Technical Procedure for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Gunshot Residue Analysis

1.0 Purpose – This technical procedure shall be followed for the operation of the Inductively Coupled Plasma Mass Spectrometer.

2.0 Scope – This method is designed to analyze for the presence of barium, antimony, and lead collected on the cotton swabbings in gunshot residue kits.

3.0 Definitions – N/A

4.0 Equipment, Materials, and Reagents

4.1 Equipment

- Perkin Elmer SCIEX Elan DRC-e Inductively Coupled Plasma Mass Spectrometer
- Perkin Elmer AS 93 Autosampler
- Polyscience Recirculator, Model 3370
- Elan ICP-MS Instrument Control Software, Version 3.0
- Dell Pentium 4 Processor w/ Microsoft Windows XP Professional
- Microsoft Excel

4.2 Materials

- Ultra High Purity Argon, Refrigerated Liquid
- 15 mL falcon tubes with caps
- 50 mL falcon tubes with caps

4.3 Reagents

- 1 % nitric acid
- De-ionized distilled water
- Smart Tune Standard Elan DRC-e Reagent

5.0 Procedure

5.1 Verification for New Instrumentation

5.1.1 A calibration curve shall be run using the following standards: Blank, 1, 2, 3, 4, 5, and 6. The QC1 and QC2 standards shall be analyzed as known samples, along with three more known samples: Standards 1, 4, and 6. All five of these known concentrations of Ba, Sb, and Pb must pass within 20 % of their actual values. If the concentration is outside of the 20 % range, a new standard shall be prepared and analyzed. If the value is still outside of the specified range, maintenance shall be performed or a service engineer called. Once maintenance is performed, the samples shall be re-examined. If the samples are within the 20 % of the actual value, the new instrument may be used for case work.

5.2 Startup Procedures for ICP-MS and Software

5.2.1 This startup procedure is for normal daily activity. If the instrument is completely off, refer to the Hardware manual. The order for switching the circuit breakers is:

CB2 | CB4 | CB3 | CB1 | Vacuum ON

5.2.2 Check the second argon regulator connected to the inlet on the back of the ICP-MS. Set the pressure to approximately 53 psi. Check level of argon. Set the regulator pressure on the tank to approximately 70 psi.

5.2.3 Turn on the recirculator. Check that the pressure reads approximately 50 psi.

5.2.4 Attach the sample tubing and drain tubing leading from the peristaltic pump to the spray chamber. When the pump turns on, it will rotate counter-clockwise. Follow the flow through the tubing as if the pump were on.

5.2.4.1 The flow direction for the sampling tubing (the smaller tubing) is from the sampling probe into the spray chamber.

5.2.4.2 The flow direction for the drain tubing (the thicker tubing) is from the bottom of the spray chamber/nebulizer to the waste collection bottle.

5.2.5 Attach the autosampler tubing in the same manner. Determine the direction of flow in the tubing if the pump turns *counter-clockwise*.

5.2.5.1 The flow direction for the rinse tubing (the smaller tubing) is from the 2 L rinse bottle (1 % HNO_3) to the autosampler rinse position.

5.2.5.2 The flow direction for the drain tubing (the thicker tubing) is from autosampler probe rinse to the waste collection bottle.

5.2.6 Fill the 2 L rinse bottle with enough 1 % HNO_3 to complete anticipated run. A full set of 17 gunshot residue kits requires approximately 1 L of 1 % HNO_3. Prepare 1 % HNO_3 according to the Trace Unit Technical Procedure for Gunshot Residue (GSR) Analysis.

5.2.7 Click on the ELAN icon on the computer desktop.

5.3 Daily Performance Check Procedure and Maintenance

5.3.1 Check the ICP-MS Daily Performance Logbook to determine if a Daily Performance Check has been done that day. If it has, proceed to **5.4**.

5.3.2 Turn on the instrument and set the instrument up for analysis in accordance with **5.2**. This requires the plasma be turned on and allowed to stabilize for approximately 20 minutes before performing the Daily Performance Check.

5.3.3 From the File menu select Daily Performance.wrk.

5.3.4 Manually place the autosampler probe into the Smart Tune Solution Standard and analyze sample.

5.3.5 Review the results in the SUMMARY section of the report to check for background levels, double charges, and oxides.

5.3.5.1 The ratios of Double Charged and Oxides are displayed in the "Net Intens. Mean" column of the SUMMARY Section of the report. The row corresponding with CeO and Ba^{++} contains the ratio value.

5.3.6 Requirements for a passing Daily Performance are:

5.3.6.1 **Background levels**: Analytes 8.5 and 220 must be < 2.5 cps (The 8.5 analyte requirement only applies when running in the dynamic reaction cell mode.)

5.3.6.2 **Double Charges:** Ratio of Ba^{++}/Ba < 0.030 or 3 % and RSD Value < 4.0 %

5.3.6.3 **Oxides:** Ratio of CeO/Ce < 0.030 or 3 % and RSD Value < 4.0 %

5.3.7 If the performance check passes, record date and initials on the instrument's Use Log. Place Daily Performance printout in ICP-MS binder. Initial and date the printout.

5.3.8 Place the capillary back in the rinse position. If values fail to meet the above criteria, follow the Daily Optimization Flowchart: Standard Mode found on p. 4-38 of the *ELAN Version 3.0 Software Guide* (See page 4). If values fail again, a service representative shall be contacted. Once service is performed and the above stated criteria are met, the instrument may be returned to service.

5.4 Procedure for performing Gunshot Residue Analysis

5.4.1 Pass/Fail Criteria for the Calibration Curve and quality control standards

5.4.1.1 The following criteria shall be used to set up the method (C:\elandata\Method\GSR.mth). The method shall be set up to stop the analysis automatically if these criteria are not met.

5.4.1.1.1 The calibration curve shall pass with a minimum correlation value of 0.995.

5.4.1.1.2 The QC1 and QC2 Standards shall be within 20 % of the known values.

5.4.1.1.3 Correction Factors: All correction factors needed for In, Ba, Pb are listed in APPENDIX 2, GSR.mth.

5.4.1.2 The automated method shall run the Blank, Std 1, 2, 3, 4, 5, 6, QC1 and QC2 before running the samples. The method shall run a QC1 (blank) and QC2 (mid-curve) standard after every 5 samples. Since gunshot residue kits consist of 5 swabbings, this means the QC1 and QC2 shall run between each gunshot residue kit.

5.4.1.3 Should one of these not pass within 20 % of its actual value, the method shall automatically stop the analysis. If the values are outside of the 20 % value, then maintenance shall be performed or the new standards shall be prepared. Then the calibration curve and quality control standards shall be run. If the values are within 20 % of the actual value, the instrument may be used for case work.

5.4.2 Setting up ICP-MS Software for Gunshot Residue Analysis

5.4.2.1 From the File menuOpen Workspace, and select GSR.wrk.

5.4.2.2 See ***Appendix 2*** for all instrumental parameters of the gunshot residue analysis.

5.4.2.3 Click on the Report Tab (located on the right-hand side of the Method window).

5.4.2.4 Create a Report Filename specific for the run. This shall be the name of the .csv file to later be converted into an EXCEL spreadsheet.

5.4.2.5 Create a new Dataset for each GSR run.

5.4.2.6 Create a new sample file for each GSR run. For the first sample, select: "Run Blank Std. and Sample" from the Measurement Action column. All other samples select "Run Sample."

5.4.2.6.1 Double-check the following settings:

- Method selected is C:\elandata\Method\GSR.mth
- Sample Type: Sample
- Aliquot Volume = 1
- Diluted to Volume = 10
- Sample Flush = 35
- Sample Flush Speed = -24
- Read Delay = 20
- Delay and Analysis Speed = -20
- Wash = 45
- Wash Speed = -24

5.4.3 Setting up Standard and Controls for GSR Analysis

5.4.3.1 All reagent preparations for the solutions, standards, and controls listed below are found in the Trace Unit Technical Procedure for Gunshot Residue (GSR) Analysis.

5.4.3.2 Place standards Blank, 1, 2, 3, 4, 5, and 6 in autosampler slots 14-20. Place QC1 Standard in autosampler slot 6. Place QC2 Standard in autosampler slot 7.

5.4.3.3 Fill the 2 L rinse bottle with enough 1 % HNO_3 to complete anticipated run. A full set of 17 gunshot residue kits requires approximately 1 L of 1 % HNO_3. Place samples in the correct autosampler slots as listed in the sample file.

5.4.4 GSR Analysis

5.4.4.1 Build the run list by highlighting all samples, and analyze the batch. Print a report for each kit in the ICP-MS run when complete.

5.5 Shutdown Procedure

5.5.1 Place the autosampler probe in a bottle of deionized water and run through the system for ~5-10 minutes. Remove the probe and let pump run until all liquid has drained from the tubing into the waste.

5.5.2 Shut off the plasma and stop the peristaltic pump.

5.5.3 Flip the power to off on the autosampler power strip.

5.5.4 Turn off the recirculator.

5.5.5 Release the tension on all tubing of the peristaltic pump and the autosampler pump. No further action shall be required for basic shutdown procedures. If there is a need to completely shut down the system for an extended period of time, flip the power switches on the left side of the ICP-MS in the following order: Vacuum Off | CB1 | CB3 | CB4 | CB2.

5.6 Maintenance for ICP-MS

5.6.1 Replace tubing for peristaltic pump and autosampler tubing when needed. Over time, the tubing will become flat from use and shall be replaced.

5.6.2 The autosampler probe may become blocked with cotton from the samples. If this happens, use the thin wire snake to loosen and remove the clog.

5.6.3 Check the condition of the oil for the roughing pump and the turbomolecular pump. The color of the oil should be clear to light tea color. Replace the oil if its color is as dark as coffee.

5.6.4 Record any maintenance performed in the Maintenance Log.

5.7 Sampling and Sample Selection

5.7.1 No sampling is performed. When sample selection occurs, it shall be based on the Forensic Scientist's training and experience.

5.8 Calculations – N/A

5.9 Uncertainty of Measurement – N/A

6.0 Limitations – N/A

7.0 Safety

7.1 Liquid argon is colorless, odorless and non-flammable. Prolonged direct contact with skin can cause frostbite. Caution shall be exercised when dealing with a gas in a pressured tank. If a problem is detected with the tank, contact the gas vendor.

7.2 Never view the ICP torch directly without eye protection.

7.3 Do not bypass interlocks and safety devices. This could cause an electrical hazard and potential lethal voltages.

7.4 1 % nitric acid waste shall be disposed of properly by following Laboratory procedures for waste.

8.0 References

ELAN ICP-MS Series Safety Manual, Perkin Elmer Instruments, 2001.

ELAN Version 3.0 Software Guide, Perkin Elmer Instruments, 2001.

Aerospace Report ATT-77 (7915)-3, "A Final Report on Particle Analysis for Gunshot Residue Detection." 1977.

Cone, R.D. "Detection of Barium, Antimony, and Lead in Gunshot Residues by Flameless Atomic Absorption Spectrophotometry." *Police, Weapons Center Bulletin* 73.6 (1973): 4-6.

Guinn, V.P. "The Determination of Traces of Barium and Antimony in Gunshot Residues by Activation Analysis." *Proceedings of the First International Conference on Forensic Activation Analysis,* 1967.

Koons, R.D., "Analysis of Gunshot Primer Residue Collection Swabs by Inductively Coupled Plasma-Mass Spectrometry." *Journal of Forensic Sciences* 43.4 (1998): 748-754.

Koons, R.D., D.G. Havekost and C.A. Peters. "Analysis of Gunshot Primer Residue Collection Swabs using Flameless Atomic Absorption Spectrophotometry: A Reexamination of Extraction and Instrument Procedures." *Journal of Forensic Sciences* 32.4 (1987): 846-865.

Saferstein, R., ed. *Forensic Science Handbook.* Volume III, 2nd edition. Englewood Cliffs, NJ: Prentice-Hall, 2010. Chapter 9: Forensic Aspect of Firearms Discharge Residue (FDR) Analysis p.467

9.0 Records

- Maintenance Log
- Use Log
- Daily Performance Report

10.0 Attachments

- Appendix 1: Daily Optimization Flowchart
- Appendix 2: Method Parameters for C:\elandata\Method\GSR.mth

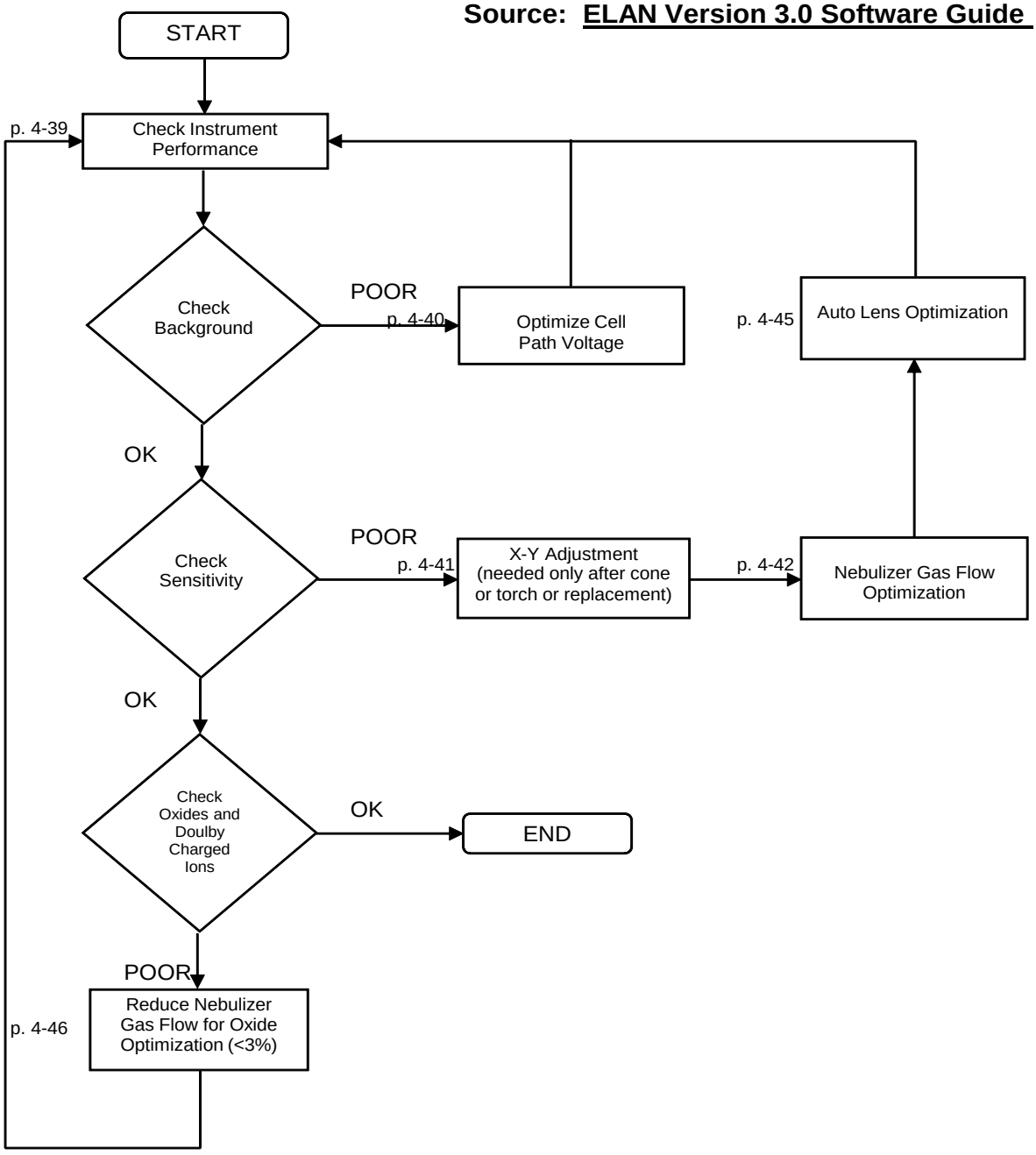
Revision History		
Effective Date	Version Number	Reason
09/17/2012	1	Original ISO Document
09/30/2013	2	Removed 5.4.5.10 through 5.4.5.12 and replaced with printing the reports. Added 5.6.4 to Maintenance and edited 5.3.13 to reflect use of Logs
10/18/2013	3	Added issuing authority to header
09/05/2014	4	Updated header to Physical Evidence Section – Trace Unit, issuing authority to Physical Evidence Section Forensic Scientist Manager. Updated all references in procedure from Trace Evidence Section to Trace Unit. Edited: 5.3.3 – Removed "click on open workspace" and added "select Daily Performance.wrk" 5.3.5 – Added "and analyze sample" to end of sentence 5.3.13 – Removed "the instrument shall be ready for analysis" and capitalized R in record 5.3.8 – Added "If values fail again, a service representative shall be contacted. Once service is performed and the above stated criteria are met, the instrument may be returned to service." 5.4.2.1 – Removed "click on" and added "and select GSR.wrk" to end of sentence 5.4.2.3 – Removed "Click on the method icon on the Elan Toolbar. Make sure C:\elandata\Method/GSR.mth is selected." 5.4.2.8 – Removed "Select the Dataset icon from the Elan toolbar. From the "File" menu, select "New". Type the desired dataset name then click "Open"." 5.4.2.9 – Removed "Select the Sample icon from the Elan toolbar. From the "File" menu, select "Open". Select the GSR template.sam then click on "Open". Fill out the following information for each sample." Added "For the first sample, select: "Run Blank Std. and Sample" from the Measurement Action column. All other samples select "Run Sample"." 5.4.4 – Removed "Begin" 5.4.4.1 – Removed "Click on Batch Index Number of the first sample in the sample file and drag down until all samples for analysis are highlighted." Added "Build the run list by highlighting all samples, and analyze the batch. Print a report for each kit in the ICP-MS run when complete." 5.5.2 – Removed "Click on "Instrument" from the Elan toolbar. Click

		on the Front Panel tab to determine the status of the instrument. Click "STOP" under Plasma. This will…" Capitalized s in Shut and moved "off" to before "the plasma". Removed: 5.3.4, 5.3.6, 5.3.7, 5.3.8, 5.3.9, 5.3.12, 5.3.15, 5.3.16, 5.4.2.2, 5.4.2.5, 5.4.2.6, 5.4.2.10, 5.4.2.11, 5.4.4.2, 5.4.4.3, 5.4.4.4, 5.4.5. Moved instructions to ICP-MS Training.

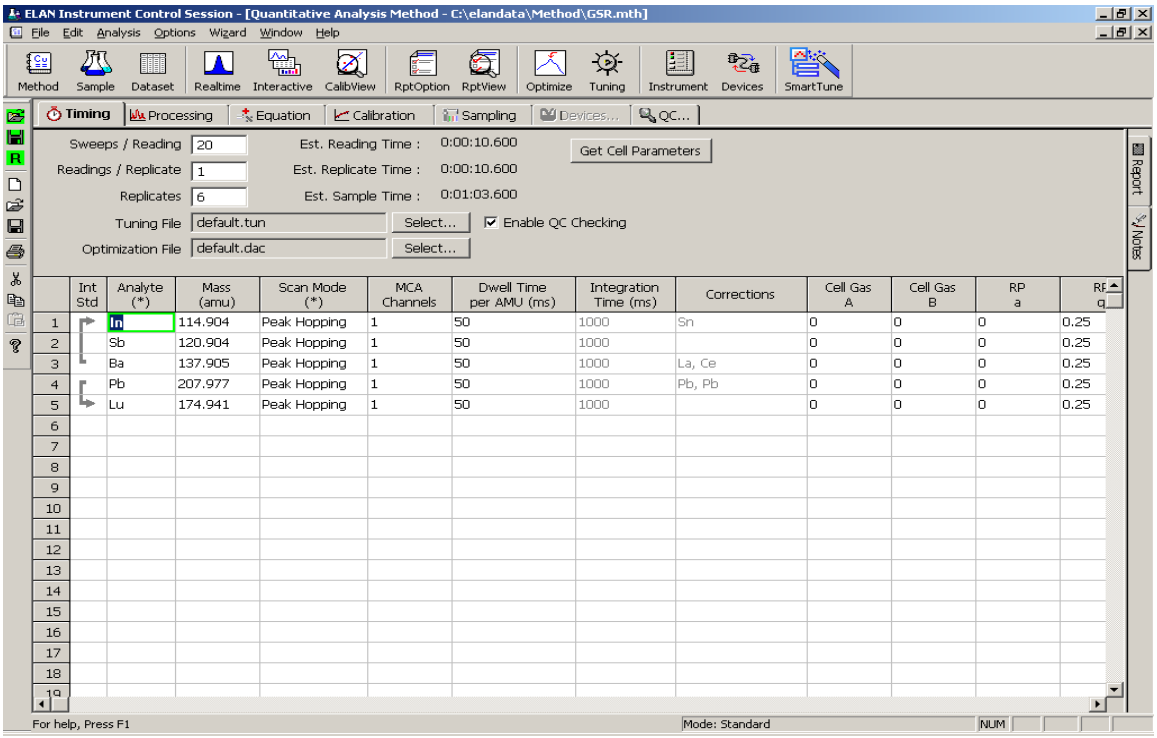
APPENDIX 1:

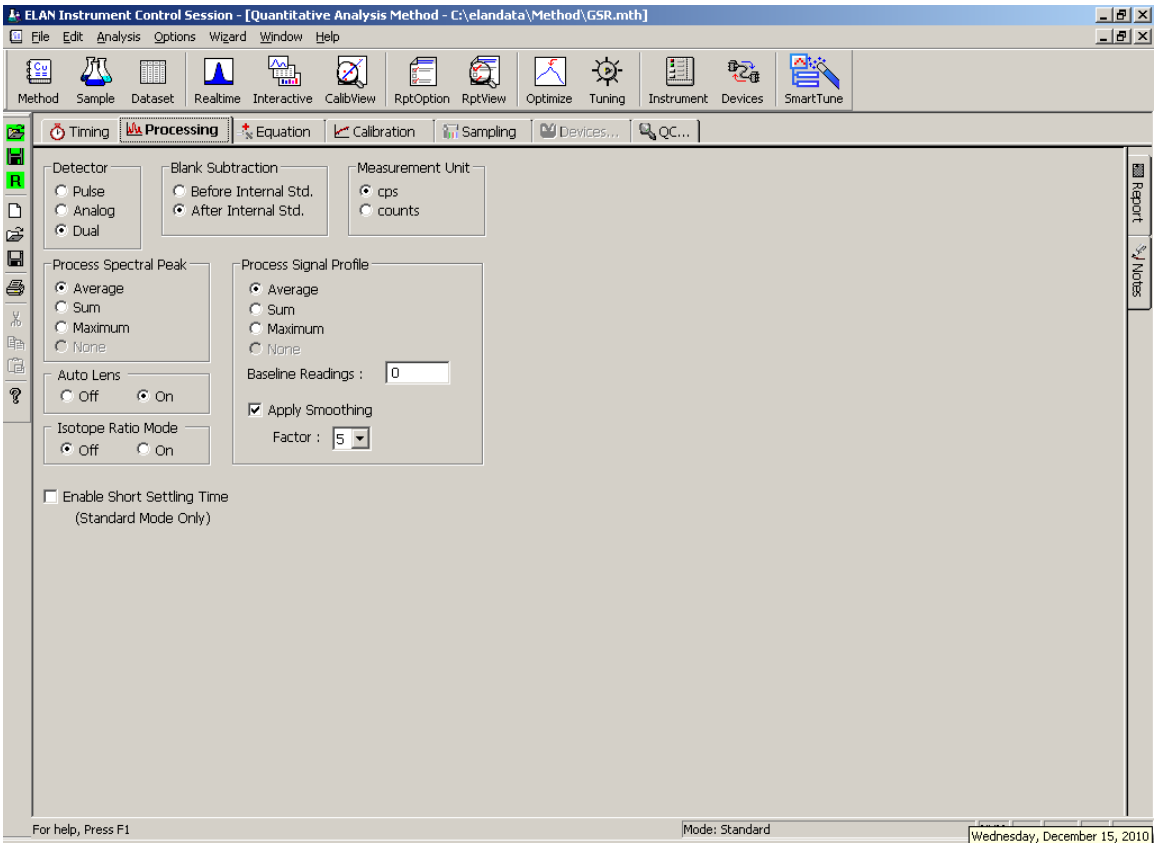
DAILY OPTIMIZATION FLOWCHART: Standard Mode

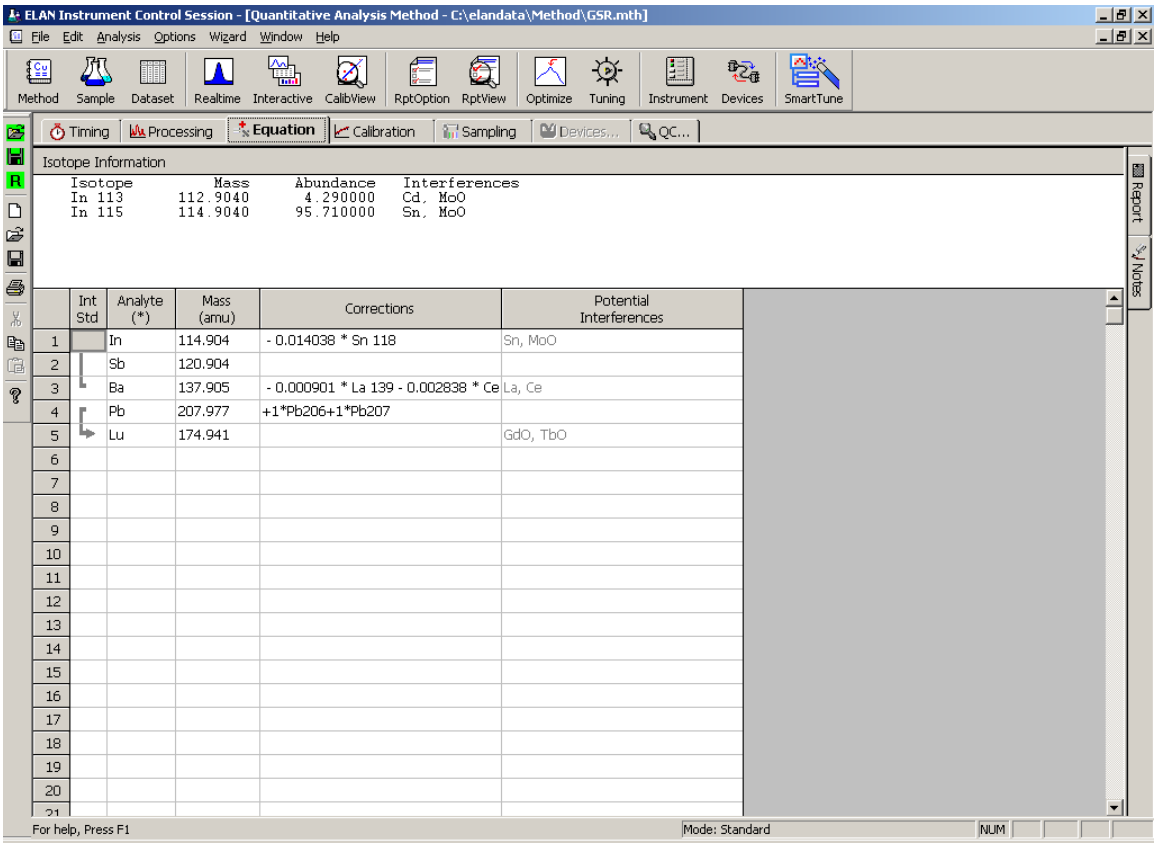
Source: ELAN Version 3.0 Software Guide

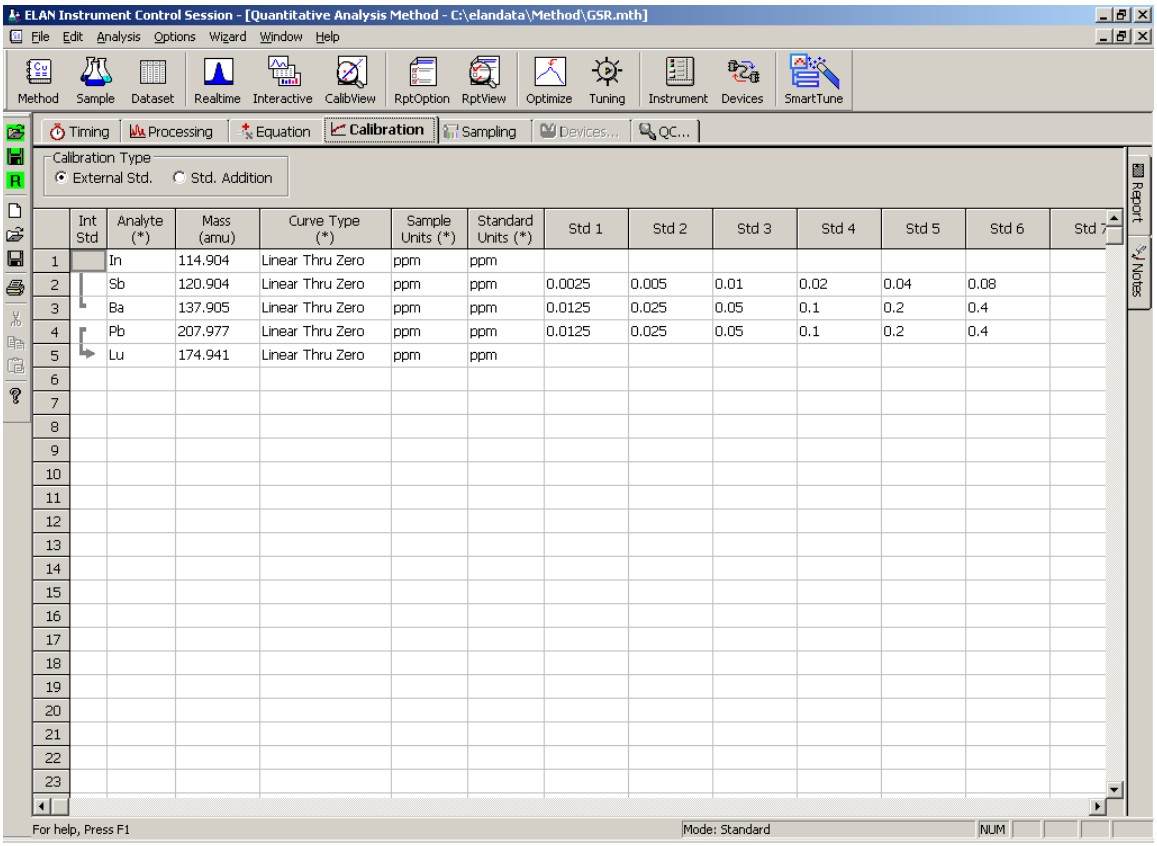


APPENDIX 2: ICP-MS Gunshot Residue Method Parameters (GSR.mth)









	Int Std	Analyte (*)	Mass (amu)	Curve Type (*)	Sample Units (*)	Standard Units (*)	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7
1		In	114.904	Linear Thru Zero	ppm	ppm							
2		Sb	120.904	Linear Thru Zero	ppm	ppm	0.0025	0.005	0.01	0.02	0.04	0.08	
3		Ba	137.905	Linear Thru Zero	ppm	ppm	0.0125	0.025	0.05	0.1	0.2	0.4	
4		Pb	207.977	Linear Thru Zero	ppm	ppm	0.0125	0.025	0.05	0.1	0.2	0.4	
5		Lu	174.941	Linear Thru Zero	ppm	ppm							
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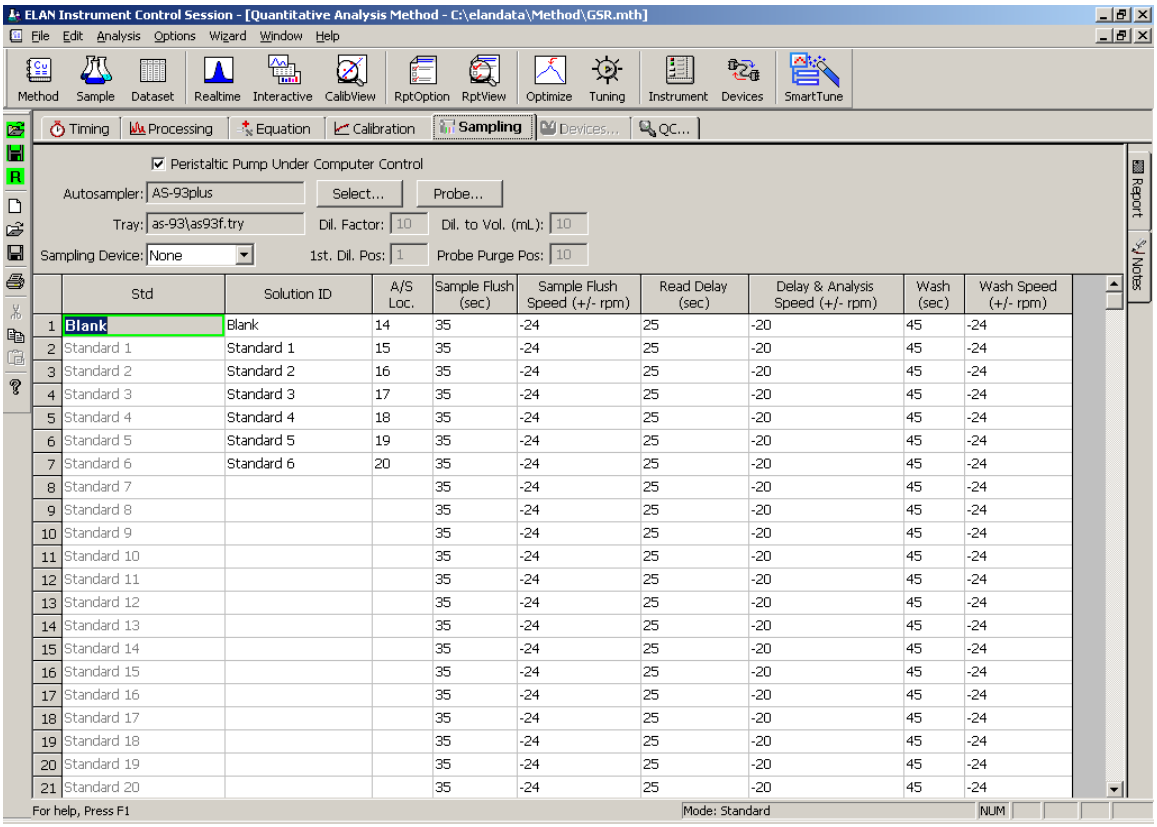

	Std	Solution ID	A/S Loc.	Sample Flush (sec)	Sample Flush Speed (+/- rpm)	Read Delay (sec)	Delay & Analysis Speed (+/- rpm)	Wash (sec)	Wash Speed (+/- rpm)
1	Blank	Blank	14	35	-24	25	-20	45	-24
2	Standard 1	Standard 1	15	35	-24	25	-20	45	-24
3	Standard 2	Standard 2	16	35	-24	25	-20	45	-24
4	Standard 3	Standard 3	17	35	-24	25	-20	45	-24
5	Standard 4	Standard 4	18	35	-24	25	-20	45	-24
6	Standard 5	Standard 5	19	35	-24	25	-20	45	-24
7	Standard 6	Standard 6	20	35	-24	25	-20	45	-24
8	Standard 7			35	-24	25	-20	45	-24
9	Standard 8			35	-24	25	-20	45	-24
10	Standard 9			35	-24	25	-20	45	-24
11	Standard 10			35	-24	25	-20	45	-24
12	Standard 11			35	-24	25	-20	45	-24
13	Standard 12			35	-24	25	-20	45	-24
14	Standard 13			35	-24	25	-20	45	-24
15	Standard 14			35	-24	25	-20	45	-24
16	Standard 15			35	-24	25	-20	45	-24
17	Standard 16			35	-24	25	-20	45	-24
18	Standard 17			35	-24	25	-20	45	-24
19	Standard 18			35	-24	25	-20	45	-24
20	Standard 19			35	-24	25	-20	45	-24
21	Standard 20			35	-24	25	-20	45	-24