Bundeskriminalamt

Investigation of changes of the refractive index of glass fragments caused by laser ablation

Dr. Stefan Becker

Bundeskriminalamt, Forensic Science Institute

Wiesbaden, Germany

Investigation of changes of the refractive index of glass fragments caused by laser ablation

Starter

Aim of study & previous work

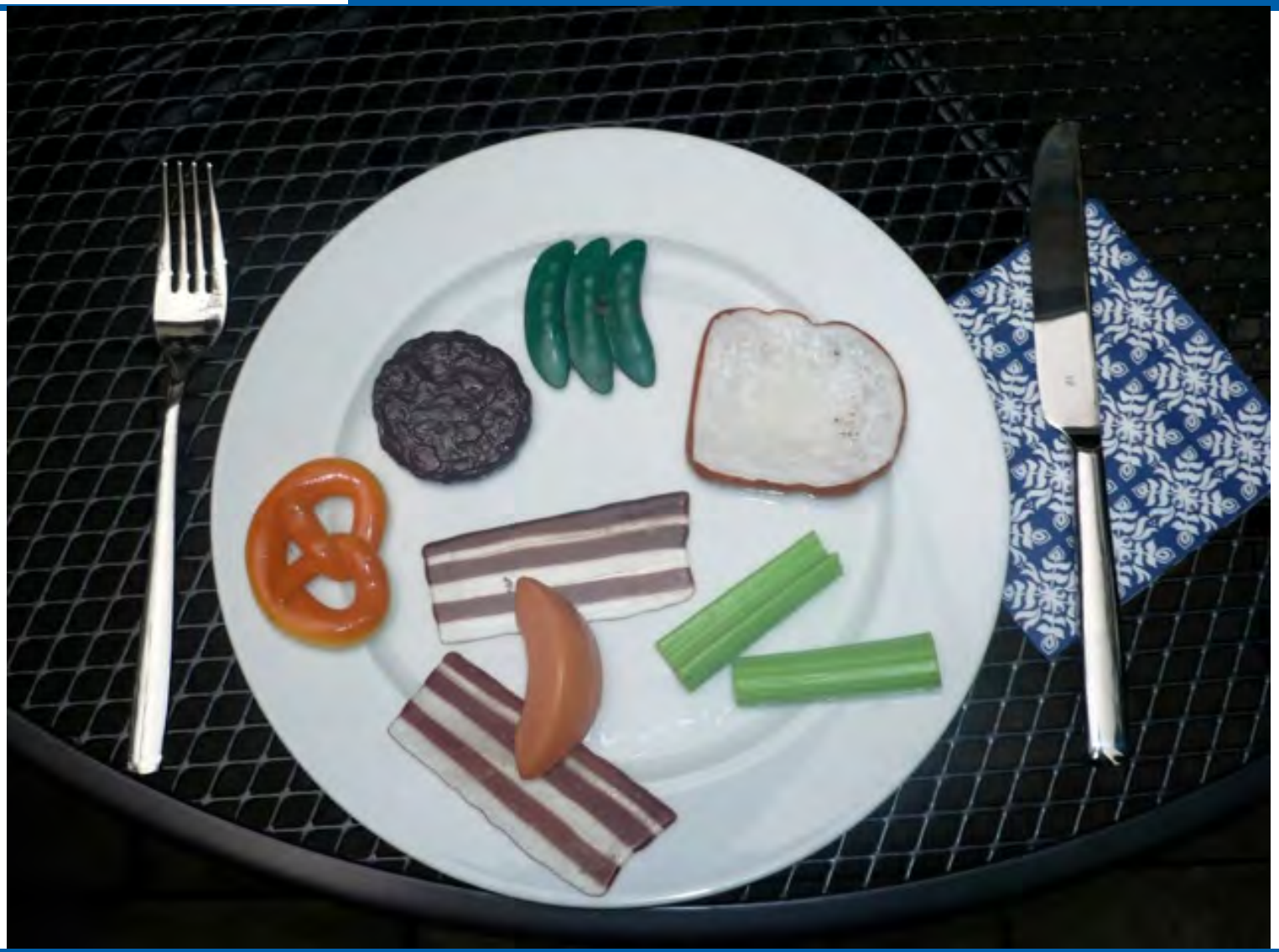
Main course

Experimental design & results

Dessert

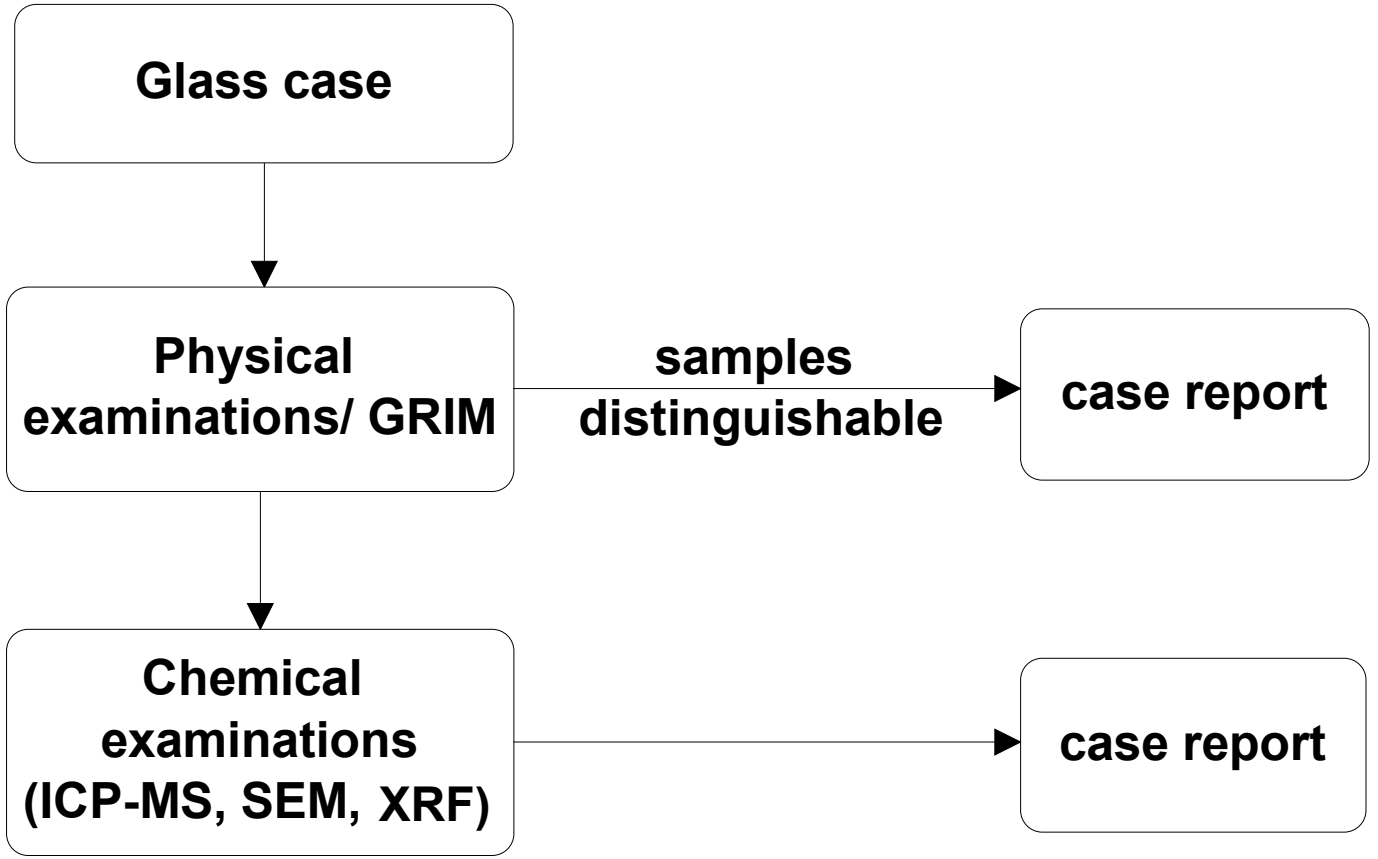
Spin off

LA vs. RI *Starter*



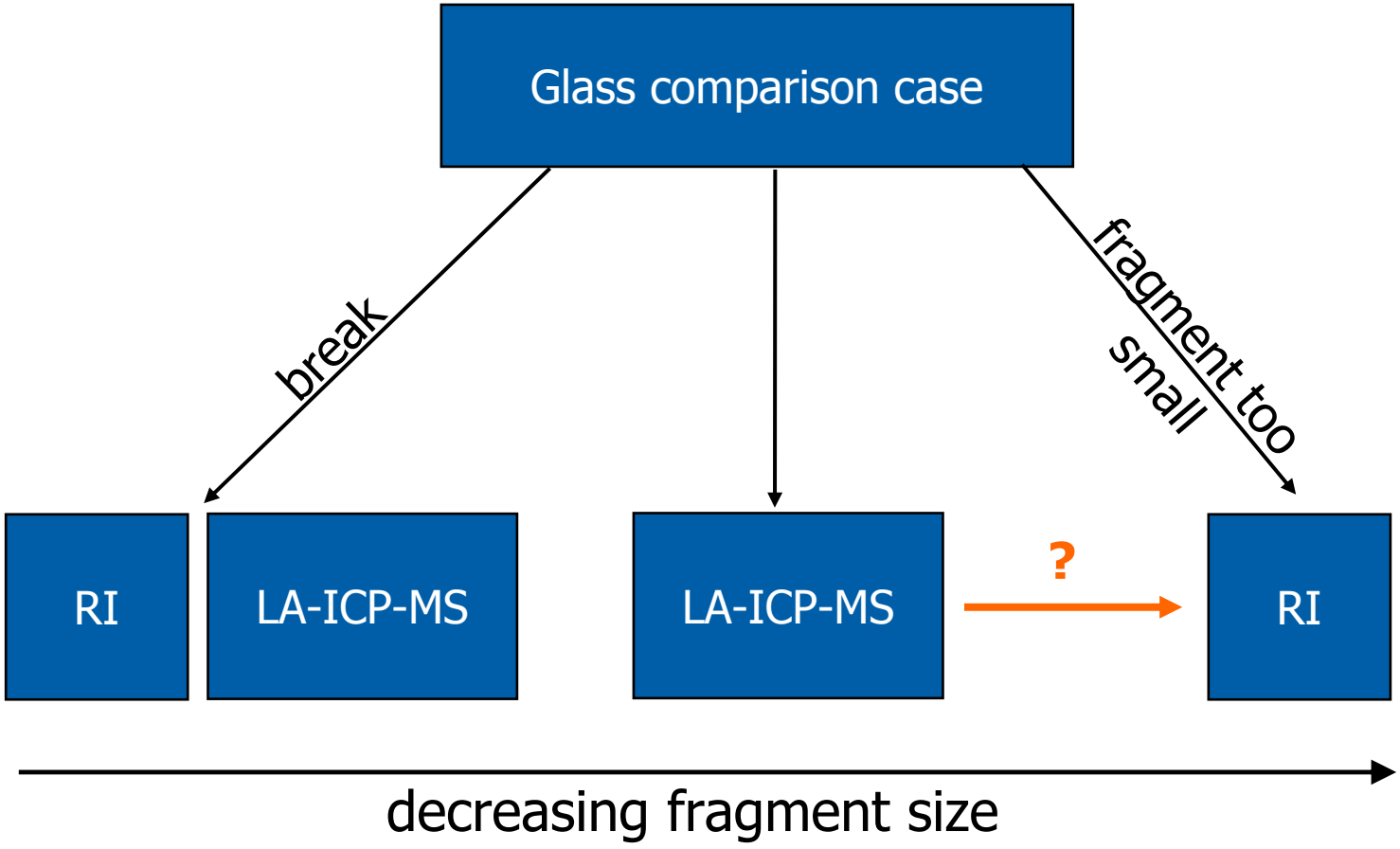
Step-by-step approach to forensic glass analysis

1970 - 2005



LA vs. RI

2005 - present



LA vs. RI

Does the laser ablation process alter the results of refractive index measurements of glass fragments?

What are the influencing factors?

mass, size, color, geometry of a glass fragment

sample preparation, laser wavelength

LA vs. RI

Third attempt to tackle this issue:

1. Oral presentation at the ENFSI Annual Meeting of the European Glass Group 2001, Oslo
2. Poster presentation at the European Winter Conference on Plasma Spectrochemistry, 30 Jan-03 February 2005, Budapest, Hungary

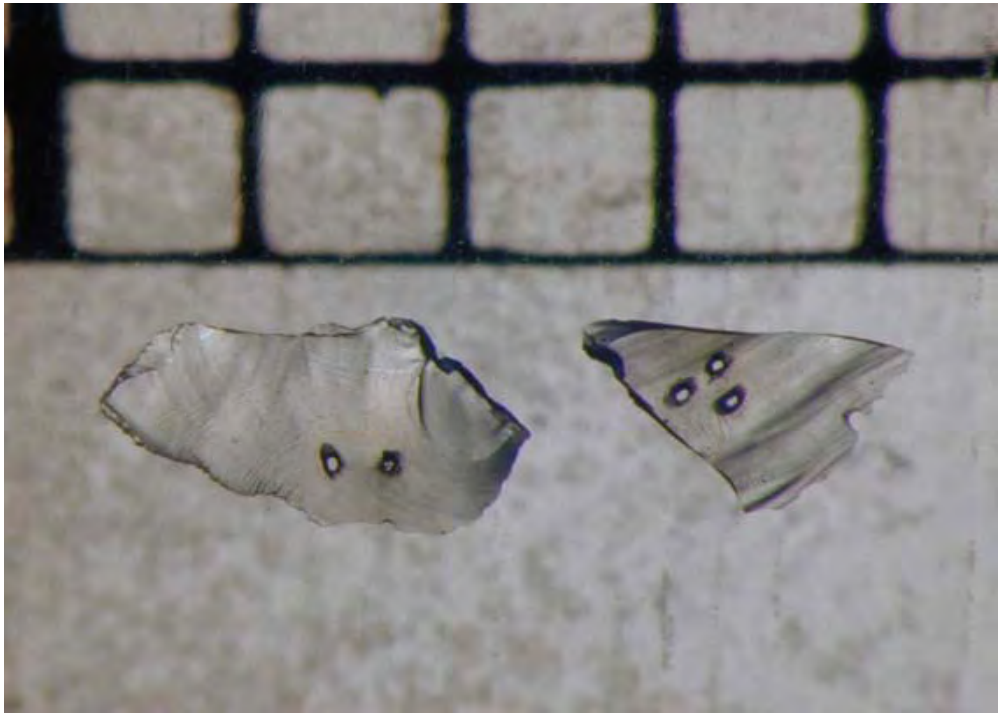
LA vs. RI

Work	Objects	# of fragments	Laser wavelength [nm]
2000/2001	K5 glass	2	266
2005	1 float glass	7	213
2010/2011	3 float glasses	71	193 213

LA vs. RI 2001

BKA-K5 standard glass for RI

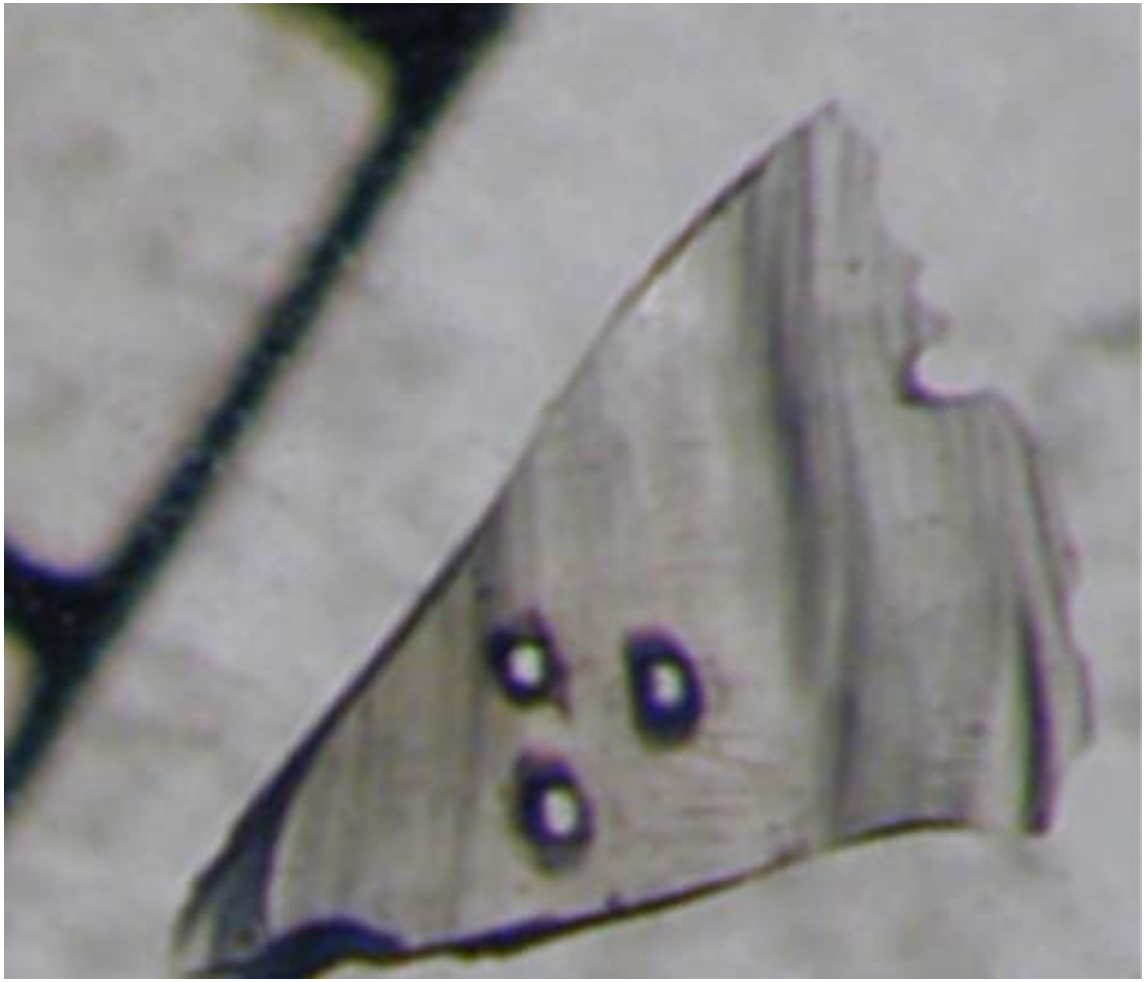
Crown glass produced by Schott AG with high optical homogeneity



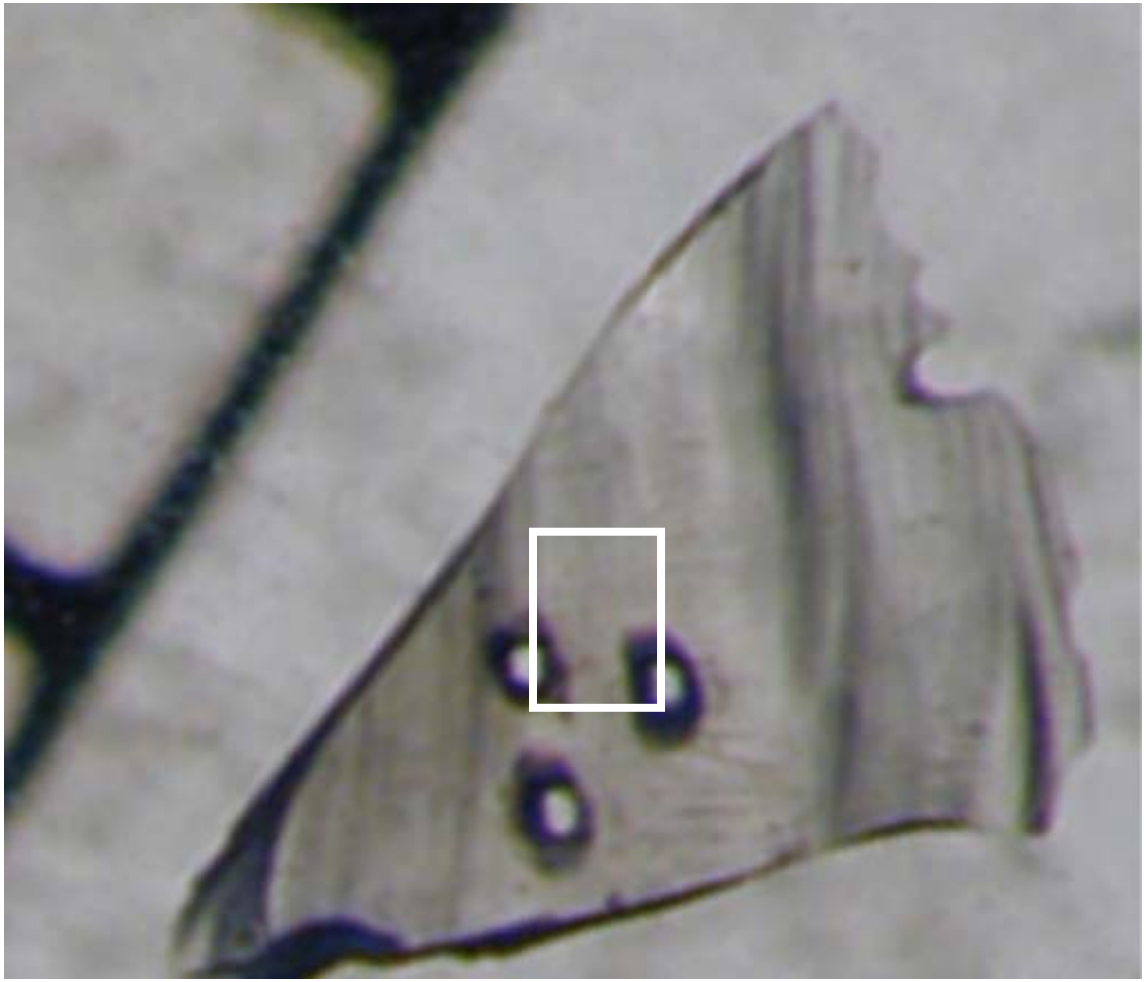
Laser Ablation:

- 10 Hz, 266 nm
- Duration: 140 s
- Energy: 0.7 mJ
- Crater-ø: 80 µm

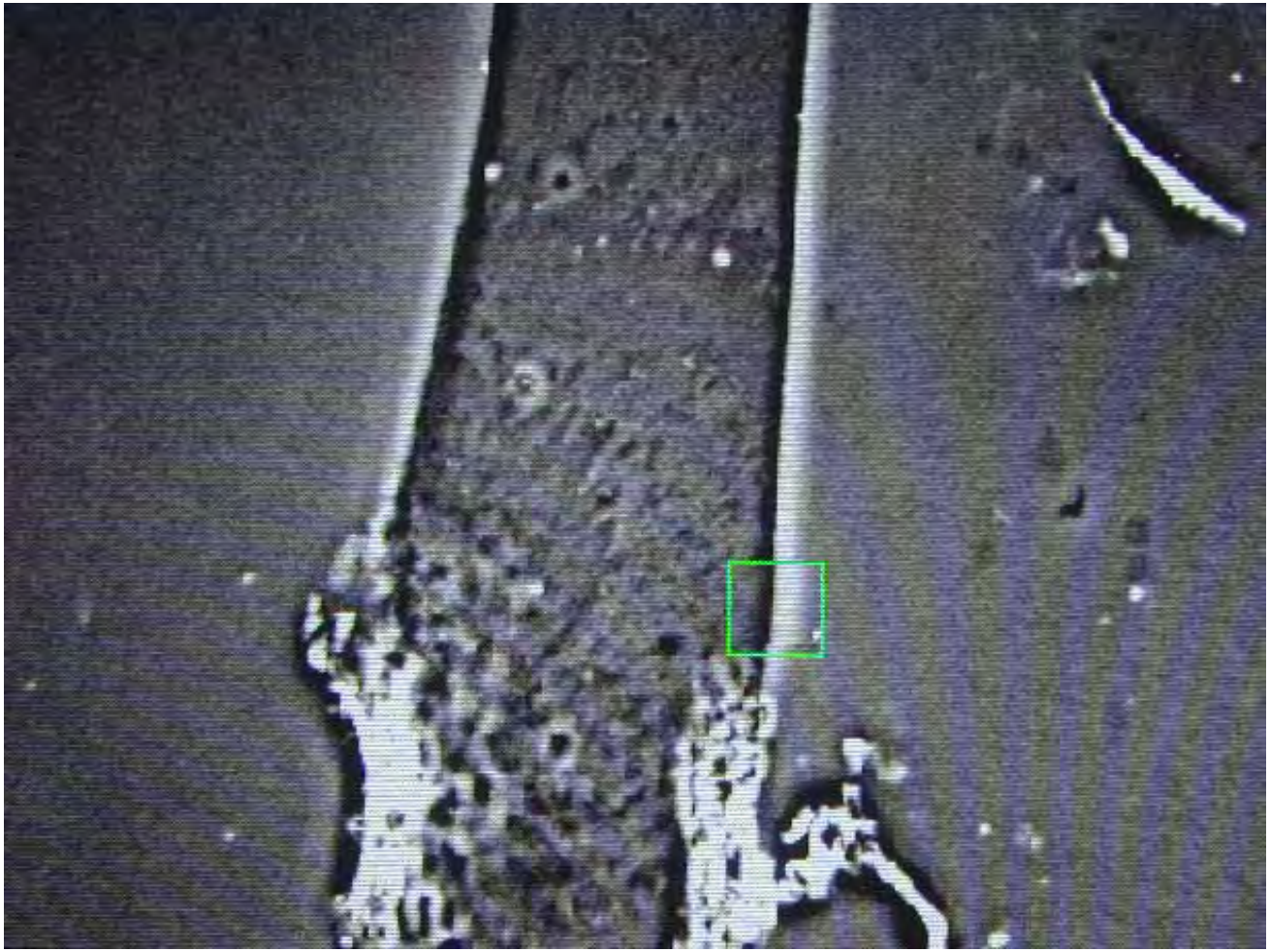
LA vs. RI 2001



LA vs. RI 2001



LA vs. RI 2001

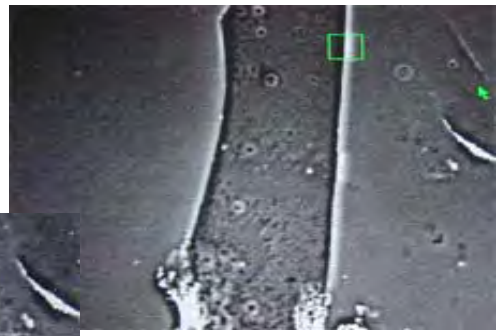


LA vs. RI 2001

Spatial change of RI

Smaller fragment:

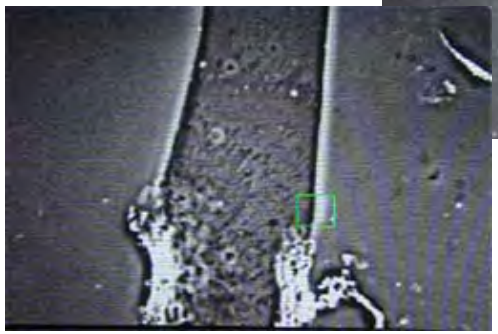
1.52239



1.52226

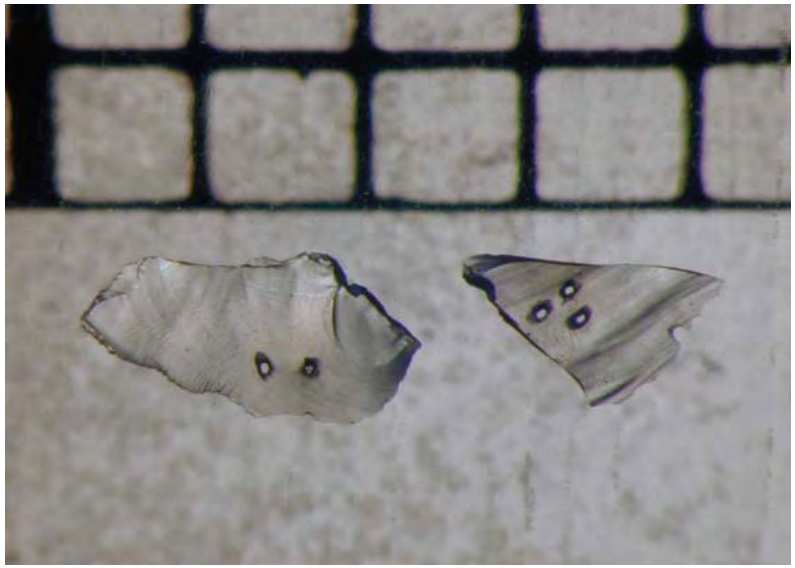
1.52225

1.52219



	mean	SD
n_D	1.52240	2.2E-05

LA vs. RI
Results presented in 2001



mm scale

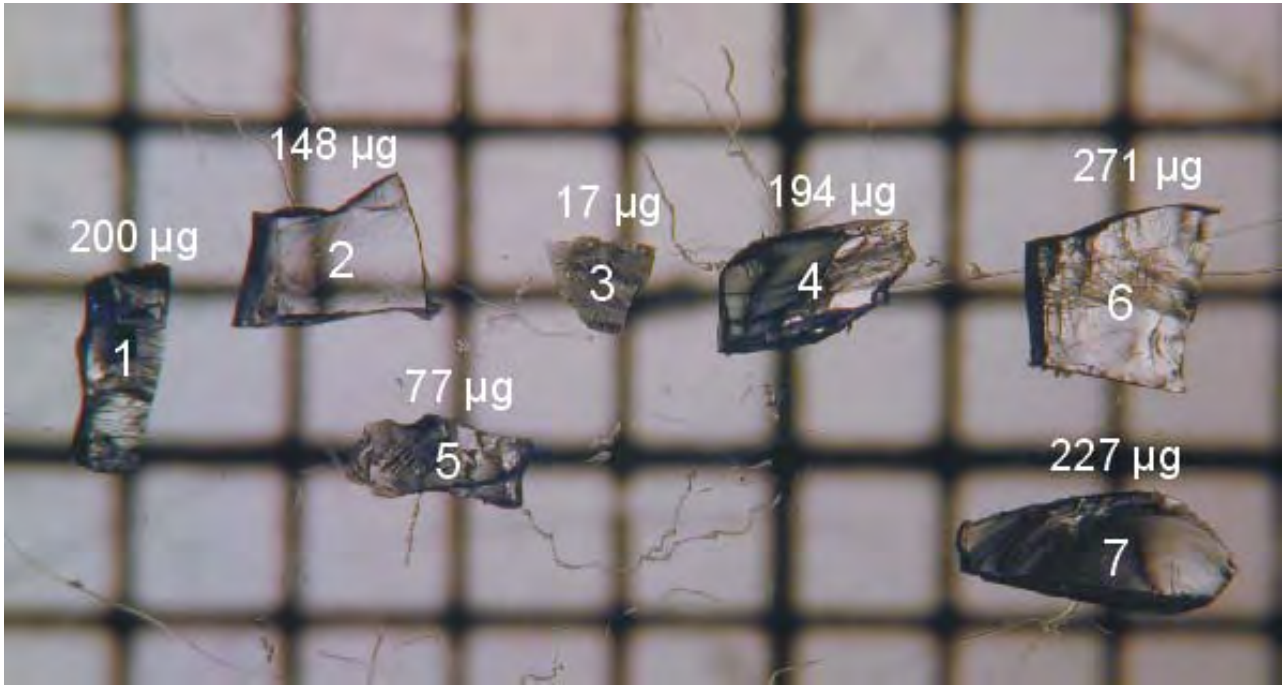
Smaller fragment/ 3 crater:

- Reduction of RI up to $2*10^{-4}$
- Spatial gradient

Bigger fragment/ 2 crater:

- No significant change of RI

LA vs. RI 2005



Fragments of float glass sample 13_2
covering a mass range from 17 µg - 271 µg

LA vs. RI 2005

Findings

1.) Morphological changes are created at the crater region by laser ablation (RI determination is not possible)

2.) Higher variation of RI values due to laser-glass interaction

3.) Effect of RI variation decreases with higher fragment size/mass

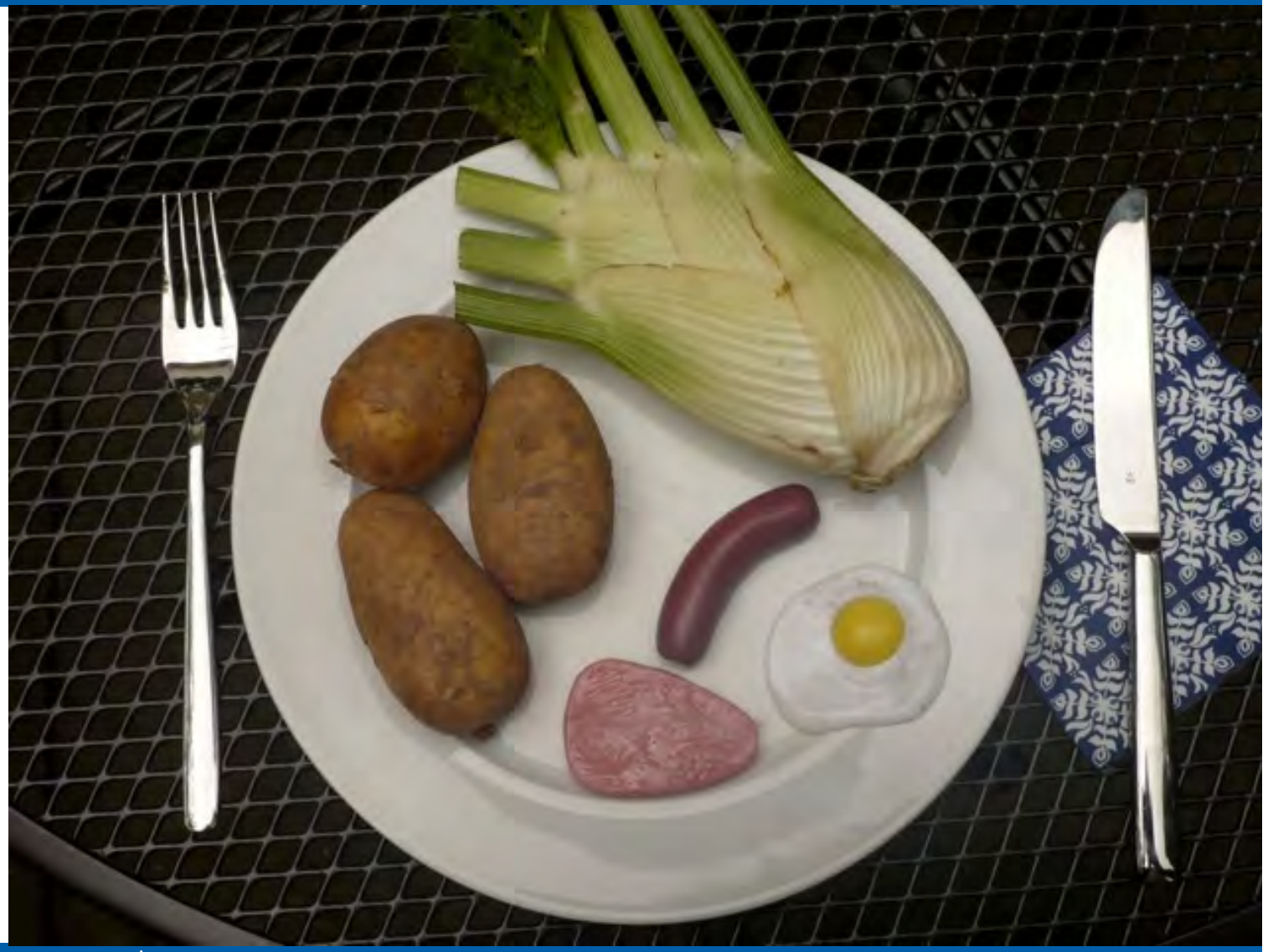
LA vs. RI 2005 Conclusion

Alteration of the RI value of small fragments may occur in the course of the laser ablation process.

More investigations on the variation of the RI of fragments of different size, mass or shape and for different laser systems (266 nm, 193 nm) are needed in order to give a universally valid statement.

LA vs. RI 2010/11

Main course



LA vs. RI 2010/11 Selection of samples

	Name	Color	heated/ tempered	Producer / plant	thickness/ mm
5_2	Parasol grün N	green	No	Vegla, Herzogenrath, Germany	4.1
13_2	Optifloat	clear	No	Flachglas, Weiherhammer 1, Germany	3.8
26_23	Dom. Heated	green	Yes	Libbey Owens Ford L.O.F., Lathrop, CA, U.S.A.	3.6

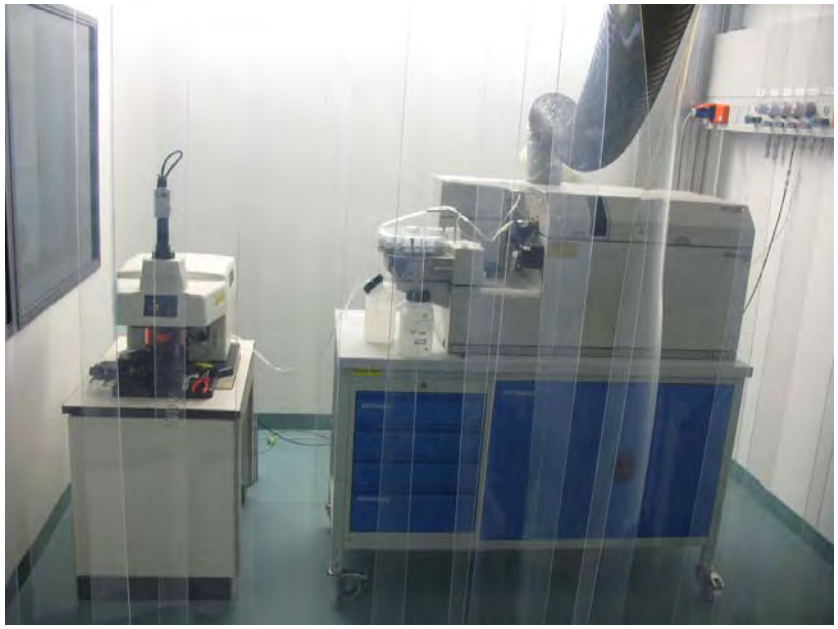
LA vs. RI 2010/11 Instrumentation

Foster & Freemann GRIM III system coupled to an existing phase contrast microscope Diaplan (Leitz, Germany) with Phaco L110/0.25 lens and Mettler Toledo FP 82 HT hotstage.

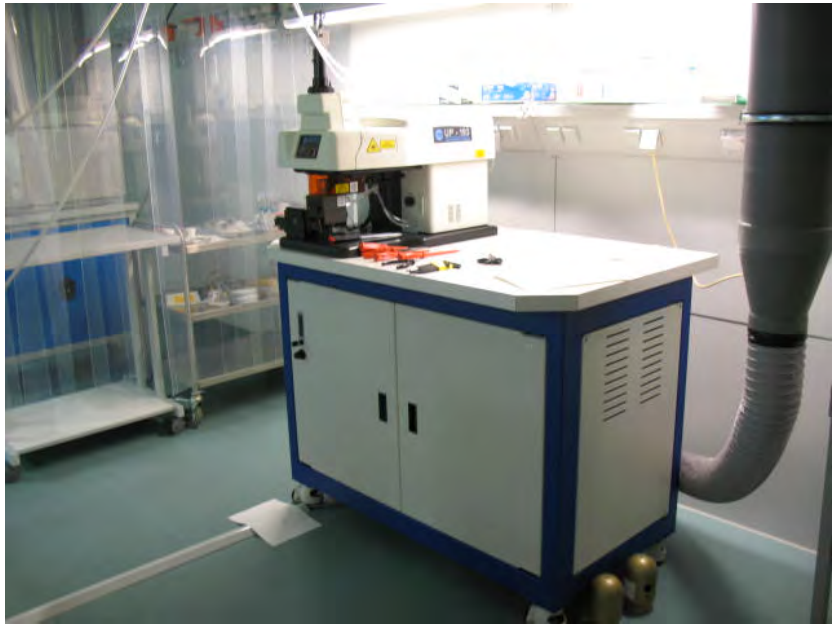
Ultra-microbalance scale:
Mettler Toledo UMX5 Comparator

LA vs. RI 2010/11 Instrumentation

Laser ablation



New Wave Research UP 213
Solid-state laser (Nd:YAG) 213 nm



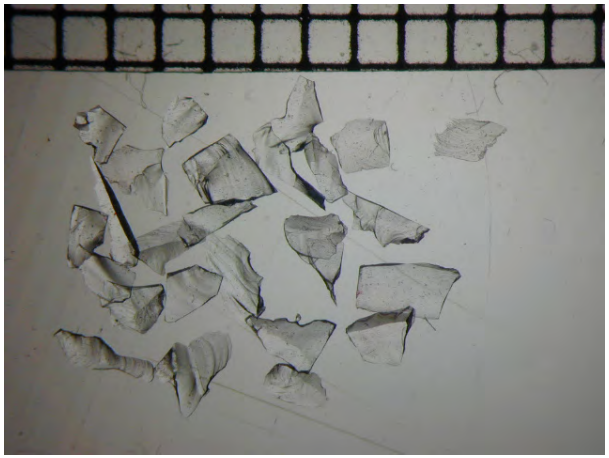
UP 193
gas laser (excimer ArF) 193 nm

LA vs. RI 2010/11 Workflow

1. Selection of three float glasses (colors, thermal history); isolation of glass fragments of different sizes
2. Documentation of physical properties (size, mass), photography
3. Laser ablation ICP-MS analysis of glass samples according to ISO 17025 accredited method for the quantitative analysis of glass fragments
4. Photographic documentation of ablated fragments
5. Sample preparation: Cleaning (EtOH/HNO_3) and breaking of fragments
6. Determination of RI using Foster & Freeman GRIM III

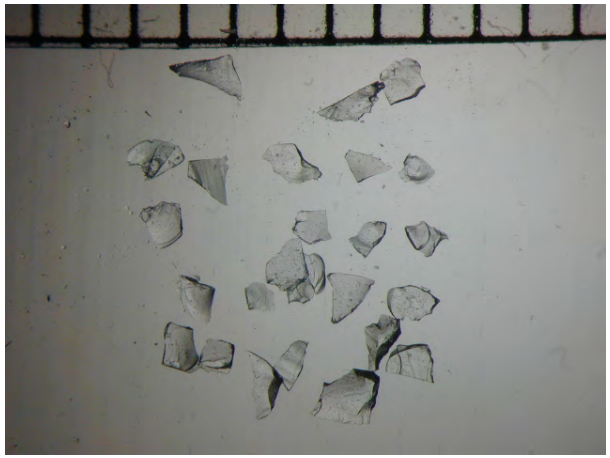
LA vs. RI 2010/11 Selection of fragments

Glass 5_2



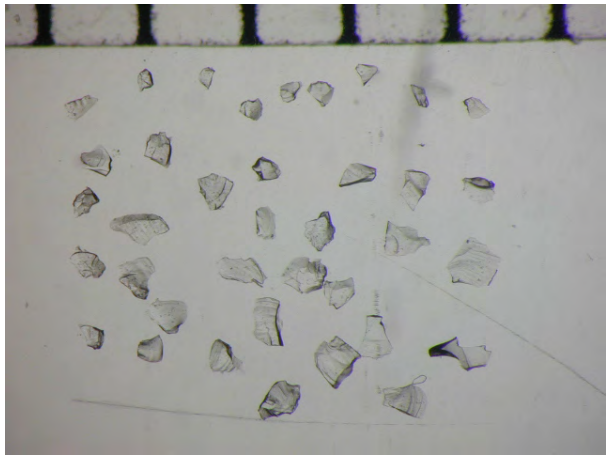
Group A:

Size length 1 mm - 2 mm



Group B:

Size length 0.5 mm - 1 mm

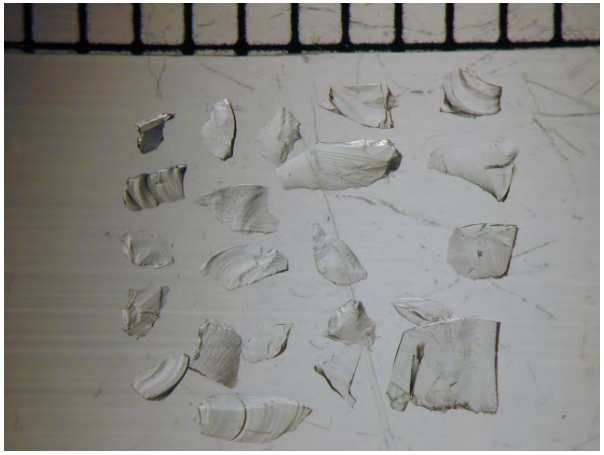


Group C:

Size length 0.2 mm - 0.5 mm

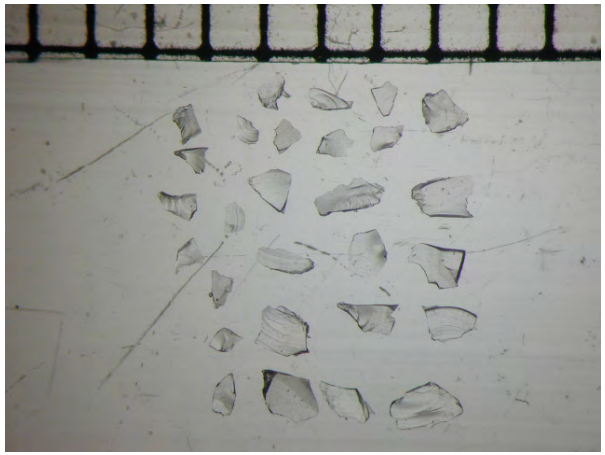
LA vs. RI 2010/11 Selection of fragments

Glass 13_2



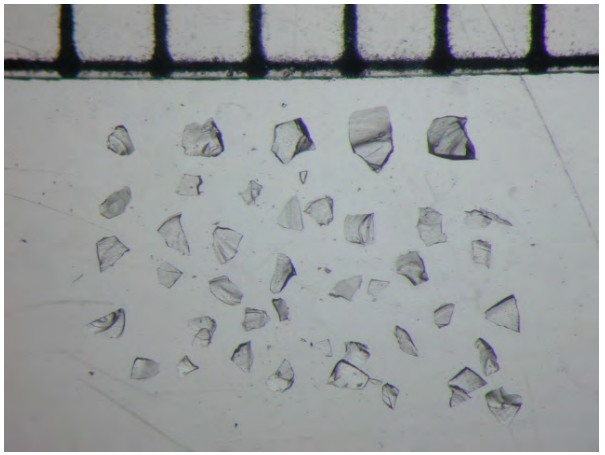
Group A:

Size length 1 mm - 2 mm



Group B:

Size length 0.5 mm -1 mm

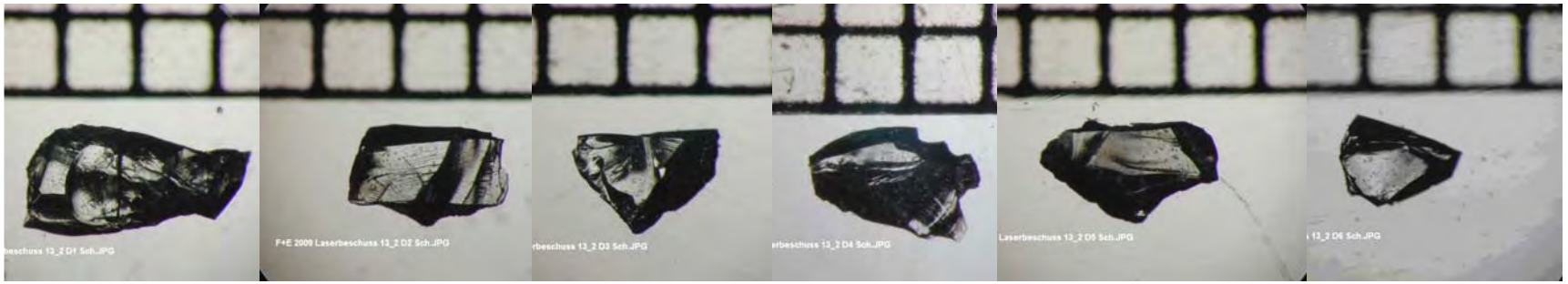


Group C:

Size length 0.2 mm -0.5 mm

LA vs. RI 2010/11 Selection of fragments

Inclusion of additional set of six ‘very big’ fragments: Glass 13_2



13_2D1
3mmx1.5mm
3.32 mg

13_2D2
2mmx1.2mm
1.86 mg

13_2D3
2mmx1.2mm
1.77 mg

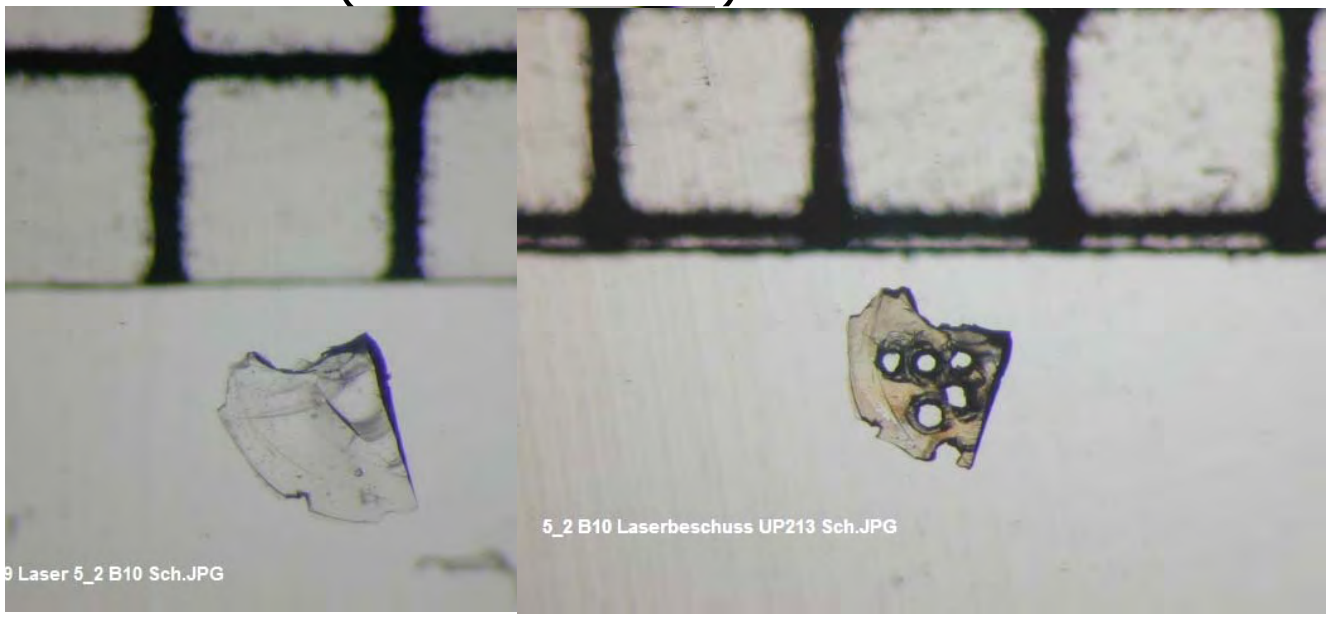
13_2D4
2.1mmx1.5mm
1.50 mg

13_2D5
2.1mmx1.6mm
2.74 mg

13_2D6
1.6mmx1.0mm
2.09 mg

LA vs. RI 2010/11 Photographical documentation

(millimeter scale)



untreated glass fragment

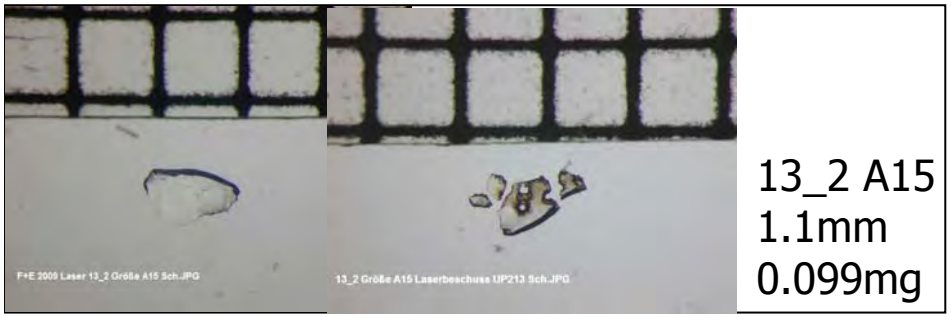
ablated glass fragment

name
5_2 B10
maximal length
0.8 mm
62 µg
mass
213
laser wavelength [nm]

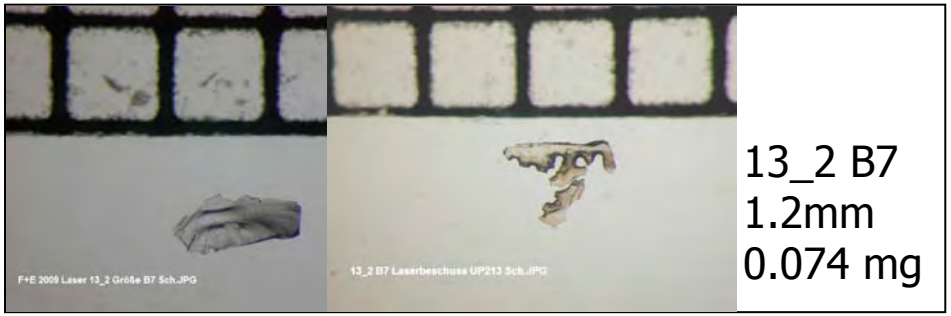
Bundeskriminalamt

LA vs. RI 2010/11

wavelength 213 nm



13_2 A15
1.1mm
0.099mg

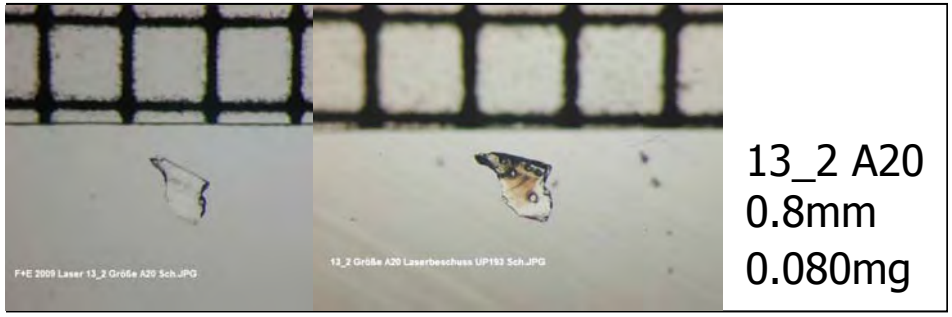


13_2 B7
1.2mm
0.074 mg

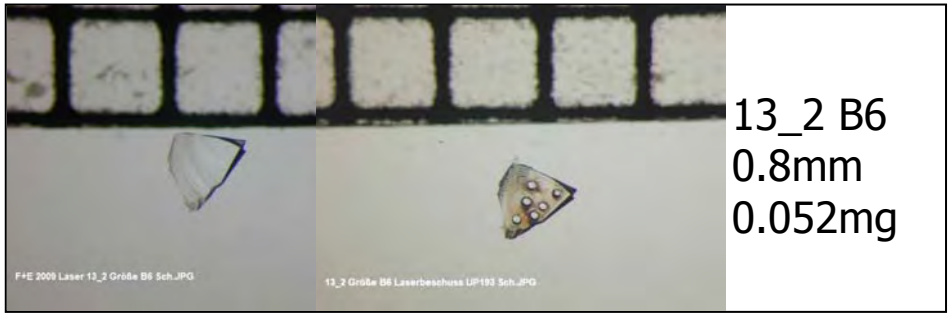
13_2 B9
1mm
0.063mg

wavelength 193 nm

13_2 A19
1.1mm
0.093mg



13_2 A20
0.8mm
0.080mg

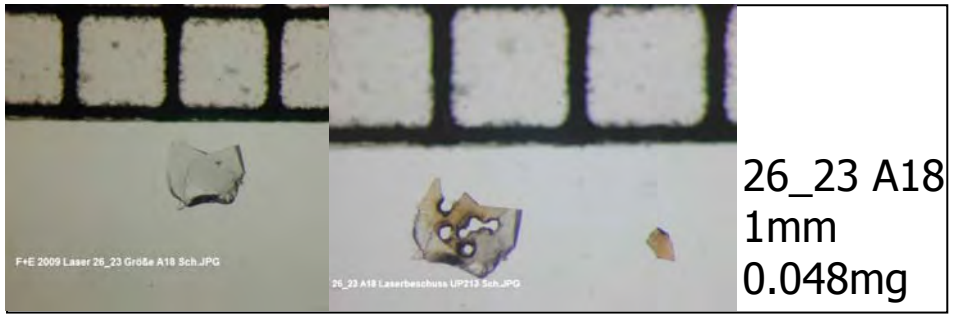


13_2 B6
0.8mm
0.052mg

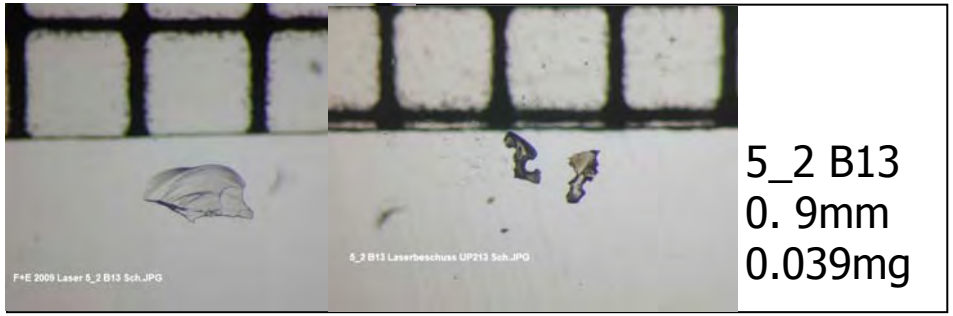
Bundeskriminalamt

LA vs. RI 2010/11

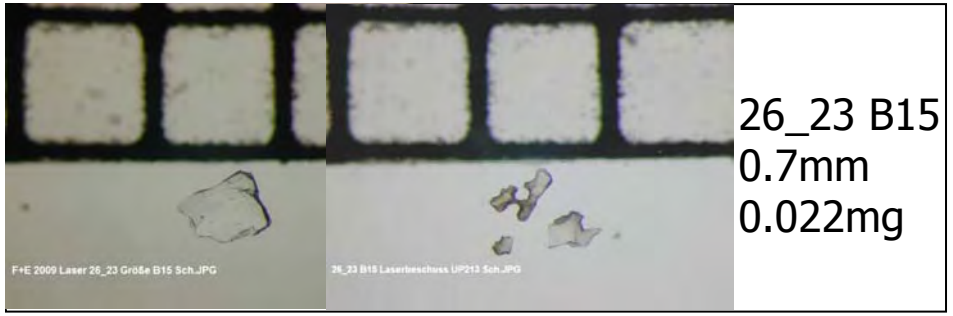
wavelength 213 nm



26_23 A18
1mm
0.048mg

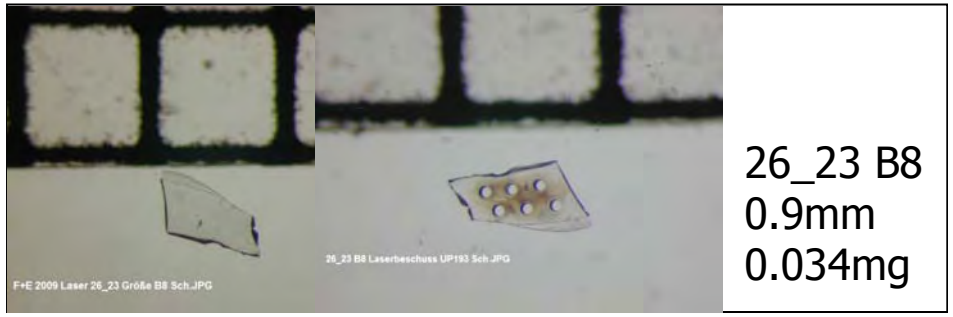


5_2 B13
0. 9mm
0.039mg

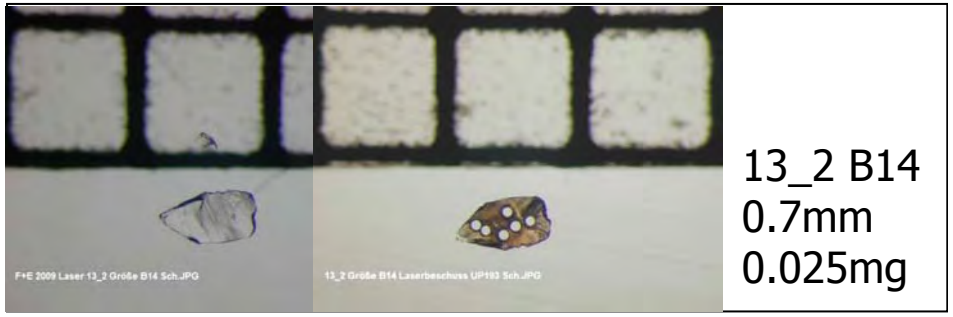


26_23 B15
0.7mm
0.022mg

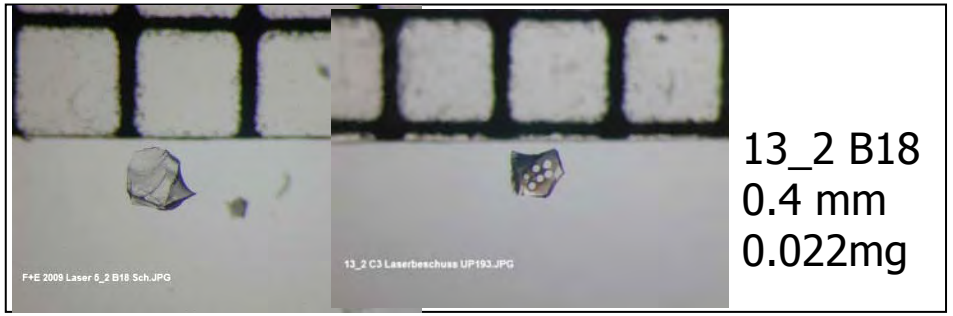
wavelength 193 nm



26_23 B8
0.9mm
0.034mg



13_2 B14
0.7mm
0.025mg

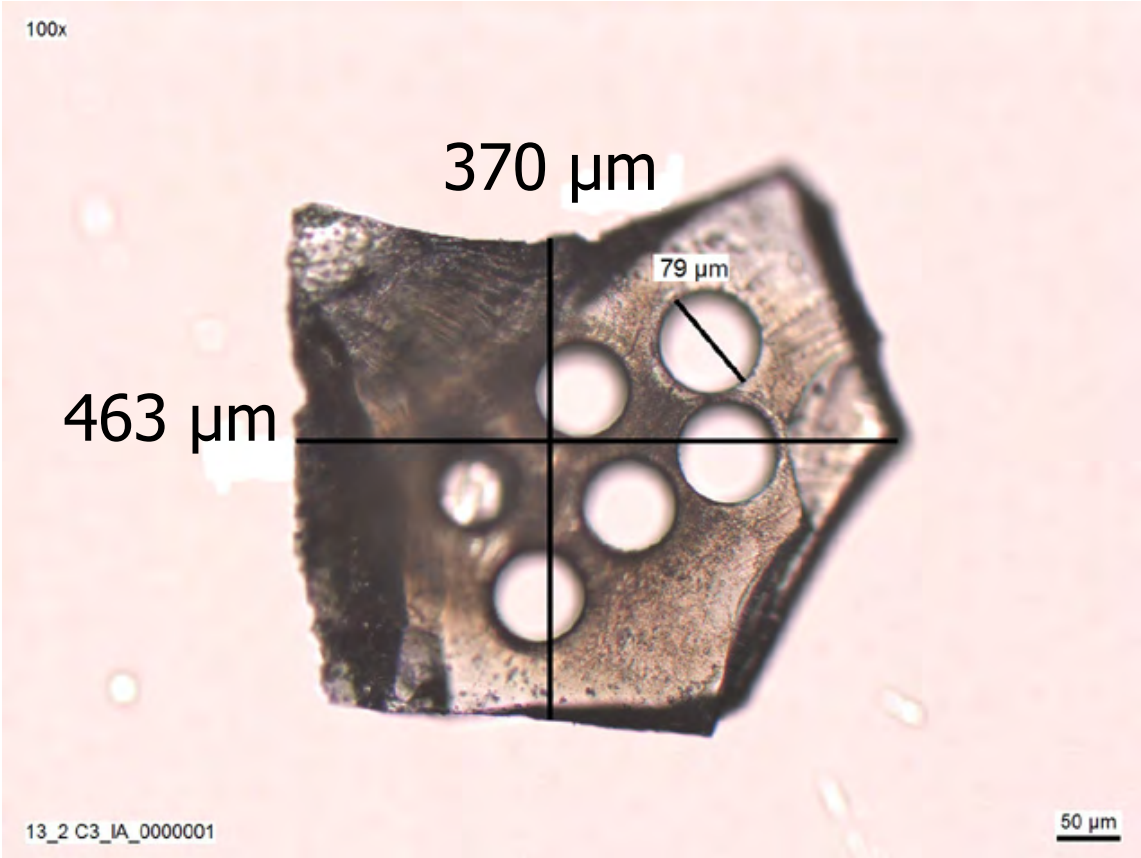


13_2 B18
0.4 mm
0.022mg

LA vs. RI
2010/11

Minimum size requirements for six replicate measurements with crater diameter of approx. 80 µm:

13_2 C3
22 µg
193 nm

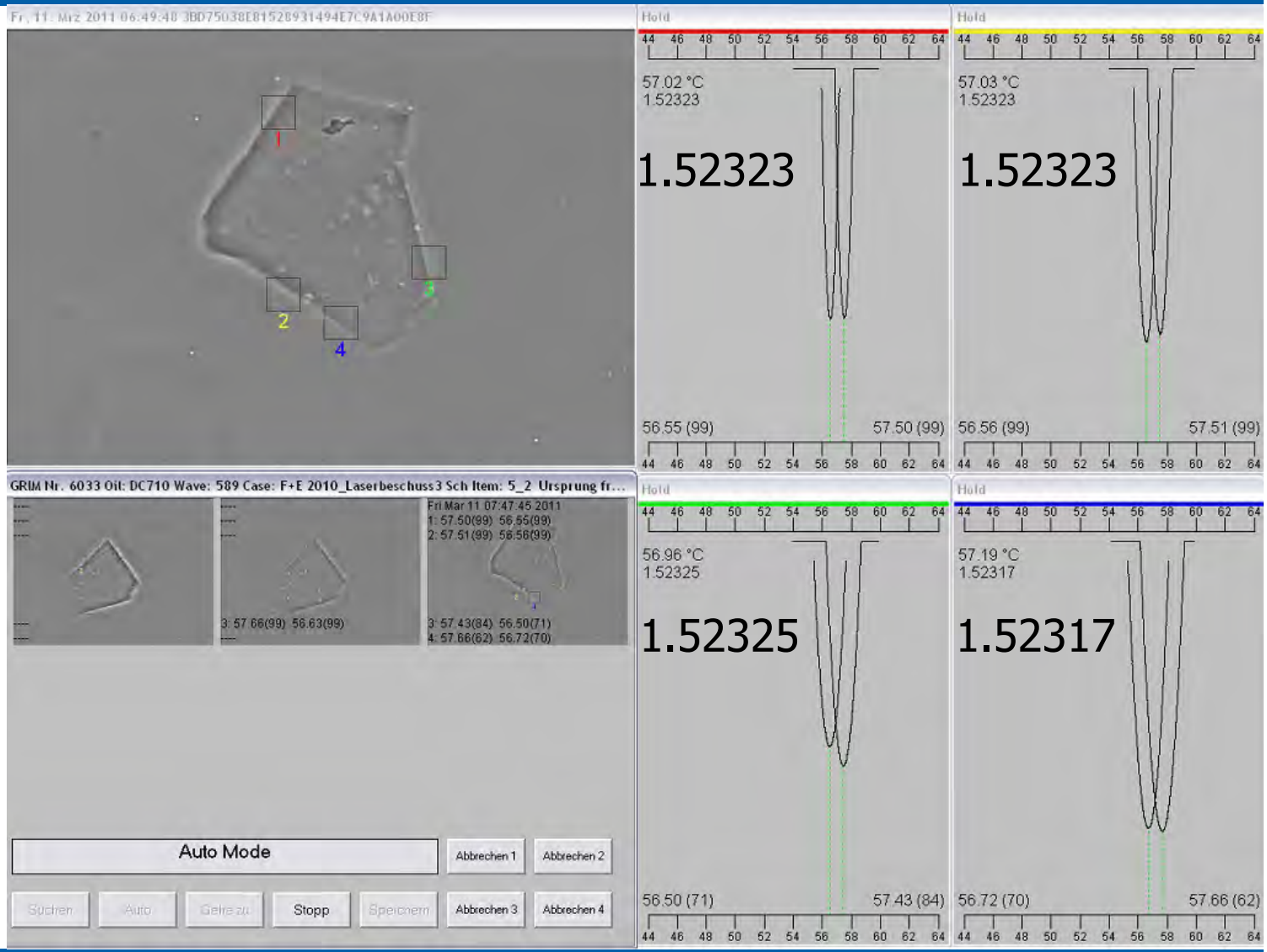


Bundeskriminalamt

LA vs. RI 2010/11

Glass 5_2
untreated

n_D=1.52323
SD = 3*10^{-5}



Bundeskriminalamt

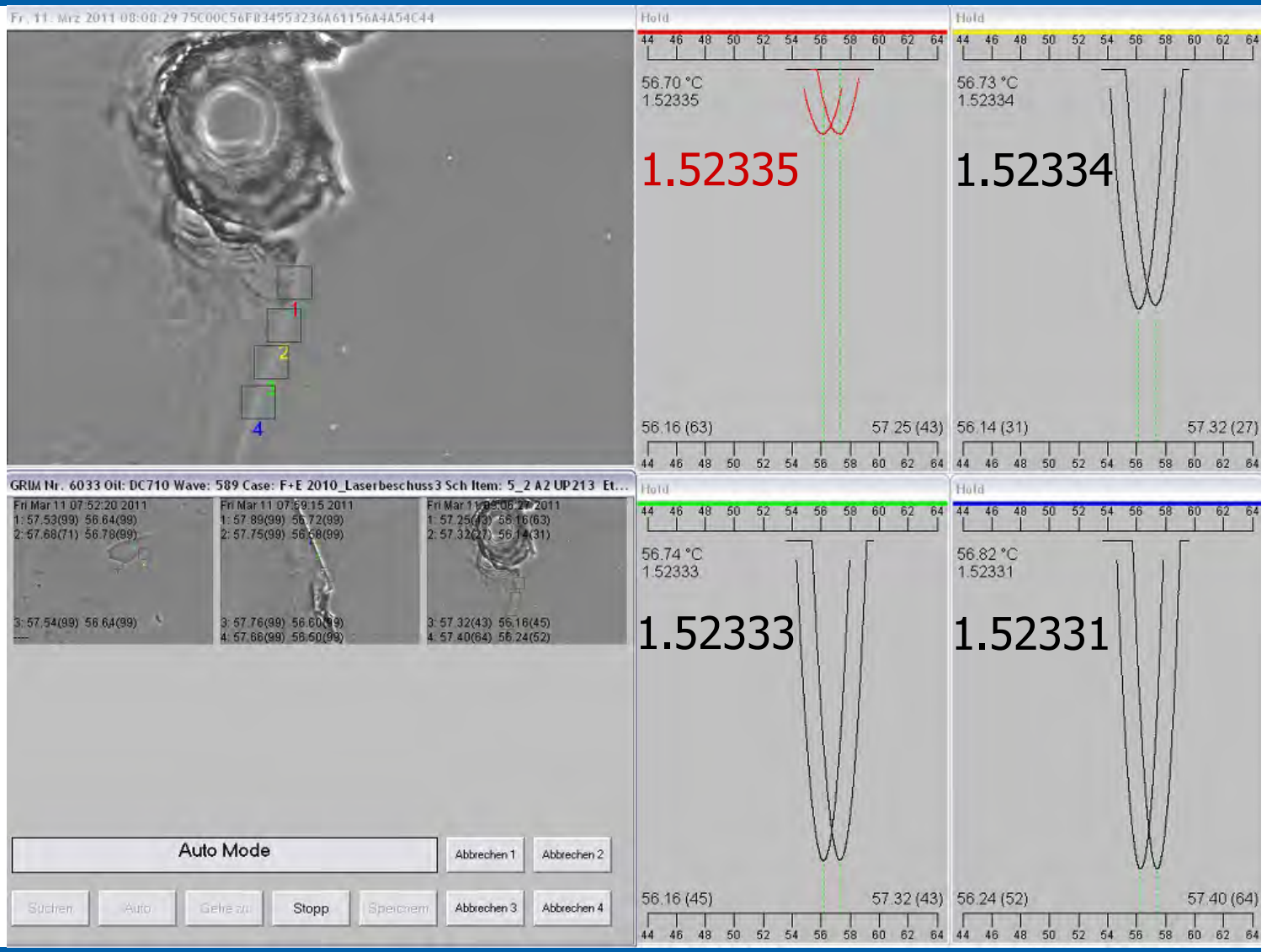
LA vs. RI 2010/11

5_2 A2
568 µg
213 nm

untreated

n_D=1.52323

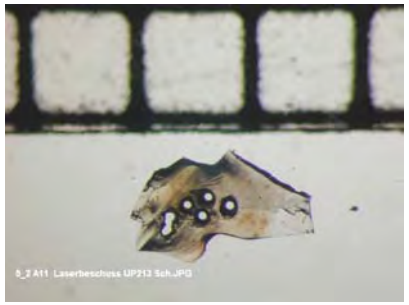
SD = $3*10^{-5}$



Bundeskriminalamt

LA vs. RI 2010/11

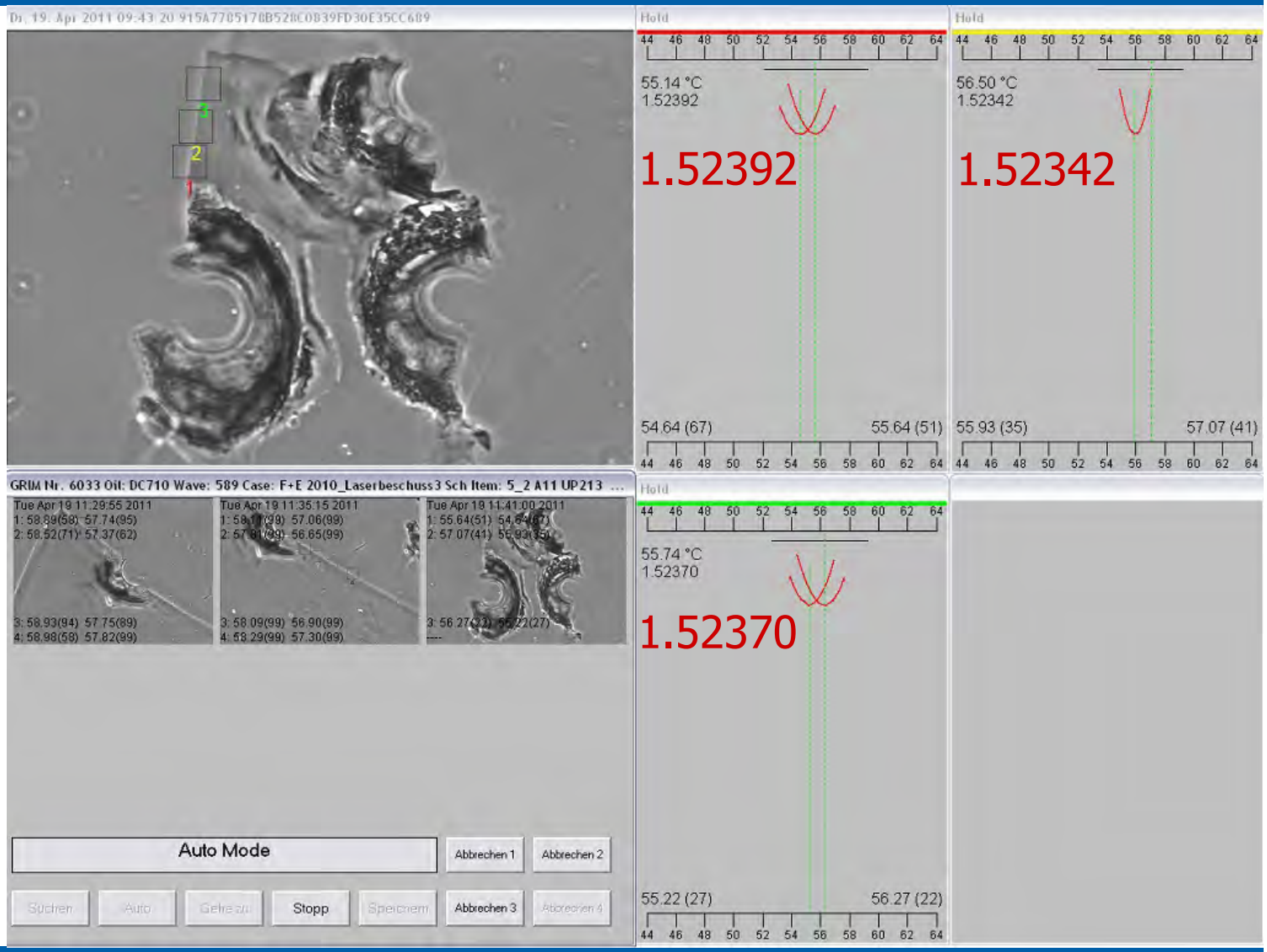
5_2 A11
178 µg
213 nm



untreated

n_D=1.52323

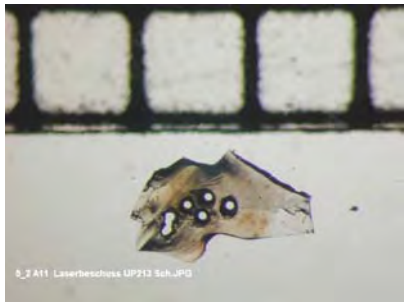
SD = 3*10^{-5}



Bundeskriminalamt

LA vs. RI 2010/11

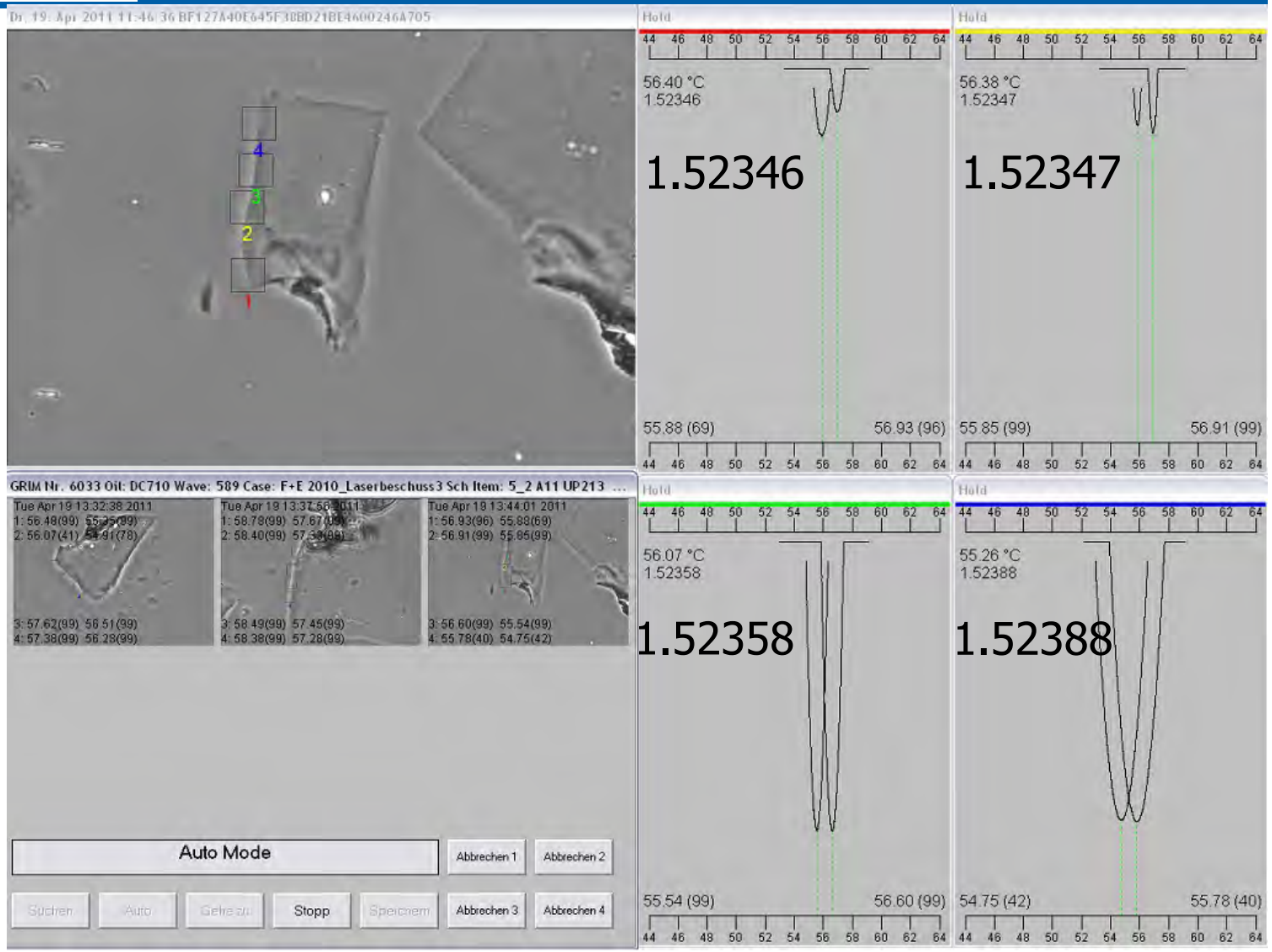
5_2 A11
178 µg
213 nm



untreated

n_D=1.52323

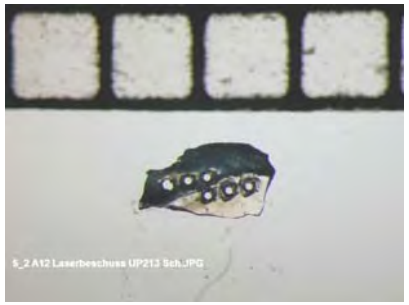
SD = 3*10^{-5}



Bundeskriminalamt

LA vs. RI 2010/11

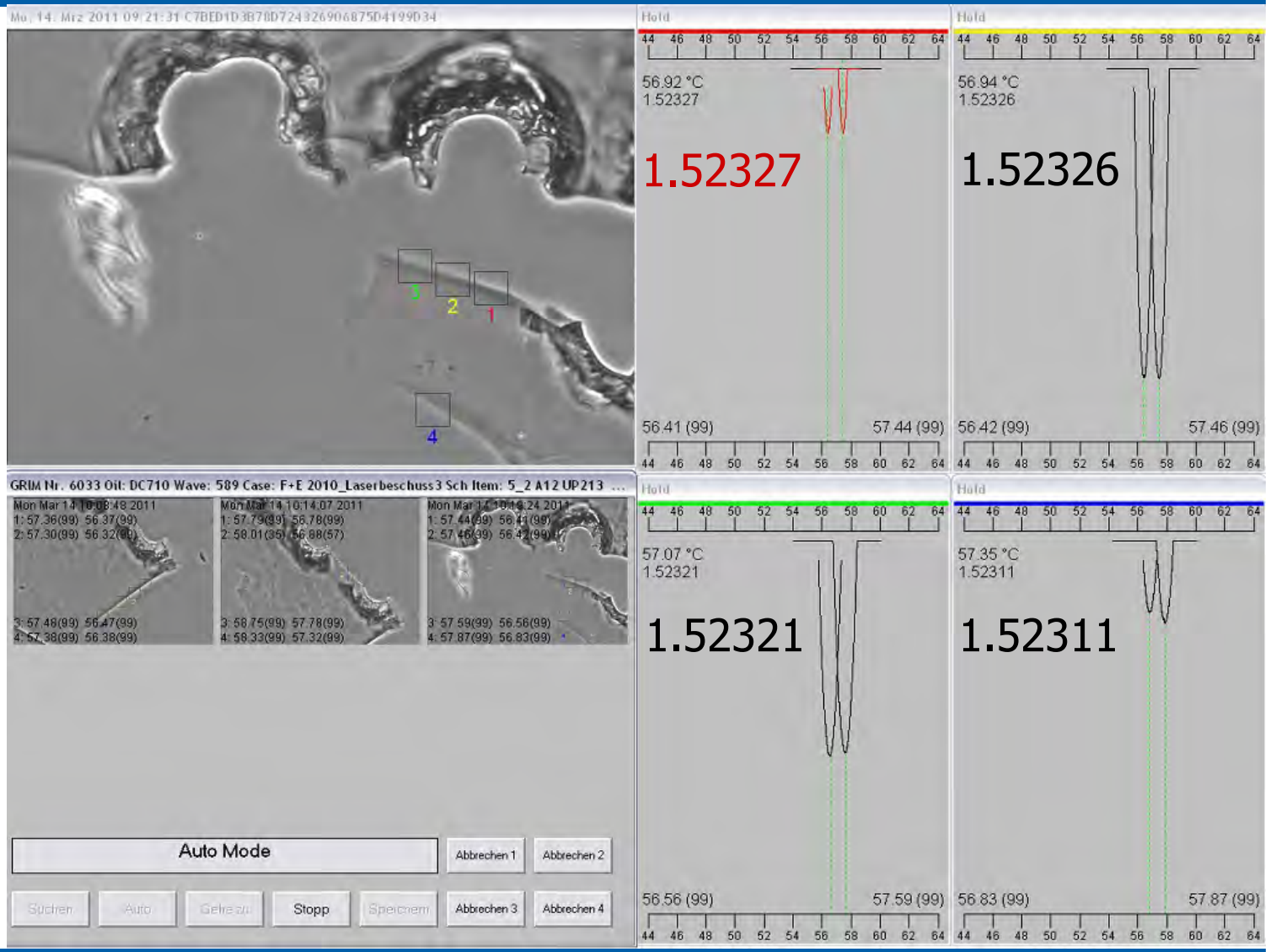
5_2 A12
148 µg
213 nm



untreated

n_D=1.52323

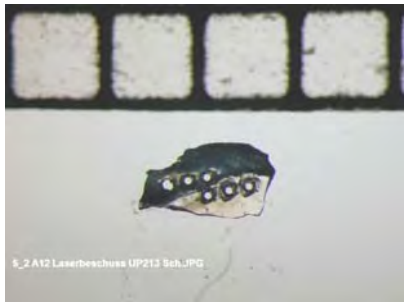
SD = $3*10^{-5}$



Bundeskriminalamt

LA vs. RI 2010/11

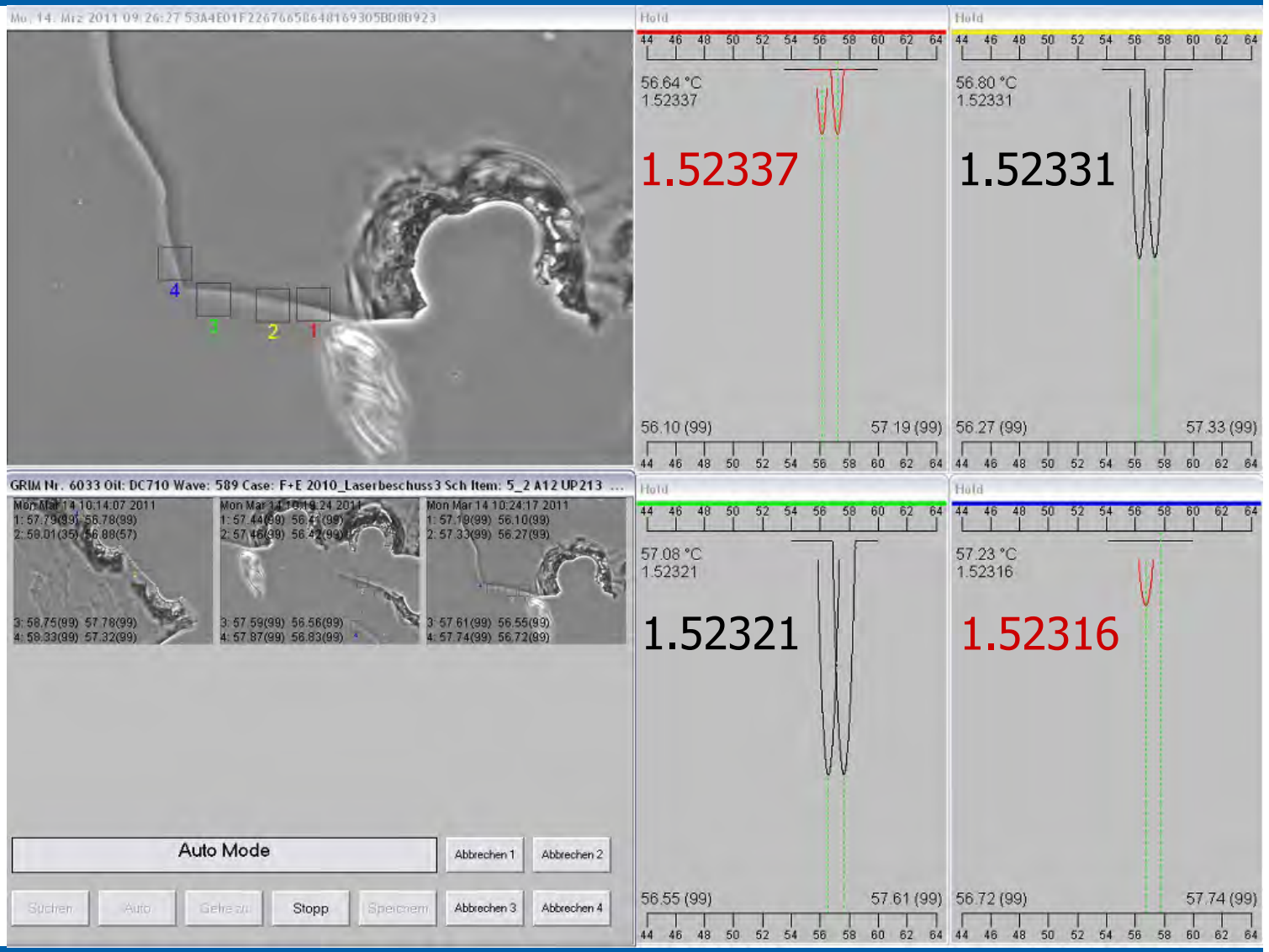
5_2 A12
148 µg
213 nm



untreated

n_D=1.52323

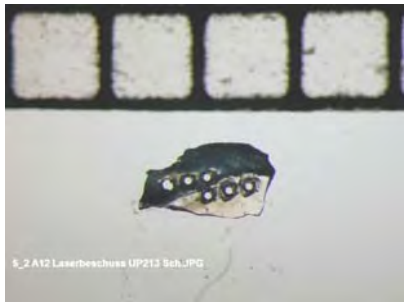
SD = $3*10^{-5}$



Bundeskriminalamt

LA vs. RI 2010/11

5_2 A12
148 µg
213 nm



untreated

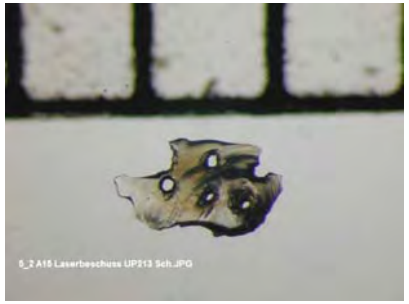
n_D=1.52323

SD = $3*10^{-5}$

Bundeskriminalamt

LA vs. RI 2010/11

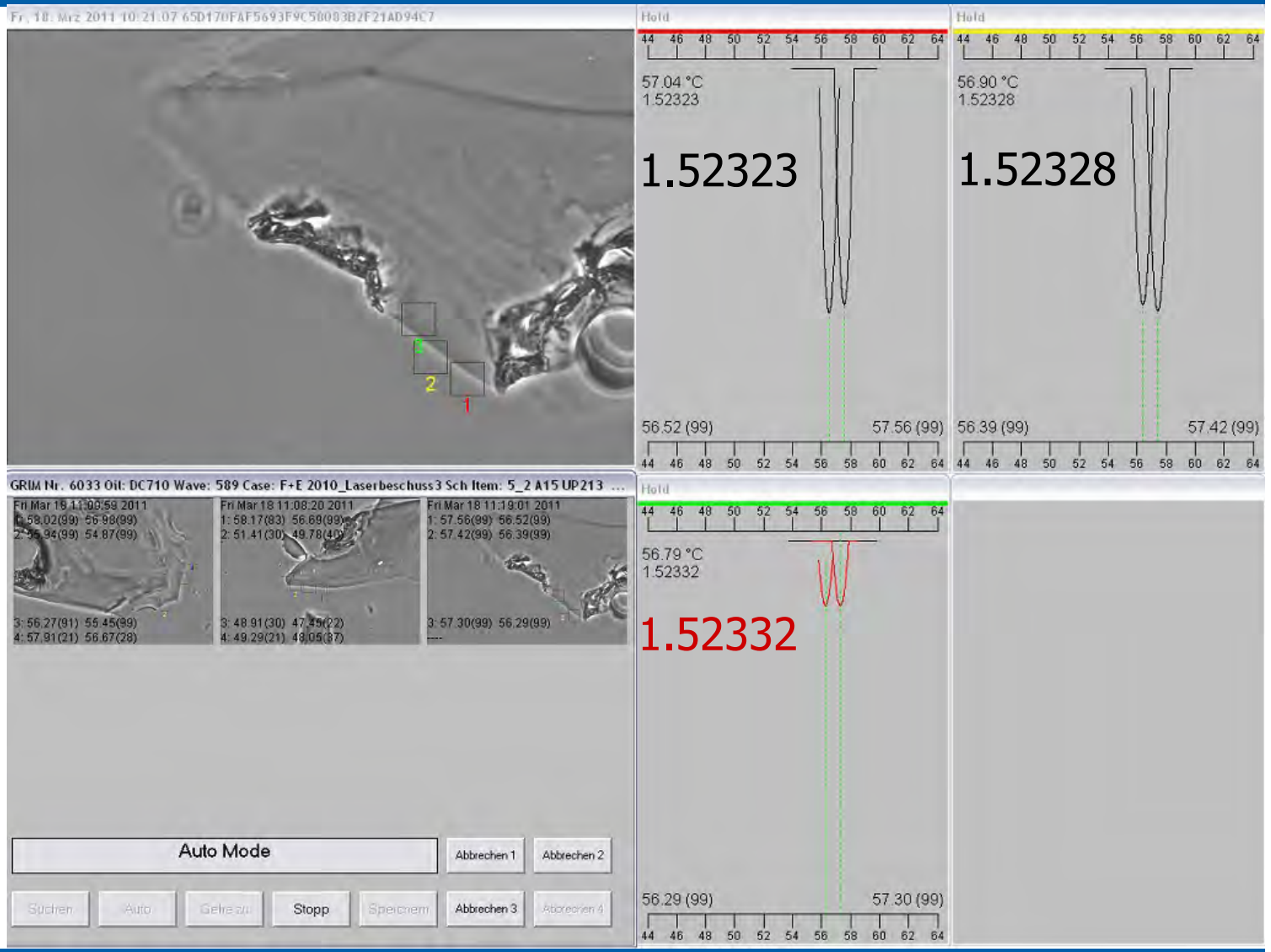
5_2 A15
150 µg
213 nm



untreated

n_D=1.52323

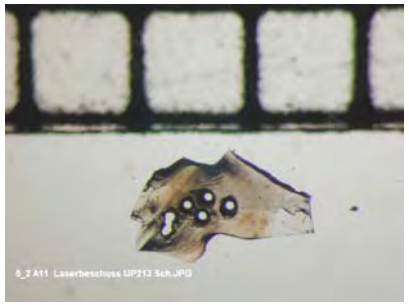
SD = $3*10^{-5}$



Bundeskriminalamt

LA vs. RI 2010/11

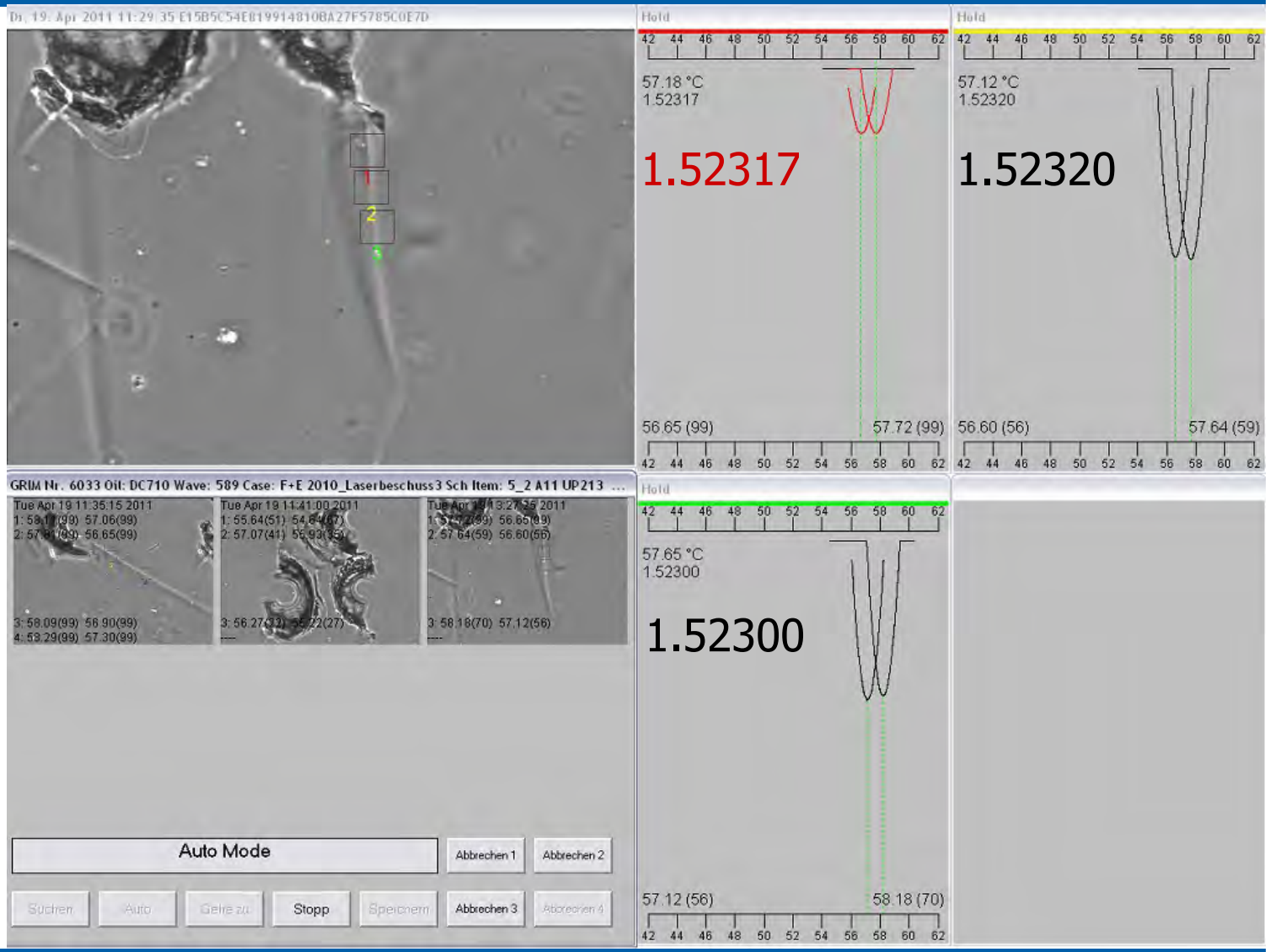
5_2 A11
178 µg
213 nm



untreated

n_D=1.52323

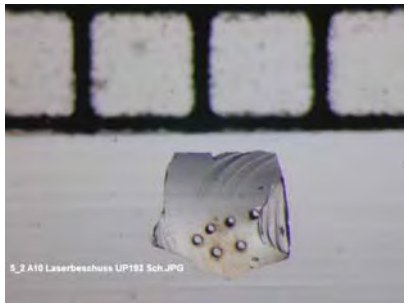
SD = $3*10^{-5}$



Bundeskriminalamt

LA vs. RI 2010/11

5_2 A10
151 µg
193 nm



untreated

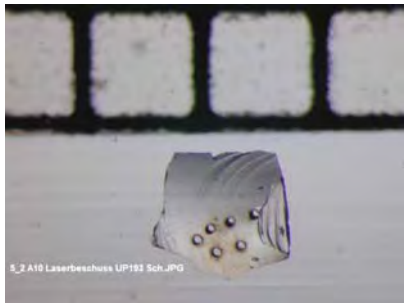
n_D=1.52323

SD = $3*10^{-5}$

Bundeskriminalamt

LA vs. RI 2010/11

5_2 A10
151 µg
193 nm



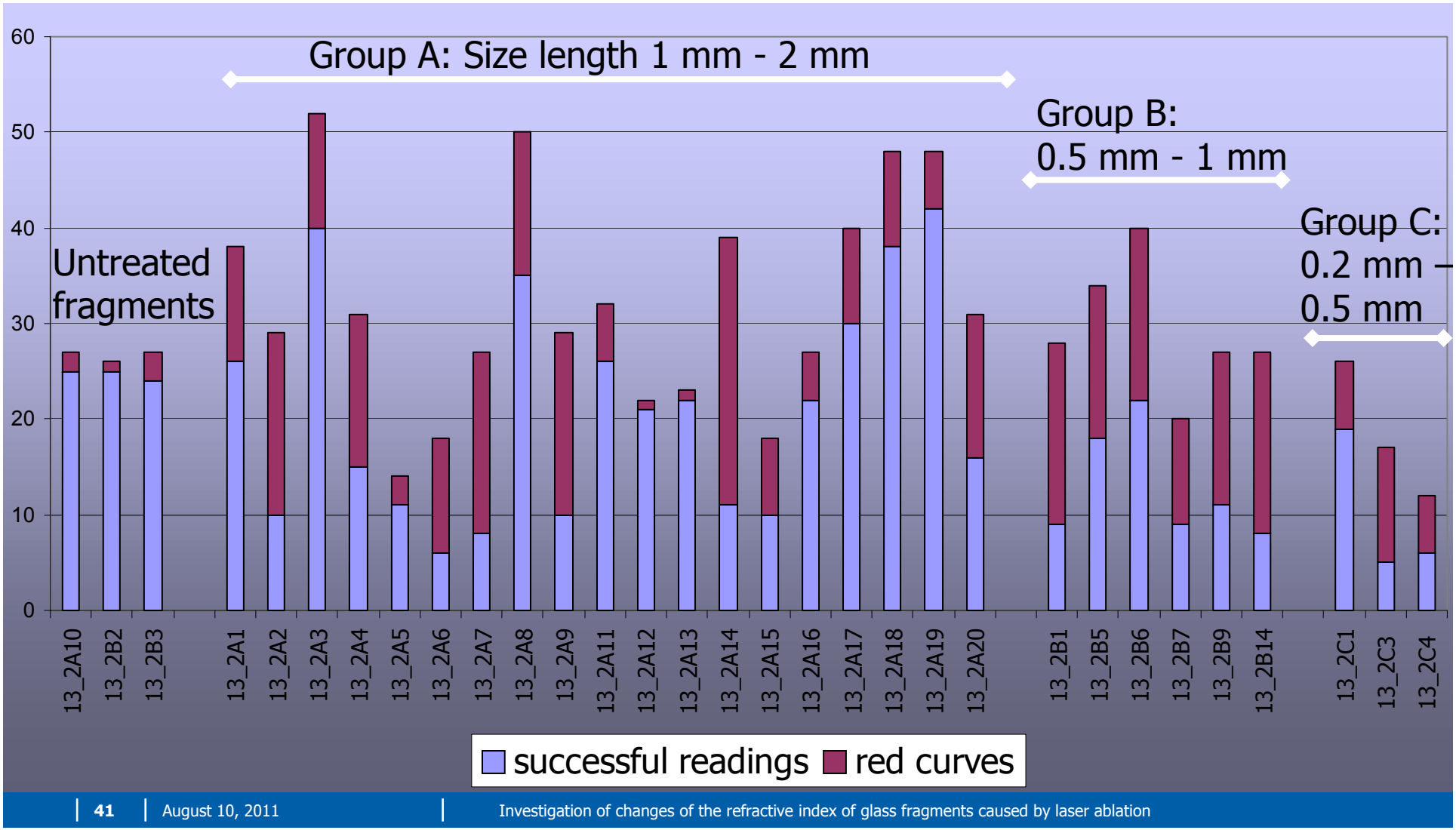
untreated

n_D=1.52323

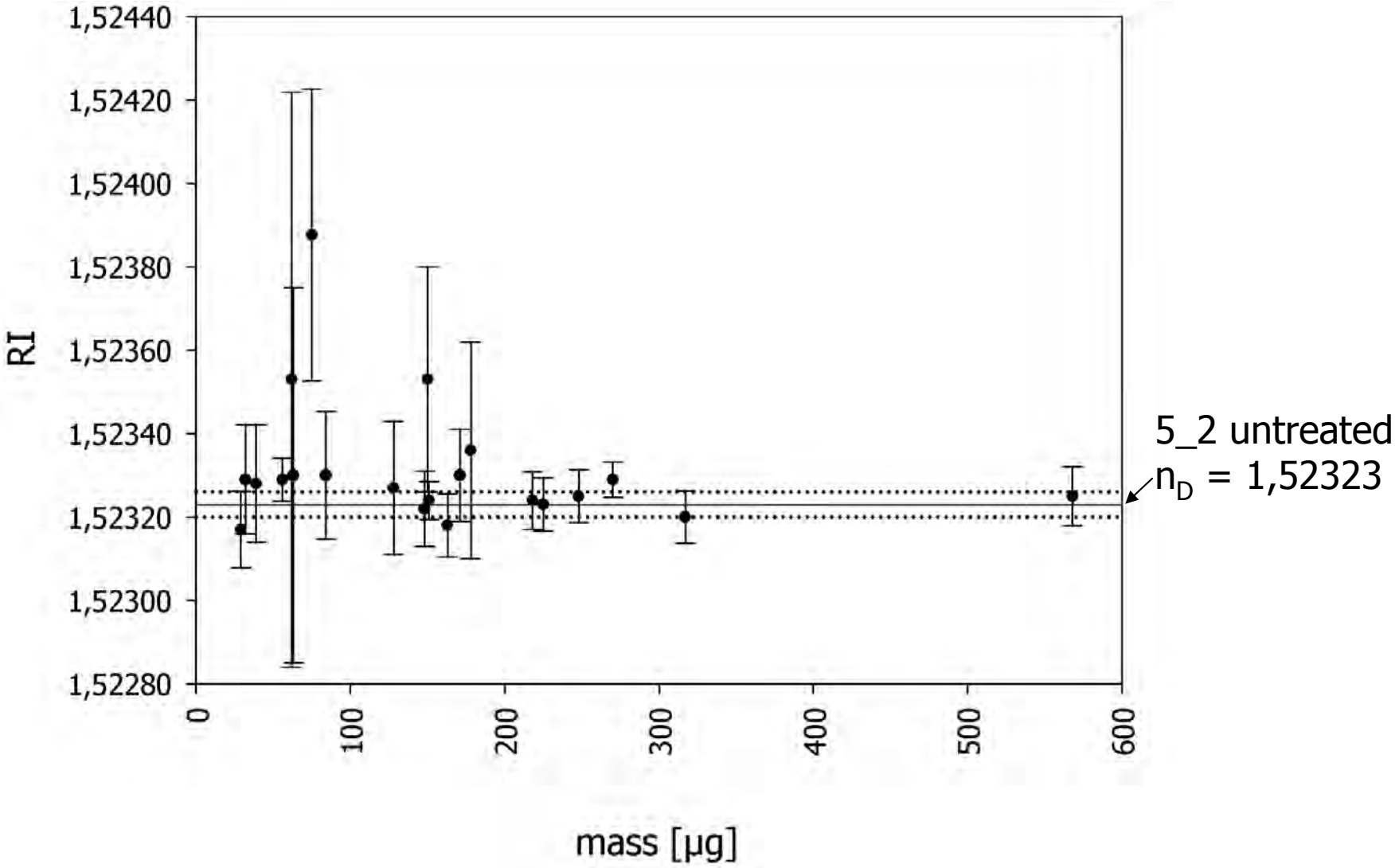
SD = 3*10^{-5}

Bundeskriminalamt

LA vs. RI
2010/11
successful measurements vs. red curve



LA vs. RI
2010/11 Results for 5_2



LA vs. RI
2010/11 Results for 5_2

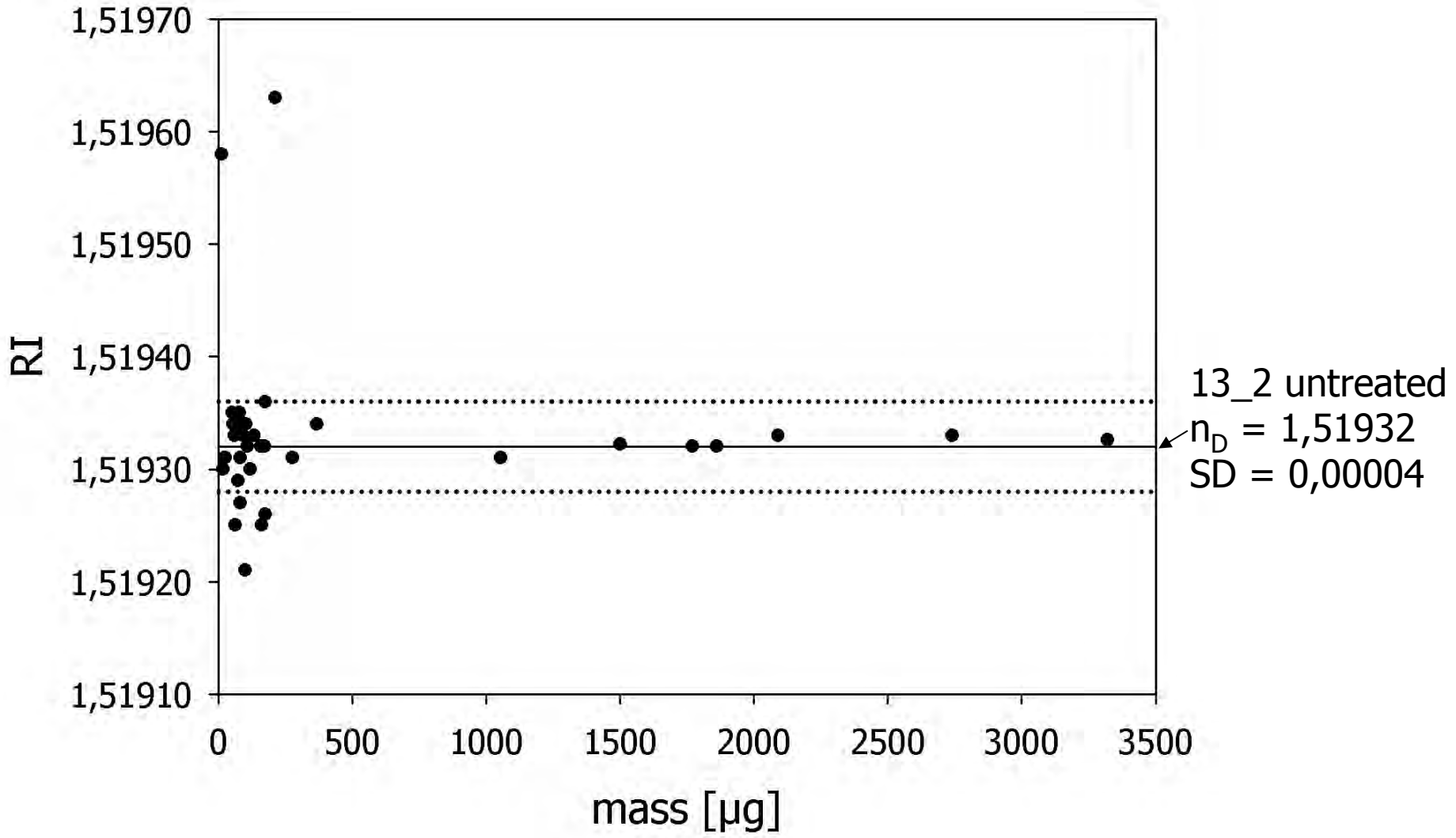
Float glass 5_2 untreated

n_D = 1,52323 SD = $3*10^{-5}$

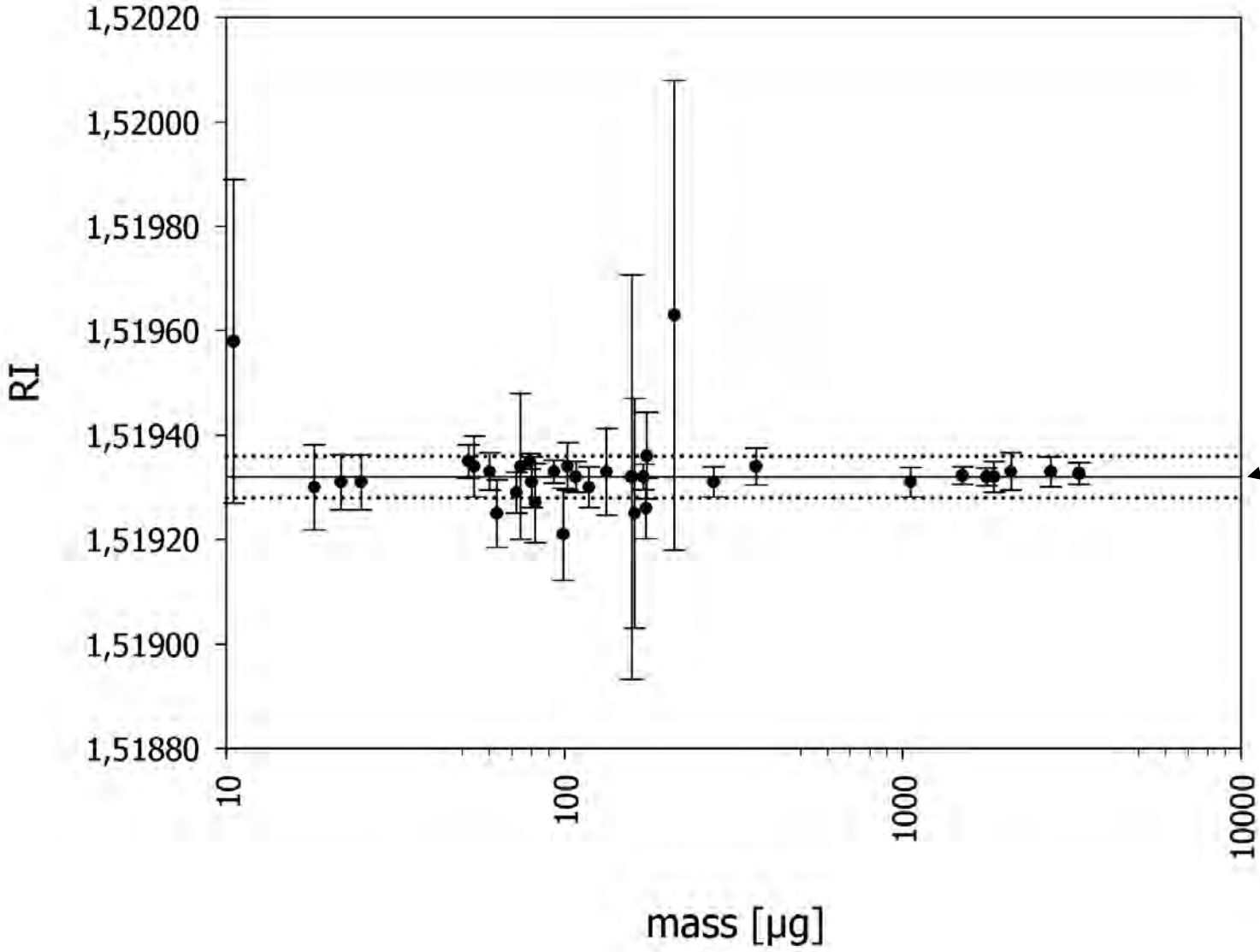
RI of 16 fragments after LA 213 nm:
mean n_D = 1,52330 SD = 1.0 E-4

RI of 5 fragments after LA 193 nm:
mean n_D = 1,52336 SD = 2.9 E-4
After exclusion of outlier
mean n_D = 1,52325 SD = 1.0 E-4

LA vs. RI
2010/11 Results for 13_2



LA vs. RI
2010/11 Results for 13_2



13_2 untreated
n_D = 1,51932
SD = 0,00004

LA vs. RI
2010/11 Results for 13_2

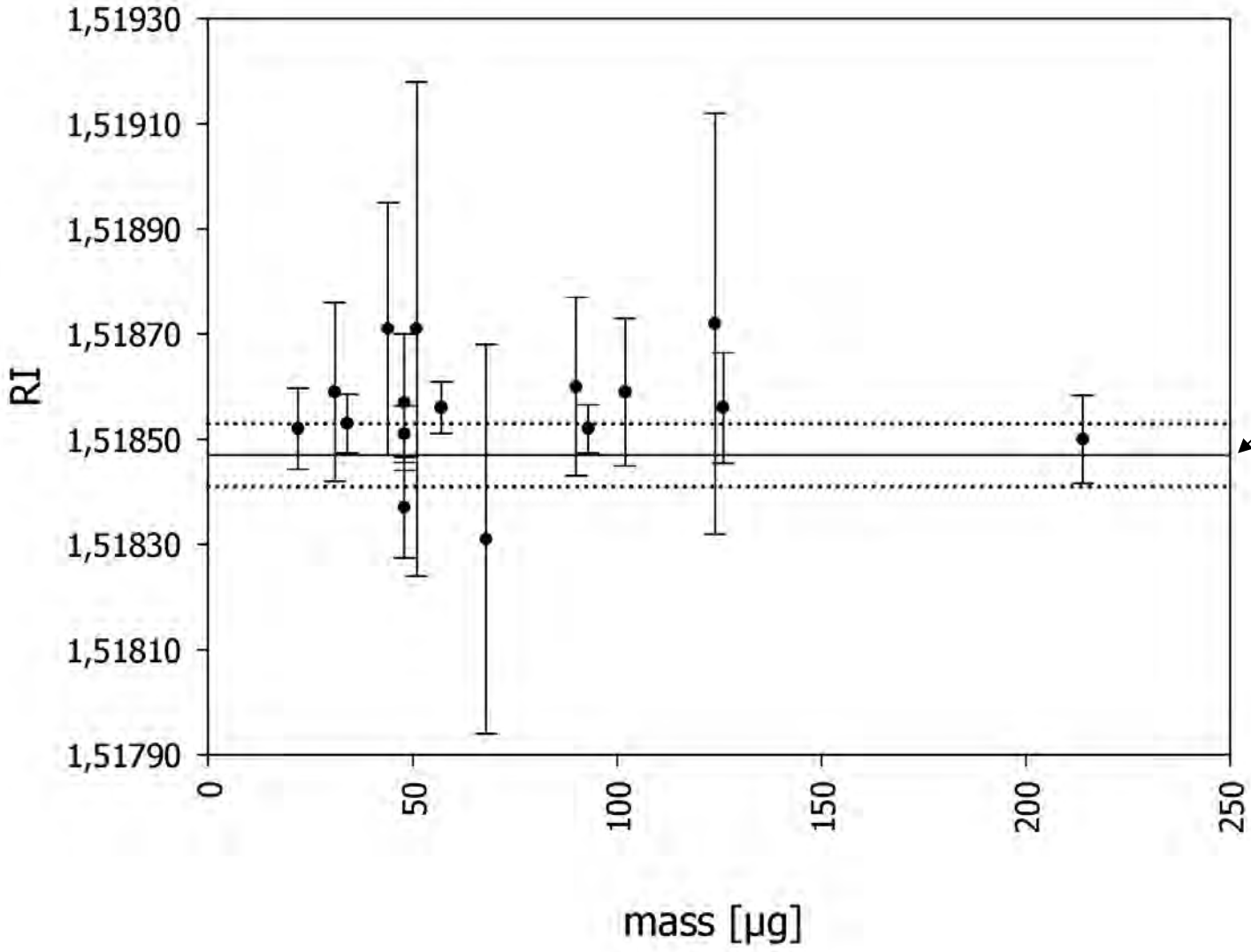
Float glass 13_2 untreated

n_D = 1,51932 SD = $4*10^{-5}$

RI of 19 fragments after LA 213 nm have been determined
mean n_D = 1,51931 SD = 4 E-5

RI of 15 fragments after LA 193 nm have been determined
mean n_D = 1,51936 SD = 8 E-5
(two outlier
mean n_D = 1,51933 SD = 2 E-5)

LA vs. RI
2010/11 Results for 26_23



26_23 untreated
n_D = 1,51847
SD = 0,00006

LA vs. RI 2010/11 Results for glass 26_23

Float glass 26_23 untreated

n_D = 1,51847 SD = 6*10-5

RI of 10 fragments after LA 213 nm:

mean n_D = 1,51854 SD = 1.3 E-4

RI of 6 fragments after LA 193 nm:

mean n_D = 1,51958 SD = 7 E-5

LA vs. RI 2010/11 Summary 1 / 2

- Ablation of small glass fragments down to the size of 0.4 mm x 0.4 mm were investigated.
- Laser ablation leads to an increased number of invalid refractive index readings (red curve).
- Decreased number of successful measurements (readings) possible.

LA vs. RI 2010/11 Summary 2 / 2

- No effects of different cleaning solvents (EtOH vs. HNO_3)
- No improvements of RI results by 193 nm LA
- Very small to negligible effects on RI for fragments > 250 µg
- Higher variations of individual RI and SD, but no significant changes of overall mean; RI of overall mean is correct.

LA vs. RI 2010/11 Suggestions

- As many as possible readings should be carried out on as many edges as possible (averaging effect)
- Results should be assessed with caution (higher variations of RI)
- Careful inspection of RI readings (outlier test)
- Match criteria should be applied with extreme caution

LA vs. RI 2010/11 Acknowledgments

Many thanks to:

Carolin	Photographic documentation, weighing, RI measurements
Marc Dücking, Peter Watzke & Peter Weis	Laser Ablation-ICPMS measurements

Bundeskriminalamt

LA vs. RI 2010/11 *Dessert*

ice cream cone
maximum length 200 µm