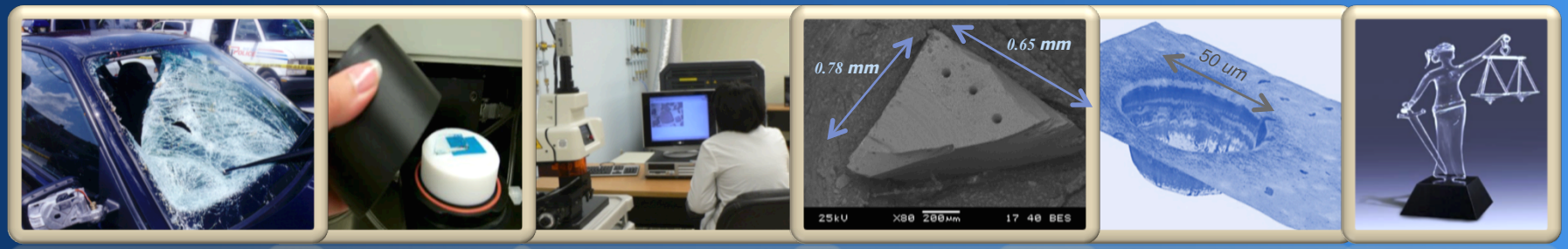


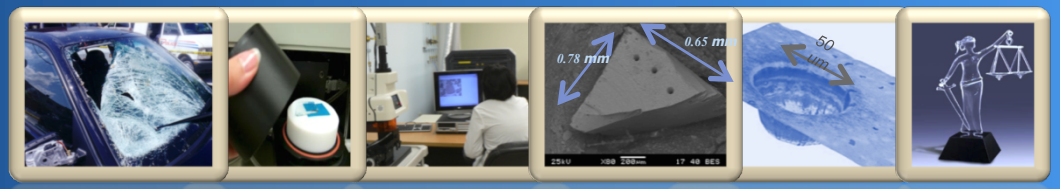
Uncertainty Associated with the Elemental Analysis and Forensic Comparison of Materials using Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Jose R. Almirall

Department of Chemistry and Biochemistry
International Forensic Research Institute
Florida International University, Miami FL USA

Forensic Science Error Management International Symposium
July 23, 2015

Outline



- Motivation for/and **advances in the use of elemental analysis** of glass evidence in forensic science
- Research in glass analysis: **our collective experience** over the last decade
- Elemental Analysis Working Group (EAWG): the **importance of standardization** of methods
- Conclusions and future directions including advances in the **interpretation of data**

CTS Proficiency Tests Reports: Laboratories reporting glass analysis

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Year – "Elemental" - RI diff. - Inconclusive/Incorrect

- 2013 - 43/111 - 0.00111 - 6/111 (5%)
- 2012 - 39/105 - 0.00113 - 3/105 (3%)
- 2011 - 43/111 - 0.00092 - 2/111 (2%)
- 2010 - 77/111 - 0.00240 - 4/111 (4%)
- 2009 – 66/114 - 0.00013 - 8/114 (≠ thickness)
- 2008 – 66/116 - 0.00040 - 8/116 (7%)
- 2007 – **85**/120 - no difference - 32/120 **(27%)**
- 2006 – 70/117 - 0.00020 - 14/117 (12%)
- 2005 – 61/110 - 0.00020 - 7/110 (7%)
- 2004 – 74/122 - 0.00390 - 7/122 (6%)

Source: http://www.collaborativetesting.com/forensics/report_list.html

General hypothesis for the use of elemental analysis in forensic comparisons (glass example)

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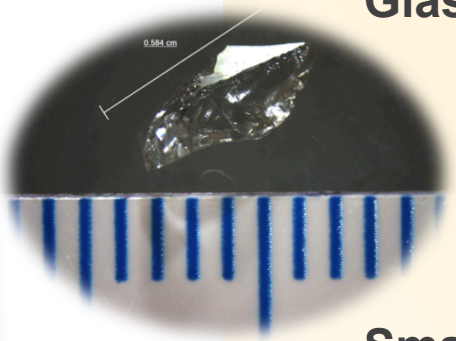

Glass contains ***an elemental signature*** originating from:

a) components added intentionally as part of their formulation

b) inorganic contaminants from the raw materials and

c) inorganic contaminants from the manufacturing process

Small ***variations*** *in the chemical composition* **remain among manufacturers and between production batches** and ***can be detected*** *and* ***used to discriminate among*** sources of glass by sensitive techniques (laser ablation coupled to ICP-MS).

Many research groups have reported distinguishing glass samples from different manufacturing sources and even from the same source when manufactured at different times.

Possible Interpretations of this data

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- **When glass fragments are analyzed and compared by these sensitive methods and NO difference is detected between the elemental signatures then the analyst may conclude that the glass fragments originated from the same manufacturing plant and was manufactured at approximately the same time period (weeks/months).**
- **Association scale:**

  Type 1 Association: Identification

  Type 2 Association: Highly likely

  Type 3 Association: Could have

  Type 4 Association: Cannot eliminate
- **Calculation of a Likelihood Ratio (LR)**

LR = 1/f, where f is probability of observing the same elemental signature in the general population.
f can be estimated by 1/ (N+1), where N is the number of samples in your database (for a database of 1000 samples, **LR ~ 1000**.)

Comparison of Profiles

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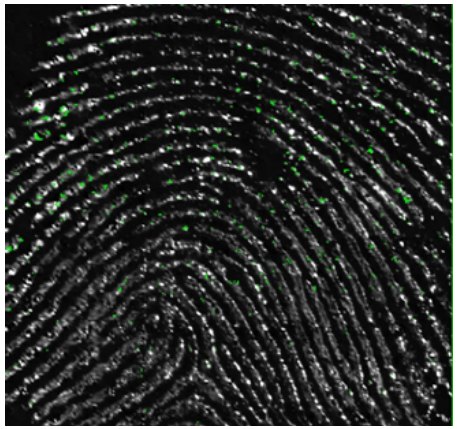
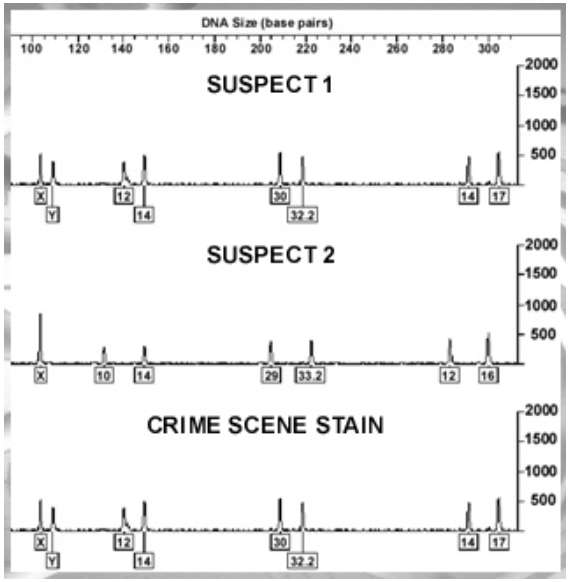
Fingerprints



Unique

Imagen: www.istockphoto.com

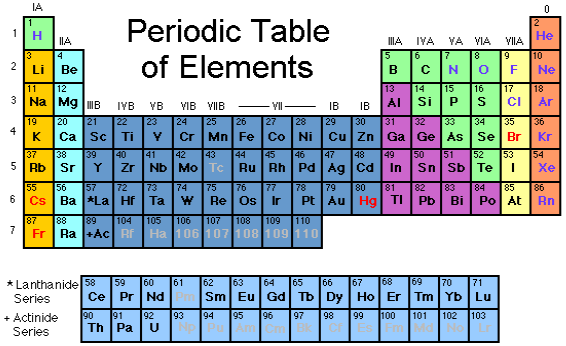
DNA

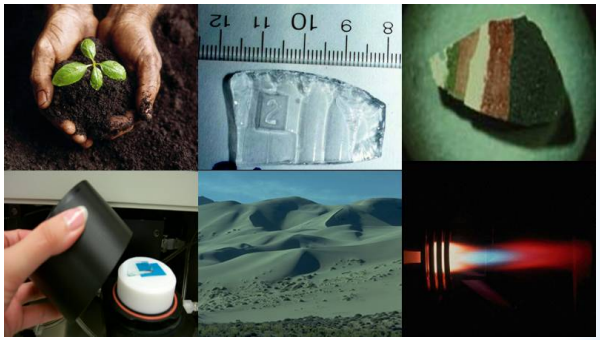


Probability < 1: 1billon

Unique
(except identical twins)

Elemental Analysis





Very high power of discrimination but not unique. <u>Depends on material and analytical method used</u>

Scientific Working Group on Materials (SWGMAT) Guidelines

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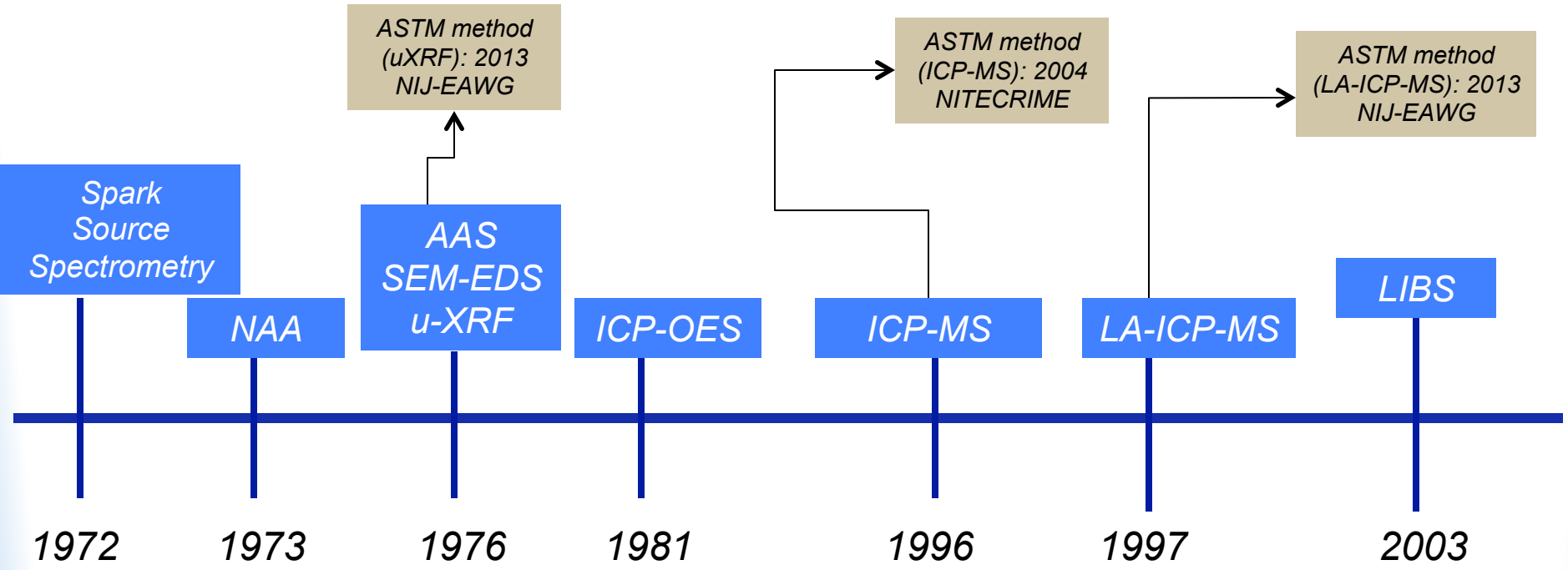
- "The discrimination potential of element concentrations in glass was documented as early as 1973. Several instrumental methods have been used by forensic scientists ……"

- "Elemental analysis methods are (***should be***) used when other methods of comparison fail to distinguish two glass fragments as having different sources…"

Source: Elemental Analysis of Glass, Forensic Science Communications, vol. 7, no. 1, 2005.

Elemental analysis of glass: timeline of progress



Over 70 peer-reviewed publications *describing method performance and utility of* ***elemental analysis of glass in forensic examinations over the past 4 decades.***

ICP Plasma as an Ionization Source

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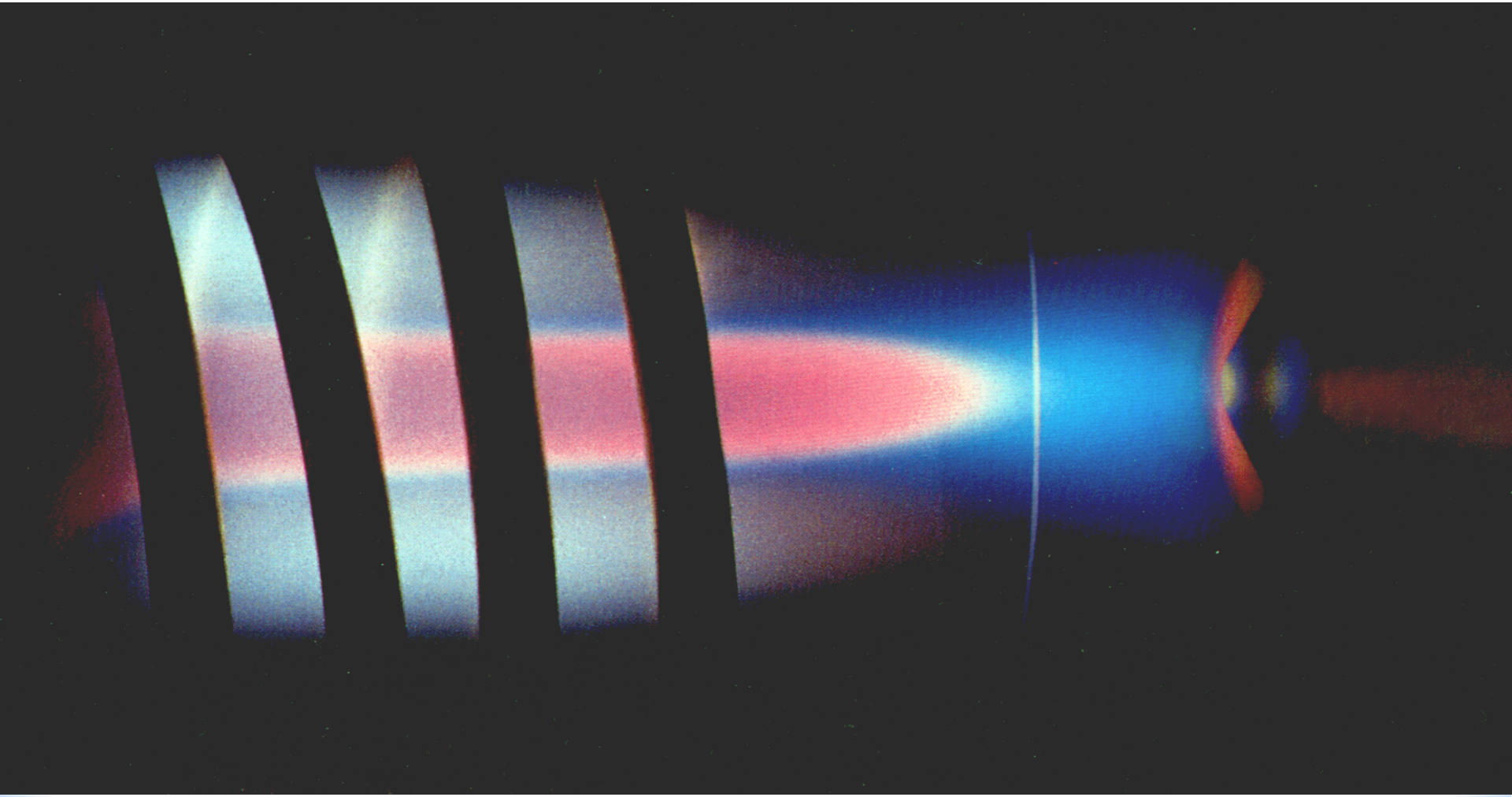

Slide courtesy of R. Sam Houk, Iowa State University

Laser Ablation micro-analysis

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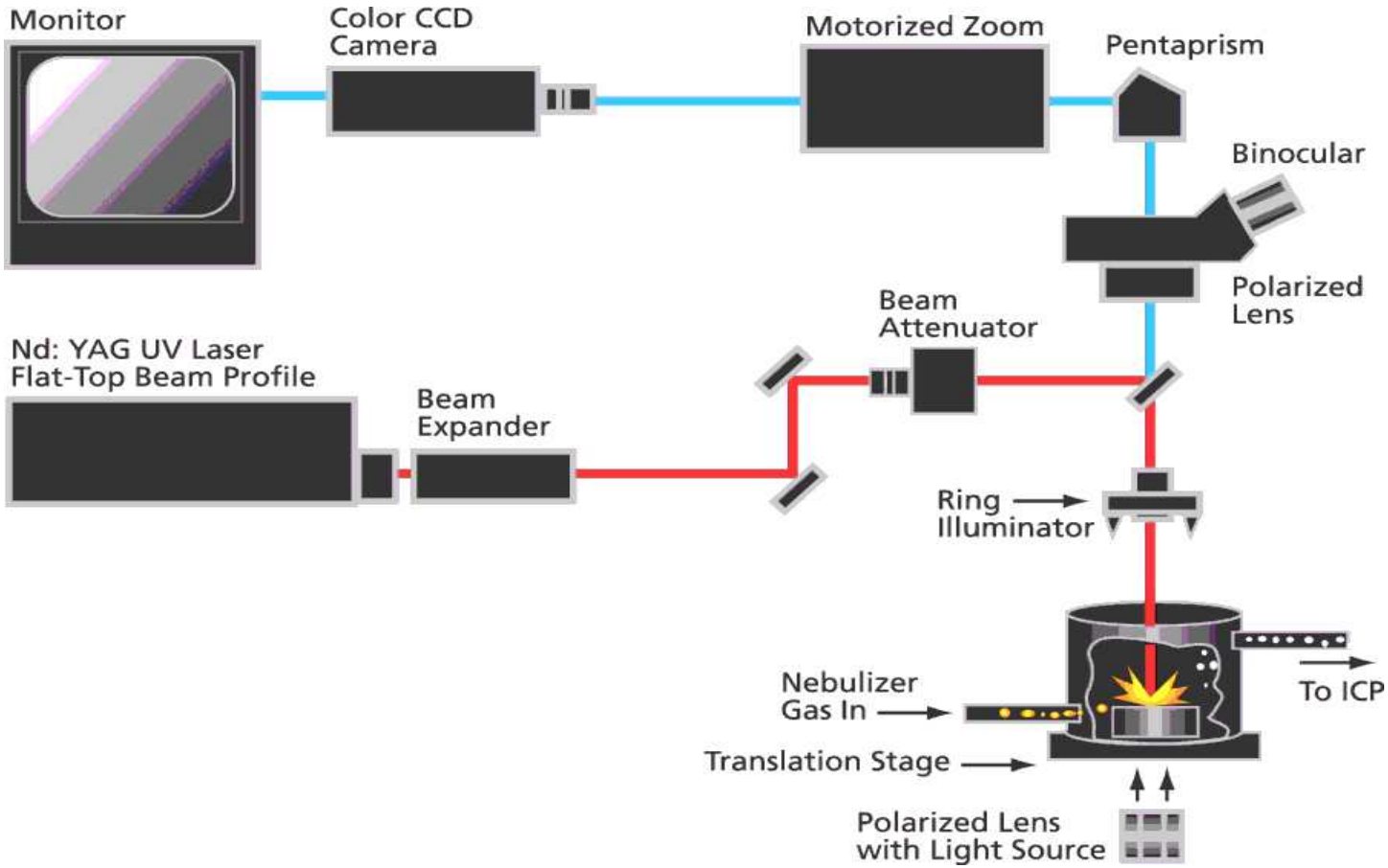

Source: CETAC Technologies

Quantitative Analysis using LA-ICP-MS

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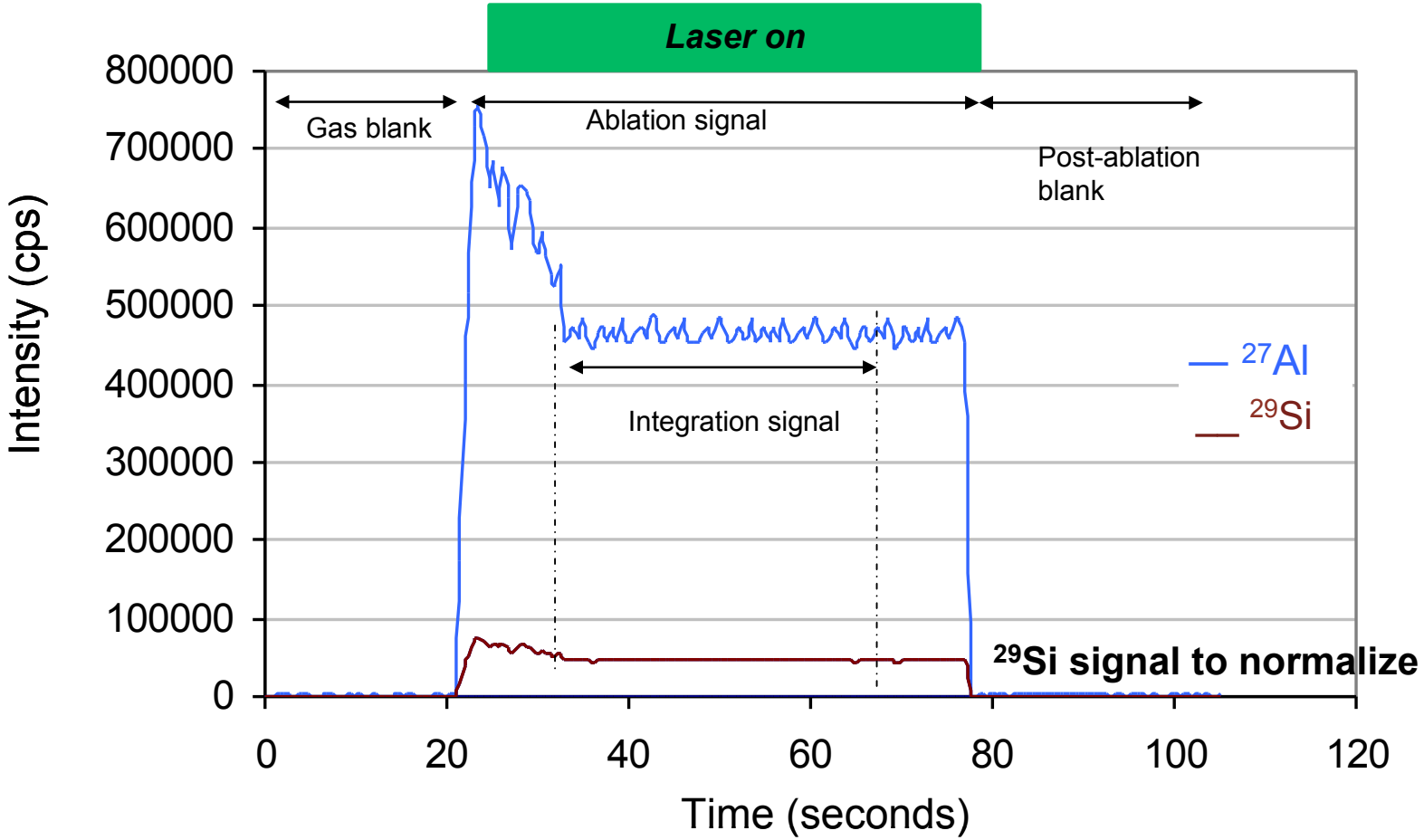
1. Normalize for ablation yield using Si as an internal std
2. Convert cps to concentration with calibration std (FGS1)

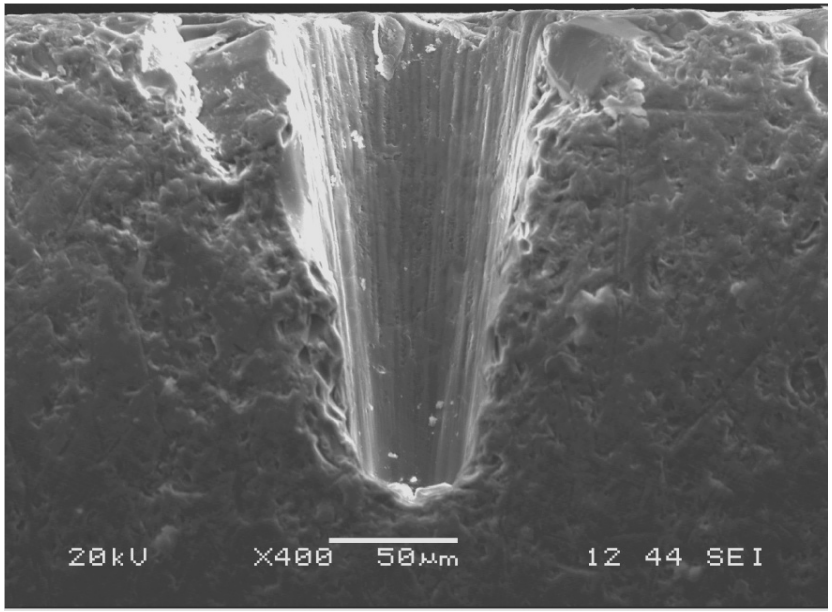


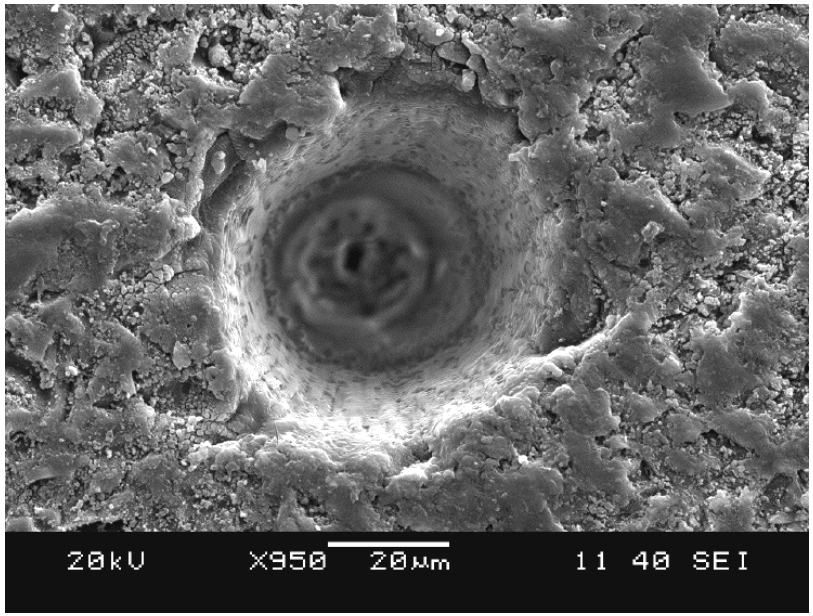
E2126 (**2013**) Standard Test Method for the Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons, **ASTM**

LODs with the New Wave UP 213 LA-ICP-MS and Elan DRC ICP-MS

Glass Standard	^{25}Mg	^{55}Mn	^{85}Rb	^{88}Sr	^{90}Zr	^{137}Ba	^{139}La	^{140}Ce	^{146}Nd	^{178}Hf
NIST 612 (ppm)	2.2	0.32	0.11	0.062	0.094	0.30	0.061	0.075	0.19	0.22
NIST 1831 (ppm)	2.1	0.32	0.10	0.072	0.10	0.24	0.053	0.065	0.17	0.21
FGS02 (ppm)	3.4	0.31	0.093	0.060	0.083	0.23	0.040	0.052	0.15	0.21

50 µm spot size, 266 nm (9 mJ), 10 Hz, 50 sec. ablation (500 shots), He carrier





T. Trejos and J.R. Almirall, Effect of fractionation on the elemental analysis of glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *Analytical Chemistry*, **2004**, 76(5) 1236-1242.

LA-ICP-MS Limit of Detection (LODs)

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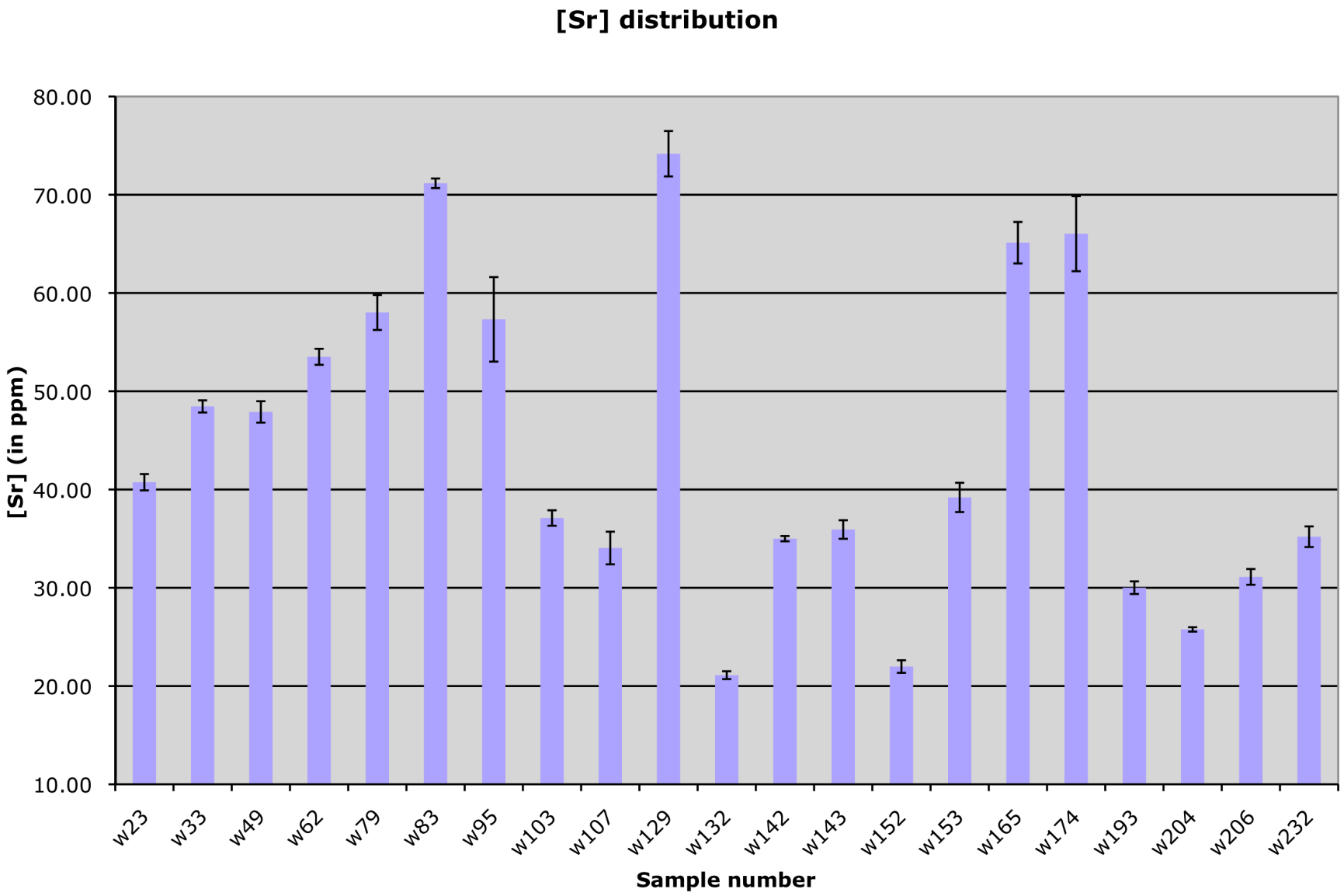
Element	*Typical* Concentration Range [ppm]	LOD (*ns*-LA-ICP-MS) [ppm]
Mg	25064 – 43136	0.79
Al	485 – 8116	0.82
Ti	51 – 463	2.80*
Mn	10 – 79	0.27
Rb	0.23 – 7	0.05
Sr	21 – 91	0.06
Zr	20 – 271	0.05
Ba	5 – 64	0.23
La	1.20 – 12	0.06
Ce	2 – 23	0.02
Hf	0.79 – 8	0.19
Pb	1.27 – 37	0.25



21 windows with the same refractive index values and similar chemical composition

Utility of Elemental Analysis of Glass

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Peer reviewed papers:

*Hickman, D, Glass types identified by chemical analysis, Forensic Science International, **1986**, 33(1), 23-46.*

*Koons, R; Fiedler, C; Rawalt, R, Classification and discrimination of sheet and container glasses by ICP-AES and pattern recognition, Journal of Forensic Sciences, **1988**, 33(1), 49-67.*

*Becker, S; Gunaratnam, L; Hicks, T; Stoecklein, W. and Warman, G, The differentiation of float glass using refractive index and elemental analysis: Comparisons of techniques, Problems of Forensic Science, Vol. XLVII, **2001**, 80-92.*

*DC Duckworth, SJ Morton, CK Bayne, S Montero, RD Koons and JR Almirall, Forensic glass analysis by ICP-MS: A multi-element assessment of discriminating power via Analysis of Variance (ANOVA) and pair-wise comparisons", J. of Analyt. and Atomic Spectrometry, **2002**, 17(7) 662-668.*

*Trejos, T and Almirall, J, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part I and Part II: micro-homogeneity study of glass and its application to the interpretation of forensic evidence, Talanta, **2005**, 67(2) 388-395 and 396-401.*

*Latzchoczy,C; Dücking, M; Becker, S; Günther, D; Hoogewerff J; Almirall, J; Buscaglia, J; Dobney, A; Koons, R; Montero, S; van der Peyl, G; Stoecklein, W; Watling, J; Zdanowicz, V, Evaluation of a standard method for the quantitative elemental analysis of float glass samples by LA-ICP-MS, J. of Forensic Sciences, **2005**, 50 (6), 1327-1341.*

Discrimination of glass comparisons using LA-ICP-MS

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Glass Subset	CFS *1	Headlamp *1	Container*1	Automobile*2
# of samples	46	45	45	41
# comparison pairs	**1035**	**990**	**990**	**820**
Discrimination power (LA-ICP-MS)	**99.7%**	**100%**	**100%**	**99%**
% false inclusions	0.3%	0%	0%	1.0%*

 # comparison pairs n(n-1)/2 = 171

% DISC = 100* (1- IP/CP)

[1] *Trejos T., Montero S. and Almirall J.R., J. of Analyt. and Bioanalyt. Chem., **2003**, 376, 8: 1255-1264.*

[2] *Naes B., Umpierrez S., Ryland S., Barnett C. and Almirall J.R., Spectrochimica Acta. B., **2008**, 63 ,1145-1150.*

Miami Junkyard Sample Collection

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- A total of 41 glass samples were collected from 14 different vehicles
- Selected vehicles were manufactured from 1995 to 2005
- 41 samples produce 820 possible comparisons

LA-ICP-MS Discrimination by Element

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Isotope	Number of indistinguishable pairs (out of 820 possible pairs)
^{140}Ce	303 (37%)
^{57}Fe	255 (31%)
^{137}Ba	191 (23%)
^{85}Rb	176 (21%)
^{49}Ti	142 (17%)
^{90}Zr	127 (15%)
^{88}Sr	76 (9%)
All (14 isotopes)	8 (1%)

*B. Naes, S. Umpierrez, S. Ryland, C. Barnett and **JR Almirall**, Spectro. Acta Part B: Atomic Spectroscopy, **2008**.*

List of indistinguishable pairs by LA-ICP-MS

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Pair #	Sample #	Vehicle make	Vehicle model	Year	Sample Location
1	6	Chevrolet	Cavalier	2004	outside windshield
	7	Chevrolet	Cavalier	2004	inside windshield
2	8	Chevrolet	Cavalier	2004	side window
	9	Chevrolet	Cavalier	2004	rear window
3	11	Oldsmobile	Intrigue	1998	outside windshield
	12	Oldsmobile	Intrigue	1998	inside windshield
4	13	Dodge	Neon	2000	outside windshield
	14	Dodge	Neon	2000	inside windshield
5	20	Chevrolet	Cavalier	2003	outside windshield
	21	Chevrolet	Cavalier	2003	inside windshield
6	23	Dodge	Stratus	1998	outside windshield
	24	Dodge	Stratus	1998	inside windshield
7	28	Ford	Expedition Eddie Bauer	2004	inside windshield
	29	Ford	Expedition Eddie Bauer	2004	outside windshield
8	37	Jeep	Grand Cherokee	2001	outside windshield
	38	Jeep	Grand Cherokee	2001	inside windshield

*B. Naes, S. Umpierrez, S. Ryland, C. Barnett and **JR Almirall**, Spectro. Acta Part B: Atomic Spectroscopy, **2008**.*

Elemental Analysis in Forensic Science: Practice

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"*Elemental analysis methods are used (**should be**) when other methods of comparison fail to distinguish two glass fragments as having different sources.*"

SWGMAT Guidelines on Elemental Analysis of Glass; 2004
http://www.swgmat.org/Elemental%20Analysis%20of%20Glass.pdf

SEM-EDS is not recommended due to limitations in sensitivity for detection of trace elements (MDL ~ 1000 ppm)
uXRF, solution/digestion ICP-MS and LA-ICP-MS are methods of choice in operational forensic laboratories.
LIBS provides a viable, sensitive (MDL ~ 1-10 ppm) alternative to uXRF and LA-ICP-MS.

Of the ~ **111** trace evidence laboratories completing the **2013 CTS glass examination**, **31 labs** reported using XRF and **11 labs** reported using ICP-MS or LA-ICP-MS, **1 lab** (+referee) LIBS (**43/111 or only 39%** follow SWGMAT Guidelines).

Six (6) incorrect responses included 1 SEM-EDS and labs with no elemental analysis .

Forensic LA-ICP-MS or LIBS labs in the U.S.	Forensic LA-ICP-MS or LIBS labs elsewhere
FBI Laboratory (CFRSU)	National Forensic Science Service, Seoul (Korea)
Sacramento County Forensic Laboratory	National Research Institute of Police Science (Japan)
Texas Department of Public Safety	Health Sciences Authority Forensic Lab (Singapore)
Tennessee Bureau of Investigation FSD	Beijing Police Forensic Science Lab (China)
U.S. Customs and Border Protection, DHS	Madrid Federal Police (Spain)
Homeland Security Investigation Laboratory, DHS	Netherlands Forensic Institute (The Hague)
New Jersey State Police Forensic Laboratory	Forensic Science Institute (BKA, Germany)
South Carolina Law Enforcement Division (SLED)	State Forensic Labs in Germany (LKAs)
Virginia Department of Forensic Sciences (LIBS)	RCMP, (Ottawa, Canada)
Food and Drug Administration Forensic Labs	Barcelona Guardia Civil (Spain)
U.S. EPA Forensic Laboratory	South Africa Police Services Lab (Pretoria, South Africa)
Several other LIBS installations in the US	Australian Federal Police (Canberra, Australia) (LIBS)
Florida International University, IFRI Lab	Brazilian Federal Police Forensic Laboratory, and more

EAWG Round Robin Design

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RR1: Performance of analytical methods, evaluation of **match criteria currently in use** in each lab

RR2 : Larger set of standard materials for standardization of methods. Larger sample sets for comparison and evaluation of **type I and type II error rates.**

RR4: extended evaluation of **sampling and match criteria effect on type I and II errors** (focused on false exclusions)

RR3: study **discrimination capabilities** from glass sources produced at different time intervals and efficiency of match criteria (focused on false inclusions)

Benefits of Inter-laboratory Exercises

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- Utilize the power of errors, “errors are good”
- Errors (mistakes) during inter-laboratory exercises are very low stakes (in comparison to casework or proficiency tests)
- Exercises are an extension of training when we have permission to learn from our mistakes
- Provides a feedback loop, provides a means to calibrate oneself with respect to everyone else
- The lessons are both individual and community
- May lead to consensus

Other Benefits of Inter-laboratory Exercises

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- Identify sources of errors (including unfit analyst, inadequate instrumentation/facilities)
- Provide necessary training
- Reveal any cognitive bias issues
- Reveal the uncertainty associated with your own individual instrument/laboratory setup
- Reveal any tendencies to overstate (or understate) the value of the evidence
- Instill confidence in the measurements and conclusions derived from same

NIJ-funded Elemental Analysis Working Group (EAWG)

Evaluation of the performance of different match criteria for the comparison of elemental composition of glass by μ-XRF, ICP-MS, LA-ICP-MS and LIBS.

Jose Almirall[1], Tatiana Trejos[1], Robert Koons[2], Stefan Becker[3], Ted Berman[4], Steve Buckley[5], JoAnn Buscaglia [6], Erica Cahoon[1] , Claude Dalpe[7] ,Tiffany Eckert-Lumsdon[8], Troy Ernst[8], Igor Gornuskin[9], Christopher Hanlon[10], Alex Heydon[11], Randall Nelson[12], Kristine Olsson[13], Christopher Palenik[14], Edward Chip Pollock[16], David Rudell[11], Scott Ryland[4], Emily Schenk[1], Anamary Tarifa[1] , Melissa Valadez[16] , Andrew van Es[17], Diane Wong[18], Vincent Zdanowicz

[1]International Forensic Research Institute at Florida International University, [2]retired Federal Bureau of Investigation (FBI laboratory CFRSU), Forensic Science Institute (BKA, Germany), [4]Florida Department of Law Enforcement, [5]Photon Machines, [6]FBI laboratory CFRSU, [7]Royal Canadian Mounted Police - Forensic Science & Identification Services, [7]US Army Criminal Investigation Lab, [8] Michigan State Police-Grand Rapids Forensic Laboratory, [9]BAM, Federal Institute of Materials Research and Testing, [10]Miami Dade Police Department, [11]Center of Forensic Sciences (Canada), [12]Tennesse Bureau of Investigation, [13]Johnson County Crime Lab, [14]Microtrace LLC, [15]Laboratory of Forensic Science, Sacramento, CA, [16] Texas Department of Public Safety, [17]Netherlands Forensic Institute, [18]Applied Spectra, [19]Department of Homeland Security, CBP Research Laboratory

Round Robin Studies

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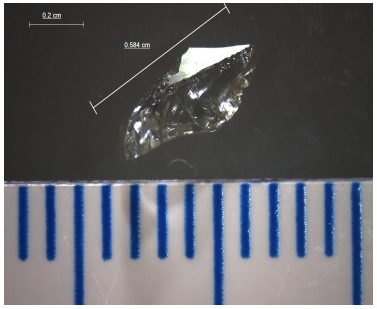
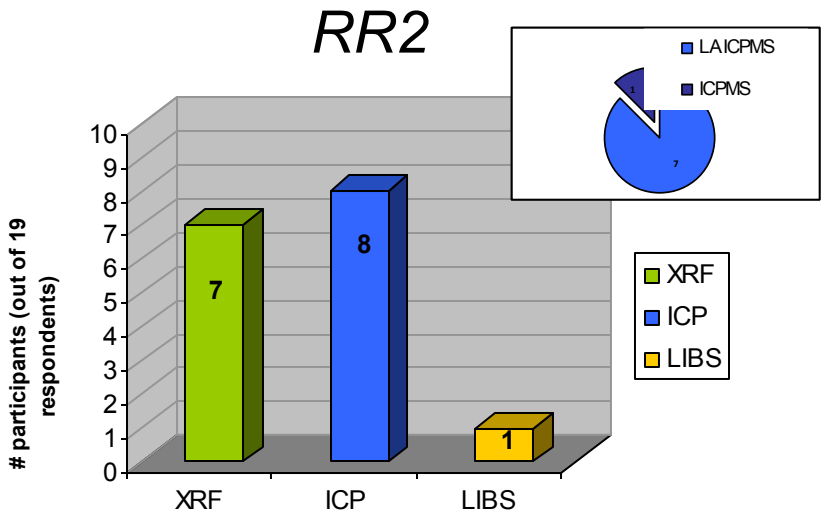
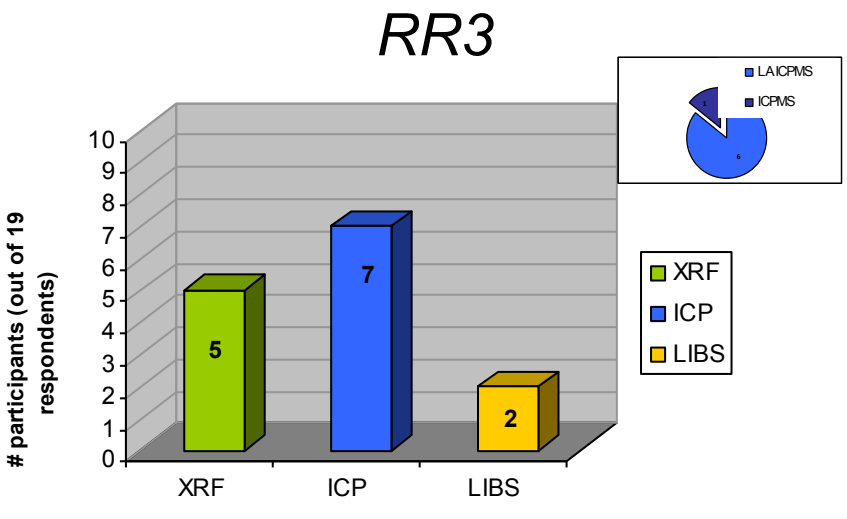
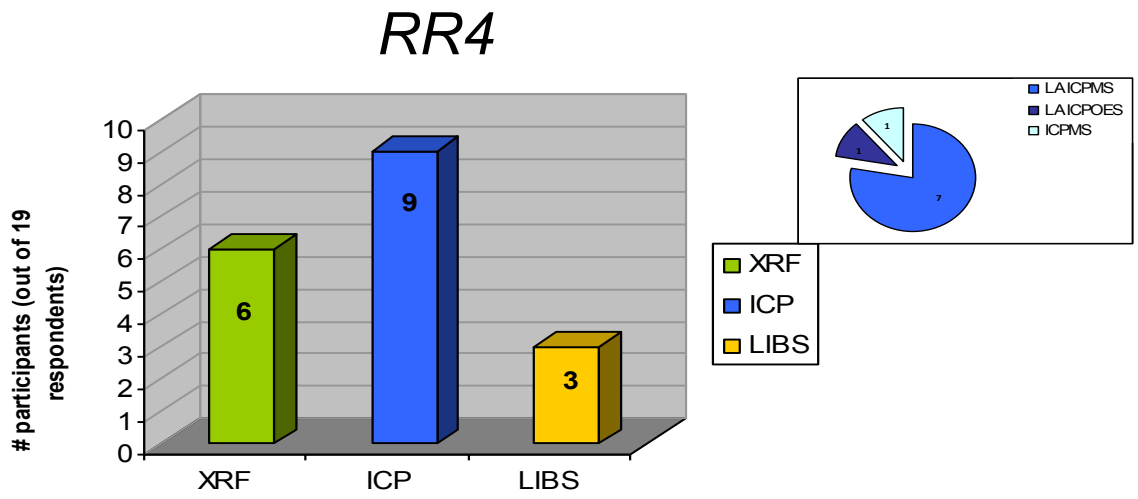
- Questions to answer
  - **ANALYTICAL PERFORMANCE**
    - How does each technique perform in comparison to the others?
      - µXRF, ICP (LA-ICP-MS, ICP-MS, LA-ICP-OES), LIBS
      - Precision (inter-lab, intra-lab)
      - Accuracy
      - Sensitivity (LOD, LOQ)
      - Interferences
      - Discrimination capabilities
    - How is the inter-laboratory performance?
      - Consistency of results
      - Standardization of the methods of analysis (ASTM methods)
  - **MATCH CRITERIA**
    - What match criteria is/are appropriate for the interpretation of the data generated from the elemental analysis of glass?
      - Evaluation of performance and error rates for different methods
      - Sampling strategies
      - Selection of practical and statistically sound comparison criteria
      - Interpretation of **significance** of the association



Participant laboratories







2nd Round Robin Objectives

Reference standard materials NIST 1831, FGS1 and FGS2

- Evaluation of **analytical performance**
- **Normalization of** XRF data
- **Improvement** and standardization of methods
- **Variations** of the measurements and inter-lab variation

- **Glass samples for comparisons**
  - Evaluation of **different match criteria** and to address the interpretation and standardization of reporting language.

Evaluation of analytical performance

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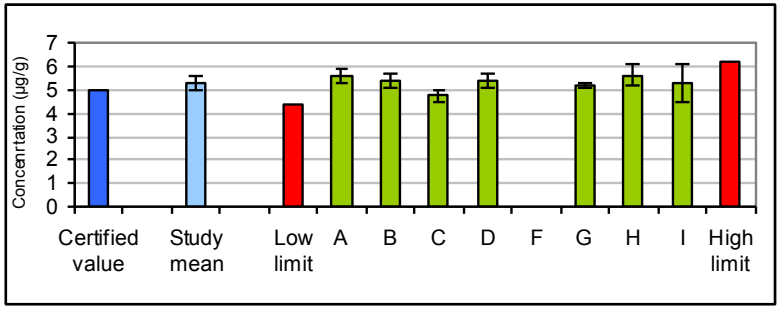
Elemental analysis of SRM 1831 — **Lithium**

Laboratory ID	mean	stdev	comments	Z scores		
A-ICP	5.63	0.27		z score Aq	0.95	acceptable
B-ICP	5.39	0.30		Z score Bq	0.16	acceptable
C-ICP	4.75	0.22		z score Cq	-1.96	acceptable
D-ICP	5.40	0.28		Z score Dq	0.21	acceptable
F-ICP			nr	z score Fq	-17.80	nr
G-ICP	5.23	0.12		z score Gq	-0.36	acceptable
H-ICP	5.66	0.44		Z score Hq	1.08	acceptable
I-ICP	5.30	0.80		z score Iq	-0.13	acceptable
Certified value	4.99					

Inter-Lab statistics

Study Mean	5.34
Study Standard Dev.	0.30
high limit (mean + 3)	6.25
low limit (mean - 3)	4.43



The study led to:
- **Standardization of methods**
- **Identification of outliers and sources of errors**
- **Method improvement**

SRM 1831: All participants passed the z score criteria only 1 lab reported Zr out of range (outlier)

Excellent agreement between participant laboratories (%RSD <10, % bias <10 for majority of elements)

Bias and precision found in SRM NIST 1831 from inter-laboratory study.

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Element	Reported value, $\mu g g^{-1}$	Average, $\mu g g^{-1}$ [D]	Bias %	Repeatability-within s_r (%)	Reproducibility-between s_R (%)
Li	5.00 [A]	5.3	7.0	**5.1**	**5.6**
Mg	21200 [B]	23900	13	**1.1**	**10**
Al	6380 [B]	6400	0.3	**1.1**	**9.3**
K	2740 [B]	2690	-1.8	**2.3**	**7.2**
Ca	58600 [B]	58000	-1.0	**2.6**	**3.9**
Fe	608 [B]	500	-18	**2.7**	**22**
Ti	114 [B]	130	14	**2.6**	**7.0**
Mn	15.00 [C]	13.1	-13	**1.8**	**2.4**
Rb	6.11 [C]	6.0	-1.8	**2.4**	**3.8**
Sr	89.12 [C]	85	-5.0	**2.0**	**4.6**
Zr	43.36 [C]	36	-17	**2.2**	**6.8**
Ba	31.5 [C]	30.0	-4.4	**2.6**	**6.7**
La	2.12 [A]	2.2	4.2	**2.6**	**6.7**
Ce	4.54 [C]	4.4	-3.1	**2.6**	**3.8**
Nd	1.69 [A]	1.8	4.1	**2.3**	**7.1**
Hf	1.10 [C]	0.96	-13	**3.7**	**8.5**
Pb	1.99 [C]	1.8	-11	**5.0**	**6.7**

Data from 7 participant laboratories using different manufacturer LA and ICP-MS instruments

Description of the glass samples – RR2

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- **Architectural float glass** manufactured at the **same manufacturing plant** (Cardinal Glass Industries, Portage, WI, USA).
- **K1 and Q1** shared a **common origin**
  - Manufactured April 1st, 2001
- **Q2** originated from a different source than sample K1
  - Manufactured August 12th, 1998

Glass Comparisons as reported by each lab using their selected match criteria

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Lab ID	Method	K1 vs Q1	K1 vs Q2	Match criteria
A-ICP	LA-ICP-MS	IN	DS	t-test (p=0.05, elements and ratios)
B-ICP	LA-ICP-MS	IN	DS	Ratios, ± 2SD
C-ICP	LA-ICP-MS	IN	DS	± 4SD (with %RSD<5%), element concentrations
D-ICP	LA-ICP-MS	IN	DS	t-test (p=0.05, element concentrations)
F-ICP	ICP-MS	IN	DS	± 3SD, element concentrations
G-ICP	LA-ICP-MS	IN	DS	Range overlap, ratios to Si^{29}
H-ICP	LA-ICP-MS	IN	DS	± 4SD (modified), elemental concentrations
I-ICP	LA-ICP-MS	IN	DS	t-test (p=0.05, element concentrations)

100 % correct association and discrimination

Match criteria:

1. t-test (p=0.05) [3labs]
2. Range overlap [1 lab]
3. ± 2 SD [1 labs]
4. ± 3 SD [1 labs]
5. ± 4 SD [2 labs]

RR3 - Source of the samples

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- All samples in set A (K1, K2, Q1, Q2, Q3) were architectural **float glass** manufactured at the **same manufacturing plant** (Cardinal Glass Industries, Portage, WI, USA).
- The samples were manufactured between **April/15/1998 and August 31/2001.**
- They were sampled from a 2 x 2.5cm glass fragment of the **FIU database**, originally collected from a **glass pane** sampled at the manufacturing plant.

Sample ID	Manufacturing date
K1	August / 17 / 2001
Q1	August / 31 / 2001
K2	April / 15 / 1998
Q2	May / 17 /1998
Q3	July / 17/ 1998

Each participant was asked to conduct elemental analysis in order to compare K1 with all the questioned items (Q1, Q2, Q3) and to compare K2 with all the questioned items (Q1, Q2, Q3).

3rd RR: comparison of samples manufactured more than 2 years apart

	2Y3M	*2Y5M*	*2Y4M*	
Lab ID	K1 vs Q2	K1 vs Q3	K2 vs Q1	Match criteria
A XRF	**DS**	**DS**	**DS**	Spectra overlap
B XRF	**DS**	**DS**	**DS**	Spectra overap, ± 3s of ratio intensities Ca/Mg, Ca/Ti Ca/Fe, Sr/Zr, Fe/Zr, Ca/K, Fe/Sr, Fe/Mn
C XRF	**DS**	**DS**	**DS**	Spectra overap, ± 3s of ratio intensities Excluded by Ca/Ti, Ca/K. Ca/Mn
E XRF	**DS**	**DS**	**DS**	Spectra overap, ± 3s of ratio intensities
F XRF	**DS**	**DS**	**DS**	± 3s of ratio intensities Ca/Fe, Sr/Zr, Ca/K, Fe/Mn, Ca/Mn, Fe/Ti, Ca/Ti
H LIBS	**DS**	**DS**	**DS**	t test at 95% and ANOVA (95%)
I LIBS	**IN***	**DS**	**DS**	PLS algorithm
A ICP	**DS**	**DS**	**DS**	± 2s
B ICP	**DS**	**DS**	**DS**	± 2s and ± 3s
C ICP	**DS**	**DS**	**DS**	modified ±4s
D ICP	**DS**	**DS ***	**DS**	t test at 95% (Bonferroni correction), *ANOVA + Tukey 95%
E ICP	**DS**	**DS**	**DS**	t test at 95% and ANOVA (95%)
F ICP	**DS**	**IC ***	**DS**	* Q3 large RSDs, Range overlap and ± 3s
H ICP	**DS**	**DS**	**DS**	modified ±4s

Regardless of the technique used, the differences on elemental profile of samples manufactured years apart was detected by all participants

3rd RR: comparison of samples manufactured weeks-months apart

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	2weeks	*1 month*	*3 months*	
Lab ID	**K1 vs Q1**	**K2 vs Q2**	**K2 vs Q3**	**Match criteria**
A XRF	**IN**	**DS**	**IN**	Spectra overlap
B XRF	**IN**	**DS**	**IN**	Spectra overap, ± 3s of ratio intensities Ca/Mg, Ca/Ti Ca/Fe, Sr/Zr, Fe/Zr, Ca/K, Fe/Sr, Fe/Mn
C XRF	**IN**	**IN**	**IN**	Spectra overap, ± 3s of ratio intensities Excluded by Ca/Ti, Ca/K. Ca/Mn
E XRF	**IN**	**IN**	**IN**	Spectra overap, ± 3s of ratio intensities
F XRF	**IN**	**DS**	**IN**	± 3s of ratio intensities Ca/Fe, Sr/Zr, Ca/K, Fe/Mn, Ca/Mn, Fe/Ti, Ca/Ti
H LIBS	**DS**	**DS**	**DS**	t test at 95% and ANOVA (95%)
I LIBS	**IN**	**DS**	**IN**	PLS algorithm
A ICP	**IN**	**DS**	**IN**	± 2s (for 10 elements menu, if number of overlaps 9 or 10 then match if <9 then non-match)
B ICP	**DS**	**DS**	**DS**	± 2s and ± 3s
C ICP	**DS**	**DS**	**DS**	modified ±4s
D ICP	**DS**	**DS**	**DS**	t test at 95% (Bonferroni correction), *ANOVA + Tukey 95%
E ICP	**IN ***	**DS**	**IN**	t test at 95% and ANOVA (95%)
F ICP	**IN**	**DS**	**IC ***	* Q3 large RSDs, Range overlap and ± 3s
H ICP	**DS**	**DS**	**DS**	modified ±4s

Summary RR3

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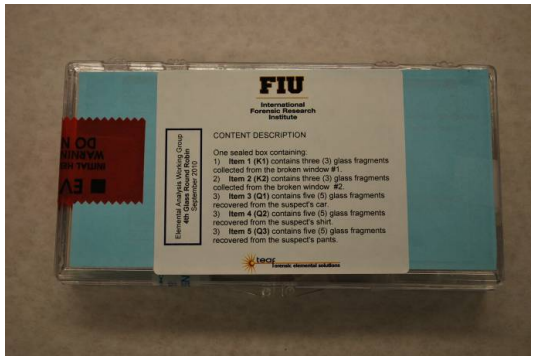
- These RR allowed the study of **type II errors** for sample sets that share **very similar composition.**
- **All techniques** were able to **differentiate samples manufactured in the same plant more than 3 months apart**, regardless of the match criteria employed.
- The samples that have very similar elemental profile and were manufactured at the same plant a few weeks or months apart were differentiated only by the more sensitive techniques (ICP and LIBS).

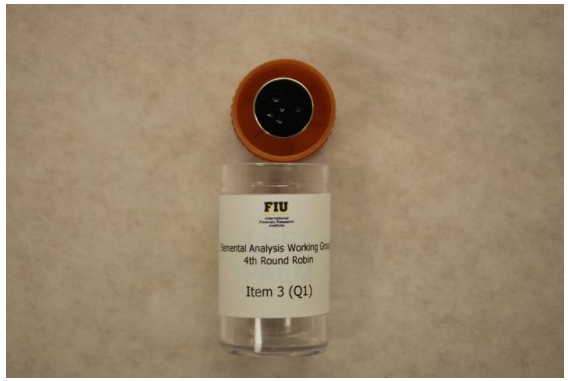
The capability to detect differences between samples manufactured within short periods of times seems to be technique-dependent but also depends on the reproducibility of the method and match criteria

4th RR: origin of the samples

- **Q1:** glass from Pilkington plant (Ohio, USA) manufactured on 02/18/2010

- **K1, K2, Q2, Q3:** all fragments from same source, glass from Pilkington plant manufactured on 03/03/2010





Pre-distribution analysis by LA-ICP-MS

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sample ID	**Q1**	**K1, K2, Q2, Q3**
manufacturing date	**021810**	030310
Li7	**6.79**	6.14
Mg25	**29287**	30487
Al27	**847**	**906**
K39	**146**	191
Ca42	**61236**	62326
Ti49	**504**	315
Mn55	**18.75**	12.08
Fe57	**4279**	3086
Rb85	**0.68**	0.76
Sr88	**47.84**	47.68
Zr90	**24.98**	21.34
Sn118	**21.29**	12.81
Sb121	**0.24**	0.23
Ba137	**8.31**	6.90
La139	**1.47**	1.48
Ce140	**2.30**	2.17
Nd146	**1.25**	1.12
Hf178	**0.67**	0.60
Pb208	**0.67**	0.65

Match Criteria Comparison

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- Each participant was later asked to conduct the following match criteria on their own data:
  - Range overlap
  - t-test (p=0.05, p=0.01)
  - ± 2s, 3s, 4s, 5s, 6s,
  - t-test with Bonferroni correction
  - Hotellings T (some sets)
  - ± 2s, 3s, 4s, 5s, 6s (min 3%RSD)

ICP methods – Type 2 error (RR2, RR3 and RR4)

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Match criteria	Type 1 error rate (%)			Type 2 error rate (%)		
	Test 2	Test 3	Test 4	Test 2	Test 3	Test 4
Range	42	-	81	0	0	0
t-test .05	74	-	93	0	1	0
t-test .01	53	-	84	0	1	0
t-test Bonf.	53	-	69	0	2	0
±2s	53	-	85	0	0	0
±2s (s>3%)	26	-	75	0	0	0
±3s	42	-	66	0	2	0
±3s (s>3%)	0	-	47	0	2	0
±4s	26	-	42	0	5	0
±4s (s>3%)	**0**	**-**	**28**	**0**	**5**	**0**
±5s	11	-	30	0	9	0
±5s (s>3%)	0	-	18	0	11	0
±6s	11	-	27	0	12	0
±6s (s>3%)	0	-	13	0	15	0

Type 1 error
*Failure to associate samples with common origin was observed in **RR4, with higher type I error** rates associated to **heterogeneity** of the sample source*

Type 2 error:
*Failure to discriminate samples that originated from different sources was observed only for samples that originated from the **same plant** manufactured **2 weeks apart** (RR3)*

Products of EAWG

FIU International Forensic Research Institute

JAAS

Journal of Analytical Atomic Spectrometry

www.rsc.org/jaas

PAPERS

1270

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

Tatiana Trejos, Robert Koons, Peter Weis, Stefan Becker, Ted Berman, Claude Dalpe, Marc Duecking, JoAnn Buscaglia, Tiffany Eckert-Lumsdon, Troy Ernst, Christopher Hanlon, Alex Heydon, Kim Mooney, Randall Nelson, Kristine Olsson, Emily Schenk, Christopher Palenik, Edward Chip Pollock, David Rudell, Scott Ryland, Anamary Tarifa, Melissa Valadez, Andrew van Es, Vincent Zdanowicz and Jose Almirall*

ASTM INTERNATIONAL

ASTM E2926 - 13

Standard Test Method for Forensic Comparison of Glass Using Micro X-ray Fluorescence (μ-XRF) Spectrometry

ASTM E2927 - 13

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

Anal Bioanal Chem

DOI 10.1007/s00216-013-6978-y

RESEARCH PAPER

Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ-XRF, ICP-MS, and LA-ICP-MS

Tatiana Trejos · Robert Koons · Stefan Becker · Ted Berman · JoAnn Buscaglia · Marc Duecking · Tiffany Eckert-Lumsdon · Troy Ernst · Christopher Hanlon · Alex Heydon · Kim Mooney · Randall Nelson · Kristine Olsson · Christopher Palenik · Edward Chip Pollock · David Rudell · Scott Ryland · Anamary Tarifa · Melissa Valadez · Peter Weis · Jose Almirall*

Research article

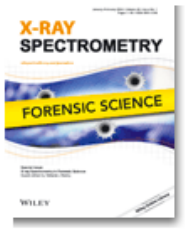
Signal-to-noise ratios in forensic glass analysis by micro X-ray fluorescence spectrometry

T. Ernst[1,*], T. Berman[2], J. Buscaglia[3], T. Eckert-Lumsdon[4], C. Hanlon[5], K. Olsson[6], C. Palenik[7], S. Ryland[2], T. Trejos[8], M. Valadez[9], J. R. Almirall[8]

Article first published online: 21 DEC 2012

DOI: 10.1002/xrs.2437

Issue



X-Ray Spectrometry

Special Issue: X-ray Spectometry in Forensic Science

Volume 43, Issue 1, pages 13–21, January/February 2014

Significance of Elemental Analysis from Trace Evidence

NCJ Number: 242325

Date Published: October 2012

Author(s): Jose Almirall

Document Type: Grant Report

NIJ Final Report

https://ncjrs.gov/pdffiles1/nij/grants/242325.pdf

ASTM Test Method-

"a definitive procedure that produces a test result"

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"An ASTM test method should represent a **consensus** as to the best currently available test procedure for the use intended. It should be supported by experience and adequate data obtained from cooperative tests."

"The **precision and bias** section of the test method shall include a brief descriptive summary of the interlaboratory study that will permit the user of the test method to judge the reliability of the data."

"**Measurement uncertainty** is an estimate of the magnitude of systematic and random measurement errors that may be reported along with the measurement result."

** Form and Style for ASTM Methods, Jan. 2015 ed. ASTM Intern.*

Final Recommendations- EAWG

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Sampling

- Use a **minimum** of 9 measurements from the known fragments (from 3 fragments, if possible). Use as many measurements as practical from the recovered fragments to calculate the mean concentrations for each element.
- Appropriate sampling techniques should be used to account for natural heterogeneity of the material.
- For XRF data, appropriate sampling should also account for varying fragment size and surface geometries, and potential critical depth effects.

Quality assurance

- The performance of the instrument must be monitored routinely and the frequency and tolerances should be set by each laboratory.
- Precision and bias should be monitored on a daily basis using a control glass, i.e. NIST 1831.
- Method detection limits and method quantitation limits should be determined by each laboratory.

Match criteria for ICP-based data

- Use interval of ± 4 SD match criterion about the mean concentration of the known for each element.
- Due to typical precision of ICP-MS data, set the match criterion to at least 3% RSD of the mean or the actual SD of the known for each element, whichever is greater.

Interpretation –

Glass samples that are manufactured in different plants or even at the same plant but after some weeks or months apart are clearly differentiated by elemental composition.

Future Directions

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- Standardization of **language** used by glass examiners in communicating the significance of a comparison that yields indistinguishable elemental signatures using sensitive methods (LA-ICP-MS or uXRF).
- Agreement between glass examiners that results in the same conclusion as to significance in a report or during testimony.
- Simplify and automate the collection of elemental data using LIBS.
- Expand the use of elemental analysis to other matrices of interest to forensic scientists.

Example Reporting Language Currently in Use

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GENERAL ASSOCIATIONS

The following descriptions are meant to provide context to the opinions reached in this report. Every type of conclusion may not be applicable in every case or for every material type.

Type 1 Association: Identification

An association in which items share individual characteristics and/or physically fit together that demonstrate the items were once from the same source.

Type 2 Association: Highly likely

An association in which items correspond in all measured physical properties, chemical composition and/or microscopic characteristics and share distinctive characteristic(s) that would not be expected to be found in the population of this evidence type. The distinctive characteristics were not sufficient for a Type 1 Association.

Type 3 Association: Could have

An association in which items correspond in all measured physical properties, chemical composition and/or microscopic characteristics and could have originated from the same source. Because it is possible for another sample to be indistinguishable from the submitted evidence, an individual source cannot be determined.

Type 4 Association: Cannot eliminate

An association in which items correspond in some but possibly not all measured physical properties, chemical composition and/or microscopic characteristics and cannot be eliminated as coming from the same source. This type of evidence may be commonly encountered in the environment, may have limited comparative value and/or there may be factor(s) limiting the comparison.

Inconclusive - No conclusion could be reached regarding an association between the items.

Elimination: Items exhibit dissimilarities in one or more of the following: physical properties, chemical composition or microscopic characteristics and, therefore, conclusively did not originate from the same source.

Non-Association: Items exhibit dissimilarities but certain details or features are not sufficient for an Elimination.

Note: All types of association may not be applicable to all types of evidence.

Likelihood Ratio (LR) Calculation

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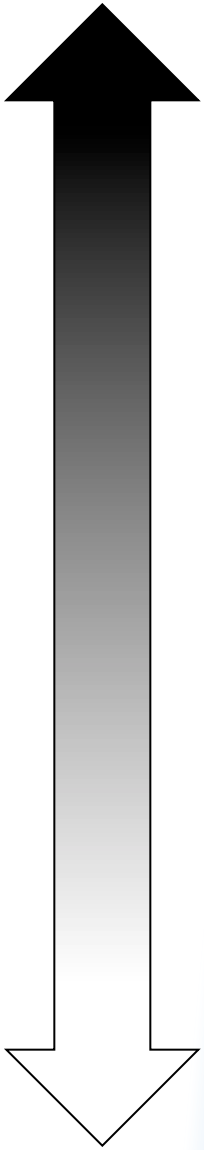
Association scale:	*Equivalent LR*
Type 1 Association: Identification	*∞*
DNA and Fingerprint Evidence	*1,000,000,000*
Type 2 Association: Very Strong Evidence	*1,000 – 10,000*
Type 3 Association: Strong Evidence	*10 – 100*
Type 4 Association: Some evidence	*1 – 10*
Inconclusive (no support for either proposition)	*1*
Evidence of poor association	*0.1*
Strong evidence of poor association	*0.001*
Very strong evidence of no association	*0.000001*
Elimination:	*0*



J. Almirall and T. Trejos, Analysis of Glass Evidence (Chapter 6) *in Forensic Chemistry: Fundamentals and Applications, J. Siegel, Ed.* ***2015****. Wiley and Sons*

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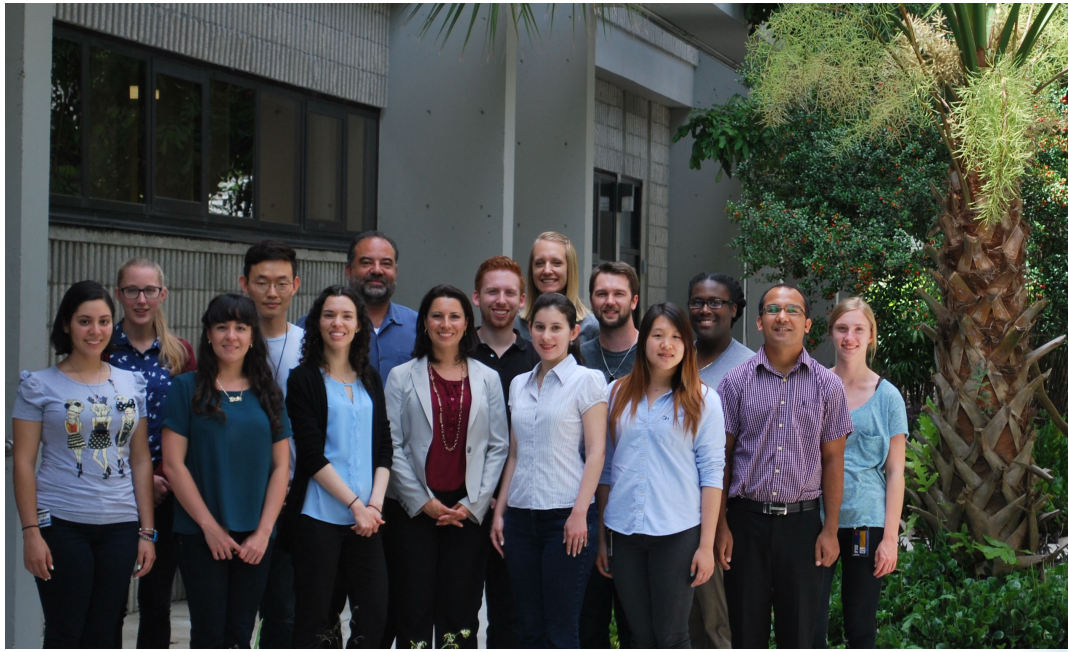

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Bulk Soil Analysis Method Development

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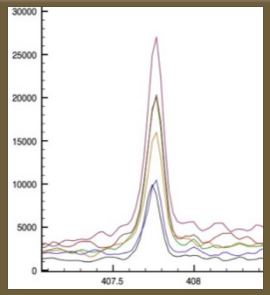
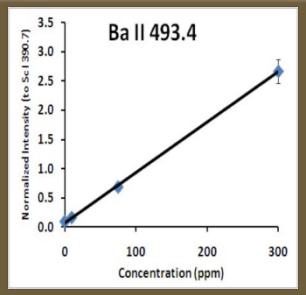
Sample Preparation

- Dry
- Sieve (optional)
- Spike with internal standard
- Homogenize
- Press into pellets



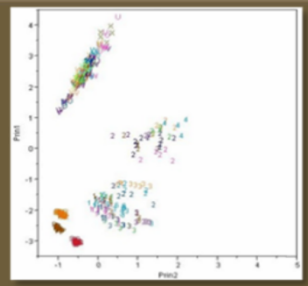
Optimization

- For each instrument
- Element menu
- Instrumental parameters
- Criteria: LOD, SNR, RSD, accuracy, selectivity



Calibration

- For each instrument
- For each element
- Linear Dynamic Range



Data Analysis

- Background subtraction
- Normalization to internal standard
- Statistical analysis: Pairwise comparison (ANOVA with Tukeys), PCA, LDA

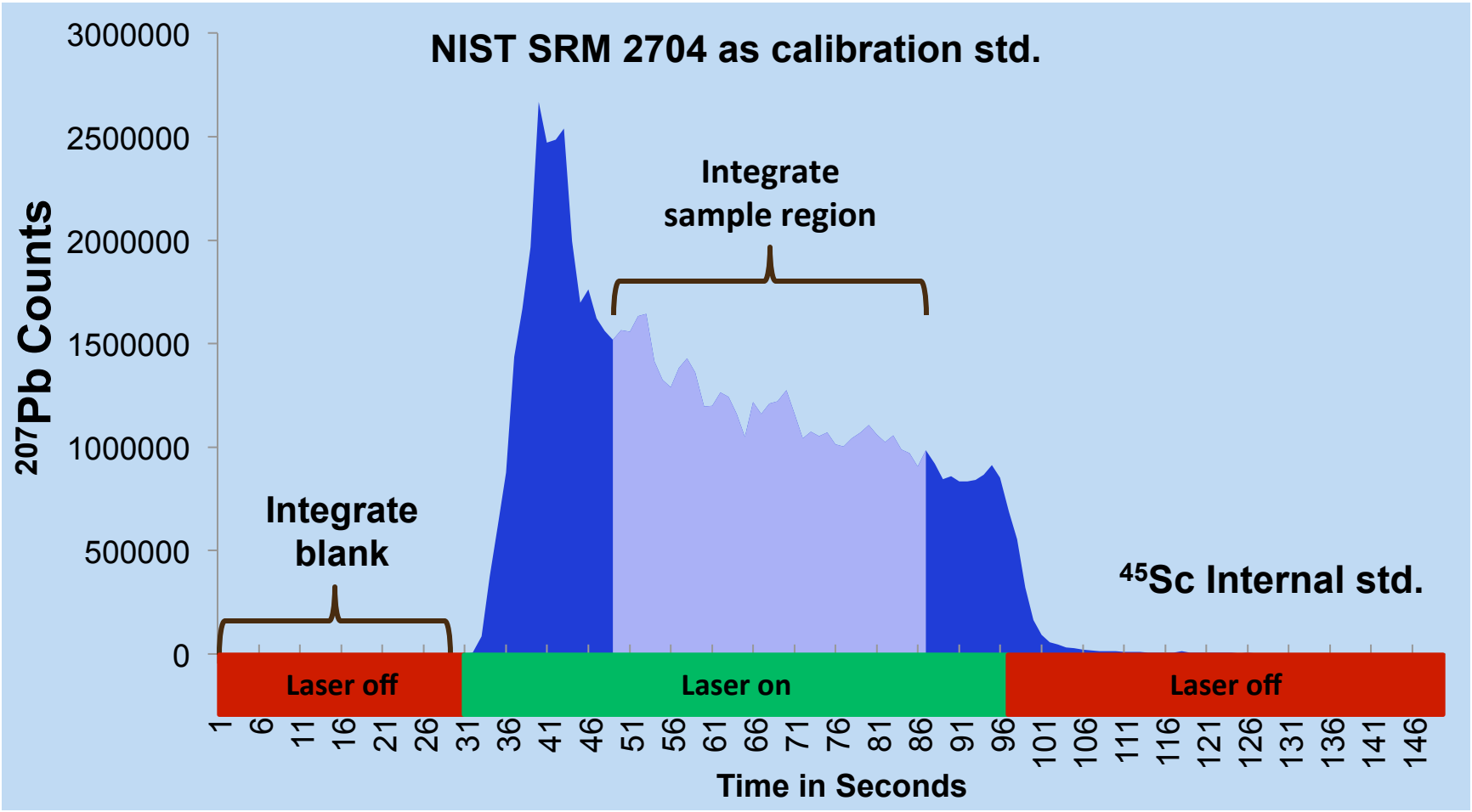
	LIBS	LA-ICP-MS
Manufacturer	Built in-house	Perkin-Elmer ELAN DRC II
Laser	New Wave Tempest 266 nm Nd:YAG (29 mJ, 4 ns pulse @ 0.667 Hz)	CETAC 266 nm Nd:YAG (3.2 mJ @ 10 Hz)
Spot	Focus at 1.4 mm into the sample surface; 137 µm spot size	Focus at sample surface; 200 µm spot size
Detector	Andor Mechelle 5000 spectrometer & iStar iCCD detector (2.0 µs gate delay, 150 µs gate width)	Quadrupole mass spectrometer
Ablation Gas	Argon	Helium
Data Collection	3 cleaning shots, 75 shots accumulated/replicate, 5 reps/ sample	10s cleaning, 30 sintegration, 4 reps/ sample
Element Menu	Ba, Ca, Fe, Li, Mg, Sr, Ti	Al, Ba, Ca, Li, Mg, Sr, Ti, U, V

Sample Preparation - Pellets

- Dry and weigh a ~ 500 mg sample
- Add internal standard
  - Dry (Eg: 80 °C overnight)
- Micromill (to reduce particle size & further homogenize) [1]
- Press the pellet
- Pros of the use of pellets:
  - Homogeneous
  - Can be used in many instruments (LA-ICP-MS, LIBS, XRF)
  - Can be stored and re-analyzed (consumes µg)
- Cons of the use of pellets:
  - Potential for loss/contamination at each step
  - Takes 2-4 days (or more if many samples)
  - Sample size requirement

1. L Arroyo, T Trejos, P.R. Gardinali, and J.R. Almirall, Optimization and Validation of a LA-ICP-MS Method for the Quantitative Analysis of Soils and Sediments, *Spectrochimica Acta Part B: Atomic Spectroscopy,* **2009**, 64 (1), 14-25.

Quantitative Analysis of Soils using LA-ICP-MS



Quantitative Analysis using LA-ICP-MS and LIBS

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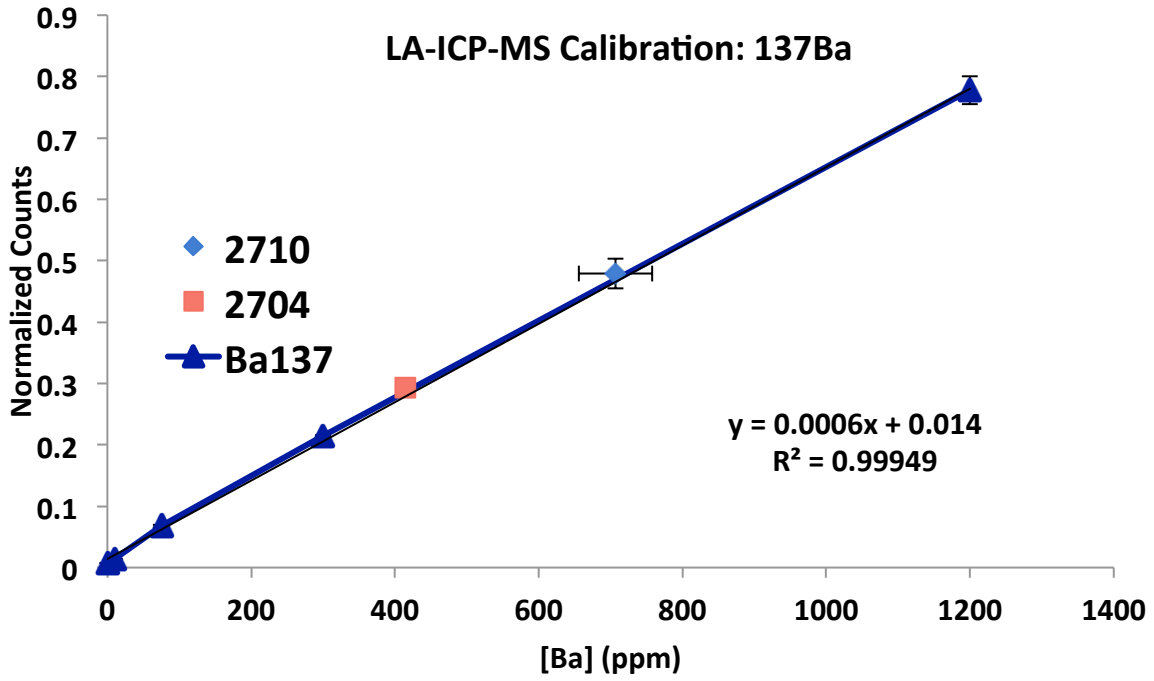

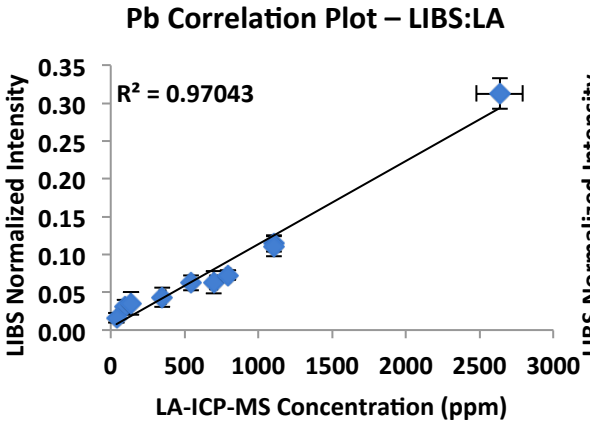

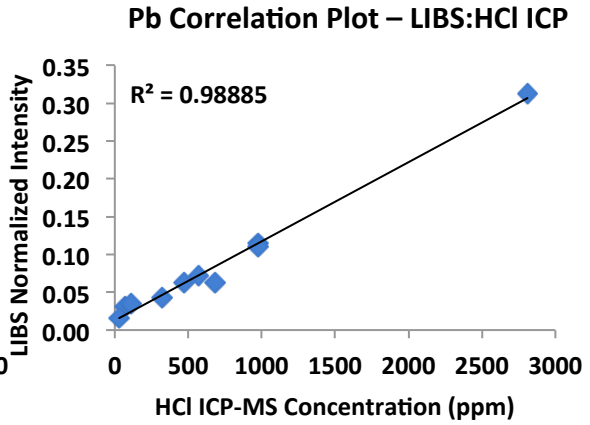

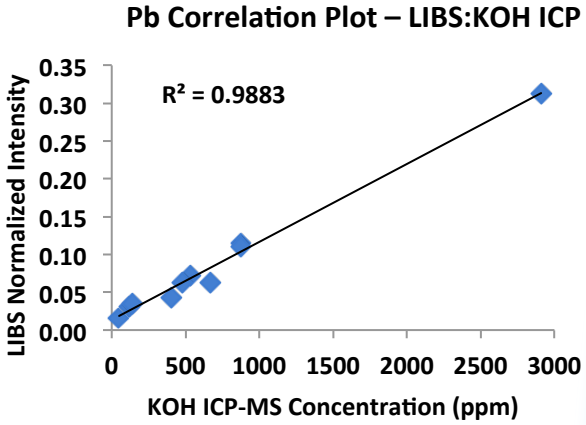

7-laboratory inter-lab LA-ICP-MS Results

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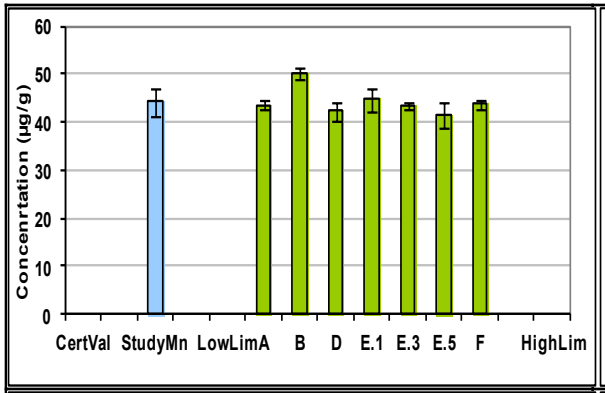
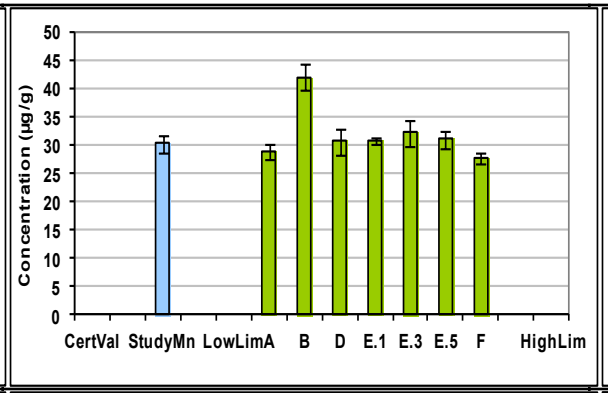
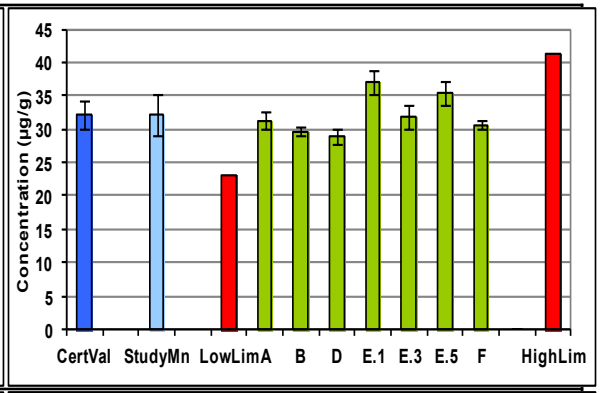
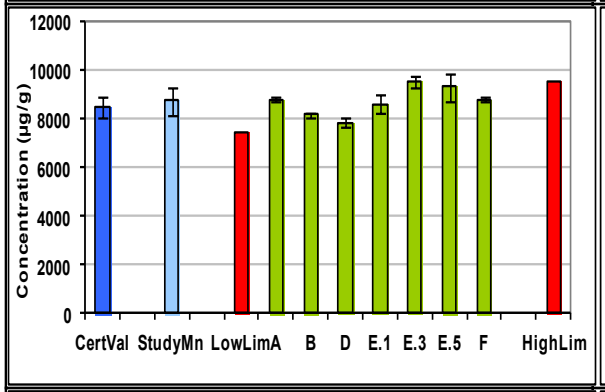
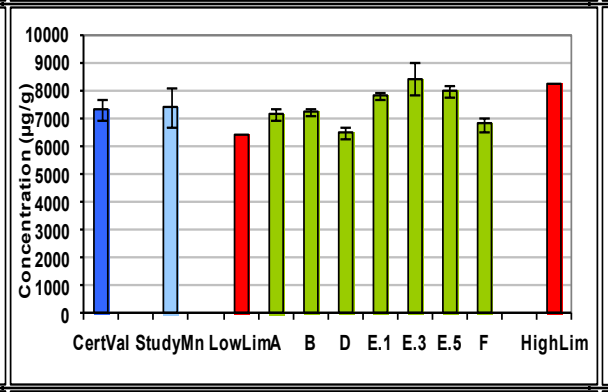
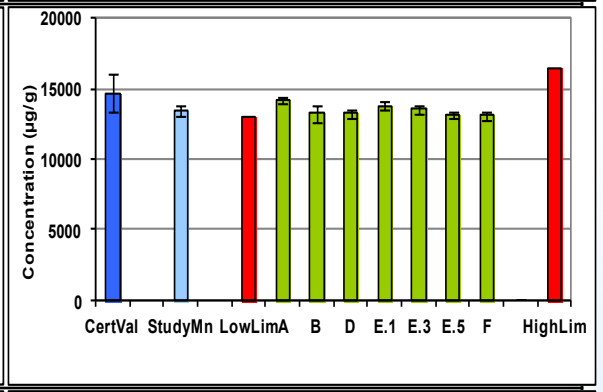
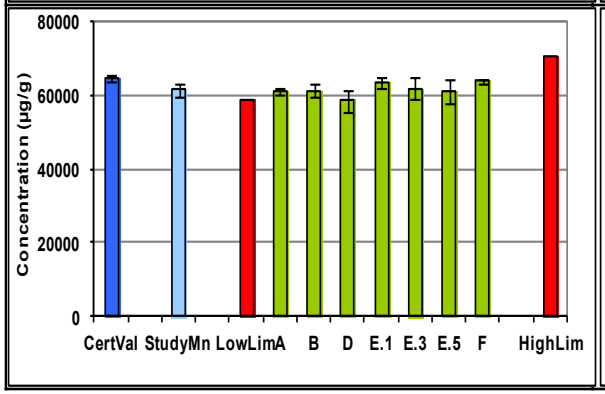
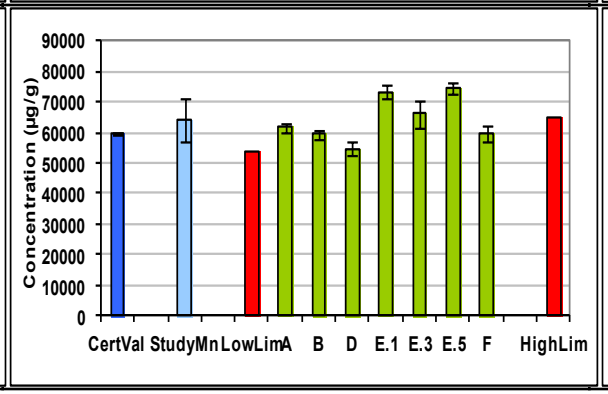
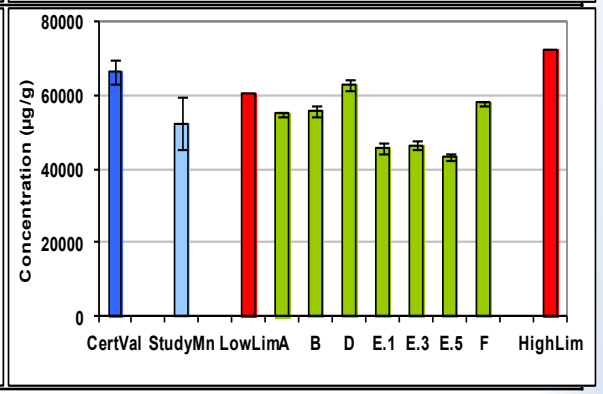
	2710	2710a	PACS-2
Li			
Mg			
Al			

7-laboratory inter-lab LA-ICP-MS Results

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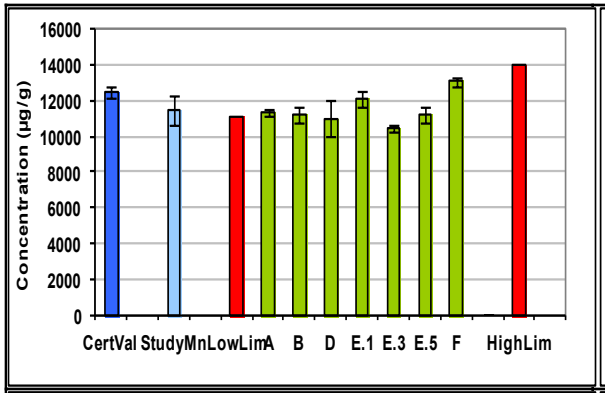
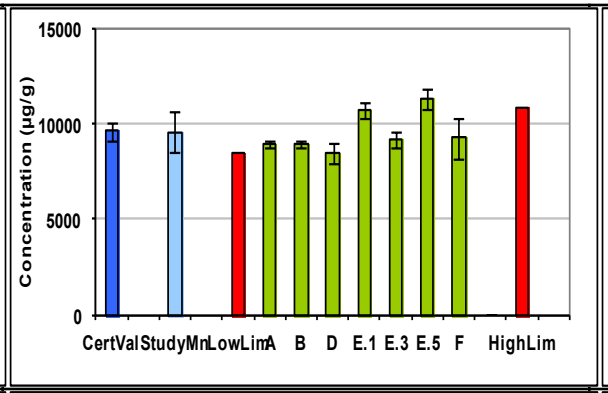
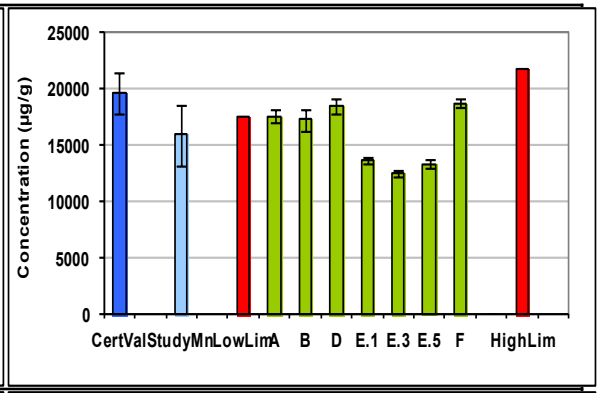
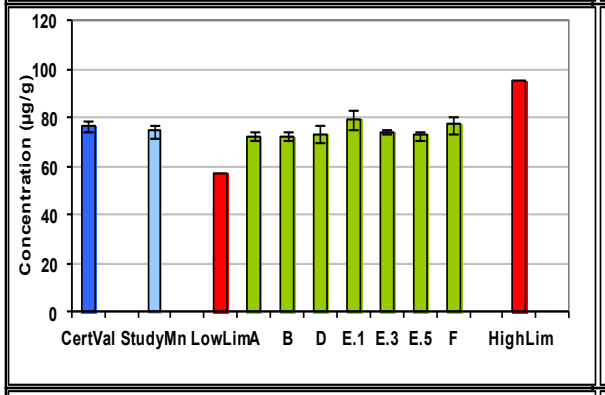
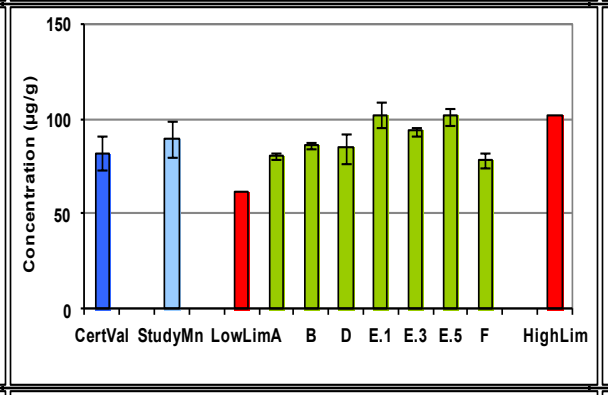
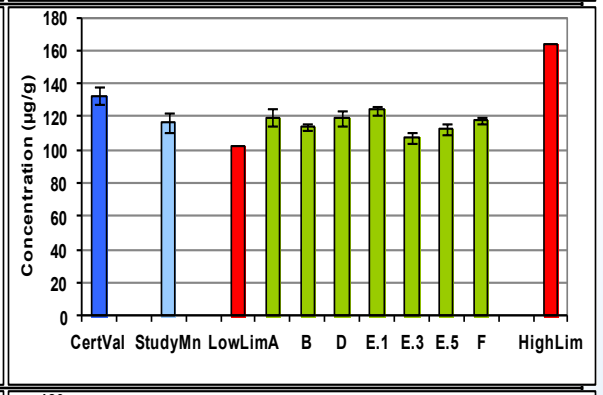
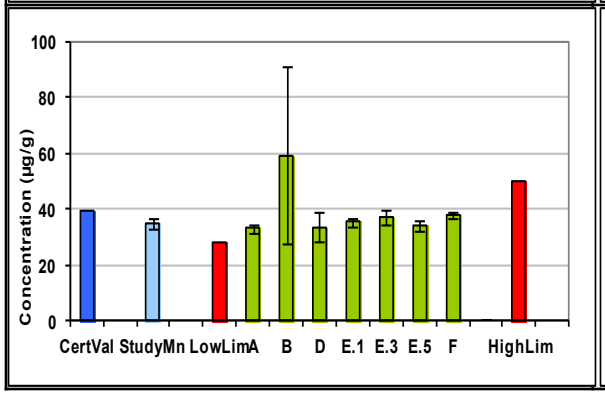
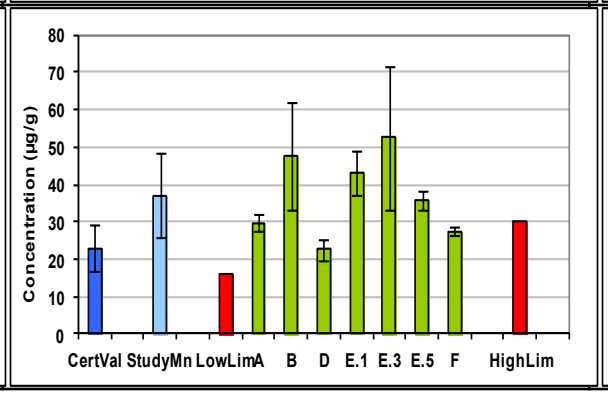
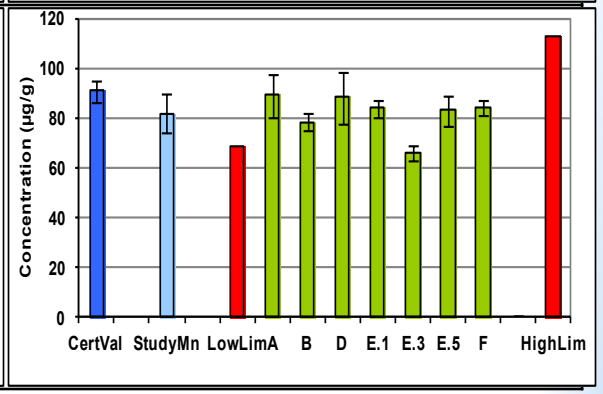
Ca			
V			
Cr			

7-laboratory inter-lab LA-ICP-MS Results

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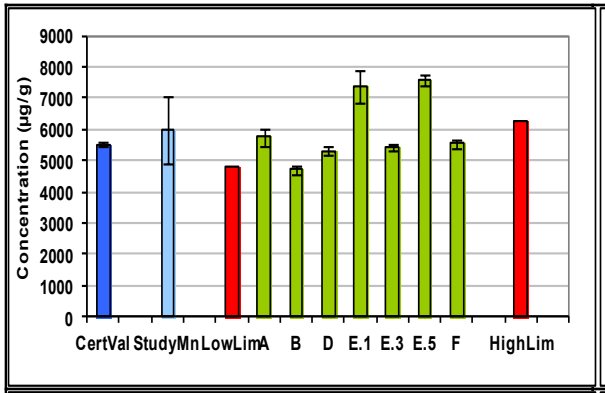
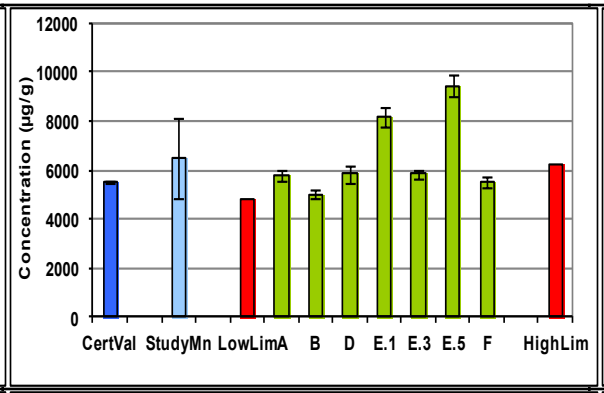
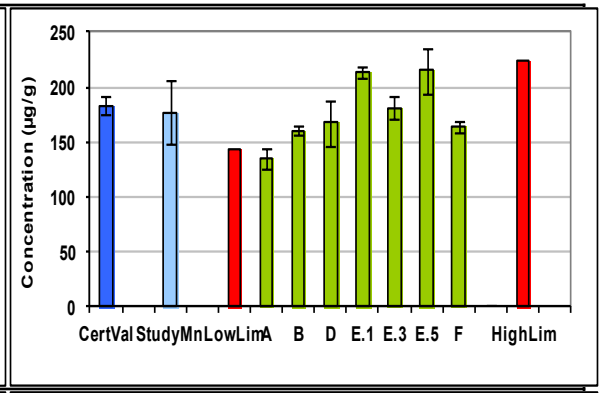
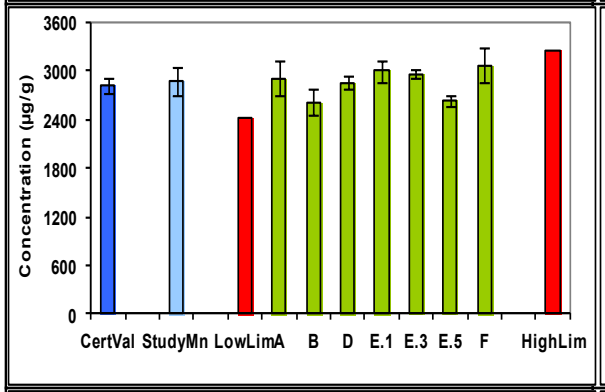
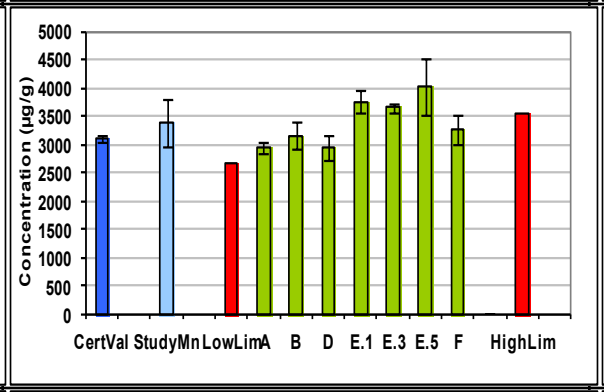
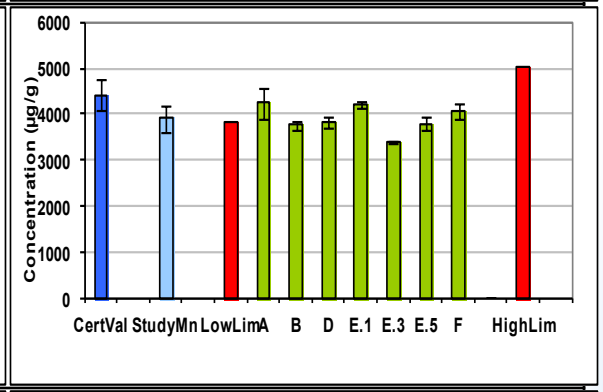
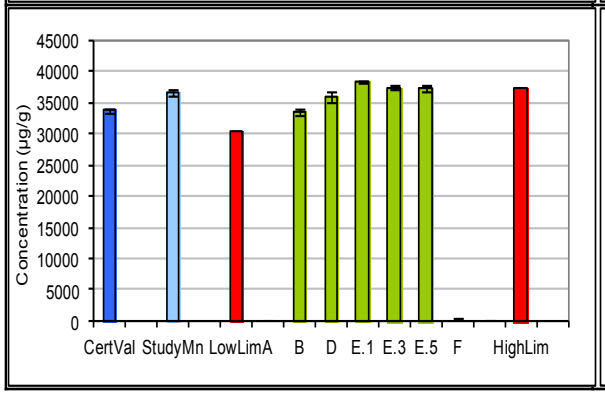
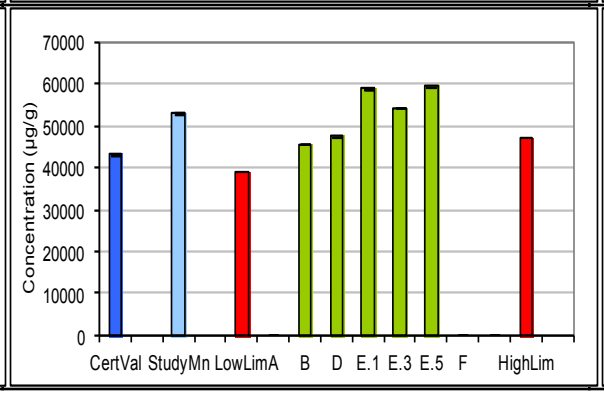
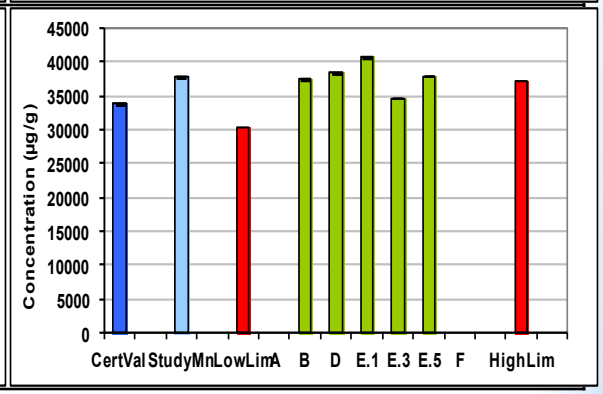
	2710	2710a	PACS-2
Pb			
Ti			
Fe			

Sample Prep: Pellets vs Tape

Pros of **pellets**:
Homogeneous
Can add internal standard
Analysis by many instruments
Easy storage & re-analysis

Cons of **pellets**:
Potential for loss/contamination
Takes 2-4 days
Requires ~500 mg for 13mm pellet
Destructive to sample

Pros of **tape**:
Fast (<1 day)
Analysis by laser-based instruments
Storage and re-analysis possible
<10 mg for ~120mm^2 tape surface
Less destructive

Cons of **tape**:
Potential for loss/contamination
Can't add internal standard
- Normalize to matrix elements
- Use ratios (as is done with glass)

Heterogeneous
- Apply fine fraction, do line/raster

Contribution from Tape?
- Raster quickly, monitor tape-only peaks

Tape sample preparation method has been reported as suitable for characterization of soils.*

** SC Jantzi and **JR Almirall,** Elemental analysis of soils by LA-ICP-MS and LIBS with multivariate discrimination using tape-mounting as an alternative to pellets for small forensic transfer specimens, Applied Spectroscopy, **2014**, 68(9), 963-974.*

α, 1-α, β and 1-β

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The significance level (α) of a statistical hypothesis test is a fixed probability of wrongly rejecting the null hypothesis H_0, if it is in fact true.

It is the probability of a Type I error.

The confidence level is 1-α.

Usually, the significance level is chosen to be 0.05 (or 5%)

$$\alpha$$

α, 1-α, β and 1-β

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- type II error occurs when H_0 is not rejected and when it is, in fact, false.
- A type II error is frequently due to sample sizes being too small.
- The probability of a type II error is symbolized by β.
- The power of the test is 1-β, which is the probability of avoiding a Type II error.

β

Truth table

Experiment Results	Truth: Hypothesis True	Truth: Hypothesis False
Accept Hypothesis	Correct	Type II Error
Reject Hypothesis	Type I Error	Correct