THE DIFFERENTIATION OF FLOAT GLASS USING REFRACTIVE INDEX AND ELEMENTAL ANALYSIS: COMPARISONS OF TECHNIQUES

Stefan BECKER[1], Lawrence GUNARATNAM[2], Tacha HICKS[3], Wilfried STOECKLEIN[1], Geoff WARMAN[4]

[1] *Bundeskriminalamt, Forensic Science Institute, Wiesbaden, Germany*

[2] *National Bureau of Investigation, Crime Laboratory, Vantaa, Finland*

[3] *Institut de Police Scientifique et de Criminologie, Lausanne, Switzerland*

[4] *Metropolitan Laboratory, Forensic Science Service, London, United Kingdom*

ABSTRACT: In order to evaluate differences between the results of elemental analysis of glass a proficiency test was carried out during the period 1999/2000. The initial work on this project was presented at the first EAFS Meeting in Lausanne in 1997. Three pairs of glass samples with similar refractive indices had to be examined using refractive index measurements and elemental analysis. In this study SEM-EDX, μXRF, and ICP/MS were used for the elemental analysis.
Based on the refractive index measurements a complete differentiation of the glasses was not possible. Annealing of the glass enabled further differentiation. After the use of the elemental techniques a full differentiation of the six glasses was possible. The strategies used by different laboratories in order to discriminate between the samples and the merits of the various techniques applied are discussed.

KEY WORDS: Annealing; Float glass; Forensic glass analysis; ICP/MS; Proficiency test; SEM-EDX; μXRF.

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INTRODUCTION

Float glass is one of the major types of evidence encountered in crimes such as burglary, traffic accidents and vandalism. One of the common methods of examination is to measure the refractive index. However as narrow limits are set for the main components used in the manufacturing process, the ability to discriminate between float glass samples by using refractive index alone may be considerably reduced.

In order to evaluate the differences between the results of elemental analysis of glass, a proficiency test was carried out during the period 1999/2000. The initial work of this project was presented at the first EAFS Meeting in Lausanne in 1997.

It required refractive index measurements and elemental analysis (main & trace elements if possible) to be made on a set of six float glasses (three pairs of glass samples with similar refractive indices). Based on the selection of the samples, glasses from different float glass plants had to be discriminated.

The following forensic laboratories took part in the analysis:
– National Bureau of Investigation, Crime Laboratory, Vantaa, Finland;
– Forensic Science Service (FSS), Metropolitan Police, London, United Kingdom;
– Institut de Police Scientifique et de Criminologie (IPSC), Lausanne, Switzerland;
– Bundeskriminalamt (BKA), Forensic Science Institute, Wiesbaden, Germany.

EXPERIMENTAL

Sample selection

Table 1 shows the glasses selected for analysis. Pairs of float glasses 1/4, 2/6, and 3/5 exhibited similar refractive indices (difference of refractive index n_d smaller than 6×10^{-5}). Samples were selected from the central float glass collection of the Forensic Science Institute/BKA.

TABLE I. SAMPLE INFORMATION OF SELECTED GLASS SAMPLES

Sample number	Production plant	Country	Company	Colour	Date of production
1	Gladbeck	Germany	Pilkington	Green	15 September 1993
2	Lahti	Finland	Pilkington	Clear	14 February 1995
3	Greenland	USA	AFG (Asahi)	Clear	App. 1995
4	Aichi 1	Japan	Asahi Glass Co.	Green	App. 1997
5	Gladbeck	Germany	Pilkington	Clear	16 March 1983
6	Halmstad	Sweden	Pilkington	Clear	1 April 1995

Instrumentation

The refractive index was determined with GRIM 1 and GRIM 2 (Foster & Freeman, UK) at the wavelength of app. 589 nm. The particles were crushed and immersed in silicon oils (Locke Scientific, UK). Annealing was performed in a tube furnace MTF 10/15 equipped with the controller Eurotherm 818P (laboratory 3). In laboratory 4 a ceramic fibre furnace produced by Kontron VMK-22 equipped with a controller Eurotherm 812 was used for annealing.

TABLE II. OPERATING PARAMETERS USED FOR ANNEALING OF THE GLASS (THE PARAMETERS REPRESENT SETTINGS OF THE TEMPERATURE PROGRAMMING AND MAY NOT REPRESENT ACTUAL FURNACE CONDITIONS)

	Laboratory 3	Laboratory 4
Ramp rate 1	200°C/min	600°/h
Dwell temperature 1	590°C	555°C
Dwell time 1	12 min	2 h
Ramp rate 2	4.5°C/min	4°C/h
Dwell temperature 2	425°C	500°C
Dwell time 2	0.5 min	0.1 h

Elemental analysis was performed using:
– EDX-μXRF/Kevex Omicron,
– EDX-μRFA/EDAX Eagle,
– SEM-EDX Jeol JXA – 8600 Super Probe/Oxford ISIS 300,
– 2 laboratories used SEM-EDX Camscan,
– ICP/MS PQ2plus VG Elemental.

Sample preparation

EDX-μXRF/Kevex Omicron: The samples were glued (Super 77, Scotch 3M) on a thread of cotton: the glue and the cotton were of a type whose elements would not interfere with those being analysed in the glass.

SEM-EDX Camscan #1: Samples were embedded in conductive Bakelite with 4 glass standards. After polishing the surface with alumina, the polished sample was carbon coated.

SEM-EDX Jeol: Samples were embedded in acrylic resin with one glass standard NBS 620. After polishing the surface with diamond paste, the polished sample was carbon coated.

EDX-μRFA / EDAX EAGLE: Samples were embedded in acrylic resin (Technovit 2000 LC/Kulzer) and the surface was polished with diamond paste. 8 standard glasses were used for calibration.

SEM-EDX Camscan #2: Samples were embedded in acrylic resin (Technovit 2000 LC/Kulzer). 8 standard glasses were used for calibration. After polishing the surface with diamond paste, the polished samples were carbon coated.

ICP/MS: The samples were first placed in a 20% w/w HNO_3 solution overnight and then immersed in a solution of demonised water and air dried. After weighing 0.5–1.4 mg of glass into a 7 ml thread PFA vessel with a concave bottom, 1000 μl of digestion acid mixture (40% HF & 60% HNO_3 1:1 w/w) was added and digestion took place in an ultrasonic bath in three 10 min periods. The digested sample was cooled and 500 μl of $HClO_4$ 70% was added. After fuming the sample to dryness and cooling, the volume was made up to 1 ml with 1 μg/l Rh in HNO_3 5%. The sample was then diluted with 1 μg/l Rh in HNO_3 2% and analysed for major and minor elements.

Conditions of analysis

TABLE III. ELEMENTS MEASURED BY DIFFERENT ANALYSING TECHNIQUES

Technique	Elements observed
EDX-μXRF/Kevex	Na, Mg, Al, Si, K, Ca, Fe, Sr, Zr
SEM-EDX Camscan #1	Na, Mg, Al, Si, S, K, Ca, Fe
SEM-EDX Jeol	Na, Mg, Al, Si, K, Ca, Fe
μXRF/Eagle	Na, Mg, Al, Si, K, Ca, Ti, Fe
SEM-EDX Camscan #2	Na, Mg, Al, Si, S, K, Ca, Ti, Fe
ICP/MS	Li, Mg, Al, Ca, Ti, Mn, Co, Rb, Sr, Y, Zr, Sn, Sb, Ba, La, Ce, Nd, Eu, Dy, Ho, Er, Hf, Pb, Bi, Th, U

TABLE IV. INSTRUMENTAL CONDITIONS FOR THE DIFFERENT TECHNIQUES

Technique	Instrumental conditions
SEM-EDX Camscan #1	Accelerating voltage: 15 kV, beam current: 1 nA; scan mode: raster, acquisition time: 200 s, detector resolution 135eV (Mn, Kα), scanned area at 2000x mag, approx. 50 x 40 μm
SEM-EDX Jeol	Accelerating voltage: 15 kV, beam current: 1 nA, scan mode: raster, acquisition time 100 s, detector resolution 138 eV (Mn, Kα)
EDX-μXRF/Kevex	X-ray source: Rhodium unfiltered radiation, accelerating voltage: 35 kV, beam current: 0.05–1 nA, collimator: 300 μm, analysis in vacuo, acquisition time 1500 s, detector resolution: 180 KeV (Mn, Kα)
μXRF/Eagle	X-ray source: Molybdenum unfiltered radiation, accelerating voltage: 30 kV, beam current: 30 nA, collimator: 100 μm, acquisition time 500 s, detector resolution: 180 KeV (Mn, Kα), analysis in vacuum
SEM-EDX Camscan #2	Accelerating voltage: 20 kV, beam current: 0.3 nA, scan mode: raster, window 250 μm, acquisition time: 500 s
ICP/MS	Plasma conditions: forward power 1350 W, reflected power < 5 W, carrier gas flow 0.8–1.1 l/min, auxiliary gas flow 0.6 l/min; cooling gas flow 14.2 l/min, uptake rate controlled by peristaltic pump 0.8 ml/min. Data acquisition: uptake time 120 s; acquisition time 60 s (3x), sample wash time 300; scanning mass: 4.6–239.4 amu

RESULTS

Differentiation by refractive index

As shown in Figure 1 differentiation of glass 1 and 4 was not possible by refractive index measurements. Only laboratory 1 stated it was able to differentiate between these two glasses with a difference in refractive index of 2×10^{-5} by using t-test with a confidence level of 5%.

As shown in Figure 2 differentiation of glass 2 and 6 was not possible by refractive index measurements.

As shown in Figure 3 differentiation of glass 3 and 6 was not possible by refractive index measurements. Only laboratory 1 stated it was able to dif-

ferentiate between these two glasses with a difference in refractive index of 3×10^{-5} by using t-test with a confidence level of 5%.

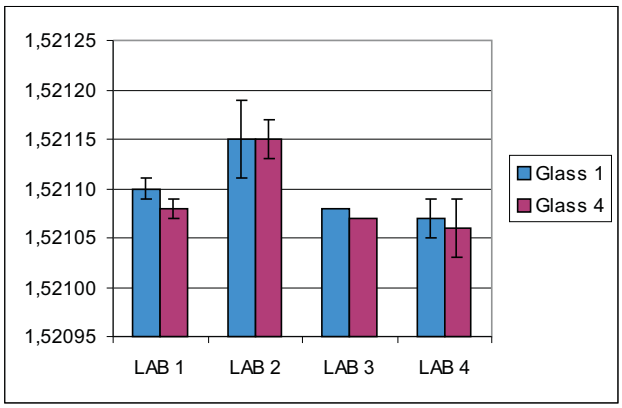

Fig. 1. Incomplete differentiation of glass 1 and 4.

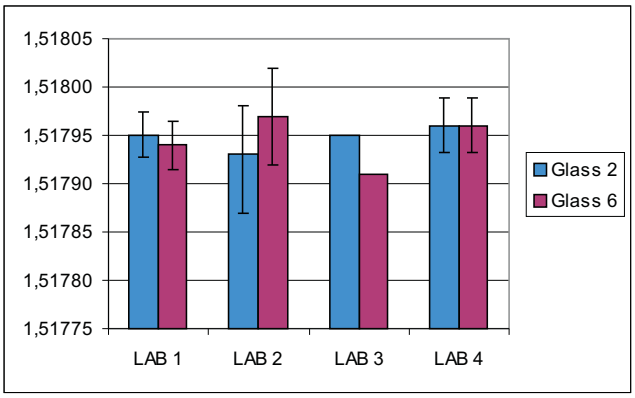

Fig. 2. Differentiation of glass 2 and 6 not possible.

Differentiation by quantitative elemental analysis with SEM-EDX or μXRF

Differentiation of glass 1 and 4: differentiation of the green glasses 1 and 4 could be easily achieved by their potassium and iron concentrations as shown in Figure 4 and Figure 5. A differentiation could also be achieved by comparing the sodium, magnesium, and aluminium concentrations of glasses 1 and 4 (see Table V).

Differentiation of glass 3 and 5: differentiation of the clear glasses 3 and 5 could only be achieved by comparing the aluminium and potassium concentrations as shown in Figure 6 and Figure 7. Laboratory 4 (SEM-EDX

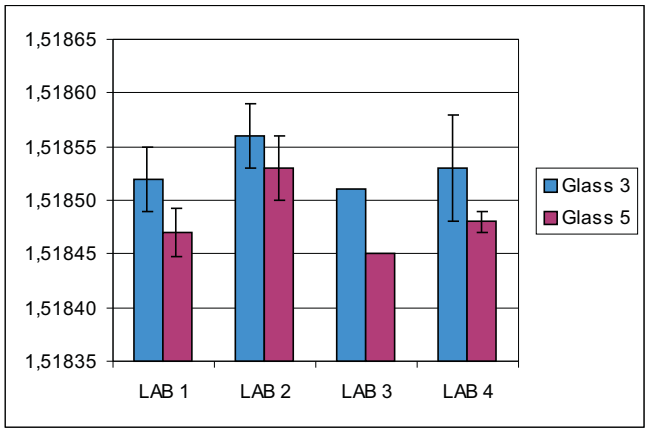

Fig. 3. Incomplete differentiation of glass 3 and 5.

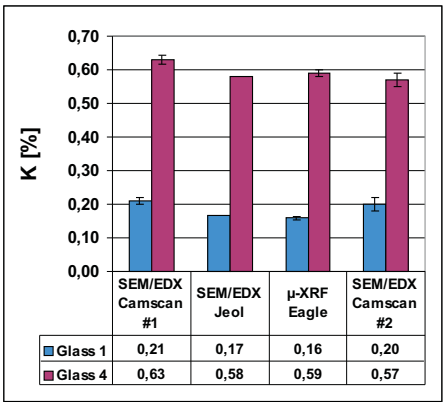

Fig. 4. Differentiation of glass 1 and 4 by potassium.

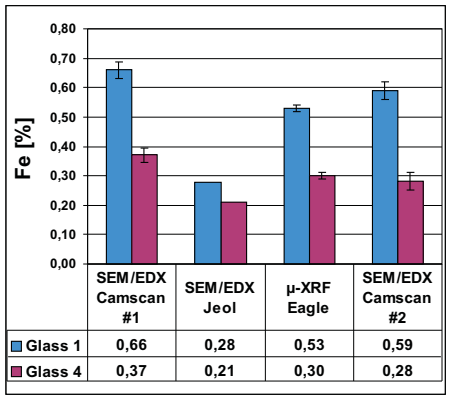

Fig. 5. Differentiation of glass 1 and 4 by iron.

Camscan 2) reported aluminium and potassium concentration to be below the detection limit (0.1%).

Differentiation of glass 2 and 6: compared to the previous pairs, differentiation of glass 2 and 6 is much more difficult. Based on the calcium concentration only, laboratory 3 (SEM-EDX Jeol) and laboratory 4 (SEM-EDX Camscan #2) were able to discriminate the glass (see Figure 8). When comparing magnesium all laboratories were able to differentiate the glass (see Figure 9).

Differentiation by quantitative elemental analysis with ICP/MS

Differentiation of glasses 1 and 4: in addition to SEM-EDX and μXRF analysis elemental analysis was carried out using ICP/MS. A differentiation of glasses 1 and 4 by a selection of elements in the concentration range from 0.4–20ppm is shown in Figure 10.

Differentiation of glasses 3 and 5: a differentiation of glasses 3 and 5 by a selection of seven elements in the concentration range from 0.5–7 ppm is shown in Figure 11.

Differentiation of glasses 2 and 6 by element concentrations: a differentiation of glasses 2 and 6 by a selection of six elements in the concentration range from 0.4–7 ppm is shown in Figure 12. Shifting to higher concentrations in Figure 13 the differentiation of glass 2 and 6 by four elements in the concentration range from 6 to 90 ppm is shown.

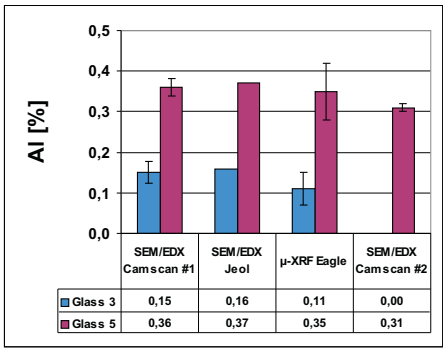

Fig. 6. Differentiation of glass 3 and 5 by aluminium concentration.

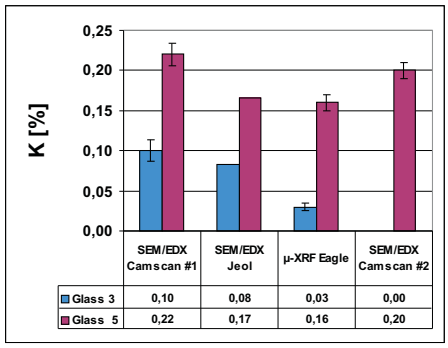

Fig. 7. Differentiation of glass 3 and 5 by potassium concentration.

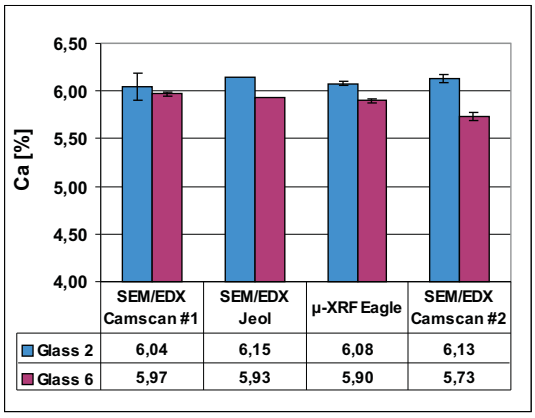

Fig. 8. Differentiation of glass 2 and 6 by calcium concentration.

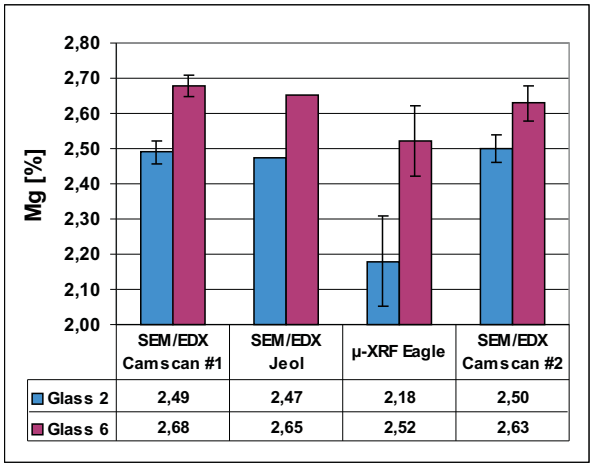

Fig. 9. Differentiation of glass 2 and 6 by magnesium concentration.

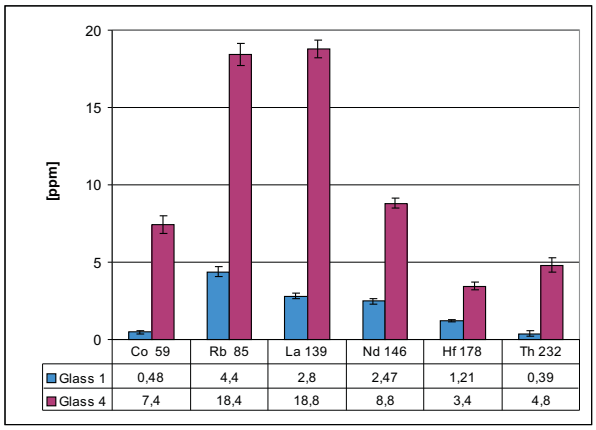

Fig. 10. Differentiation of glass 1 and 4 by six trace element concentrations measured by ICP/MS.

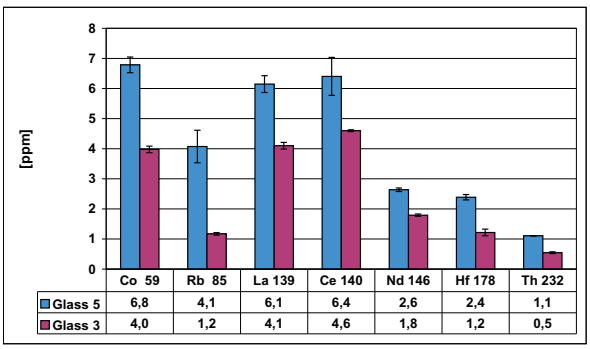

Fig. 11. Differentiation of glass 3 and 5 by seven trace element concentrations as measured by ICP/MS.

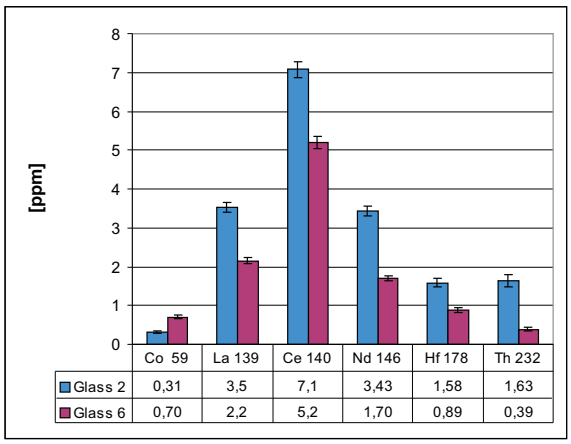

Fig. 12. Differentiation of glass 2 and 6 by trace element concentration as measured by ICP/MS.

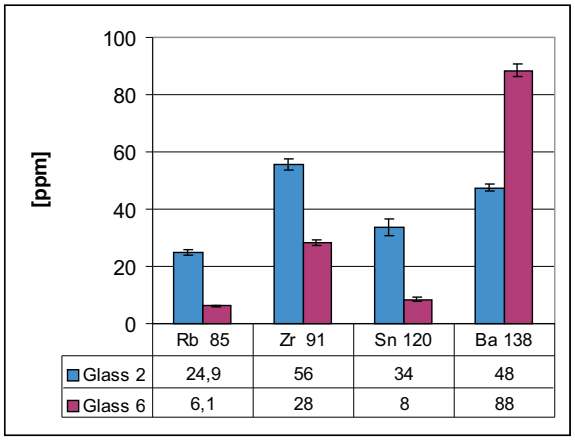

Fig. 13. Differentiation of glass 2/6 by trace element concentration as measured by ICP/MS.

TABLE V. COMPILATION OF QUANTITATIVE ELEMENTAL ANALYSES CARRIED OUT BY SEM-EDX AND μXRF

	Na	Mg	Al	Si	K	Ca	Fe
Sample 1							
SEM-EDX Camscan 1	9.84	2.31	0.34	33.88	0.21	6.09	**0.66**
SEM-EDX Jeol	10.09	2.17	0.37	33.84	0.17	6.15	**0.28**
μXRF	10.00	2.21	0.32	33.79	0.16	6.07	**0.53**
SEM-EDX Camscan 2	10.28	2.29	0.34	33.86	0.20	6.00	**0.59**
Inter-laboratory mean	10.05	2.25	0.34	33.84	0.18	6.08	0.51
Inter-laboratory SD	0.18	0.07	0.02	0.04	0.02	0.06	0.17
Inter-laboratory RSD [%]	1.8	2.9	6.1	0.1	13.4	1.0	32.1
Sample 2							
SEM-EDX Camscan 1	9.54	2.49	0.37	34.31	0.24	6.04	0.07
SEM-EDX Jeol	9.87	2.47	0.37	34.03	0.17	6.15	0.07

TABLE V. CONTINUATION

	Na	Mg	Al	Si	K	Ca	Fe
µXRF	9.71	2.18	0.27	33.81	0.18	6.08	0.08
SEM-EDX Camscan 2	10.16	2.50	0.35	34.40	0.22	6.13	< 0.10
Inter-laboratory mean	9.82	2.41	0.34	34.14	0.20	6.10	0.07
Inter-laboratory SD	0.26	0.15	0.05	0.27	0.03	0.05	0.01
Inter-laboratory RSD [%]	2.68	6.40	14.03	0.79	17.06	0.79	7.90
Sample 3							
SEM-EDX Camscan 1	**10.21**	2.36	0.15	34.18	0.10	6.15	0.07
SEM-EDX Jeol	**10.39**	2.29	0.16	34.03	0.08	6.22	0.07
µ-XRF	**10.36**	2.21	0.11	33.99	0.03	6.14	0.06
SEM-EDX Camscan 2	**10.80**	2.30	< 0.1	33.63	< 0.1	5.89	< 0.10
Inter-laboratory mean	10.44	2.29	0.14	33.96	0.07	6.10	0.07
Inter-laboratory SD	0.25	0.06	0.03	0.23	0.04	0.14	0.01
Inter-laboratory RSD [%]	2.42	2.69	18.62	0.69	51.42	2.36	8.64
Sample 4							
SEM-EDX Camscan 1	9.31	2.60	**0.90**	33.32	**0.63**	6.18	**0.37**
SEM-EDX Jeol	9.27	2.53	**0.90**	33.42	**0.58**	6.07	**0.21**
µ-XRF	9.68	2.54	**0.96**	33.15	**0.59**	6.14	**0.30**
Camscan 2	9.61	2.64	**0.96**	33.95	**0.57**	6.16	**0.28**
Inter-laboratory mean	9.47	2.58	0.93	33.46	0.59	6.14	0.29
InterSEM-EDX-laboratory SD	0.21	0.05	0.03	0.35	0.03	0.05	0.07
Inter-laboratory RSD [%]	2.18	1.98	3.73	1.03	4.41	0.74	22.73
Sample 5							
SEM-EDX Camscan 1	9.84	2.31	0.36	34.15	0.22	6.20	0.07
SEM-EDX Jeol	10.09	2.29	0.37	34.03	0.17	6.15	0.07
µ-XRF	10.07	2.22	0.35	33.76	0.16	6.11	0.07
SEM-EDX Camscan 2	10.28	2.24	0.31	34.00	0.20	6.16	< 0.10
Inter-laboratory mean	10.07	2.27	0.35	33.99	0.19	6.15	0.07
Inter-laboratory SD	0.18	0.04	0.03	0.16	0.03	0.04	0.00
Inter-laboratory RSD [%]	1.79	1.87	7.60	0.48	15.25	0.60	0.05
Sample 6							
SEM-EDX Camscan 1	9.61	2.68	0.38	34.12	0.25	5.97	0.08
SEM-EDX Jeol	9.72	2.65	0.37	33.80	0.25	5.93	0.07
µ-XRF	9.93	2.52	0.38	33.78	0.19	5.90	0.06
SEM-EDX Camscan 2	10.01	2.63	0.36	33.63	0.23	5.73	< 0.10
Inter-laboratory mean	9.82	2.62	0.37	33.83	0.23	5.88	0.07
Inter-laboratory SD	0.18	0.07	0.01	0.21	0.03	0.11	0.01
Inter-laboratory RSD [%]	1.88	2.68	2.56	0.61	12.21	1.80	14.29
Pairs with similar *RI* = 1/4, 3/5, 2/6							

Grey values represent the lowest values of the data set whereas; the bold values represent the highest concentrations of the datasheet.

The inter-laboratory deviation for Na, Si, Ca, and Mg (one exception with RSD of 7%) is below 3%. Taking into account the small number of laboratories (n = 4) it is certainly difficult to draw any general conclusions for the comparison of data resulting from elemental analysis. Still the low inter-laboratory standard deviation for most elements implies the good capability of SEM and μXRF for quantitative elemental analysis in forensic glass case work.

Differentiation strategies

Laboratory 1 included a t-test for refractive index values with a confidence level of 1 %, which resulted in a grouping of three pairs of glass. After further application of the t-test with a confidence level of 5% a differentiation of glasses 3/5 and 1/4 was possible. Qualitative analysis of Rb enabled a further differentiation of pair 2/6. Also semiquantitative analysis by SEM followed by calculation of several elemental ratios (Mg/Ca, Al/Ca, K/Ca Fe/Ca, Sr/Zr) enabled differentiation of the pairs 3/5 and 1/4 (see Figure 14).

Glass	RI	RI	Elemental analysis	Elemental analysis
	including t-test with confidence level 1%	including t-test with c. l. 5 %	Qualitative analysis of Rb	Semi-quantitative Mg/Ca, Al/Ca, K/Ca Fe/Ca, Sr/Zr
	Pairs of 2/6, 3/5, 1/4	All differentiated except 2/6	Differentiation of 2/6 possible	Differentiation of 3/5, 1/4 possible
2			Rb -qualitative	
6			Rb -qualitative	
3				K, Sr/Zr
5				K, Sr/Zr
1				Fe, K, Sr/Zr
4				Fe, K, Sr/Zr

Fig. 14. Differentiation strategy of laboratory 1.

After application of refractive index measurements laboratory 2 was able to group the samples into three pairs of glasses (Figure 15). Quantitative elemental analysis by SEM-EDX enabled a complete differentiation. Important elements for differentiation of these glass samples are aluminium (pair 3/5) and iron, potassium, and the strontium/zirconium ration (pair 1/4).

After refractive index measurements laboratory 3 was able to discriminate the samples into three pairs of glass (Figure 15). A further differentia-

Glass	RI	Elemental analysis	RI	RI	Elemental analysis
		SEM/EDX		annealing	SEM/EDX
	Pairs of 2/6, 3/5, 1/4	Complete differentiation	Pairs of 2/6, 3/5, 1/4	Differentiation except 1/4	Complete differentiation
2		Mg			Mg, Ca
6		Mg			Mg, Ca
3		Al			Al, K
5		Al			Al, K
1		Na, Mg, Al, K, Fe			Na, Mg, Al, K, Fe
4		Na, Mg, Al, K, Fe			Na, Mg, Al, K, Fe

Fig. 15. Differentiation strategy of laboratory 2 (left) and laboratory 3 (right).

tion of two pairs (2/6 and 3/5) could be achieved by refractive index measurements after annealing of the glass. Quantitative elemental analysis by SEM-EDX enabled a complete differentiation of all glass. Elements permitting differentiation were calcium, magnesium (pair 2/6), aluminium, potassium (pair 3/5) and potassium, iron (pair 1/4).

A differentiation into three pairs of glass after refractive index measurements was achieved by laboratory 4. After annealing of the glass two pairs (2/6 and 3/5) could be differentiated by refractive index measurements. Quantitative elemental analysis by SEM-EDX and μ-XRF enabled complete differentiation of all glass (see Figure 16).

The elements used for differentiation were calcium, magnesium (pair 2/6), aluminium and potassium (pair 3/5) and aluminium, potassium and iron (pair 1/4).

Glass	RI	RI	Elemental analysis
		annealing	SEM/EDX μXRF
	Pairs of 2/6, 3/5, 1/4	Differentiation except 1/4	Complete differentiation
2			Mg, Ca
6			Mg, Ca
3			Al, K
5			Al, K
1			Na, Mg, Al, K, Fe
4			Na, Mg, Al, K, Fe

Fig. 16. Differentiation strategy of laboratory 4.

Beside by SEM-EDX and μ-XRF analysis by inductively coupled plasma mass spectrometry (ICP/MS) was carried out. A full differentiation by at least six elements could be detected for all glass.

CONCLUSION

It was shown that refractive index measurements do not enable all samples of glasses to be fully differentiated. Since many of the float glasses have a similar composition only techniques with a high analytical sensitivity providing measurements of good precision can be used to achieve discrimination. The experiments have shown that microsamples of float glass with indistinguishable refractive index coming from different float glass plants can be differentiated by the methods used in this proficiency test.

This study shows the necessity of annealing of the glass as an important tool for further discrimination. However, only the use of several elemental analytical techniques such as SEM-EDX, μXRF, and ICP/MS allowed a complete discrimination of all float glasses.

With two pairs of glass (1/4) and (3/5) several elements could be used for differentiation whereas with the glass pair 2/6 only Mg and Ca enable a differentiation to be made (SEM-EDX, μXRF). Still the low inter-laboratory standard deviation for most elements implies the good capability of SEM and μXRF for quantitative elemental analysis in forensic glass case work.

The application of ICP/MS enabled a complete differentiation of all glasses to be made based on individual differences of at least six elements.

Further work should be carried out on the discrimination of float glass from the same geographical origin and/or the same float glass plant. Especially the time-dependent variation of elemental concentrations of glass from the same float glass plant (and the same furnace) has to be investigated.