Analysis of Obsidian using HH XRF

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What is Obsidian?

- Obsidian is rapidly chilled lava, which lends itself to tool making thanks to its easy workability and hardness. (FELSIC, RYOLITHIC) composition

“Silverware” of the stone age, Tool stone and weapon!

Still in use today…
Wikipedia trivia…

- Obsidian has been used for blades in surgery, as well-crafted obsidian blades have a cutting edge many times sharper than high-quality steel surgical scalpels, the cutting edge of the blade being only about 3 nanometers thick.[13] Even the sharpest metal knife has a jagged, irregular blade when viewed under a strong enough microscope; when examined even under an electron microscope an obsidian blade is still smooth and even. One study found that obsidian incisions produced narrower scars, fewer inflammatory cells, and less granulation tissue in a group of rats.[14]

13 Buck, BA (March 1982). "Ancient technology in contemporary surgery". *The Western journal of medicine* **136** (3): 265–269. ISSN 0093-0415. OCLC 115633208. PMC 1273673. PMID 7046256.

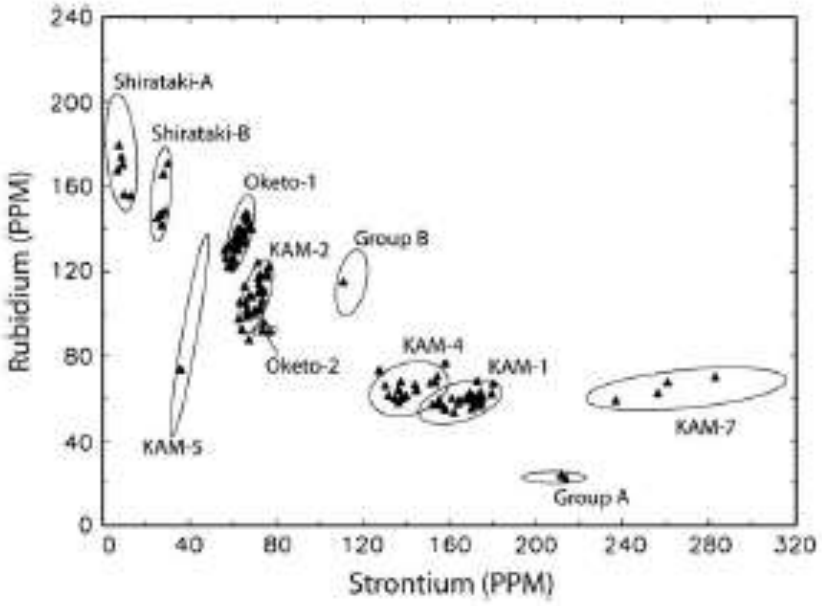
14 Disa, JJ; Vossoughi, J; Goldberg, NH (October 1993). "A comparison of obsidian and surgical steel scalpel wound healing in rats". *Plastic and reconstructive surgery* **92** (5): 884–887. doi:10.1097/00006534-199392050-00015. ISSN 0032-1052. OCLC 121212765. PMID 8415970. http://www.ncbi.nlm.nih.gov/pubmed/8415970?dopt=AbstractPlus. Retrieved 2007-11-20.

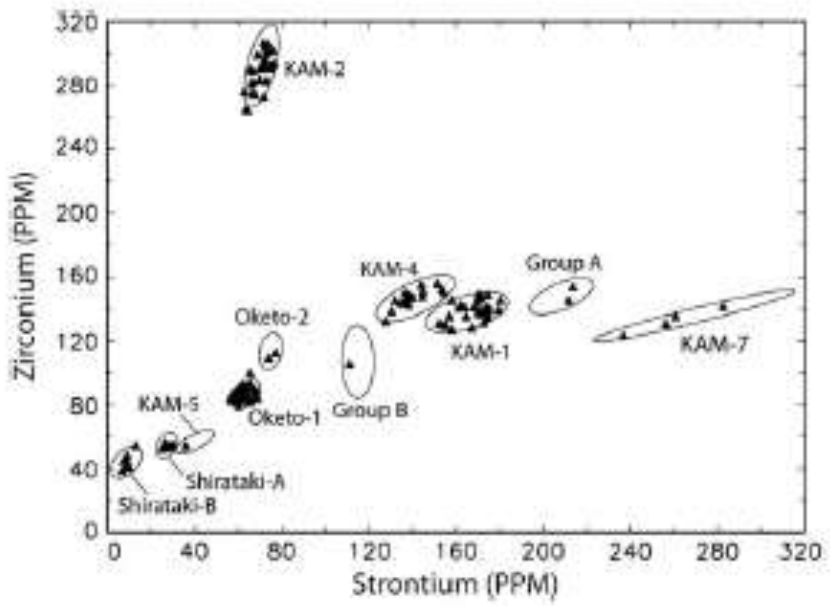
Why do we want to analyze obsidian?

- Obsidian based tools allow the tracking of migration (or immigration) paths in the”former” time… e.g. Siberia to North America, Olmecs and Maya …..

Sourcing and Clustering

- The trace elements found in “basalt” can be used to establish sources for the magma but allow us also to define localities from which the obsidian was mined.

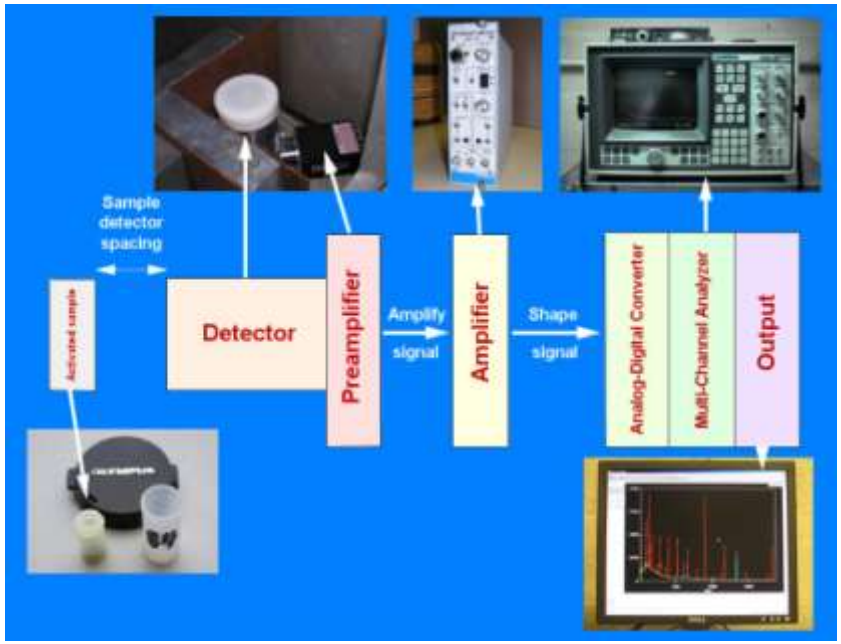




S. Colby Phillips, Robert J. Speakman, Initial source evaluation of archaeological obsidian from the Kuril Islands of the..., J. Archaeol. Sci. (2009), doi:10.1016/j.jas.2009.01.014

The past…

- Instrumental Neutron Activation Analysis (INAA)
  - Get a reactor
  - Make sample radioactive: $^{58}Fe + {}^{1}n \rightarrow {}^{59}Fe + Beta^{-}$ + gamma rays
  - Take sample and measure GAMMA emission!
  - Gamma emission is chracteristic for element and direct proportional of c

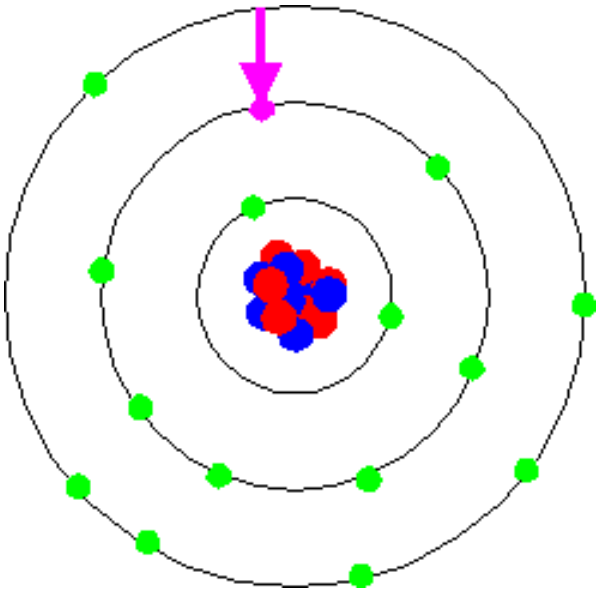


The lab based technique

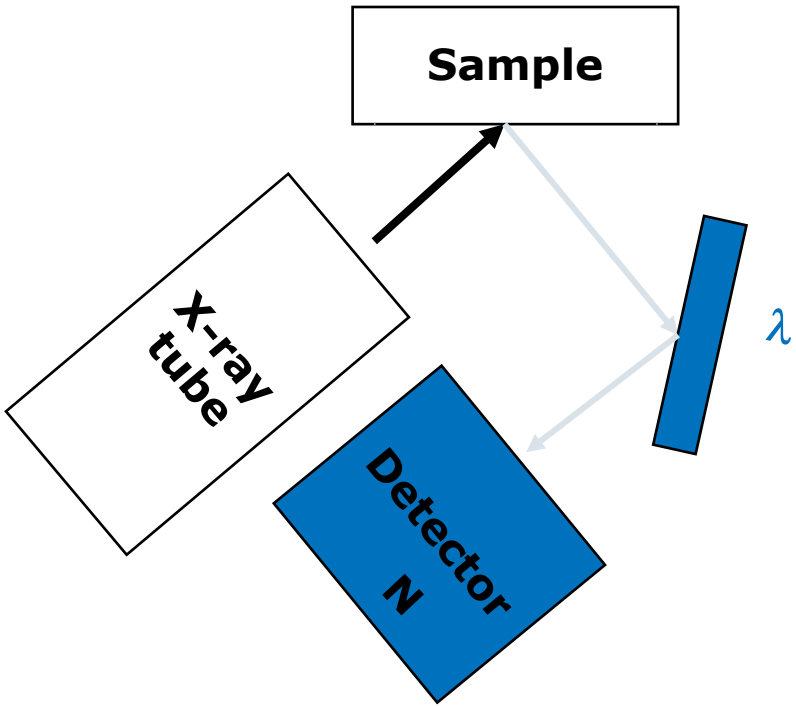
- Laser induced inductively coupled plasma mass spectrometry
- LI-ICP-MS
  - destructive (although much less than INAA): Laser vaporizes the sample
  - Equipment around 200 K $
  - Laboratory infrastructure needed
  - High consumable cost (Ar)
  - Best dynamic range from ppm to ppt
  - Calibration traceable to single element solutions

Why use X-rays?

- X-Rays spectrometry makes use of the characteristic emissions from inner shell transitions of the elements in the sample
  - Solid and liquid samples can be used directly
  - NON DESTRUCTIVE!
  - Relative technique, comparison between known and unknown samples

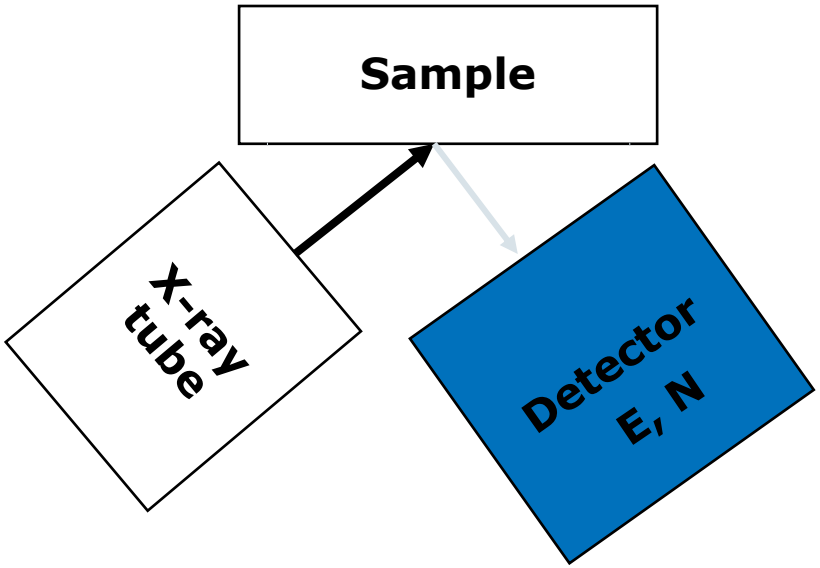


The different XRF approaches
Wavelength dispersive XRF (WD XRF)



- An analyzer crystal separates the various wavelengths, λ (energies)
- The detector records only the number, N, of X-ray photons at a given wavelength (energy)

The different XRF approaches
Energy dispersive XRF (ED XRF)



The detector is used to record both:

- the energy, E, and
- the number, N, of X-ray photons

What is PXRF?

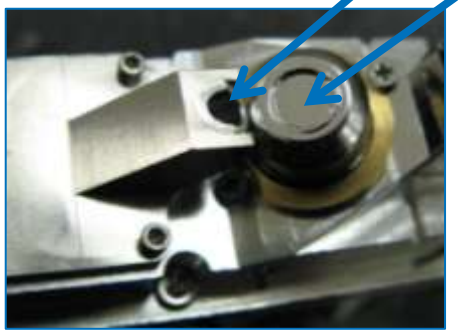
- Portable or Hand Held XRF is the miniaturization of traditional direct excitation ED XRF, made possible by small "PC"s, small x-ray tubes and the XRF detectors developed for NASA's ROVER. The

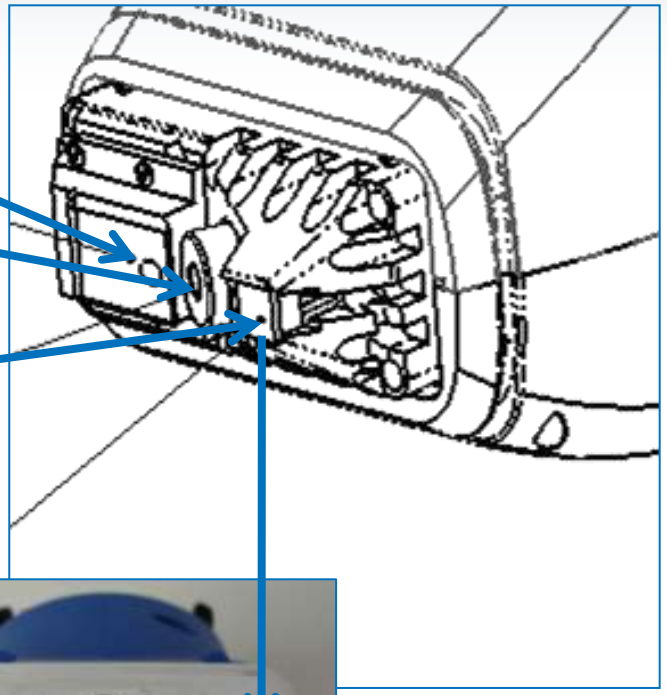
ED XRF

Tube (Rh)

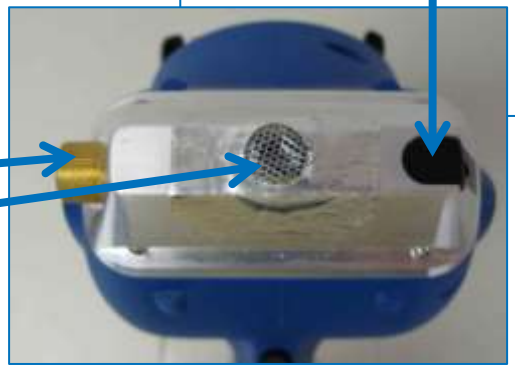
XFlash™ Detector

IR SENSOR



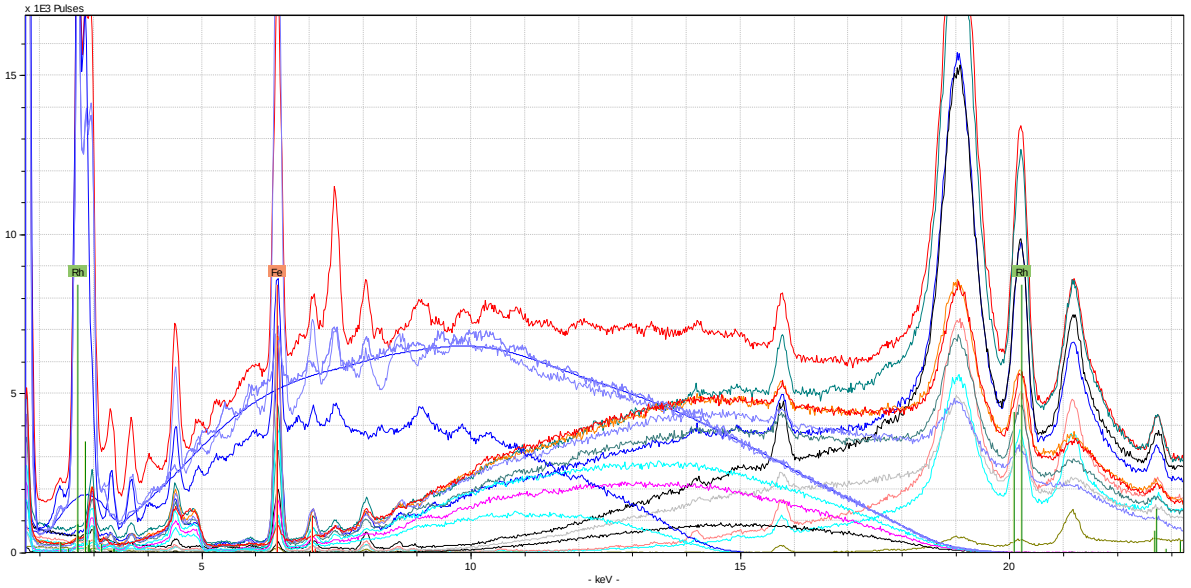


FILTER /TARGET
EXIT WINDOW

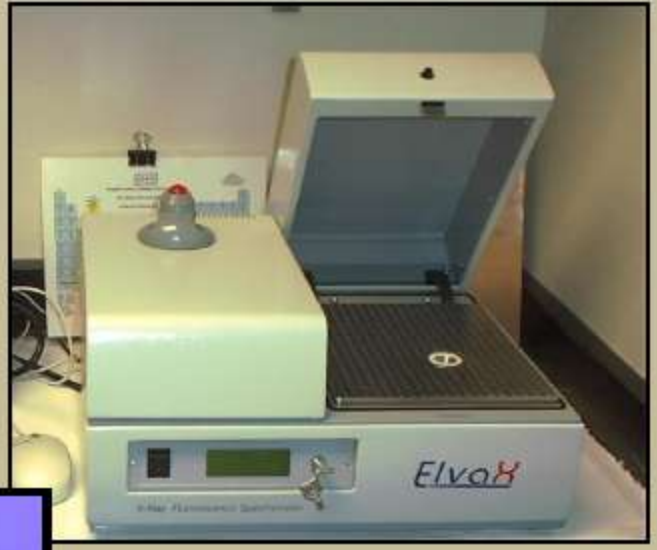


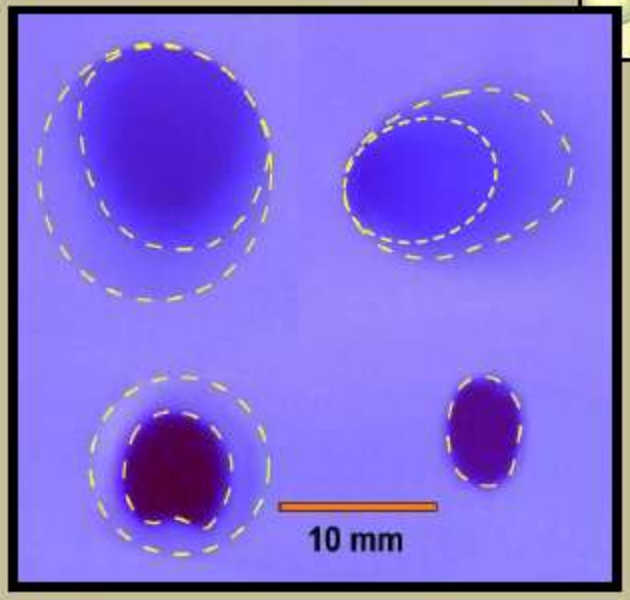
Resolution , Signal : Noise and Sensitivity Parameters you need to know!

- Critical components: (FLEXIBILITY)
  - Detector: resolution < 145 eV stable up to high count rates
  - Ability to use beam conditioning (Filters to work on background)
  - Ability to tune excitation (high kV!)
  - Software for spectral evaluation and calibration



Portable-XRF





Comparison of beam diameter and shape for 4 commercially- available portable XRF spectrometers. Darker color corresponds to intensity of X-ray beam.

Smithsonian
Museum Conservation Institute

*currently owned by MCI

What do we need to analyze?

- The elements of interest are Rb, Sr, Y, Zr and Nb, with a detection limit of less than 1 ppm
- Due to matrix effects we also need to be able to measure Ca, Ti, Fe, Mn, Ba
- Reference Material needs to be referenced to ICP-MS or INAA to be suitable for sourcing

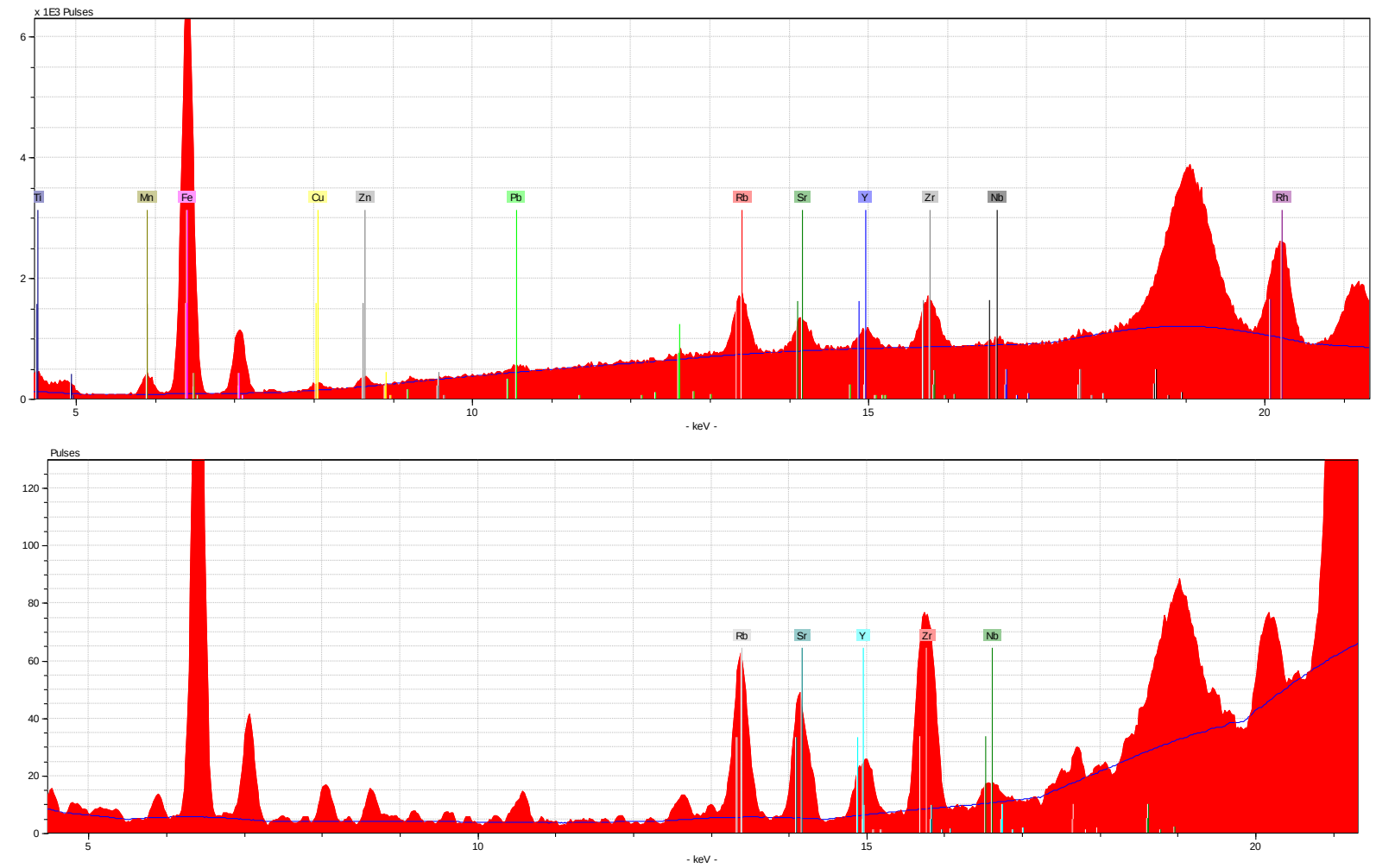
Sample ID	**MLZ1023**	**XMC014**	**LGB-STD**	**BGID01**	**YOC001**
Element	Batza Tena-1, AK	Wrangell Mtn, AK	Little Glass Butte, OR	Bear Gulch, ID	Obsidian Cliff, WY
XRF data					
Mn (ppm)	568	350	327	330	192
Fe (ppm)	4824	8535	6200	11361	8677
Zn (ppm)	38	35	31	62	61
Ga (ppm)	15	15	16	17	22
Th (ppm)	38	11	8	23	28
Rb (ppm)	172	107	95	170	237
Sr (ppm)	10	115	67	48	9
Y (ppm)	32	22	26	44	74
Zr (ppm)	119	156	106	308	177
Nb (ppm)	32	13	8	56	44

Concentrations in various sources of Obsidian provided

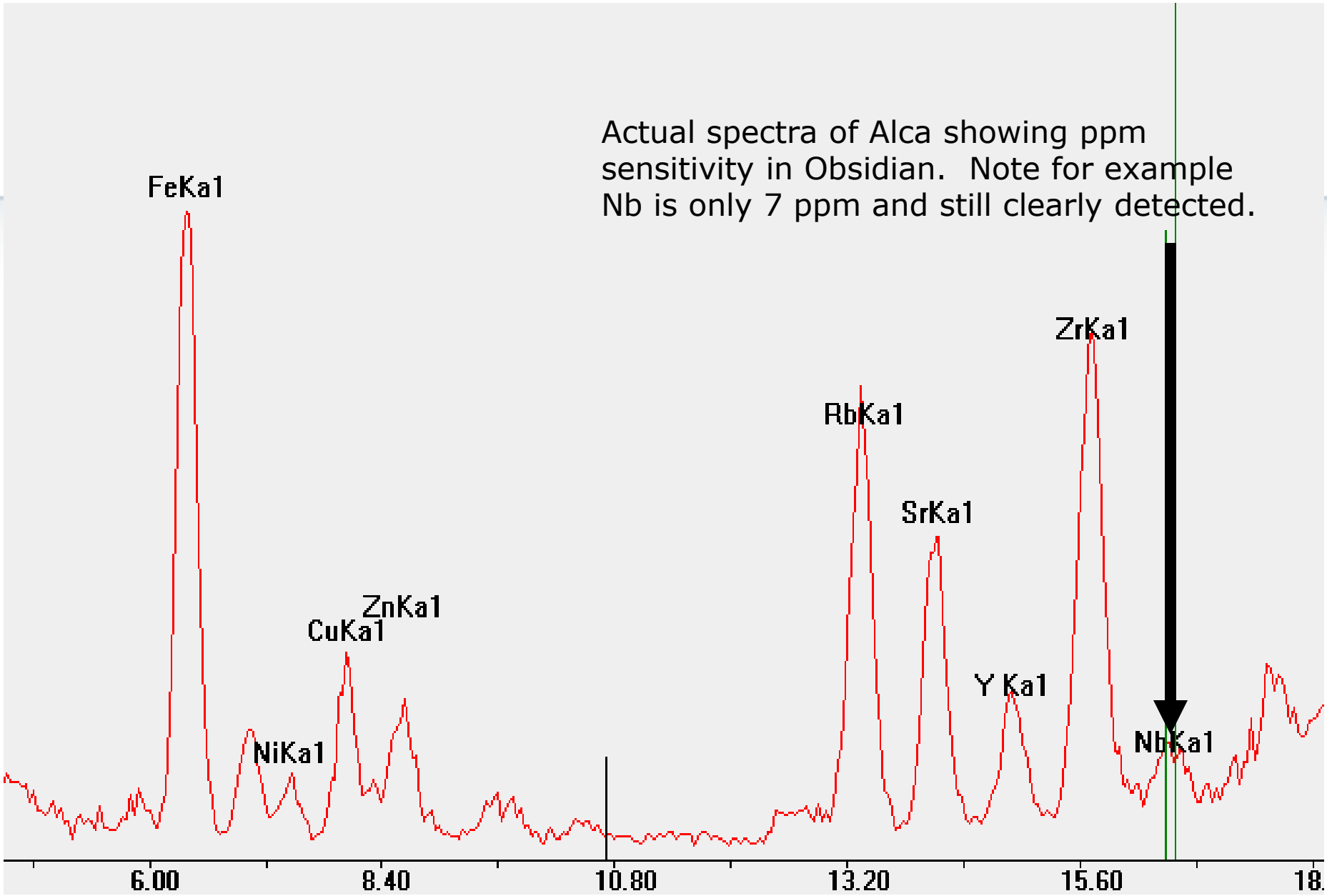
Values are in ppm

	K	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb
Chivay	36952	723	4865	35	19	23	245	39	20	70	16
Ixtepeque	32815	435	8917	29	15	7	95	154	19	167	6
Mono Glass Mtn	38853	353	5427	32	18	22	196	2	32	79	22
Otumba	33000	362	8019	40	17	10	117	121	24	132	10
Pico de Orizaba	35216	554	3545	25	15	6	100	26	17	42	8
Quispisisa	37806	366	5616	32	18	20	175	131	18	93	10
Alca	**36747**	**475**	**5435**	**39**	**15.3**	**13.7**	**136**	**71**	**14**	**82**	**7**
Ucareo	34848	146	7427	34	17	14	144	12	29	111	11
Yellowstone	41062	192	8666	66	22	28	237	2	77	155	35
CRG 0002	38500	495	27091	215		33	238	3		1552	
MLZ 1019	39400	563	4876	38		36	170	5		104	
Sierra de Pachuca	24113	1146	15843	191	28	18	192	3	111	914	72
UNL-050_1	32000	718	19622	110		9	99	82		400	
XMC 020	35460	350	8535	34		11.3	107	114		170	

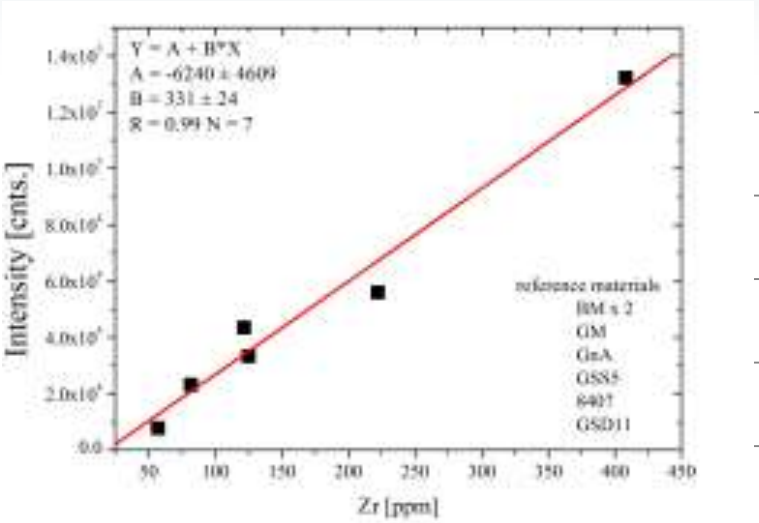
Establish instrument settings and sensitivity for application



Actual spectra of Alca showing ppm sensitivity in Obsidian. Note for example Nb is only 7 ppm and still clearly detected.

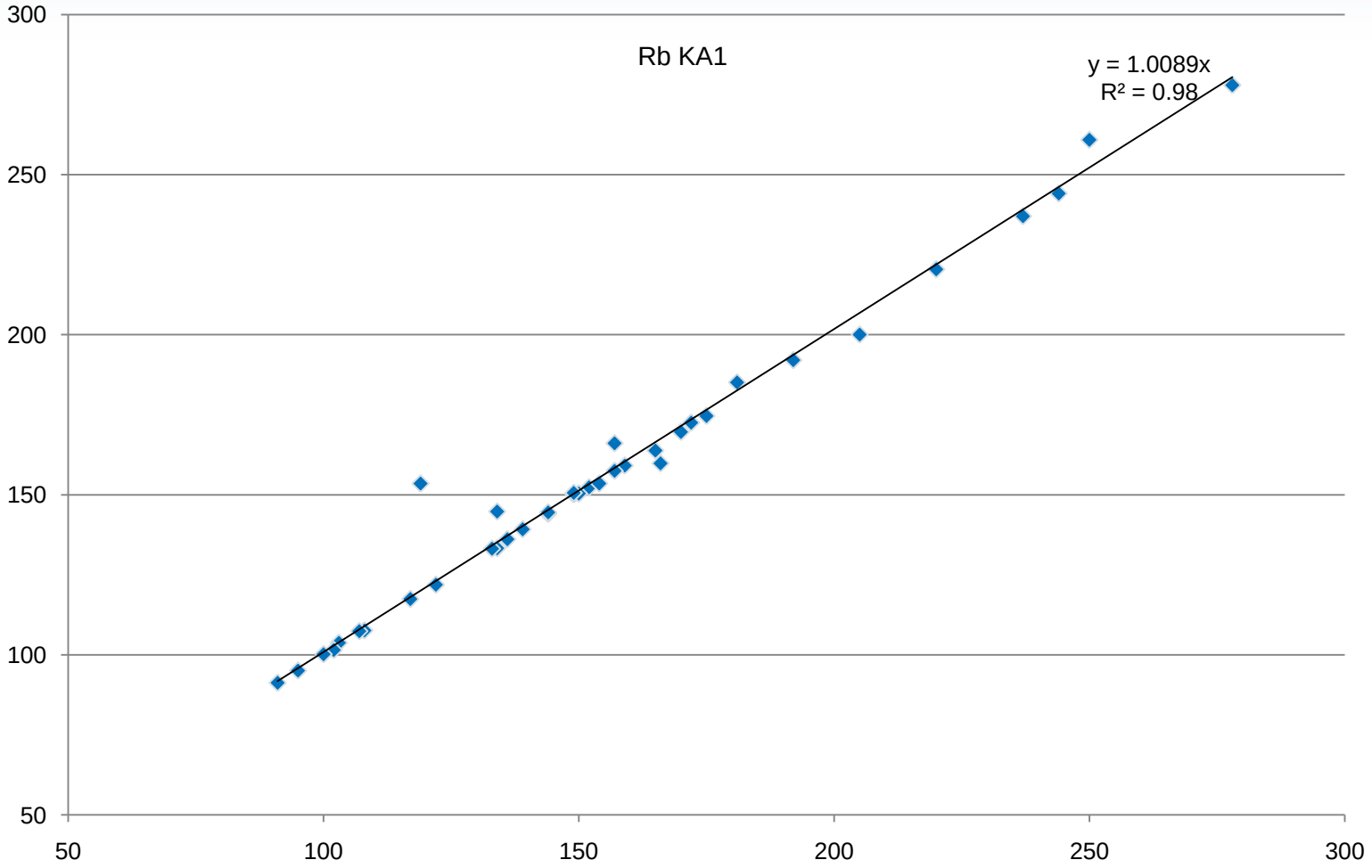


Calibrate the unit using known reference material and validate….



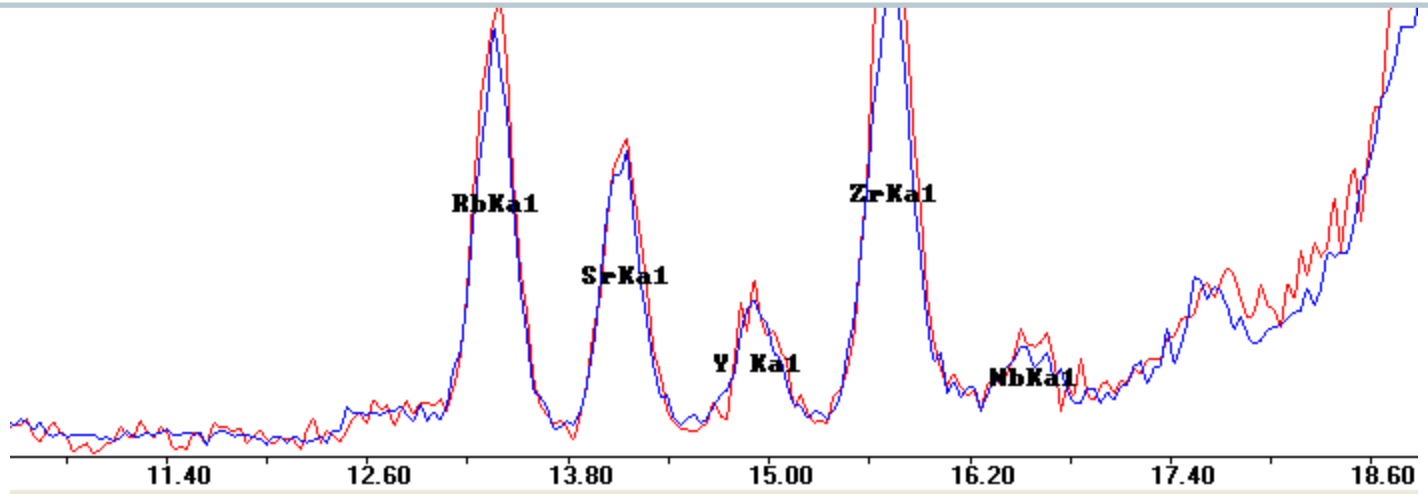
Y Ka1

Validation vs. INAA



Transfer calibrations…

Alca obsidian Spectra taken 2 years apart on 2 different Tracer III V systems and 2 pieces of Alca obsidian collected a different times showing the response from 11 to 18 keV. They are statistically identical at the ppm level.

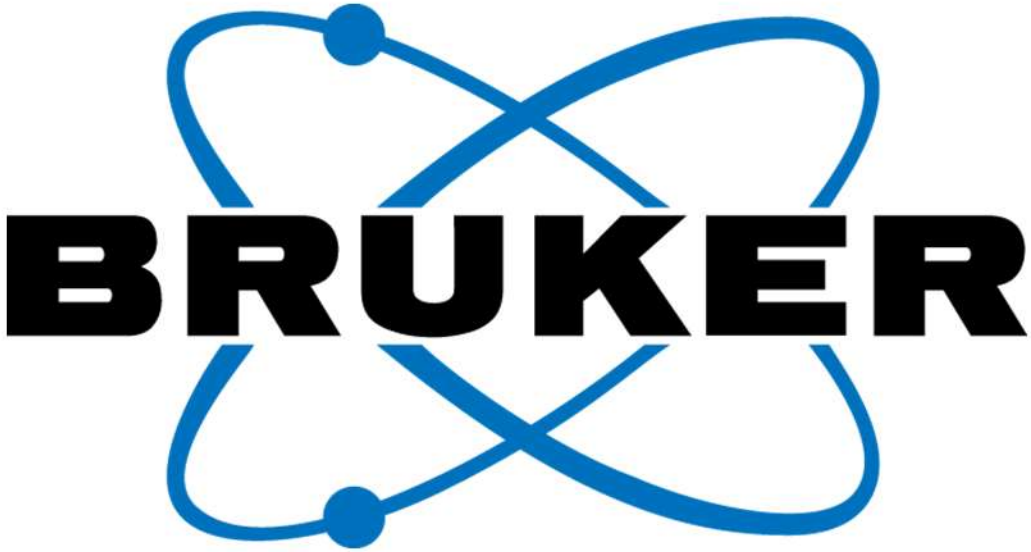


Conclusion

- HH or PXRF provides quality data, very comparable to laboratory instruments
- Care need to be taken to calibrate and validate it
- Data is checked so the INAA based database for provenance can be used
- "Peer" group used HH XRF to gather more data trough collection campaigns in Museums

Acknowledgments

- John Speakman: Smithsonian Conservation Institute
- Robert Tykot:L U South Florida
  - http://shell.cas.usf.edu/~rtykot/
- JELMER W. EERKENS: UC Davis
- Dr. Bruce Kaiser: Bruker Inc.



www.bruker.com