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.

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EAWG Round Robin Design

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

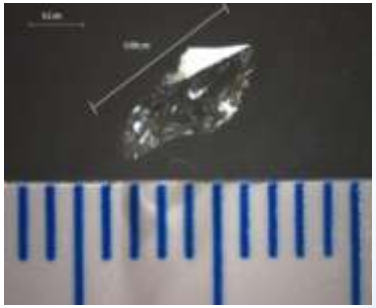
RR2 : Larger set of standard materials for standardization of methods. Larger sample sets for comparison and evaluation of **type I and type II error rates.**

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

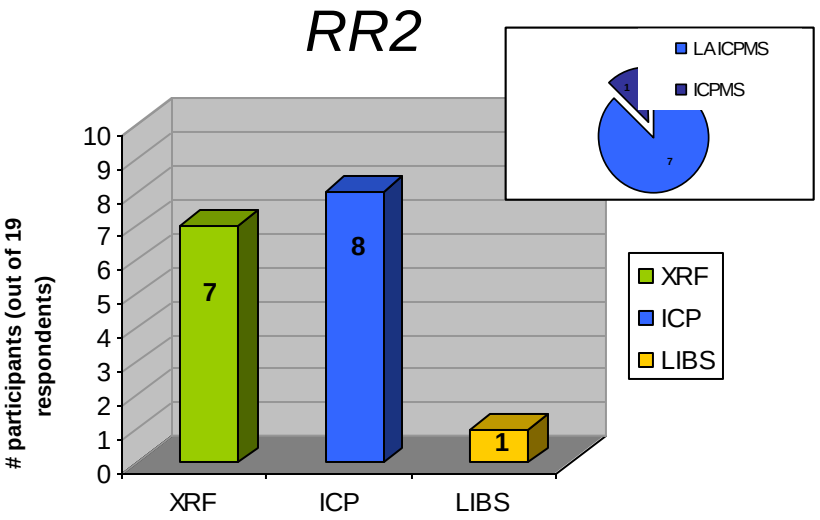
RR3: study **discrimination capabilities** from glass sources produced at different time intervals and efficiency of match criteria (focused on false inclusions)

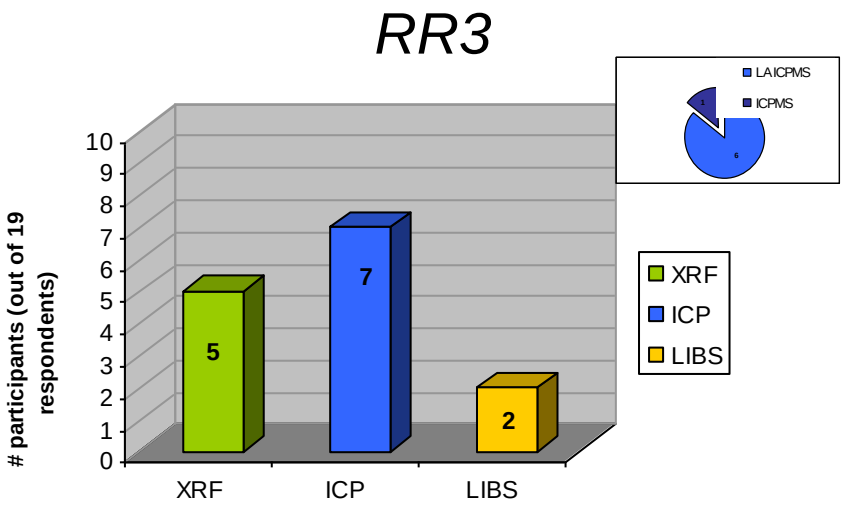
Round Robin Studies- Questions to answer

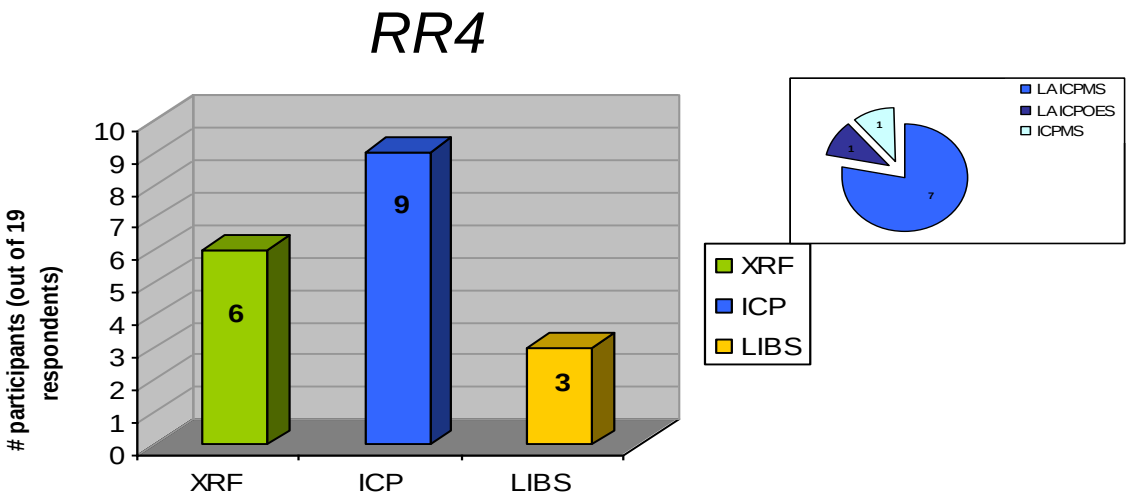
- **ANALYTICAL PERFORMANCE**
  - How does each technique perform in comparison to the others?
    - µXRF, ICP (LA-ICP-MS, ICP-MS, LA-ICP-OES), LIBS
    - Precision (inter-lab, intra-lab)
    - Accuracy
    - Sensitivity (LOD, LOQ)
    - Interferences
    - Discrimination capabilities
  - How is the inter-laboratory 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







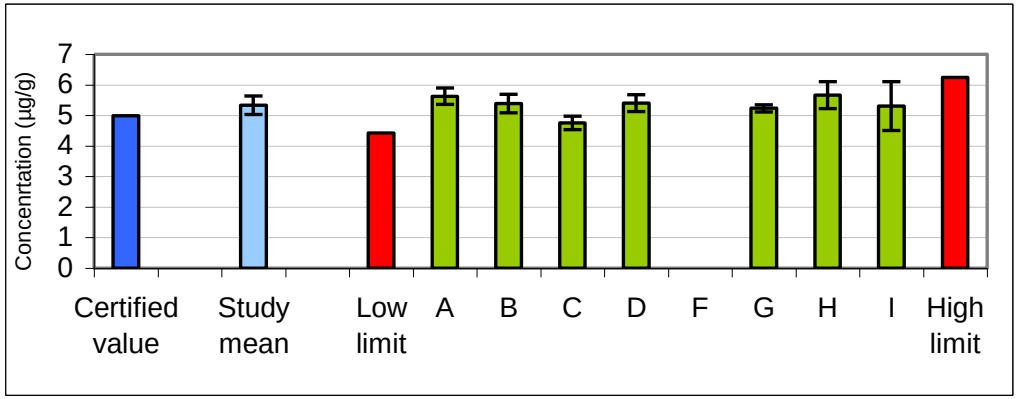
Evaluation of analytical performance

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	)	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 + 3δ)	6.25
low limit (mean - 3δ)	4.43



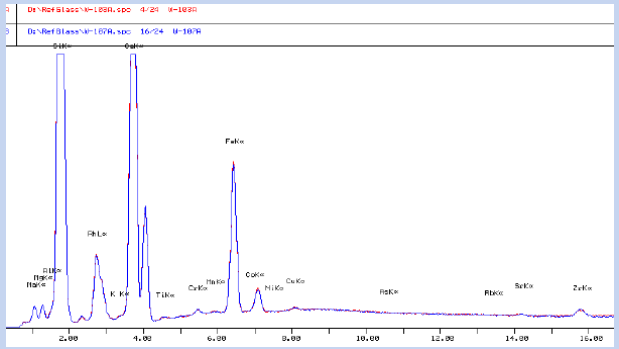
Excellent agreement between participant laboratories (%RSD <10, % bias <10 for majority of elements)

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

Description of the glass samples – RR2

- **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

ICP-MS and XRF data

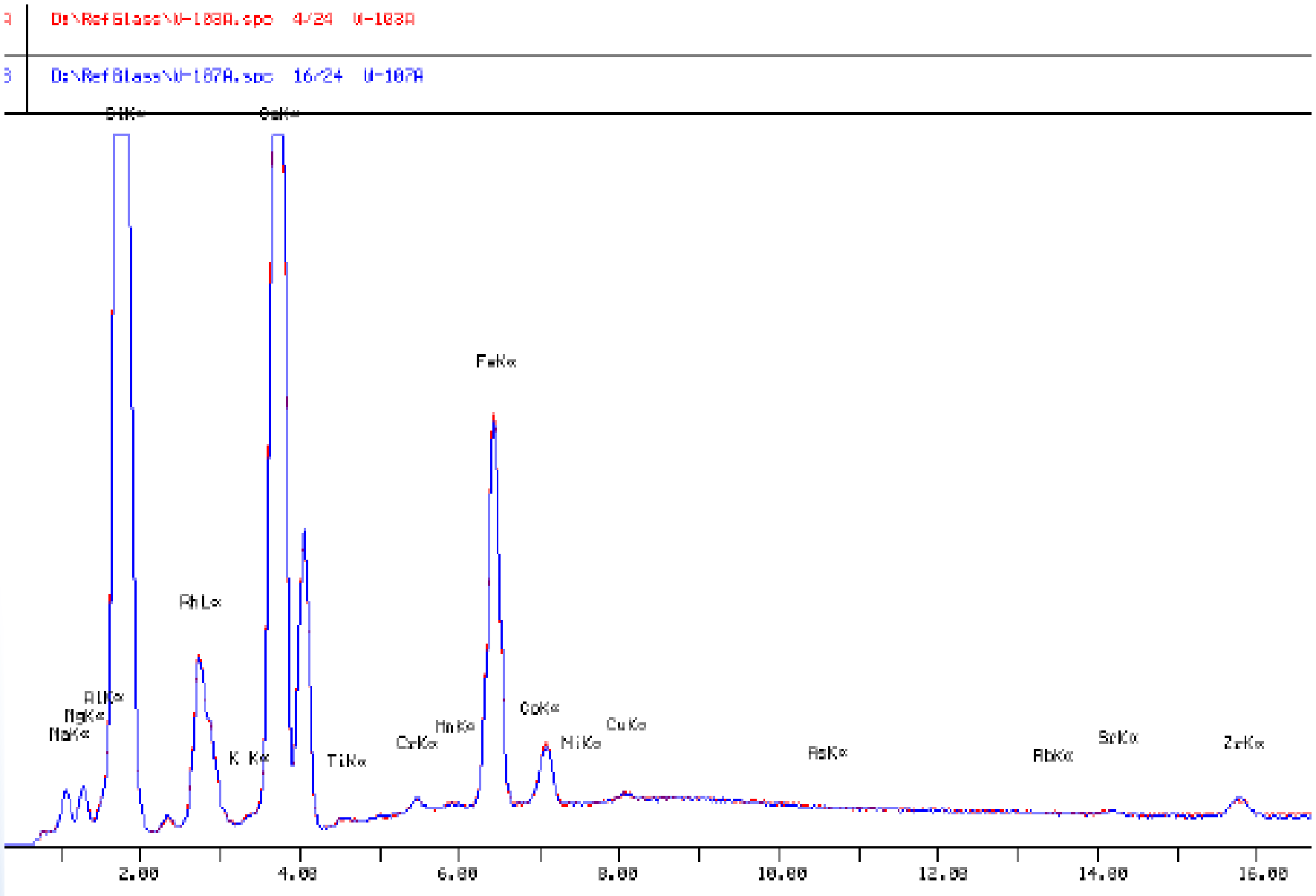


XRF typical data display

Item K1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
K1-1	40.81	600	20.71	0.87	8.18	80.37	9.40	37.98
K1-2	40.96	491	20.84	0.85	9.90	83.33	11.65	33.10
K1-3	40.98	460	20.67	0.92	9.25	84.49	10.05	42.57
K1-4	41.83	916	20.34	0.96	10.34	84.27	10.74	45.06
K1-5	42.02	570	20.55	0.67	8.16	88.52	12.25	44.62
K1-6	41.17	650	20.63	0.68	7.39	84.93	10.91	92.21
K1-7	41.42	480	20.76	0.97	8.96	89.19	9.20	54.03
K1-8	41.30	599	20.74	0.56	7.00	87.06	12.56	65.12
K1-9	40.95	621	20.75	0.90	9.39	82.75	10.47	55.55
K1-10	41.79	672	20.70	0.90	9.12	85.67	10.15	41.57
mean	**41.32**	**606**	**20.67**	**0.83**	**8.77**	**85.06**	**10.74**	**52.14**
stdev	0.43	131	0.14	0.14	1.07	2.68	1.13	17.93
%RSD	**1%**	**22%**	**1%**	**17%**	**12%**	**3%**	**11%**	**34%**

Item Q1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
Q1-fragment 1-1	41.49	554	20.52	0.91	7.72	84.34	8.47	49.53
Q1-fragment 1-2	41.76	1022	20.46	1.14	11.60	83.22	10.20	81.19
Q1-fragment 1-3	40.52	825	20.23	0.73	7.16	88.03	9.78	47.68
mean	**41.26**	**800.31**	**20.40**	**0.93**	**8.82**	**85.19**	**9.48**	**59.47**
stdev	0.65	235.18	0.15	0.20	2.42	2.52	0.90	18.84
%RSD	**2%**	**29%**	**1%**	**22%**	**27%**	**3%**	**10%**	**32%**

ICP-MS and XRF data



ICP-MS and XRF data

Item K1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
K1-1	40.81	600	20.71	0.87	8.18	80.37	9.40	37.98
K1-2	40.96	491	20.84	0.85	9.90	83.33	11.65	33.10
K1-3	40.98	460	20.67	0.92	9.25	84.49	10.05	42.57
K1-4	41.83	916	20.34	0.96	10.34	84.27	10.74	45.06
K1-5	42.02	570	20.55	0.67	8.16	88.52	12.25	44.62
K1-6	41.17	650	20.63	0.68	7.39	84.93	10.91	92.21
K1-7	41.42	480	20.76	0.97	8.96	89.19	9.20	54.03
K1-8	41.30	599	20.74	0.56	7.00	87.06	12.56	65.12
K1-9	40.95	621	20.75	0.90	9.39	82.75	10.47	55.55
K1-10	41.79	672	20.70	0.90	9.12	85.67	10.15	41.57
mean	**41.32**	**606**	**20.67**	**0.83**	**8.77**	**85.06**	**10.74**	**52.14**
stdev	0.43	131	0.14	0.14	1.07	2.68	1.13	17.93
%RSD	**1%**	**22%**	**1%**	**17%**	**12%**	**3%**	**11%**	**34%**

Item Q1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
Q1-fragment 1-1	41.49	554	20.52	0.91	7.72	84.34	8.47	49.53
Q1-fragment 1-2	41.76	1022	20.46	1.14	11.60	83.22	10.20	81.19
Q1-fragment 1-3	40.52	825	20.23	0.73	7.16	88.03	9.78	47.68
mean	**41.26**	**800.31**	**20.40**	**0.93**	**8.82**	**85.19**	**9.48**	**59.47**
stdev	0.65	235.18	0.15	0.20	2.42	2.52	0.90	18.84
%RSD	**2%**	**29%**	**1%**	**22%**	**27%**	**3%**	**10%**	**32%**

ICP-MS and XRF data

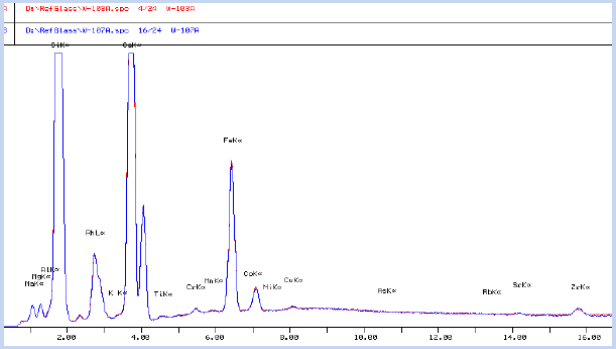
FIU International Forensic Research Institute

ICP-MS typical data

Item K1	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe57	Rb85	Sr88	Zr90	Ba137	La139	Ce140	Nd146	Hf178	Pbsum
K1-1	4.18	22324	2796	1185	63951	68.82	19.16	515	1.93	30.70	30.03	10.69	2.49	4.18	2.00	0.81	1.15
K1-2	4.14	22212	2753	1171	63222	68.48	18.31	514	1.65	29.86	29.30	9.82	2.62	4.14	1.90	0.81	1.06
K1-3	4.22	22358	2757	1176	63513	72.87	18.58	528	1.63	29.70	29.89	10.04	2.53	4.22	1.87	0.71	1.17
K1-4	4.23	22419	2760	1172	63703	72.43	18.78	511	1.62	29.87	30.08	9.78	2.50	4.23	1.87	0.72	1.21
K1-5	4.05	22272	2675	1134	61850	66.02	18.06	504	1.56	28.90	32.00	9.54	2.43	4.05	1.65	0.81	1.04
K1-6	4.20	22587	2701	1151	62681	67.05	18.30	504	1.66	29.42	32.41	9.95	2.45	4.20	1.96	0.85	1.01
K1-7	4.09	22315	2654	1148	61297	66.80	18.13	503	1.58	28.65	31.33	9.71	2.45	4.09	1.71	0.80	1.13
K1-8	4.14	22815	2694	1131	63036	68.21	18.56	503	1.52	28.95	29.74	9.44	2.38	4.14	1.86	0.80	1.10
K1-9	4.21	22508	2683	1130	62232	69.20	18.42	506	1.61	29.07	29.88	9.35	2.43	4.21	1.81	0.73	1.02
K1-10	4.10	22551	2652	1142	62639	66.75	17.78	509	1.57	28.84	28.75	9.55	2.44	4.10	1.95	0.63	1.09
mean	**4.16**	**22436**	**2712**	**1154**	**62812**	**68.66**	**18.41**	**510**	**1.63**	**29.40**	**30.34**	**9.79**	**2.47**	**4.16**	**1.86**	**0.77**	**1.10**
stdev	0.06	181	50	20	844	2.34	0.39	7.78	0.11	0.64	1.18	0.39	0.07	0.06	0.11	0.07	0.07
%RSD	1.5%	0.8%	1.9%	1.8%	1.3%	3.4%	2.1%	1.5%	7.0%	2.2%	3.9%	3.9%	2.7%	1.5%	6.0%	8.7%	6.2%

Item Q1	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe57	Rb85	Sr88	Zr90	Ba137	La139	Ce140	Nd146	Hf178	Pbsum
Q1-fragment 1-1	4.19	23476	2793	1144	64121	70.26	18.61	518	1.55	29.68	32.58	9.88	2.47	4.19	1.90	0.90	1.00
Q1-fragment 1-2	4.09	23315	2753	1140	64052	70.19	18.27	510	1.56	29.37	29.22	9.31	2.40	4.09	1.85	0.75	1.01
Q1-fragment 1-3	4.18	23430	2741	1145	63722	70.74	18.35	526	1.49	29.51	28.16	9.42	2.43	4.18	1.72	0.74	1.14
mean	**4.15**	**23407**	**2763**	**1143**	**63965**	**70.40**	**18.41**	**518**	**1.53**	**29.52**	**29.99**	**9.54**	**2.43**	**4.15**	**1.82**	**0.80**	**1.05**
stdev	0.06	83	27	3	213	0.30	0.18	8.03	0.04	0.16	2.31	0.30	0.03	0.06	0.09	0.09	0.08
%RSD	**1.3%**	**0.4%**	**1.0%**	**0.2%**	**0.3%**	**0.4%**	**1.0%**	**1.6%**	**2.4%**	**0.5%**	**7.7%**	**3.2%**	**1.4%**	**1.3%**	**5.1%**	**11.4%**	**7.5%**

ICP-MS and XRF data



XRF typical data display

Item K1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
K1-1	40.81	600	20.71	0.87	8.18	80.37	9.40	37.98
K1-2	40.96	491	20.84	0.85	9.90	83.33	11.65	33.10
K1-3	40.98	460	20.67	0.92	9.25	84.49	10.05	42.57
K1-4	41.83	916	20.34	0.96	10.34	84.27	10.74	45.06
K1-5	42.02	570	20.55	0.67	8.16	88.52	12.25	44.62
K1-6	41.17	650	20.63	0.68	7.39	84.93	10.91	92.21
K1-7	41.42	480	20.76	0.97	8.96	89.19	9.20	54.03
K1-8	41.30	599	20.74	0.56	7.00	87.06	12.56	65.12
K1-9	40.95	621	20.75	0.90	9.39	82.75	10.47	55.55
K1-10	41.79	672	20.70	0.90	9.12	85.67	10.15	41.57
mean	**41.32**	**606**	**20.67**	**0.83**	**8.77**	**85.06**	**10.74**	**52.14**
stdev	0.43	131	0.14	0.14	1.07	2.68	1.13	17.93
%RSD	**1%**	**22%**	**1%**	**17%**	**12%**	**3%**	**11%**	**34%**

Item Q1	Ca/Mg	Ca/Ti	Ca/Fe	Sr/Zr	Fe/Zr	Ca/K	Fe/Sr	Fe/Mn
Q1-fragment 1-1	41.49	554	20.52	0.91	7.72	84.34	8.47	49.53
Q1-fragment 1-2	41.76	1022	20.46	1.14	11.60	83.22	10.20	81.19
Q1-fragment 1-3	40.52	825	20.23	0.73	7.16	88.03	9.78	47.68
mean	**41.26**	**800.31**	**20.40**	**0.93**	**8.82**	**85.19**	**9.48**	**59.47**
stdev	0.65	235.18	0.15	0.20	2.42	2.52	0.90	18.84
%RSD	**2%**	**29%**	**1%**	**22%**	**27%**	**3%**	**10%**	**32%**

*If the K and the Q are significantly different by **at least one element** (or ratio), they can be excluded to have come from the same source*

Item K1	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe57	Rb85	Sr88	Zr90	Ba137	La139	Ce140	Nd146	Hf178	Pbsum
K1-1	4.18	22324	2796	1185	63951	68.82	19.16	515	1.93	30.70	30.03	10.69	2.49	4.18	2.00	0.81	1.15
K1-2	4.14	22212	2753	1171	63222	68.48	18.31	514	1.65	29.86	29.30	9.82	2.62	4.14	1.90	0.81	1.06
K1-3	4.22	22358	2757	1176	63513	72.87	18.58	528	1.63	29.70	29.89	10.04	2.53	4.22	1.87	0.71	1.17
K1-4	4.23	22419	2760	1172	63703	72.43	18.78	511	1.62	29.87	30.08	9.78	2.50	4.23	1.87	0.72	1.21
K1-5	4.05	22272	2675	1134	61850	66.02	18.06	504	1.56	28.90	32.00	9.54	2.43	4.05	1.65	0.81	1.04
K1-6	4.20	22587	2701	1151	62681	67.05	18.30	504	1.66	29.42	32.41	9.95	2.45	4.20	1.96	0.85	1.01
K1-7	4.09	22315	2654	1148	61297	66.80	18.13	503	1.58	28.65	31.33	9.71	2.45	4.09	1.71	0.80	1.13
K1-8	4.14	22815	2694	1131	63036	68.21	18.56	503	1.52	28.95	29.74	9.44	2.38	4.14	1.86	0.80	1.10
K1-9	4.21	22508	2683	1130	62232	69.20	18.42	506	1.61	29.07	29.88	9.35	2.43	4.21	1.81	0.73	1.02
K1-10	4.10	22551	2652	1142	62639	66.75	17.78	509	1.57	28.84	28.75	9.55	2.44	4.10	1.95	0.63	1.09
mean	**4.16**	**22436**	**2712**	**1154**	**62812**	**68.66**	**18.41**	**510**	**1.63**	**29.40**	**30.34**	**9.79**	**2.47**	**4.16**	**1.86**	**0.77**	**1.10**
stdev	0.06	181	50	20	844	2.34	0.39	7.78	0.11	0.64	1.18	0.39	0.07	0.06	0.11	0.07	0.07
%RSD	1.5%	0.8%	1.9%	1.8%	1.3%	3.4%	2.1%	1.5%	7.0%	2.2%	3.9%	3.9%	2.7%	1.5%	6.0%	8.7%	6.2%

Item Q1	Li7	Mg25	Al27	K39	Ca42	Ti49	Mn55	Fe57	Rb85	Sr88	Zr90	Ba137	La139	Ce140	Nd146	Hf178	Pbsum
Q1-fragment 1-1	4.19	23476	2793	1144	64121	70.26	18.61	518	1.55	29.68	32.58	9.88	2.47	4.19	1.90	0.90	1.00
Q1-fragment 1-2	4.09	23315	2753	1140	64052	70.19	18.27	510	1.56	29.37	29.22	9.31	2.40	4.09	1.85	0.75	1.01
Q1-fragment 1-3	4.18	23430	2741	1145	63722	70.74	18.35	526	1.49	29.51	28.16	9.42	2.43	4.18	1.72	0.74	1.14
mean	**4.15**	**23407**	**2763**	**1143**	**63965**	**70.40**	**18.41**	**518**	**1.53**	**29.52**	**29.99**	**9.54**	**2.43**	**4.15**	**1.82**	**0.80**	**1.05**
stdev	0.06	83	27	3	213	0.30	0.18	8.03	0.04	0.16	2.31	0.30	0.03	0.06	0.09	0.09	0.08
%RSD	**1.3%**	**0.4%**	**1.0%**	**0.2%**	**0.3%**	**0.4%**	**1.0%**	**1.6%**	**2.4%**	**0.5%**	**7.7%**	**3.2%**	**1.4%**	**1.3%**	**5.1%**	**11.4%**	**7.5%**

ICP-MS typical data

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

FIU International Forensic Research Institute

Lab ID	Method	K1 vs Q1	K1 vs Q2	Match Criteria
A-ICP	LA-ICP- MS	nr	D**	t-test (p=0.05, for elements and ratios), data analysis incomplete
B- ICP	LA-ICP- MS	I*	D**	Ratios, ± 2SD
C-ICP	LA-ICP- MS	I*	D**	± 4SD (with RSD<5%), element concentrations
D-ICP	LA-ICP- MS	I*	D**	t-test (p =0.05), element concentrations
F-ICP	ICP-MS	I*	D**	± 3SD, element concentrations
G-ICP	LA-ICP-MS	I*	D**	Range overlap, ratios to Si^{29}
H-ICP	LA-ICP-MS	I*	D**	± 4SD with system relative standard deviations, element concentrations
I-ICP	LA-ICP-MS	I*	D**	t-test (p =0.05), element concentrations
A-XRF	XRF	I*	D**	Spectra overlap, (Levels of K, Ti, and Mn caused exclusion of Q2: Level of Al in Q2 was also different, but alone may not have caused total exclusion)
B-XRF	XRF	I*	D**	Spectra overlap, ± 3SD ratios of intensities Ca/Mg, Ca/Ti Ca/Fe, Sr/Zr, Fe/Zr, Ca/K, Fe/Sr, Fe/Mn
C-XRF	XRF	I*	D**	Spectra overlap, range overlap for Ca/Mg, Ca/Fe, Sr/Zr, Fe/Zr, and Ca/K
D-XRF	XRF	I*	D**	Spectra overlap, ± 3SD ratios of intensities Ca/Mg, Ca/Ti ,Ca/Fe, Ca/K, Fe/Sr, Fe/Mn
E-XRF	XRF	I*	D**	Spectra overlap, ± 3SD ratios of intensities Ca/Mg, Ca/Ti Ca/Fe, Sr/Zr, Fe/Zr, Ca/K,
F-XRF	XRF	I*	D**	Spectra overlap, ± 3SD ratios of intensities Ca/Fe, Sr/Zr, Ca/K
G-XRF	XRF	I*	D**	Spectra overlap, ± 2SD of ratios of Ca/Mg, Ca/Ti Ca/Fe, Sr/Zr, Fe/Zr, Ca/K, Fe/Mn
H-LIBS	LIBS	I*	D**	t-test (p =0.05), ratios of intensities for Al/Sr, Fe/Sr, Ca/K, Al/Ca, Al/Na, Ba/Sr

100 % correct association and discrimination

Match criteria:

1. t-test (p=0.05) [4labs]
2. Range overlap [2 labs]
3. ± 2 SD [2 labs]
4. ± 3 SD [5 labs]
5. ± 4 SD [2 labs]
6. Spectra overlap [6 labs]

RR3 - Source of the samples

- 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).

Pre-distribution analysis (RI, digestion-ICP-MS, LA-ICP-MS)

ID	K1	Q1	K2	Q2	Q3
manufacturing date	8/17/2001	8/31/2001	4/15/1998	5/17/1998	7/17/1998
Mg	11499	13365	21704	19887	21069
Ti	58.97	57.51	118.2	**155.3**	125.7
Mn	17.27	17.15	92.26	**158.5**	100.1
Fe	391.3	420.7	147.3	137.0	155.7
Rb	1.64	1.62	0.63	0.92	0.72
Sr	31.73	29.31	37.34	41.89	37.59
Zr	28.98	31.20	32.70	36.45	34.18
Ba	**9.34**	**11.86**	15.90	**23.03**	17.63
La	2.77	2.70	3.48	4.04	3.51
Ce	4.54	4.49	6.08	7.42	6.27
Sm	0.35	0.34	0.46	0.62	0.51
Hf	0.70	0.77	0.78	0.87	0.74
Pb	1.66	1.02	0.93	0.86	0.71

All samples discriminated vs each other (except K1 vs Q1, depending on the match criteria used)

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

Comparison of samples manufactured weeks-months apart

	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

- This RR allowed the study of **type 2 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 Round Robin- 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

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

XRF Results as reported by each participant using their selected match criteria

Lab ID	K1 vs Q1-1	K1 vs Q1-2	K1 vs Q1-3	K1 vs Q2-1	K1 vs Q2-2	K1 vs Q2-3	K1 vs Q3-1	K1 vs Q3-2	K1 vs Q3-3	match criteria
XRF-A	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay
XRF-B	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-C	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-D	DS	DS	DS	IN	IN	IN	IN	IN	IN	3s
XRF-F	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-I	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, range overlap
XRF-H	DS	DS	DS	IN	IN	IN	IN	IN	IN	3s
Lab ID	K2 vs Q1-1	K2 vs Q1-2	K2 vs Q1-3	K2 vs Q2-1	K2 vs Q2-2	K2 vs Q2-3	K2 vs Q3-1	K2 vs Q3-2	K2 vs Q3-3	
XRF-A	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay
XRF-B	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-C	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-D	DS	DS	DS	IN	IN	IN	IN	IN	IN	3s
XRF-F	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, 3s
XRF-I	DS	DS	DS	IN	IN	IN	IN	IN	IN	spectra overlay, range overlap
XRF-H	DS	DS	DS	IN	IN	IN	IN	IN	IN	3s

ICP Results as reported by each participant using their selected match criteria

Lab ID	K1 vs Q1-1	K1 vs Q1-2	K1 vs Q1-3	K1 vs Q2-1	K1 vs Q2-2	K1 vs Q2-3	K1 vs Q3-1	K1 vs Q3-2	K1 vs Q3-3	Match criteria	# elements
ICP-A	DS	DS	DS	IN	IN	IN	IN	IN	IN	2s interval, 9 of 10	10
ICP-B	DS	DS	DS	inc	inc	inc	inc	inc	inc	2s, 3s	18
ICP-C	DS	DS	DS	IN	IN	IN	IN	IN	DS	modified 4s	11
ICP-D	DS	DS	DS	IN	DS	DS	IN	DS	DS	t-test bonfer.	18
ICP-E	DS	DS	DS	IN	IN	IN	IN	IN	IN	2s	16
ICP-F	DS			DS (1)			IN			3s, grouped Qs	17
ICP-H	DS	DS	DS	IN	IN	IN	IN	IN	IN		16
ICP-J	DS	DS	DS	DS	DS	DS	DS	IN	DS	t-test bonfer.	10
ICP-K	DS	DS	DS	IN	IN	IN	IN	IN	IN	4s	18
Lab ID	K2 vs Q1-1	K2 vs Q1-2	K2 vs Q1-3	K2 vs Q2-1	K2 vs Q2-2	K2 vs Q2-3	K2 vs Q3-1	K2 vs Q3-2	K2 vs Q3-3	Match criteria	# elements
ICP-A	DS	DS	DS	IN	IN	IN	IN	IN	IN	2s interval, 9 of 10	10
ICP-B	DS	DS	DS	inc	inc	inc	inc	inc	inc	2s, 3s	18
ICP-C	DS	DS	DS	IN	IN	IN	IN	IN	IN	modified 4s	11
ICP-D	DS	DS	DS	IN	IN	DS	IN	DS	IN	t-test bonfer.	18
ICP-E	DS	DS	DS	IN	IN	IN	IN	IN	IN	2s	16
ICP-F	DS			IN			IN			3s, grouped Qs	17
ICP-H	DS	DS	DS	IN	IN	IN	IN	IN	IN	modified 4s	16
ICP-J	DS	DS	DS	DS	IN	DS	DS	IN	IN	t-test bonfer.	10
ICP-K	DS	DS	DS	IN	IN	IN	IN	IN	IN	4s	18

LIBS Results as reported by each participant using their selected match criteria

Lab ID	K1 vs Q1-1	K1 vs Q1-2	K1 vs Q1-3	K1 vs Q2-1	K1 vs Q2-2	K1 vs Q2-3	K1 vs Q3-1	K1 vs Q3-2	K1 vs Q3-3	match criteria	# elements
LIBS-H	DS	DS	DS	IN	DS	DS	DS	IN	IN	ttest bonfer.	8 elements, 11ratios
LIBS-I	IN	IN	IN	DS	DS	IN	IN	IN	IN	ttest (0.01)	7 elements, 6 ratios
LIBS-K	DS	DS	IN	DS	DS	DS	IN	IN	IN	ttest (0.01)	8 elements, 14 ratios
Lab ID	**K2 vs Q1-1**	**K2 vs Q1-2**	**K2 vs Q1-3**	**K2 vs Q2-1**	**K2 vs Q2-2**	**K2 vs Q2-3**	**K2 vs Q3-1**	**K2 vs Q3-2**	**K2 vs Q3-3**		
LIBS-H	DS	DS	DS	IN	DS	DS	DS	IN	DS	ttest bonfer.	8 elements, 11ratios
LIBS-I	IN	IN	DS	IN	DS	IN	IN	IN	IN	ttest (0.01)	7 elements, 6 ratios
LIBS-K	inc	inc	IN	DS	DS	DS	inc	IN	IN	ttest (0.01)	8 elements, 14 ratios

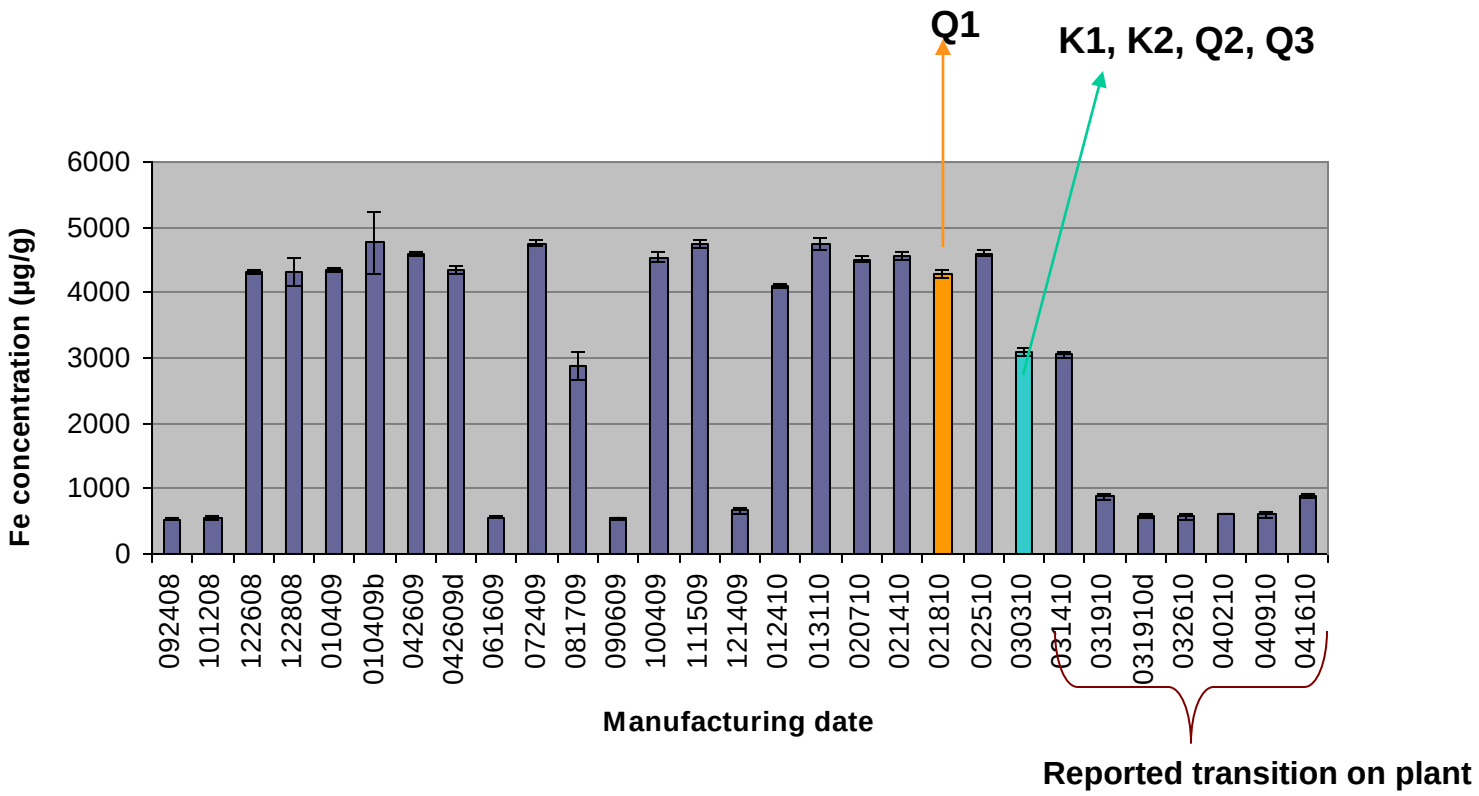
Ratios used for analysis:

LIBS-H: Ti 366 / Al 394, Fe 438/Ca643, Fe 438/Al394, Mg 517/Ti 336, Sr407/Al394, Fe 438/Ti336, Fe 438/Ba455, Al396/Ti336, Sr407/Ca616, Fe438/Na818, Mg517/Ba493

LIBS-I: Ca396/Mg279, Ti335/Ca396, Ca396/Fe275, Sr407/Na818, Fe275/Na818, Ca396/K766

LIBS-K: Ca428/Mg518, Ti498/Ca428, Ca428/Fe372, Al396/Ca317, Na818/Fe372, Al396/Fe372, Ca318/Fe3172, Na818/Al396, Sr407/Al396, Sr407/Ca428, Al396/Mg518

Pilkington Glass – Fe transition

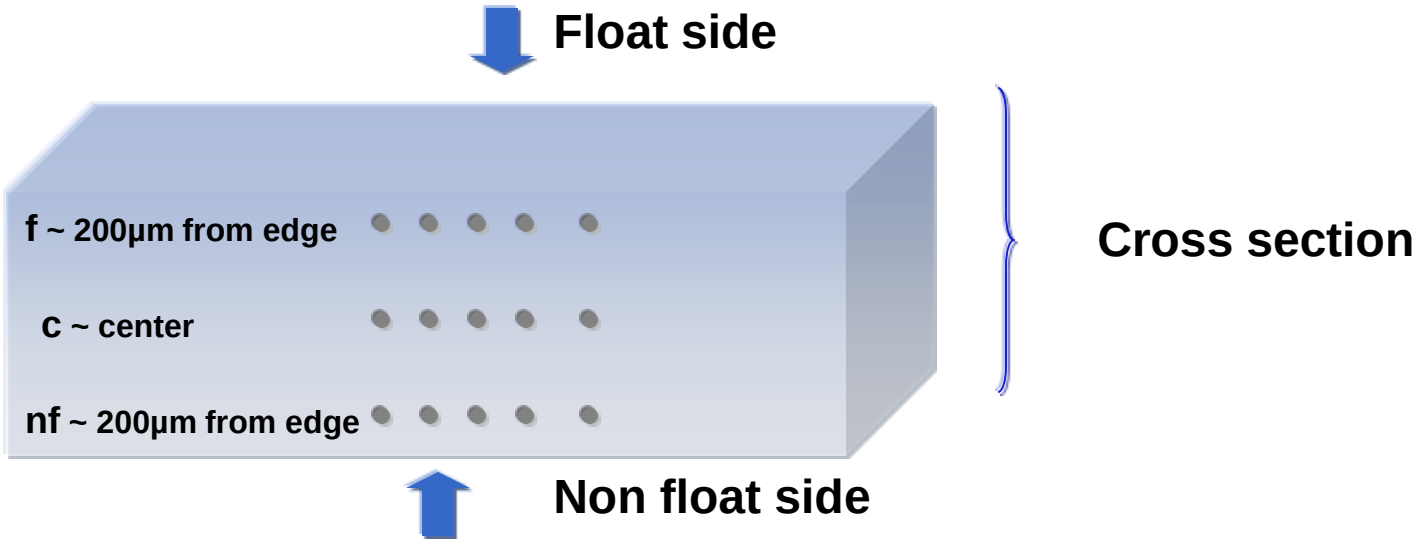


EAWG – glass homogeneity study

PLANT - SAMPLES:
Pilkington 030310
Pilkington 021810
Cardinal 010817

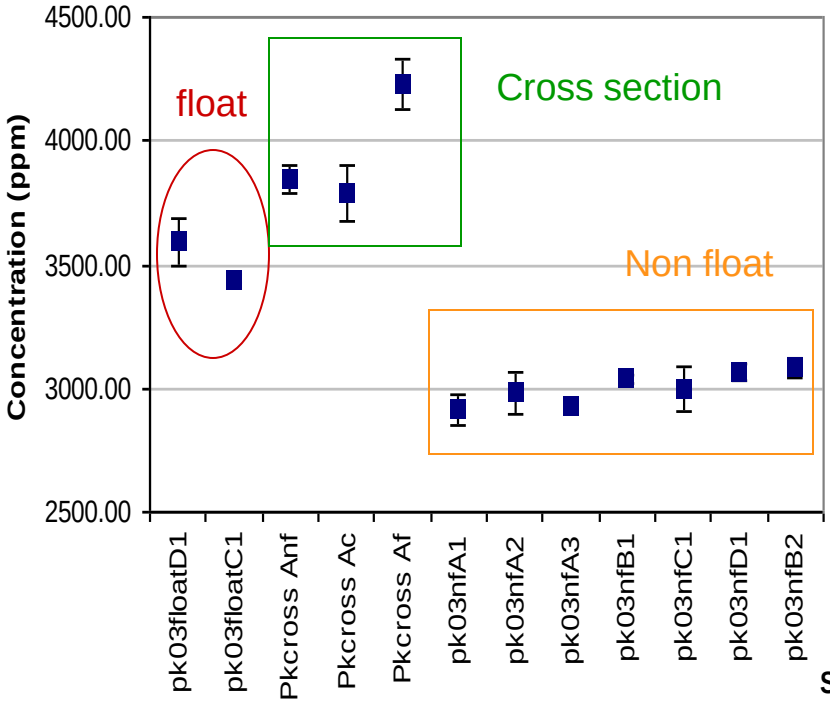
Between fragments variation:
5-7 fragments per set (3 replicates each)

Within fragment variation (spatial):
non float side
float side
cross section

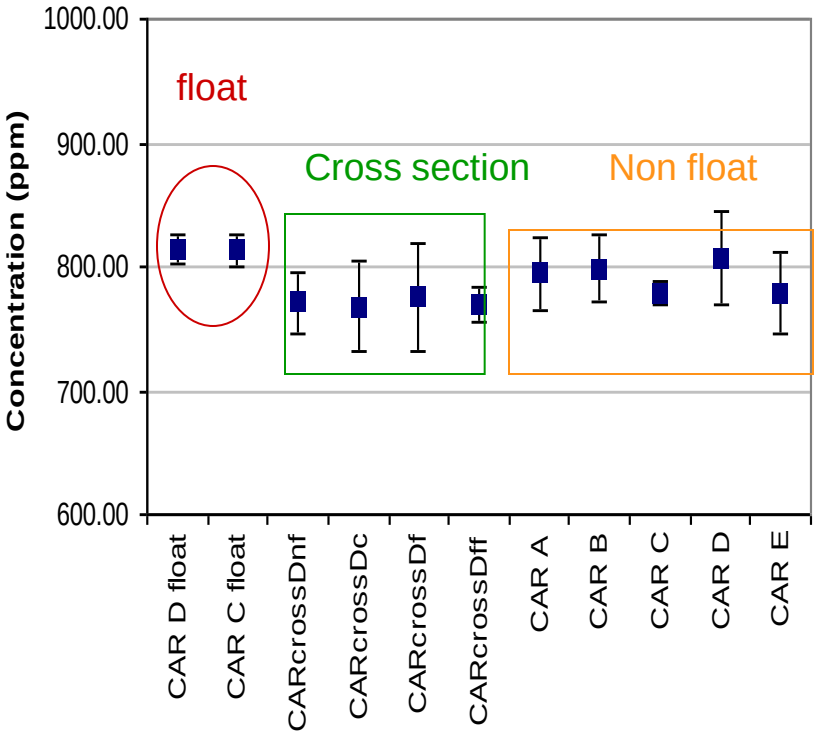


Fe variation

PK030310



CAR021810



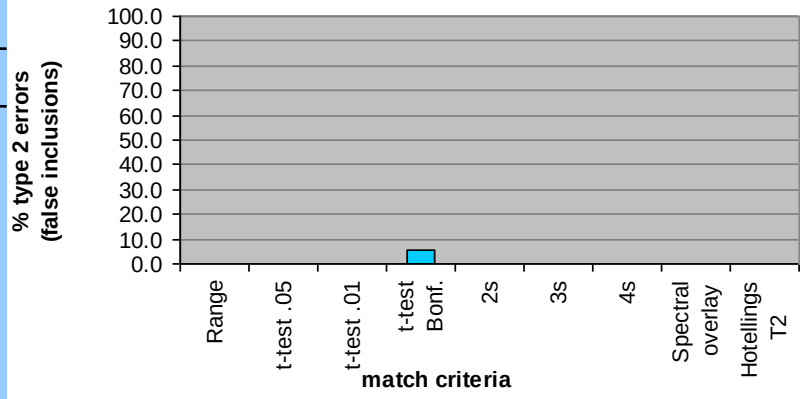
Match Criteria Comparison

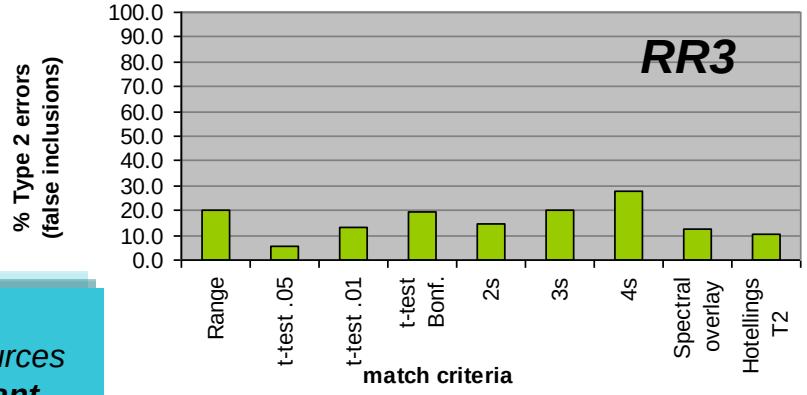
- Each participant was later asked to conduct the following match criteria on their own data:
  - Range overlap
  - t-test (p=0.05, p=0.01)
  - t-test with Bonferroni correction
  - Hotellings T (some sets)
  - ± 2s, 3s, 4s, 5s, 6s
  - ± 2s, 3s, 4s, 5s, 6s (min 3%RSD)

µXRF – Type 2 error (RR2, RR3 and RR4)

Match criteria	% Type II		
	RR2	RR3	RR4
Range	0	20	0
t-test .05	0	6	0
t-test .01	0	13	0
t-test Bonf.	6	19	0
2s	0	15	0
3s	0	20	0
4s	0	28	0
Spectral overlay	0	12	0
Hotellings T^2	0	10	0

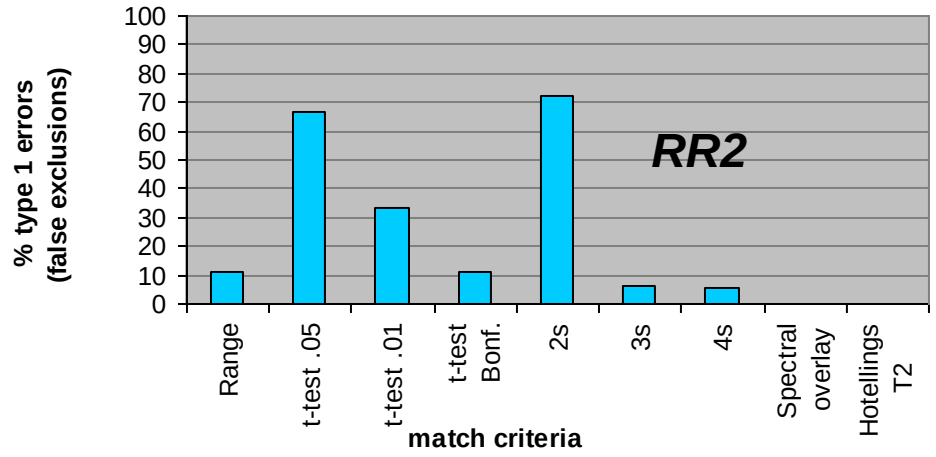
RR2

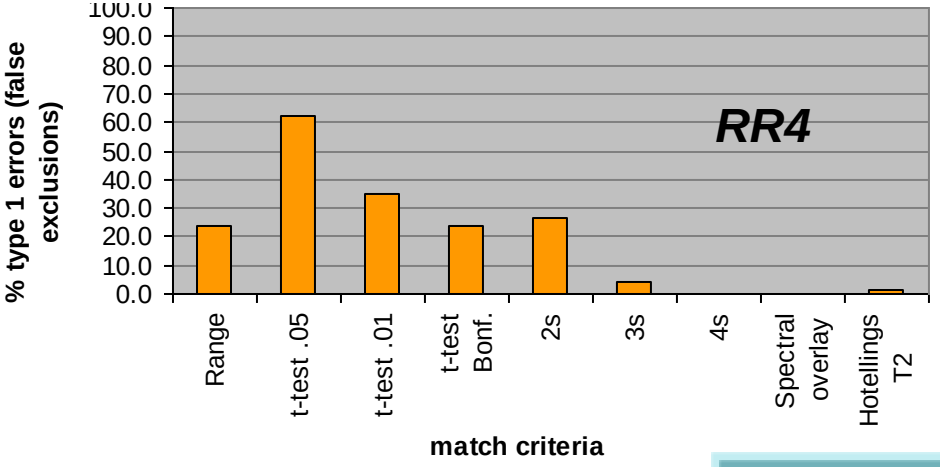




Type 2 error:
Failure to discriminate samples that originated from different sources was observed only for samples that originated from the ***same plant*** *manufactured* ***2 weeks and 3 months*** *apart (RR3)*

µXRF – Type I error (RR2, RR3 and RR4)



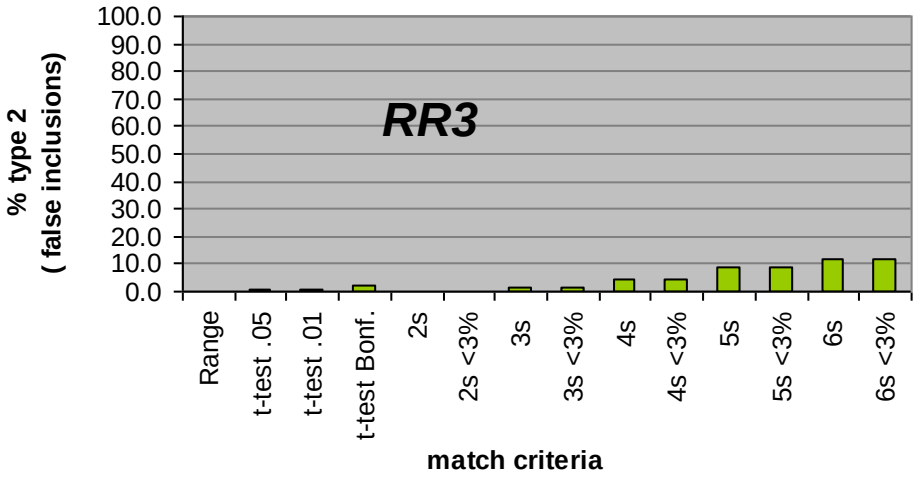


Match criteria	% Type I		
	RR2	RR3	RR4
Range	11	n/a	24
t-test .05	67	n/a	63
t-test .01	33	n/a	35
t-test Bonf.	11	n/a	24
2s	72	n/a	26
3s	6	n/a	4
4s	6	n/a	0
Spectral overlay	0	n/a	0
Hotellings T^2	0	n/a	1

Type 1 error

In most cases, failure to associate samples with common origin was observed for 1 out of 6 to 8 elemental ratios.

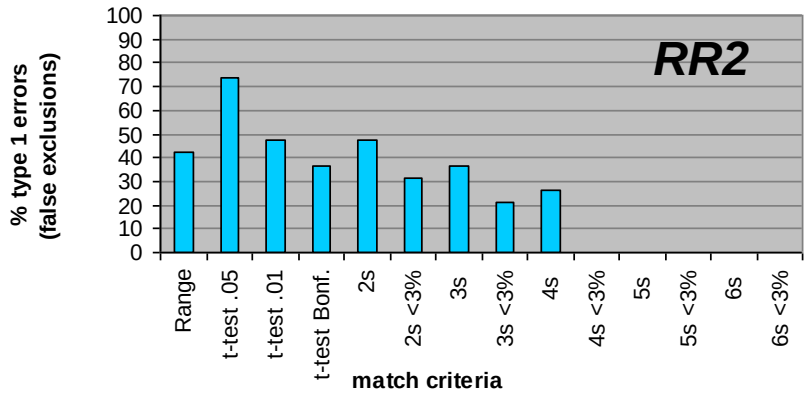
ICP methods – Type 2 error (RR2, RR3 and RR4)

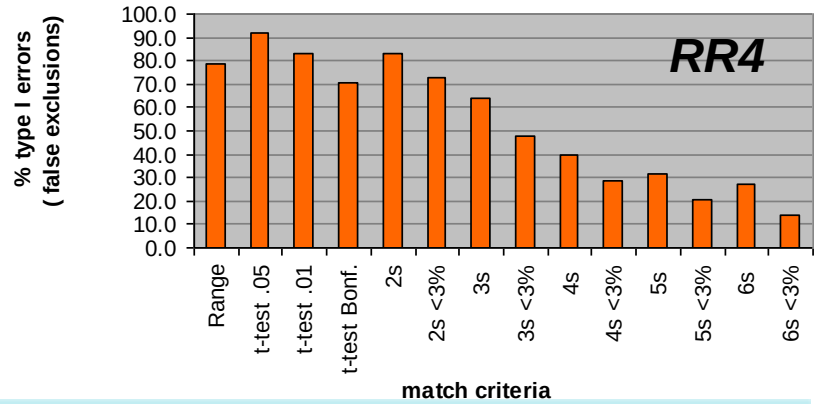


Type 2 error:
Failure to discriminate samples that originated from different sources was observed by ***some labs*** *only for samples that originated from the* ***same plant*** *manufactured* ***2 weeks apart*** *(RR3)*

Match criteria	% Type II		
	RR2	RR3	RR4
Range	0	0	0
t-test .05	0	1	0
t-test .01	0	1	0
t-test Bonf.	5	2	0
2s	0	0	0
2s <3%	0	0	0
3s	0	2	0
3s <3%	0	2	0
4s	0	5	0
4s <3%	0	5	0
5s	0	9	0
5s <3%	0	9	0
6s	0	12	0
6s <3%	0	12	0

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

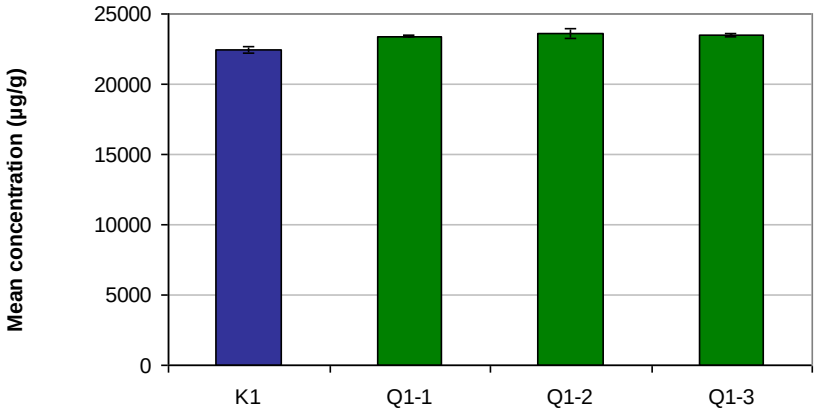




Type 1 error
Failure to associate samples with common origin was observed in ***RR2*** *only for* ***2 out of 7 labs, only for 1 out of 16-18 elements.***

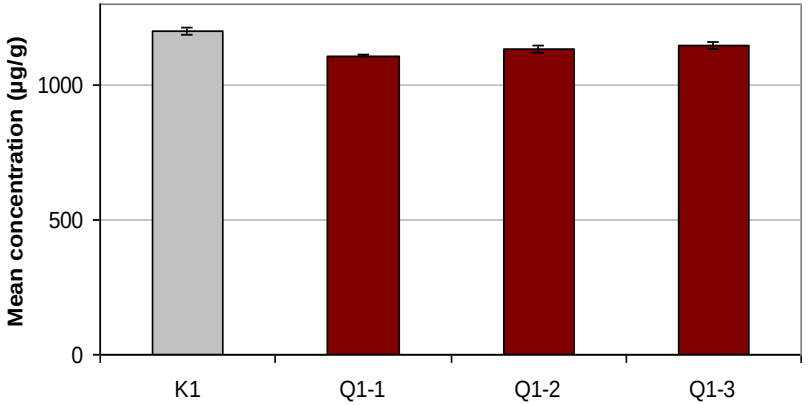
RR4 higher type I error *rates are associated to* ***heterogeneity*** *of the sample source*

	% Type I		
Match criteria	**RR2**	**RR3**	**RR4**
Range	42	n/a	79
t-test .05	74	n/a	92
t-test .01	47	n/a	83
t-test Bonf.	37	n/a	70
2s	47	n/a	83
2s <3%	32	n/a	73
3s	37	n/a	64
3s <3%	21	n/a	48
4s	26	n/a	40
4s <3%	0	n/a	29
5s	0	n/a	31
5s <3%	0	n/a	20
6s	0	n/a	27
6s <3%	0	n/a	14



4s range
21711 - 23161

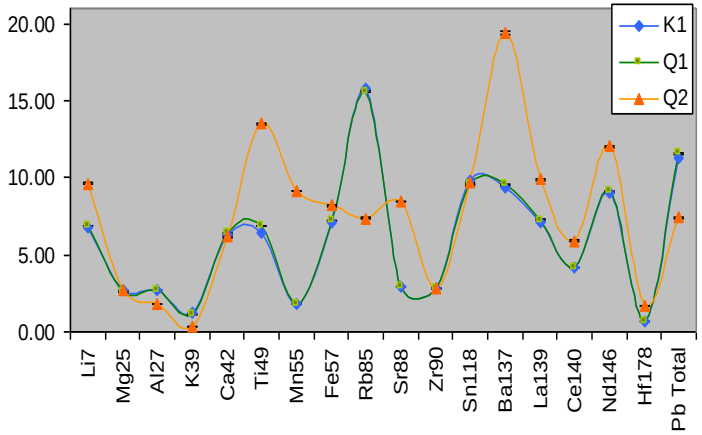
	Mg mean	stdev	%RSD
K1	22436	181	0.8%
Q1-1	23407	83	0.4%
Q1-2	23610	325	1.4%
Q1-3	23518	113	0.5%



4s range
1253-1142

	K mean	stdev	%RSD
K1	1198	14	1.2%
Q1-1	1110	6	0.5%
Q1-2	1131	14	1.2%
Q1-3	1147	13	1.2%

5 out of 19 comparisons gave 26% **type I error** on RR2 for **4s**
2 out of 7 labs, **one element only**
Precision **< 1.2%RSD**



P. Weis et al, J. Anal. At. Spectrom., 2011, 26, 1273

EAWG Recommendations

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 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.

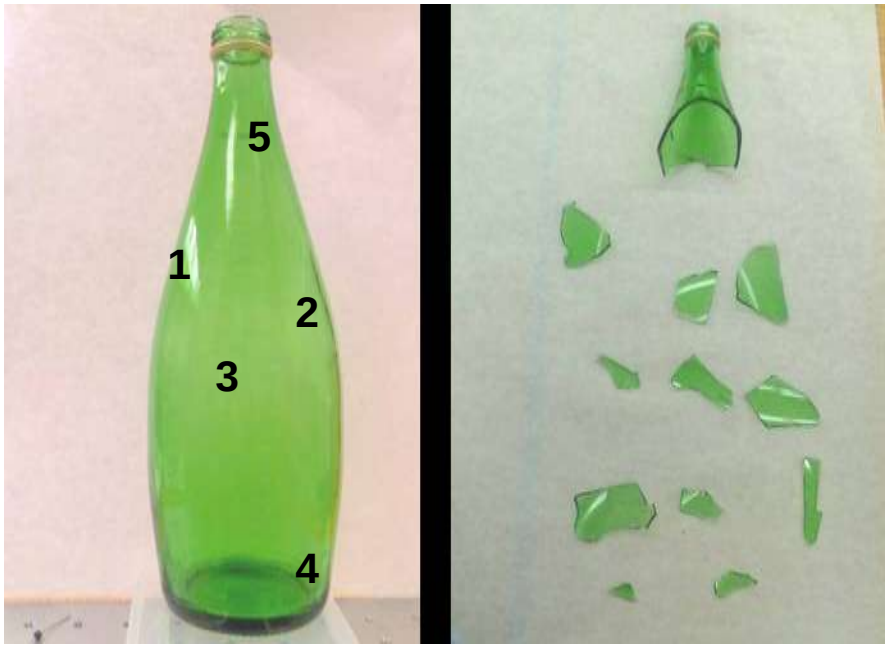
- **Match criteria for XRF-based data**
  - Use spectral overlay as a preliminary comparison method.
  - Ratios for comparison can include Fe/Ca, Ti/Ca, K/Ca, Sr/Zr, Zr/Fe, Mn/Fe and Sr/Fe, if those elements are present above minimum quantification levels
  - ± 3s criteria performs better than range overlap but both can be applied as a comparison criteria for the elemental ratios.
  - Hotelling's T (multivariate t-test) also performs well and can be considered as an alternative match criteria for elemental comparisons.

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

Acknowledgments

- The authors would like to acknowledge the National Institute of Justice (Grant # NIJ-2009-DN-BX-K252) for funding the Elemental Analysis Working Group through a grant to Florida International University.
- We also want to thank all the EAWG participants and their agencies for their contributions to the EAWG.
- Dr. Robert Koons for his contribution on data analysis and interpretation

Set B: homogeneity test design



- Green bottle labeled “Perrier water with lime”.
- A fragment of approximately 3 cm was selected from each area and washed with methanol, nitric acid (0.8M).
- Once the samples were dried, they were carefully broken and measured with a caliper to group them by size and make sure all participants had series of fragments of similar size and shape.
- Each sample was prepared in a separate clean area to avoid cross contamination.

Homogeneity has been reported in the past for ICPMS and LA-ICP-MS only

In general, **regardless of the micro-sampling technique** used for the analysis of these container fragments, there is **evidence of heterogeneity** in the elemental composition of the bottle. Therefore, it is recommended to **sample more glass fragments** (5-10) from different areas of the known container and use the overall mean values and variation of the measurements for the comparison to questioned glass.