A forensic study: Lead determination in gunshot residues

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A B S T R A C T

Electrochemical lead analyses of gunshot residues (GSRs) were performed using an acidic solution with a bare gold microelectrode in the presence of chloride ions. GSRs from four different guns (0.38 in. revolver, 12 caliber pump-action shotgun, 0.38 repeating rifle, and a 0.22 caliber semi-automatic rifle) and six different types of ammunition (CleanRange®, normal, semi-jacketed, especial 24g®, 3T®, CBC®, and Eley®) were analyzed. Results obtained with the proposed methodology were compared with those from an atomic absorption spectrometry analysis, and a paired Student’s t-test indicated that there was no significant difference between them at the 95% confidence level. With this methodology, a detection limit of 1.7 nmol L−1 (3σ/slope), a linear range between 10 and 100 nmol L−1, and a relative standard deviation of 2.5% from 10 measurements were obtained.

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1. Introduction

Forensic analysis has improved significantly over the past few years, mainly owing to the continued increase in the requirement for more reliable results in order to diminish erroneous convictions. Lead determination in the forensic field can be performed on different kinds of samples, such as drugs [1,2], disease cases [3,4], teeth [5,6], and particularly gunshot residues (GSRs) [7–18]. GSRs are residues from firearm discharge, and they consist of vapors and particulate materials that are deposited onto the hands (mainly the index fingers and thumbs), face, and clothes of the shooters. If these particles are collected and reliably analyzed, the suspect can be successfully identified. GSRs have three main inorganic elements: lead, barium, and antimony. The analysis of lead from GSRs can be used as an indicator of the presence of the residues.

Electrochemistry methods, particularly stripping analysis, are often used for the determination of metals such as lead [19–24]. In the past few years, efforts have been made to replace the commonly used mercury electrode [25–27] with less toxic ones. Nowadays, the most common alternative is the bismuth film electrode [28–32], but carbon [33–35] and gold electrodes [36,37] have also been used.

As for other metallic substrates, the deposition of another metal (e.g., lead) onto gold electrodes occurs through bulk and underpotential deposition (upd) [38]. The upd is a consequence of the stronger bonding force between the metal being deposited and the substrate as compared to the bonding force between similar atoms [38,39]. This difference in bonding energy results in the formation of a monolayer of the metal, which is followed by the formation of successive layers owing to the bulk deposition [38].

The use of a microelectrode to perform stripping analysis has some advantages, such as the possibility of carrying out the experiment in low-volume samples and the miniaturization of the apparatus [36]. In addition, since one of the dimensions of a microelectrode is smaller than the thickness of the Nernst diffusion layer, an efficient mass transport to the electrode surface is achieved, resulting in a steady-state response in a very short time. The efficiency of mass transport eliminates the need to stir the solution in the pre-concentration step (as required when a conventional sized electrode is used in stripping analysis), considerably reducing an important source of errors.

In this study, the amount of lead in GSR samples was quantified using a gold microelectrode and stripping analysis. All of the parameters involved in the lead determination, including the amount of chloride used, were optimized. The results obtained by the electrochemistry technique were compared with those of an atomic absorption analysis.

2. Experimental section

2.1. Reagents

Solutions of lead nitrate, potassium chloride, potassium ferricyanide, and EDTA were prepared by dissolving the reagents in deionized water processed through a water purification system (18.0 MΩ cm−1, Nanopure Infinity, Barnstead, Iowa, USA). The nitric acid solution was prepared by diluting the stock solution as necessary. All solid reagents (Merck, Darmstadt, Germany) were of analytical grade, and were used without further purification.
2.2. GSR collection and analysis

The GSR was collected during a shooting lesson of the “Dr. Coriolano Nogueira Cobra” police academy (ACADEPOL) of São Paulo, and at a shooting range (Centaurus®) in São Paulo, Brazil. Four different guns were used: one handgun (0.38 in. revolver) and three long-barreled guns (12 caliber pump-action shotgun, 0.38 repeating rifle, and a 0.22 caliber semi-automatic rifle). The ammunition types used were CleanRange®, normal, semi-jacketed, especial 24g®, 3T®, CBC®, and Eley®.

GSRs were collected from the right hand of the shooters immediately after the shoot, using a cotton swab soaked in a 2% (m/v) EDTA solution, as recommended by Reis et al. [40]. The entire hand was scrubbed in order to collect the gunshot residue. The cotton swabs were then placed in sterile vials, and 10 mL of a 10% (m/v) HNO₃ solution was added. The vials were subjected to ultrasound for 2 h at 60 °C, before the extracted solutions were analyzed by square wave anodic voltammetry (SWV) and atomic absorption spectrometry (AAS).

2.2.1. Square wave voltammetry

An Autolab PGSTAT30 bipotentiostat (Eco Chemie, Utrecht, Netherlands) connected to a microcomputer was used for the voltammetric measurements. The gold microelectrode was constructed by connecting a gold microfiber (diameter = 25 μm) to a nickel/chromium wire with a silver ink conductive paint (Joint Metal Comércio LTDA, São Paulo, Brazil), which was then inserted in a glass capillary and flame-sealed. The surface of the microelectrode was polished with alumina powder (1 μm, Alfa Aesar, Ward Hill, MA, USA) on a microcloth polishing pad. The radius of the microelectrode was determined by measuring the steady-state current in a potassium ferricyanide solution of known concentration.

Prior to each lead analysis, the microelectrode surface was polished with the alumina powder and washed with deionized water.

The lead analysis was then conducted on the extraction solution plus a known amount of chloride using SWV. And if necessary, the sample was diluted. The analysis parameters were optimized to the following values: E_cleaning = 0.7 V, t_cleaning = 120 s, E_deposition = −0.7 V, E_final = 0.1 V, t_deposition = 480 s, t_equilibrium = 15 s, frequency = 500 Hz, E_step = 5 mV, and E_amplitude = 25 mV.

2.2.2. Atomic absorption spectrometry (AAS)

The lead content of the samples was also determined using a Zeenit 600 graphite furnace atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). This apparatus has transverse heated graphite tubes with integrated pyrolytically coated platforms, a Zeeman-effect background correction system, and a hollow lead cathode lamp (Analytik Jena AG, Jena, Germany). The instrument settings for the spectrometer were 4 mA of lamp current, a band-pass of 0.8 nm, and a hollow lead cathode lamp (diameter=25 μm). The calibration curve (2 μg Pb in 15% (v/v) HNO₃ and 10 g L⁻¹ Mg, prepared from Pb(NO₃)₂ and Mg(NO₃)₂ salts, respectively (Merck, Darmstadt, Germany). The calibration curve (2–40 μg L⁻¹) was constructed using analytical grade Tritisol® solutions of 1000 mg L⁻¹ of Pb (Pb(NO₃)₂) diluted in 0.1% v/v HNO₃. The samples were analyzed without prior treatment. Samples with high concentrations of lead were diluted in high-purity water, and the analytical signals of each sample were recorded in triplicate.

Fig. 1. Square wave voltammograms obtained with a gold microelectrode (r = 12.5 μm) in a solution containing 0.1% (m/v) HNO₃, 0.01% (m/v) EDTA, and 0.1 μmol L⁻¹ Pb(II). Parameters: E_cleaning = 0.7 V, t_cleaning = 120 s, E_depot = −0.7 V, t_depot = 480 s, E_final = 0.1 V, frequency: 500 Hz, E_step = 5 mV, E_amplitude = 25 mV, t_equilibrium = 10 s.

3. Results and discussion

3.1. Optimization of parameters of SW stripping voltammetry

As described in Section 1, the use of microelectrodes in stripping analysis can be highly advantageous, as the efficiency of the mass transport eliminates the need to stir the solution in the pre-concentration step, considerably reducing an important source of errors in stripping analysis. Fig. 1 shows ten successive stripping voltammograms, recorded without stirring the solution using a gold microelectrode in a 0.1% (m/v) HNO₃ + 0.01% (m/v) EDTA + 0.1 μmol L⁻¹ Pb(II) solution. In all voltammograms a peak at −0.6 V can be observed, which can be related to the electrochemical oxidation of lead. The peak current varied between 49 and 53 nA with a mean current peak of 51 nA and a relative standard deviation of 2.5%. These results confirm the good repeatability obtained using a microelectrode in stripping analysis.

Experiments to optimize the SWV stripping parameters for the lead analysis were performed using a 0.05% (m/v) HNO₃ + 0.01% (m/v) EDTA + 0.1 μmol L⁻¹ Pb(II) solution. All parameters involved in the SWV were evaluated and were chosen according to the highest current obtained for each parameter.

Fig. 2. Influence of frequency on peak current. Depositing solution: 0.1% (m/v) HNO₃, 0.01% (m/v) EDTA, 50 mM L⁻¹ Cl⁻, and 0.1 μmol L⁻¹ Pb(II). Studied frequencies: 20, 50, 90, 120, 150, 200, 250, 300, 400, 500, and 1000 Hz. Parameters: E_cleaning = 0.7 V, t_cleaning = 120 s, E_depot = −0.6 V, t_depot = 480 s, E_final = 0.1 V, frequency: 500 Hz, E_step = 5 mV, E_amplitude = 25 mV, t_equilibrium = 10 s.
The effect of the deposition time on the peak current was evaluated at seven different values (30, 60, 120, 240, 480, 600, and 720 s). A significant increase in the current value was observed as the deposition time was increased to 480 s; beyond this value, the enhancement was negligible and so the deposition time was chosen to be 480 s.

The parameter most affected by the current value was the frequency. A significant increase in the peak current was observed as the frequency changed to higher values (Fig. 2). As reported by Bard and Faulkner [22], frequencies between 1 and 500 Hz are usually used in SWV, and therefore, we chose to work at a frequency of 500 Hz.

Seven different values of the deposition potential were studied (−0.4, −0.5, −0.6, −0.7, −0.8, −0.9, and −1.0 V). An applied potential of −0.7 V was chosen, as this presented the highest current value not to be significantly influenced by hydrogen evolution. Finally, the step potential and amplitude potential were optimized, from experimental ranges of 1–15 mV and 5–35 mV, respectively. No significant change in these parameters with respect to the current was observed, and thus, values of 5 mV for the step potential and 25 mV for the amplitude potential were chosen. All optimized parameters and the chosen values are summarized in Table 1.

As already reported [37], the addition of chloride ions to the depositing solution plays an important role in lead deposition. Therefore, the amount of chloride added to the solution was studied. Fig. 3 shows the effect on the current peak, relative to the electrochemical oxidation stripping lead. An increase in the current of a factor of three, until the chloride concentration of lead, with variation in the chloride concentration. An increase in the current peak, relative to the electrochemical oxidation stripping current. Subsequently, the figures of merit (listed in Table 2) were determined using the previously optimized parameters and conditions.

### 3.2. GSR analysis

As detailed in the Experimental section, samples were obtained from a 0.38 in. revolver, 12 caliber pump-action shotgun, 0.38 repeating rifle, and a 0.22 caliber semi-automatic rifle. The ammunition types used were CleanRange®, normal, semi-jacketed, especial 24g®, 3T®, CBC®, and Eley®. With the CleanRange® ammunition, each shooter fired 18 times in a row, while only one shot was discharged with the other types of ammunition.

After the extraction process, the lead content of the GSRs was determined using both the proposed method and a reference method (AAS). It is important to note that the lead determination by SWV stripping required the use of the standard addition method (see Fig. 4).

The Student's t-test was applied to the results obtained by SWV stripping and those found using AAS, and a comparison is shown in Table 3. The paired Student's t-test indicated that there was no significant difference between the results obtained from both methods at the 95% confidence level. Hence, it can be concluded that the proposed strategy is reliable and can be successfully applied to lead determination in GSR analysis.

Two interesting aspects can be highlighted from analysis of the results. Firstly, it can be seen that the amount of lead present in the GSR from the revolver is smaller than that from long-barreled guns. Secondly, the CleanRange® ammunition is not supposed to have lead as a constituent [41]. However, as shown here, lead was detected in the residues originating from the discharge of a gun containing this type of ammunition. Sarkis et al. have already reported the presence of lead in this ammunition [42]. Our result also corroborates reports from police officers, who declared that they felt a slight sweet taste in their mouth following shooting lessons with the CleanRange® ammunition, indicating the presence of lead in the air.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition time</td>
<td>480 s</td>
</tr>
<tr>
<td>Deposition potential</td>
<td>−0.7 V Ag/AgCl</td>
</tr>
<tr>
<td>Frequency</td>
<td>500 Hz</td>
</tr>
<tr>
<td>Step potential</td>
<td>5 mV</td>
</tr>
<tr>
<td>Amplitude potential</td>
<td>25 mV</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Equation</th>
<th>( U/nA = 3 \times 10^{-10} \pm 1 \times 10^{-10} + 0.28 \pm 2 \times 10^{-3} \cdot [Pb^{2+}] \cdot \text{mol L}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear range</td>
<td>( 1 \times 10^{-9} \cdot 1 \times 10^{-10} \cdot \text{mol L}^{-1} )</td>
</tr>
<tr>
<td>Detection limit (3σ/slope)</td>
<td>1.8 mmol L(^{-1})</td>
</tr>
<tr>
<td>Quantification limit (10σ/slope)</td>
<td>5.6 mmol L(^{-1})</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of Cl\(^{-}\) concentration on I\(_p\) of the stripping of lead. Parameters: \( E_{\text{cleaning}} \): 0.7 V, \( t_{\text{cleaning}} \): 120 s, \( E_{\text{dep}} \): −0.7 V, \( t_{\text{dep}} \): 480 s, \( E_{\text{amplitude}} \): 0.1 V, frequency: 500 Hz, \( E_{\text{amplitude}} \): 25 mV, \( t_{\text{equilibrium}} \): 10 s, Deposit solution: 0.1% (m/v) HNO\(_3\), 0.01% (m/v) EDTA, 50 mmol L\(^{-1}\) Cl\(^{-}\), and 0.1 mmol L\(^{-1}\) Pb(II).

Fig. 4. Square wave voltammograms obtained with a gold microelectrode (r = 12.5 μm) in the presence of a solution containing GSR (full line) and successive additions of a Pb(II) solution of known concentration (dashed lines). Parameters: \( E_{\text{cleaning}} \): 0.7 V, \( t_{\text{cleaning}} \): 120 s, \( E_{\text{dep}} \): −0.7 V, \( t_{\text{dep}} \): 480 s, \( E_{\text{amplitude}} \): 0.1 V, frequency: 500 Hz, \( E_{\text{amplitude}} \): 5 mV, \( E_{\text{amplitude}} \): 25 mV, \( t_{\text{equilibrium}} \): 10 s. Inset: calibration curve obtained from the voltammograms.
Table 3

Results obtained from two different methods (stripping and AAS) for analysis of GSR samples.

<table>
<thead>
<tr>
<th>Gun</th>
<th>Ammunition</th>
<th>Number of shots</th>
<th>“Stripping” mg Pb&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>AAS/mg Pb&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>f&lt;sub&gt;recovered&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38 revolver</td>
<td>CleanRange®</td>
<td>18</td>
<td>0.014±0.001</td>
<td>0.017±0.0001</td>
<td>1.00±0.0001</td>
</tr>
<tr>
<td>0.38 revolver</td>
<td>CleanRange®</td>
<td>18</td>
<td>0.015±0.002</td>
<td>0.014±0.0001</td>
<td>0.30±0.0001</td>
</tr>
<tr>
<td>0.38 revolver</td>
<td>CleanRange®</td>
<td>18</td>
<td>0.017±0.002</td>
<td>0.0154±0.0001</td>
<td>1.12±0.0001</td>
</tr>
<tr>
<td>0.38 revolver</td>
<td>Normal</td>
<td>1</td>
<td>0.019±0.008</td>
<td>0.026±0.001</td>
<td>1.47±0.0001</td>
</tr>
<tr>
<td>12-caliber pump-action shotgun</td>
<td>3T®</td>
<td>1</td>
<td>0.021±0.008</td>
<td>0.019±0.002</td>
<td>0.40±0.0001</td>
</tr>
<tr>
<td>12-caliber pump-action shotgun</td>
<td>3T®</td>
<td>1</td>
<td>0.021±0.008</td>
<td>0.022±0.0004</td>
<td>0.07±0.0004</td>
</tr>
<tr>
<td>0.38 repeating rifle</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.022±0.008</td>
<td>0.022±0.0002</td>
<td>0.20±0.0002</td>
</tr>
<tr>
<td>0.38 repeating rifle</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.03±0.01</td>
<td>0.031±0.0005</td>
<td>0.91±0.0005</td>
</tr>
<tr>
<td>Semi automatic 0.22 caliber rifle</td>
<td>Eley®</td>
<td>1</td>
<td>0.039±0.006</td>
<td>0.046±0.001</td>
<td>1.9±0.0001</td>
</tr>
<tr>
<td>0.38 repeating rifle</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.04±0.01</td>
<td>0.0445±0.0004</td>
<td>0.28±0.0004</td>
</tr>
<tr>
<td>Semi automatic 0.22 caliber rifle</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.04±0.02</td>
<td>0.0519±0.0005</td>
<td>1.16±0.0005</td>
</tr>
<tr>
<td>12-caliber pump-action shotgun</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.06±0.01</td>
<td>0.067±0.0008</td>
<td>1.03±0.0003</td>
</tr>
<tr>
<td>12-caliber pump-action shotgun</td>
<td>Special 24g®</td>
<td>1</td>
<td>0.07±0.02</td>
<td>0.078±0.0002</td>
<td>1.28±0.0002</td>
</tr>
<tr>
<td>0.38 repeating rifle</td>
<td>Semi jacketed</td>
<td>1</td>
<td>0.12±0.02</td>
<td>0.1441±0.0004</td>
<td>2.22±0.0004</td>
</tr>
</tbody>
</table>

4 f<sub>recovered</sub> 95% = 2.132 (n = 4; n = degrees of freedom).
5 f<sub>recovered</sub> 95% = 2.353 (n = 3; n = degrees of freedom).
6 f<sub>recovered</sub> 95% = 6.314 (n = 1; n = degrees of freedom).

4 Conclusions

The possibility of using a gold microelectrode in acidic media in the presence of chloride ions to analyze lead originating from GSRs has been demonstrated. The proposed method was compared with results from AAS, and a paired Student’s t-test indicated that there was no significant difference between the methods at the 95% confidence level.

The results showed that the lead content in GSRs obtained from the same ammunition (semi jacketed, caliber 0.38 in.), but different guns (revolver (0.38 in.)) and long-barreled gun (0.38 repeating rifle), was not the same. The amount of lead found in the GSR from the revolver was lower, and this is likely to be due to a more significant dispersion of the residues from the revolver in comparison with the long-barreled gun. The major difference between the gunshot residues from two different ammunitions (Special 24g® and 3T®) was noticed using the 12-caliber pump-action shotgun. Finally, it was found that the CleanRange® ammunition contained a small amount of lead, which is unexpected since this kind of ammunition is not supposed to have this metal as a constituent in order to avoid exposure of policemen.

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References


