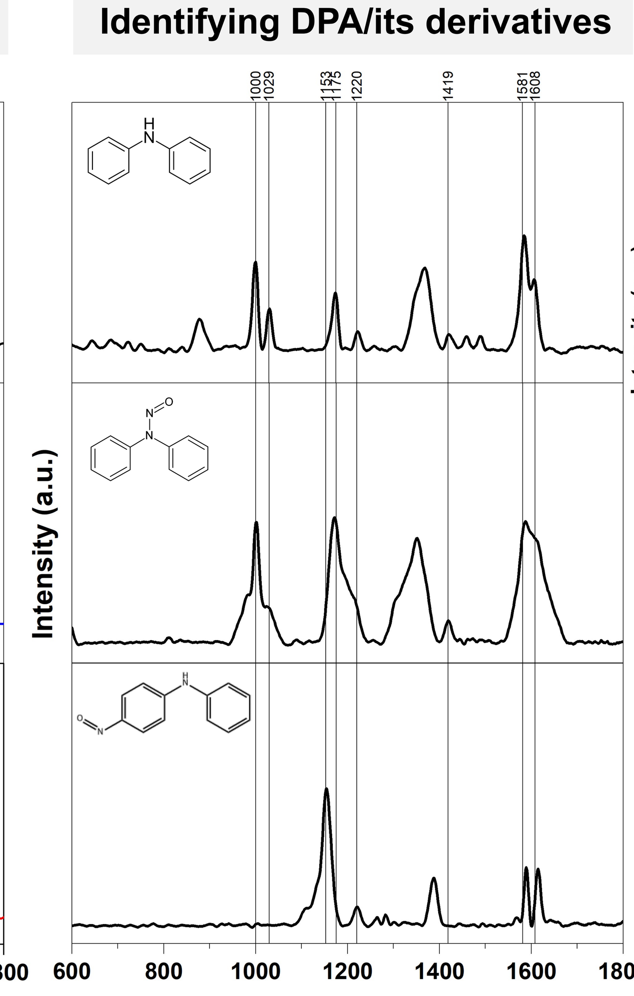

Fig. 7. SERS detection of diphenylamine (DPA) standards aligned with its nitro derivatives (*N*-nitroso-DPA and 4-nitroso-DPA).

Calibration of DPA | Detection of smokeless powder

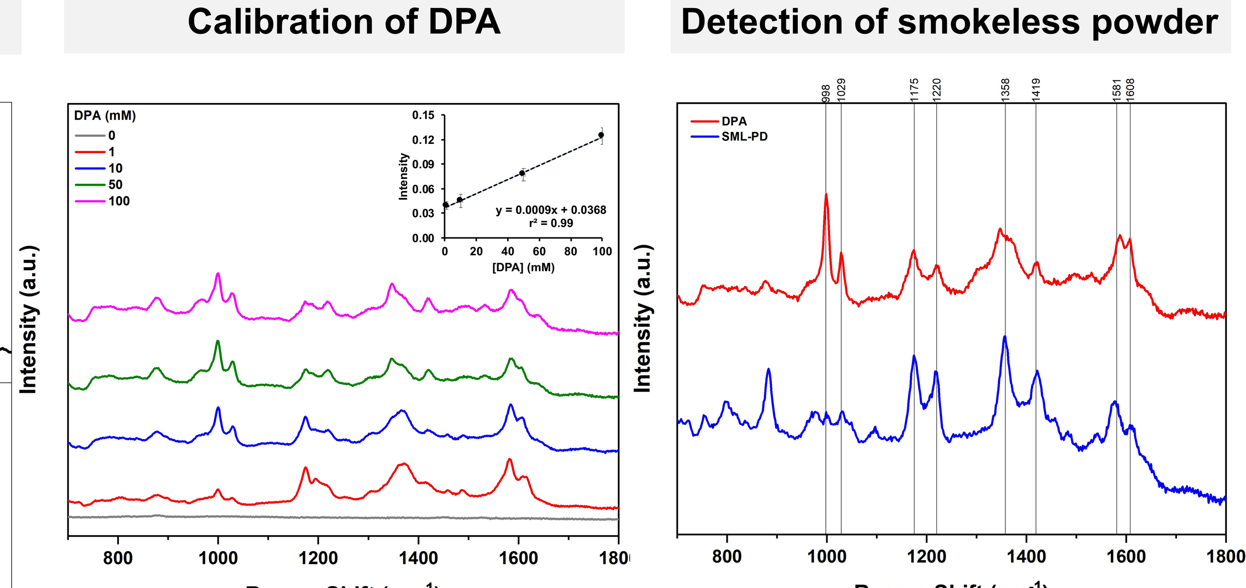

Fig. 8. SERS spectra and its calibration plot of DPA in 0-100 mM (left) and detection of smokeless powder compared to DPA standard (right).

Conclusion

- For the sensor surface enhancement, 5 min for Au electrodeposition was selected.
- The method offers rapid sensing of KNO_3, $KClO_4$, C_6H_5COONa, DPA and its derivatives aiming for low explosives and GSR analyses.

Reference

1. López-López, et al. Anal Bioanal Chem 408, 4965–4973 (2016).
2. Ott, C.E. et al. Forensic Chemistry, 34, p. 100492 (2023).