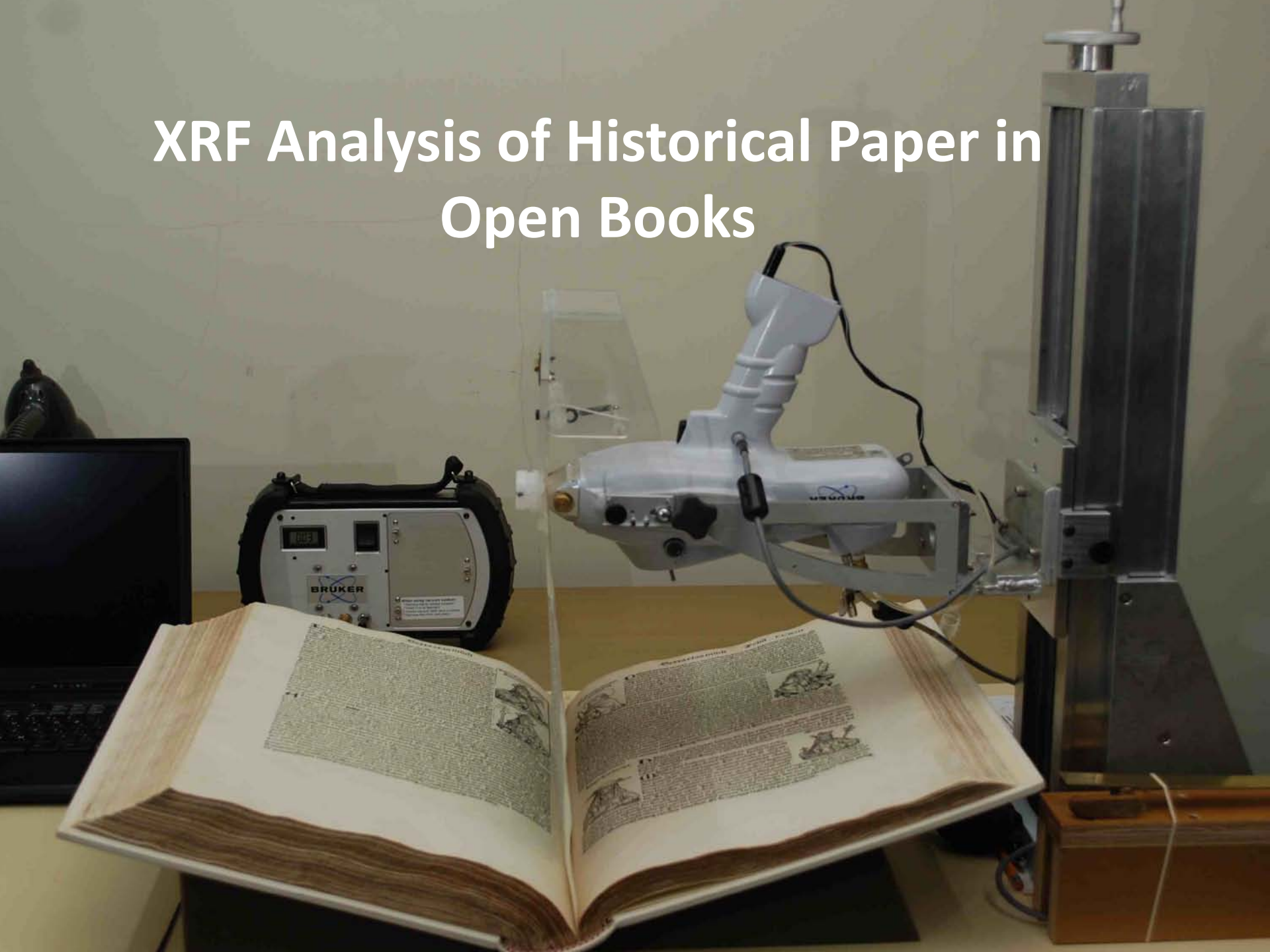
XRF Analysis of Historical Paper in Open Books



XRF Analysis of Historical Paper in Open Books

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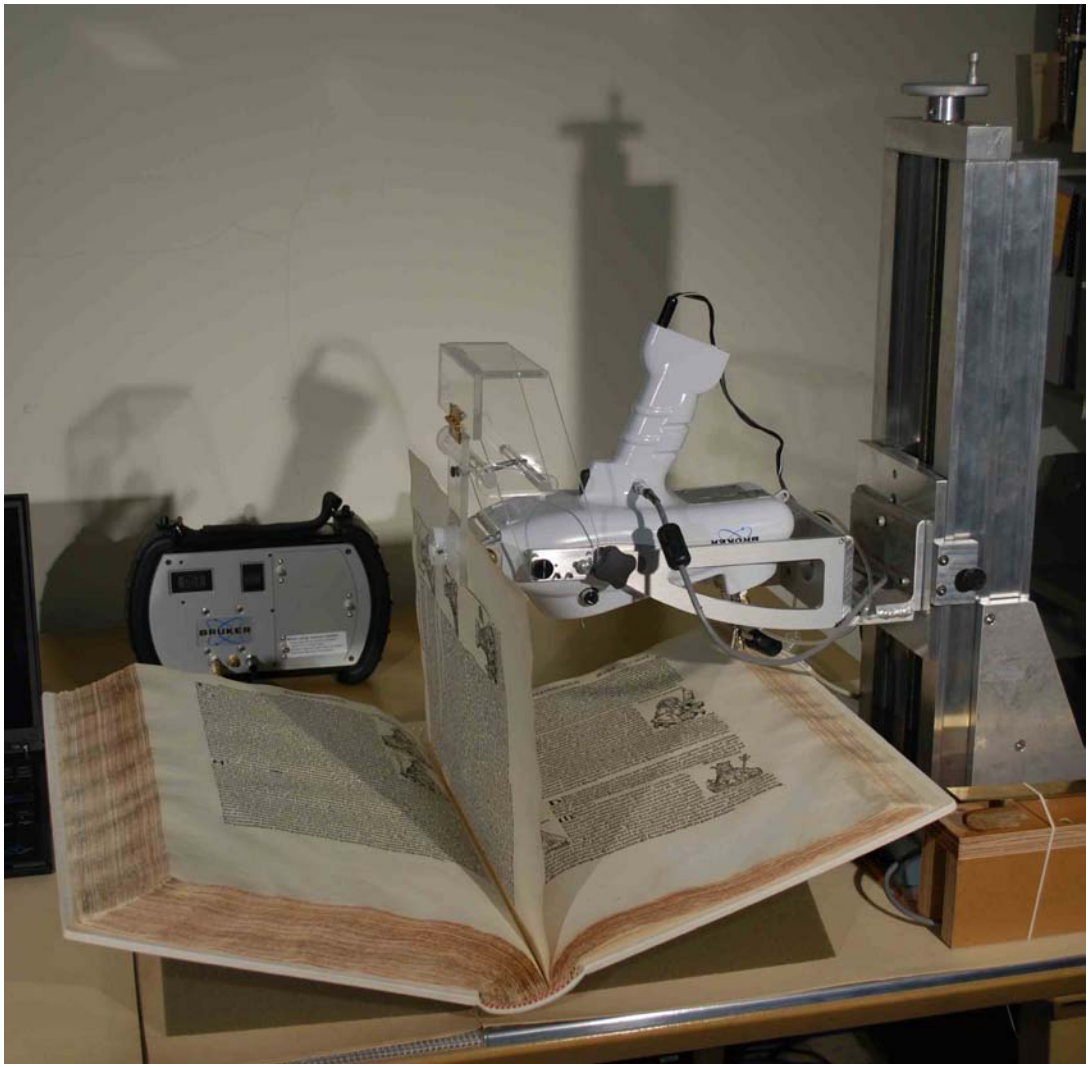
IMLS funded UICB research

- 1500 papers in manuscripts and printed books; 14th through 19th C
- Elements of interest: K, Al and S (Alum), Ca, and Fe

Steps for XRF analysis of paper in books

1. Select instrument and tube type
2. Design instrument positioning device for analysis
3. Normalize spectra
4. Establish method to correct for the variation in paper thickness/density
5. Select paper specimens for destructive testing and calibration
6. Create the calibration
7. Estimate the overall predictive ability of the calibration
8. Acquire data; output results

1. Selection of instrument and tube type
2. Instrument positioning

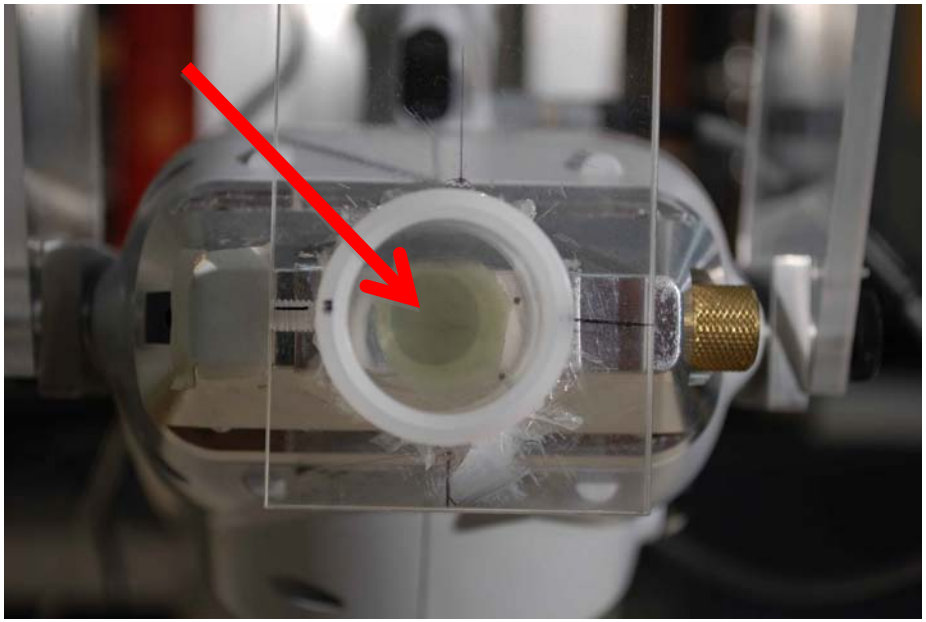


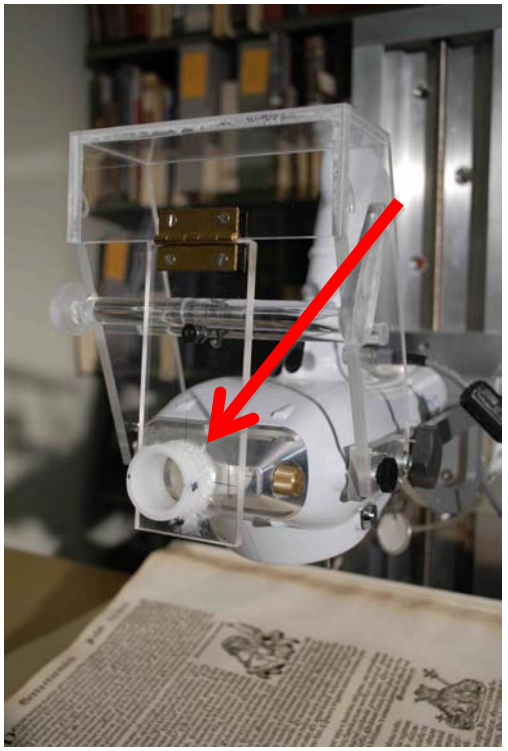
3. Normalize spectra
4. Correct for thickness/density

- BrKa1 (12KeV XRF line)
- CrKa1 (5.4KeV XRF line)

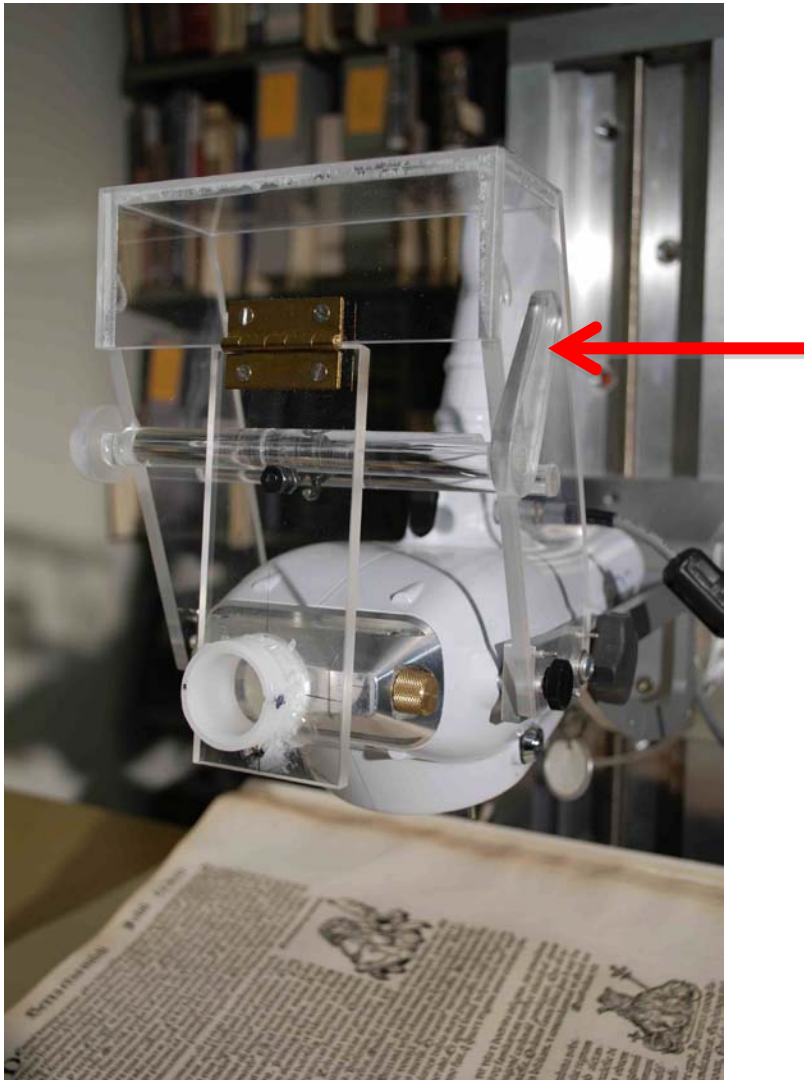
Cr Br artifact

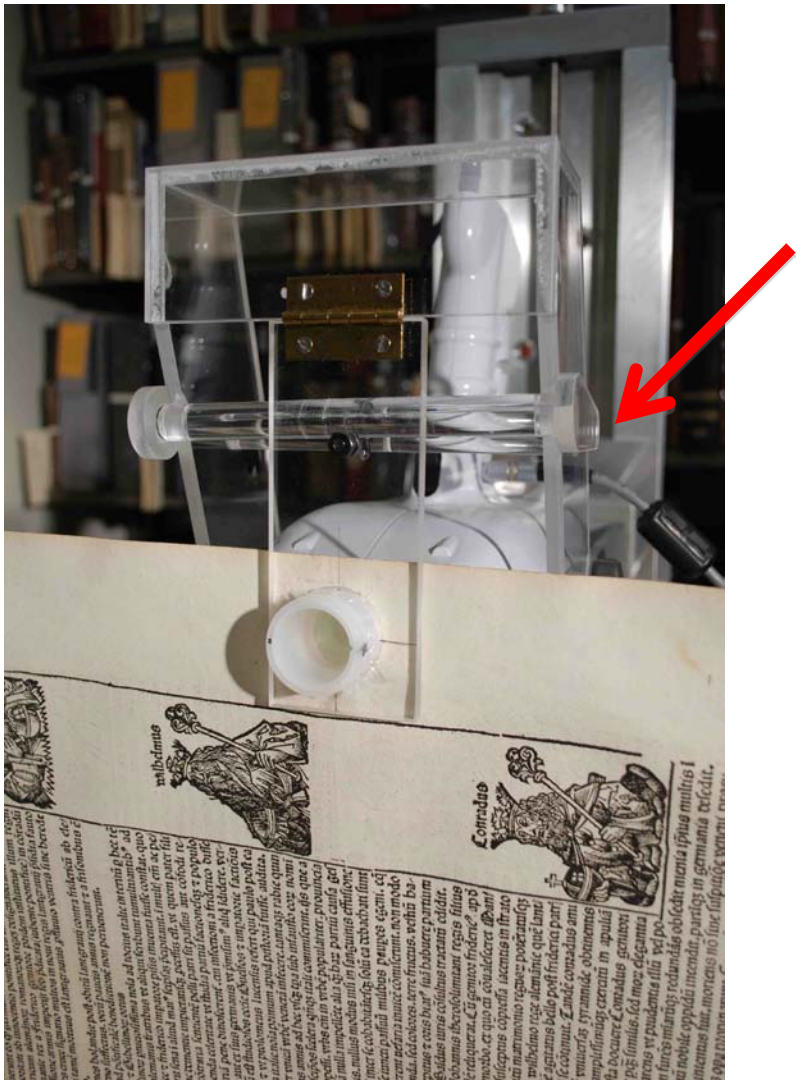
- Chromium(III) 2-ethylhexanoate in 2-ethylhexanoic acid [$Cr(C_8H_{15}O_2)_3$]
- 3,3',5,5'-Tetrabromobisphenol A [$C_{15}H_{12}Br_4O_2$]
- Fiberglass resin

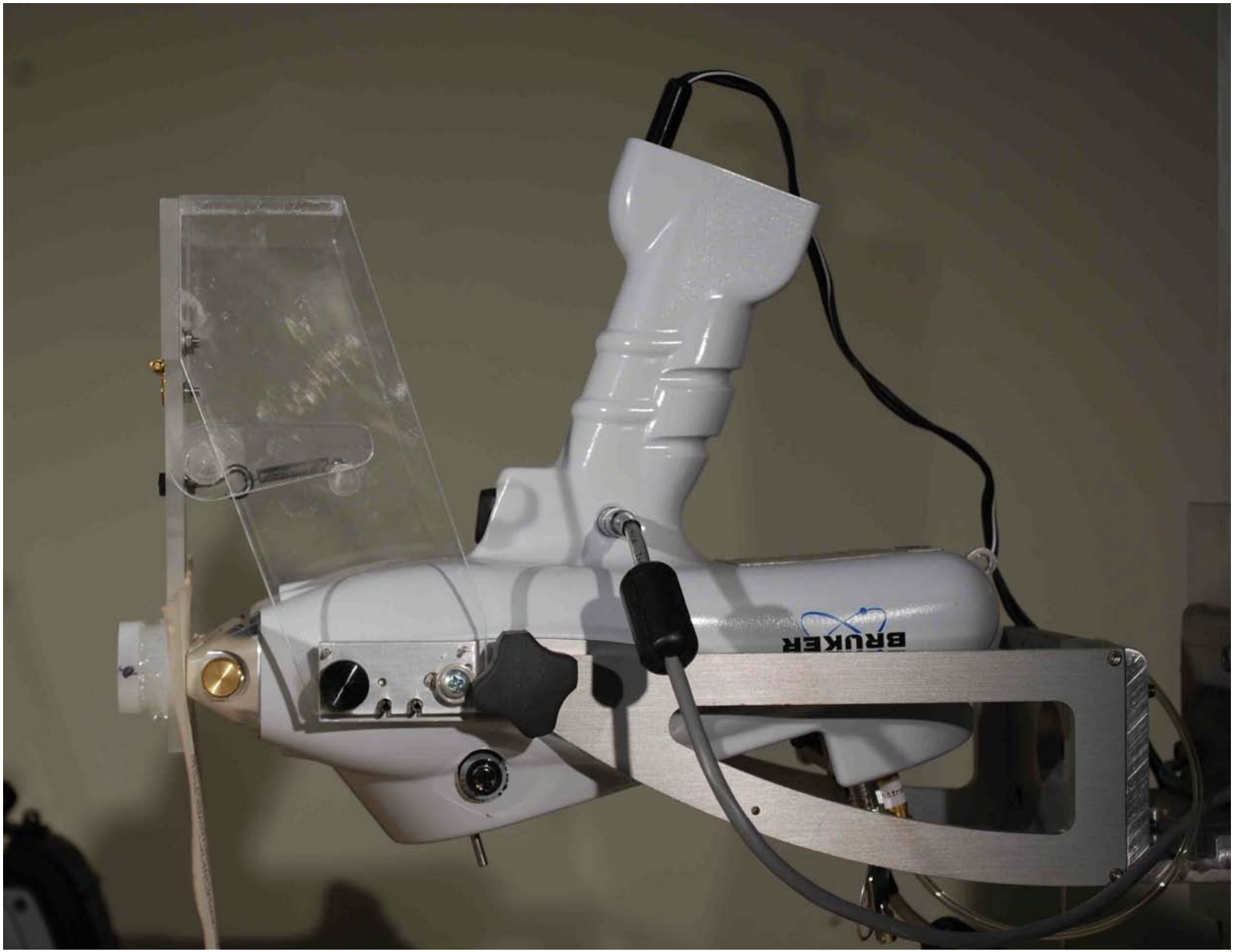


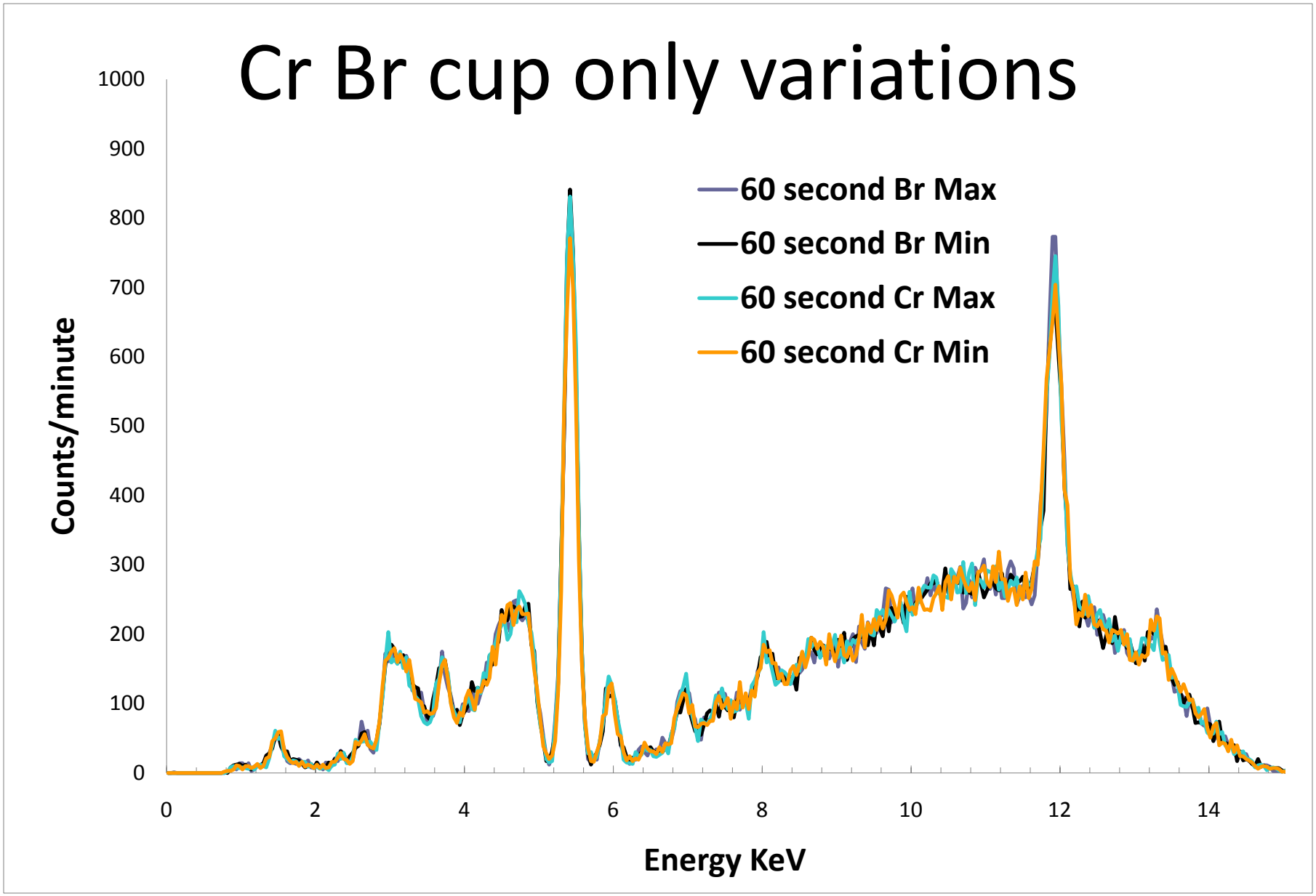


Cr Br cup positioning





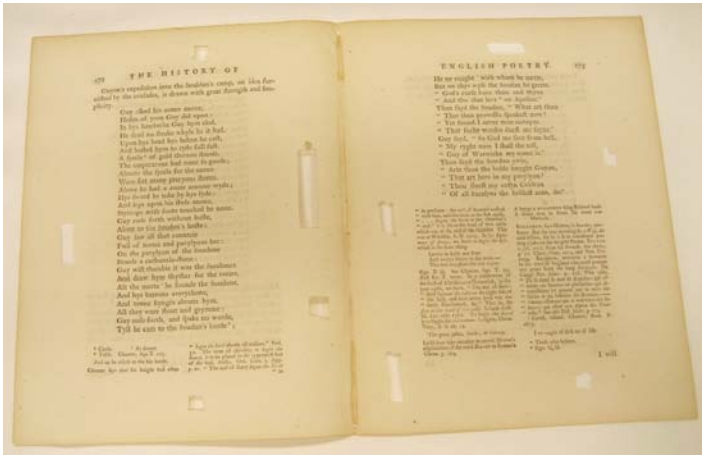

BRUKER


Cr Br cup only variations
60 second Br Max
60 second Br Min
60 second Cr Max
60 second Cr Min
Counts/minute
Energy KeV
0
100
200
300
400
500
600
700
800
900
1000
0
2
4
6
8
10
12
14

5. Select paper specimens for destructive testing and calibration

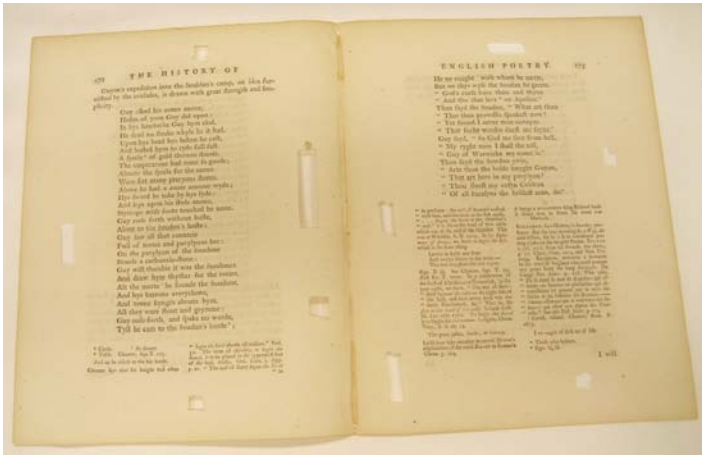
Preparation of samples for elemental analysis

Sampled each specimen with a diamond blade (near 10 random places already sampled for gelatin, etc.)



Preparation of samples for elemental analysis

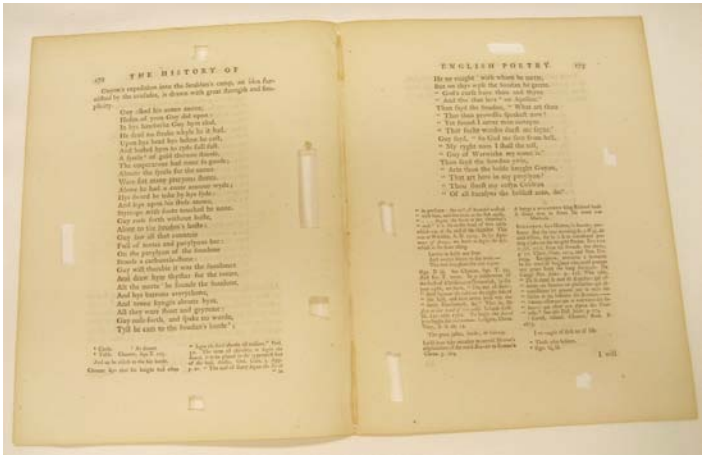
Sampled each specimen with a diamond blade (near 10 random places already sampled for gelatin, etc.)



weighed out ~100mg of paper

Preparation of samples for elemental analysis

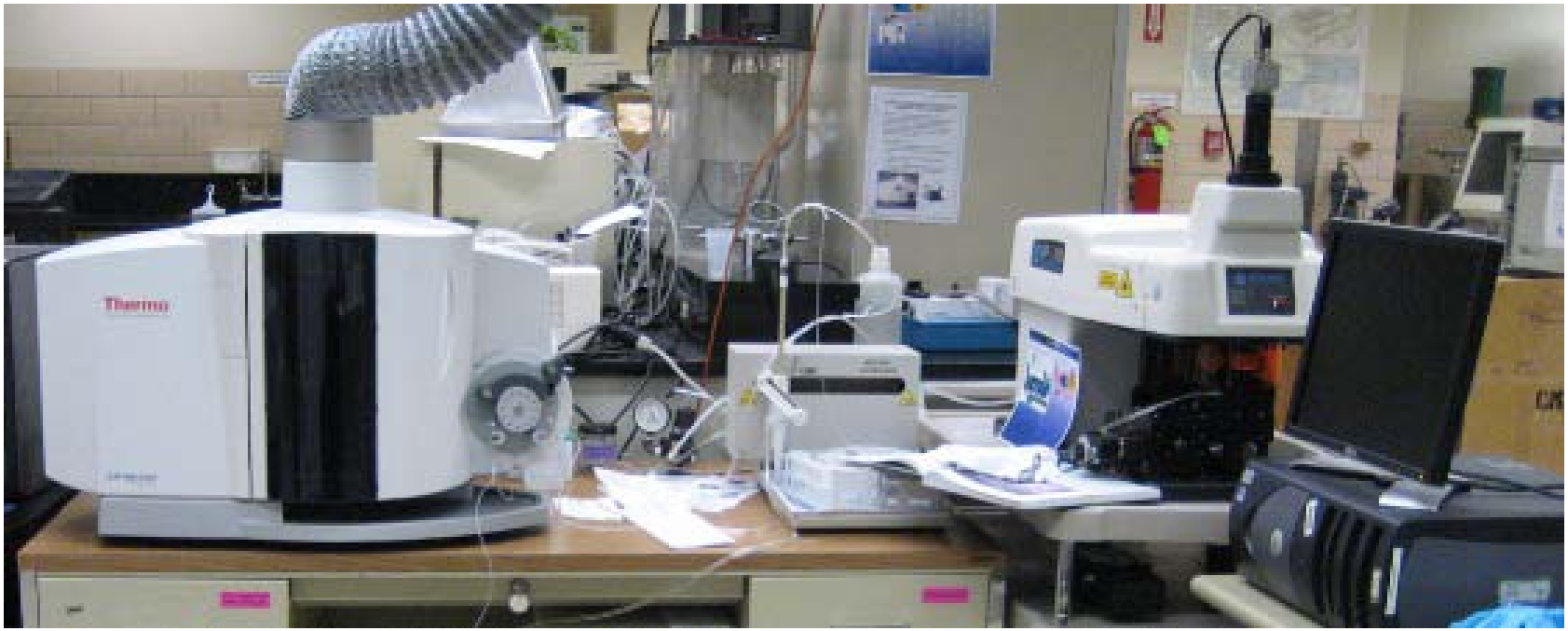
Sampled each specimen with a diamond blade (near 10 random places already sampled for gelatin, etc.)



weighed out ~100mg of paper

digested the samples in individual Teflon vials with Nitric and HF acids

ICP-OES elemental analysis



Thermo iCAP ICP-OES at the Library of Congress

*(**I**nductively **C**oupled **P**lasma – **O**ptical **E**missions **S**pectrometer)*


KODAK Color Control Patches
Kodak

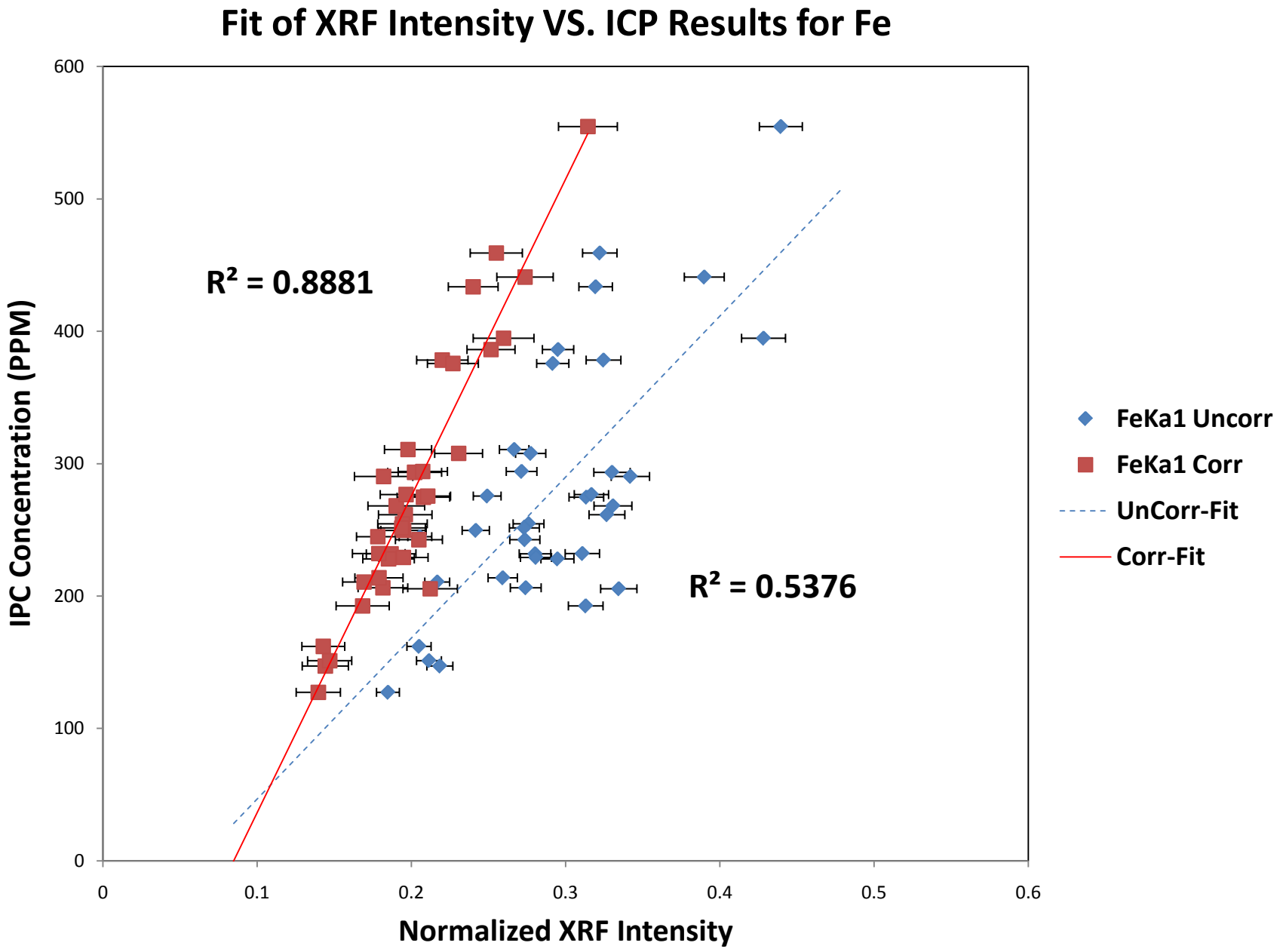
6. Create the calibration

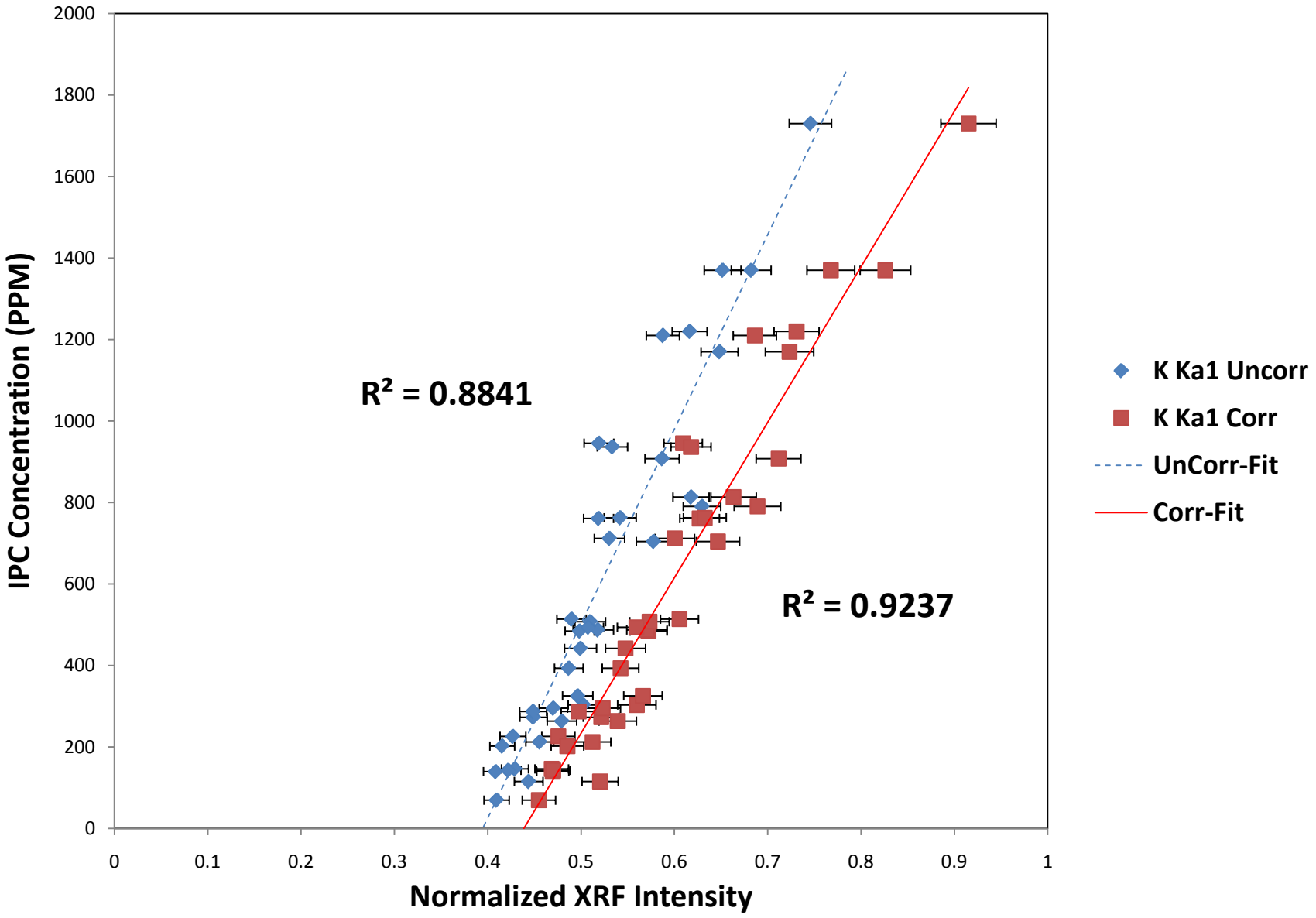
Standard Lucas Tooth equation:

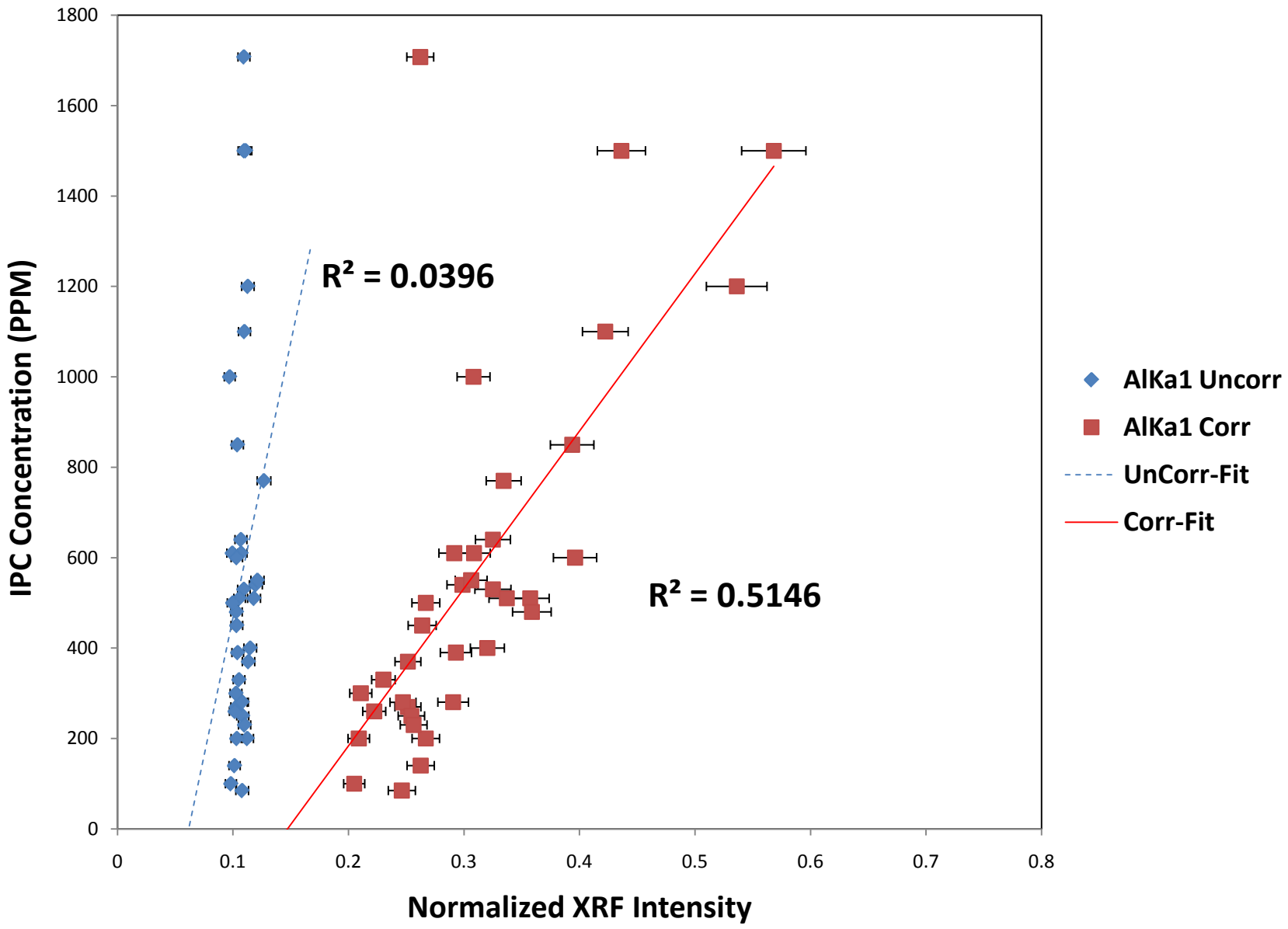
$$W_{nm} = I_{nm}\left(K_0 + \sum_x K_{nm} I_{xm}\right) + b_n$$

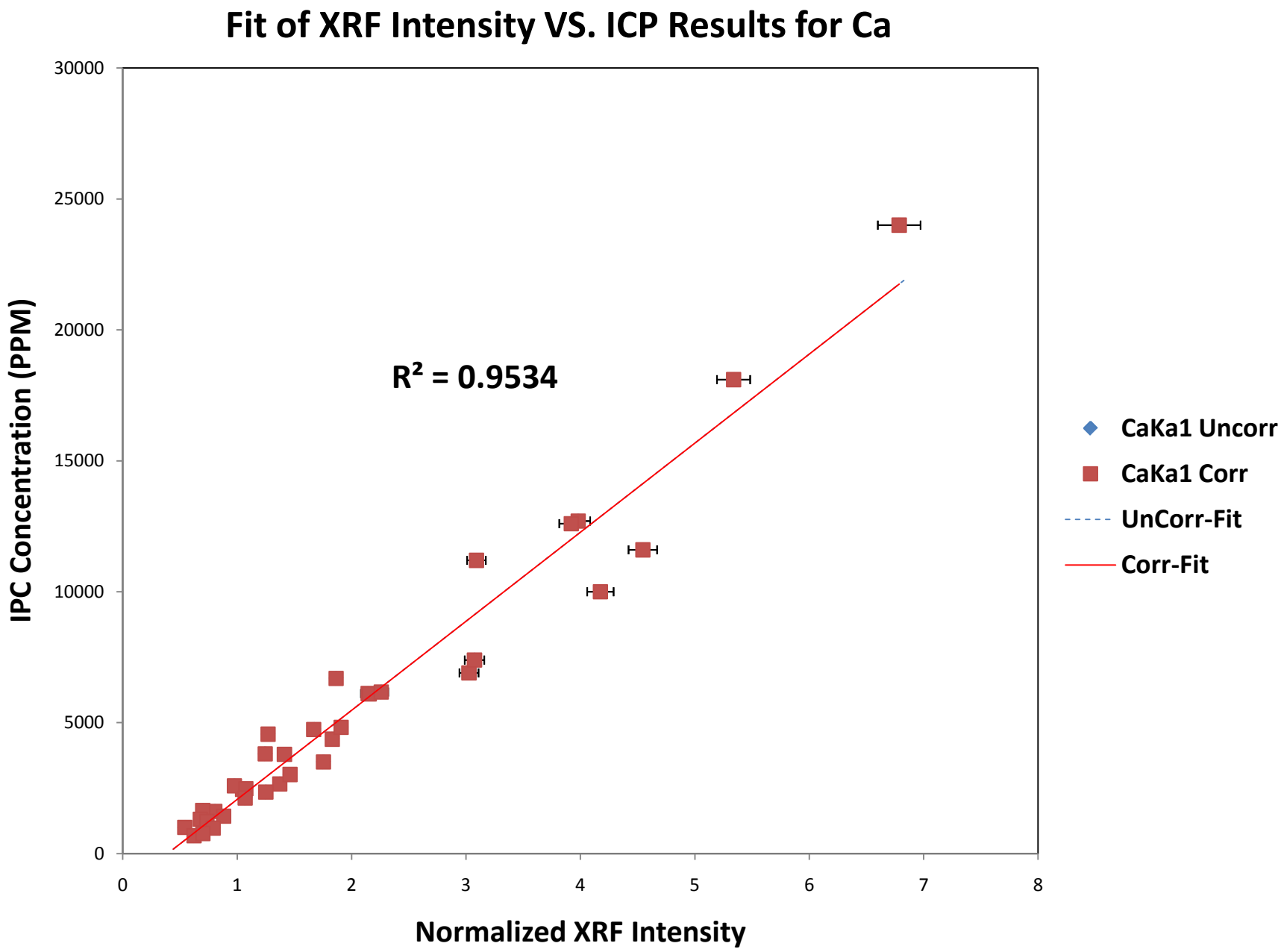
Beer-Lambert law:

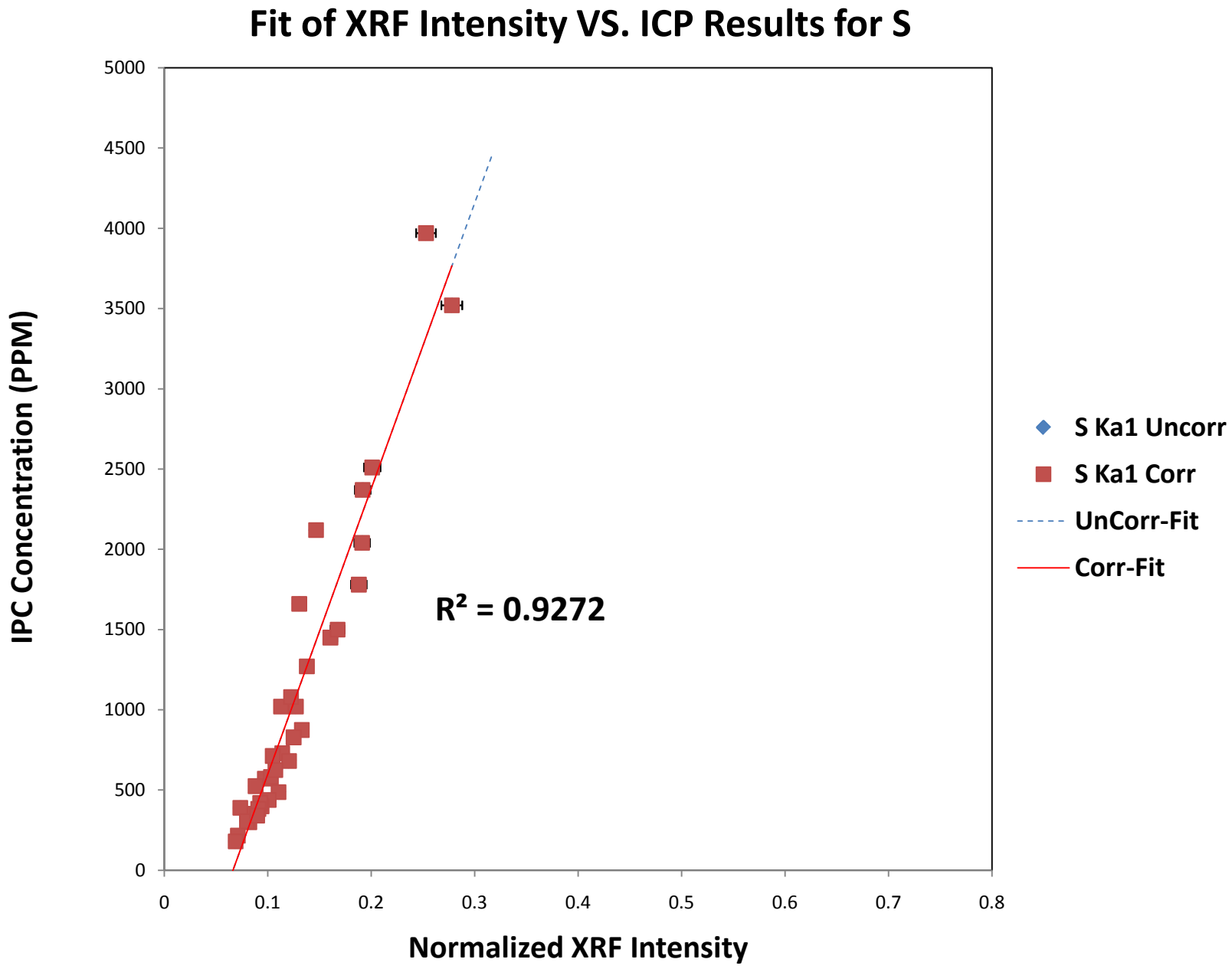
$$I(E) = I_o e^{-\mu\rho x}$$


Fit of XRF Intensity VS. ICP Results for Fe
IPC Concentration (PPM)
Normalized XRF Intensity
R² = 0.8881
R² = 0.5376
FeKa1 Uncorr
FeKa1 Corr
UnCorr-Fit
Corr-Fit
0
100
200
300
400
500
600
0
0.1
0.2
0.3
0.4
0.5
0.6


Fit of XRF Intensity VS. ICP Results for K
IPC Concentration (PPM)
Normalized XRF Intensity
R² = 0.8841
R² = 0.9237
K Ka1 Uncorr
K Ka1 Corr
UnCorr-Fit
Corr-Fit
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


Fit of XRF Intensity VS. ICP Results for Al
IPC Concentration (PPM)
Normalized XRF Intensity
R² = 0.0396
R² = 0.5146
AlKa1 Uncorr
AlKa1 Corr
UnCorr-Fit
Corr-Fit
0
200
400
600
800
1000
1200
1400
1600
1800
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8


Fit of XRF Intensity VS. ICP Results for Ca
IPC Concentration (PPM)
Normalized XRF Intensity
R² = 0.9534
30000
25000
20000
15000
10000
5000
0
0
1
2
3
4
5
6
7
8
CaKa1 Uncorr
CaKa1 Corr
UnCorr-Fit
Corr-Fit


Fit of XRF Intensity VS. ICP Results for S
IPC Concentration (PPM)
Normalized XRF Intensity
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
R² = 0.9272
S Ka1 Uncorr
S Ka1 Corr
UnCorr-Fit
Corr-Fit

Sources of uncertainty impacting accuracy and precision

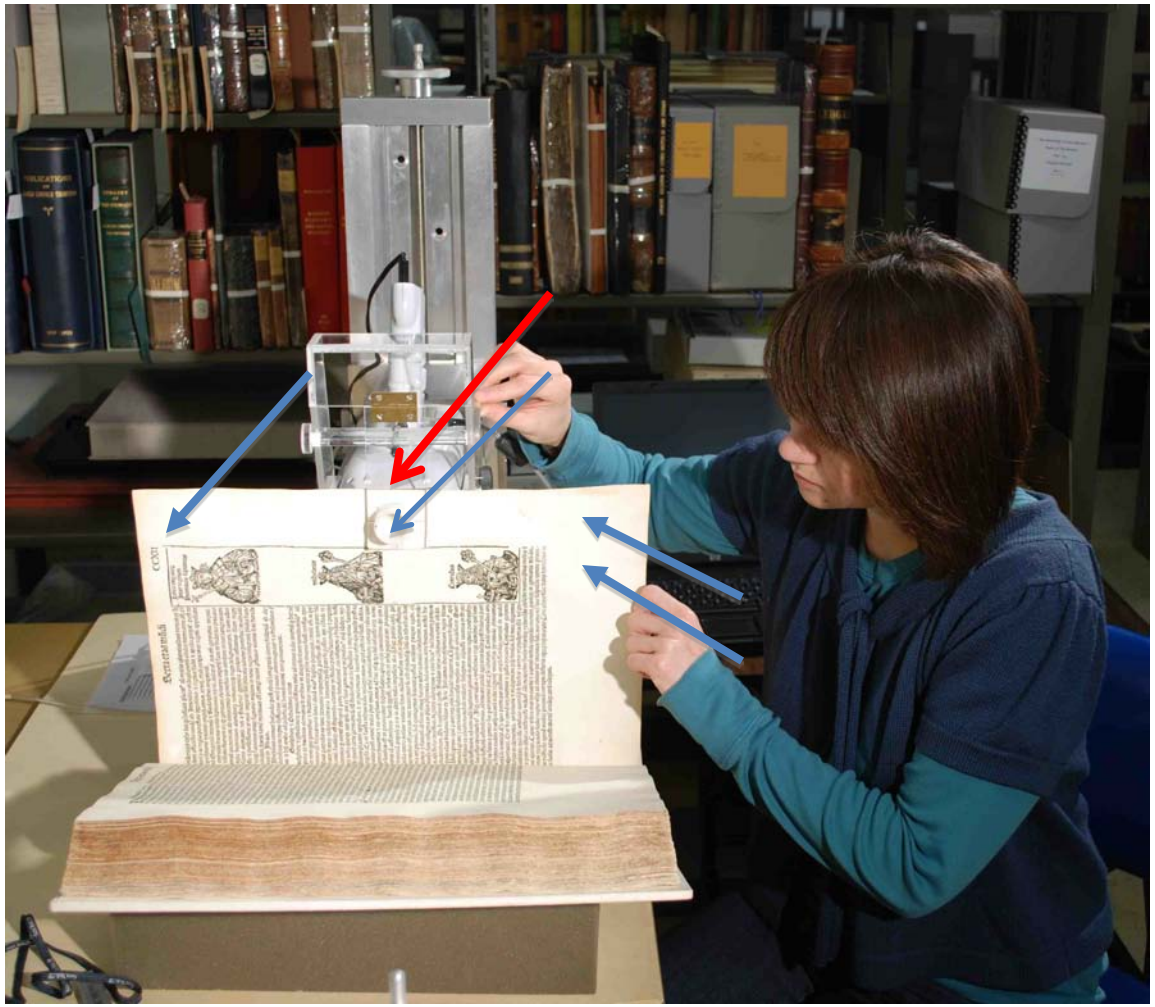
- Instrument error (addressed by 2 x SD precision value)
- Specimen placement/geometry*
- Specimen thickness*
- Calibration accuracy (from the 4 ICP specimens not used in the calibration)

*included in the calibration

7. Estimate overall predictive ability

- Precision of +/- 20% at a 90% confidence level when concentrations are close to 1000ppm
- Improves at higher concentrations, is poorer at lower concentrations
- Elemental variations also impact results

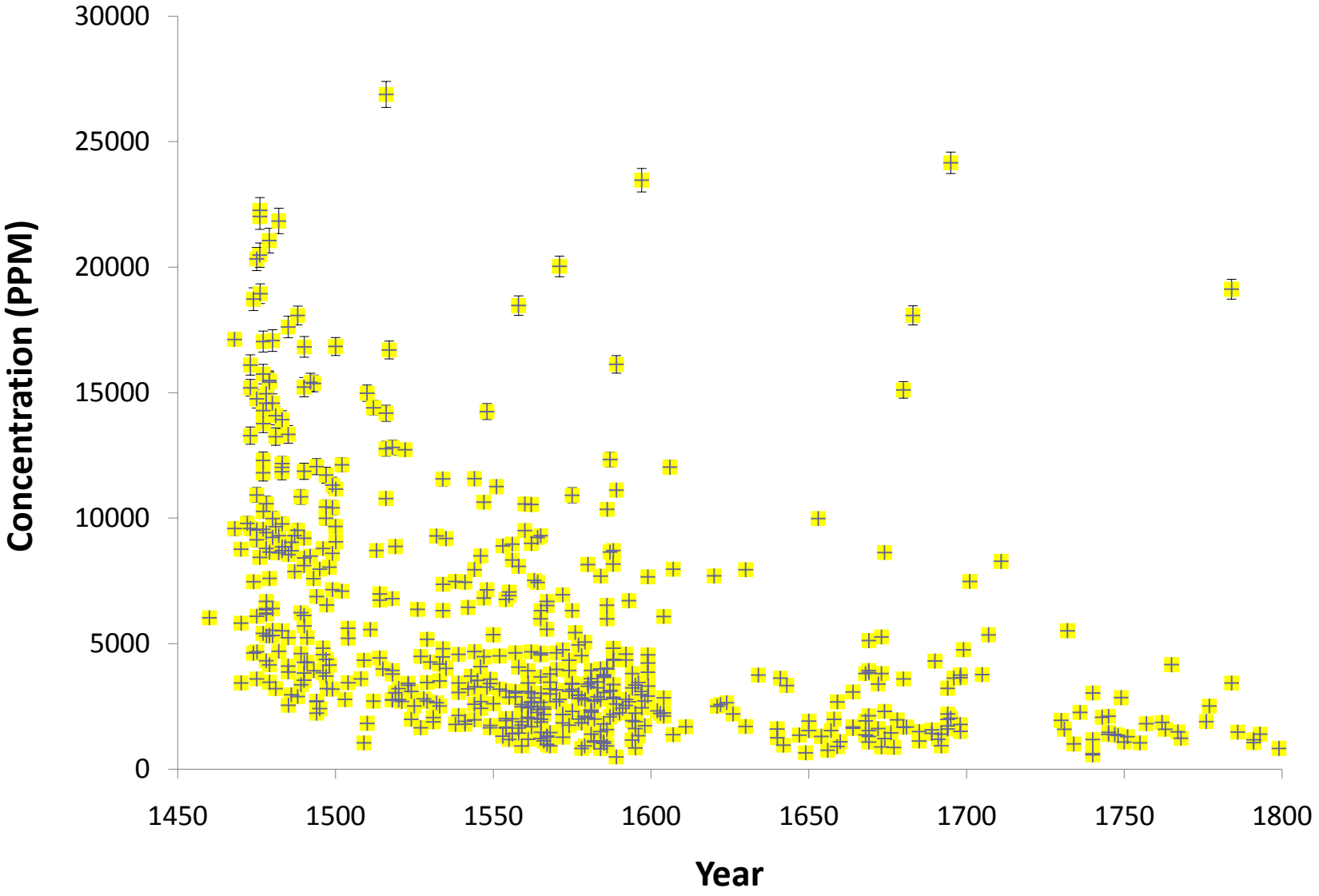
8. Acquire data; output results



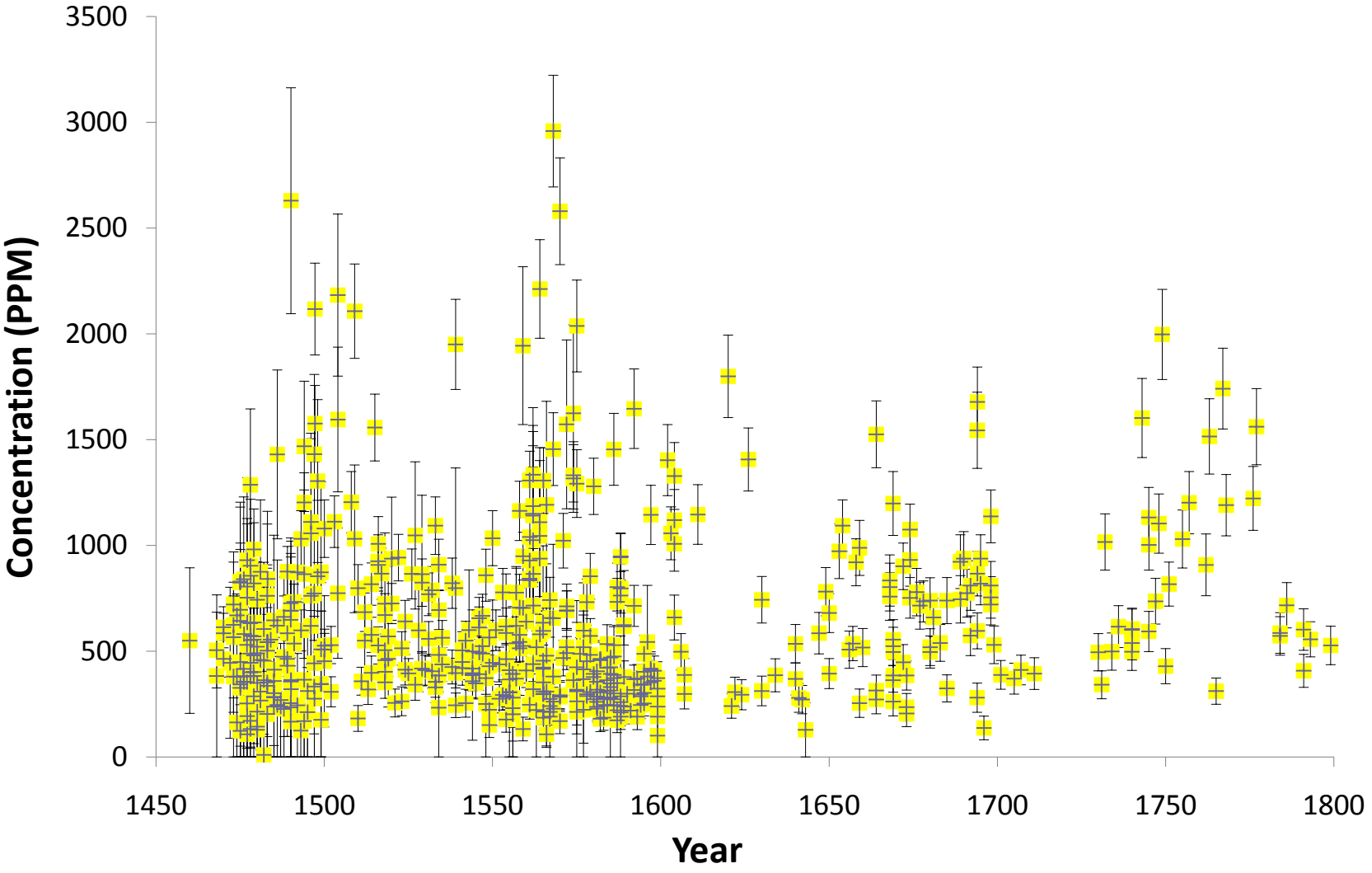
8. Acquire data; output results

IMLS#	Date Tested	Al Symbol	Al	Al Precision	S Symbol	S	S Precision
1502-002	10/17/08		529	88		567	167
1503-001	11/14/08		1112	122		2089	207
1504-001	2/28/08		774	308		1178	270
1504-002	3/7/08	+	2183	383		2518	462
1504-003	3/7/08		1595	342		1976	390
1508-001	9/12/08		1204	145		2584	245
1509-001	3/6/08		1031	349		2171	318
1509-002	9/5/08	+	2107	223	+	4962	322
1510-002	9/30/08		798	111		1587	208
1510-003	1/15/09		182	61	-	178	144

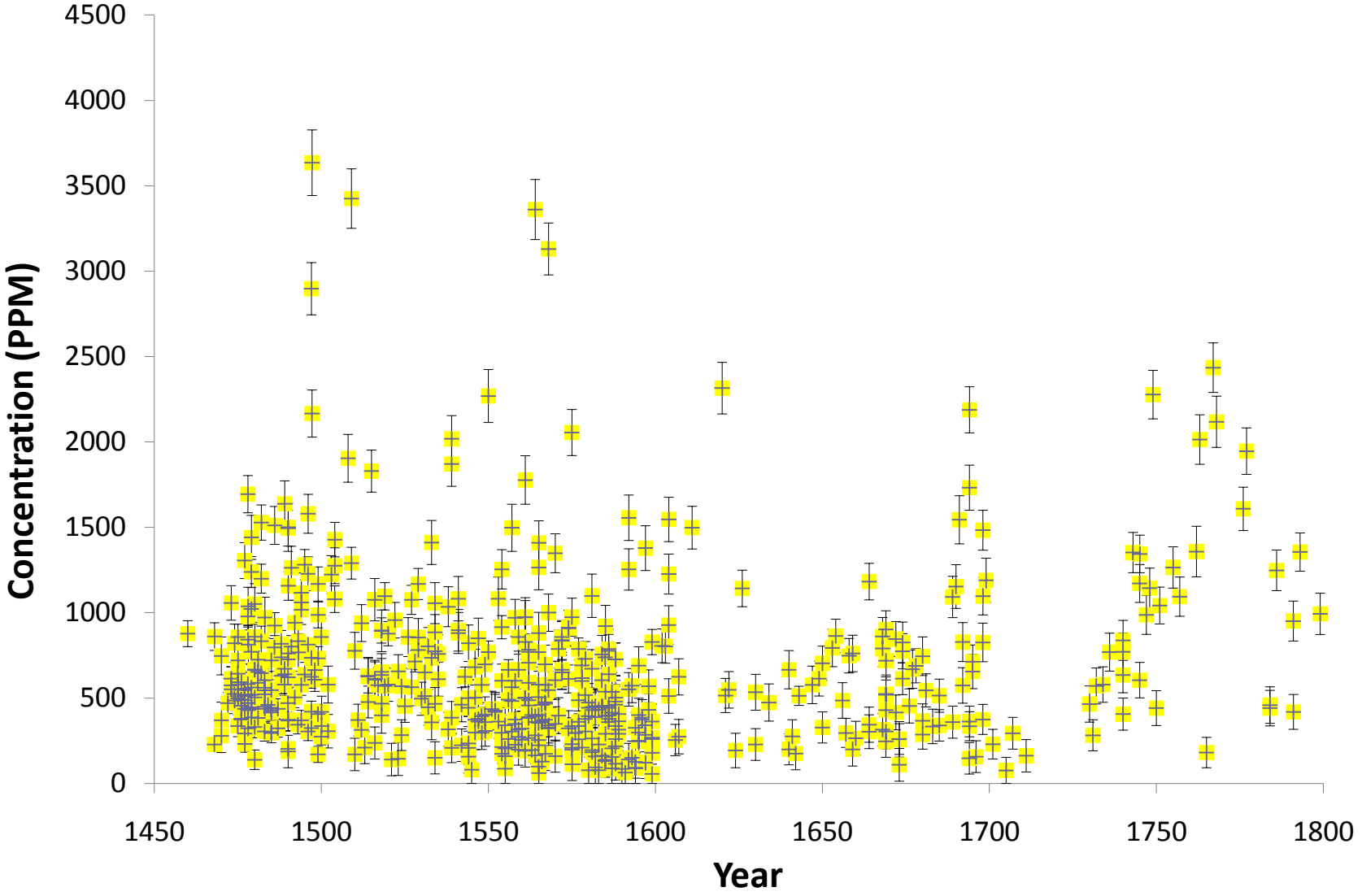
Early research results; Ca



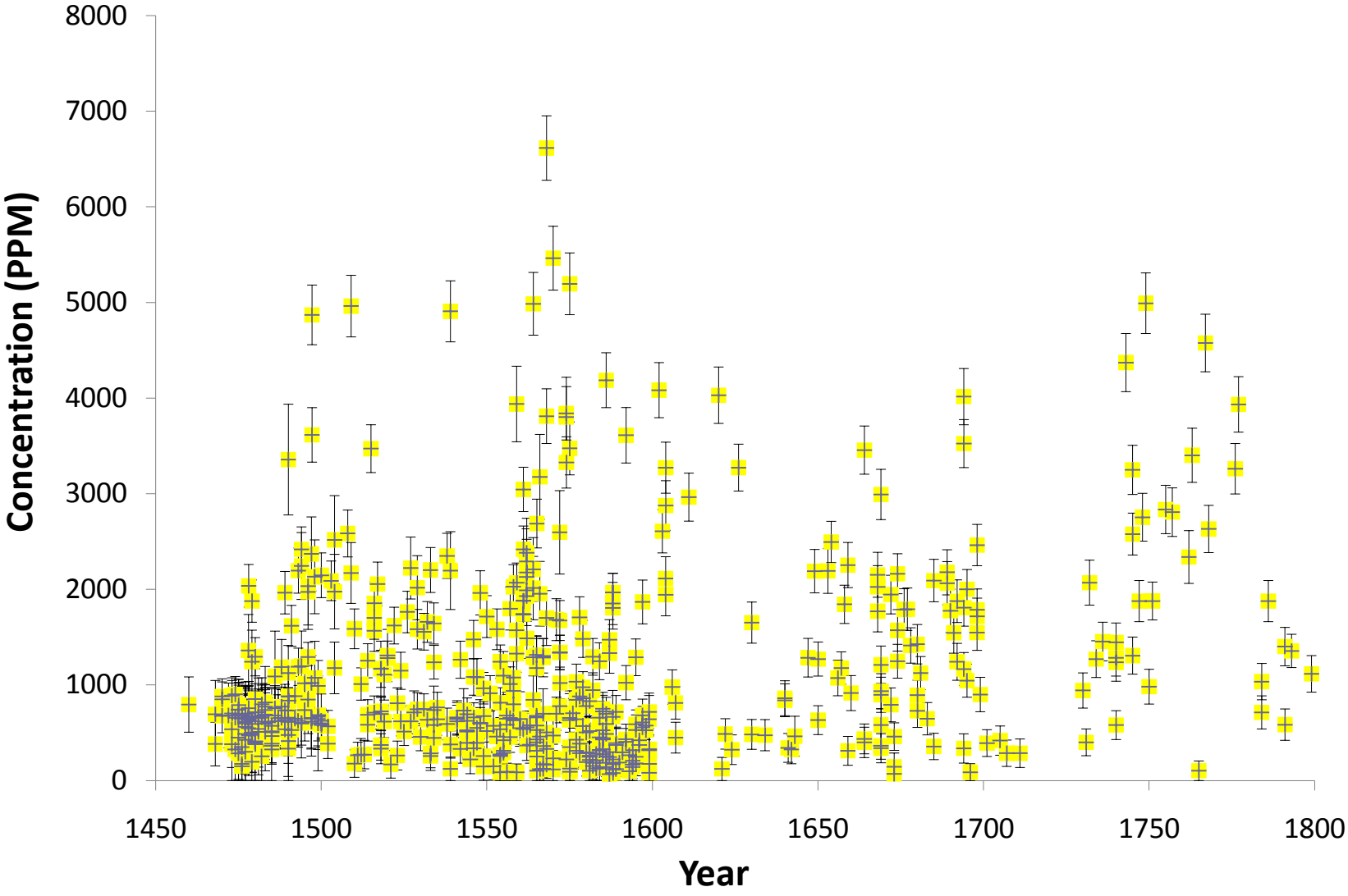
Early research results; Al



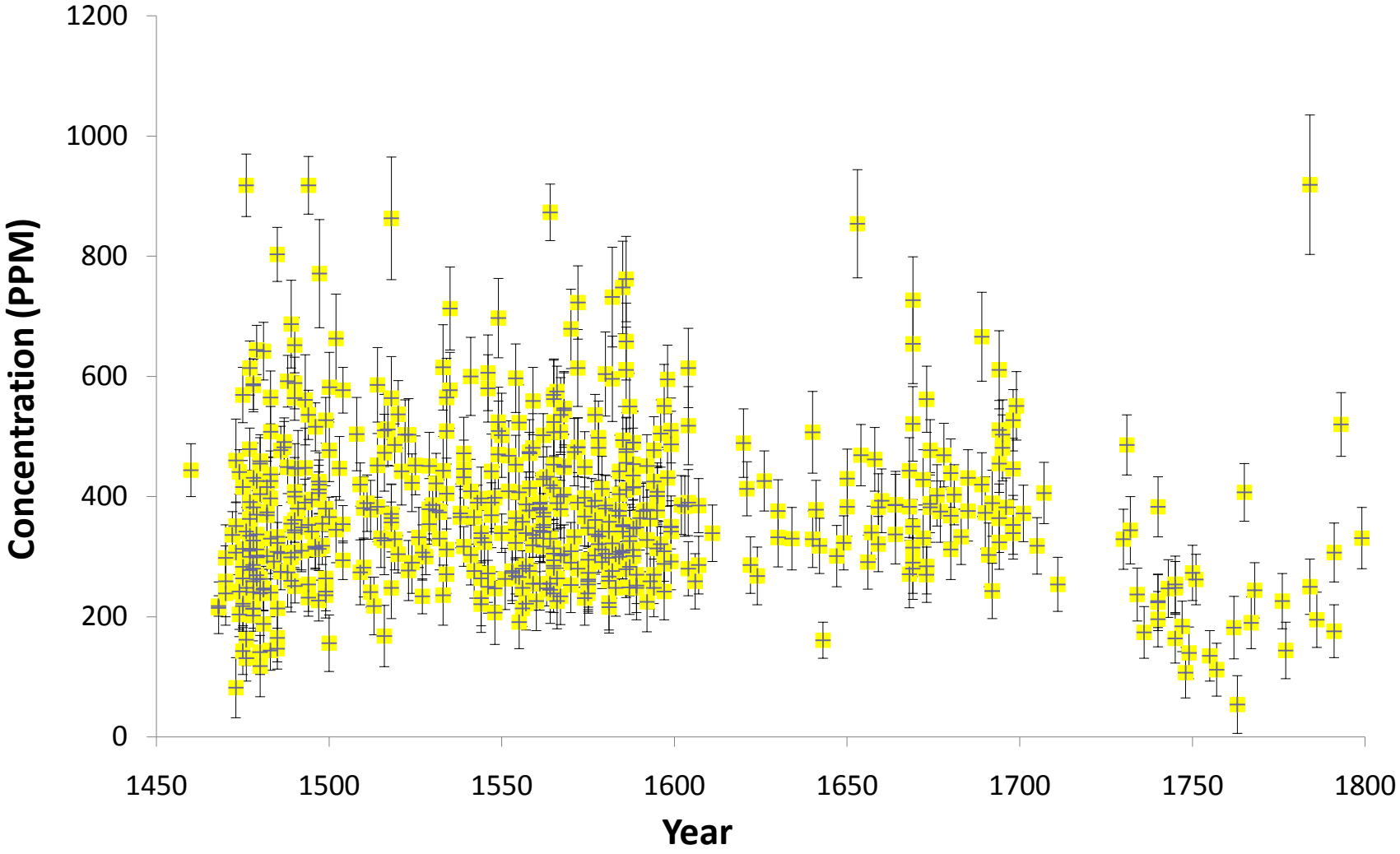
Early research results; K



Early research results; S



Early research results; Fe



Conclusions

- Handheld XRF instrumentation equipped with the proper accessories and software holds promise for estimation of elemental concentration of elements of interest in historical paper specimens in open books or at the perimeter of works of art on paper.
- Predictive power is enhanced by the number of unknowns analyzed. Thus surveys of large numbers of items in collections result in the most reliable data.

Conclusions Continued

- More research is necessary before this method can be recommended for monitoring of elemental changes during single item treatment, however predictive capability may improve over the work shown here because single artifacts consist of essentially the same substrate (with similar thickness and density) during treatment steps.

Acknowledgements

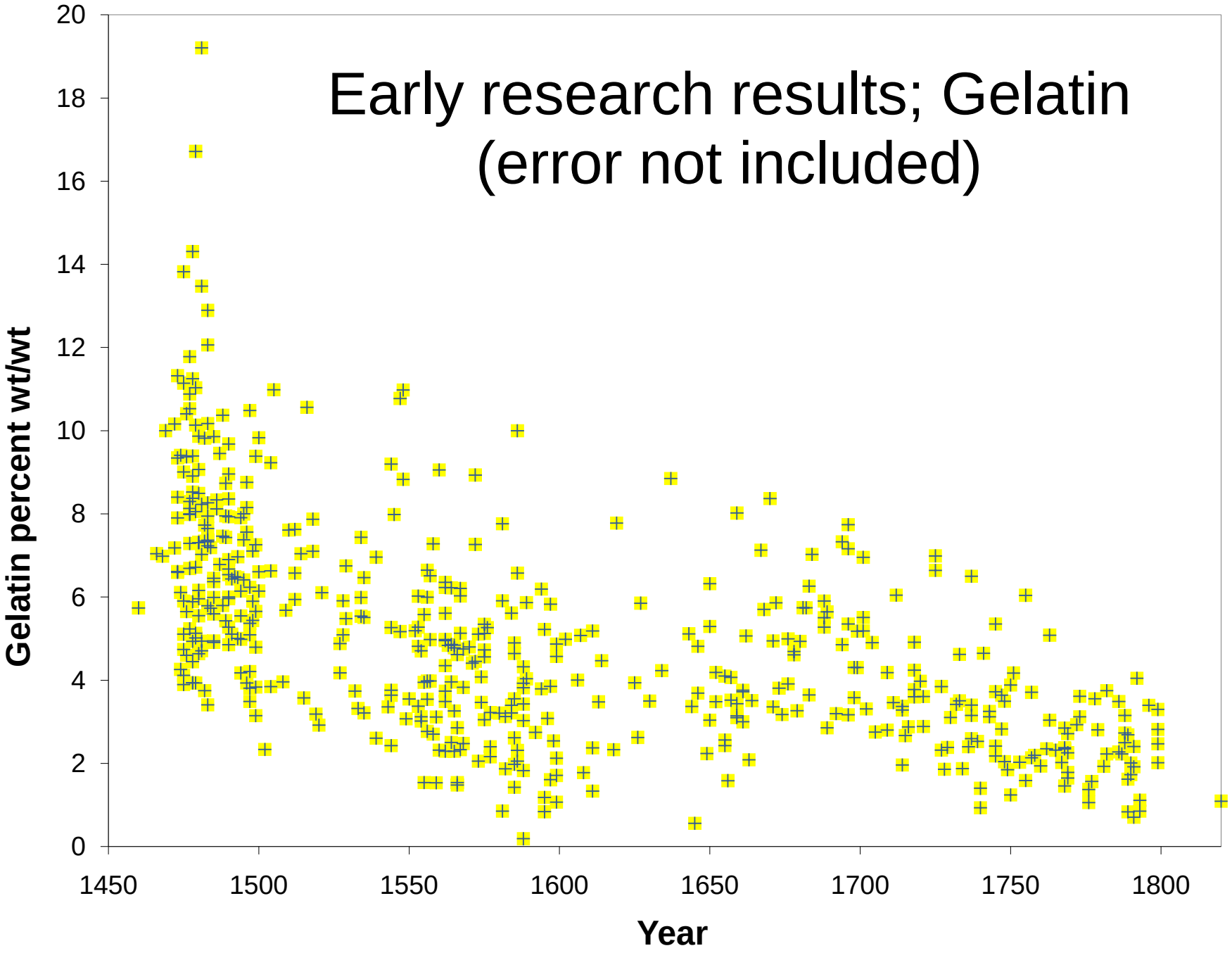
- Institute for Museum and Library Services
- University of Iowa Center for the Book
- Bruker AXS
- Library of Congress, Preservation Research and Testing Division
- The Kress Foundation

Four ICP Test Samples Not used in Calibration

		Sample Accuracy					Sample Precision			
	Sample Label	D16	D5	L19	L2	Sample Label	D16	D5	L19	L2
AlKa1	Conc.(ppm)	1300	1200	160	240	2STDEV	170	334	114	130
	Bias (ppm)	-258	143	100	350	Est. Prec.	147	191	75	115
S Ka1	Conc.(ppm)	2620	3220	361	665	2STDEV	240	522	173	255
	Bias (ppm)	-102	283	-114	174	Est. Prec.	292	366	160	212
K Ka1	Conc.(ppm)	1670	1260	282	468	2STDEV	163	261	211	180
	Bias (ppm)	-119	251	-96	48	Est. Prec.	250	234	154	182
CaKa1	Conc.(ppm)	759	1140	5280	19900	2STDEV	119	109	514	796
	Bias (ppm)	-26	-169	326	-3982	Est. Prec.	134	149	411	1190
FeKa1	Conc.(ppm)	188	106	291	302	2STDEV	36	42	37	26
	Bias (ppm)	19	-45	-35	15	Est. Prec.	76	76	84	100

Final data to be published as an interactive website in early 2010

- Alum, Ca, Fe and gelatin content
- Color
- Sheet thickness
- Sheet size
- Strength
- Publication information; title, country, date, etc.
- Photo
- Materials and workmanship (MW) quality grade
- Good and poor MW sheets in the same book?
- Binding original?


Early research results; Gelatin
(error not included)
Gelatin percent wt/wt
Year
0
2
4
6
8
10
12
14
16
18
20
1450
1500
1550
1600
1650
1700
1750
1800

Surprises? Chlorine