Elemental Analysis of Glass by Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS)

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1 INTRODUCTION

This document provides the procedure for the identification and quantitation of numerous elements in glass. The concentrations of selected elements in glass serve to chemically characterize the source of the glass. The concentrations of several elements are intentionally controlled by the manufacturers to impart specific end-use properties to a particular glass product. These manufacturer-controlled elements help to chemically characterize a glass fragment by placing it into a particular product use class. The concentrations of trace elements are generally not controlled by the manufacturers. Subtle and distinct differences in the concentrations of manufacturer-controlled elements and uncontrolled trace elements provide a means of differentiating among glasses made by different manufacturers, among glasses from different product lines of a single manufacturer, and over time along an individual production line of glass from a single manufacturer.

This technical procedure is implementing through incorporation by reference the ASTM International E2927, Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using LA-ICP-MS for Forensic Comparisons. ASTM E2927 is on the Organization of Standard Area Committees (OSAC) Registry of Approved Standards.

1.1 Principle

This procedure is for the quantitative analysis of seventeen elements: lithium (Li), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), iron (Fe), titanium (Ti), manganese (Mn), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), hafnium (Hf), and lead (Pb) by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the forensic analysis of glass fragments. The precision, accuracy, and limits of detection of these elements were established during the validation of the method. Silicon (Si) is also monitored for use as a normalization standard. Additional elements may be added as needed, for example, tin (Sn) can be used to monitor the orientation of float glass fragments. The concentrations of the elements listed above range from the low parts per million ($\mu g g^{-1}$) to percent (%) levels in soda-lime-silicate glass, the most common type encountered in forensic cases. This standard method may be applied for the quantitative analysis of other glass types; however, some modifications in the standard reference glasses and the element menu may be required.

1.2 Specimens

This procedure is used for the analysis of small fragments of broken glass objects such as: windows, windshields, or containers. The method consumes approximately 0.4 to 3.1 µg of glass per replicate and is suitable for the analysis of full thickness samples as well as irregularly shaped fragments as small as 0.1 mm by 0.1 mm by 0.2 mm in dimension.

2 SCOPE

This document applies to Geologist-Forensic Examiners and qualified analysts in the Trace Evidence Unit (TEU).

3 EQUIPMENT

- Cleaning solution (e.g., Cavicide, Windex)
- Compressed air
- Deionized water (18.2 megohm-cm or higher)
- Distilled water
- Ethanol
- Glass Standard Reference Materials (SRMs) NIST 612, NIST 1831, Schott FGS 1, Schott FGS 2, Deutsche Glastechnische Gesellschaft (DGG 1) or equivalent
- *Glitter* data analysis software or equivalent
- Grinder/Polisher
- Helium
- Kimwipes, Techwipes, or equivalent low lint paper tissue
- Laboratory coat
- Nitrile gloves or equivalent
- NWR UP213 Nd:YAG Laser Ablation System or equivalent with an accompanying personal computer containing the instrument software (i.e., *ActiveView 2*)
- Safety goggles
- Sonicator
- Tape, double sided
- Agilent 7900 ICP-MS or equivalent with an accompanying personal computer containing the instrument software (i.e., *Masshunter*)
- Tweezers

4 STANDARDS AND CONTROLS

A. *Calibration*: A single point calibration curve using a single glass standard is used for quantitation. Calibration standards must be matrix-matched to the sample and well characterized. For routine soda-lime-silicate glass analysis, use FGS 2. For other glass types, NIST 612 may be used.
    1. Analyze at least three spots of the calibration standard at the beginning of the sample sequence, and at least three spots of the calibration standard the end of each sample sequence.
        i. If the sample sequence exceeds more than one hour in duration, at least three replicates of both the calibration (FGS 2 or NIST 612) SRM and accuracy and precision (DGG 1 or NIST 1831) SRM should be run intermittently throughout the sample sequence, approximately every 20 replicates.

B. *Accuracy and Precision*: In addition to the calibration standard, measure at least three spots of an additional glass standard reference material, such as DGG 1 or NIST 1831, with each sample sequence as a check of accuracy and precision.

1. Assess each standard glass measured against the control charts for the method. Mean concentration values have been established or verified for each of the glass SRMs by measuring at least six spots over five days. From these analyses, a standard deviation was calculated. See Table 1 for concentrations and standard deviations, as well as recorded literature values. A control is acceptable if the calculated mean value of each element is within three standard deviations (± 3SD) of the control chart mean, and the relative standard deviation (RSD) is ≤15%.

Table 1: Control Chart Values

	Mean Measured Concentration, ppm ($\mu g g^{-1}$)			Standard Deviation, ppm ($\mu g g^{-1}$)			Literature Recorded Values ppm ($\mu g g^{-1}$)		
Element	**NIST 612**	**FGS 2**	**DGG 1**	**NIST 612**	**FGS 2**	**DGG 1**	**NIST 612**	**FGS 2**	**DGG 1**
Li	45.894	29.072	26.287	1.775	1.204	1.237	40.2	29	26.3
Mg	45.558	23522.106	25316.500	3.380	659.679	1690.207	68	23400	25207
Al	10790.649	7436.105	6687.158	434.063	211.856	419.923	10744	7400	6509
K	43.343	4616.714	3127.398	1.254	91.859	99.957	62.3	4600	2984
Ca	86251.938	59409.427	45973.009	4477.623	1800.081	4287.987	85050	59300	47555
Ti	39.334	327.097	780.721	1.568	8.736	45.625	44	326	785
Mn	37.145	221.806	60.635	2.099	7.261	4.871	38.7	221	64.32
Fe	95.263	2608.170	1211.802	18.387	65.623	74.210	51	2600	1221
Rb	30.418	35.206	2.239	1.198	0.995	0.307	31.4	35	2.14
Sr	59.982	254.029	12.178	4.104	9.991	1.203	78.4	253	15.06
Zr	36.675	224.351	25.708	1.411	5.689	1.655	37.9	223	24.98
Ba	38.099	200.083	61.318	1.460	5.150	3.775	39.3	199	61.26
La	33.825	18.104	1.893	1.254	0.450	0.127	36	18	1.86
Ce	36.547	23.124	3.687	1.228	0.703	0.214	38.4	23	3.71
Nd	34.308	25.144	1.890	1.303	0.635	0.144	35.5	25	1.87
Hf	37.634	15.095	0.746	1.344	0.408	0.054	36.7	15	0.73
Pb	42.143	24.055	6.094	1.716	1.285	0.418	38.57	24	6.11

2. When precision (measured as RSD) among the glass replicate measurements for SRMs is >15% for elements present at higher concentrations, take appropriate measures to determine the cause of the discrepancy. When the measured concentrations of several elements in a standard glass have RSDs >15%, measurement of additional standard glass samples may be warranted. When the measured concentrations of several elements in the additional standard glass have RSDs >20%, the run will be discontinued.

C. *Normalization*: The use of a normalization standard is needed to adjust for differences in ablation yield between the ablated materials (i.e., to normalize the signal). Because silicon (Si) is present as a major component in all soda-lime-silicate glass (~70 to 72% as SiO), use ^{29}Si as the normalization standard during the analysis of these glass samples. If analyzing other glass types, the concentration of the normalization standard used must be determined prior to quantitative analysis.

1. In Glitter software, in the standard window, select ^{29}Si as the normalization standard, and set to the appropriate value of SiO for each sample (see standard values in ASTM E2927).

D. Store glass SRMs at ambient temperature and pressure in separate, closed containers to prevent deleterious change. Glasses maintained in this fashion have an indefinite shelf life.
    1. When the glass SRM samples have been ablated multiple times and there is no longer enough of a flat surface for analysis, they can be re-polished or replaced.

5 SAMPLING

A. When sufficient glass is available, select several fragments from each exemplar item to represent the range of potential compositions of the glass.
    1. For each known source, measure twelve replicates (spots) (three replicates from at least four fragments if possible) and calculate the mean for each element.
    2. For each questioned fragment, measure four to six replicates (spots) and calculate the mean for each element.
B. If the known or questioned glass fragments are limited in size, fewer replicates may be analyzed at the discretion of the Geologist-Forensic Examiner. However, if it is not possible to analyze the minimum recommended number of known replicates the elemental heterogeneity may not be captured in the source. This could potentially increase the false exclusion rate. Document this in the case records.

6 PROCEDURE

6.1 Startup

A. Ensure that the water level of the chiller is at least ¾ full and set to 20°C. If needed, add fluid.
B. Turn on the laser computer.
C. Turn on the LA-ICP-MS blower.
D. Turn on the helium (He) carrier gas.
    1. The pressure should be ~10 psi. If not, adjust the wall gauge.
E. Open *ActiveView 2*.
    1. Purge the ablation cell for ~120 seconds.
    2. Enable MCF1 and set the He gas flow rate to 800 mL/min at a ramp rate of ~10 mL/min.
    3. Save the new batch.
        i. Ensure the settings are correct.
F. Open *Masshunter*.
    1. Select <Instrument Control>.
    2. Save the new batch.
        i. Ensure the settings are correct.

G. In Masshunter:
    1. Select <External Device> and connect to <Local Host>.
    2. In Tune Modes ensure the Argon (Ar) makeup gas is set to 0.
    3. Open the Maintenance Panel, and set the makeup gas to 1.5 L/min.
H. Allow instrument to run with He and Ar for 1-2 mins to clear the lines of air.
I. In *ActiveView 2* disable MCF1.
J. From *Masshunter* ignite the plasma.
    1. After ignition, in Tune Modes, slowly ramp the makeup gas to 0.95 L/min.
    2. Allow the plasma to warm up for at least 20 minutes.
K. In *ActiveView 2*:
    1. Set the flow rate to 800 mL/min at a ramp rate of ~7 to 10 mL/min.
    2. When the flow rate reaches the set point, purge the ablation cell.
    3. Set the following parameters:
        - Mode: continuous
        - Energy: 0%
        - Spot Size: any µm
    4. Fire the laser for 20 minutes with the shutter closed.

6.2 Tuning

6.2.1 Batch Tune

A. After warming up the laser and the plasma (see section 6.1), use NIST 612 programmed with an approximate eight-minute line (~3 mm length) to tune the ICP-MS.
B. Set the following parameters in *ActiveView 2*:
    - Mode: continuous
    - Energy: 65%
    - Rep Rate: 10 Hz
    - Spot Size: 50 µm
    - Passes: 1
    - Scan Speed: 5
    - Depth/Pass: 5
C. Allow the laser to ablate for approximately 10 to 20 seconds to stabilize the signal.
D. In *Masshunter* select <Auto Tune>.
    1. If the Tune Check Report indicates the failure of any parameter, repeat the Auto Tune.
    2. Repeated failure of the sensitivity or stability test reports may indicate that the system needs cleaning or maintenance. Follow the guidance in the ICP-MS instrument manual for cleaning and maintenance.
    3. If the instrument continues to fail the performance report after cleaning and maintenance, the instrument will be taken out of service until the failure is remediated.

6.2.2 Electron Multiplier (EM) Tune

A. In *Masshunter* run EM Tune.
    1. Use the User Tune parameters generated during the Batch Tune.
    2. Ensure that the makeup gas is set to 0.95 L/min.
    3. Select <Send to ICP-MS>.
    4. Save the batch.
B. In ActiveView 2:
    1. Set a ~2.5mm line using NIST 612 with the following parameters:
        - Mode: continuous
        - Energy: 80%
        - Rep Rate: 20hz
        - Aperture Wheel: 110 µm (max aperture size)
        - Passes: 1
        - Scan Speed: 5 µm/sec
        - Depth/Pass: 5
C. Manually start the EM Tune in *ActiveView 2*.
D. Allow the laser to ablate for approximately 10 to 20 seconds to stabilize the signal.
E. In *Masshunter* select <Run EM Auto Setting>.
    1. Ensure that the makeup gas is at 0.95 L/min.

6.2.3 Pulse/Analog (P/A) Factor Tune

A. Complete the EM Tune before starting the P/A Factor Tune.
B. In *Masshunter* run a P/A Factor Tune.
    1. Use NIST 612 and the EM Tune parameters (See Section 6.2.2.B).
    2. Manually start the P/A Factor Tune Line in *ActiveView 2*.
    3. Allow the signal about 20-30 seconds to stabilize once the laser begins firing.
    4. Select <Run P/A Factor Auto Setting>.
        i. Ensure that the makeup gas is still 0.95 L/min.
C. Certain elements (^{25}Mg, ^{29}Ti, ^{57}Fe, ^{137}Ba, ^{78}Se, and $^{206/207}$Pb) may show “Signal too low”. The concentrations of these elements are low in NIST 612, so this result is expected.

6.3 Performance Report

A. Generate a Performance Report every week if the instrument is in regular use. If the instrument is being run intermittently, conduct the Performance Report prior to analysis.
B. In *Masshunter*, run a Performance Report.
    1. Use NIST 612 with an approximate eight-minute line (~2.5 mm length) and the Batch Tune parameters (See Section 6.2.1.B).
    2. Select <Send to ICPMS> and save the batch.
C. In *Masshunter*, go to <Performance Report>.
D. Manually start the laser firing in *ActiveView 2*.
    1. Allow the signal about 20-30 seconds to stabilize once the laser begins firing.

E. Select <Run Performance Report>.
F. Review the results of the Performance Report in "History View". Save using <Generate>.
    1. If the Performance Report fails, repeat the Performance Report.
        i. If the instrument fails after at least two attempts, the instrument may need to be cleaned or serviced by the manufacturer.
        ii. If the instrument continues to fail after cleaning and maintenance, the instrument will be taken out of service until the failure is remediated.
        iii. All failures of performance will be logged in the record book.

6.4 Sample Preparation

A. If necessary, clean the samples to remove surface contamination. This can be done by washing, pre-ablation, or both.
    1. Wash samples with an appropriate solvent with or without sonication. Appropriate solvents should be chosen based on their ability to remove the contamination without altering the glass and can include soap and water, organic solvents, or bleach. Following washing, rinse the samples with deionized water, followed by ethanol (or equivalent). Allow to dry completely.
    2. See section 6.5.E for pre-ablation settings. Pre-ablation is done immediately prior to signal acquisition as part of the program settings.
B. Load samples into the ablation cell.
    1. Secure samples in the ablation cell using double-sided tape or other appropriate adhesive. If necessary, use a glass microscope slide(s) or equivalent to raise the samples to ensure they are in focus.
    2. If samples are suspected to be float glass, load the samples with the float side down.
C. In *ActiveView 2* purge the ablation cell for ~120 seconds after loading samples.

6.5 Analysis

A. Follow instrument startup and warmup per section 6.1.
B. Tune the instrument per section 6.2.
C. In *ActiveView 2*, open a new experiment and choose replicate spots for each glass sample (See sections 4 and 5).
    1. Select spots on different locations on the fragment.
    2. Place the locations of each spot sufficiently apart from each other to avoid possible debris from other ablation halos.
    3. Label each spot with a unique identifier.
    4. Ensure that each spot is in focus.
D. Set the following analysis conditions in *ActiveView 2*:
    - Mode: continuous
    - Passes: 1

- Depth: 5 µm
- Energy: 65% (Fluence ~10 J/cm^2)
- Rep Rate: 10 Hz
- Spot Size: 50 µm
- Dwell Time: 60 seconds
- Select “Close Shutter after Scan”
- Select “Enable Pre-Ablation Pass”

E. Set the following conditions for the pre-ablation in *ActiveView 2*:
- Mode: continuous
- Passes: 1
- Depth: 0 µm
- Energy: 65%
- Rep Rate: 10 Hz
- Spot Size: 75 µm
- Dwell Time: 20 seconds
- Laser Warmup: 20 seconds
- Select “Enable Laser During Scans”

F. Create procedure blanks using the same parameters as above but set the energy to 0% for both pre-ablation and ablation energy.

G. Each data acquisition sequence will consist of a 20-30 second gas blank (i.e., background), followed by 50-60 seconds of sample ablation, followed by at least 60 seconds of post-ablation blank (i.e., washout time). Absolute times will vary according to sample requirements (e.g., fragment size, glass type, etc.).

H. Add samples to the queue in *ActiveView 2* from either the Layer Management or the Pattern Management tab.

I. In *Masshunter*, ensure the External Device control panel is open.
1. Confirm that the numbers listed for the laser-warmup and washout delay are the same as those listed in *ActiveView 2*.
2. Go to Sample List and add in the sample sequence.
3. Select <Add to Queue> to start the run.

6.6 Data Processing

A. When analysis is complete, open *Glitter*.
1. Select <Element Concentrations>.
2. Select “IS in ppm”, then <Update>.

B. In File, select <Load Data>.
1. In the standards window, change the reference material if necessary (e.g., FGS 2).
2. Select ^{29}Si as the internal standard.
3. Change the dwell times to match your settings for the integration times of each element.
4. Enter the SiO_2 values for the samples as follows, then select <Accept>:
   - Blank – 0.00001
   - FGS 2 – 72.0010

- DGG 1 – 71.72
- NIST 612 – 71.86
- NIST 1831 – 72
- FGS 1 – 72
- Unknown/Control (float glass) – 72

C. Export the data in the desired format (e.g., .csv, .txt, etc.) and add the sample identifiers.
D. Run outlier tests on the compositional data to identify outliers in the data (e.g., Grubbs test).

6.7 Shutdown

A. In *ActiveView 2*:
    1. Purge the ablation chamber for at least 120 seconds.
    2. Disable the gas flow.
    3. Close *ActiveView* 2 and switch the laser off.
B. In *Masshunter*:
    1. Shut off the plasma.
    2. Allow the instrument to transition from analysis mode completely to standby mode, then close *Masshunter*.
C. Turn off He gas at the wall and the LA-ICP-MS blower.

7 Interpretation of the Analytical Results

A. Following the recommendations of Trejos et al (2013), use a modified 4σ confidence interval as the comparison criterion for the comparative analysis of glass fragments by LA-ICP-MS. If the average elemental concentration for any element in the item being compared falls outside of the modified 4σ confidence interval for that element in an exemplar sample, the items are considered distinguishable (an exclusion conclusion).
    1. See Section 6.6.D for outlier testing and apply as necessary.
B. If measured elemental concentrations are between the limit of detection and the limit of quantitation of the instrument, measured concentration values are unreliable and may produce unacceptably high RSDs. In this case, reanalysis of the samples is not useful. While it is possible to report the presence of an element if the concentration of the element is between the limit of detection and the limit of quantitation, the elements will not be considered during a comparison.
C. The detection limits of this method vary slightly from day to day. Approximate method detection limits have been stated in the validation records and are supported by literature values (see Trejos et al., 2013). These values may be used as a guide.

8 Calculations

A modified 4σ confidence interval is calculated by taking either the measured standard deviation or 3% of the average for each element, whichever is greater, and multiplying it by

four. The confidence interval for an element is the average value of the elemental concentration ± the modified 4σ.

9 Measurement Uncertainty

Uncertainty values for each element were determined during instrument validation. Additional uncertainty information for LA-ICP-MS can be found in the appendix of ASTM E2927.

10 Limitations

A. Fragments smaller than 0.2 mm x 0.1 mm by 0.1 mm may be too small for analysis with the current operating conditions.
B. Laser ablation may change the refractive index of the glass fragment. Therefore, refractive index measurements on glass fragments that have been ablated is not recommended.

11 Safety

A. Commercial laser ablation units are enclosed type I lasers. However, laser systems typically used for analysis of glass generate high energy radiation that may pose serious risks to eye safety if exposed to the eye. Interlocks must not be bypassed or disconnected.
B. ICP-MS instruments generate high amounts of radiofrequency energy in their RF power supply and torch boxes that is potentially hazardous if allowed to escape. Safety devices and safety interlocks must not be bypassed or disconnected.
C. Breaking glass can cause glass fragments to be ejected in unpredictable trajectories. Use caution to break the glass in a way that minimizes blowback. Broken glass can cause cuts and damage to eyes and exposed skin. PPE must be worn when handling or breaking glass including gloves, safety glasses, and a laboratory coat.

12 References

ASTM International, Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons (E2927)

Trejos, Tatiana, et al., Forensic Analysis of Glass by µ-XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: Evaluation of the Performance of Different Criteria for Comparing Elemental Composition, *Journal of Analytical Atomic Spectrometry*, 28; 1270-1282, 2013

Trejos, Tatiana, et al., Cross Validation and Evaluation of the Performance Methods for the Elemental Analysis of of Forensic Glass by µ-XRF, ICP-MS and LA-ICP-MS, Analytical and Bioanalytical Chemistry, 405; 5393-5409, 2013

FBI Laboratory Safety Manual (current version)

Agilent 7900 ICP-MS manual

ESI NWR213 Laser and *ActiveView* 2 Manuals

13 REVISION HISTORY

Revision	Issue Date	Changes
02	1/28/2022	Reformatted entire document and references. Added 'qualified analyst' to the Scope.
03	11/15/2023	Significant revisions to Sections 6 and 7 to include instruction for new LA-ICP-MS setup.