Elemental Analysis of Glass by SEM-EDS, XRF, LIBS and Laser Ablation-ICP-MS

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Elemental Analysis of Glass

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.

Trejos, T and Almirall, J, Effect of fractionation on the elemental analysis of glass using LA-ICP-MS, *Analytical Chemistry,* **2004**, 76(5) 1236-1242.

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

Trejos, T and Almirall, J, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II: sample size and sample shape considerations, *Talanta*, **2005**, 67(2) 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.

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ASTM Standards

INTERNATIONAL

Designation: E 1967 – 98 (REapproved 2003)

Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase Contrast Microscope[1]

This standard is issued under the fixed designation E 1967; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

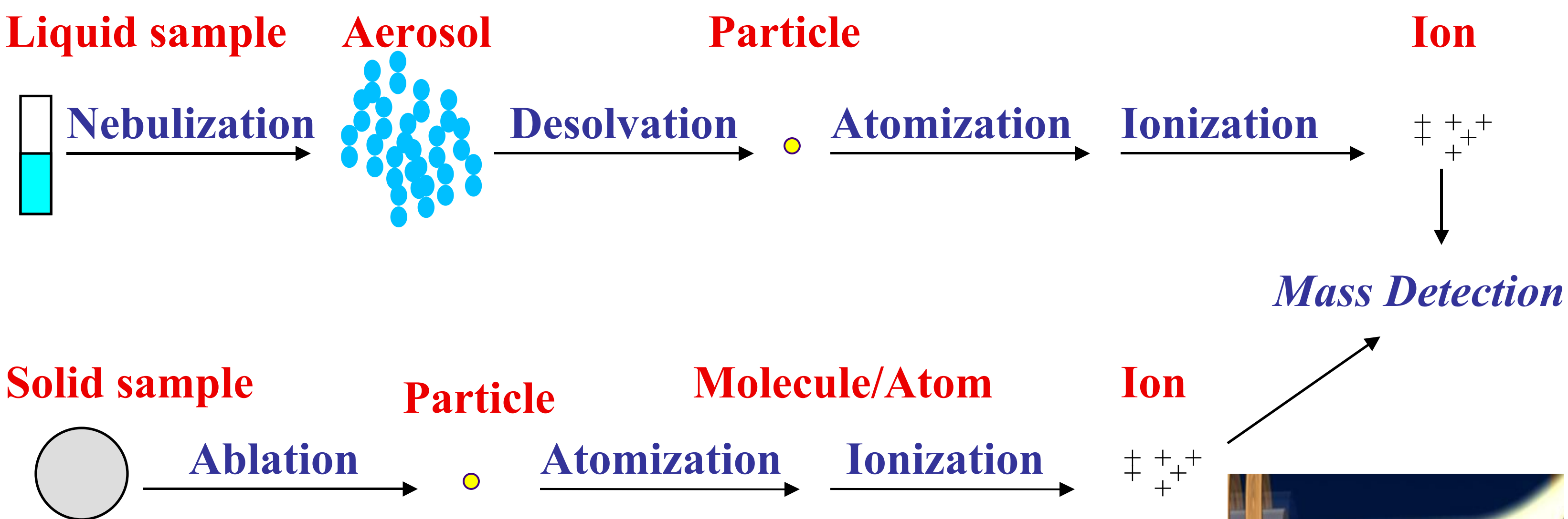
INTERNATIONAL

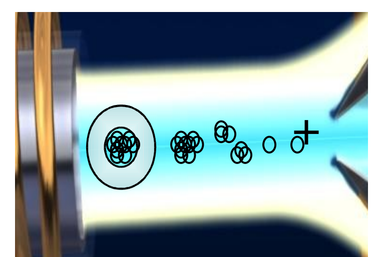
Designation: E 2330 – 04

Standard Test Method for Determination of Trace Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

This standard is issued under the fixed designation E 2330; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

Processes in ICP-MS and LA-ICP-MS

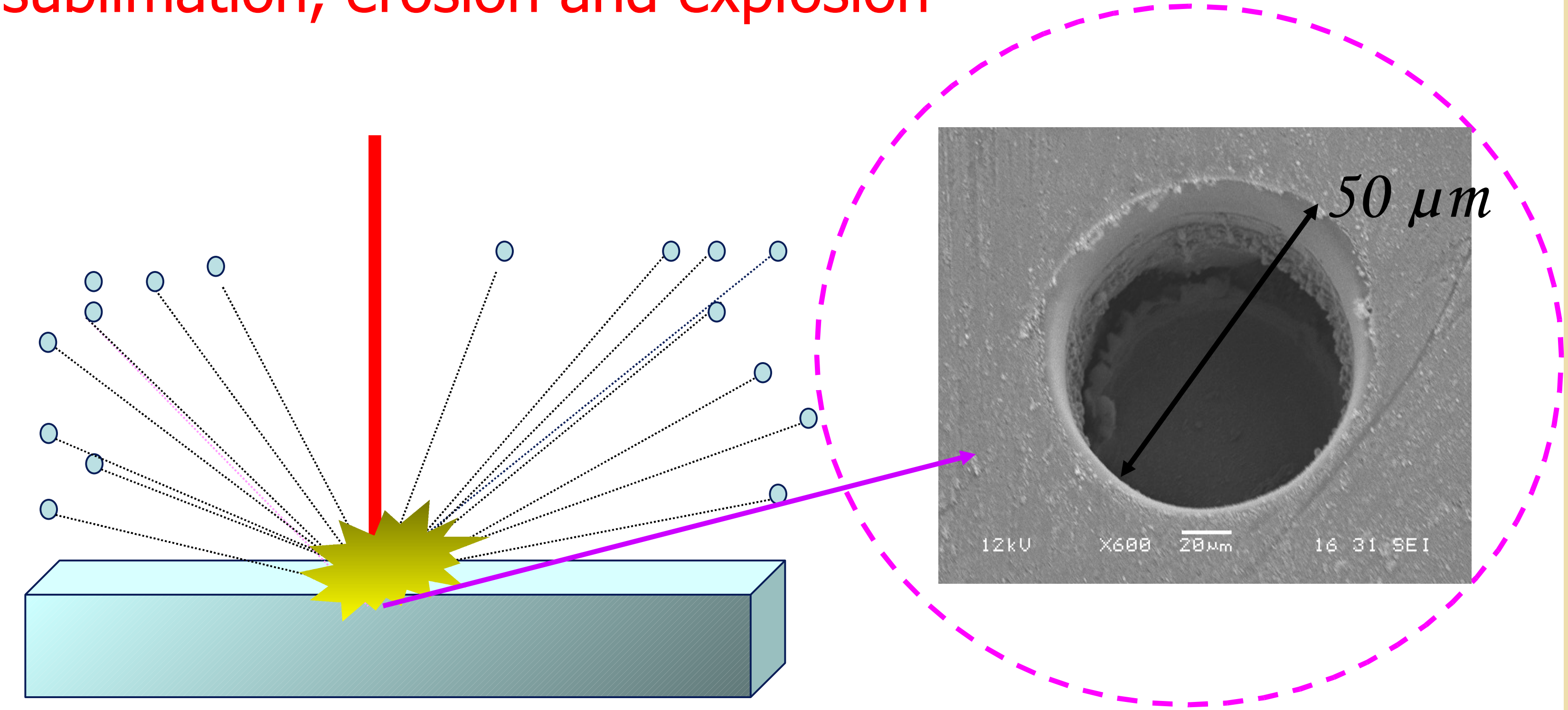




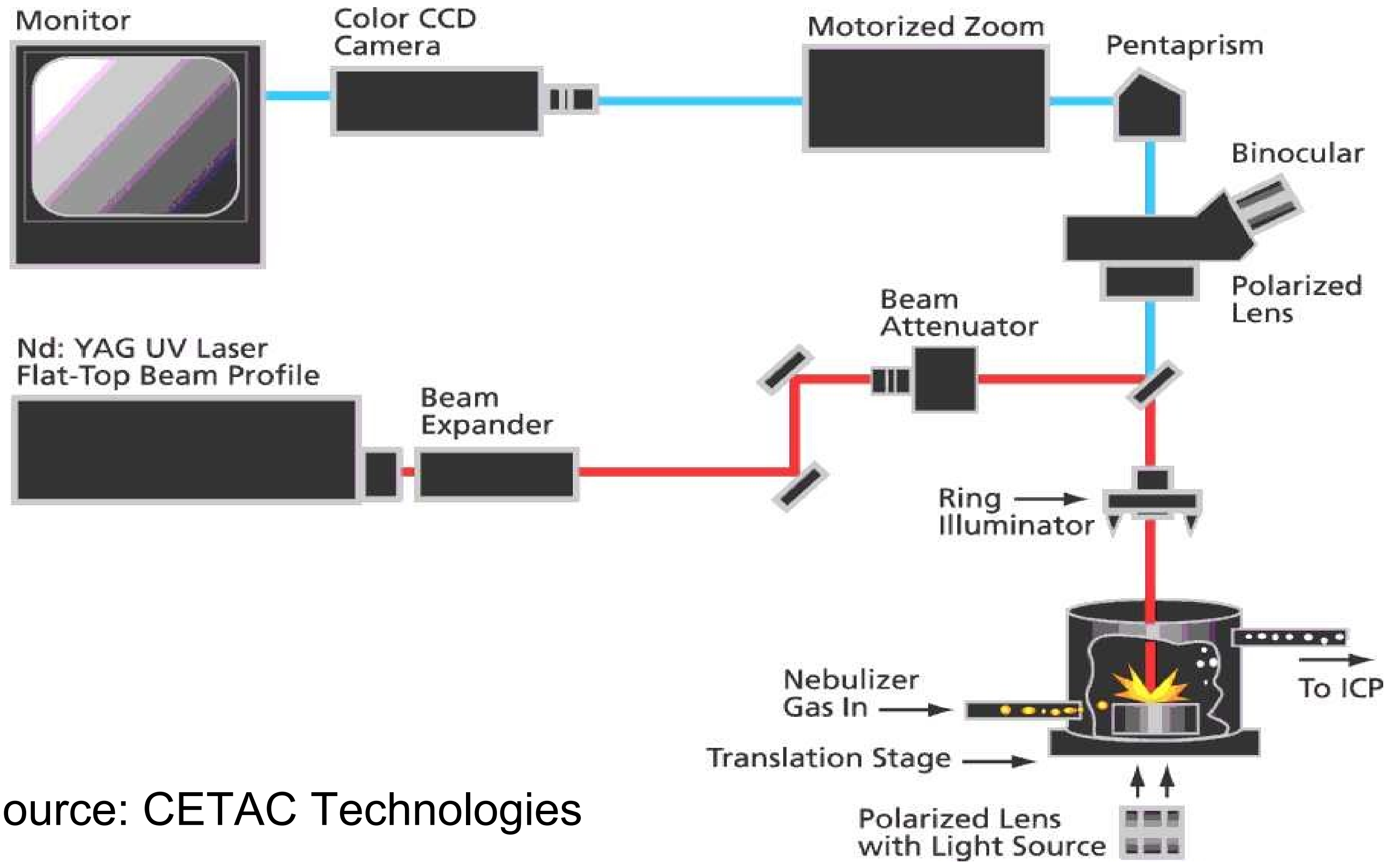
When a laser of enough power density strikes a solid material it generates a particle aerosol into the gas phase.

Laser Ablation

"Ablation is a progressive and superficial destruction of a material by melting, fusion, sublimation, erosion and explosion "



Laser Ablation Diagram



Source: CETAC Technologies

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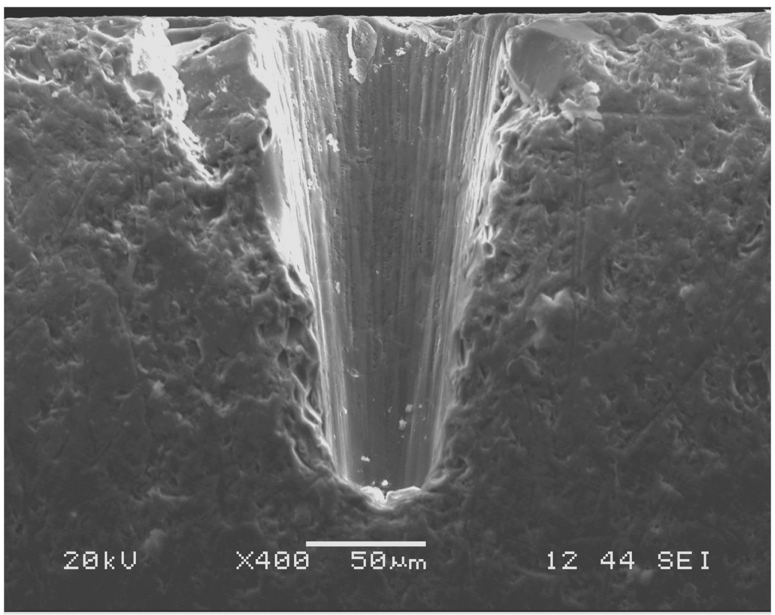
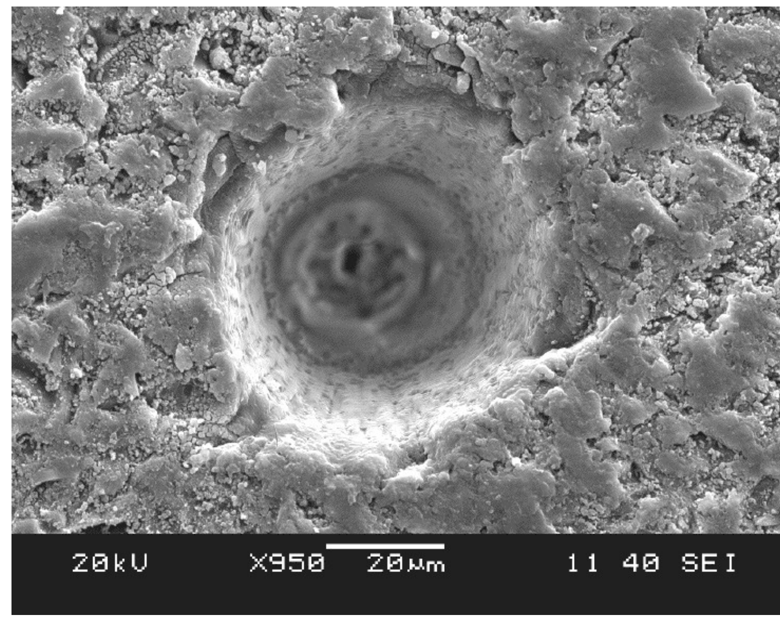
LODs with the New Wave UP 213 LA-ICP-MS

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

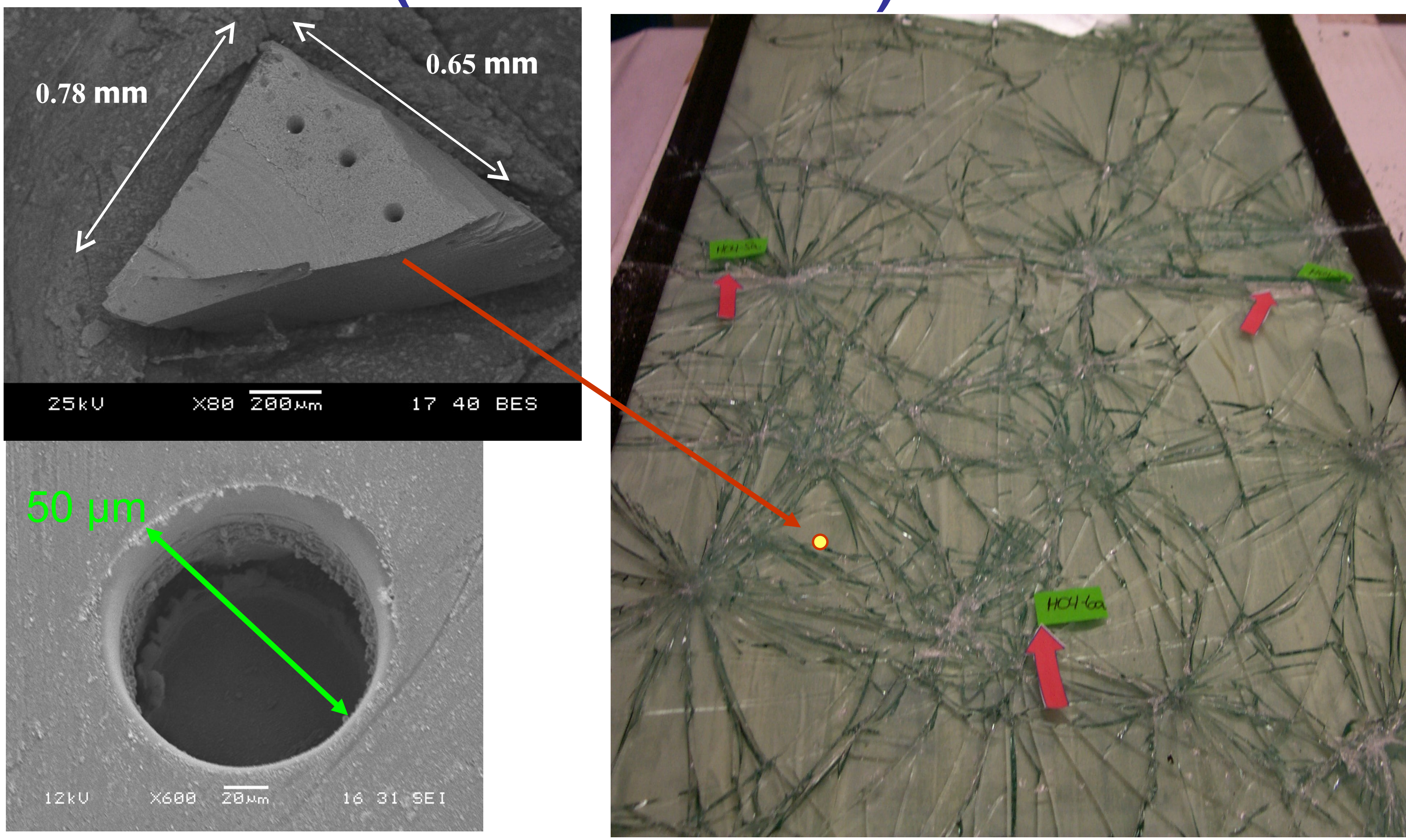
50 µm spot size 266 nm (9 mJ), 10 Hz, 50 sec. ablation (500 shots)



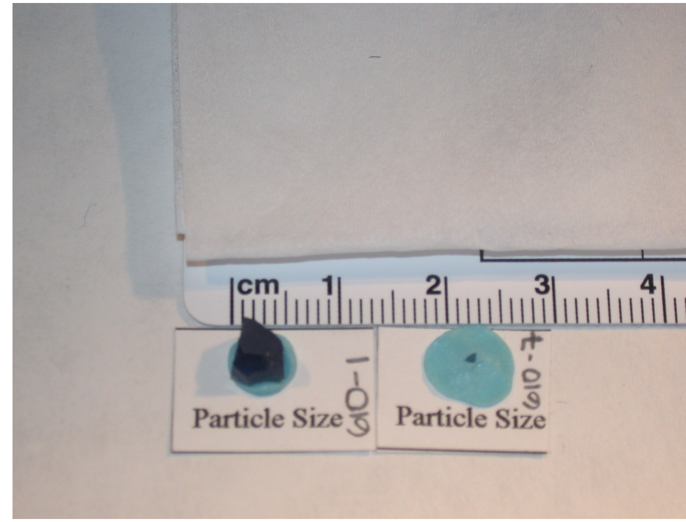


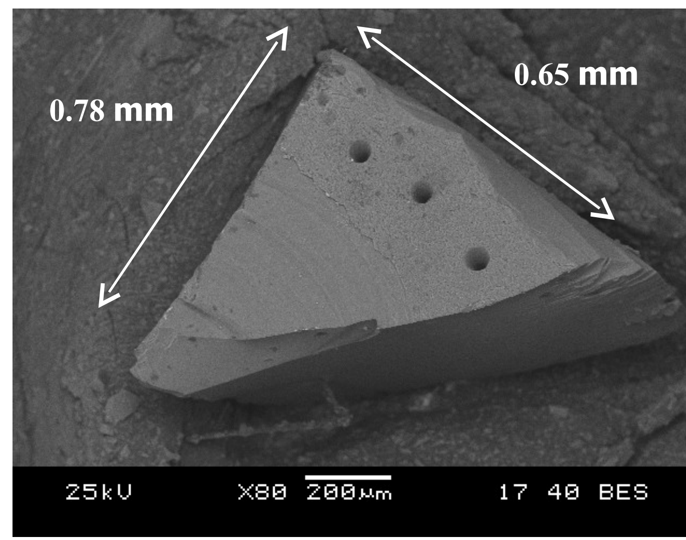
T. Trejos and J.R. Almirall, Effect of fractionation on the elemental analysis of glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), Analytical Chemistry, **2004**, 76(5) 1236-1242.

Homogeneity at micro-scale (0.5 – 1mm)



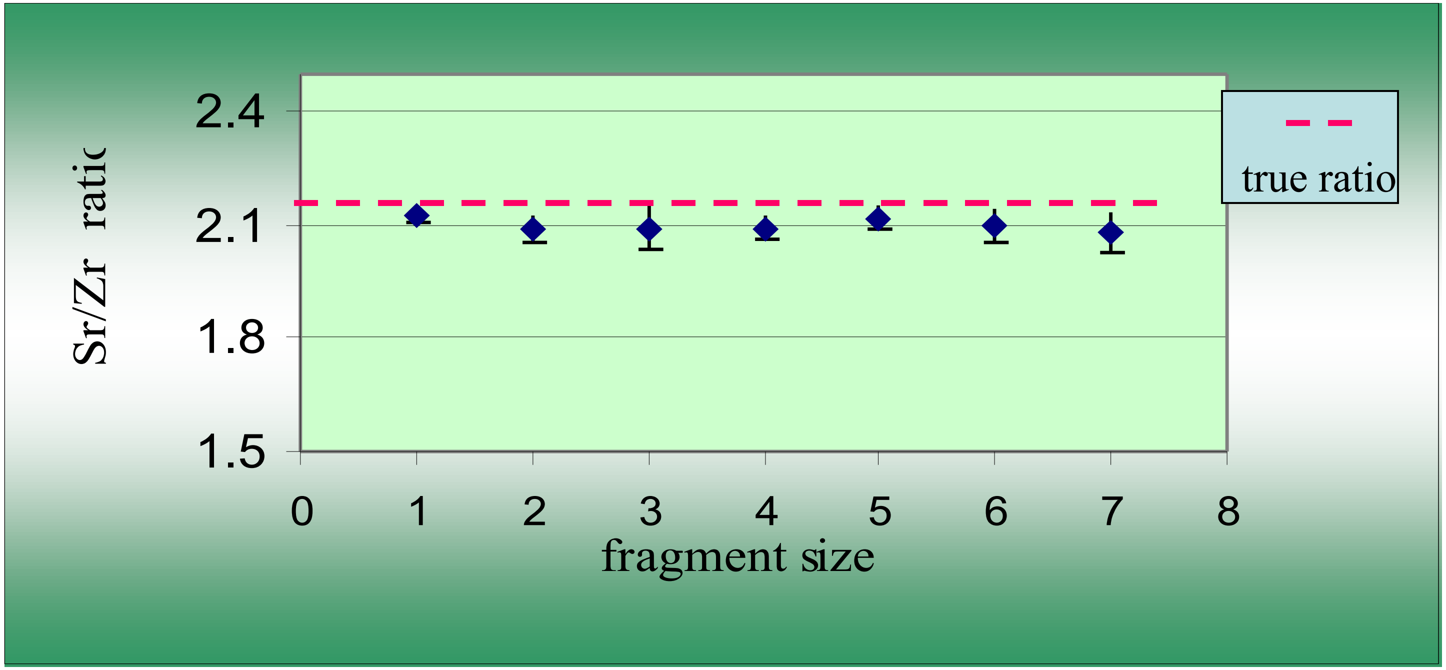
T. Trejos and J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part I: micro-homogeneity study of glass and its application to the interpretation of forensic evidence, *Talanta*, **2005**, 67(2) 388-395





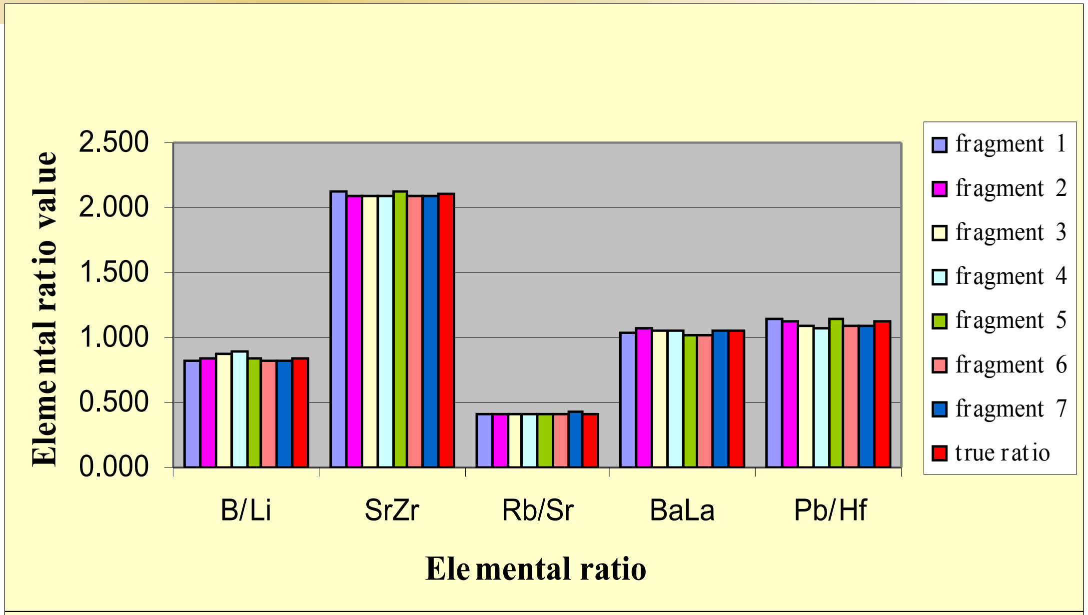
T. Trejos and J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II: sample size and sample shape considerations, *Talanta*, **2005**, 67(2) 395-401.

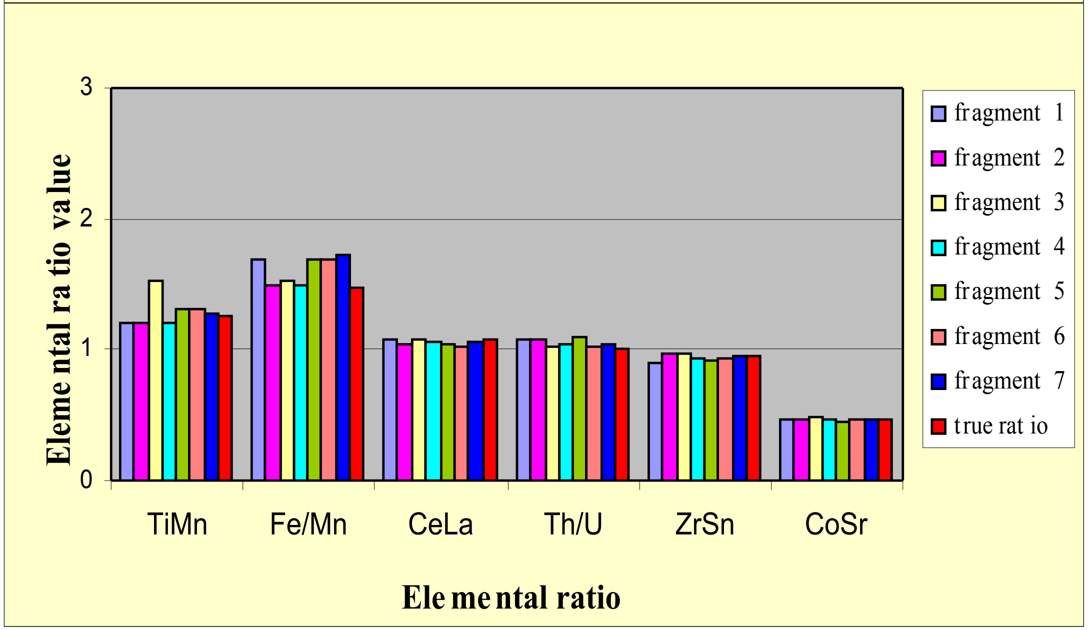
Mean values and standard deviations of Sr/Zr for 7 glass fragments (SRM 612)



No significant
difference between the fragments ($p>0.05$)

T. Trejos and J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II: sample size and sample shape considerations, *Talanta*, **2005**, 67(2) 395-401.

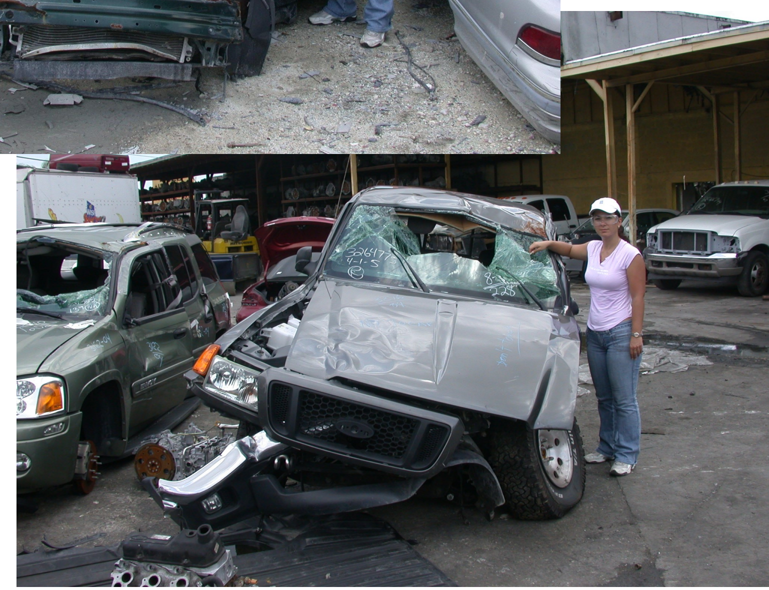




T. Trejos and J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II: sample size and sample shape considerations, *Talanta*, **2005**, 67(2) 395-401.

Miami Junkyard Sample Collection (August 2005)

- A total of 41 glass samples were collected from 14 different vehicles in various junk yards
- Selected vehicles were manufactured from 1995 to 2005

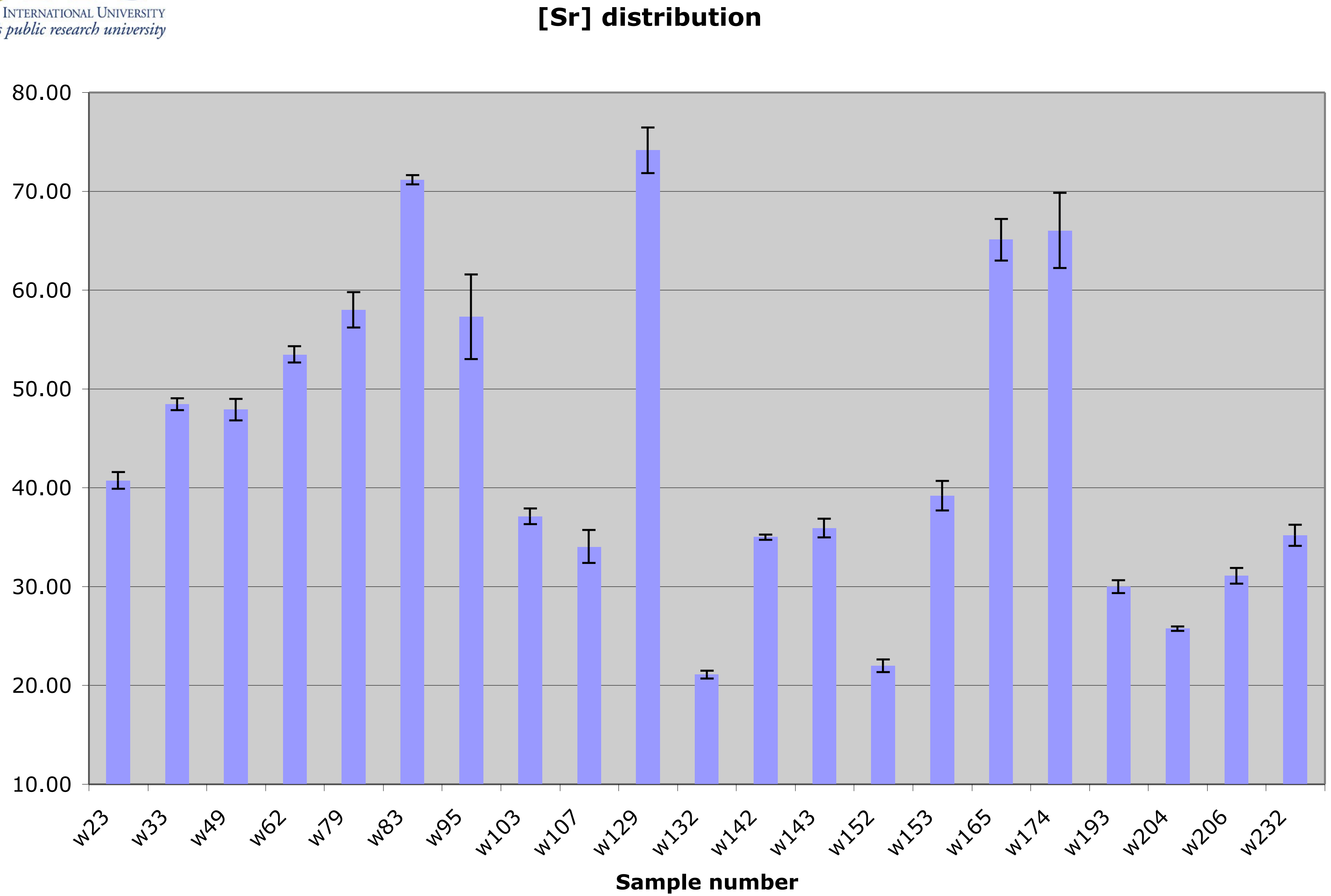


Discrimination by Isotope

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%)

Description of indistinguishable pairs

Pair #	Sample #	Vehicle make	Vehicle model	Year	Sample collected from
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



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

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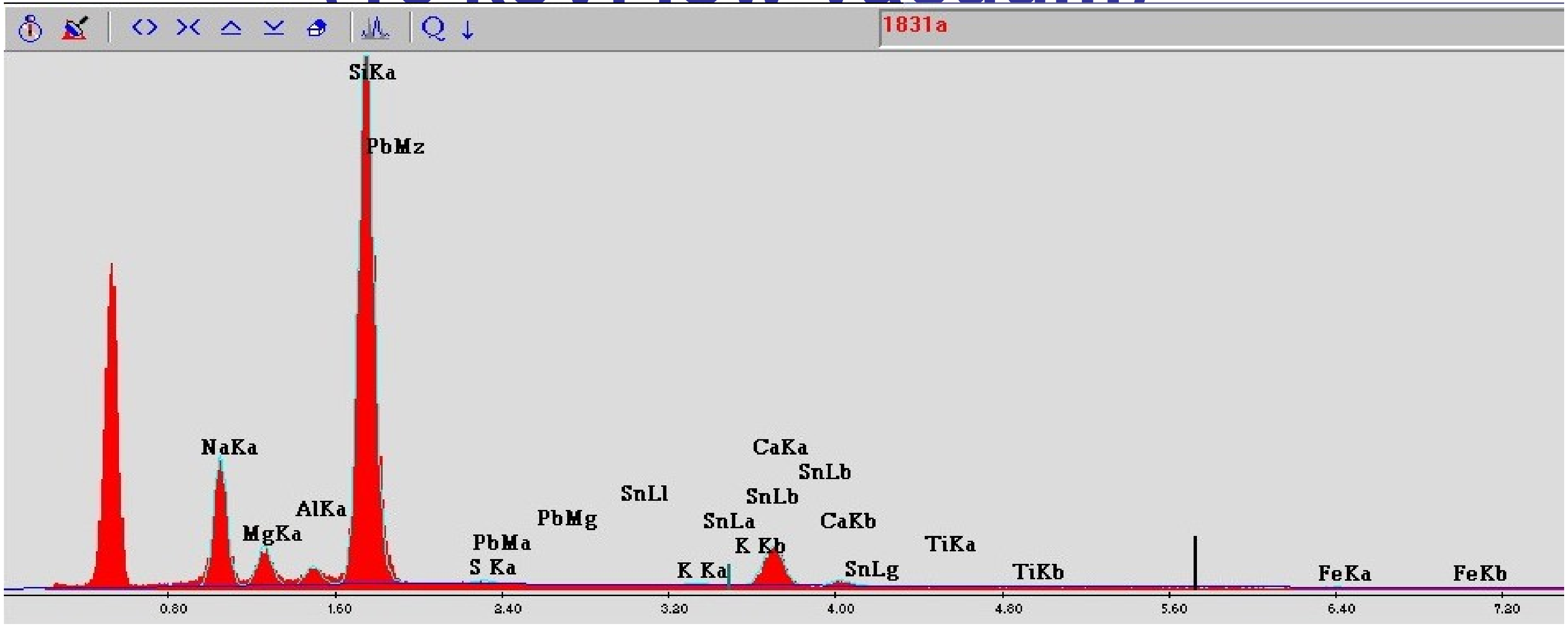
Limits of Detection for LA-ICP-MS

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

SEM spectra and conditions (16 keV, low vacuum)



ANALYSIS OF WINDOW GLASSES BY SEM-EDS

Limit of detection ~ 1000 ppm (0.1 %)

accelerating voltage=16KV
low vacuum
work distance=9 mm
single point
back scatter detector
resolution=1024x800

time of collection=100s
pressure=29 Pa
spot size=50
magnification=110

SEM Analysis of NIST 1831 (Float Glass) at 16 keV

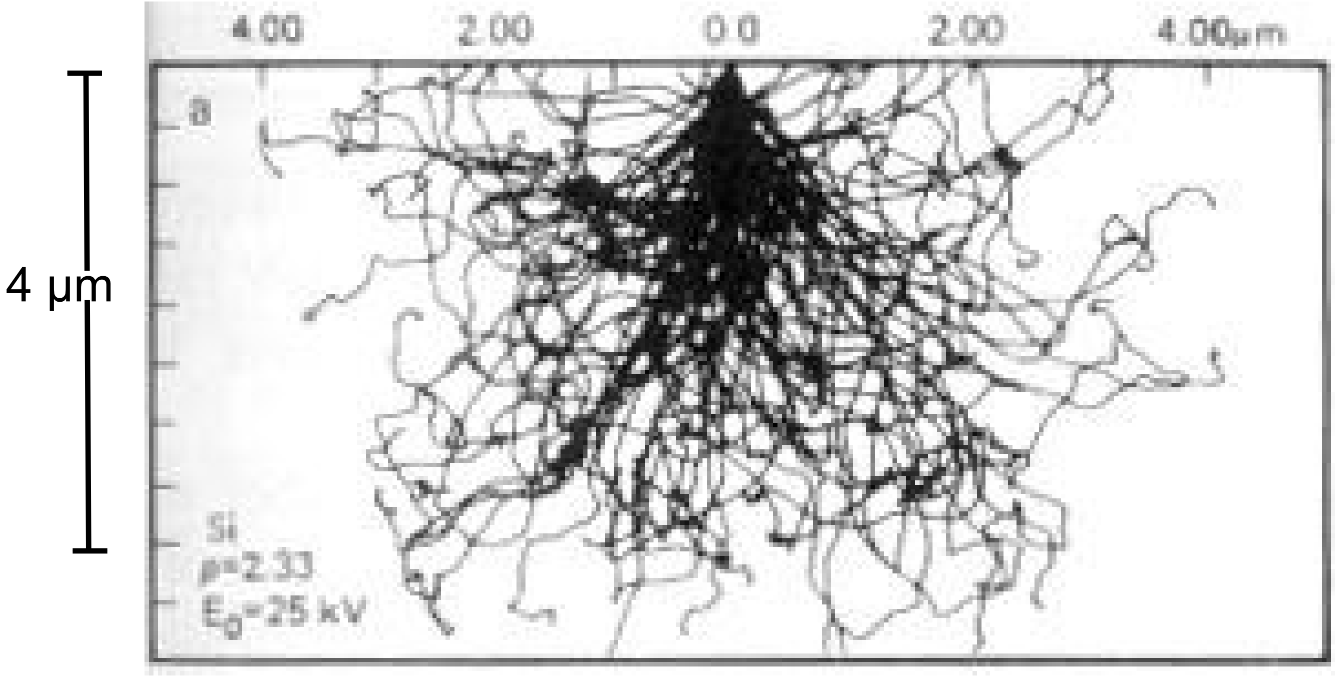
Element	1831a	1831b	1831c	Mean	SD	RSD	Certified Values (as % Oxides)	uncertainty
Si	65.70	65.64	65.56	65.63	0.07	0.11	73.08	0.08
Na	14.82	14.91	15.25	14.99	0.23	1.51	13.32	0.05
Ca	10.31	10.38	10.32	10.34	0.04	0.37	8.2	0.05
Mg	4.53	4.63	4.71	4.62	0.09	1.95	3.51	0.05
Al	2.46	2.44	2.48	2.46	0.02	0.81	1.21	0.04
K	0.64	0.55	0.53	0.57	0.06	10.22	0.33	0.02
S	0.41	0.55	0.56	0.51	0.08	16.55	0.25	0.01
Fe	0.38	0.21	0.32	0.30	0.09	28.42	0.087	0.003
Ti	0.00	0.12	0.28	0.13	0.14	105.36	0.019	0.002
Sn	0.49	0.37	0.00	0.29	0.26	89.10	0	
				99.85			100.01	

Trace metals in 1831 (Float Glass, measured by ICP-MS)

element	reported value, $\mu g g^{-1}$	average, $\mu g g^{-1}$	Bias, %	repeatability-within, s_r (%)	reproducibility-between, s_R (%)
Ti	114[a]	123	7.9	3.0	5.8
Mn		15.00		6.6	8.8
Rb		6.11		2.1	9.2
Sr		89.12		2.8	10
Zr		43.36		4.8	11
Sb		2.06[b]		85	-
Ba		31.52		2.4	4.2
Ce		4.54		2.0	7.4
Sm		0.40		7.7	9.9
Hf		1.10		19	5.7
Pb		1.99		10	7.7

SEM penetration profile (sampling)

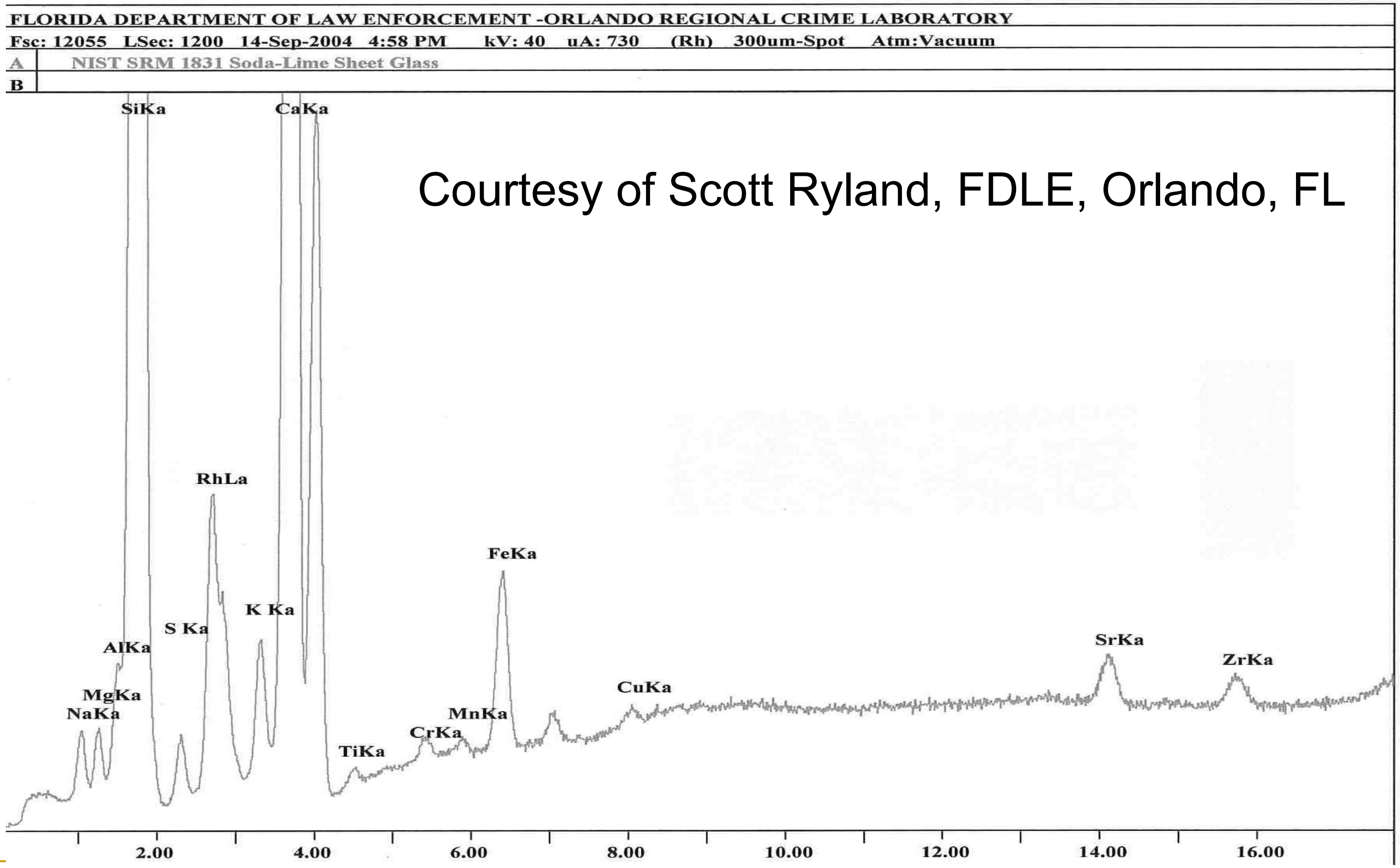
~ 2 μm for 15 keV and ~ 5 μm for 25 keV



Monte Carlo Dynamics
(Reimer, Ludwig, Scanning Electron Microscopy, Springer-Verlag, 1985, p. 99)

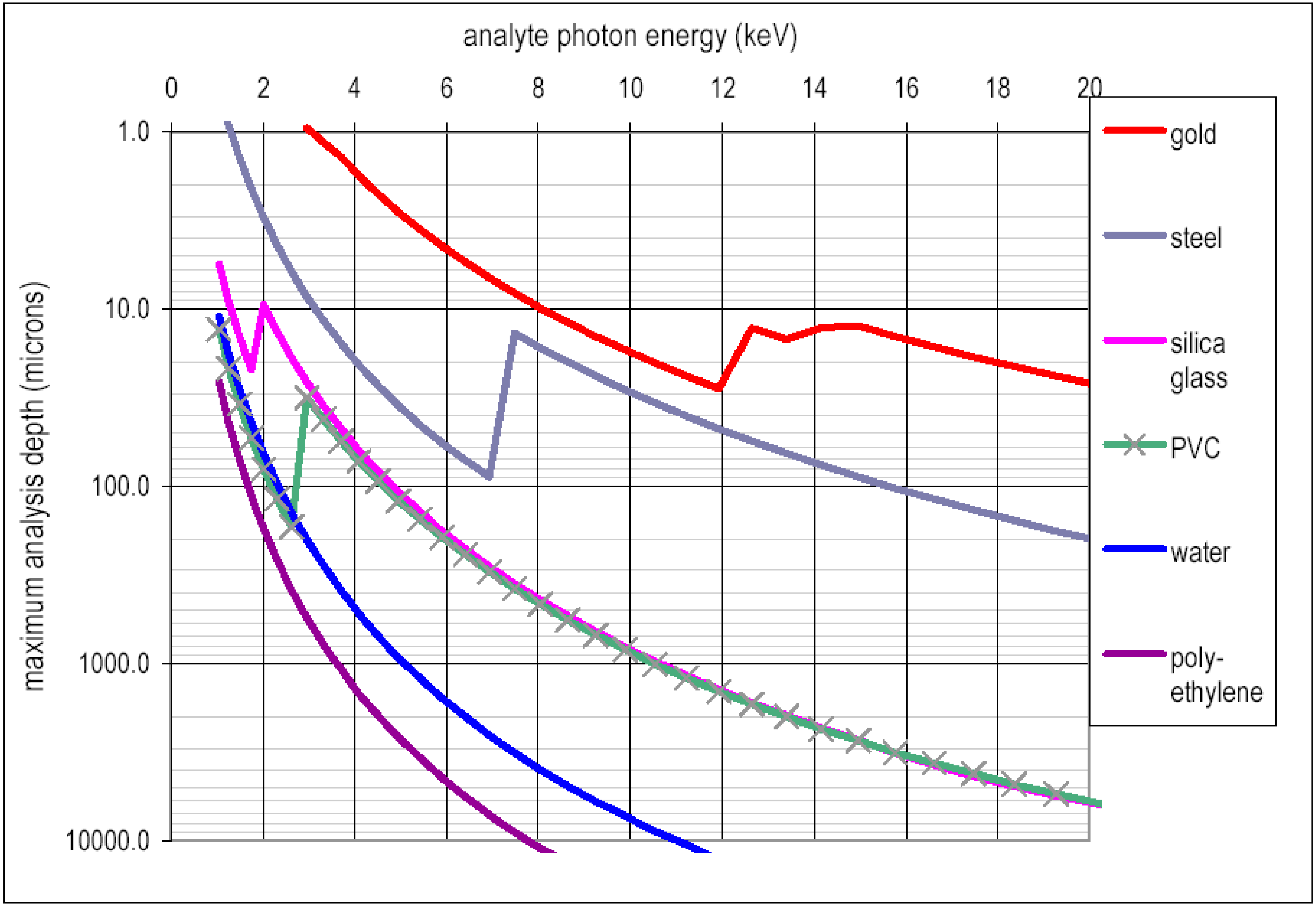
XRF spectra and conditions

Rh x-ray tube
40 keV beam potential
300 micron diameter monocapillary focusing collimator
SiLi EDS with beryllium window
beam current @ 35% dead time (approximately 760 microamps)
17 microsecond time constant
resolution approximately 156 eV



Courtesy of Scott Ryland, FDLE, Orlando, FL

Analysis Depths for Energies up to 20 keV



Seaman, EDAX Application Note "Analysis Depth for μ-EDXRF Methods"

Description of indistinguishable pairs (XRF)

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
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	29	Ford	Expedition Eddie Bauer	2004	outside windshield
8	37	Jeep	Grand Cherokee	2001	outside windshield
	38	Jeep	Grand Cherokee	2001	inside windshield

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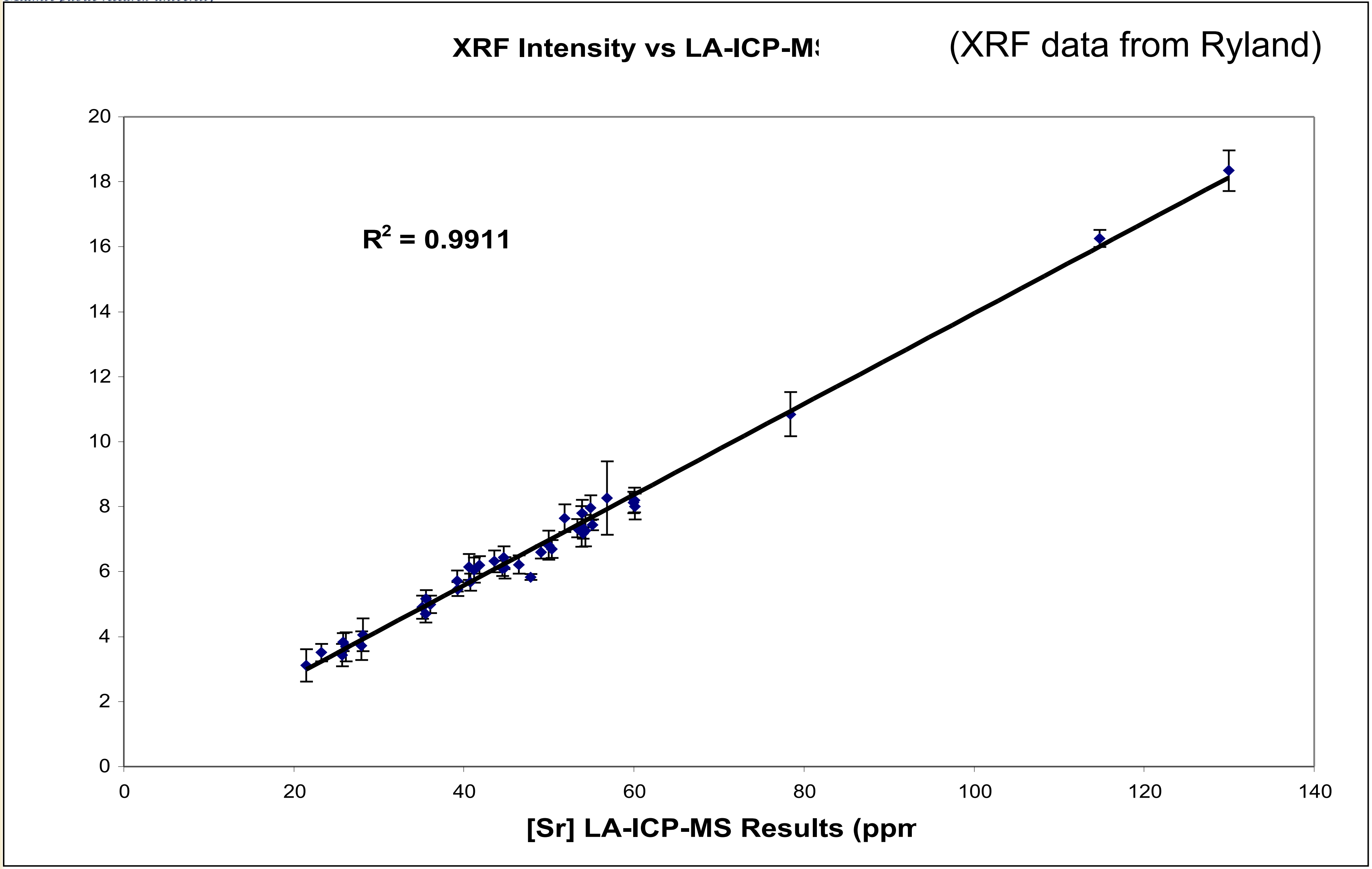

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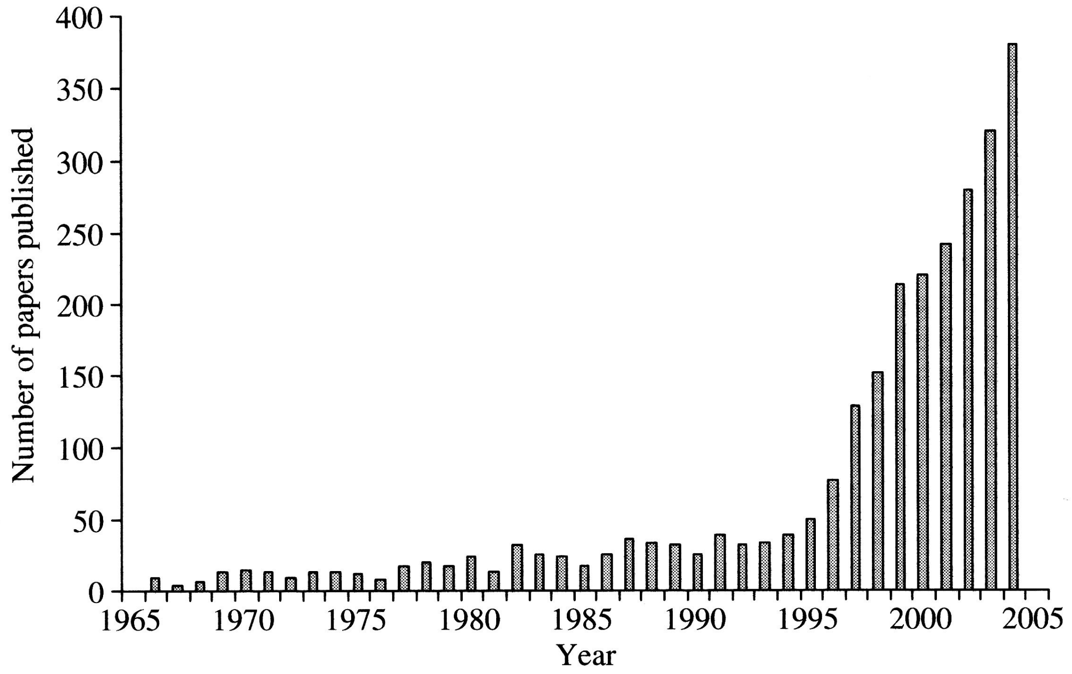
LIBS Background

<u>First reported by Maker, Terhune and Savage in 1963</u>

- A focused laser pulse interacts with a target material to generate a practically totally ionized gas (plasma).
- The plasma then excites the substrate's atoms and ions.
- A characteristic emission is detected.
- The emission spectrum is spectrally resolved to provide qualitative and (semi) quantitative analysis of the material.
- Direct sampling of gases, liquids and <u>**solids**</u> to determine elemental composition.

LIBS Developments



Number of publications over the last 40 years (but still less mature than ICP and XRF as an analytical method)

Source: M. Sabsabi from Cremers and Radziemsk, 2006

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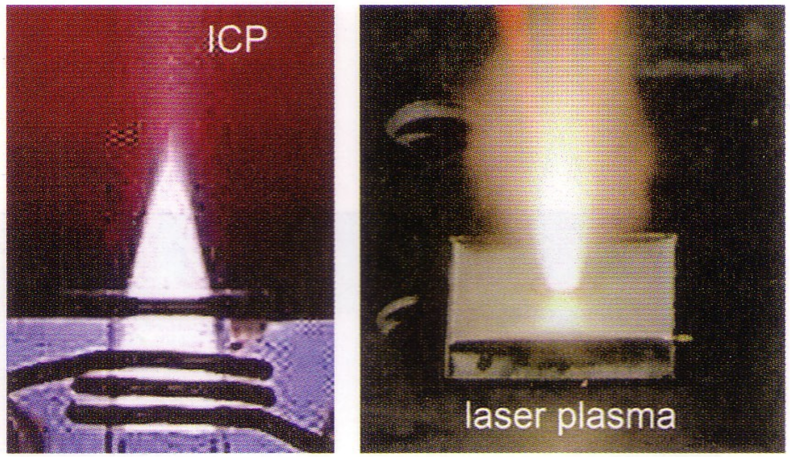
Atomic Emission Spectroscopy

- Ability to detect all elements
- ***Simultaneous*** multi-element detection
- Fast and easy to operate
- No sample preparation
- Almost non-destructive
- Good sensitivity for a wide range of elements
- Capability of field and stand-off analyses

Plasma as an Excitation Source



* Not on same scale

ICP Plasma:

- ~ cm in length
- sustained and controlled with gas flow
- $n_e \sim 1 \times 10^{15}/cm^3$
- Temperature ~ 8000 ^{0}K

Laser Plasma:

- ~ mm in length
- created with ns laser pulse
- ~ microseconds lifetime
- $n_e \sim 1 \times 10^{16}/cm^3$
- Temperature ~ 10000 ^{0}K

Source of photo: Cremers and Radziemski 2006

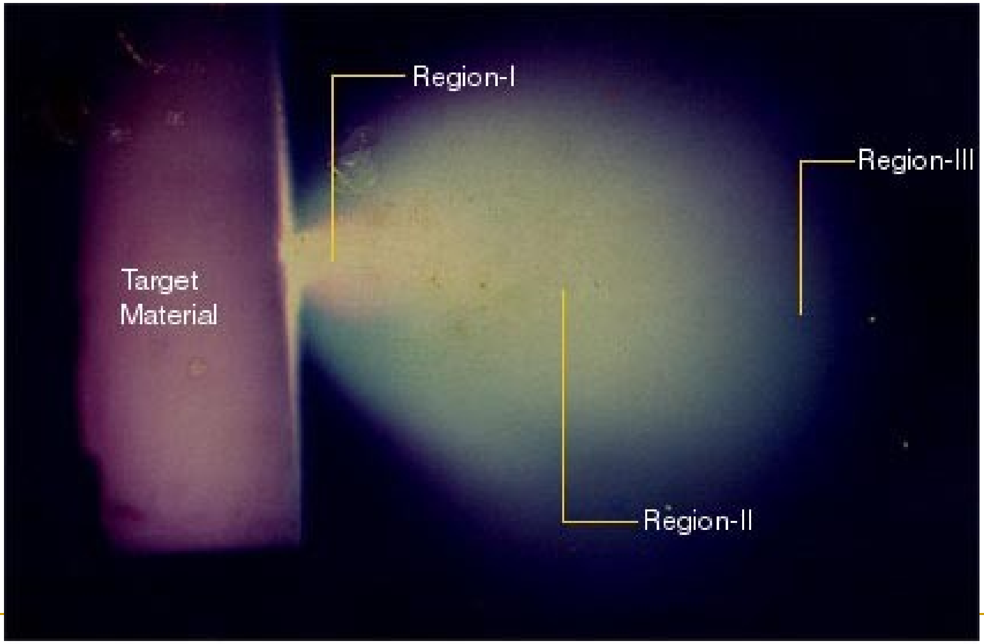
LIBS mechanism

Multi-photon ionization (MPI)

$$M + mh\nu \longrightarrow M^{+} + e^{-}$$

Cascade Breakdown (exponential increase of e^{-})

$$e^{-} + M \longrightarrow 2e^{-} + M^{+}$$

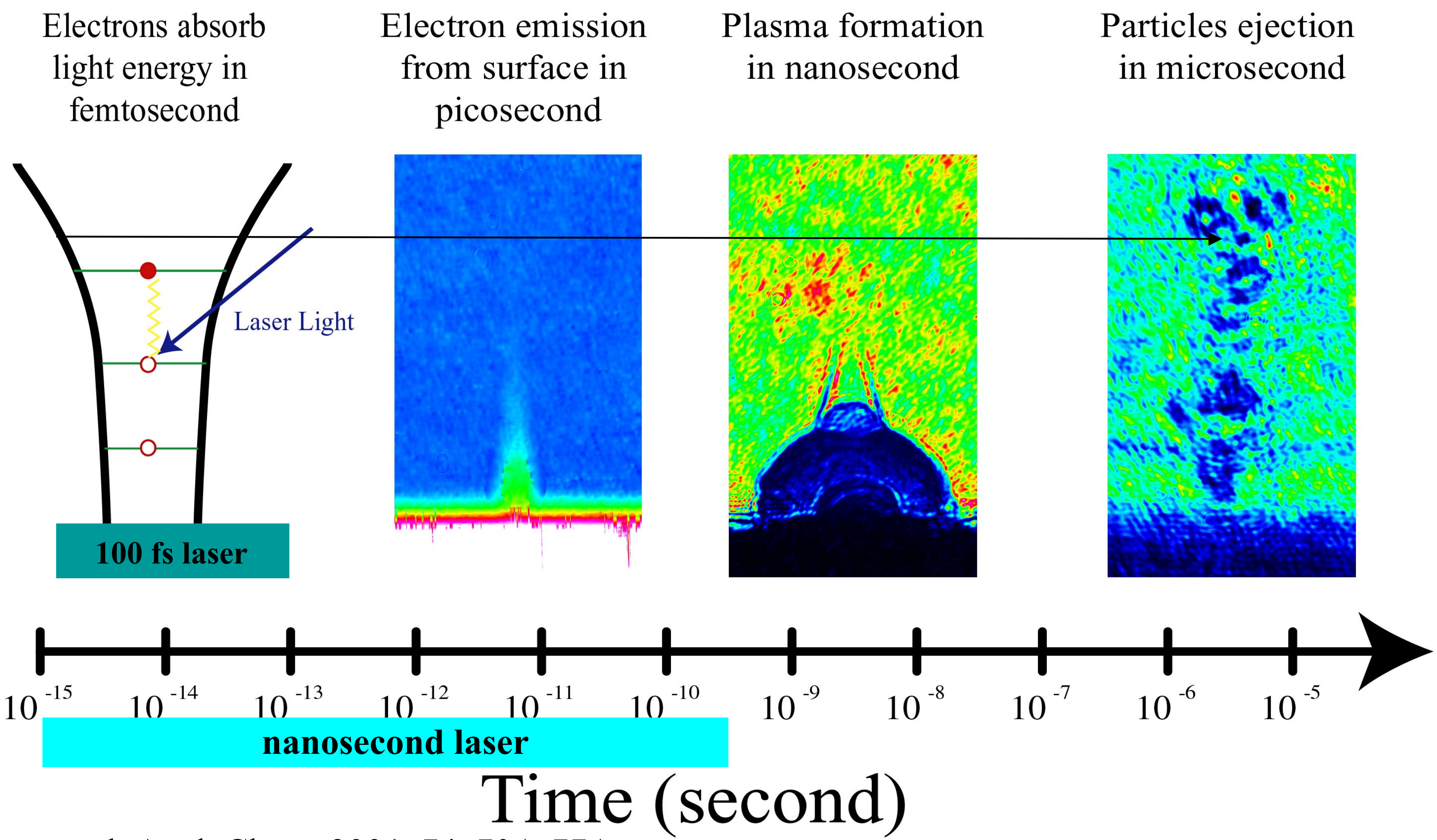


Laser produced plasma plume from a metal target

← Laser Source

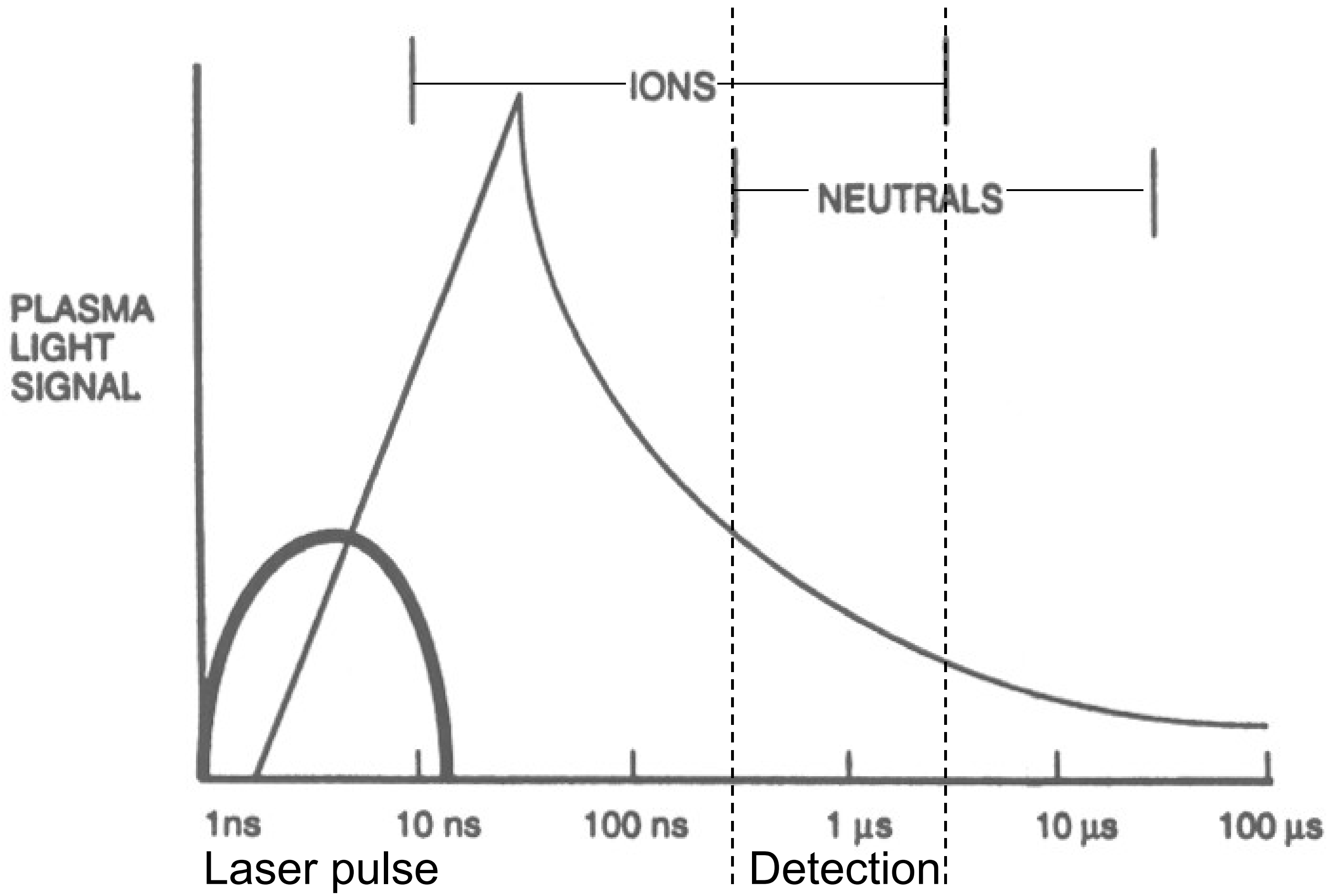
Nd: YAG λ = 1064 nm
10 ns pulse focused to
100 μm beam at target surface
~ 50 mJ (10^{9}-10^{11} W/cm^{2})

Laser-sample interaction time scale

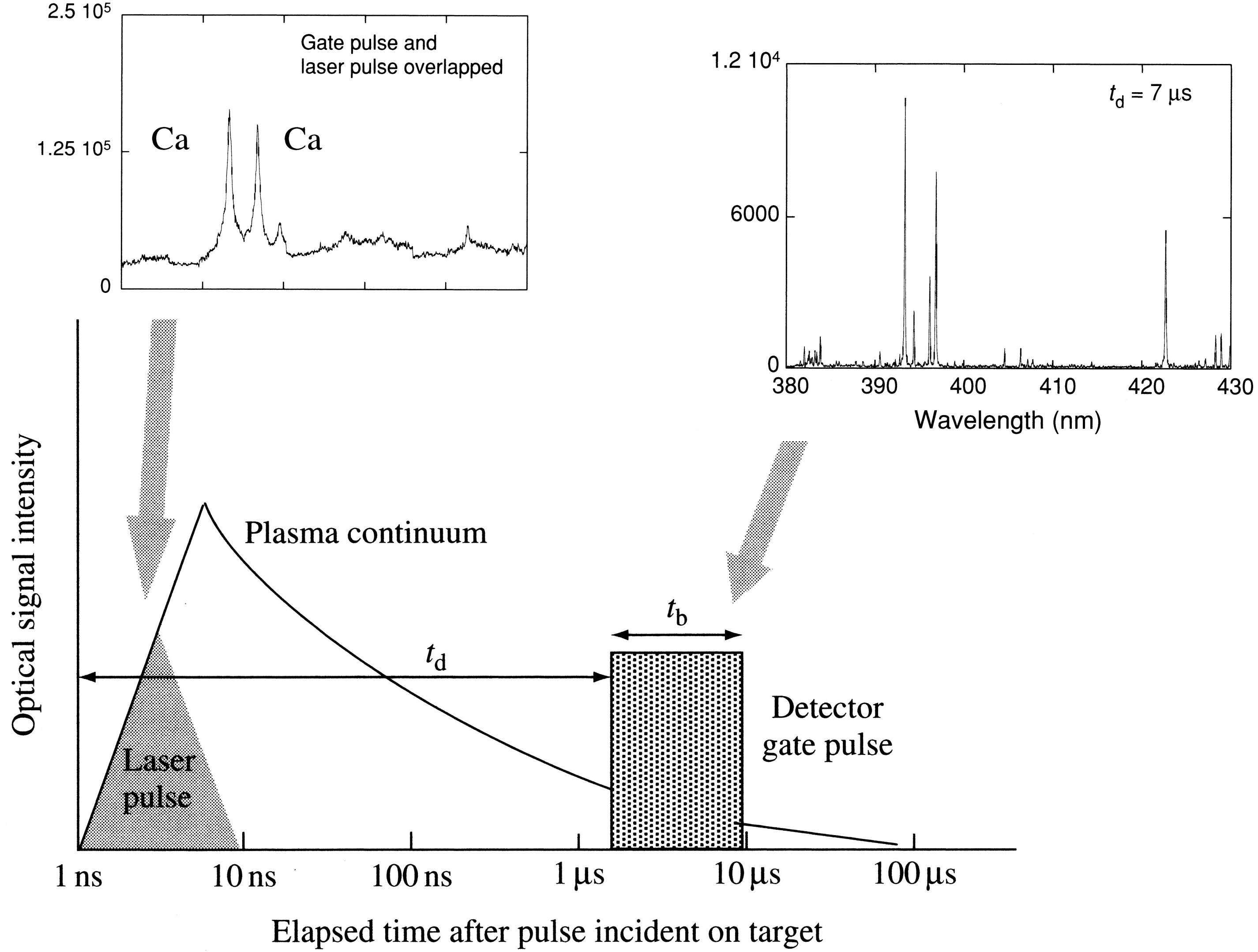


Russo, et al, Anal. Chem. **2001**, 74, 70A-77A

Plasma temporal analysis

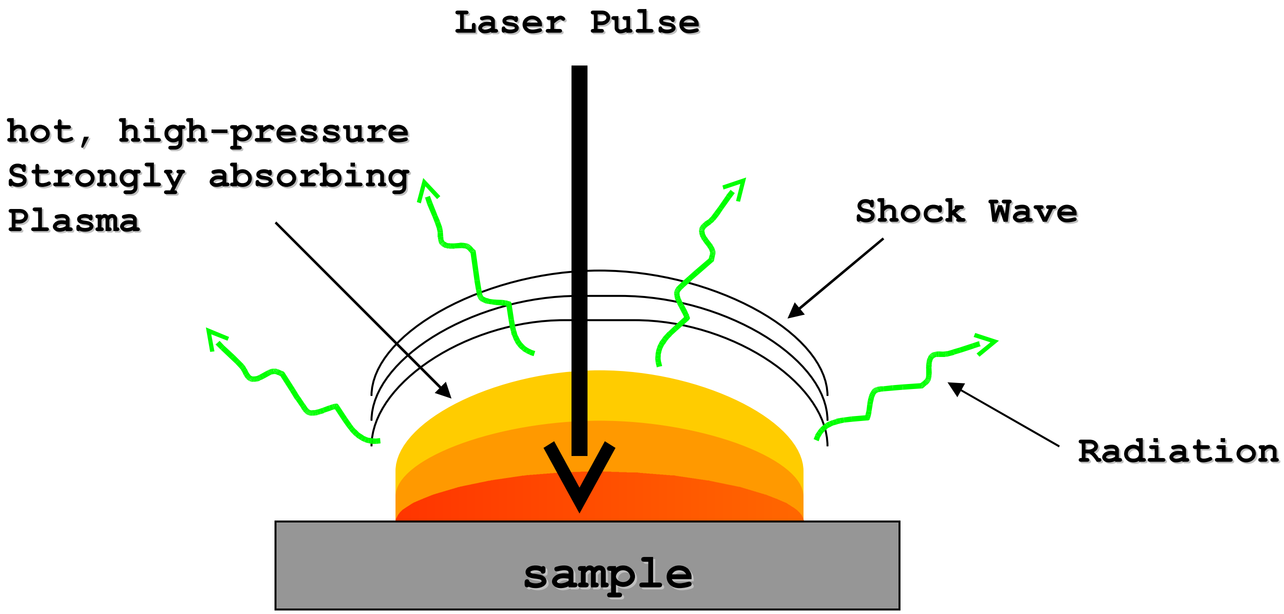


Plasma temporal analysis



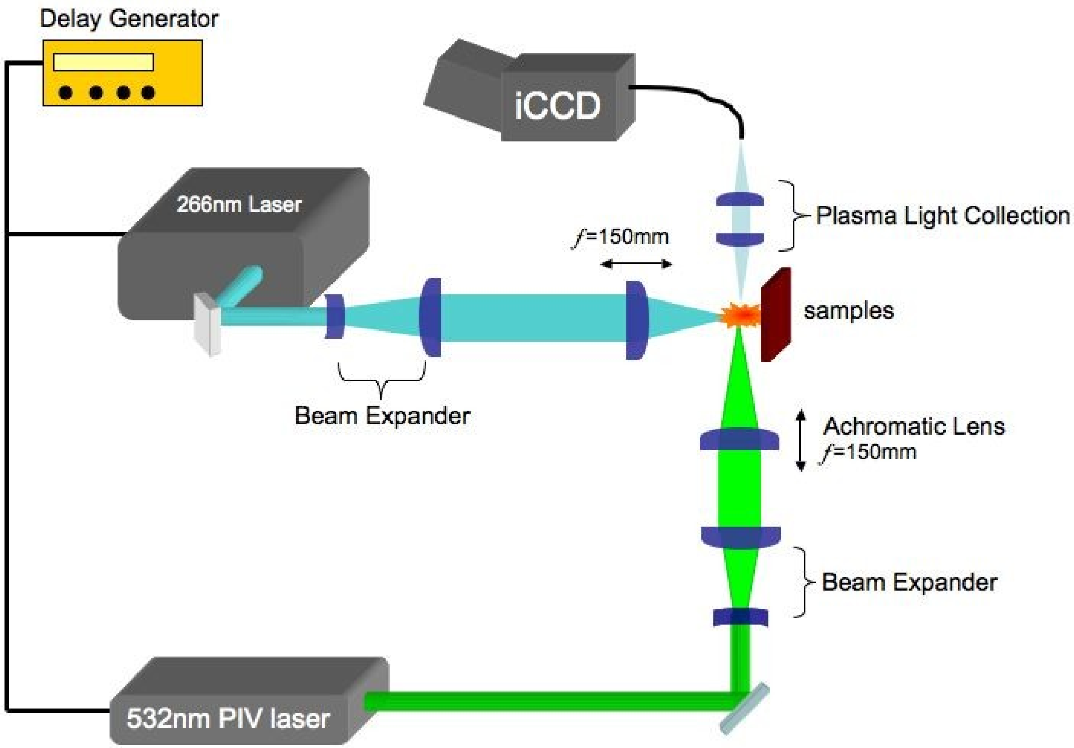
Source: Cremers and Radziemski 2006

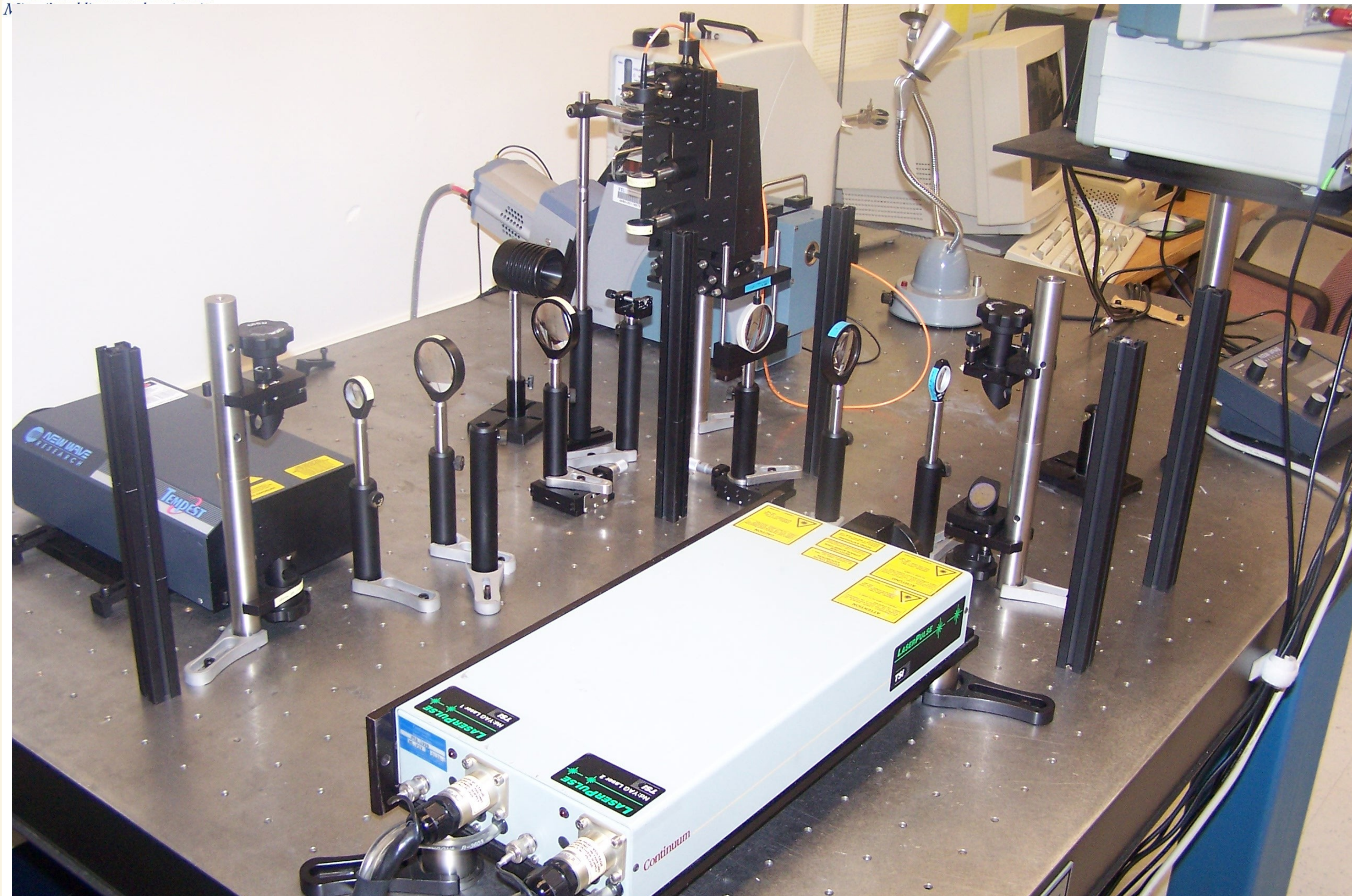
Plasma creation

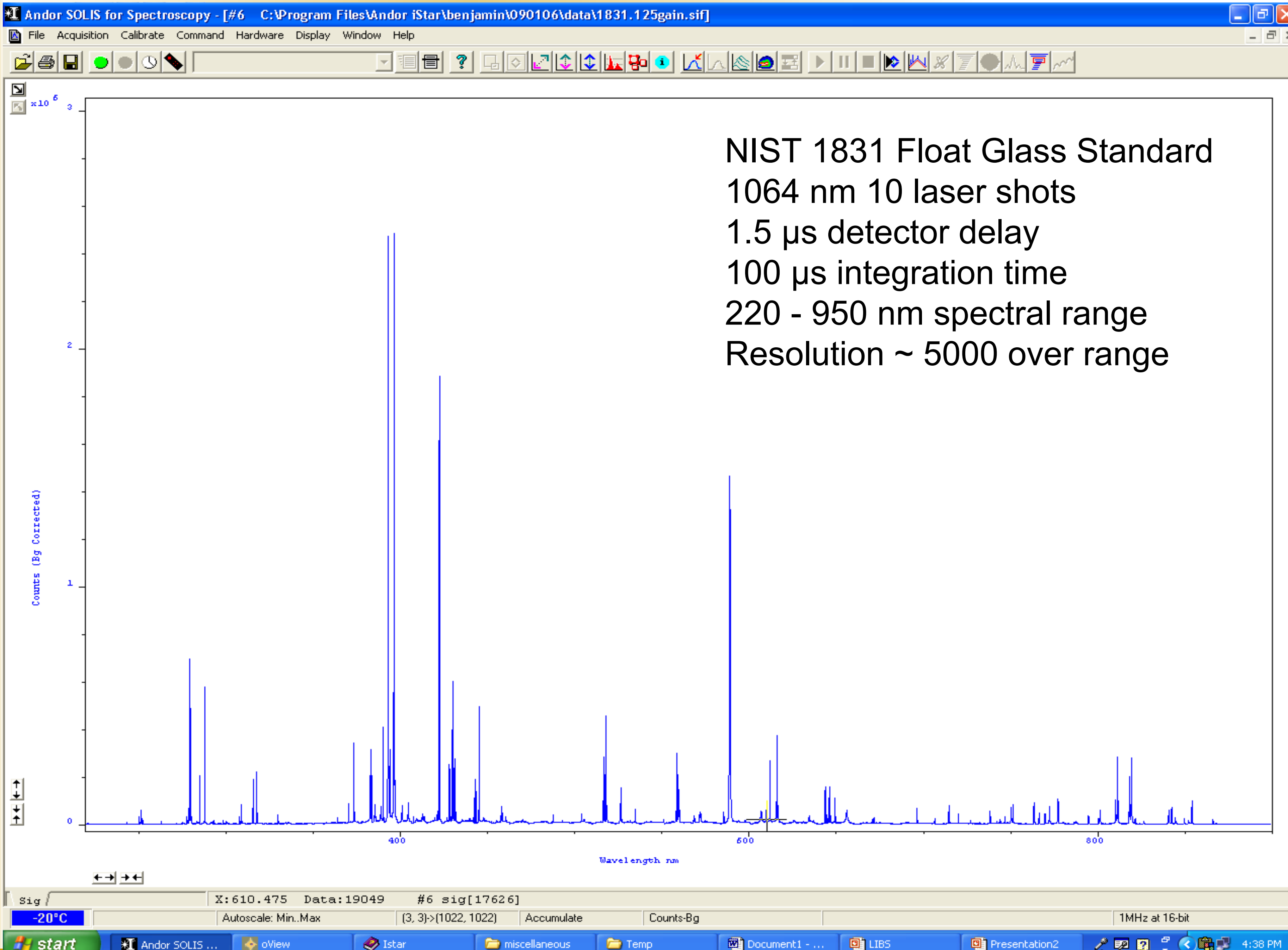


Experimental Setup

- Continuum MiniLite Nd:YAGs
  - Two lasers (PIV) system
  - 2nd harmonic 532nm
  - 22 mJ max energy per pulse
  - 0.67 Hz Rep Rate
- New Wave Tempest
  - 4th harmonic 266 nm
  - 27 mJ max energy per pulse
  - 0.67 Hz Rep Rate
- Focal length = 150 mm
- Varying focus positions wrt sample surface
- Delay between laser pulses varied from 0.0 - 10.0 μs.
- Spectrometer
  - Mechelle 200-900nm
  - Resolving power 5000
- Detector
  - Andor iCCD Camera




NEW WAVE
RESEARCH
TEMPEST
LASERPULSE
Continuum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File Acquisition Calibrate Command Hardware Display Window Help
NIST 1831 Float Glass Standard
1064 nm 10 laser shots
1.5 μs detector delay
100 μs integration time
220 - 950 nm spectral range
Resolution ~ 5000 over range
x10^6
Counts (Bg Corrected)
Wavelength nm
400
600
800
X:610.475 Data:19049 #6 sig[17626]
-20°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
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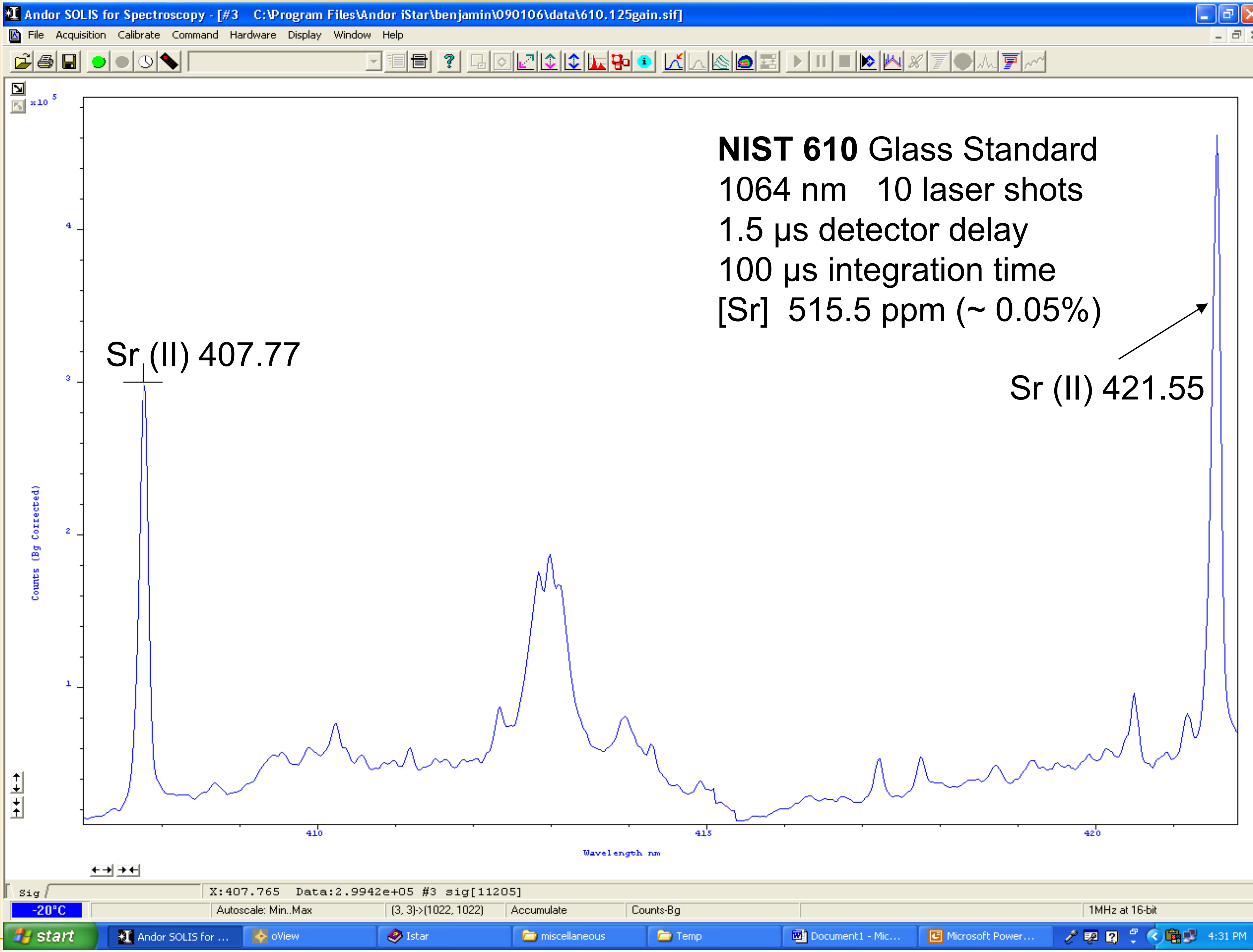
Andor SOLIS for Spectroscopy - [#3 C:\Program Files\Andor iStar\benjamin\090106\data\610.125gain.sif]
File Acquisition Calibrate Command Hardware Display Window Help
NIST 610 Glass Standard
1064 nm 10 laser shots
1.5 µs detector delay
100 µs integration time
[Sr] 515.5 ppm (~ 0.05%)
Sr (II) 407.77
Sr (II) 421.55
x10 5
Counts (Bg Corrected)
1
2
3
4
410
415
420
Wavelength nm
Sig
X:407.765 Data:2.9942e+05 #3 sig[11205]
-20°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
Andor SOLIS for ...
oView
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miscellaneous
Temp
Document1 - Mic...
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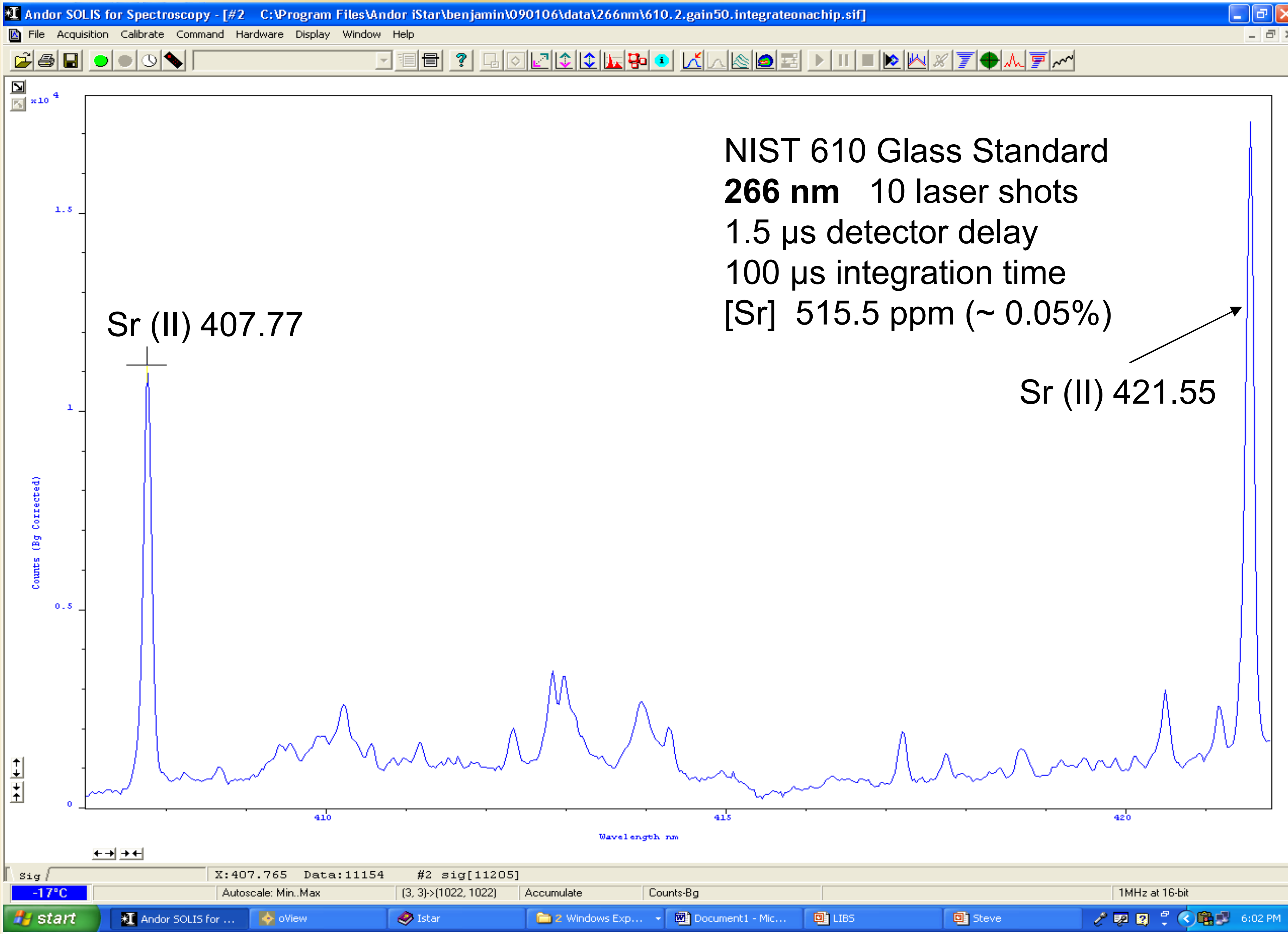
Andor SOLIS for Spectroscopy - [#2 C:\Program Files\Andor iStar\benjamin\090106\data\266nm\610.2.gain50.integrateonachip.sif]
File Acquisition Calibrate Command Hardware Display Window Help
NIST 610 Glass Standard
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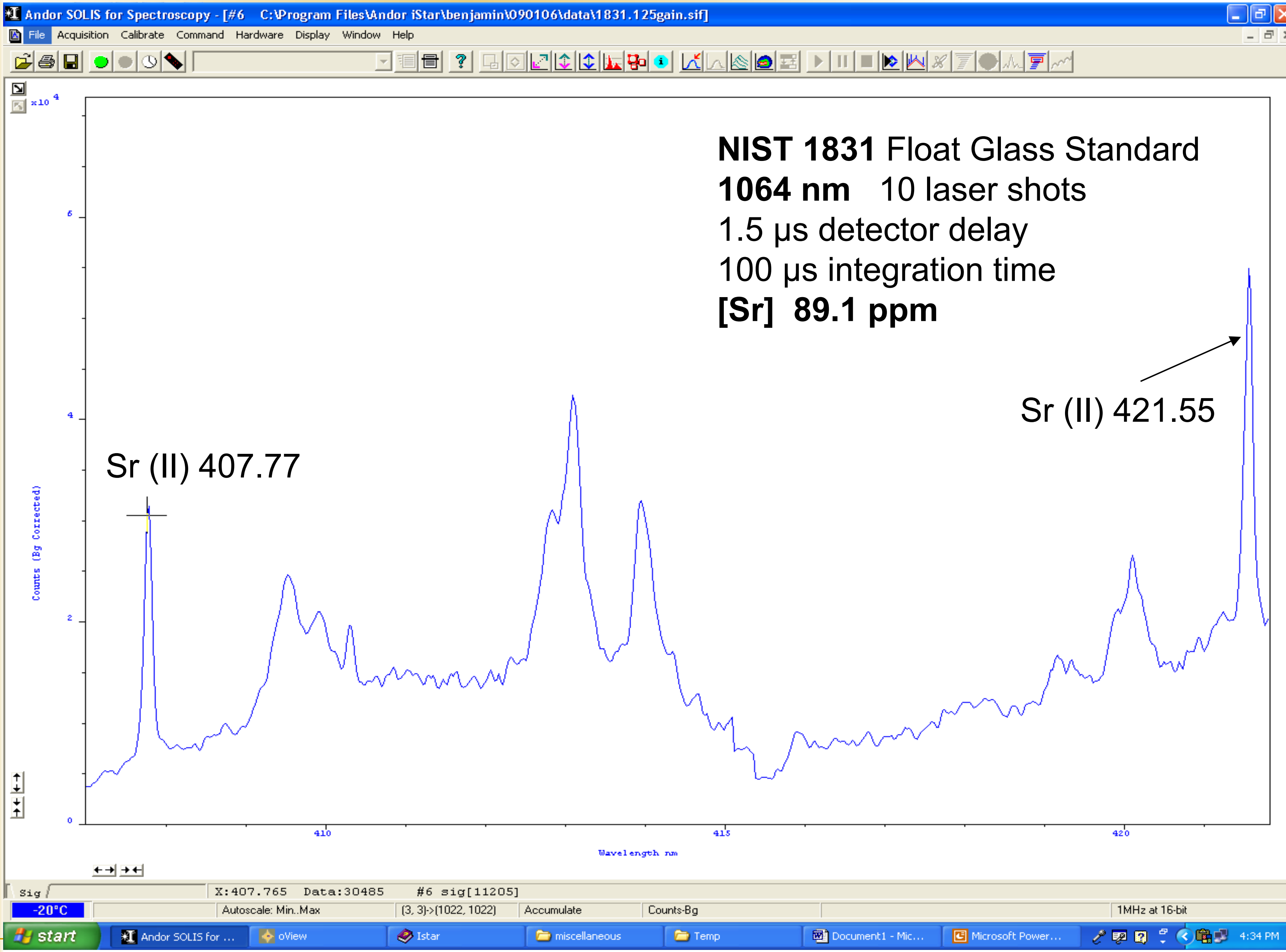
x10 4
1.5
1
0.5
0
Counts (Bg Corrected)
410
415
420
Wavelength nm
Sig
X:407.765 Data:11154 #2 sig[11205]
-17°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
Andor SOLIS for ...
oView
Istar
2 Windows Exp...
Document1 - Mic...
LIBS
Steve
6:02 PM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File Acquisition Calibrate Command Hardware Display Window Help
NIST 1831 Float Glass Standard
1064 nm 10 laser shots
1.5 µs detector delay
100 µs integration time
[Sr] 89.1 ppm
Sr (II) 421.55
Sr (II) 407.77
x10 4
6
4
2
0
Counts (Bg Corrected)
410
415
420
Wavelength nm
Sig
X:407.765 Data:30485 #6 sig[11205]
-20°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
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miscellaneous
Temp
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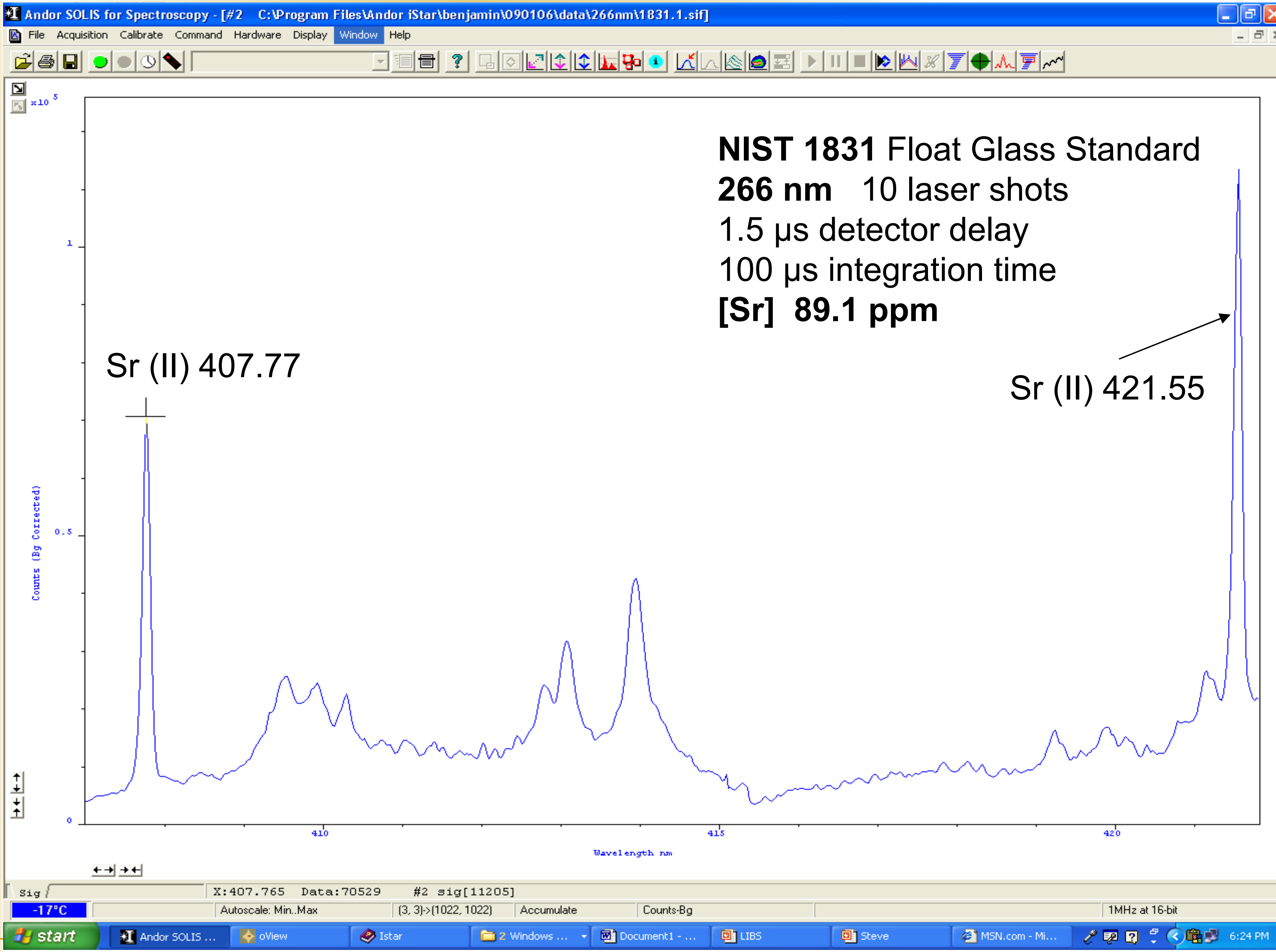
4:34 PM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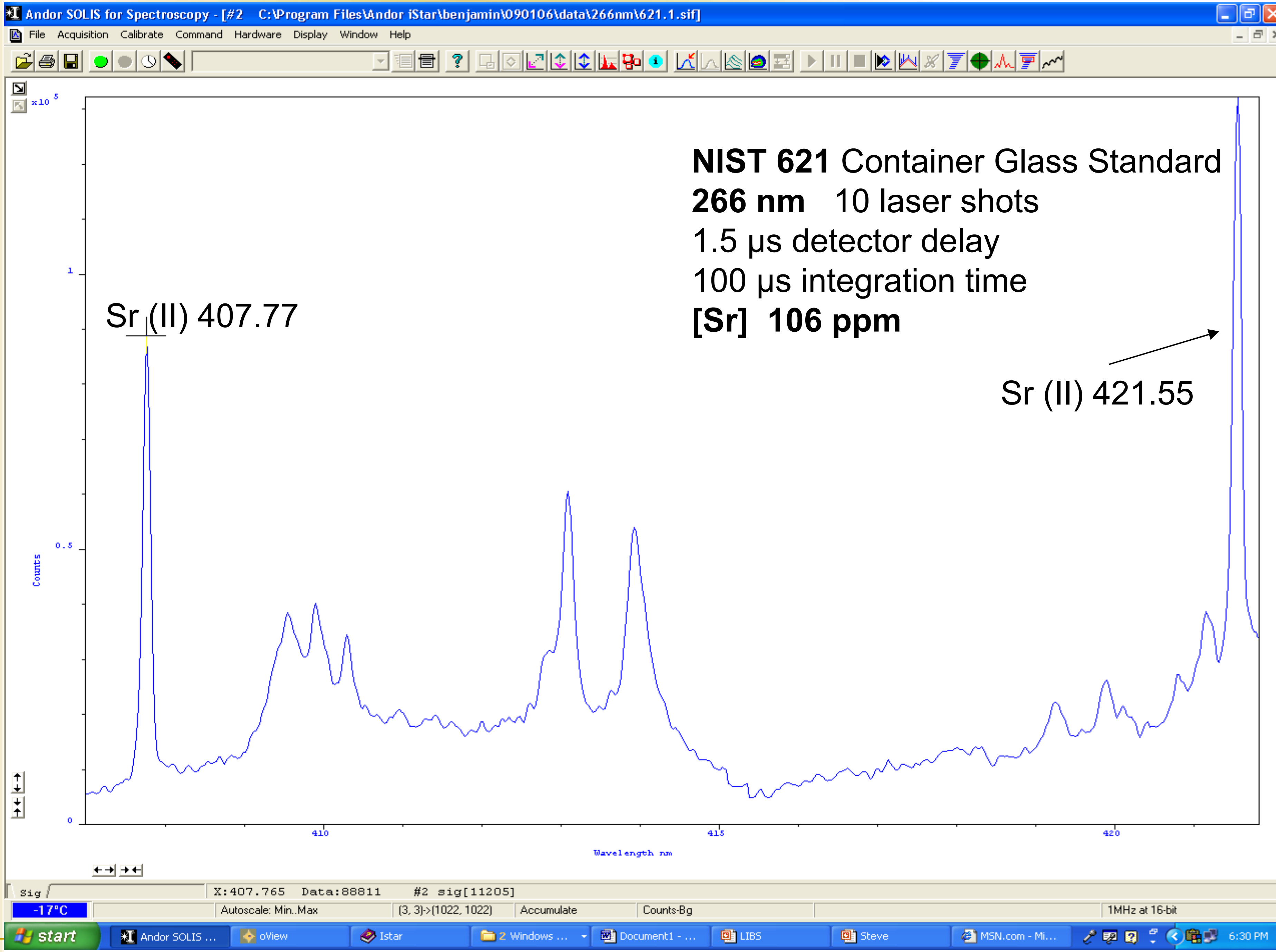
NIST 1831 Float Glass Standard
266 nm 10 laser shots
1.5 µs detector delay
100 µs integration time
[Sr] 89.1 ppm
Sr (II) 407.77
Sr (II) 421.55
x10 5
1
0.5
0
Counts (Bg Corrected)
410
415
420
Wavelength nm
Sig
X:407.765 Data:70529 #2 sig[11205]
-17°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
Andor SOLIS ...
oView
Istar
2 Windows ...
Document1 - ...
LIBS
Steve
MSN.com - Mi...
6:24 PM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File Acquisition Calibrate Command Hardware Display Window Help
NIST 621 Container Glass Standard
266 nm 10 laser shots
1.5 μs detector delay
100 μs integration time
[Sr] 106 ppm
Sr (II) 407.77
Sr (II) 421.55
x10 5
1
0.5
0
Counts
410
415
420
Wavelength nm
Sig
X:407.765 Data:88811 #2 sig[11205]
-17°C
Autoscale: Min..Max
(3, 3)->(1022, 1022)
Accumulate
Counts-Bg
1MHz at 16-bit
start
6:30 PM

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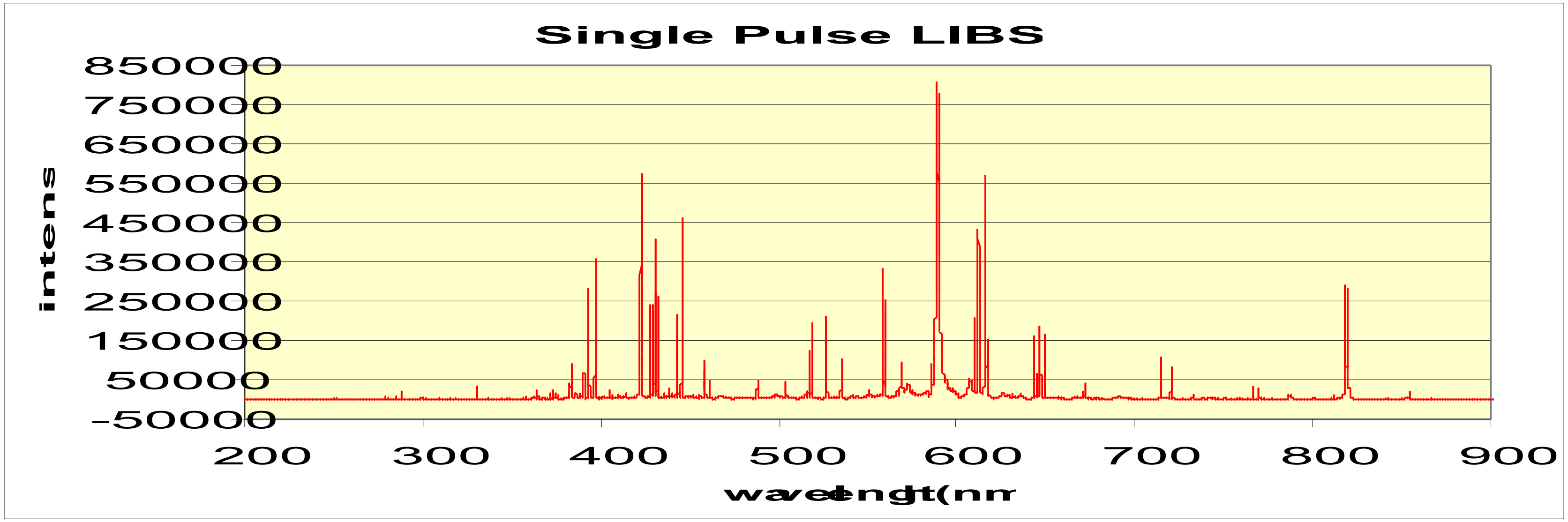
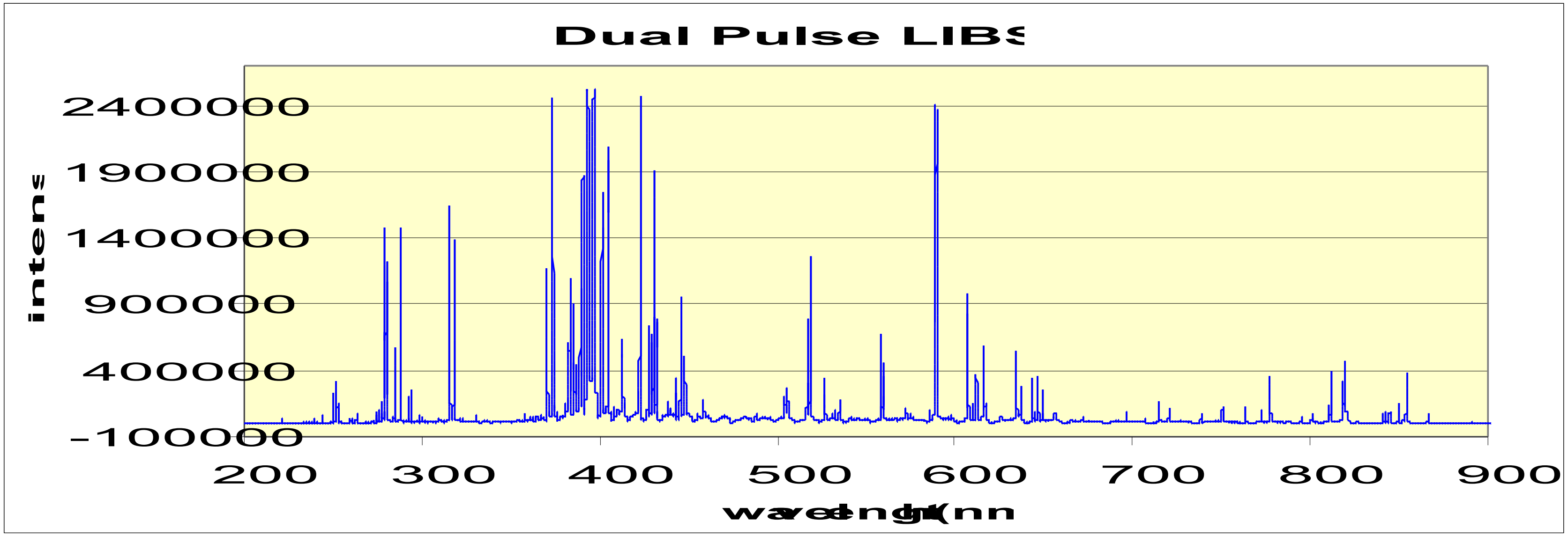
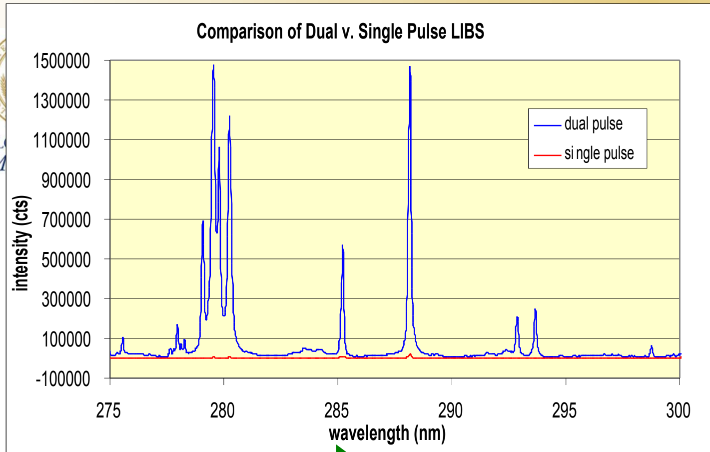
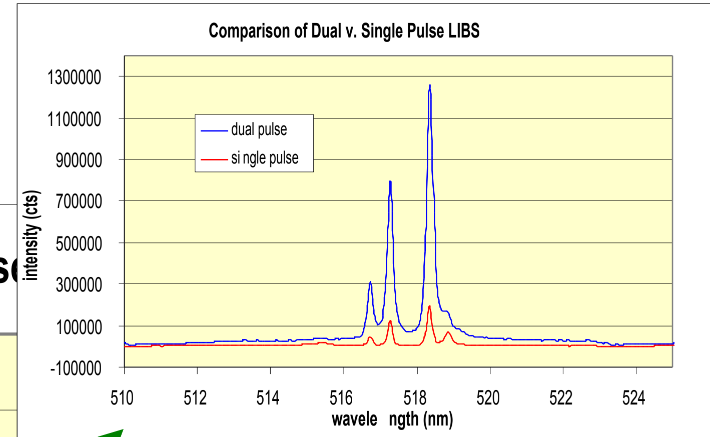




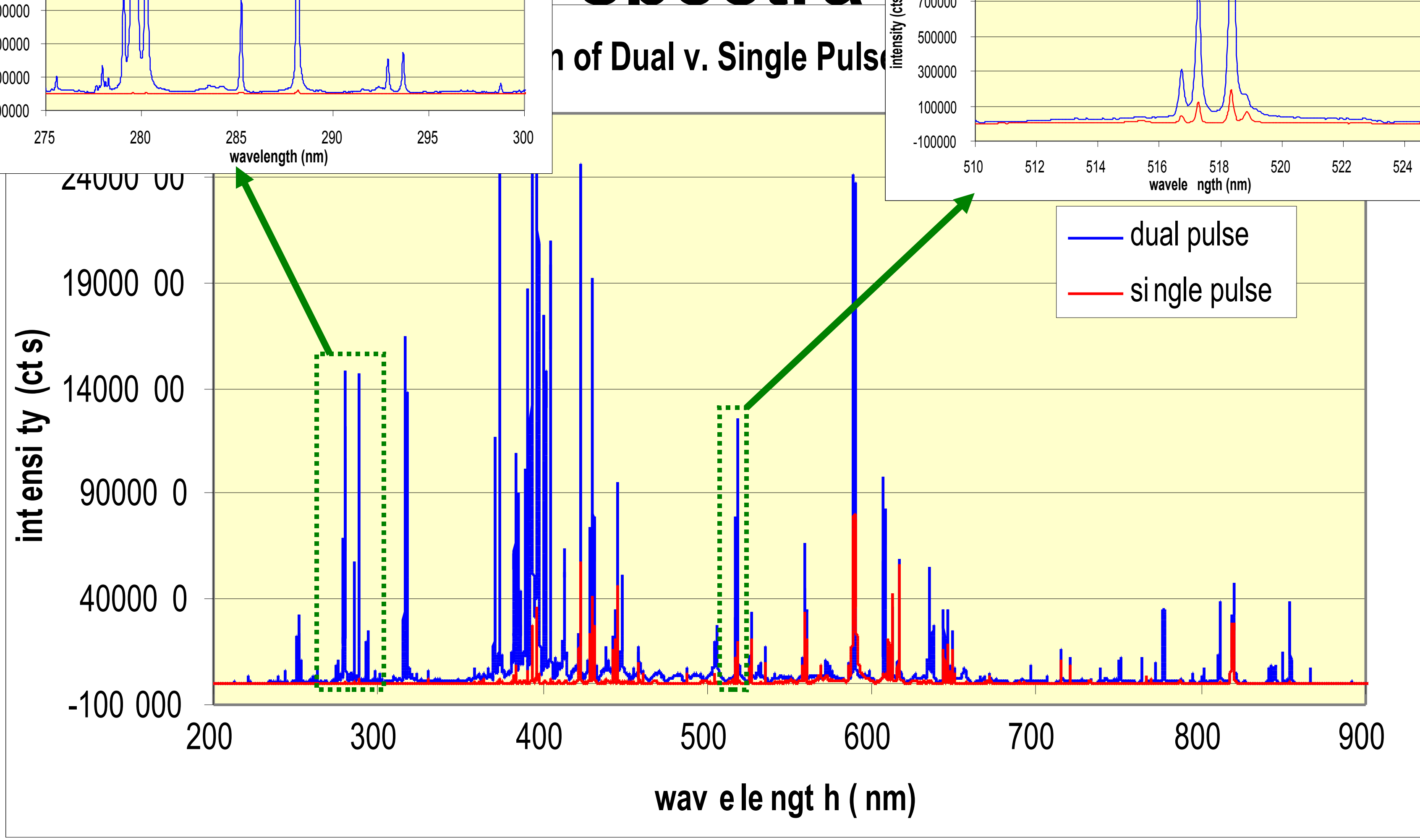
spectra



Comparison of Dual v. Single Pulse LIBS
1500000
1300000
1100000
900000
700000
500000
300000
100000
-100000
intensity (cts)
275
280
285
290
295
300
wavelength (nm)
dual pulse
si ngle pulse

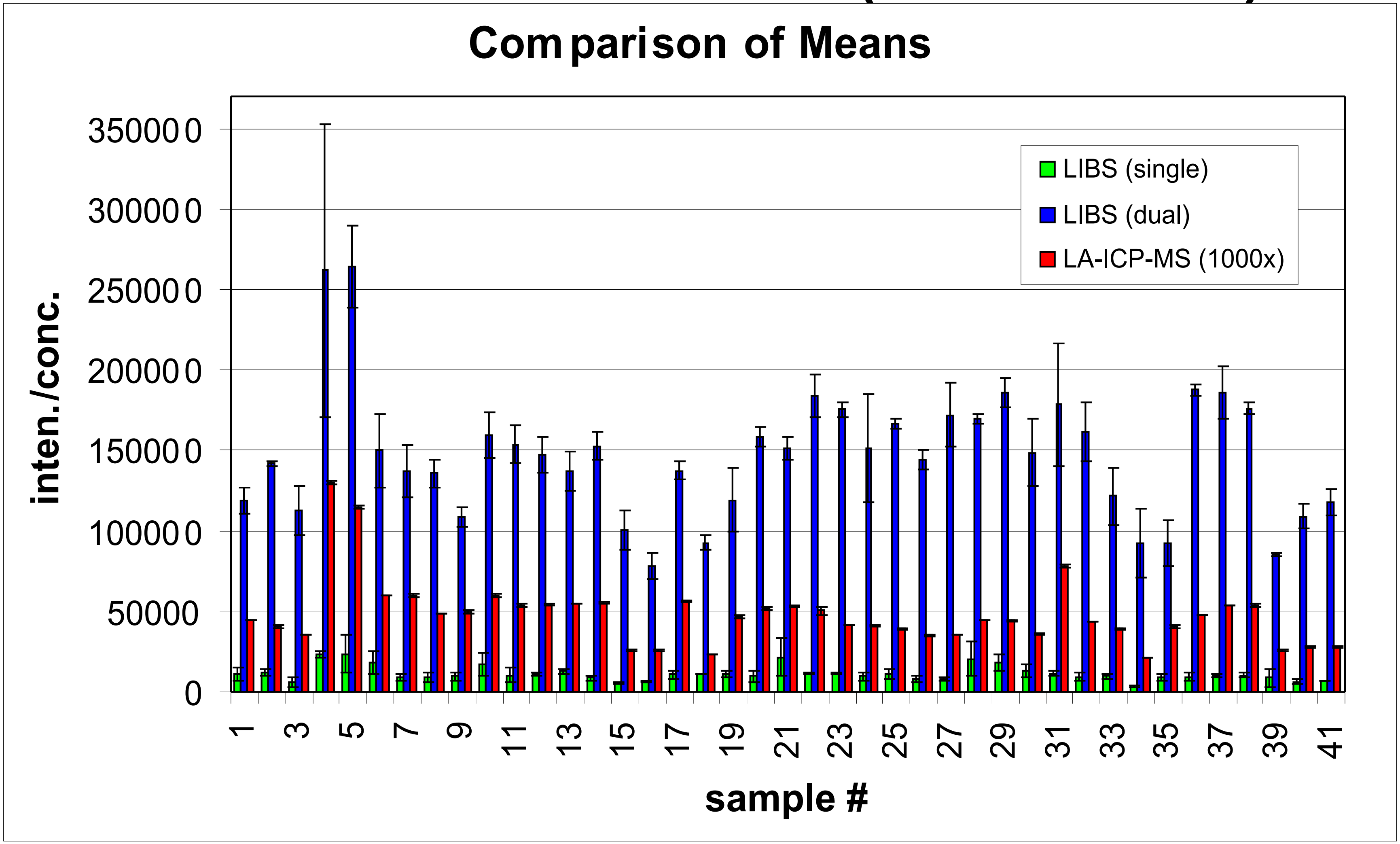


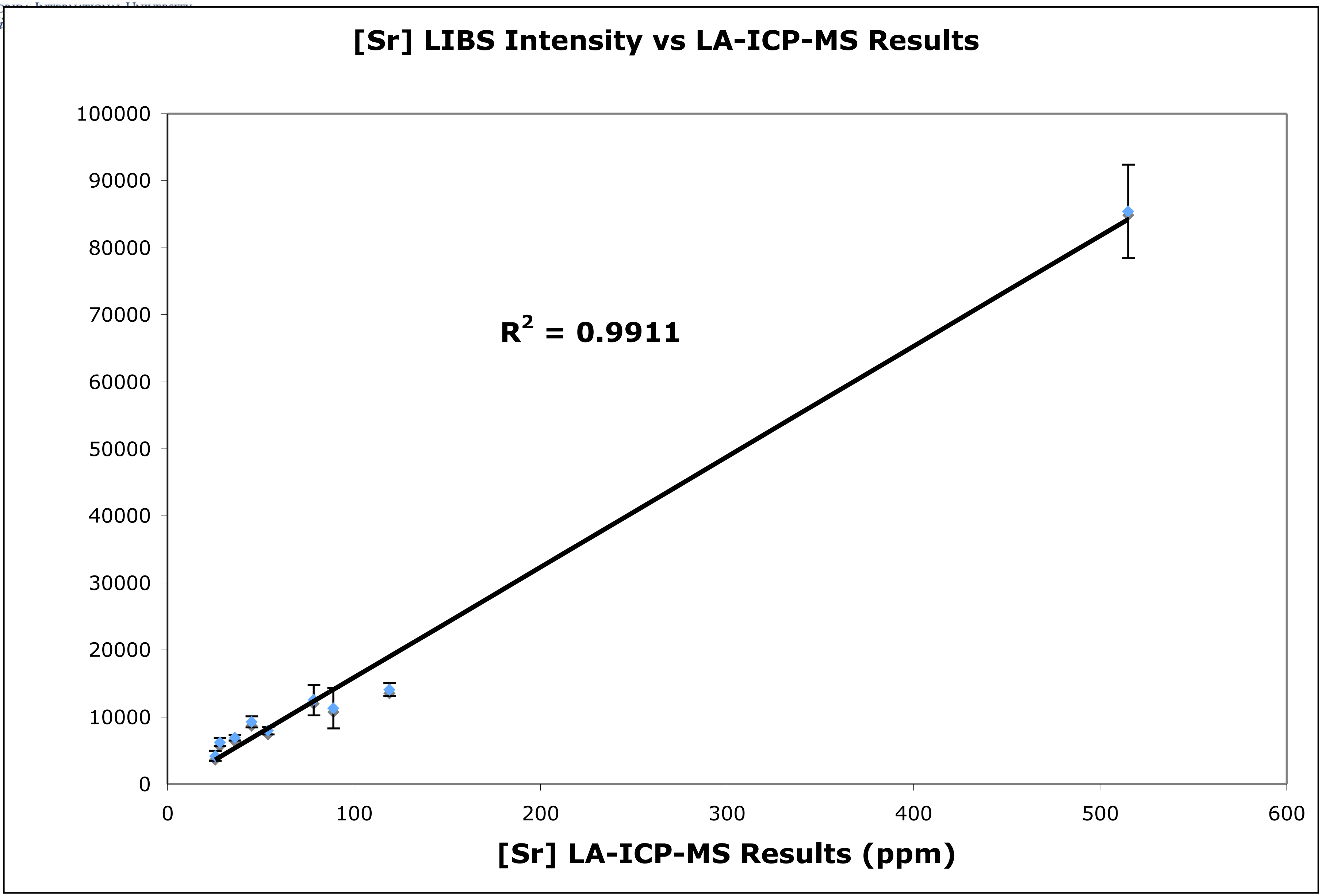
Comparison of Dual v. Single Pulse LIBS
1300000
1100000
900000
700000
500000
300000
100000
-100000
intensity (cts)
510
512
514
516
518
520
522
524
wavele ngth (nm)
dual pulse
si ngle pulse



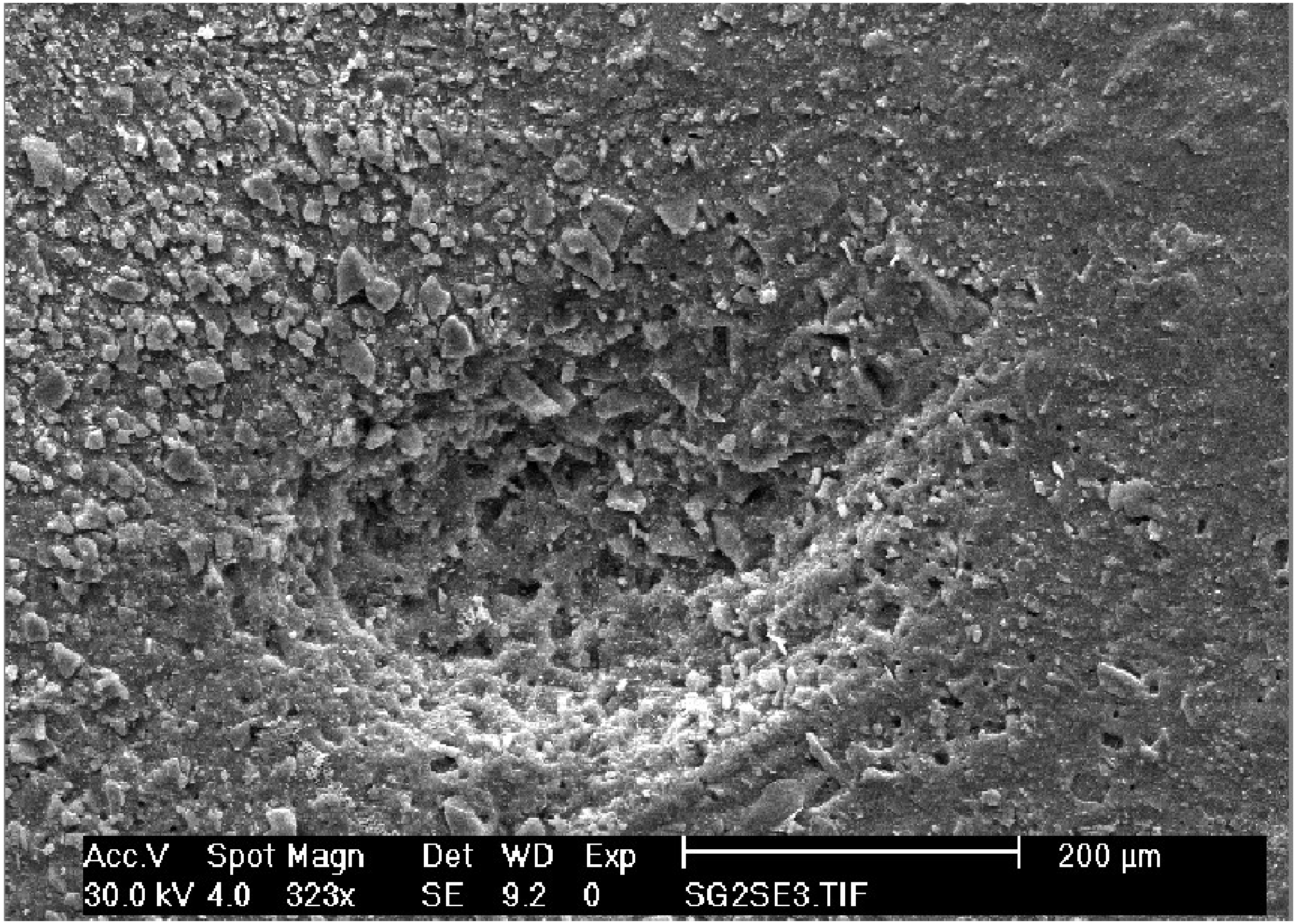
n of Dual v. Single Pulse
19000 00
14000 00
90000 0
40000 0
-100 000
int ensi ty (ct s)
200
300
400
500
600
700
800
900
wav e le ngt h (nm)
dual pulse
si ngle pulse

LIBS & LA-ICP-MS (strontium)





[Sr] LIBS Intensity vs LA-ICP-MS Results
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
100
200
300
400
500
600
R2 = 0.9911
[Sr] LA-ICP-MS Results (ppm)


Acc.V Spot Magn Det WD Exp
30.0 kV 4.0 323x SE 9.2 0
200 µm
SG2SE3.TIF

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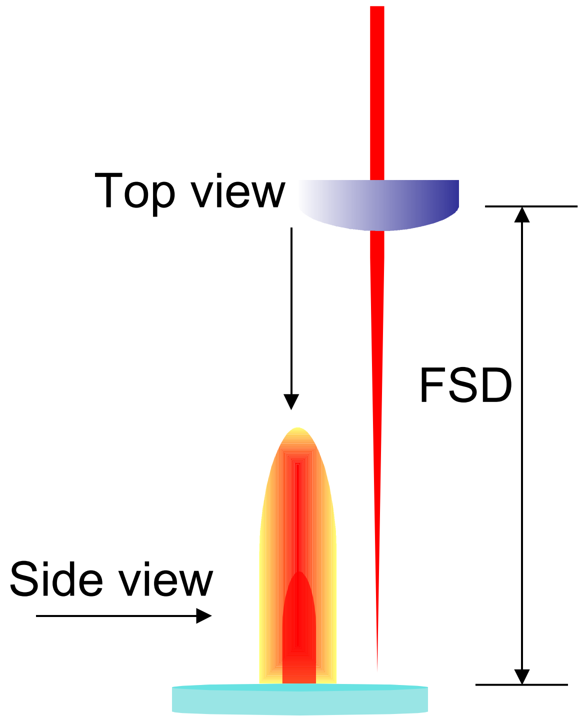
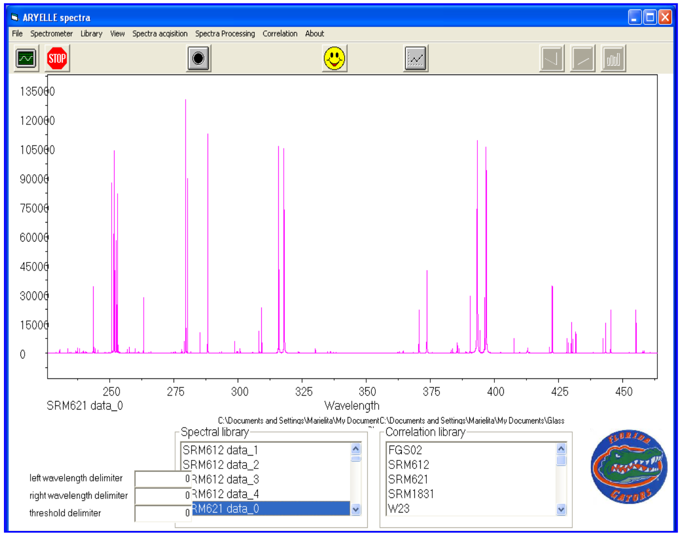
Reproducibility

- **Sampling and homogeneity (> 50 shots for sampling are necessary to sample enough material)**
- Laser stability
  - 266nm ± 7
  - 1064nm ± 4

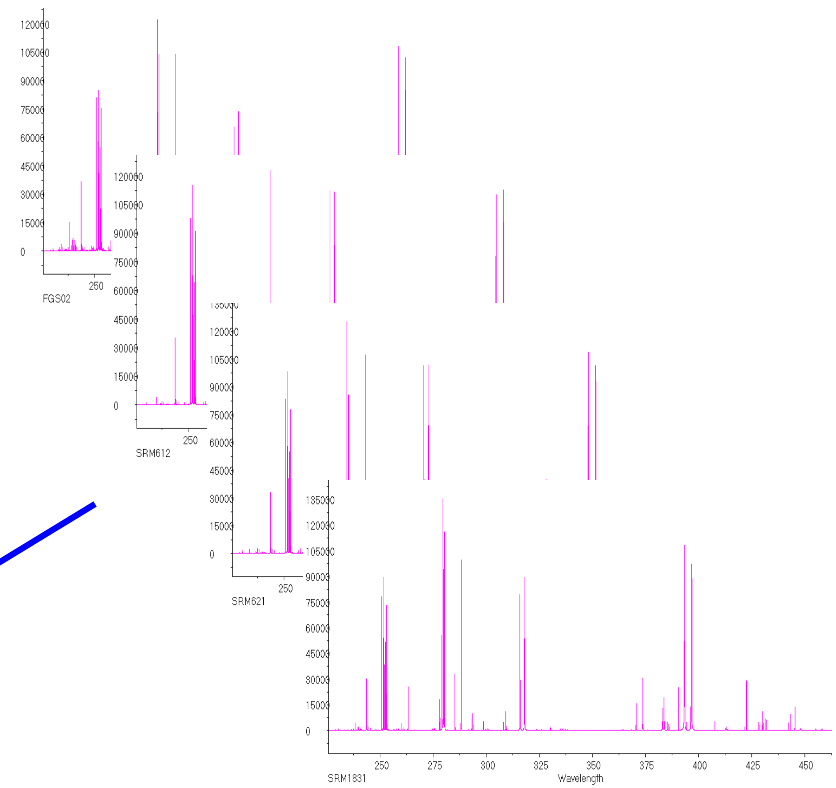
    (After 30 min warm up)

- Focus to Sample Distance (FSD)
- Single pulse intensity usually less reproducible than dual pulse intensity
- Emission observation
  - Top view of plasma S/N are generally larger when the plasma is viewed on the axis parallel with the incoming laser beam
  - Plasma expands in the lateral and perpendicular direction in dual pulse scheme

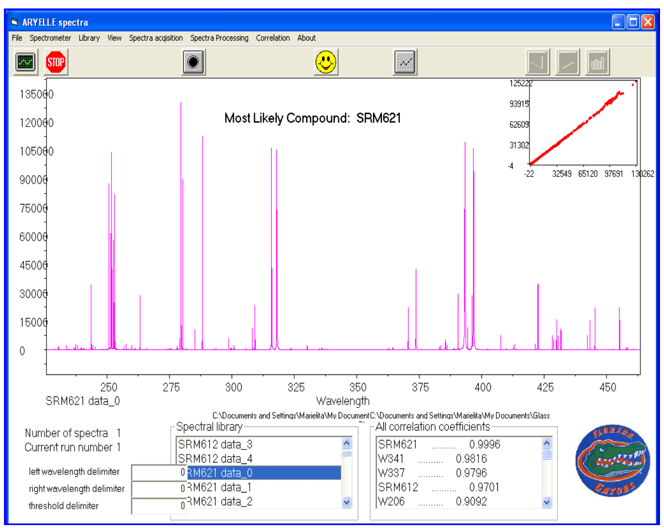




1. *Spectrum from unknown source*



2. *Search through spectral library*

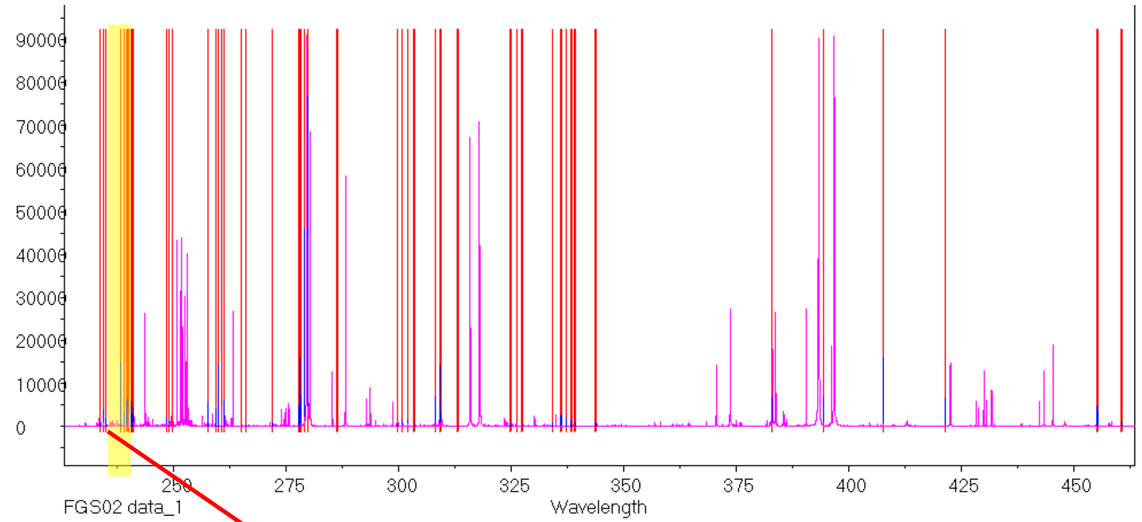


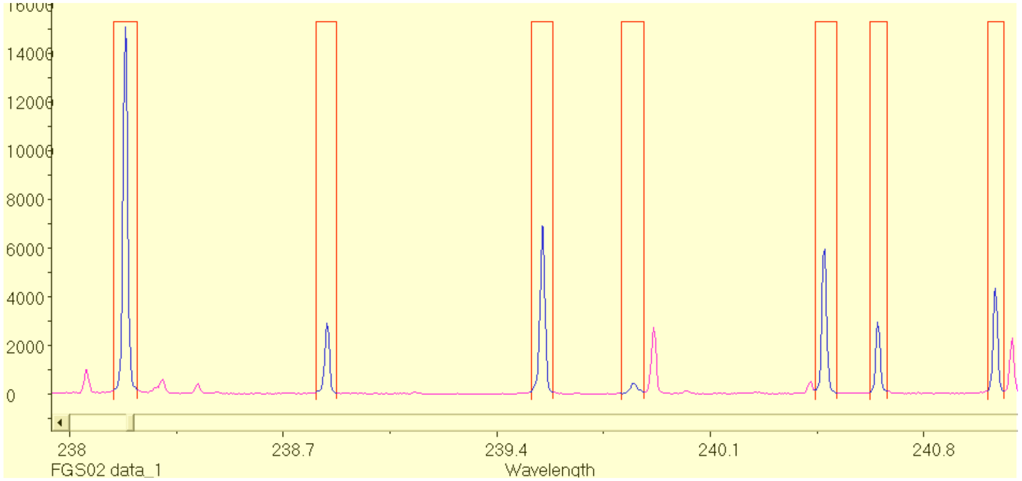
3. *Determining the most likely material*

Courtesy of Mariela Rodriguez and Igor Gornushkin, Dept. of Chemistry, UF

Element	wavelength (nm)
Al I	266.039
Al I	308.215
Al I	309.284
Al I	394.401
BI	249.677
BaII	233.527
BaII	455.403
BeI	234.861
BeI	265.062
BeII	313.042
BeII	313.107
CaI	239.856
CaI	299.732
CaI	300.686
CuI	324.754
CuI	327.396
FeI	248.327
FeI	248.814
FeI	271.903
FeI	302.064
FeII	234.35
FeII	238.204
FeII	238.863
FeII	239.563
FeII	240.489
FeII	240.666
FeII	241.052
FeII	259.94
FeII	261.187
MgI	277.669
MgI	277.827
MgI	277.983
MgI	278.142
MgI	278.297
MgI	382.936
MgII	279.078
MgII	279.8
MnII	257.61
MnII	259.372
MnII	260.568
SnI	286.332
SnI	303.412
SnI	326.234
SrI	460.733
SrII	407.771
SrII	421.552
TiI	334.187
TiII	334.941
TiII	336.122
TiII	337.28
TiII	338.377
ZrII	339.198
ZrII	343.823

Selection of characteristic lines for the correlation





Courtesy of Mariela Rodriguez and Igor Gornushkin, Dept. of Chemistry, UF

Linear Correlation (67%)

Glass ID	Correctly Identified	Incorrectly Identified	Confused with sample ID	%Correctly identified
SRM 612	5	0		100
SRM 621	5	0		100
SRM 1831	5	0		100
FGS02	5	0	W310, W153	60
1	2	3	2, 31, 14	60
2	1	4	10, 11, 14	20
3	5	0		100
4	1	4	2, 4, 11	20
5	4	1	13	80
6	4	1	7	80
7	3	2	6, 15	60
8	3	2	9, 20, 38	60
9	4	1	19	80
10	5	0		100
11	4	1	2	80
12	5	0		100
13	3	2	2, 11	60
14	4	1	10	80
15	3	2	6, 10	60
16	3	2	33, 39	60
17	3	2	16, 25	60
18	5	0		100
19	3	2	19, 22	60
20	4	1	8	80
21	2	3	20, 22, 38	40
22	5	0		100
23	2	3	24, 28, 33	40
24	3	2	23, 28	60
25	4	1	38	80
26	1	4	30, 35, 39	20
27	2	3	16, 25	40
28	3	2	29	60
29	3	2	10, 33	60
30	4	1	1	80
31	4	1	33	80
32	2	3	10, 30, 33	40
33	3	2	25, 34	60
34	4	1	16	80
35	1	4	10, 25, 26, 33	20
36	2	3	19, 20, 39	40
37	1	4	21, 38, 39	20
38	2	3	37, 39	40
39	3	2	10, 27	60
40	4	1	41	80
41	2	3	9, 40	40

Rank Correlation (99%)

Glass ID	Correctly Identified	Incorrectly Identified	Confused with sample ID	%Correctly identified
SRM 612	5	0		100
SRM 621	5	0		100
SRM 1831	5	0		100
FGS02	5	0		100
1	5	0		100
2	3	2	1	60
3	5	0		100
4	5	0		100
5	5	0		100
6	3	2	7	60
7	5	0		100
8	5	0		100
9	5	0		100
10	5	0		100
11	3	2	12	60
12	5	0		100
13	5	0		100
14	5	0		100
15	5	0		100
16	5	0		100
17	5	0		100
18	5	0		100
19	5	0		100
20	5	0		100
21	5	0		100
22	5	0		100
23	5	0		100
24	5	0		100
25	5	0		100
26	5	0		100
27	5	0		100
28	5	0		100
29	5	0		100
30	5	0		100
31	5	0		100
32	5	0		100
33	5	0		100
34	5	0		100
35	5	0		100
36	5	0		100
37	5	0		100
38	5	0		100
39	5	0		100
40	5	0		100
41	5	0		100

Courtesy of Mariela Rodriguez and Igor Gornushkin, Dept. of Chemistry, UF

Comparison between methods for elemental analysis of glass samples

Parameter	SEM/EDS	EMPA	XRF	LIBS	LA-ICP-MS
Operating Principle	**Energetic (20kV) electrons knock off inner shell electron. Relaxation of outer shell electron to the vacant position causes emission of characteristic X-Rays.**	**An energetic (15kV) electron beam interacts with the material producing the emission of characteristic X-Rays, backscattered and secondary electrons.**	**High energy X-Rays knock off inner shell electron. Relaxation of outer shell electron to vacant position causes emission of characteristic X-Rays.**	**Laser photons induce breakdown on sample surface. Deionization radiation in the UV/VIS is characteristic of element.**	**Laser photons ablate (remove) material from sample surface. Sub-micron sized particles are transported into ICP followed by MS detection.**
Sample penetration	~ 5 microns	<< 1 micron	> 100 microns	~ 50 microns (operator controlled)	~ 80 microns (operator controlled)
Sensitivity (detection limit)	1000 ppm (0.1%)[1]	100 ppm (0.01%)	100 ppm (0.01%)[1]	10-50 ppm[2]	< 1 ppm[3]
Precision	Poor	Fair	Fair-good	Fair-good	Excellent
Accuracy	Qualitative	Semi-quantitative	Semi-quantitative	Semi-quantitative	Quantitative
Analysis time	Slow	Slow	Very Slow	Fast	Slow
Sample Consumption	non-destructive	non-destructive	non-destructive	almost non-destructive	almost non-destructive
Complexity	Easy to Use	Complicated	Easy to Use	Very Easy to Use	Complicated
Cost	$250,000.00	$600,000.00	$130,000.00	$60,000.00	$300,000.00
Discrimination	Poor	Fair	Good	Good	Excellent

1. P.G. Statham, et al, X-ray spectrometry in electron beam instruments, Plenum, N.Y., NY **1995**: 103.
2. K. Loebe, Microanalysis of tool Steel and glass with laser-induced breakdown spectroscopy. Applied Optics, **2003**, 42(30)
3. T. Trejos and J.R. Almirall, Analytical Chemistry, **2004**, 76(5) 1236-1242.

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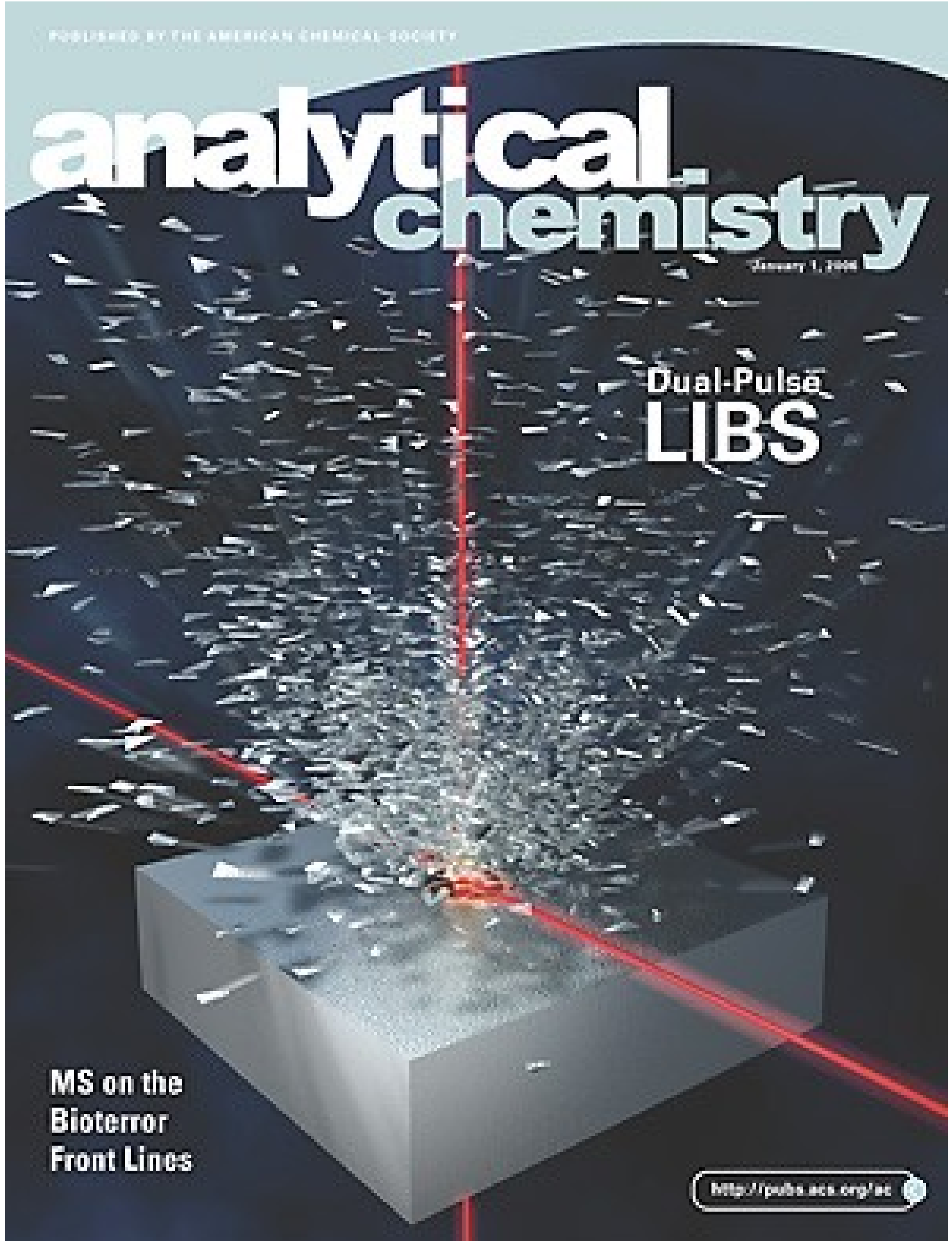

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CSI, Las Vegas episode: "What's eating Gil Grisham"

Slide courtesy of John Roy, New Wave Research

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Acknowledgements

- Collaborators in the NITECRIME network
- UF and FDLE Collaborators
- MDPD, Miami - CFS, Toronto
- NIJ -LA-ICP-MS- (2003-IJ-CX-K004)
- NSF - Major Instrumentation - (CHE-0420874)
- FIU Provost Research Award - LIBS
- NIJ -LIBS- (2005-IJ-CX-K069)
- Dr. Cleon Barnett (Post-doc)
- All current and former students

No official endorsement from the government should be inferred

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PhD Chem
PhD Chem
MSFS
BS Chem
Post-Doc

* Presenting at this AAFS meeting

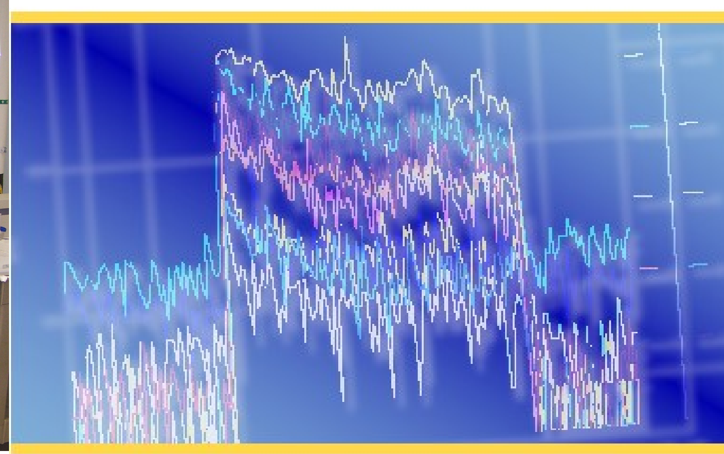
Elemental Analysis of Forensic Evidence

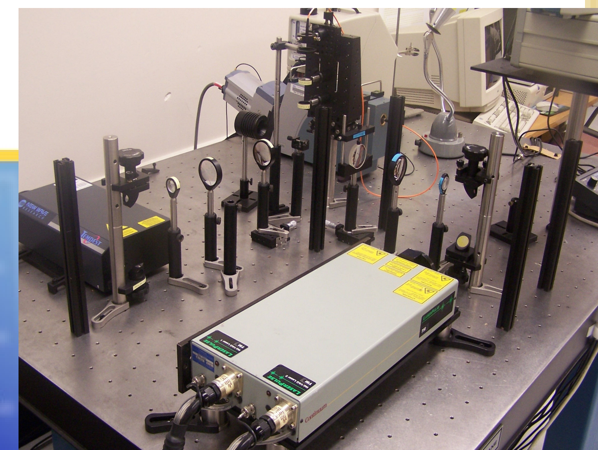
"Hands-on" Workshop

Dec. 10-14, 2007

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

teaf forensic elemental solutions





Florida International University - Miami, FL
Department of Chemistry and Biochemistry and
International Forensic Research Institute (IFRI)

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XRF Results

- **when fragment sizes are > 2-3 mm, 3 of 210 possible pairs are not distinguished**
- **for fragments sizes ~ 2 mm, 5 of 210 are not distinguished**
- **11 of 210 pairs are not distinguished for sample sizes between 1 and 1.5 mm in length**

- For the large glass sample size (> 2-3 mm, and using a +/- 3 SD criterion for the Ca/Fe net intensity ratios, 35 pairs were found to be indistinguishable (17% indistinguishable).
- Using a +/- 3 SD criterion for the Sr/Zr net intensity ratios, 102 pairs were found to be indistinguishable (49% indistinguishable).
- Using both elemental ratios, 15 pairs (7%) were found to be indistinguishable
- Adding the Ca/Mg ratios permitted 4 additional pairs to be discriminated so 95 percent of the 210 pairs were discriminated using calculated Ca/Fe, Sr/Zr, and Ca/Mg ratios alone.
- Direct comparison of the remaining eleven pairs' spectra permitted discrimination of eight more pairs (either by Ca/Si ratios or other trace elemental components such as Ti or K levels), resulting in 98% of the sample pairs being differentiated.

Casework examples

Hit-and-run

Hit-and-run

Hit-and-run

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Hit-and-run

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Hit-and-run

Hit-and-run

Hit-and-Run

Item # 14: 1 sealed glassine bag containing glass found in shower .

Item # 15: 1 sealed glassine bag containing glass found in the living room .

Item # 16: 1 sealed glassine bag containing glass found on the black pants.

Item # 17: 10 sealed glassine bags containing glass samples from the standard [Windshield standard].

Item # 18: 1 sealed glassine bag containing glass collected from the black shirt.

Analysis Procedure

The concentrations of each of the following 37 metal isotopes were measured for each of the recovered samples (Items # 14, 15, 16 and 18) with the standard glass recovered from the windshield of the vehicle.

^{7}Li, ^{11}B, ^{25}Mg, ^{27}Al, ^{39}K, ^{42}Ca, ^{49}Ti, ^{55}Mn, ^{59}Co, ^{65}Cu, ^{66}Zn, ^{71}Ga, ^{85}Rb,^{88}Sr, ^{90}Zr, ^{93}Nb, ^{118}Sn, ^{123}Sb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{147}Sm, ^{151}Eu,^{159}Tb, ^{165}Ho, ^{169}Tm, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{197}Au, ^{208}Pb, ^{209}Bi, ^{232}Th, and ^{238}U.

The concentrations of each of the following 15 metal isotopes were used for comparison for each of the recovered samples (Items # 14, 15, 16 and 18) with the standard glass recovered from the windshield of the vehicle.

^{27}Al, ^{39}K , ^{49}Ti, ^{55}Mn, ^{57}Fe, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{137}Ba, ^{139}La, ^{140}Ce, ^{178}Hf, ^{208}Pb, ^{232}Th, and ^{238}U

Truth table

QuickTime™ and a
TIFF (Uncompressed) decompressor
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