ELEMENTAL ANALYSIS OF GLASS BY LA-ICP-OES FOR FORENSIC DISCRIMINATION PURPOSES

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FIU

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SWGMAT GUIDELINES

"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 used when other methods of comparison fail to distinguish two glass fragments as having different sources…"

- Elemental Analysis of Glass, *Forensic Science Communications*, vol. 7, no. 1, 2005.

OUTLINE

- **Research motivation**
- **Instrumentation**
- **Experimental parameters**
- **Analytical performance**
- **Test set of automotive glass samples**
- **Conclusions**

RESEARCH MOTIVATION

Current elemental analysis techniques:

Solution-based sampling:
1. **ICP-OES** (Koons et al, 1988)
2. **ICP-MS** (S. Montero et al., 2001) ASTM E 2330-04

Solid sampling:
1. **SEM-EDS** (Ryland, 1986)
2. **XRF** (Reeve et al, 1976)
3. **LA-ICP-MS** (Latzchoczy et al, 2005)
4. **LA-ICP-OES**

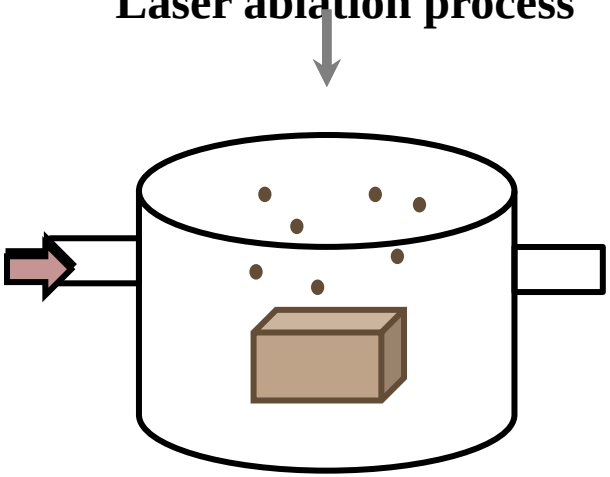
Advantages:
1. Reduced cost
2. Reduced complexity
3. Sensitivity
4. Reduced sample consumption

Characteristics of a "good" technique:

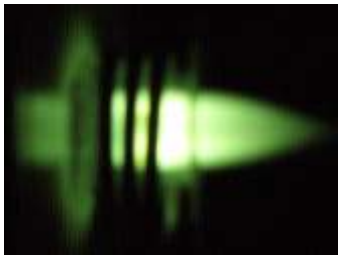
1. Detection limits ~ 10x expected concentration
2. Quantitative analysis
3. Precision adequate for the intended purpose
4. Accuracy adequate for the intended purpose

COUPLING THE TECHNIQUES

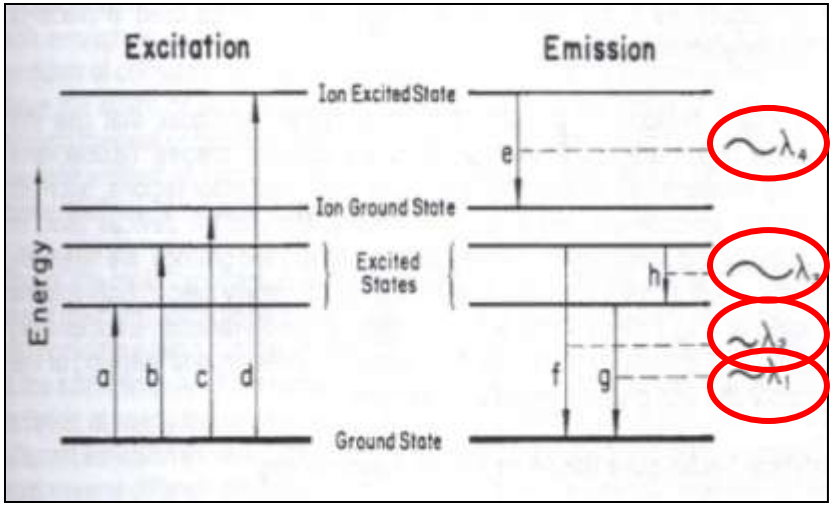
Laser ablation process



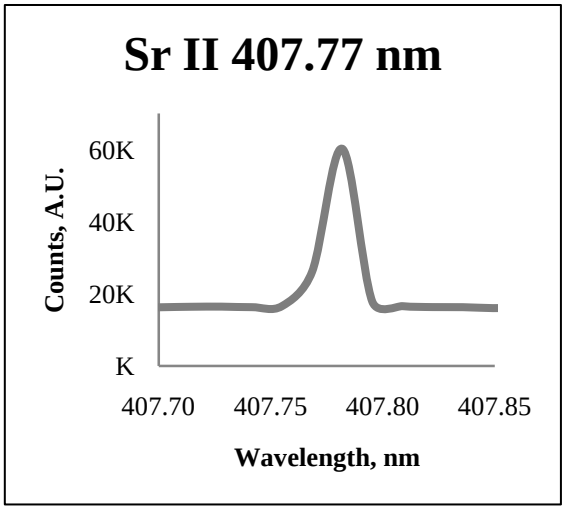
ICP



Excitation, ionization and emission processes



Resulting emission line



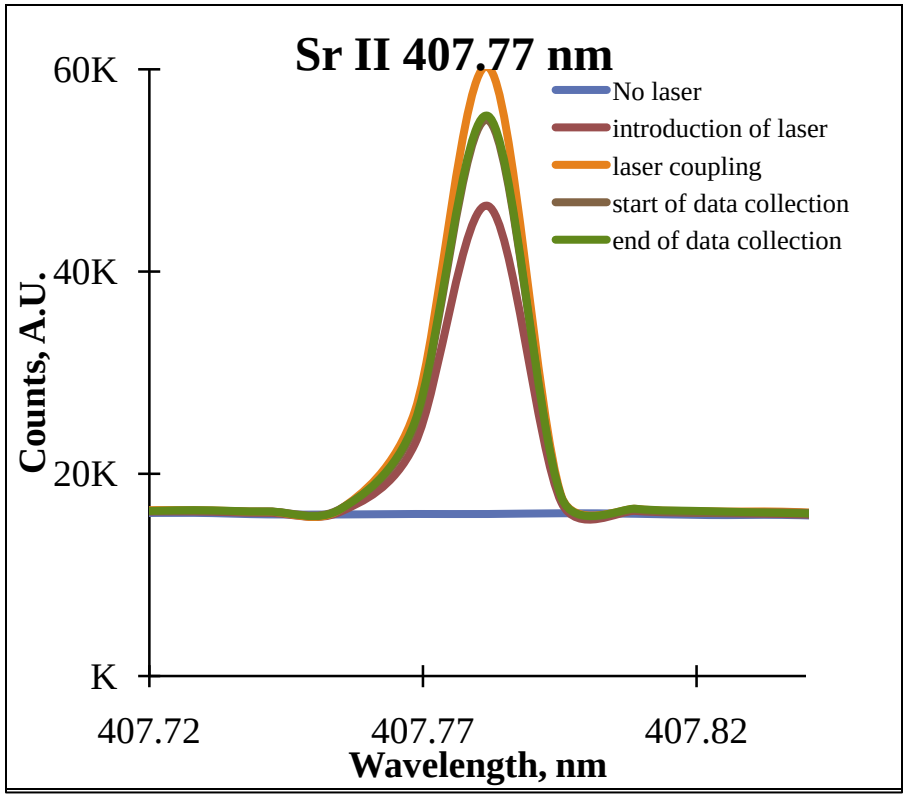
Output

Detection of emission process

Spectrometer

INSTRUMENTATION

Obtaining a transient signal



INSTRUMENTATION

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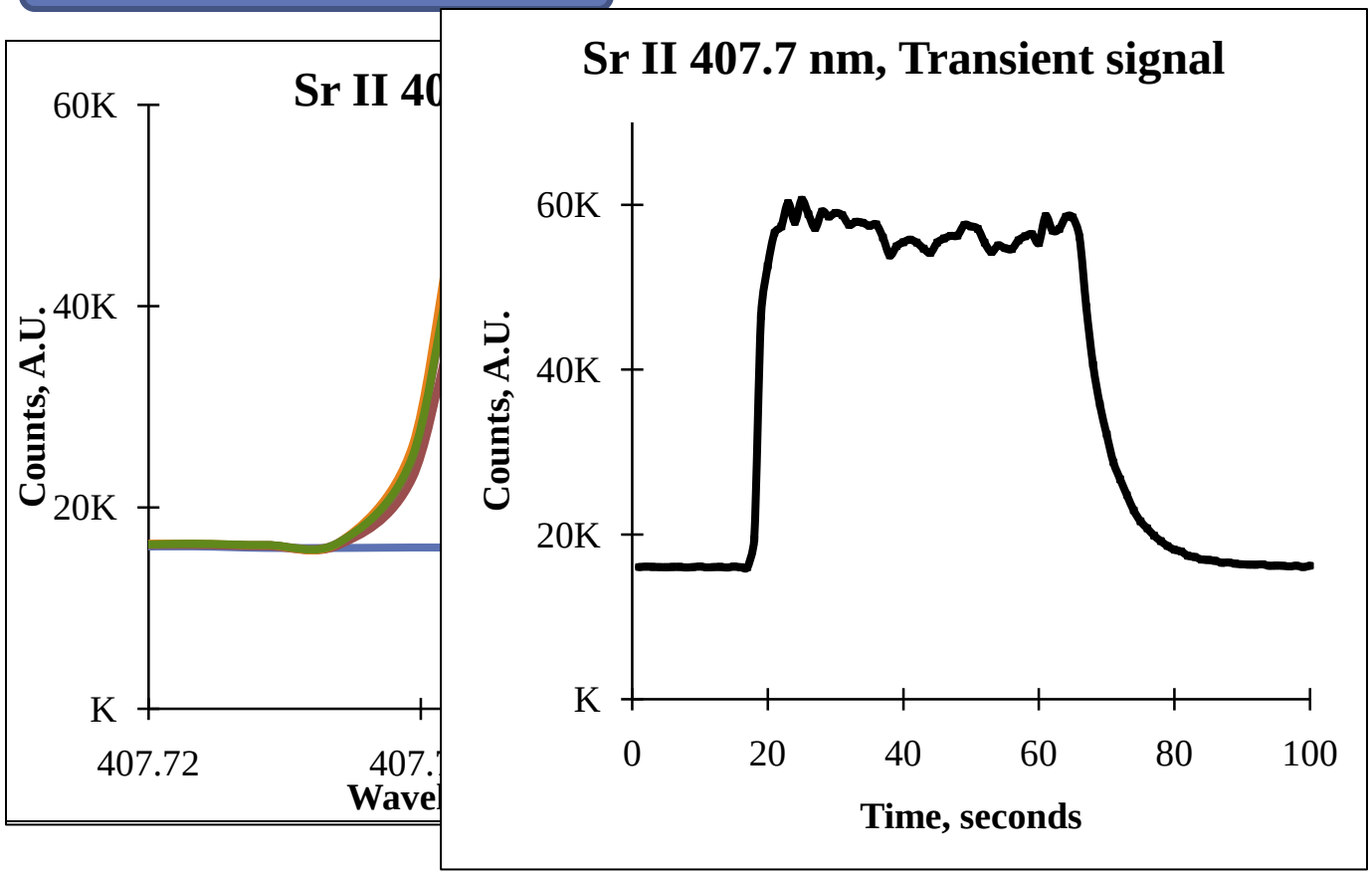

INSTRUMENTATION

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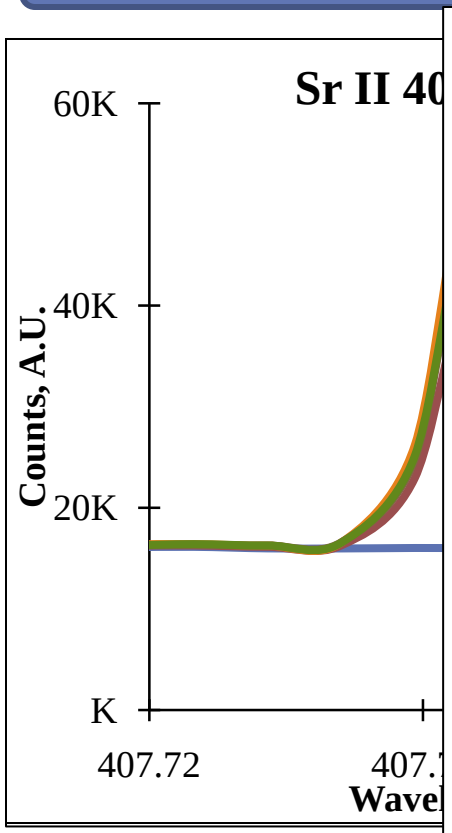
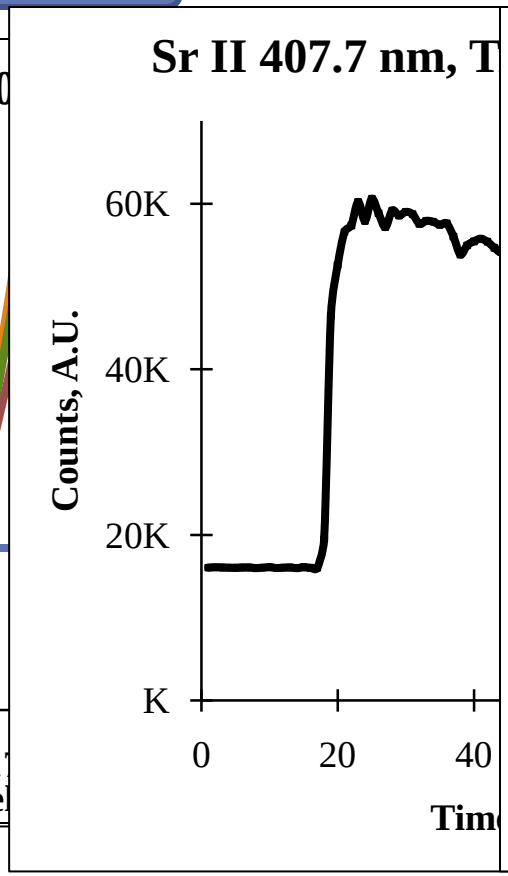
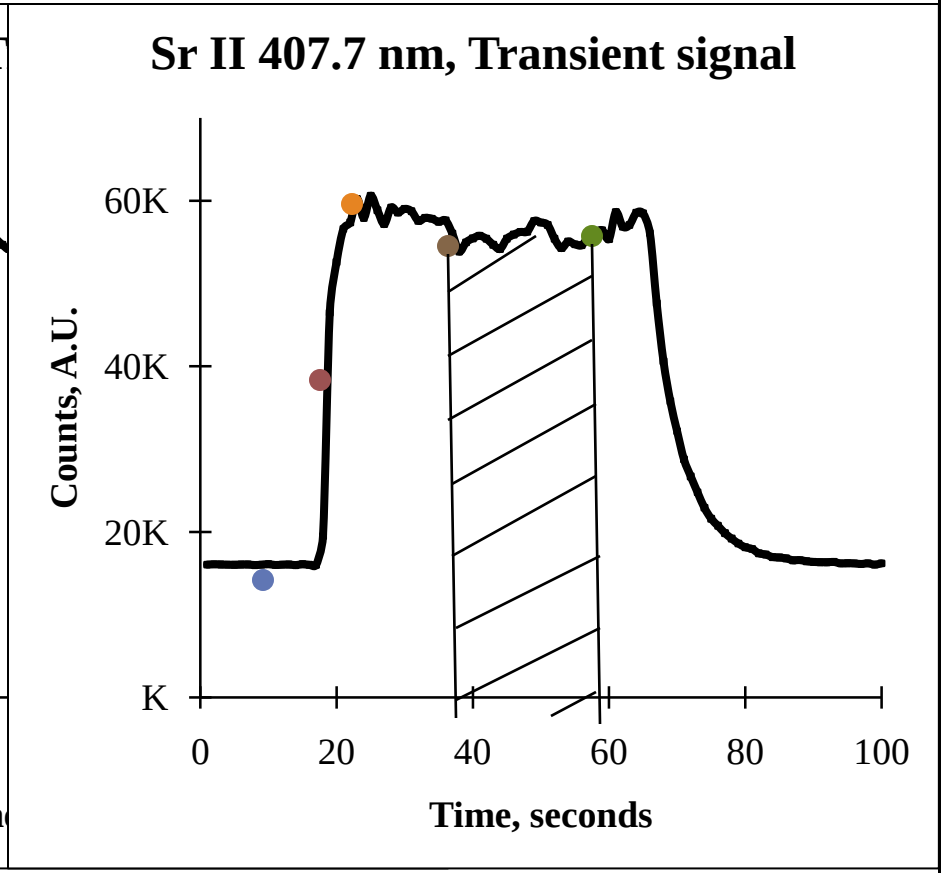






EXPERIMENTAL PARAMETERS

ICP-OES Parameters, PerkinElmer Optima DV7300

Outer plasma gas : 15 L/min

Auxiliary plasma gas : 0.5L/min

Makeup gas : 0.5L/min

} Argon

Forward power : 1500 W

Read parameters : 0.1 s integration, 1 s read time

Laser Parameters, New Wave Research Inc., UP-213

Wavelength : 213 nm, 4 ns pulse duration

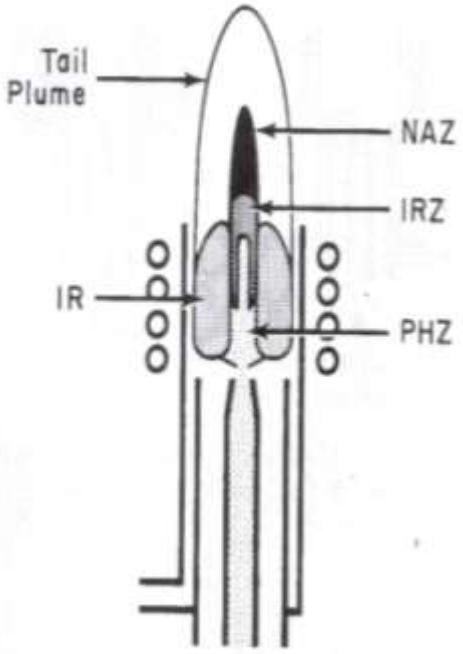
Fluence : 24 J/cm^2

Frequency : 10 Hz

Ablation cell volume : 30 cm^3

Ablation mode : 100 µm spot, 60 s ablation

ICP and torch layout



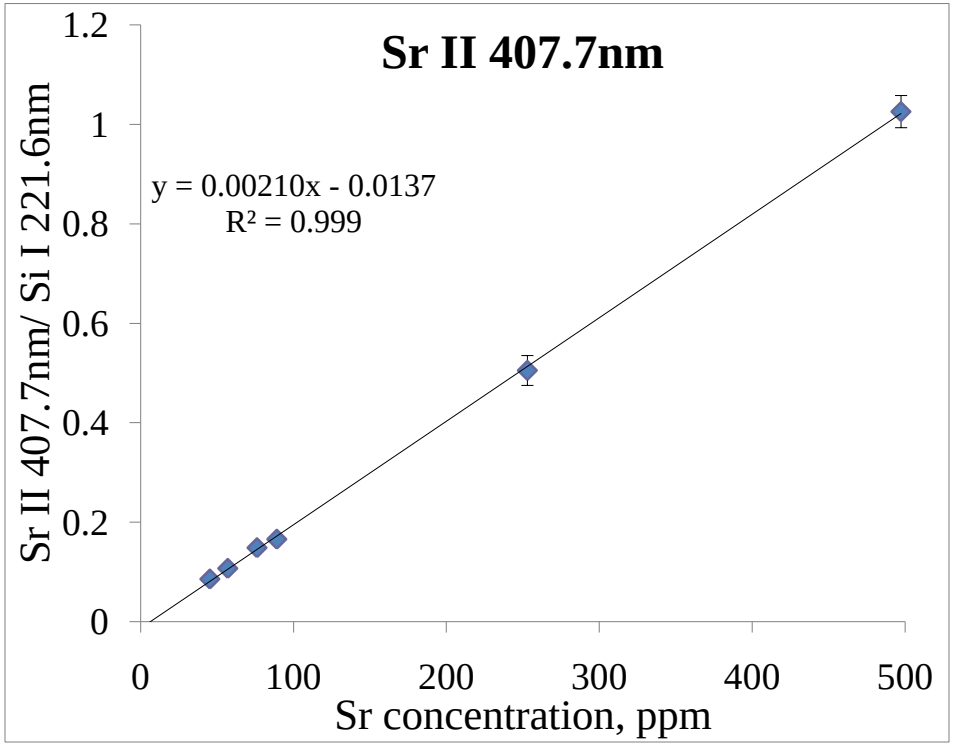
Courtesy of PerkinElmer ICP Guide

METHODOLOGY

Emission lines of interest :

Element	Wavelength (nm)
Al (I)	396.15
Ba (II)	455.40
Ca (II)	315.88
Fe (II)	238.20
Li (I)	670.78
Mg (I)	285.21
Sr (II)	407.77
Ti (II)	368.51
Zr (II)	343.82
Si (I) (Internal std)	221.66

Atomic emission : I
Ionic emission : II



Establishing a calibration using NIST glass standards

LIMITS OF DETECTION

Emission line (nm)	Limit of detection ($\mu g\ g^{-1}$)	Limit of quantitation ($\mu g\ g^{-1}$)	Typical sample Range ($\mu g\ g^{-1}$)
Al I 396.15	3.6	12.1	298-11,940[a]
Ba II 455.40	0.6	1.7	3-384[b]
Ca II 315.88	559	1862	46,086-69,767[b]
Fe II 238.20	13.1	39.3	461-6063[a]
Li I 670.78	0.38	1.31	0.8-7.0[a]
Mg I 285.21	8.1	26.9	6273-51,076[b]
Sr II 407.77	0.2	0.7	19-576[b]
Ti II 368.51	6.9	23.1	39-3226[b]
Zr II 343.82	7.1	22.3	19-269[b]

[a] Determined from actual measurements made of 127 soda-lime glass samples consisting of vehicle and architectural windows.

[b] Determined from actual measurements made of 286 soda-lime glass samples from vehicle and architectural windows.

ANALYTICAL FIGURES OF MERIT

Comparison of LA-ICP-OES and LA-ICP-MS using NIST 1831

Analyte information		LA-ICP-OES			LA-ICP-MS		
Element	Reported value (µg g^{-1})	Average (µg g^{-1})	Bias (%)	Precision (%)	Average (µg g^{-1})	Bias (%)	Precision (%)
Al	6381[a]	6232	-2.3	1.4	6828	7.0	12.0
Ca	58604[a]	58020	-1.0	1.8	58391	-0.4	2.6
Mg	21166[a]	21177	0.1	1.1	25809	21.9	6.5
Ti	114[a]	108	-5.3	6.6	135.5	18.9	15.0
Ba	31.5[b]	29.1	-7.6	3.0	29.1	-7.6	3.5
Sr	89.1[b]	85.9	-3.6	6.6	75.9	-14.8	2.4
Zr	43.4[b]	37.5	-13.6	9.5	31.3	-28.3	2.3
Fe	610[c]	581	-4.8	2.8	530	-13.1	12.4
Li	4.99[c]	5.21	4.5	6.8	5.13	2.8	2.9

[a] Certified by NIST

[b] Reported in ASTM method E 2330-04, not certified

[c] Historical data from a single lab over a one year period

***Bias and precision measurements obtained from 20 readings over approximately 2 months**

DESCRIPTION OF TEST SET

- Automobile glass from vehicles produced 1995-2004
- 41 glass fragments from 14 vehicles
  - Windshield (inner and outer)
  - Side windows (tempered)
  - Rear windows (tempered)
- Analyzed by LA-ICP-OES using a 9 element menu
- Analyzed by other techniques
  - LA-ICP-MS
  - µXRF
  - LIBS

The performance of LA-ICP-OES using this test set allows for a direct evaluation of the **analytical capabilities** and **informing power** that can be obtained in comparison to other elemental analysis techniques.

TEST SET – STATISTICAL ANALYSIS

Initial data analysis

1. **ANOVA with Tukey's, followed by a t-test ($\alpha = 0.05$) for indistinguishable pairs by ANOVA+Tukey's**
   - LA-ICP-OES, LA-ICP-MS[1], μXRF[1], LIBS[1]

Additional data analysis

2. **Broader match criteria**
   - LA-ICP-OES and LA-ICP-MS
     - Standard deviation
       - +/- 3
       - +/- 4

[1] Naes et. al. Spectrochim. Acta B, 2008.

TEST SET – INTERPRETATION

Definition of a source

1. Glass originating from the same pane

   or

2. Glass originating from the same manufacturing plant around the same time

Type I Error : False exclusion

Distinguishing samples thought to originate from the same source

Example : inner and outer windshields from the same vehicle not being associated

Type II Error : False inclusion

Associating samples known to originate from different sources

Example : side and rear windows from two different vehicles being associated

LA-ICP-OES Glass Data Statistical Comparisons

Pair #	Vehicle make	Vehicle model	Year	Sample location	IN by Pairwise/ t-test (9 ele)	IN by +/- 4s (9 ele)	IN Hotelling's T^2 (8 ele)
1	Chevrolet	Cavalier	2004	outside windshield	Yes	Yes	Yes
	Chevrolet	Cavalier	2004	inside windshield			
2	Dodge	Stratus	1998	outside windshield	Yes	Yes	Yes
	Dodge	Stratus	1998	inside windshield			
3	Ford	Expedition	2004	inside windshield	Yes	Yes	Yes
	Ford	Expedition	2004	outside windshield			
4	Jeep	Grd. Cher.	2001	outside windshield	Yes	Yes	No – Type I Error
	Jeep	Grd. Cher.	2001	inside windshield			
5	GMC	Envoy	2004	outside windshield	No – Type I Error	No – Type I Error	No – Type I Error
	GMC	Envoy	2004	inside windshield			
6	Oldsmobile	Intrigue	1998	outside windshield	No – Type I Error	Yes	Yes
	Oldsmobile	Intrigue	1998	inside windshield			
7	Dodge	Neon	2000	outside windshield	No – Type I Error	Yes	Yes
	Dodge	Neon	2000	inside windshield			
8	Chevrolet	Cavalier	2003	outside windshield	No – Type I Error	Yes	Yes
	Chevrolet	Cavalier	2003	inside windshield			
9	Ford	Explorer	2001	outside windshield	No – Type I Error	No – Type I Error	No – Type I Error
	Ford	Explorer	2001	inside windshield			
10	Jeep	Grd. Cher. Laredo	2001	outside windshield	No – Type I Error	No – Type I Error	Yes
	Jeep	Grd. Cher. Laredo	2001	inside windshield			
11	Ford	Ranger XLT	2001	outside windshield	No – Type I Error	Yes	Yes
	Ford	Ranger XLT	2001	inside windshield			
12	Chevrolet	Cavalier	2003	Side window	No	Yes – Type II Error ??	Yes – Type II Error ??
	Chevrolet	Cavalier	2003	Rear window			
13	Chevrolet	Cavalier	2004	Side window	No	Yes – Type II Error ??	Yes – Type II Error ??
	Chevrolet	Cavalier	2004	Rear window			

LA-ICP-OES VS LA-ICP-MS

Comparison of broader match criteria

Inner and outer windshield from the **same** vehicle **should** be associated but are **not**

Side and rear window from the **same** vehicle **are** associated

	False exclusions		False inclusions			
	Same vehicle		Different vehicle		Same vehicle	
	+/- 3 s	+/- 4s	+/- 3s	+/- 4s	+/- 3s	+/- 4s
LA-ICP-OES	3	3	0	0	2	2
LA-ICP-MS	5	4	0	0	2	2

Overlap of pairs

Same pairs

WHAT DOES THIS MEAN?

LA-ICP-OES | LA-ICP-MS

Technique	Type 1 Errors		Type I Error Rate		Type 2 Errors		Type II Error rate	
Pairwise/ t-test	8	7	1 %	0.9 %	0	0	0	0
+/- 3s	3	5	0.4 %	0.6 %	2	2	0.2 %	0.2 %
+/- 4s	3	4	0.4 %	0.5 %	2	2	0.2 %	0.2 %
Hotelling's	3	-	0.4 %	-	2	-	0.2%	-

Definition of a source

1. Glass originating from the same pane

or

2. Glass originating from the same manufacturing plant around the same time

SUMMARY

- **LA-ICP-OES is capable of achieving similar analytical performance to LA-ICP-MS.**
- **LA-ICP-OES provides similar informing power as LA-ICP-MS for the forensic analysis of glass.**
- **LA-ICP-OES offers advantages over LA-ICP-MS including reduced cost and complexity.**
- **The report output of LA-ICP-OES is not straightforward due to the few applications of this coupled technique. However, once this is addressed this analytical approach will be more conducive to implementation in a forensic laboratory setting.**

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