

Appendix D

Firing experiments and analysis of gunshot residues for Pb(II) and Cu(II) by SWASV

This Appendix describes the firing experiments carried out to simulate gunshot residues (GSRs) for lead bullets and copper-jacketed bullets as well as the analysis of GSRs using the nanostructure modified gold leaf (section 3.5) by SWASV.

1. Firing experiments

GSR was produced on a zinc metal sheet target (2-mm thick, cut to 300 mm × 300 mm, MARTON, Thailand) by firing a single bullet at the zinc target. The firearm was a CZ 75B CAL.9 mm LUGER semi-automatic pistol (Czech Republic). The bullet was discharged horizontally at the target that was clamped onto a square metallic frame on a table (750 mm in height). The shooter is seated on a chair with the gun pointing at the center of the target at the distance of 50 mm between the nozzle and the target. Each firing was carried out in triplicates for the two types of 9 mm bullets, viz. (i) lead round nose (Thai Arms Co. Ltd., Thailand) and (ii) copper-jacketed lead core hollow point bullets (Bullet Master Co., Ltd., Thailand).

2. Swab sampling, extraction and analysis of GSR by SWASV

A 100 µL aliquot of 5% (v/v) nitric acid was added to one end of a cotton bud. The cotton bud was then swabbed along the internal edge of bullet hole for 20 cycles. The same bud was then rubbed along the peripheral area surrounding the entrance bullet hole *ca.* 15 mm from the center of the hole. The bud was then immersed into 3.00 mL of 5%(v/v) nitric acid. The solution was stirred using the bud for 5 s and then the bud was left in the acid for 20 s for extracting the GSR. After extraction, the bud was removed and the acid extract analyzed (see below) using the modified gold leaf sensor.

3. Analysis of GSR extract by SWASV

A 20 μL aliquot of the acid GSR extract was dispensed into 30.00 mL of the supporting electrolyte (0.1 mmol L^{-1} acetate buffer pH 4.5, containing 1.0 mmol L^{-1} NaCl). Square wave anodic stripping voltammetry (SWASV) was employed for the quantification of Pb(II) and Cu(II) using the modified gold leaf sensor. The sequence for SWASV was as follows: (i) conditioning step: 0.3 V vs Ag/AgCl for 15 s; (ii) electrodeposition of Pb(0): -0.8 V vs Ag/AgCl for 120 s; (iii) stripping step: -0.8 V to 0.3 V vs Ag/AgCl, ($t_{\text{equilibration}} = 10$ s; $E_{\text{step}} = 5$ mV, amplitude = 25 mV and frequency = 50 Hz) and (iv) cleaning step: 0.3 V vs Ag/AgCl for 30 s. Magnetic stirring was only applied at steps (i), (ii) and (iv), respectively. The anodic peak current was used to calculate the concentration of Pb(II) and Cu(II) in the extract. The concentrations of these metals were measured in all the swabs of both lead-bullet and copper-jacketed bullet firings.

Control analysis was carried out under the same condition for extracts of swabs obtained from three unused zinc metal sheets. In one sampling cycle, the acid moistened bud was rubbed on the edge of an unused zinc metal sheet at the distance of 7.85 cm. The same acid moistened bud was repeatedly rubbed on the same path for 20 cycles prior immersing the bud into the vial containing 3.00 mL of 5%(v/v) nitric acid. or preparing the control extract. The 7.85-cm distance is approximately equal to the rubbing path length for collecting the GSR in one cycle of the internal edge (*ca.* 3.2 cm) plus the peripheral length surrounding the entrance of the bullet hole (*ca.* 4.7 cm).