Characterization of Corning Standard Glasses 95IRV, 95IRW, and 95IRX

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Outline: Corning 95-Series Standards

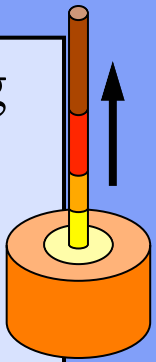
- History.
- Analytical methods summary.
- X-ray spectra -- EDS and WDS.
- EPMA element migration and homogeneity measurements.
- ICP-AES and XRF analysis.
- Results and comparision of analyses.
- Summary.
- Contact information.

History

- 1971: Art Chodos and Arden Albee at Caltech contracted Corning Glass Works to prepare glasses. Ultimately to be used as microanalysis trace element standards.
- NIST SRM 612-616 are Na-bearing high SiO_2 glasses. EPMA use is problematic due to migration and beam damage. Utilized as secondary standards.
- Higher trace element concentrations requested.
- Trace element inventory chosen to avoid peak overlaps as well as possible.
- Ca-Al-Mg borosilicate matrix chosen to avoid migration and beam damage.
- 22 elements were batched at a nominal concentration of ~0.79 % oxide in 3 glasses.

History

- Each batch subjected to two cycles of melting and stirring in Pt-Rh lined container.
- Continuous ~ 0.25 inch glass rod was formed by slowly drawing from the melt.
- Master rod cut into 9 sections and numbered.
- Material made available to MAS. End users were supplied with ~ 1/8-inch thick disc from the end of each rod.
- Glasses were distributed as GLV, GLW, and GLX.
- Bulk wet chemistry performed on material from beginning of rod; also middle and end were used to evaluate homogeneity along length.



Matrix Composition and Dopant Inventory

Average Matrix Composition, Weight %		
B_2O_3	4.4	Similar to An_{40-60} Plagioclase Feldspar
MgO	9.2	95 (-B, Mg, dopants) + (Na) ~ = Plagioclase
Al_2O_3	19.2	Recommend 20 µm minimum beam diameter
SiO_2	60	Probe current ~100 nA
CaO	6.7	
Sum	~ 95	
Dopants	~ 5	

95IRV	K Ti Cr Fe Ce Hf	Green
95IRW	V Mn Co Cu Cs Ba La Th	Blue
95IRX	Ni Zn Rb Sr Y Zr Pb U	Brown

Source Materials: 95-Series Glasses

		95IRV		95IRW		95IRX	
Oxide	**Source Material**	**Oxide g**	**Weight %**	**Oxide g**	**Weight %**	**Oxide g**	**Weight %**
B_2O_3	Anhydrous B_2O_3	56.00	4.42	56.00	4.36	56.00	4.35
MgO	Magnesium Oxide MgO (Bac)	112.00	8.84	112.00	8.72	112.00	8.70
Al_2O_3	T 61 Alumina, 100 mesh (Al_2O_3)	226.00	17.84	226.00	17.60	226.00	17.56
SiO_2	Milled African Sand (SiO_2)	733.00	57.86	733.00	57.09	733.00	56.95
K_2O	K_2CO_3 dry (5.6 g)	3.82	0.30				
K_2O	$K_2Cr_2O_7$ (19.4 g)	6.21	0.49				
CaO	$CaSO_4$*1/2 H_2O (208 g)	80.36	6.34	80.36	6.26	80.36	6.24
TiO_2	Titanium Dioxide TiO_2 (F.M.A.)	10.00	0.79				
V_2O_3	Vandium Pentoxide A.R. (V_2O_5 10 g)			8.24	0.64		
Cr_2O_3	$K_2Cr_2O_7$ (19.4 g)	10.02	0.79				
MnO	Manganese Dioxide A.R. (MnO_2 10 g)			8.16	0.64		
FeO	Iron Oxide Fe_2O_3 (10 g)	9.00	0.71				
CoO	Cobalt Oxide, A.R. (CoO)			10.00	0.78		
NiO	Nickel Oxide NiO, A.R.					10.00	0.78

Source Materials: 95-Series Glasses, Cont.

		95IRV		95IRW		95IRX	
Oxide	**Source Material**	**Oxide g**	**Weight %**	**Oxide g**	**Weight %**	**Oxide g**	**Weight %**
CuO	Copper Oxide, Black, A.R. (CuO)			10.00	0.78		
ZnO	Zinc Oxide ZnO (F.G.S.-8)					10.00	0.78
Rb_2O	Rb_2CO_3 (12.4 g)					10.04	0.78
SrO	$SrCO_3$, Allied, (14.4 g)					10.11	0.79
Y_2O_3	Yttrium Oxide (Y_2O_3)					10.00	0.78
ZrO_2	ZrO_2 (Tizon)					10.00	0.78
Cs_2O	Cs_2CO_3 (11.7 g)			10.12	0.79		
BaO	$BaCO_3$ Allied 1404 (12.9 g)			10.02	0.78		
La_2O_3	Lanthanum Oxide (La_2O_3)			10.00	0.78		
Ce_2O_3	CeO_2 (W.R. Grace, 10 g)	10.49	0.83				
HfO_2	Hafnium Oxide (HfO_2)	10.00	0.79				
PbO	Lead Oxide PbO (E.F.)					10.00	0.78
ThO_2	Thorium Oxide (ThO_2)			10.00	0.78		
UO_2	Uranium Oxide U_3O_8 (10 g)					9.62	0.75
Sum		1266.9	100	1283.90	100	1287.13	100

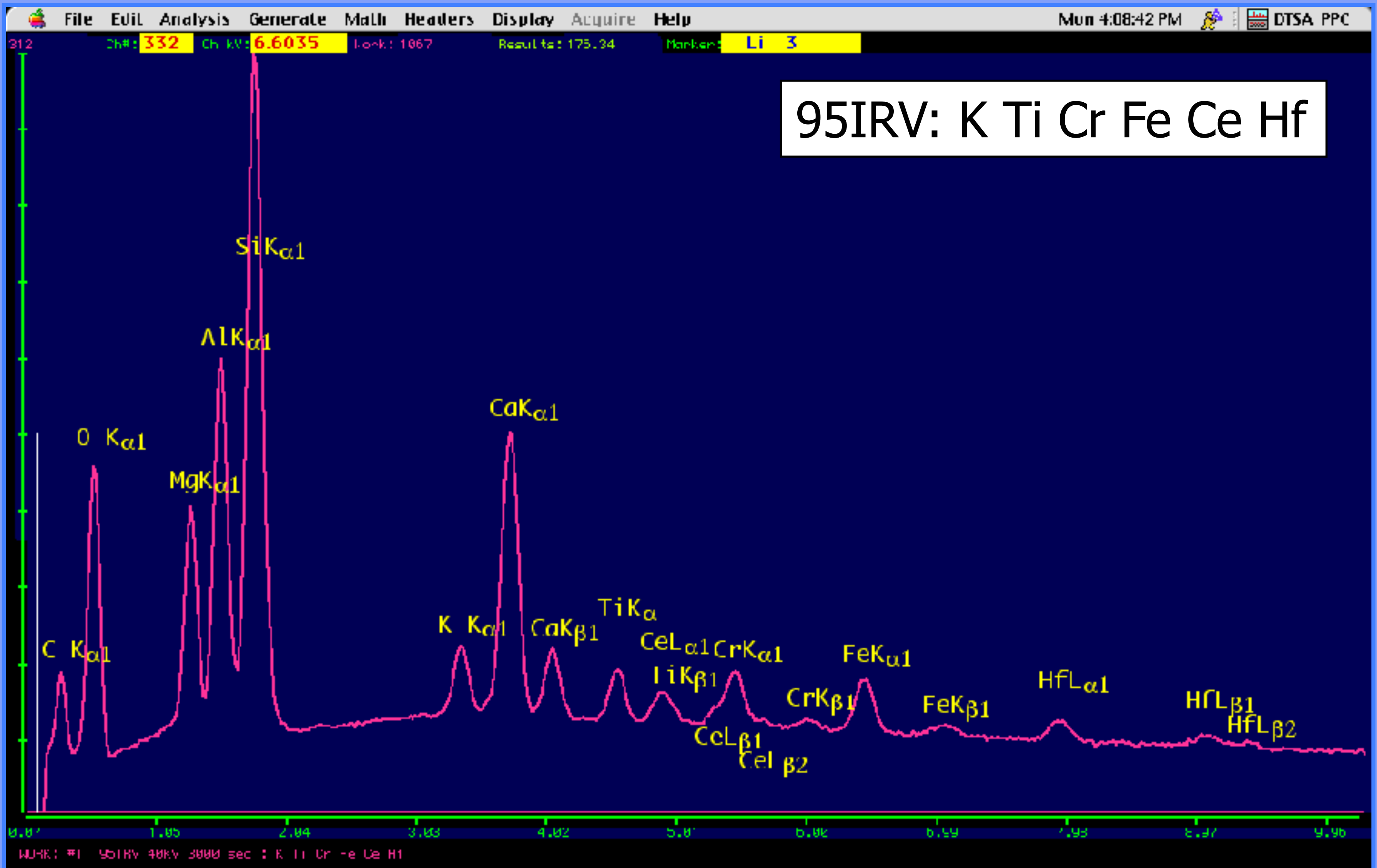
Analytical Methods 1971 - 1990's Excluding EPMA

- Atomic Absorption Spectrophotometry, Colorimetry:
  Eugene Jarosewich, Smithsonian Institution
  Jun Ito, University of Chicago (including analyses at 3 positions along length of rod)
- Gravimetry:
  Corning Glass Works
- X-ray Fluorescence Spectrometry:
  Corning Glass Works
  NASA, Johnson Space Center
- Instrumental Neutron Activation Analysis:
  Oregon State University, Undergraduate Project.

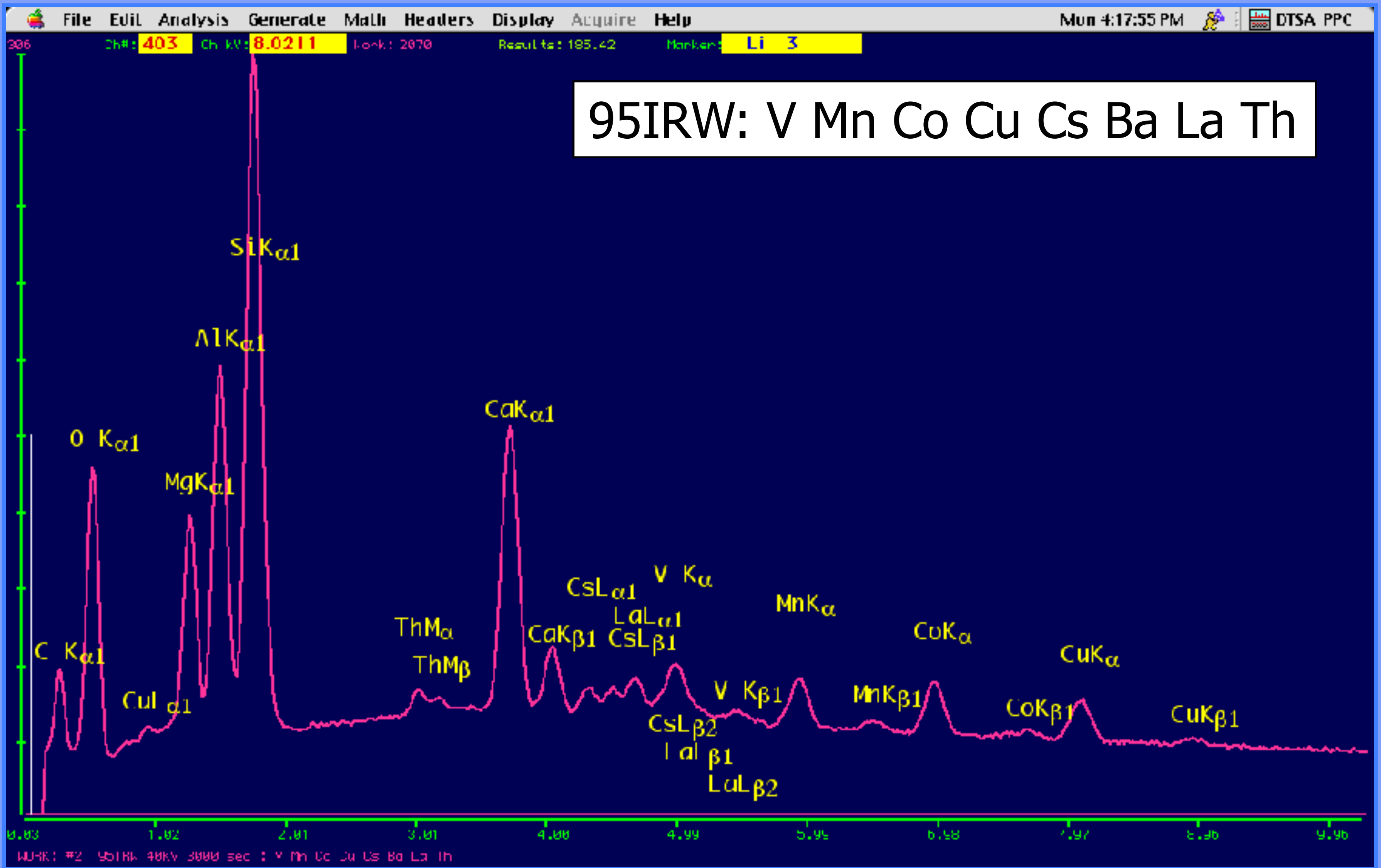
Analytical Methods 1990's - Present

- Electron probe microanalysis:
  Paul Carpenter, Caltech and MSFC
  No formal EPMA Round Robin Program
- X-ray fluorescence spectrometry:
  Emily Kluk, Los Alamos National Laboratory (WDXRF)
  Paul Carpenter, Caltech (EDXRF)
- Inductively-coupled plasma atomic-emission spectrometry:
  Dale Counce, Los Alamos National Laboratory
  Carol Nabelek, University of Missouri

EDS: 95IRV 40 KeV 3000 sec

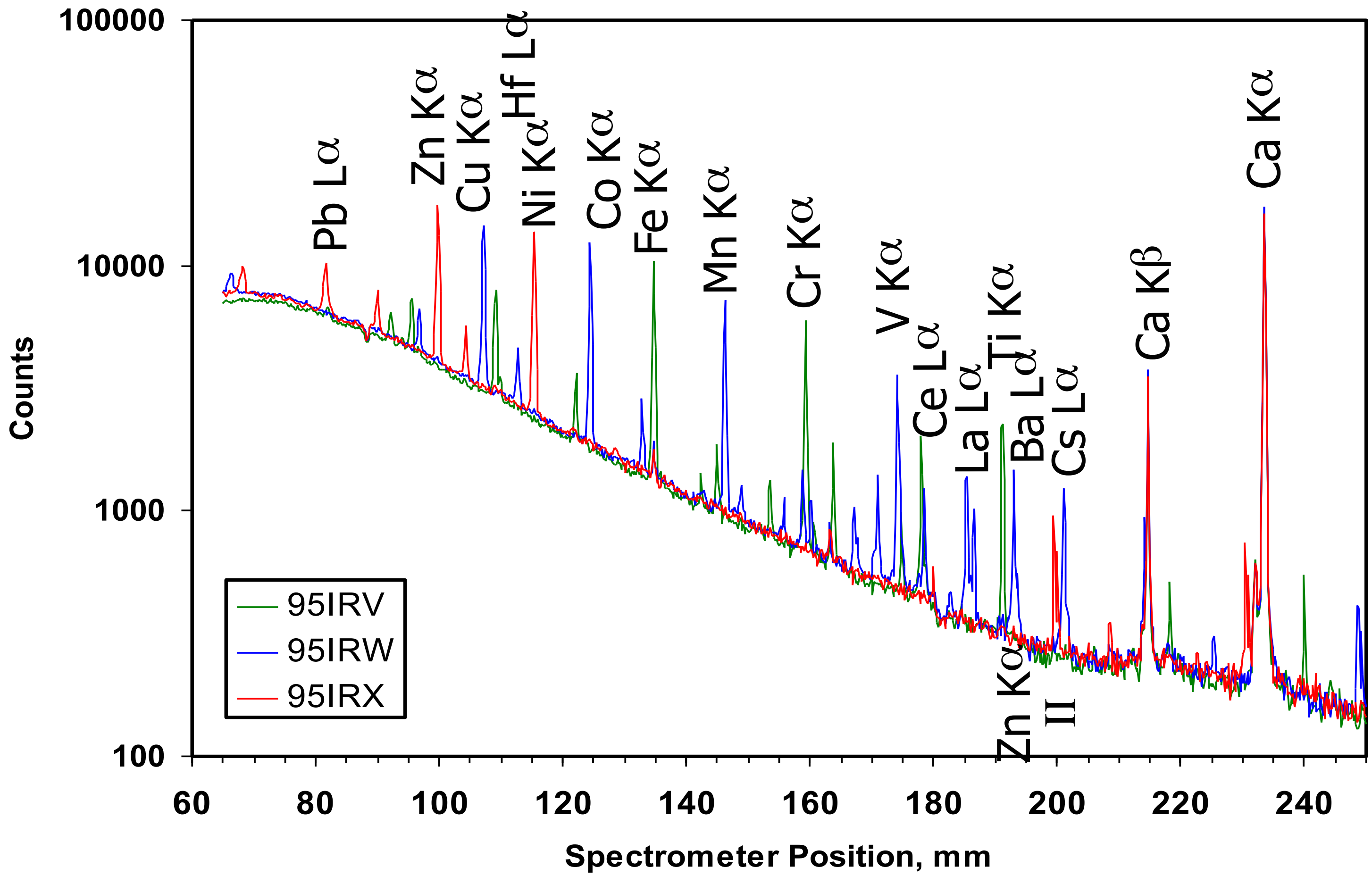


EDS: 95IRW 40 KeV 3000 sec

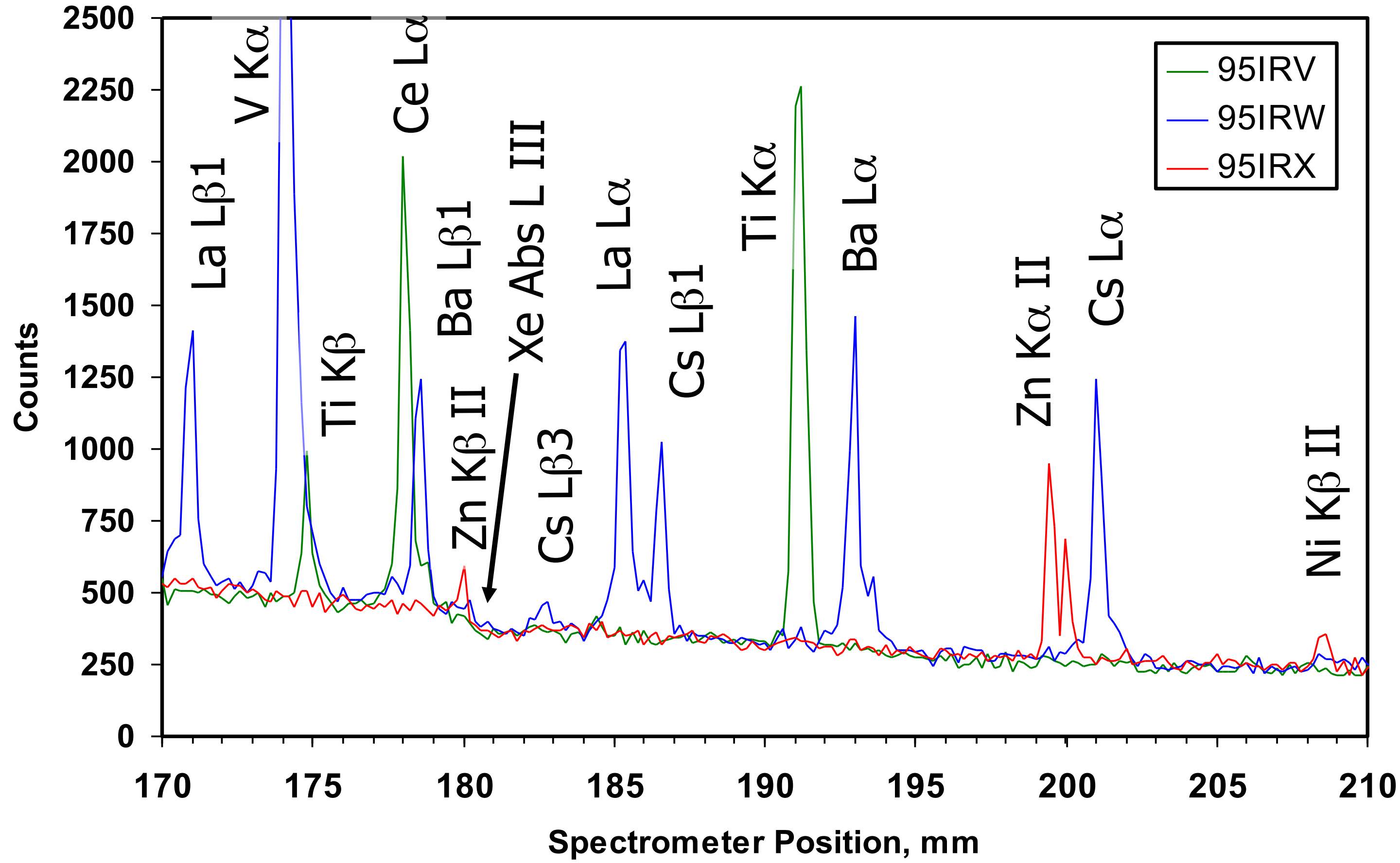


EDS: 95IRX 40 KeV 3000 sec

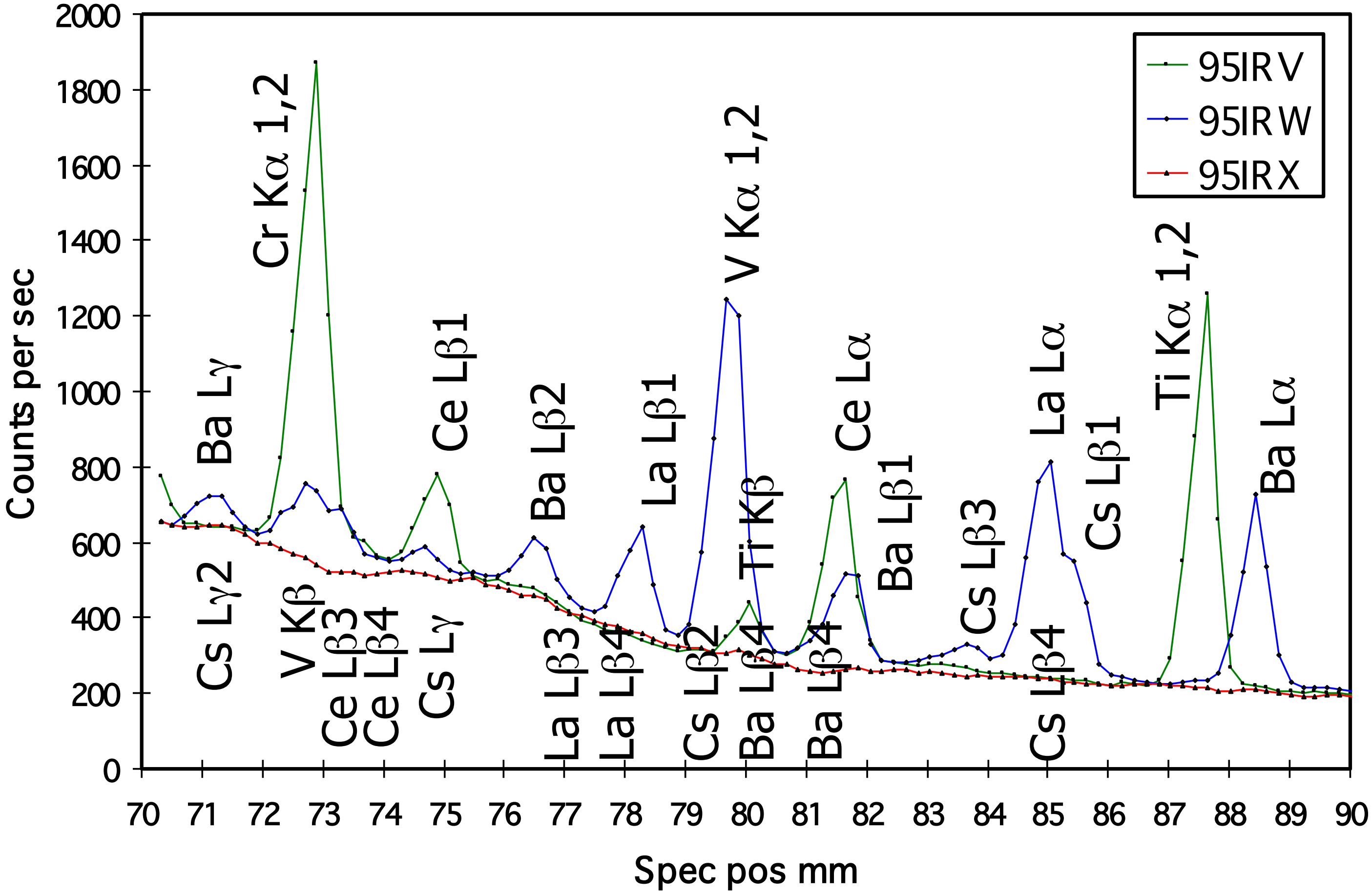
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red



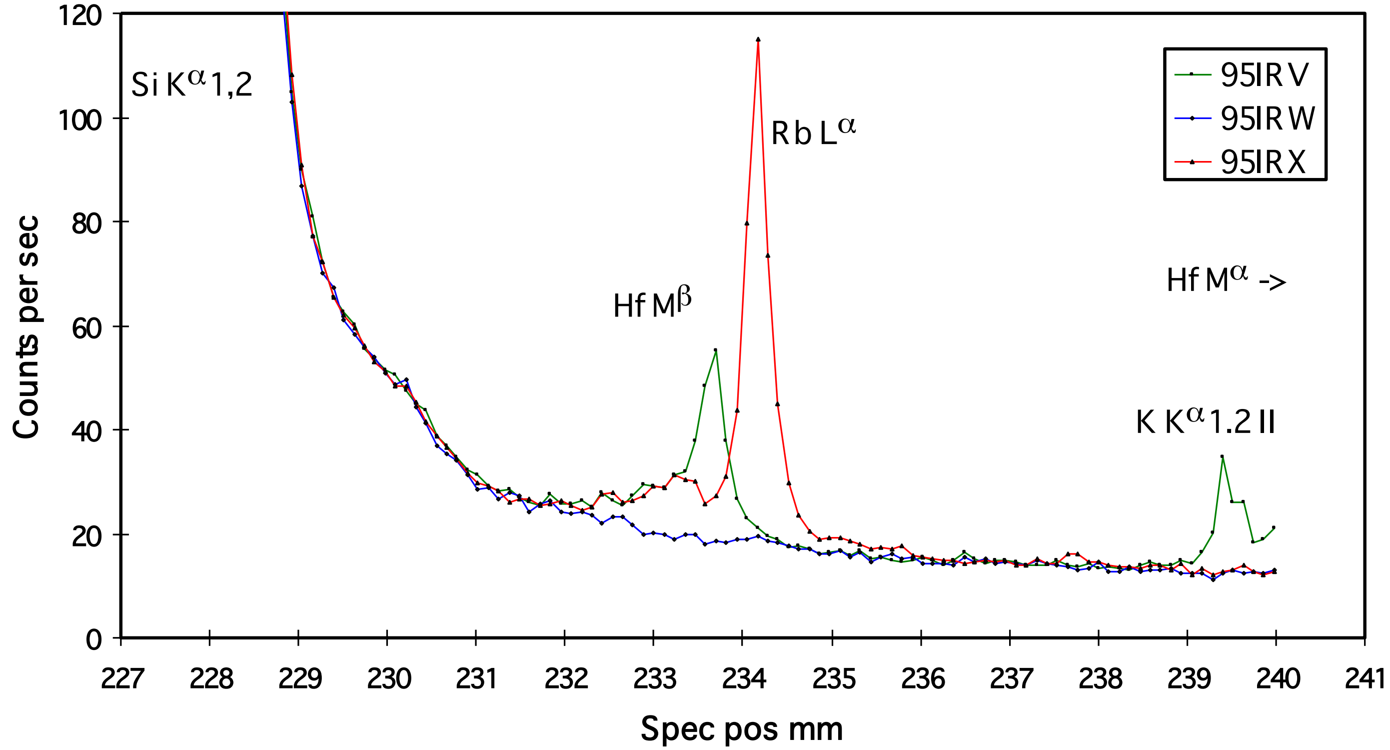
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red



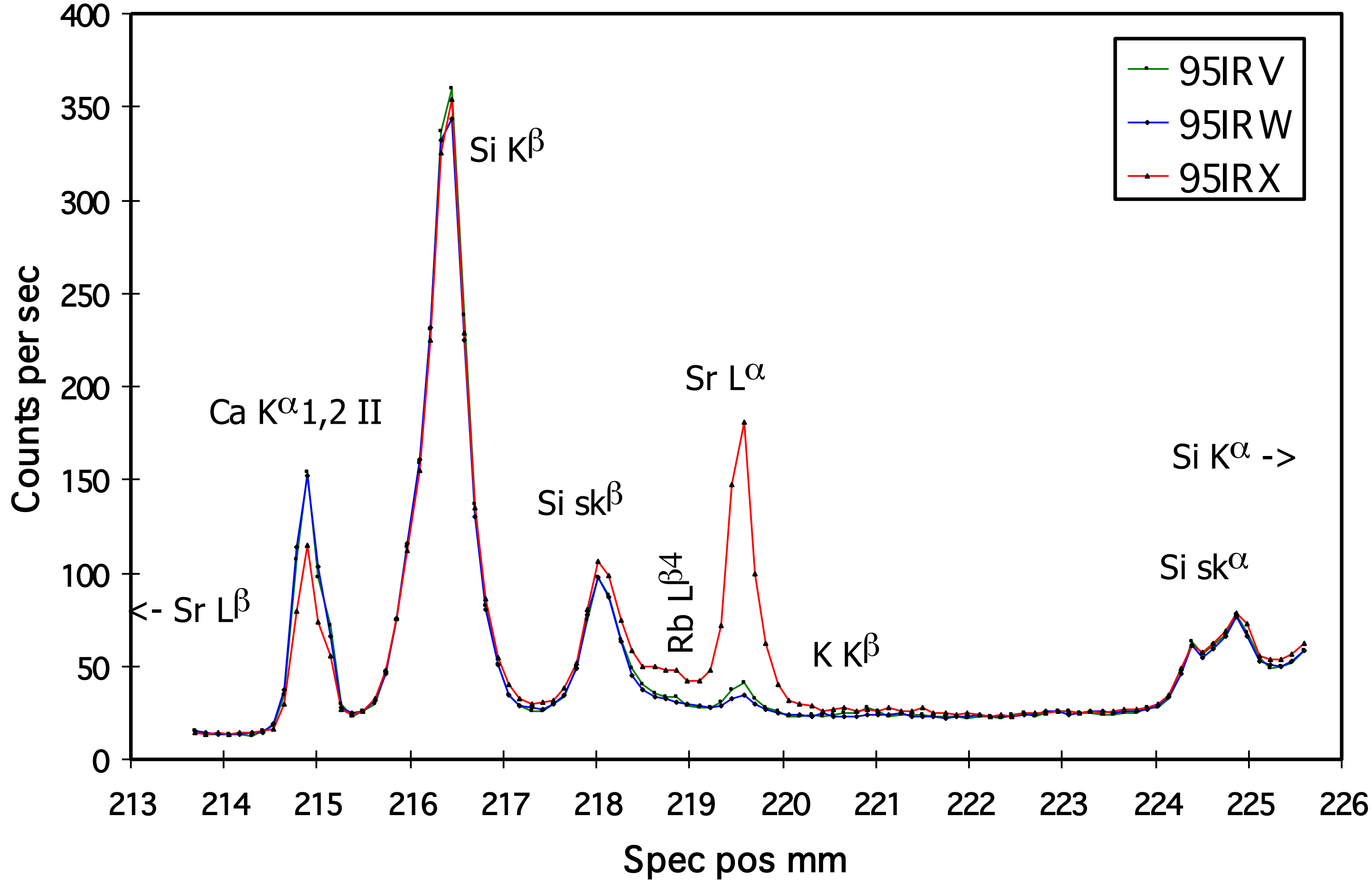
WDS Scan: PET Crystal
95IRV Green, 95IRW Blue, 95 IRX Red



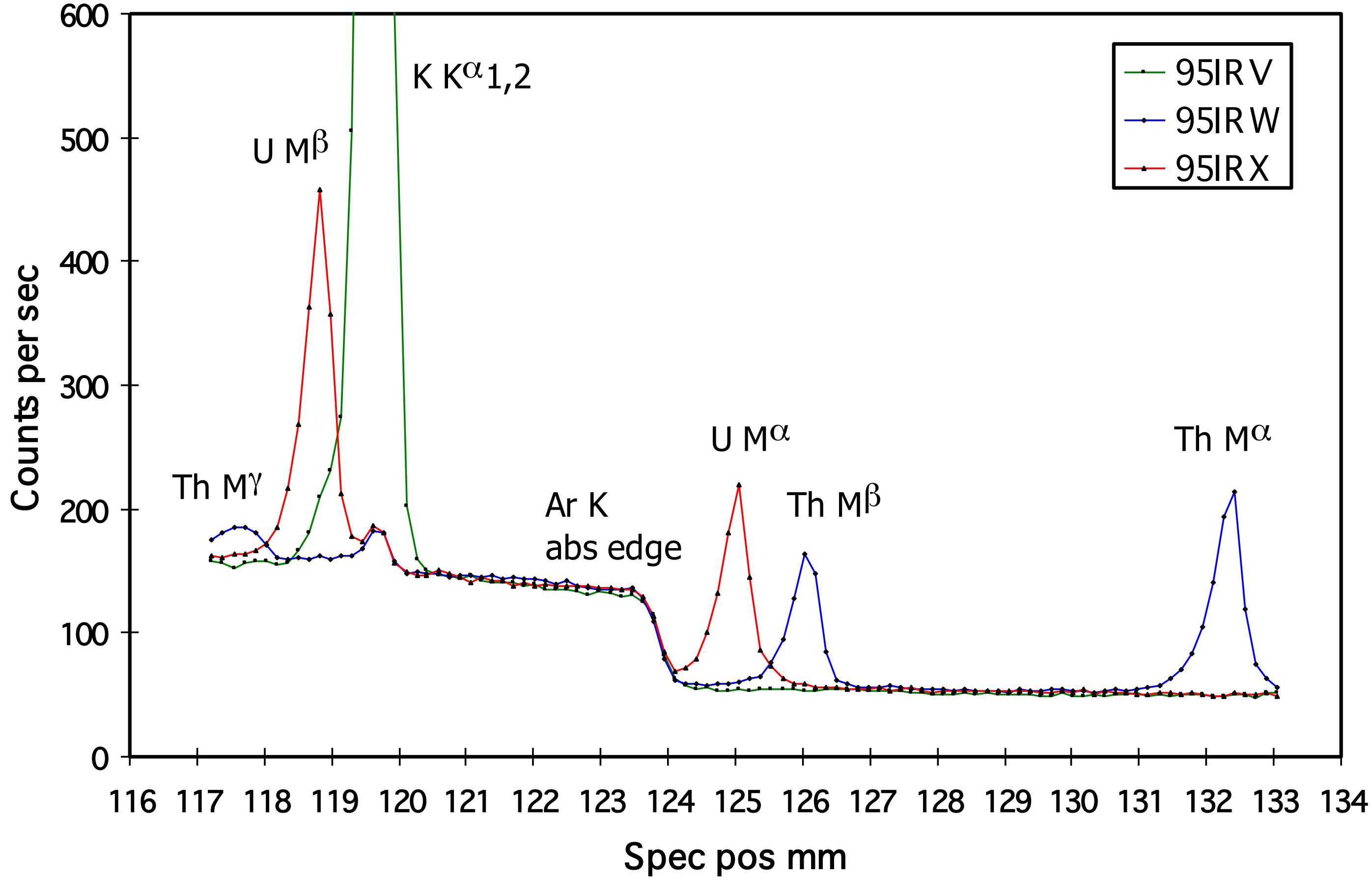
WDS Scan: PET Crystal
Si Kα limb and Hf Mβ Overlap on Rb Lα



WDS Scan: PET Crystal
Sr Lα Peaks, Rb Lβ family overlaps



WDS Scan: PET Crystal
Th Mβ on U Mα, K Kα Peaks & Ovlp U Mβ



Element Migration Studies: K, Rb, Cs

- Element migration measured at 20 KeV, 100 nA, variable beam diameter: 100 µm, 50, 20, 10, 5, focused beam.
- Count interval of 20 sec, total count time ~ 30 minutes.
- Immediate migration:
  5 µm beam: K 95IRV
  Focused beam: Cs 95IRW, Rb 95IRX
- Slow migration:
  10 µm: ~1000 sec K 95IRV
  5 µm: X00 sec Rb 95IRX
- No migration: 20 µm or greater @ 100 nA
- ΔT (degrees K) calculated using Castaing equation:

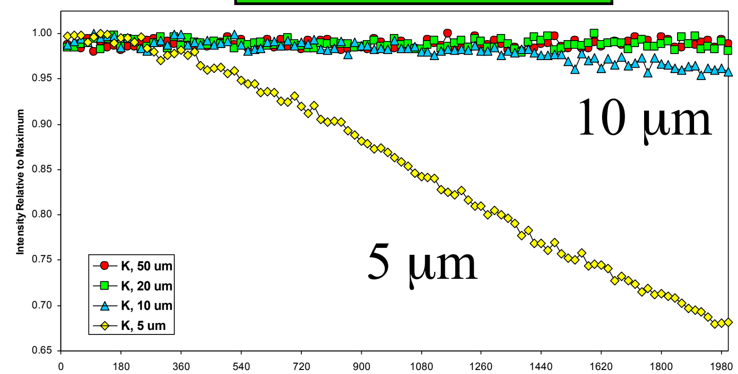
  $$\Delta T = 4.8\ E_o\ i / \lambda\ d$$

  E_o = beam voltage KeV, i probe current uA, λ thermal conductivity W/cm deg K, d beam diameter in µm

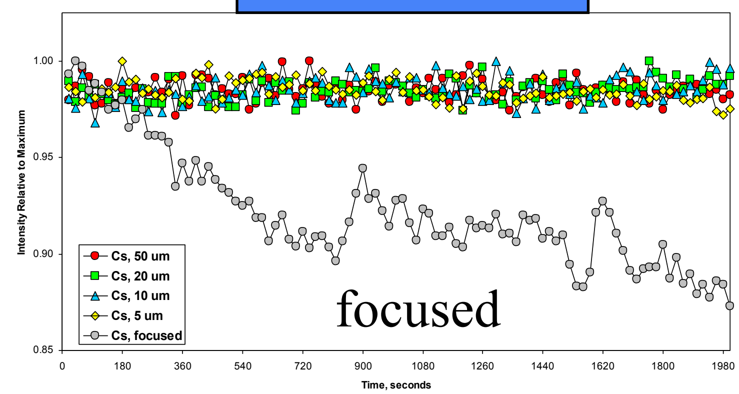
Element Migration Studies: K, Rb, Cs

Normalized X-ray Intensity vs. Time (2000 sec FS)

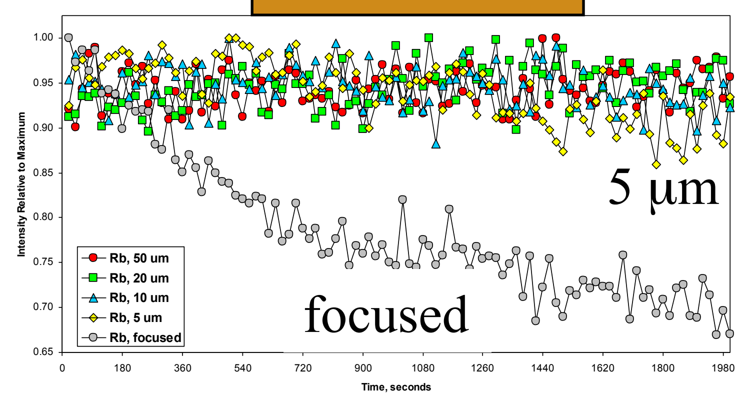
95IRV: K



95IRW: Cs



95IRX: Rb



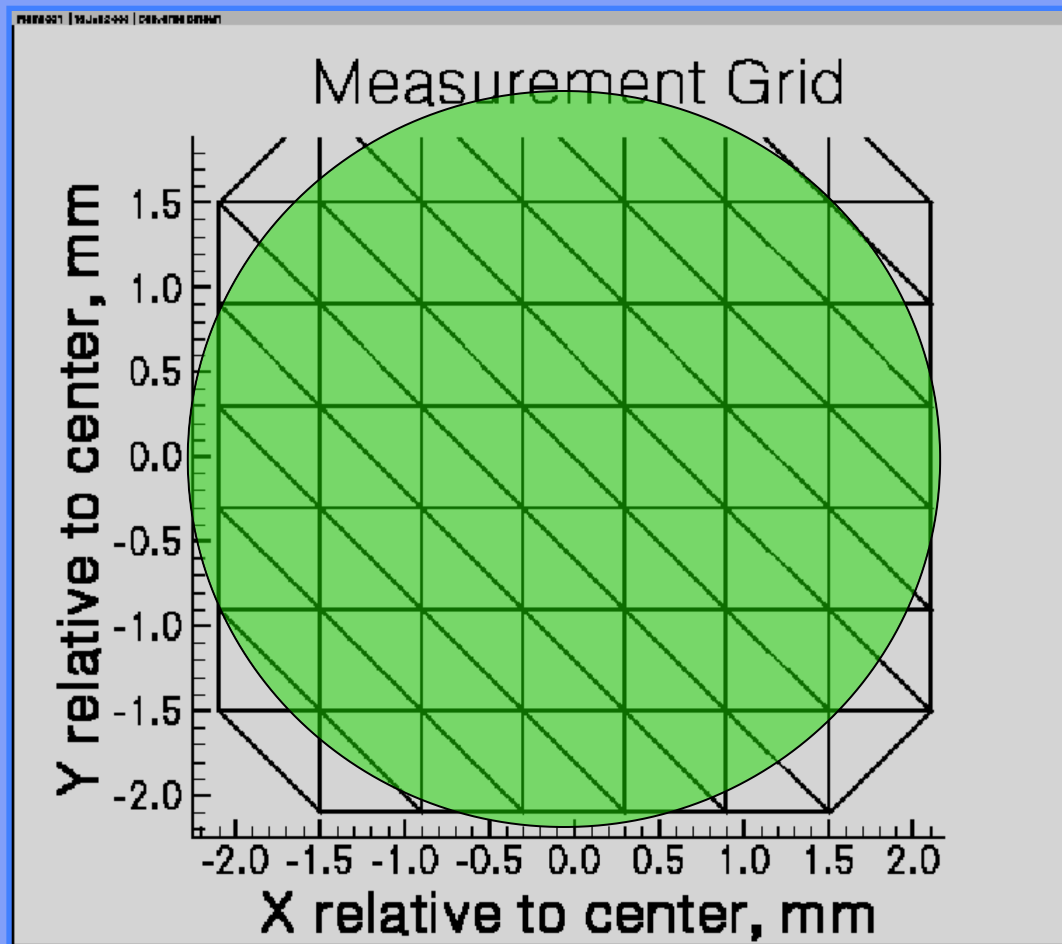
Calculated ΔT for i, d

	1 µm	5 µm	10 µm	20 µm	100 µm
100 nA	96 K	19	10	5	1
250 nA	240	48	24	12	2.4

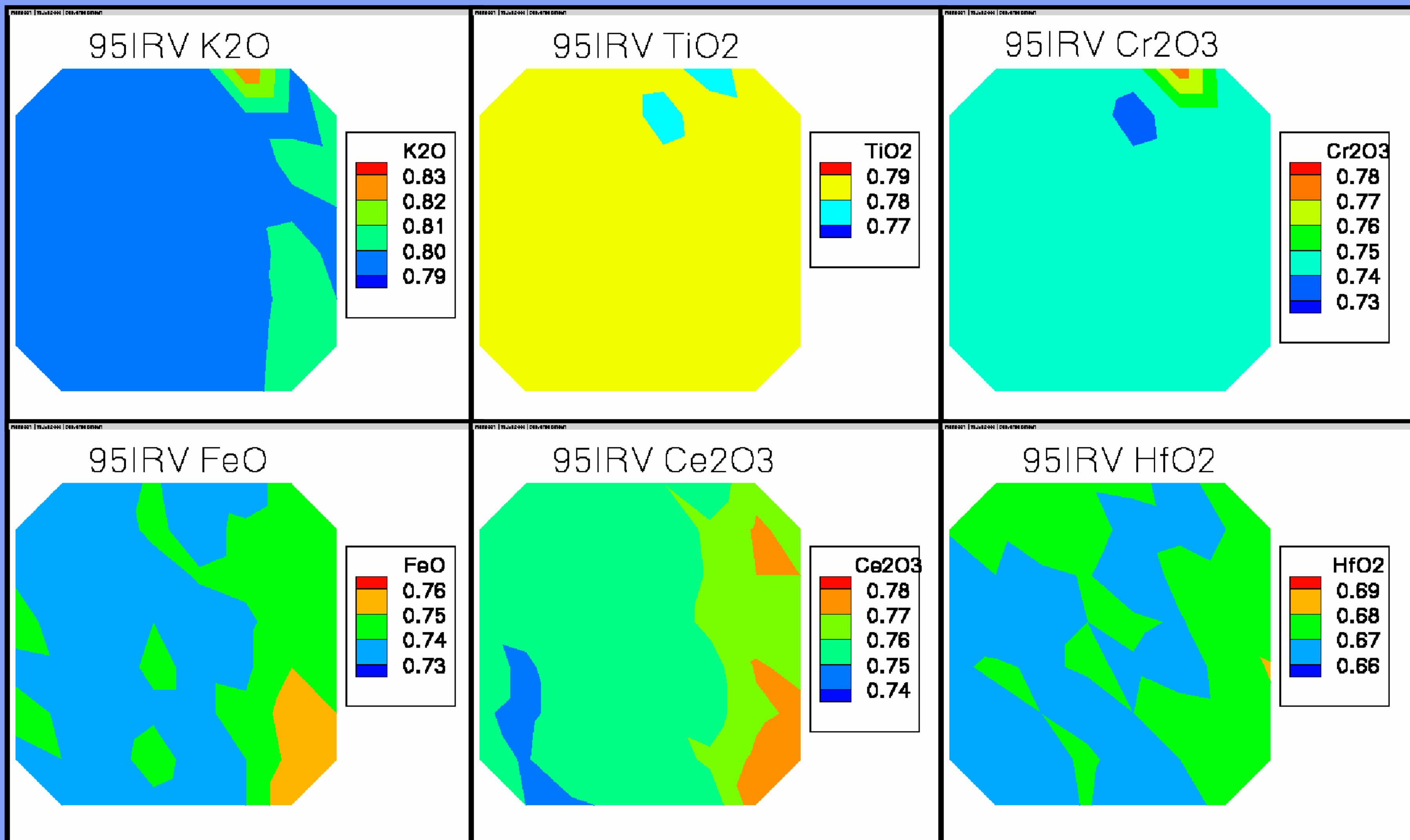
EPMA Homogeneity Measurements

- Bulk chemistry data along rod length (Ito): variation similar to or less than quoted analytical error of ± 0.01 wt% oxide.
- EPMA point count technique applied to circular cross-section of each glass rod, using a 60 point grid with 600 μm point spacing.
- Analysis conditions:
  25 keV, 100-250 nA probe current
  100 μm probe diameter
  250-500 sec peak, 100-200 sec background
- Asynchronous and synchronous data collection modes used. Instrument must be very stable!
- Contour plots generated using Tecplot
- Sigma ratio = $\sigma_{act} / \sigma_{counting\ statistics}$

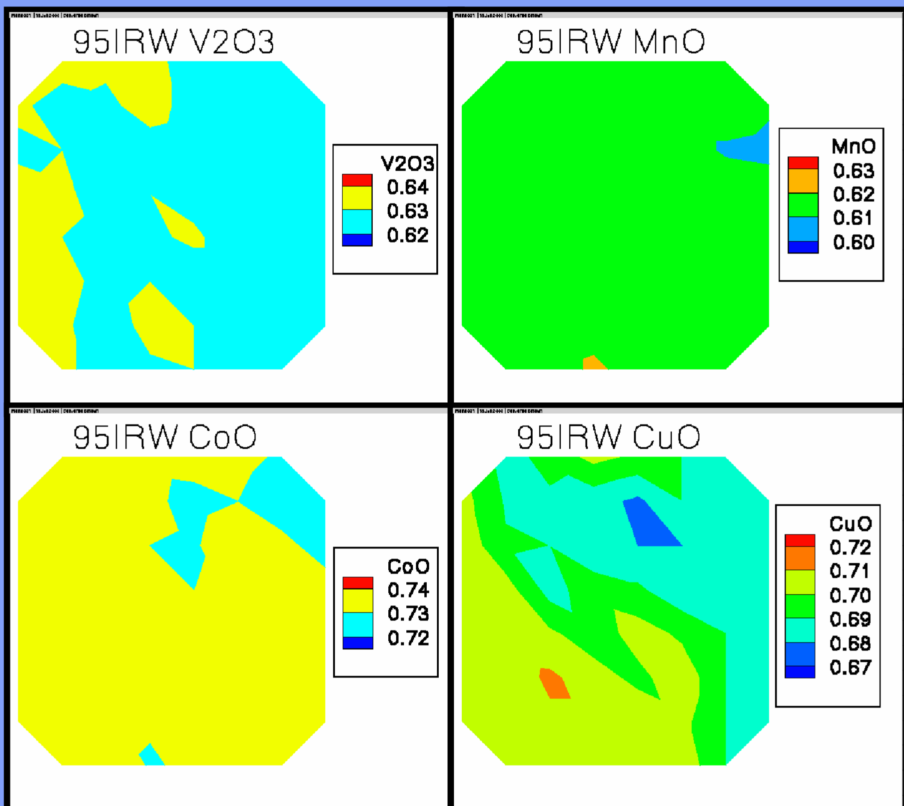
Homogeneity Point Count Grid
Tecplot Triangulation Mesh

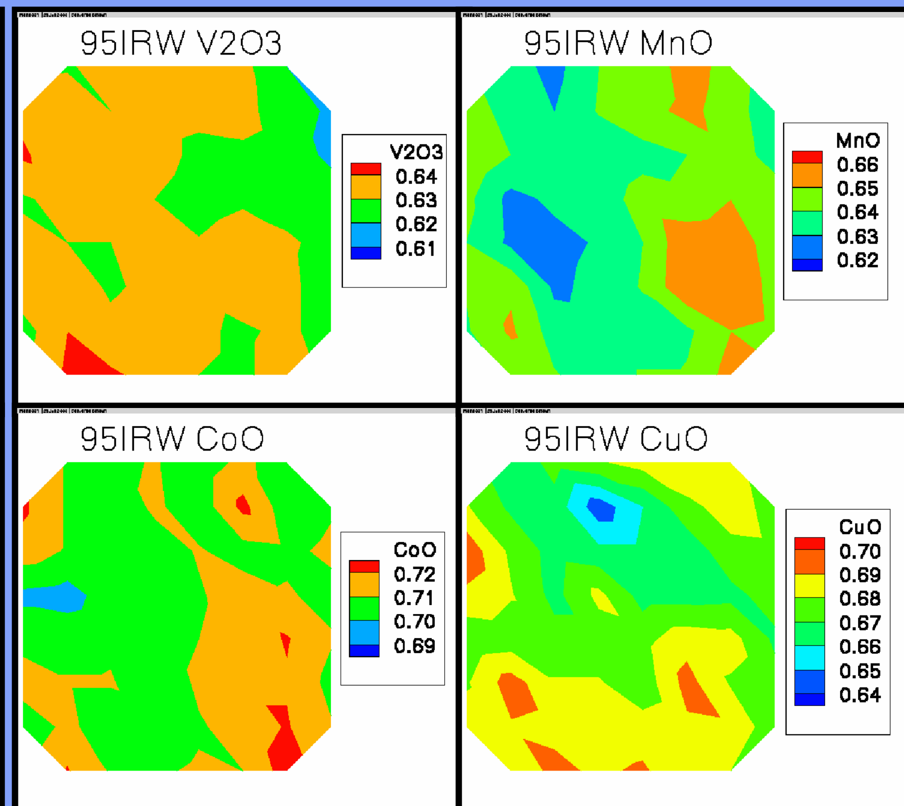


95IRV Homogeneity Maps:
K, Ti, Cr, Fe, Ce, & Hf Contour 0.01 Wt. %



95IRW Homogeneity Maps:
V, Mn, Co, & Cu Contour 0.01 Wt. % Two Runs

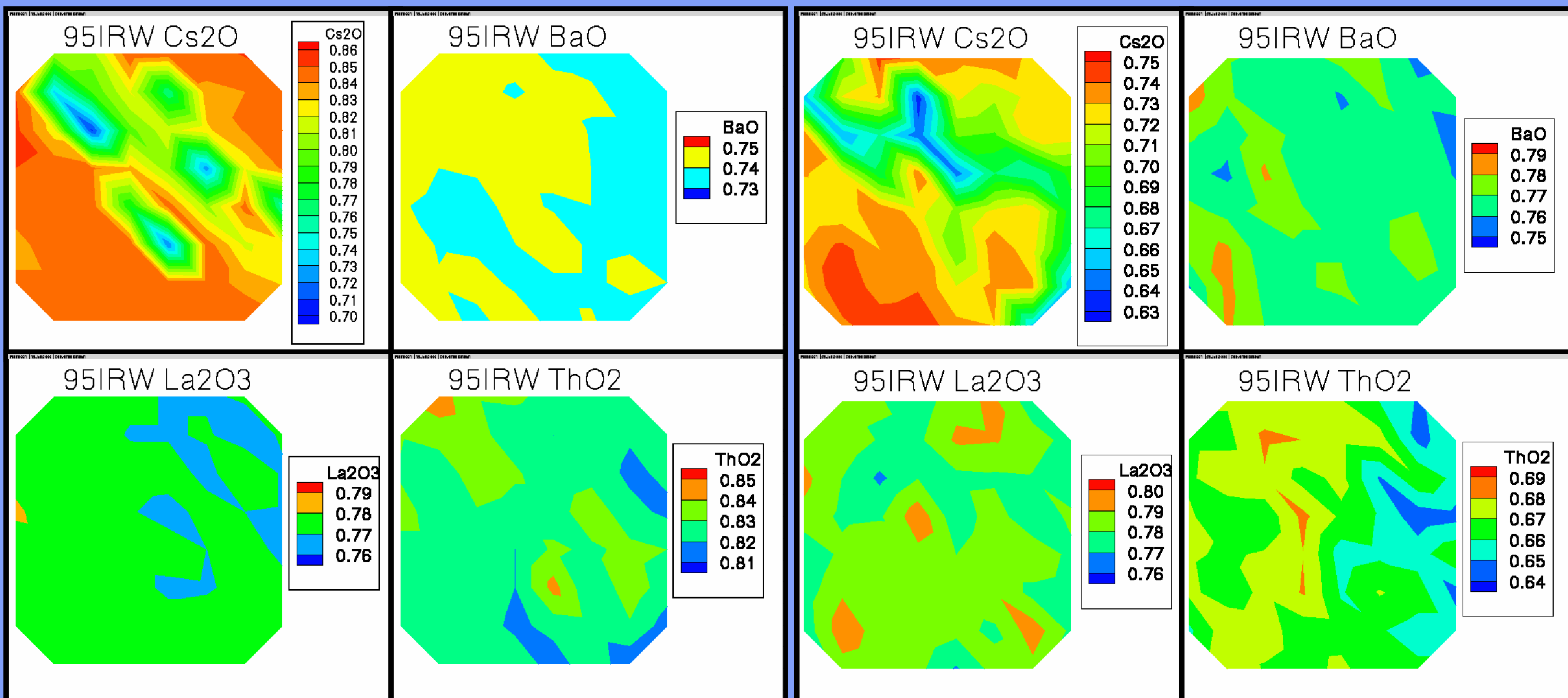




First Run

Second Run

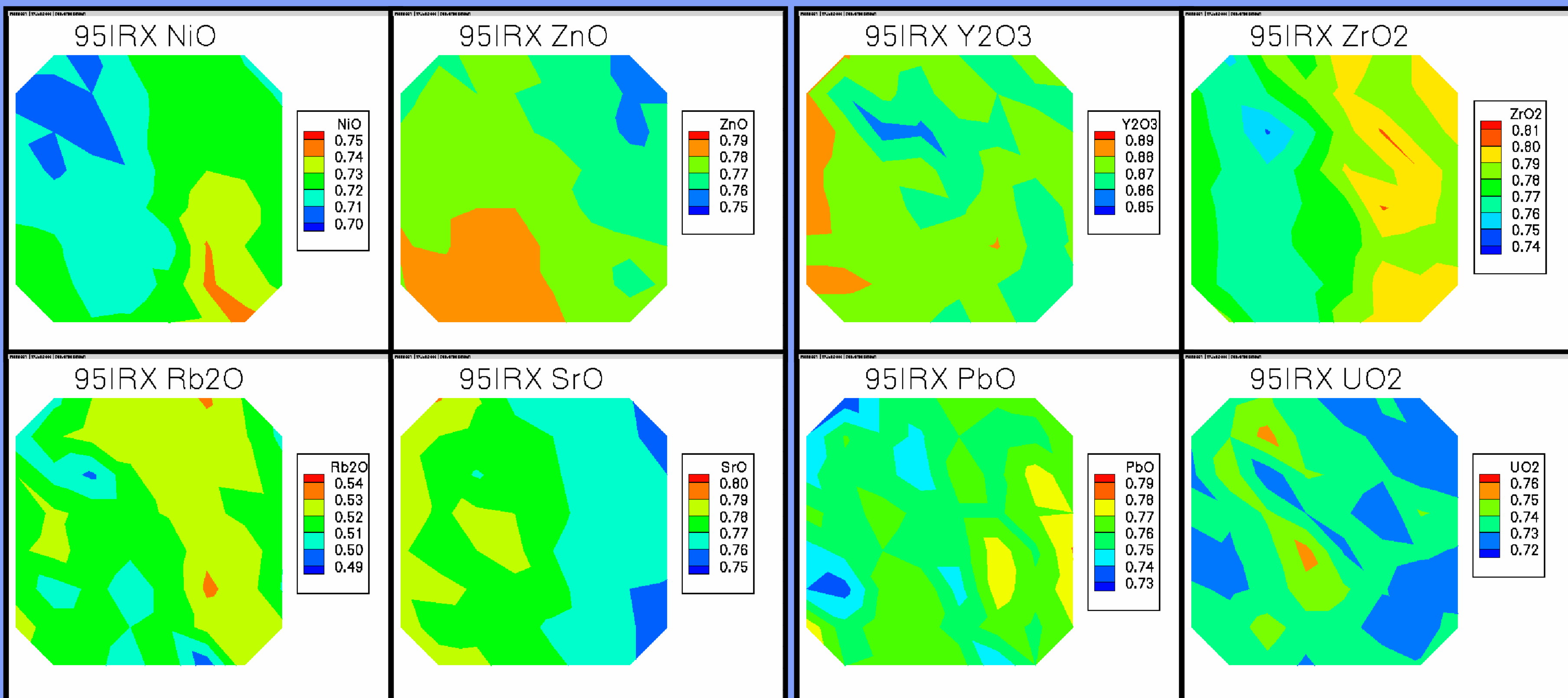
95IRW Homogeneity Maps:
Cs, Ba, La, & Th Contour 0.01 Wt. % Two Runs



First Run

Second Run

95IRX Homogeneity Maps:
(L) Ni, Zn, Rb, & Sr
(R) Y, Zr, Pb, & U   Contour 0.01 Wt. %



Analytical Method – ICP-AES

- Microwave digestion:
  From 5 g allotment, ~0.25 g sample, 3.5 ml HCL, 2 ml HNO_3, and 1.5 ml HF all combined. Heated to 200 psi for 30 minutes in digestion bombs.
- Digestion good: K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, U.
  Digestion bad (?): Ti, Sr, Y, Ba, La, Ce, Th.
- Fusion:
  From 5 g allotment, ~0.25 g sample, 2 g $LiBO_2$ flux all combined. Heated at 950 degrees C for 30 minutes, followed by dissolution of the fused bead in 5% HNO_3.
- Fusion good: Ti, Sr, Y, Zr, Ba, La, Ce, Hf, Th, U
- Problem: Some elements present at higher concentration than established working ranges by ICP-AES for silicate rocks at LANL.

Analytical Method – WDXRF

- ~5 g total glass rod was pulverized in an alumina shatterbox.
- Separate aliquots prepared by fusion:
  Sample fused in $LiBO_2$ flux at 9:1 and 36:1 dilutions and poured into disc mold for subsequent analysis.
- Crucible contamination procedures used for V.
- Normal XRF procedures at LANL for analysis of trace elements in silicate rock samples were used.
- Problem: Some elements are present at higher concentration than the primary XRF standards.
- X-ray peak overlaps similar to those seen in EPMA

95IRV Analytical Data

Oxide	Weighed In, %	Avg Bulk	1σ Bulk	Rel WI	Sigma Ratio $\sigma_{act} / \sigma_{cs}$
K_2O	0.79	0.792	0.073	+ 0.3%	3.4
TiO_2	0.79	0.787	0.040	- 0.4	3.7
Cr_2O_3	0.79	0.747	0.023	- 5.5	2.8
FeO	0.71	0.744	0.039	+ 4.7	2.8
Ce_2O_3	0.83	0.760	0.076	- 8.4	2.6
HfO_2	0.79	0.744	0.055	- 5.8	3.6

Analytical Data – Blank values 95IRV

Oxide	Bulk avg	Bulk 1 σ	EPMA avg	EPMA 1 σ	EPMA comments
V_2O_3	0.001	0.000x	0.006	0.001	Ti Kβ int
MnO	0.005	0.001	0.005	0.001	Mn Kα peak, Cr Kβ int
CoO	0.001	0.000x	0.002	0.001	Hf LL int, Fe Kβ int
NiO	0.011	0.011	0.00x		
CuO	0.002	0.001	0.00x		Hf Lα int
ZnO	0.004	0.003	0.006	0.003	Zn Kα peak, Hf Lβ1 int
Rb_2O					Si Kα limb, Hf Mβ int
SrO	0.080	0.011	0.111	0.004	Sr Lα peak
Y_2O_3	0.007	0.003	0.00x		
ZrO_2	0.027	0.003	0.033	0.004	Zr Lα peak
Cs_2O			0.015	0.001	Ti Kα int
BaO	0.016	0.003	0.014	0.001	Ba Lα peak, Ti Kα int
La_2O_3	0.002		0.00x		Ti Kα int
PbO	0.007	0.001	0.083	0.007	Hf Lγ1 int
ThO_2	0.012	0.010	0.00x		
UO_2			0.037	0.004	Ar K edge, flow counter

95IRW Analytical Data

Oxide	Weighed In, %	Avg Bulk	1 σ Bulk	Rel WI	Sigma Ratio $\sigma_{act} / \sigma_{cs}$
V_2O_3	0.64	0.638	0.011	- 0.3%	3.5
MnO	0.64	0.637	0.018	- 0.5	2.1
CoO	0.78	0.734	0.018	- 6.0	2.9
CuO	0.78	0.700	0.019	-10.2	3.4
Cs_2O	0.79	0.710	0.012	-10.1	6.5
BaO	0.78	0.776	0.012	- 0.6	3.5
La_2O_3	0.78	0.783	0.004	+ 0.4	(3.3)*
ThO_2	0.78	0.838		+ 7.4	2.8

* La in 95IRW has built-in overlap by Cs Lβ1 and Lβ4

Analytical Data – Blank values 95IRW

Oxide	Bulk avg	Bulk 1 σ	EPMA avg	EPMA 1 σ	EPMA comments
K_2O	0.019	0.004	0.011	0.001	K Kα peak
TiO_2	0.008	0.005	0.046	0.001	Ba Lα int
Cr_2O_3	0.002	0.000x	0.021	0.001	V Kβ int, La Lβ2 int
FeO	0.084	0.003	0.034	0.001	Fe Kα peak, Mn Kβ int
NiO	0.005	0.003	0.007	0.001	Ni Kα peak, Co Kβ int
ZnO	0.008	0.001	0.007	0.002	Zn Kα peak, Cu Kβ int
Rb_2O					Si Kα limb
SrO	0.044	0.004	0.075	0.003	Sr Lα peak
Y_2O_3	0.009	0.005	0.003	0.003	Small Y Lα peak
ZrO_2	0.007	0.002	0.005	0.004	Small Zr Lα peak
Ce_2O_3			0.064	0.002	Ba Lβ1,Lβ4 int
HfO_2	0.003	0.001	0.001	0.002	Cu Kα int, Co Kβ int
PbO	0.006	0.000x	0.004	0.004	
UO_2	0.001	0.000x	0.049	0.005	Th Mβ int, Ar K edge

95IRX Analytical Data

Oxide	Weighed In, %	Avg Bulk	1 σ Bulk	Rel WI	Sigma Ratio $\sigma_{act} / \sigma_{cs}$
NiO	0.78	0.730	0.022	- 6.4 %	4.4
ZnO	0.78	0.787	0.019	+ 1.0	3.8
Rb_2O	0.78	0.494	0.016	- 36.7	5.2
SrO	0.79	0.762	0.034	- 3.6	3.3
Y_2O_3	0.78	0.851	0.049	+ 9.1	2.8
ZrO_2	0.78	0.789	0.032	+ 1.1	3.1
PbO	0.78	0.754	0.009	- 3.3	4.6
UO_2	0.75	0.754	0.010	+ 0.5	3.1

Analytical Data – Blank values 95IRX

Oxide	Bulk avg	Bulk 1 σ	EPMA avg	EPMA 1 σ	EPMA comments
K_2O	0.028	0.008	0.017	0.000x	K Kα peak, U Mβ tail
TiO_2	0.006	0.002	0.028	0.002	
V_2O_3	0.003	0.001	0.003	0.001	
Cr_2O_3	0.001	0.000x	0.001	0.001	
MnO	0.005	0.001	0.004	0.001	Mn Kα peak
FeO	0.063	0.010	0.030	0.001	Fe Kα peak
CoO	0.004	0.000x	0.003	0.001	
CuO	0.005	0.001	0.002	0.001	Cu Kα peak, Ni Kβ int
Cs_2O			0.003	0.001	
BaO	0.017	0.002	0.017	0.001	Ba Lα peak
La_2O_3	0.004	0.002	0.000x	0.000x	
Ce_2O_3			0.009	0.002	Zn Kβ1,3 II int
HfO_2	0.019	0.006	0.018	0.003	Zr Kα II int
ThO_2	0.016	0.002	0.000x	0.001	

Summary 95IRV

- Very good agreement between analytical methods:
  Cr (best), Fe, Ti, Hf, K, Ce (worst)
  95IRV poorest agreement relative to 95IRW and 95IRX
- Ce: need more analyses
- Blank values (increasing, ppm oxide):
  - <50: V, Co, Cu, La, Zn, P
  - <100: Mn, Y, Pb
  - <200: Th, Ba, Na
  - Zr: 270 (EPMA 330)
  - Sr: 800 (EPMA 1110)
- Excellent homogeneity:
  Cr (lowest σ), Fe, Ce, K, Ti, Hf (highest σ)
  100 - 150 ppm oxide range on contour maps

Summary 95IRW

- Excellent agreement between analytical methods:
  Th (best, n = 1), La, V, Cs, Ba, Mn, Co, Cu (worst)
  95IRW best agreement relative to 95IRV and 95IRX
- Th: value needs refining
  La: built-in overlap from Cs $L\beta_1$ and $L\beta_4$; Use La $L\beta_1$
- Blank values (increasing, ppm oxide):
  - <50: U, Cr, Na, Hf
  - <100: P, Ni, Pb, Zr, Ti, Zn, Y
  - <200: K
  - Fe: 840 (EPMA 340)
  - Sr: 440 (EPMA 750)
- Excellent homogeneity, except Cs
  Mn (lowest σ), Th, Co, La, Cu, V, Ba, Cs (highest σ)
  200 - 350 ppm oxide range on contour maps (Cs: 1000)

Summary 95IRX

- Very good agreement between analytical methods:
  Pb (best), U, Rb, Zn, Ni, Zr, Sr, Y (worst, n = 2)
  95IRX intermediate agreement relative to 95IRV and 95IRW
- Apparently ~37% of Rb lost relative to weighed-in qty.
- Blank values (increasing, ppm oxide):
  - <50: Cr, V, Co, La
  - <100: Mn, Cu, P, Ti
  - <200: Th, Ba, Hf
  - K: 280 (EPMA 170)
  - Fe: 630 (EPMA 300)
- Excellent homogeneity, including Rb:
  Y (lowest σ), Zr, U, Sr, Zn, Ni, Pb, Rb (highest σ)
  250 - 400 ppm oxide range on contour maps

What can these glasses be used for?

- As primary standards for trace elements.
- Spectrometer peaking and primary calibration can be performed by WDS — carefully.
- As secondary standards to check against primary calibration presumably performed using higher concentration standards. Check of trace element setup.
- Peak overlaps at trace element concentration.
- Much needed standards for Rb, Sr, Cs, Th, and U.
- Other techniques: SIMS etc.

What Needs to Be Done in the Future

- Round Robin EPMA:
  Values relative to EPMA standards.
  Consensus values relative to bulk chemistry.
- SIMS and other probe techniques.
- Oxidation state: Valences are assumed.
- Traceability? Certified values? How does the EPMA community pursue this?
- EPMA Analysts: Please use these standards.

Conclusions

- Corning 95-series trace element glasses characterized by bulk chemical and x-ray analytical techniques. Excellent agreement.
- Doped and blank values determined. Can be used as primary and secondary EPMA standards.
- Homogeneous on micro and macro scales.
- EPMA wavelength scans available to aid selection of background offsets, illustrate overlaps, etc.
- All analytical work done on gratis basis by volunteers.
- Distribution program set up with Smithsonian Institution.

How to Obtain Corning 95-Series Glasses

- Smithsonian Institution will be distribute material as a crushed glass, placed in a vial.
- USNM numbers have been assigned:
  95IRV = USNM 117083
  95IRW = USNM 117084
  95IRX = USNM117085
- Contact:

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