

Onsite Measurement of Lead in Gunshot Residues Using Linear Sweep Voltammetry

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Abstract: This work presents a method for the measurement of Pb by linear sweep anodic stripping voltammetry on an Hg film electrode. The linear working range for Pb was up to $100 \ \mu g L^{-1}$, whilst the limit of detection was 19 ng L⁻¹ (360 seconds accumulation time) and per cent residual standard deviation across 10 measurements was 0.98%. The method was applied to gunshot residues for the onsite monitoring of Pb at a public shooting range.

Key words: mercury film electrode, lead, anodic stripping voltammetry, gunshot residue

1. Introduction

Exposure to lead (Pb) has been linked with a number of negative health impacts [1], exposure to Pb is therefore undesirable and should be avoided or minimised where possible. The use of firearms at indoor shooting ranges poses a risk of Pb exposure to patrons and employees.

When a firearm is discharged, primer mix containing lead styphnate, barium nitrate and antimony sulphide is ignited [2]. The combustion product, gunshot residue (GSR) contains Pb and is expelled into the environment. GSR is therefore a potentially hazardous source of Pb exposure [3]. The use of firearms in enclosed spaces such as indoor shooting ranges poses a risk to patrons and employees, since high concentrations of Pb can accumulate [3].

Traditional analytical techniques used for the measurement of lead, such as atomic absorption spectroscopy and inductively coupled plasma mass spectroscopy (ICP-MS), although highly accurate, are expensive, require laboratory infrastructure and are not suitable to onsite analysis [2, 4]. Onsite analysis for the presence of Pb at shooting ranges would provide employees with the ability to monitor for the presence of Pb and improve their ability to contain and clean-up Pb residues [4]. Modern voltammetric instruments offer an inexpensive and portable alternative to traditional analytical techniques [2, 4].

The aim of this project was to develop and validate an analytical procedure for the measurement of Pb in GSR samples.

2. Experimental

2.1 Reagents and Materials

Supporting electrolyte containing 20 mmol.L⁻¹CH₃COOH, 30 mmol.L⁻¹NaCH₃COO and 0.25 mol.L⁻¹NaCl was prepared from supra pure grade reagents, Sigma Aldrich; 20 mg.L⁻¹ Hg solution was prepared from 1000 mg.L⁻¹ Hg standard, Australian Chemical Reagents; 10 mg.L⁻¹ Pb standard was prepared from 1000 mg.L⁻¹ Pb standard, Australian Chemical Reagents; 0.45 mol.L⁻¹ HNO₃ was prepared from supra pure 70% HNO₃, Sigma Aldrich.

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GhostWipesTM Lead Sampling Wipes and a certified GhostWipesTM Lead Standard Wipe (Environmental Express) were used as supplied.

2.2 Apparatus

All electrochemical experiments were performed on a Modern Water PDV6000plus voltammetric instrument fitted with an Ag/AgCl reference electrode, glassy carbon working electrode and Pt wire auxiliary electrode. The glassy carbon working electrode (surface area 3.0 mm²) was polished using 0.1 μ m alumina slurry on a Buehler polishing pad daily and modified with an Hg film by plating 20 mg.L⁻¹ Hg solution for 300s at -1300 mV.

2.3 Procedure

2.3.1 Limit of Detection, Reproducibility and Linear Working Range

The limit of detection, reproducibility and linear working range for the PDV6000 plus instrument using the ASV method were determined by analyzing Pb standards ranging from 0.20 μ g.L⁻¹ to 200 μ g.L⁻¹. The procedure is described in section 2.3.3.

2.3.2 Sample Collection and Digestion

Various surfaces inside an indoor shooting range were sampled for GSR, by wiping a 100 cm² area using a commercial wipe, GhostWipesTM [5]. Used GhostWipesTM were placed into 50 mL plastic sample tubes with 15 mL of 0.45 mol.L⁻¹ HNO₃. Tubes were shaken vigorously for 30 minutes using a laboratory shaker and filtered through 0.45 μ m filters prior to analysis. A blank was prepared from an unused GhostWipesTM and a standard from the certified Pb GhostWipesTM standard.

2.3.3 Analysis of GSR Samples

Solutions were analyzed by dispensing 5.00 mL of supporting electrolyte and 5.00 mL of blank/standard/sample (diluted as required) into the voltametric cell. Pb was accumulated (with stirring) at -1000 mV for 30 to 360 s, depending on sample concentration; after a 15 s equilibration period a linear

sweep was recorded from -850 mV to -50 mV at 500 mVs⁻¹ and the Hg film cleaned at -50 mV for 15 s. Peaks were quantified by 3 standard additions, $R^2 > 0.990$. Blanks, standard and samples were analyzed in triplicate, and by ICP-MS at a NATA certified laboratory for comparison.

3. Results and Discussion

3.1 Limit of Detection

Analysis of a 0.20 μ g.L⁻¹ Pb standard (0.1 μ g.L⁻¹ cell concentration) using a 360 s accumulation period produced a response of 601 nA; the baseline noise was found to be 38 nA (Fig. 1). The limit of detection was defined as three times the baseline noise and calculated to be 19 ng.L⁻¹.

3.2 Reproducibility

Analysis of ten 20 μ g.L⁻¹ Pb standards (10 μ g.L⁻¹ cell concentration) using a 30 s accumulation period produced a mean response of 1.62 μ A, standard deviation 0.0158 μ A. The residual standard deviation was therefore 0.98%, indicating the response for lead was consistent and the method stable.

3.3 Linear Working Range

Analysis of Pb standards from 2.0 to 200 μ g.L⁻¹ (1.0 to 100 μ g.L⁻¹ cell concentration) using a 60 s accumulation period produced a linear calibration, R² = 0.9995 (Fig. 2) indicating the response was directly proportional to Pb concentration.



Fig. 1 Response for 0.10 μ g.L⁻¹ (Cell Concentration) Pb Standard, Accumulation Period 360 s



Fig. 2 Response for Pb Standards between 1.0 and 100 μ g.L⁻¹ (Cell Concentration), Accumulation Period 60s. Response (μ A) = 0.5115 [Pb μ g.L⁻¹], R² = 0.9995.

3.4 GSR Results

Analysis of the sample blank solution returned an average value of 0.04 mg.L⁻¹, which was negligible compared with sample values. Analysis of the certified GhostWipesTM Pb standard returned an average value of 4.32 mg.L⁻¹ by ASV and 4.54 mg.L⁻¹ by ICP-MS; giving percentage recoveries of 94.6% and 99.6%, respectively. Whilst the recovery for ASV was lower than ICP-MS both these recoveries were considered acceptable.

Results obtain from the analysis of 26 GSR samples by ASV and ICP-MS are shown in Table 1. Pb present in the surface sample can be calculated by multiplying mg.L⁻¹ values by 1.5. The surface Pb concentration at the shooting range ranged from 0.46 to 110 mg.m⁻².

Correlation of ASV and ICP-MS results returned a Pearson's R value of 0.9879, indicating a very strong correlation between the methods (Fig. 3). Construction of a Bland-Altman plot (Fig. 4) and calculation of the 95% limits of agreement revealed a slight positive bias (3.6 mg.L⁻¹) for the ASV results and a 95% limit of variation of $\pm 7 \text{ mg.L}^{-1}$ between the two methods. The plot also shows that the difference between the methods was much less for samples lower than 5 mg. L^{-1} . This indicates that sample dilution is likely to be the cause of this variation.

Table 1ValuesObtained from the Analysis of GSRSamples by ASV and ICP-MS.

1 2	16 30	0.22	17
2	30	2.1	
		5.1	36
3	14	0.68	16
4	23	0.63	26
5	28	1.93	27
6	14	0.39	15
7	75	1.7	77
8	20	1.0	23
9	10	0.42	9.4
10	13	0.93	11
11	0.86	0.0029	0.86
12	1.1	0.013	1.3
13	0.24	0.007	0.28
14	0.44	0.033	0.50
15	0.71	0.042	0.79
16	0.31	0.028	0.35
17	48	2.1	43
18	26	2.3	29
19	18	1.3	19
20	39	2.9	42
21	28	1.3	29
22	10	0.59	9.6
23	51	6.9	63
24	54	12	57
25	31	0.72	40
26	37	2.0	44



Fig. 3 Correlation of ASV results and ICP-MS results. ASV $(mg.L^{-1}) = 1.078(ICP-MS (mg.L^{-1})), R^2 = 0.9795.$



Fig. 4 Bland-Altman Plot Comparing the Difference for ICP-MS (A) and ASV (B) Results

4. Conclusions

This study demonstrates that the PDV6000plus instrument is capable of accurately and reliably measuring Pb concentrations in GSR using ASV. This technique could be of practical use for the on-site monitoring of Pb present at shooting ranges. A simpler, field-deployable analytical technique for Pb would provide shooting range staff with the ability to monitor for the presence of Pb. This would improve the capacity of staff to contain and clean-upGSR, reducing the risk of employee and patron exposure to Pb.

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