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

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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 16 gunshot residue kits requires approximately 1 L of 1 % HNO_3. Prepare 1 % HNO_3 according to the Trace Evidence Section 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, click on Open Workspace.

5.3.4 Select Daily Performance.wrk and click Open.

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5.3.5 Manually place the autosampler probe into the Smart Tune Solution Standard.

5.3.6 Let the solution flush through the system for approximately 1-2 minutes.

5.3.7 Click once on Sample on the Elan Toolbar (This is the toolbar with the picture icons across the top of the ELAN software window). Make sure the Manual tab is selected and the option box is checked for "Write to Dataset After Each Analysis." Click once on "Details Check" to ensure the RPM value under READ DELAY is set to -20. Close Details window.

5.3.8 Click on Analyze Sample.

5.3.9 A Daily Performance Report will print after analysis is complete.

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

5.3.10.1 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.

5.3.11 Requirements for a passing Daily Performance are:

5.3.11.1 **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.)

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

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

5.3.12 Compare sensitivity to manufacture's recommended values for:

- Mg >50,000 cps/10ppb
- In >250,000 cps/10ppb
- U >200,000 cps/10ppb

5.3.13 If the performance check passes, the instrument shall be ready for analysis. Place printout in ICP-MS Logbook. Initial and date the printout.

5.3.14 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).

5.3.15 If performance fails to pass, perform a complete optimization (see page 5) and/or perform maintenance. If further unsatisfactory results occur, a service representative shall be contacted. Once service is performed and the above stated criteria are met, the instrument may be returned to service.

5.3.16 See ***Appendix 1*** for additional optimization steps.

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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 menu, click on Open Workspace.

5.4.2.2 Select GSR.wrk and click OK.

5.4.2.3 Click on the Method icon on the Elan Toolbar. Make sure C:\elandata\Method\GSR.mth is selected. See ***Appendix 2*** for all instrumental parameters of the gunshot residue analysis.

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

5.4.2.5 Select the following Report Option Template: C:\elandata\ReportOptions\quant summary1.rop

5.4.2.6 To create data files for each sample, under “Report to File,” select “Send to File” by clicking on its box. Select the following Report Option Template: C:\elandata\ReportOptions\exportdata.rop

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5.4.2.7 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.

5.4.2.8 Create a new Dataset for each GSR run. 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 Create a new sample file for each GSR run. 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:

5.4.2.9.1 Type the filename desired for each sample in the Sample ID column (SMITH C).

5.4.2.9.2 Type the Laboratory Case # in the Description column that corresponds to the "C" row for each kit.

5.4.2.9.3 Check that the autosampler location starts with location 38; maximum of 85 samples per run (17 GSR kits).

5.4.2.9.4 For the first sample, select: "Run Blank Std. and Sample" from the Measurement Action column; all other samples select "Run Sample."

5.4.2.9.5 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

5.4.2.10 The unused rows in the template shall be deleted when not performing a full 85 sample analysis. Left click on the Batch Index of the first <u>unused</u> row and drag down to the last Batch Index. The unused rows shall now be highlighted. Right click and select Delete.

5.4.2.11 Save the new sample file with a new name. From the "File" menu, select "Save As." Type the new file name. Click "Save."

5.4.3 Setting up Standard and Controls for GSR Analysis

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5.4.3.1 All reagent preparations for the solutions, standards, and controls listed below are found in the Trace Evidence Section 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 16 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 Begin GSR Analysis

5.4.4.1 Click on Batch Index Number of the first sample in the sample file and drag down until all samples for analysis are highlighted.

5.4.4.2 Click on "Build Run List." (If a warning window pops up and says, "Do you want to clear previously acquired QC Data before proceeding with the batch?" Click "Yes.")

5.4.4.3 Click on "Analyze Batch." The run will start.

5.4.4.4 If the user would like the instrument to shut off after run is complete: Click on Instrument Icon and click on Auto stop tab.

5.4.5 Data Analysis

5.4.5.1 In WINDOWS, right click on the "START" button and select "Explore."

5.4.5.2 Click on the folder: C:\Elandata\ReportOutput.

5.4.5.3 Click on the appropriate .csv file for the GSR run. This will open the file into an EXCEL spreadsheet.

5.4.5.4 Highlight all of the data in the .csv file.

5.4.5.5 Go to the "Edit" menu and select "Copy."

5.4.5.6 From the File menu select "Open." Select the file: C:\GSR Casework\GSR-ICP-MS-template.xls

5.4.5.7 Click on "Enable Macros."

5.4.5.8 Click on the A1 cell which reads "Paste Data Here."

5.4.5.9 Go to the "Edit" menu and select "Paste."

5.4.5.10 Save this file under a new name.

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5.4.5.11 Select all tabs for the kits that were run and print.

5.4.5.12 Each Forensic Scientist shall then move all dataset, sample, .csv, and excel files from the general locations to his/her personal folders.

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 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 shut the plasma off 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.

5.7 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

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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

- ICP-MS Maintenance Log
- ICP-MS QC Daily Performance/Use Log
- Daily Performance Reports

10.0 Attachments

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

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Revision History		
Effective Date	Version Number	Reason
09/17/2012	1	Original ISO Document

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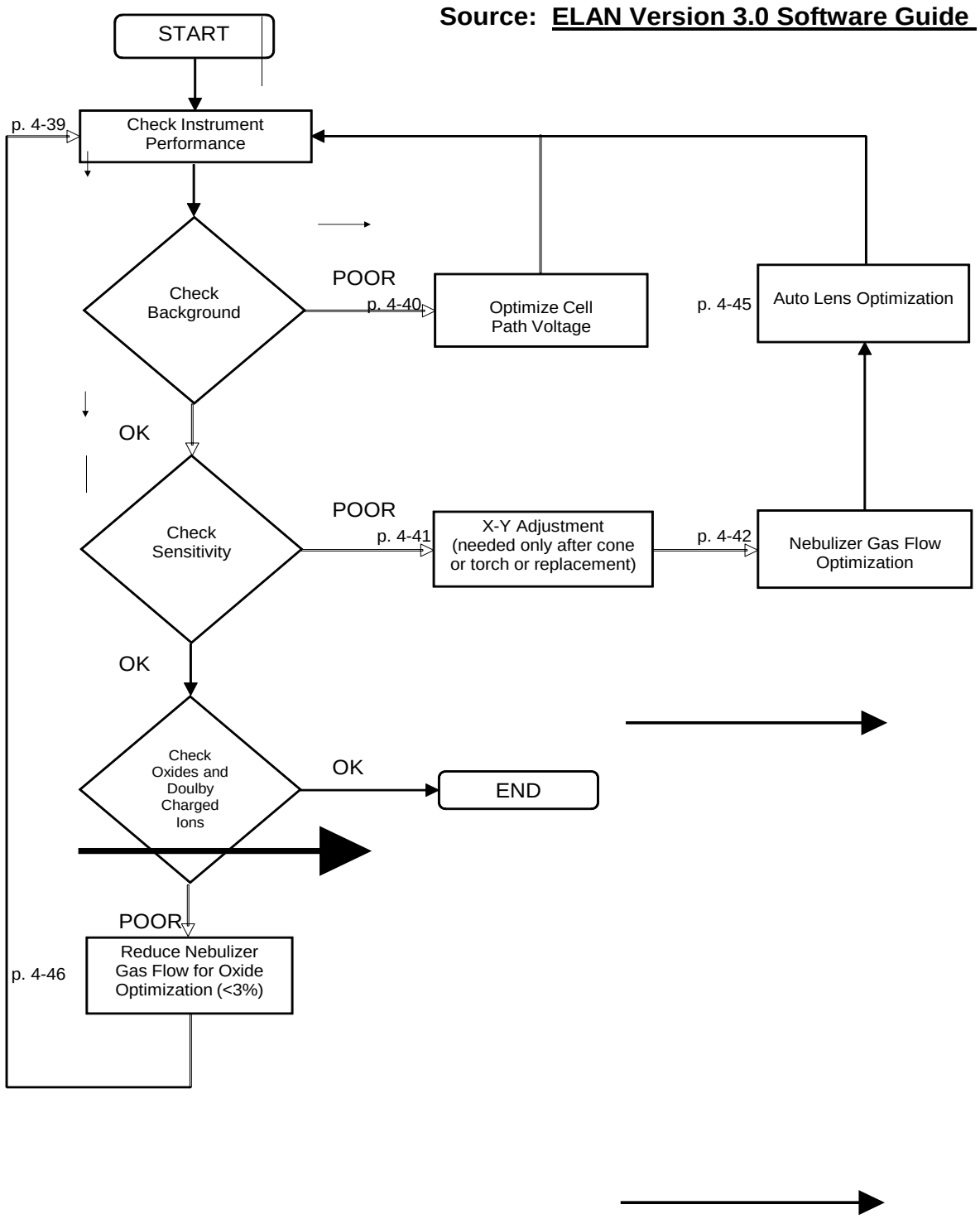
APPENDIX 1:

DAILY OPTIMIZATION FLOWCHART: Standard Mode

Source: ELAN Version 3.0 Software Guide



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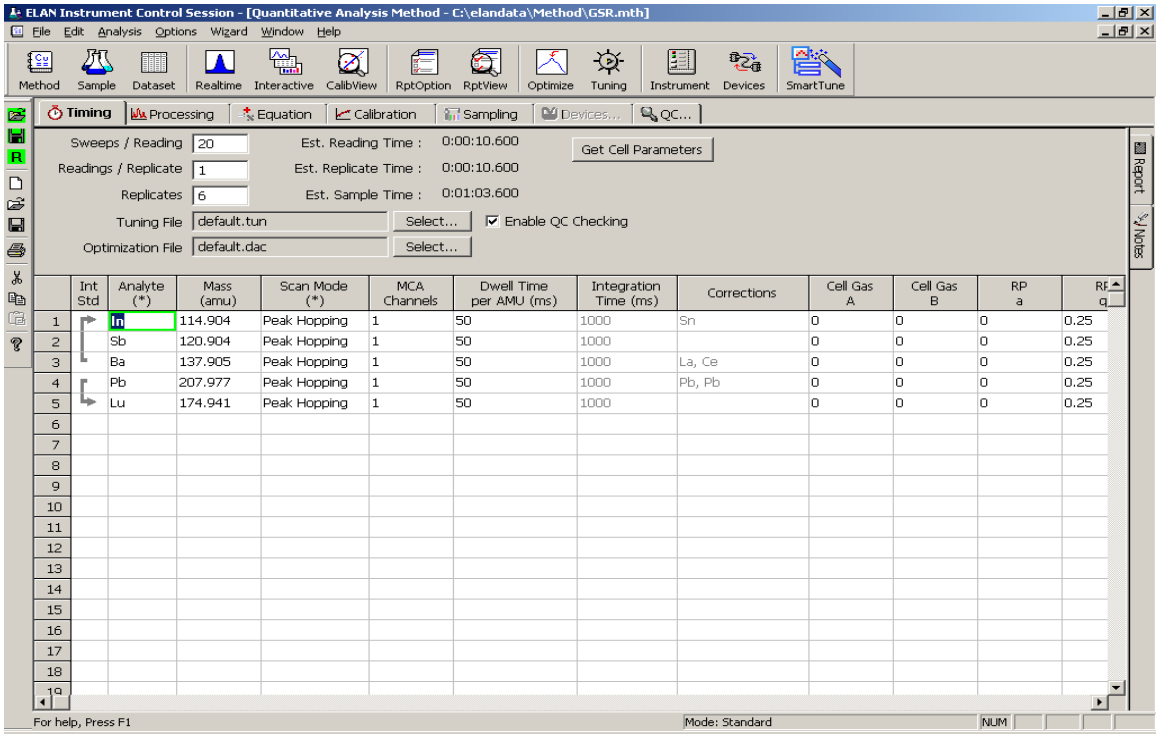
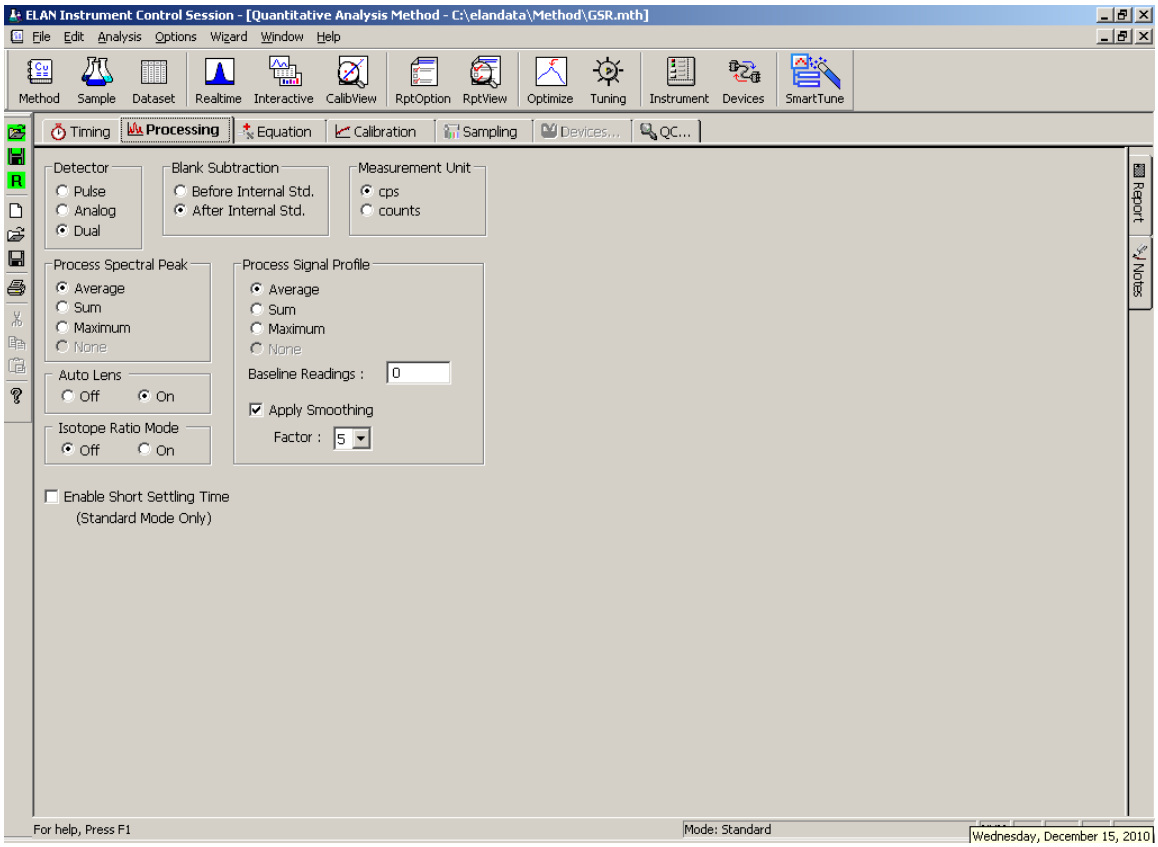
APPENDIX 2: ICP-MS Gunshot Residue Method Parameters (GSR.mth)



	Int Std	Analyte (*)	Mass (amu)	Scan Mode (*)	MCA Channels	Dwell Time per AMU (ms)	Integration Time (ms)	Corrections	Cell Gas A	Cell Gas B	RP a	RF q
1		In	114.904	Peak Hopping	1	50	1000	Sn	0	0	0	0.25
2		Sb	120.904	Peak Hopping	1	50	1000		0	0	0	0.25
3		Ba	137.905	Peak Hopping	1	50	1000	La, Ce	0	0	0	0.25
4		Pb	207.977	Peak Hopping	1	50	1000	Pb, Pb	0	0	0	0.25
5		Lu	174.941	Peak Hopping	1	50	1000		0	0	0	0.25
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												



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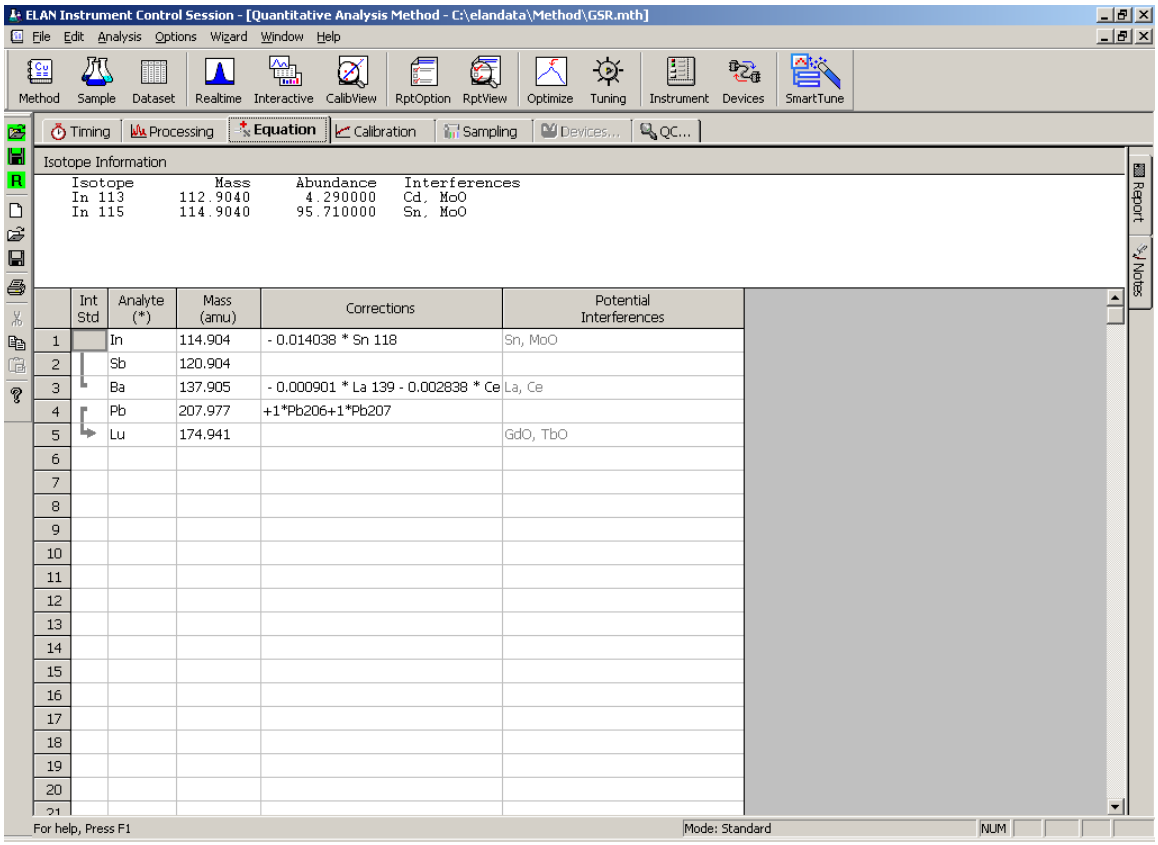

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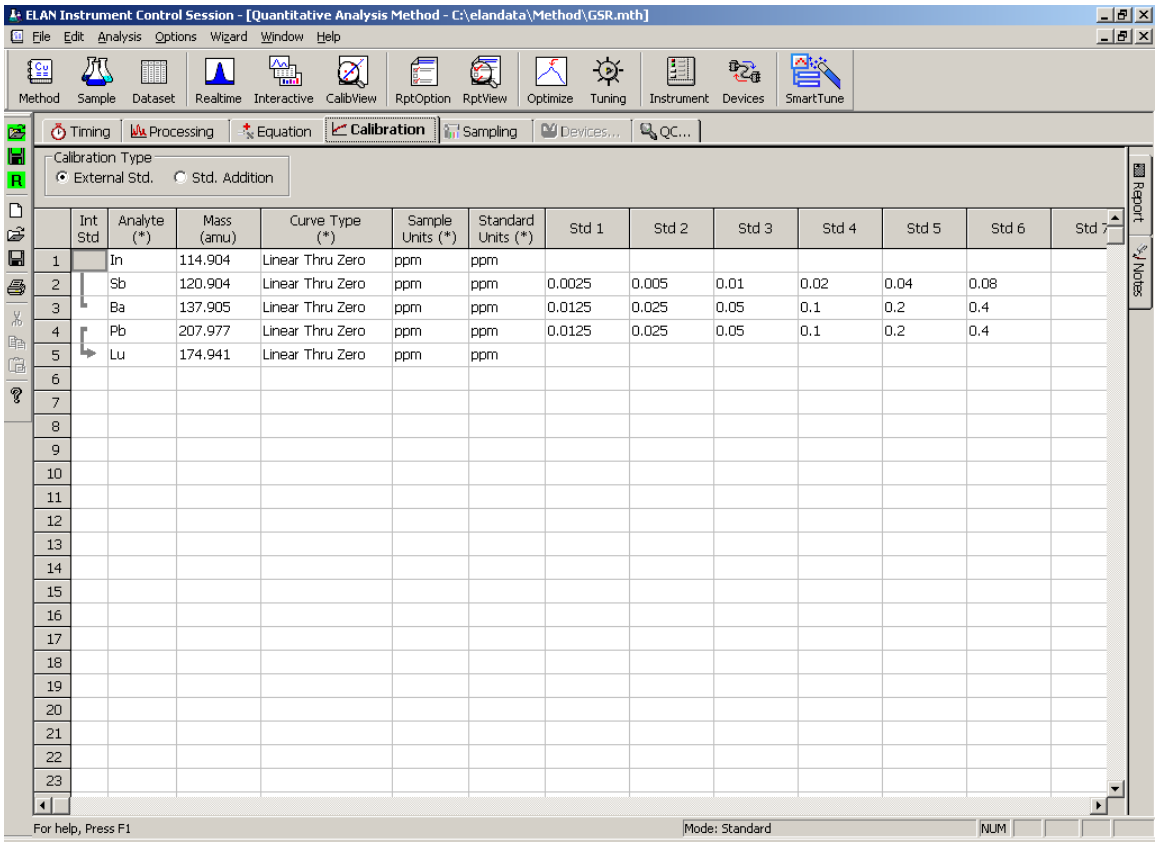
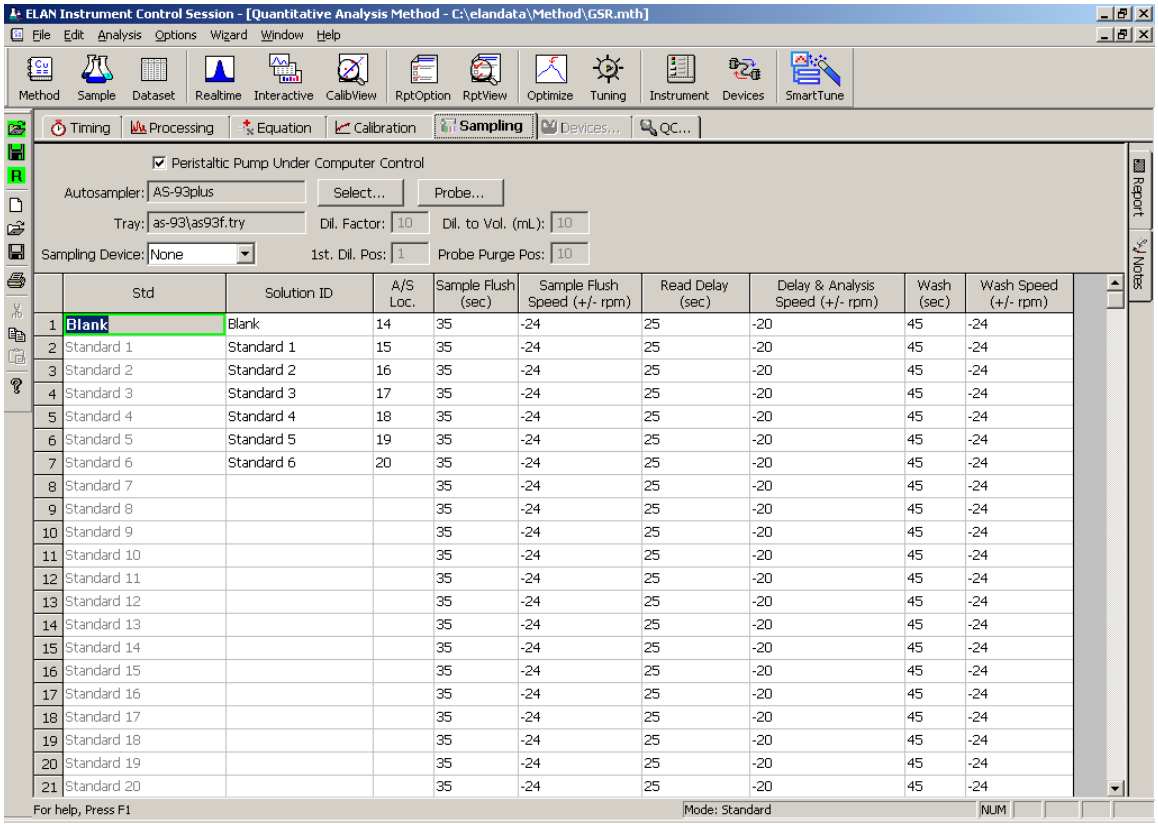


	Int Std	Analyte (*)	Mass (amu)	Curve Type (*)	Sample Units (*)	Standard Units (*)	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7
1		In	114.904	Linear Thru Zero	ppm	ppm							
2		Sb	120.904	Linear Thru Zero	ppm	ppm	0.0025	0.005	0.01	0.02	0.04	0.08	
3		Ba	137.905	Linear Thru Zero	ppm	ppm	0.0125	0.025	0.05	0.1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



	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

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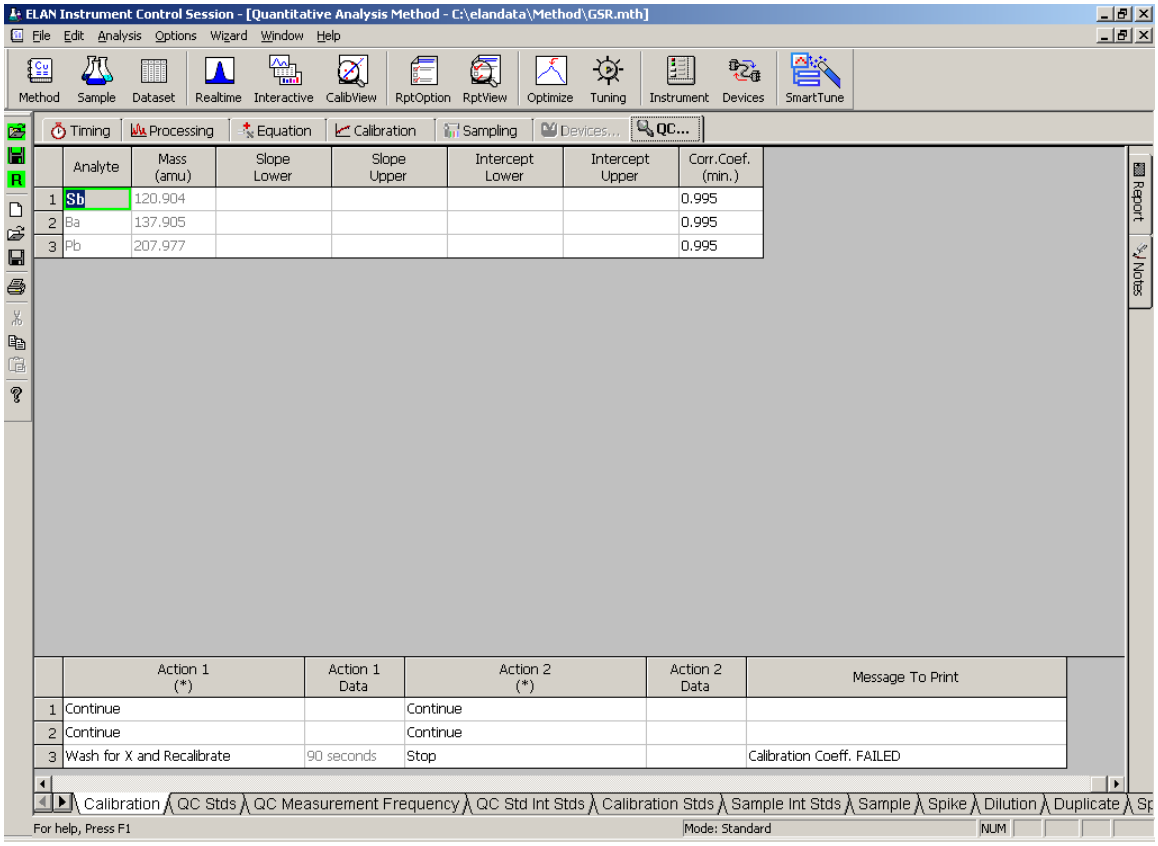

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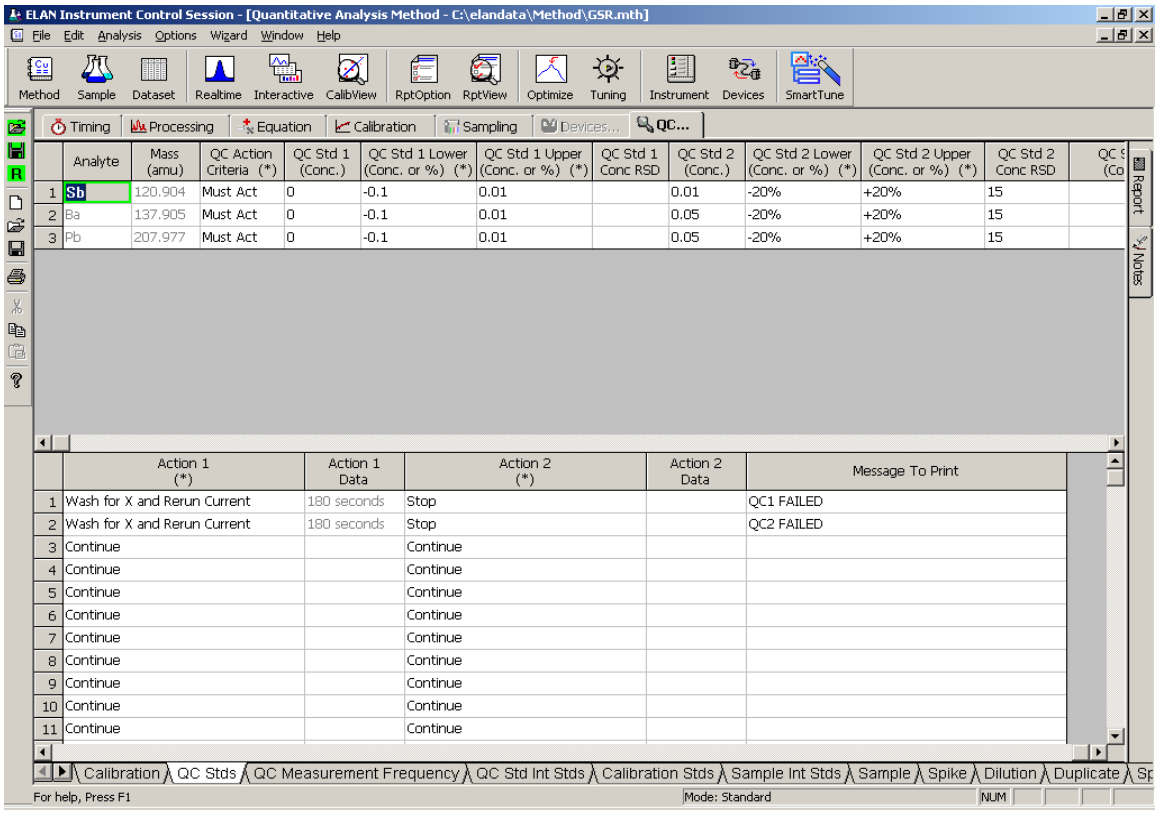
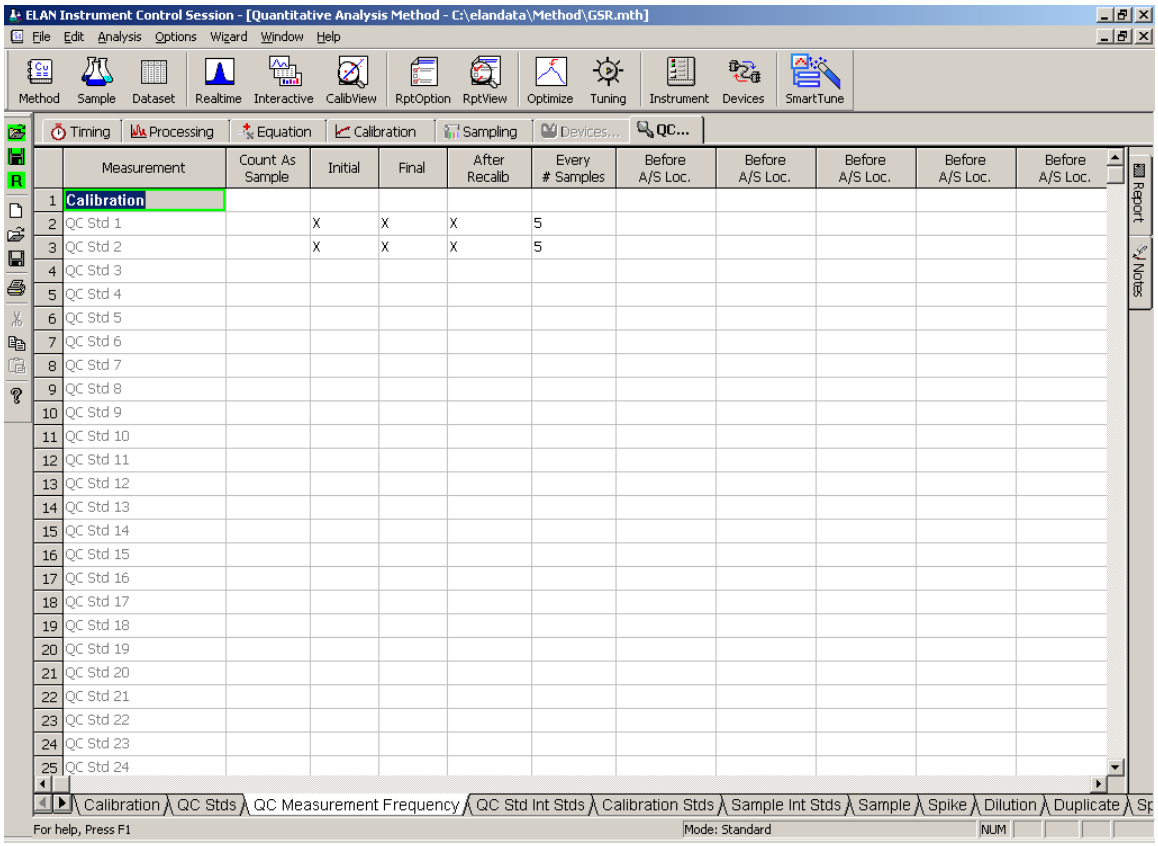


	Analyte	Mass (amu)	QC Action Criteria (*)	QC Std 1 (Conc.)	QC Std 1 Lower (Conc. or %) (*)	QC Std 1 Upper (Conc. or %) (*)	QC Std 1 Conc RSD	QC Std 2 (Conc.)	QC Std 2 Lower (Conc. or %) (*)	QC Std 2 Upper (Conc. or %) (*)	QC Std 2 Conc RSD
1	Sb	120.904	Must Act	0	-0.1	0.01		0.01	-20%	+20%	15
2	Ba	137.905	Must Act	0	-0.1	0.01		0.05	-20%	+20%	15
3	Pb	207.977	Must Act	0	-0.1	0.01		0.05	-20%	+20%	15

	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data	Message To Print
1	Wash for X and Rerun Current	180 seconds	Stop		QC1 FAILED
2	Wash for X and Rerun Current	180 seconds	Stop		QC2 FAILED
3	Continue		Continue		
4	Continue		Continue		
5	Continue		Continue		
6	Continue		Continue		
7	Continue		Continue		
8	Continue		Continue		
9	Continue		Continue		
10	Continue		Continue		
11	Continue		Continue		



	Measurement	Count As Sample	Initial	Final	After Recalib	Every # Samples	Before A/S Loc.	Before A/S Loc.	Before A/S Loc.	Before A/S Loc.	Before A/S Loc.
1	Calibration										
2	QC Std 1		X	X	X	5					
3	QC Std 2		X	X	X	5					
4	QC Std 3										
5	QC Std 4										
6	QC Std 5										
7	QC Std 6										
8	QC Std 7										
9	QC Std 8										
10	QC Std 9										
11	QC Std 10										
12	QC Std 11										
13	QC Std 12										
14	QC Std 13										
15	QC Std 14										
16	QC Std 15										
17	QC Std 16										
18	QC Std 17										
19	QC Std 18										
20	QC Std 19										
21	QC Std 20										
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24	QC Std 23										
25	QC Std 24										

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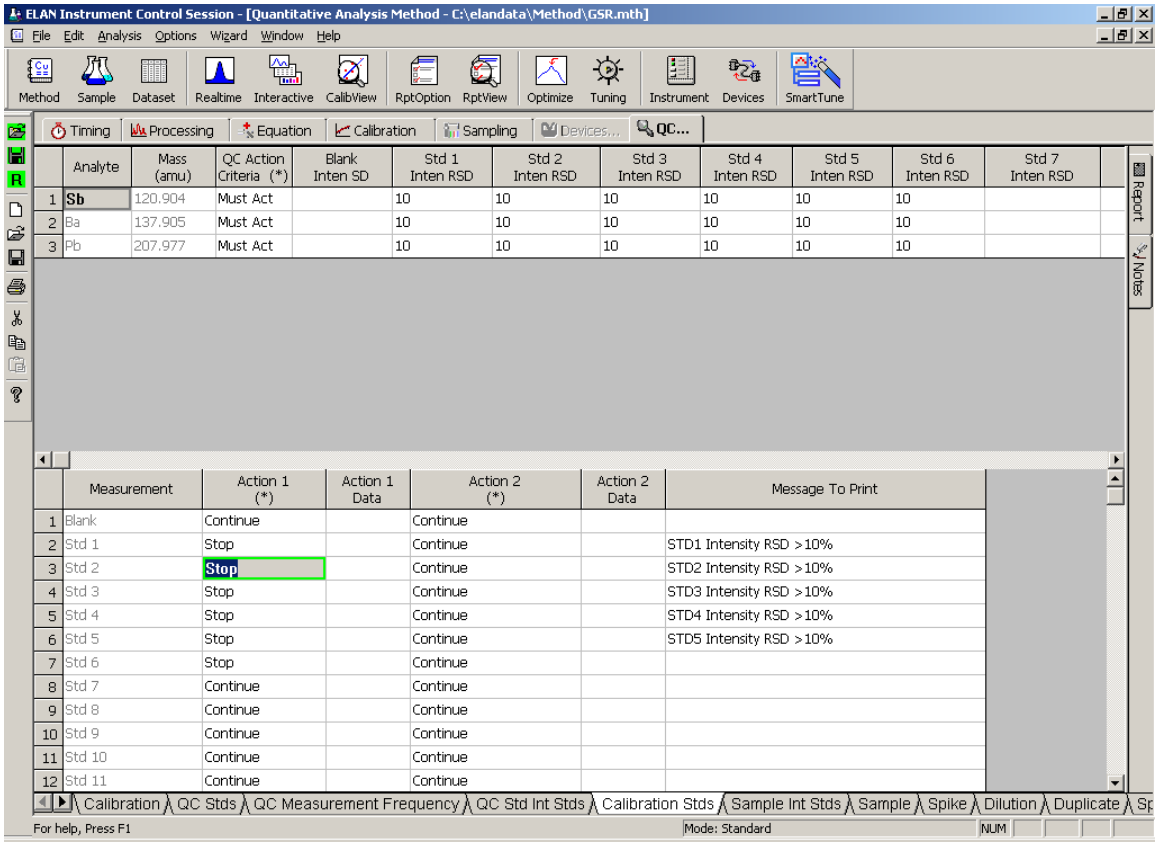

	Analyte	Mass (amu)	QC Action Criteria (*)	Blank Inten SD	Std 1 Inten RSD	Std 2 Inten RSD	Std 3 Inten RSD	Std 4 Inten RSD	Std 5 Inten RSD	Std 6 Inten RSD	Std 7 Inten RSD
1	Sb	120.904	Must Act		10	10	10	10	10	10	
2	Ba	137.905	Must Act		10	10	10	10	10	10	
3	Pb	207.977	Must Act		10	10	10	10	10	10	

	Measurement	Action 1 (*)	Action 1 Data	Action 2 (*)	Action 2 Data	Message To Print
1	Blank	Continue		Continue		
2	Std 1	Stop		Continue		STD1 Intensity RSD >10%
3	Std 2	Stop		Continue		STD2 Intensity RSD >10%
4	Std 3	Stop		Continue		STD3 Intensity RSD >10%
5	Std 4	Stop		Continue		STD4 Intensity RSD >10%
6	Std 5	Stop		Continue		STD5 Intensity RSD >10%
7	Std 6	Stop		Continue		
8	Std 7	Continue		Continue		
9	Std 8	Continue		Continue		
10	Std 9	Continue		Continue		
11	Std 10	Continue		Continue		
12	Std 11	Continue		Continue		

Calibration | QC Stds | QC Measurement Frequency | QC Std Int Stds | Calibration Stds | Sample Int Stds | Sample | Spike | Dilution | Duplicate | Sp

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