

# **Detailed Elemental Analysis of 1650,s Bronze materials found in Illinois Utilizing x ray beams from the Tracer III V+ and The Artax systems**

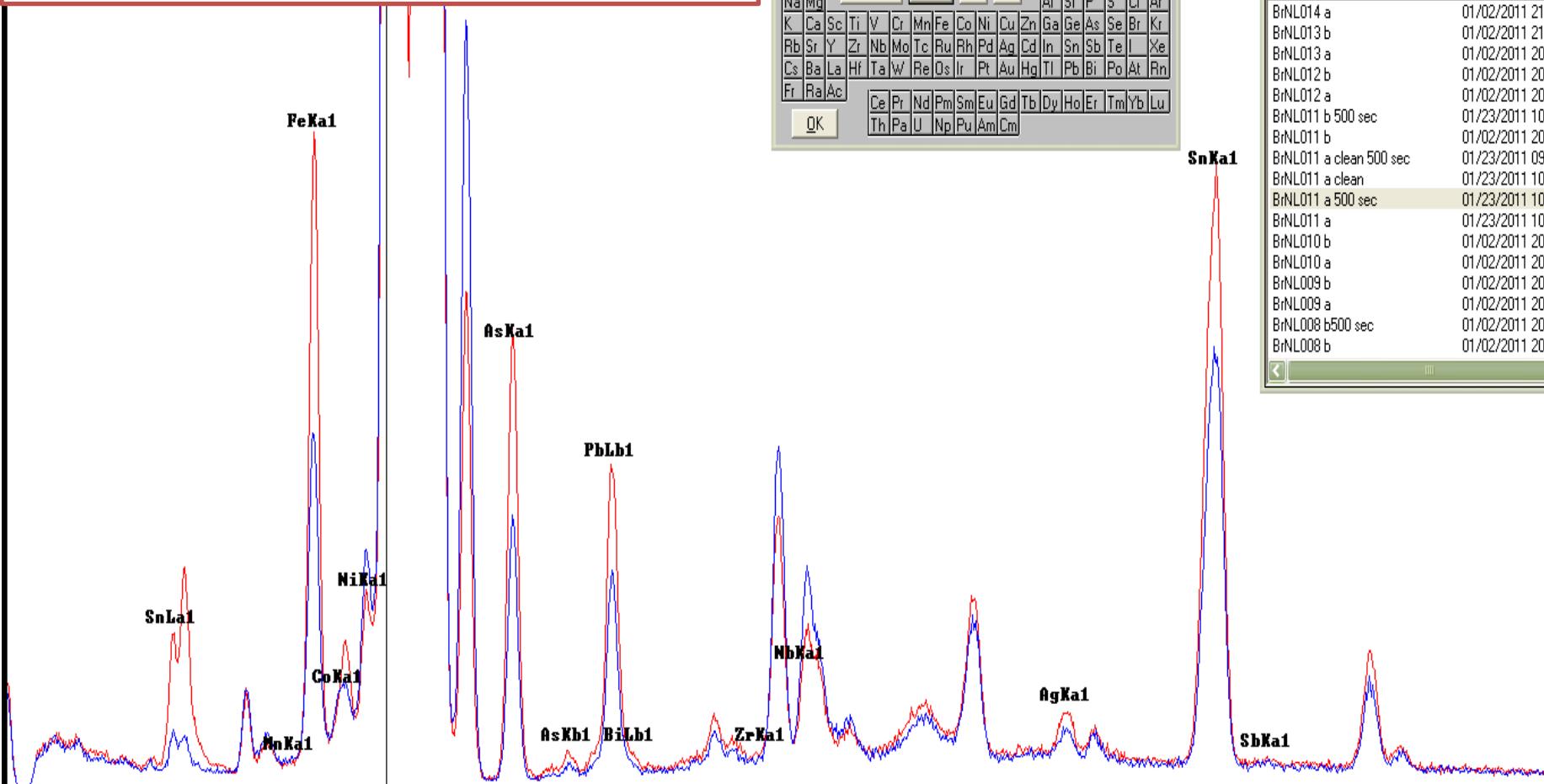
Comparison of as found surface and cleaned surface  
Artifacts BrNL011, BrNL102, BrNL105

The following 3 slides are typical spectra of samples in a clean are and a natural area. “Cleaning” was done by scraping away the corrosion layer, until bright metal was visible.

**The Tracer measurements without “Clean” in the name were taken through the corrosion layer. Artax scans were set up to cover part of the cleaned area an part of the natural area. This is clearly evident in the photographs and the plots of each element distribution.** It is very important to understand it is impossible for xrf analysis to give quantitative answers when a corrosion layer is present as this material is by its nature very non uniform and x ray physics precludes quantification of these materials. So any quantitative numbers in these situations are just ~~mean~~ to be indicative of the possible greater or lesser presence of a element, and only logical deduction can help one with the knowledge whether the element is in the corrosion or in th base metal ;as you are measuring both in some unknown proportion. It is for this reason that when ever possible both clean and corroded surfaces where measured. Also where possible the front and back of each item was measured as early Cu alloys by there very nature are very non uniform.

The measurements with the Tracer were taken with the Rh X ray tube set at 40 Kv and 3 micro amps, with a .001” Ti - .012” Al beam filter for 500 sec to assure that the trace elements could be detected in the raw spectrum.

***Below are the actual raw spectra of each location “scanned “ with the Artax are overlayed so one can easily see the elemental differences for 3 artifacts BrNL011, BrNL102, BrNL105 cleaned and natural.***

**CuKa1****BrNL011 a 500 sec/BrNL011 a clean 500 sec**

Select Elements

H	SnLa1 - 50	<input type="radio"/> K	<input checked="" type="radio"/> L	<input type="radio"/> M	He
Li	Be	<input type="radio"/> Clear All	<input type="radio"/> Add	<input type="radio"/> Z-	<input type="radio"/> Z+
Na	Mg			<input type="radio"/> Al	<input type="radio"/> Si
K	Ca	<input type="radio"/> Sc	<input type="radio"/> Ti	<input type="radio"/> V	<input type="radio"/> Cr
Rb	Sr	<input type="radio"/> Y	<input type="radio"/> Zr	<input type="radio"/> Nb	<input type="radio"/> Mo
Cs	Ba	<input type="radio"/> La	<input type="radio"/> Hf	<input type="radio"/> Ta	<input type="radio"/> W
Fr	Ra	<input type="radio"/> Ac		<input type="radio"/> Re	<input type="radio"/> Os
				<input type="radio"/> Ir	<input type="radio"/> Pt
				<input type="radio"/> Au	<input type="radio"/> Hg
				<input type="radio"/> Tl	<input type="radio"/> Pb
				<input type="radio"/> Bi	<input type="radio"/> Po
				<input type="radio"/> At	<input type="radio"/> Rn
				<input type="radio"/> Ce	<input type="radio"/> Pr
				<input type="radio"/> Nd	<input type="radio"/> Pm
				<input type="radio"/> Sm	<input type="radio"/> Eu
				<input type="radio"/> Gd	<input type="radio"/> Tb
				<input type="radio"/> Dy	<input type="radio"/> Ho
				<input type="radio"/> Er	<input type="radio"/> Tm
				<input type="radio"/> Yb	<input type="radio"/> Lu
			<input type="radio"/> Th	<input type="radio"/> Pa	<input type="radio"/> U
			<input type="radio"/> Np	<input type="radio"/> Pu	<input type="radio"/> Am
			<input type="radio"/> Cm		

OK

PDZ Preview

Path OK

Name	Date
BrNL014 a	01/02/2011 21:
BrNL013 b	01/02/2011 21:
BrNL013 a	01/02/2011 20:
BrNL012 b	01/02/2011 20:
BrNL012 a	01/02/2011 20:
BrNL011 b 500 sec	01/23/2011 10:
BrNL011 b	01/23/2011 09:
BrNL011 a clean 500 sec	01/23/2011 10:
BrNL011 a clean	01/23/2011 10:
BrNL011 a 500 sec	01/23/2011 10:
BrNL011 a	01/23/2011 10:
BrNL010 b	01/02/2011 20:
BrNL010 a	01/02/2011 20:
BrNL009 b	01/02/2011 20:
BrNL009 a	01/02/2011 20:
BrNL008 b500 sec	01/02/2011 20:
BrNL008 b	01/02/2011 20:

Cnt:41357

LSec:500.00

Chan:395.638

Kev:7.9233

Det:-40.0C

Amb:91.4F

Raw:9.795.00

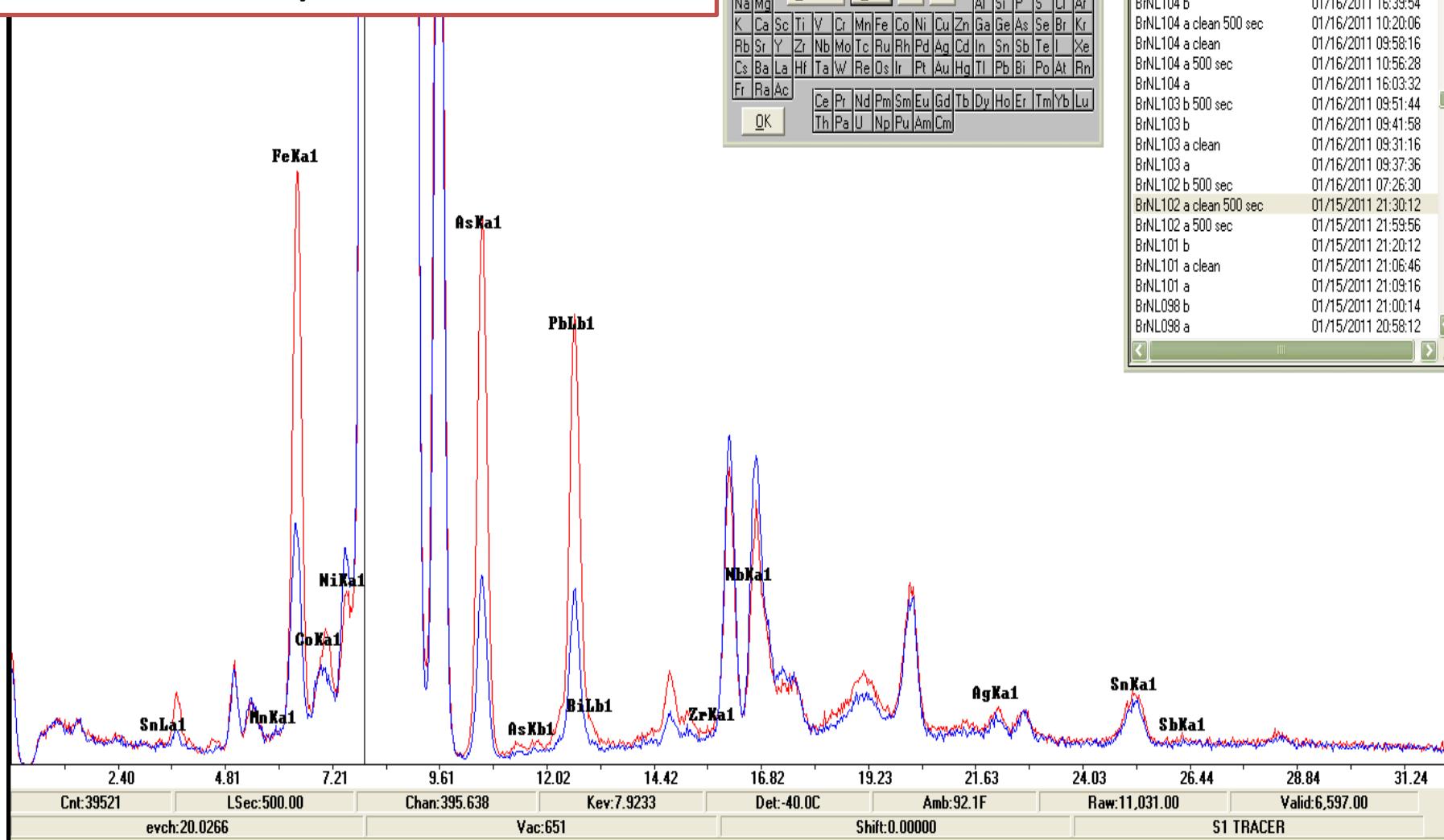
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evch:20.0266

Vac:654

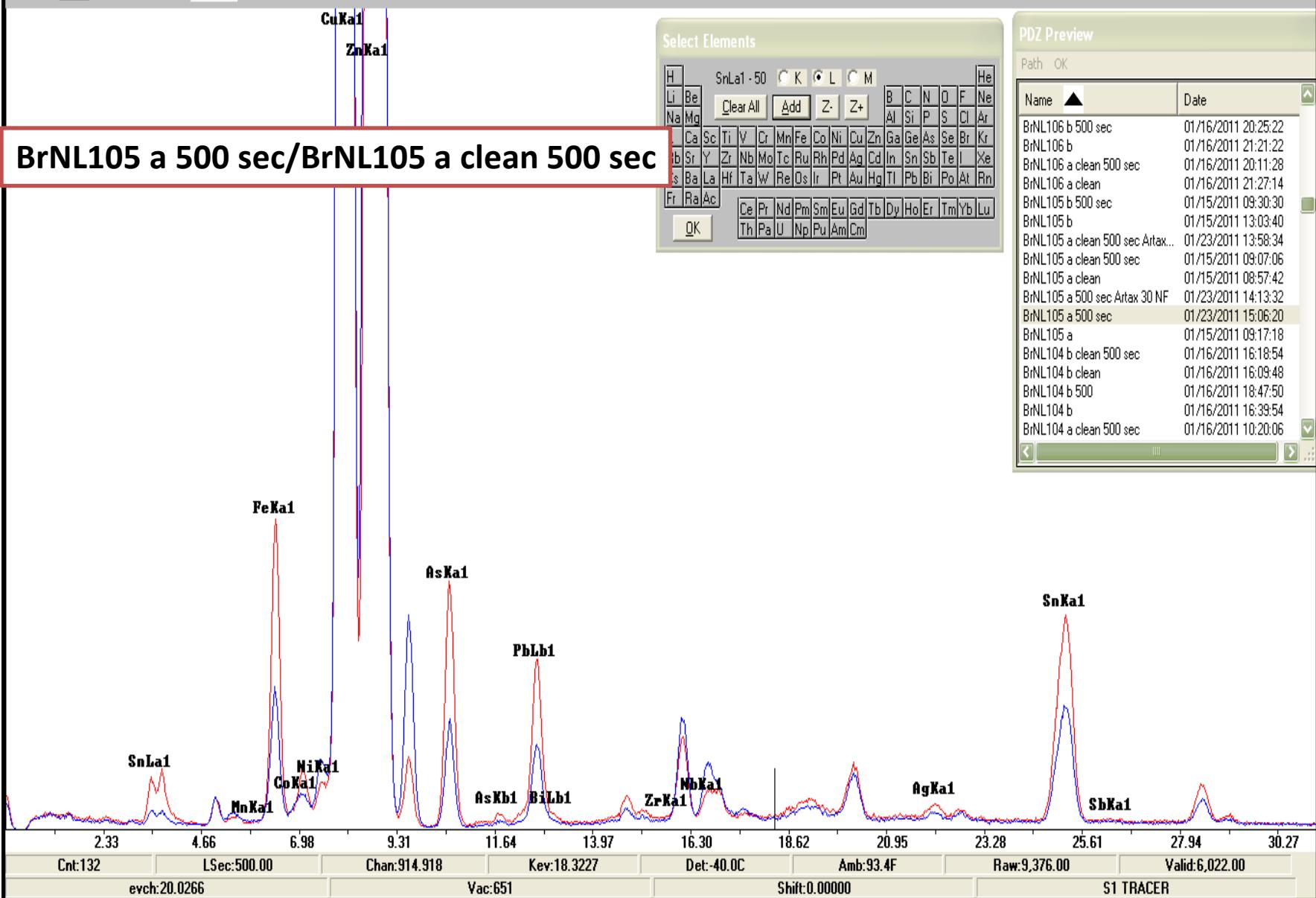
Shift:0.00000

S1 TRACER

Clear B/A **INST FILE #** KTI (.PDZ 40.00kV, 3.00pA)**CuKa1****BrNL102 a 500 sec/BrNL102 a clean 500 sec****PDZ Preview**

Path OK

Name	Date
BrNL104 b	01/16/2011 16:39:54
BrNL104 a clean 500 sec	01/16/2011 10:20:06
BrNL104 a clean	01/16/2011 09:58:16
BrNL104 a 500 sec	01/16/2011 10:56:28
BrNL104 a	01/16/2011 16:03:32
BrNL103 b 500 sec	01/16/2011 09:51:44
BrNL103 b	01/16/2011 09:41:58
BrNL103 a clean	01/16/2011 09:31:16
BrNL103 a	01/16/2011 09:37:36
BrNL102 b 500 sec	01/16/2011 07:26:30
BrNL102 a clean 500 sec	01/15/2011 21:30:12
BrNL102 a 500 sec	01/15/2011 21:59:56
BrNL101 b	01/15/2011 21:20:12
BrNL101 a clean	01/15/2011 21:06:46
BrNL101 a	01/15/2011 21:09:16
BrNL098 b	01/15/2011 21:00:14
BrNL098 a	01/15/2011 20:58:12

Clear A/B **BrNL105 a 500 sec/BrNL105 a clear****INST FILE #**KTI (.PDZ 40.00kV, 3.00 $\mu$ A)

## Tracer III V + quantitative analysis of each analysis

Note that the in all cases for the clean metal analysis the Fe, Cu, As, Pb, Sn, Ag, and Sb are lower and the Zn and Ni are higher. This is also clearly evident in the the Artax scans which follow. Note only the Clean analysis below is accurate.

	BrNL011 a 500 sec	BrNL011 a clean 500 sec		BrNL105 a clean 500 sec	BrNL102 a 500 sec	BrNL102 a clean 500 sec
FeKa1	0.90	0.39	1.52	0.49	0.76	0.20
NiKa1	0.15	0.19	0.06	0.17	0.08	0.13
CuKa1	75.96	75.94	77.80	77.16	71.56	70.83
ZnKa1	14.79	17.10	10.10	15.89	22.58	25.01
AsKa1	0.17	0.04	0.62	0.06	0.07	0.01
PbLb1	1.79	1.09	3.37	1.39	2.46	0.84
AgKa1	0.05	0.02	0.08	0.02	0.02	0.01
SnKa1	4.60	3.12	5.57	2.71	0.37	0.28
SbKa1	0.06	0.03	0.13	0.04	0.05	0.00
SUM	98.49	97.92	99.27	97.93	97.95	97.32

The slides below depict the same samples as above but the measurement parameters were set to match those used in the area elemental area analysis done with the Artax. The Artax is a 0.065 mm micro focus xrf analyzer capable of scanning and object to produce a detailed elemental map. The spacing between the analysis locations was .060 mm. The results of the maps are shown after the Tracer analysis below.

To assure that one clearly understood the detail of the spectra. The Tracer was run at the same setting on the same sample . Thus producing another perspective on what was mapped.

*In detail for the 3 sets of spectra below the presence of Si, P, and increase Sn and Fe, as well as, the increase in the Rh L x rays scattered back to the detector from the samples that have not been “cleaned”. This is because of the significantly higher percent of low mass elements present in the corrosion layer. Note these are not “measured” by xrf because the x rays they emit are too low in energy to detect. For instance H, O, N and C also make up the corrosion layer and are undetected but increase the scatter of the x rays from the surface of the sample.*

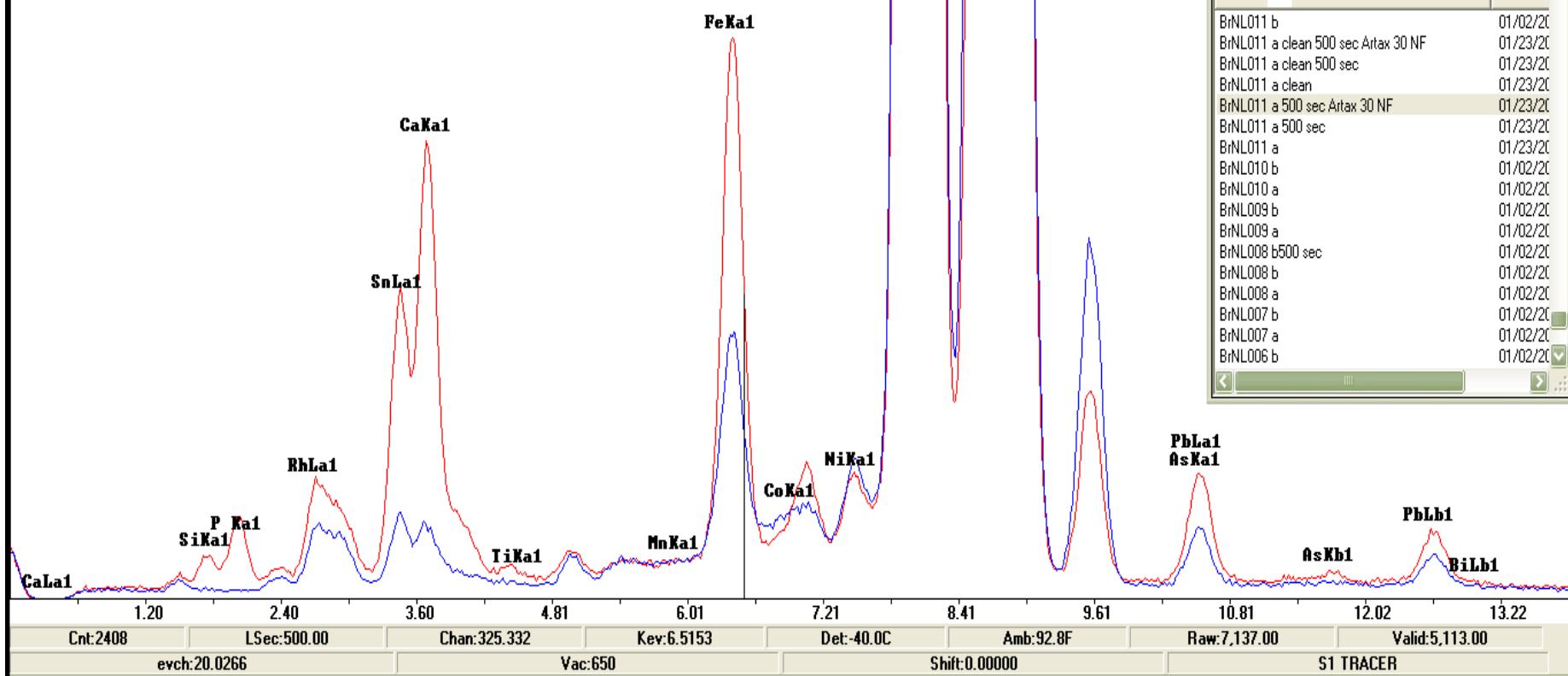
Clear A/B

BrNL011 a 500 sec Artax 30 NF/BrNL011

INST FILE #

KTI (.PDZ 30.00kV, 1.00 $\mu$ A)

## BrNL011 a 500 sec Artax 30 NF/BrNL011 a clean 500 sec Artax 30 NF



Select Elements

H	PbLa1 - 82	<input type="radio"/> K	<input checked="" type="radio"/> L	<input type="radio"/> M	He
Li		<input type="radio"/> Clear All	<input type="radio"/> Add	<input type="radio"/> Z-	<input type="radio"/> Z+
Be					
Na					
Mg					
K					
Ca					
Sc					
Ti					
V					
Cr					
Mn					
Fe					
Co					
Ni					
Cu					
Zn					
Ga					
Ge					
As					
Se					
Br					
Kr					
Rb					
Sr					
Y					
Zr					
Nb					
Mo					
Tc					
Ru					
Rh					
Pd					
Ag					
Cd					
In					
Sn					
Sb					
Te					
Xe					
Cs					
Ba					
La					
Hf					
Ta					
Re					
Ds					
Ir					
Pt					
Au					
Hg					
Tl					
Pb					
Bi					
Po					
At					
Rn					
Fr					
Ra					
Ac					
Ce					
Pr					
Nd					
Pm					
Sm					
Eu					
Gd					
Tb					
Dy					
Ho					
Er					
Tm					
Yb					
Lu					
Th					
Pa					
U					
Np					
Pu					
Am					
Cm					

Spectrum Ove...

Move A &gt;&gt; B

Clear B

OK

PDZ Preview

Path OK

Name	Date
BrNL011 b	01/02/20
BrNL011 a clean 500 sec Artax 30 NF	01/23/20
BrNL011 a clean 500 sec	01/23/20
BrNL011 a clean	01/23/20
BrNL011 a 500 sec Artax 30 NF	01/23/20
BrNL011 a 500 sec	01/23/20
BrNL011 a	01/23/20
BrNL010 b	01/02/20
BrNL010 a	01/02/20
BrNL009 b	01/02/20
BrNL009 a	01/02/20
BrNL008 b 500 sec	01/02/20
BrNL008 b	01/02/20
BrNL008 a	01/02/20
BrNL007 b	01/02/20
BrNL007 a	01/02/20
BrNL006 b	01/02/20



...

File Setup ID DownLoad Timed Tube Help

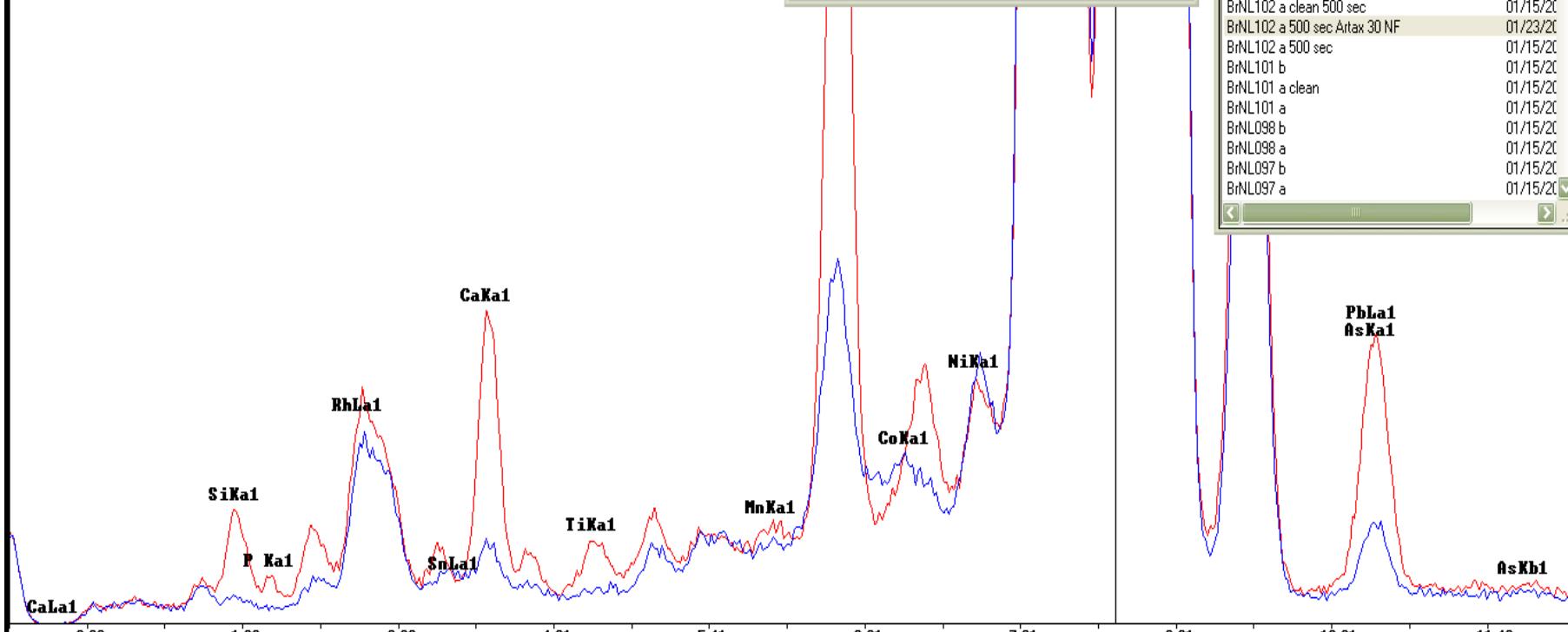
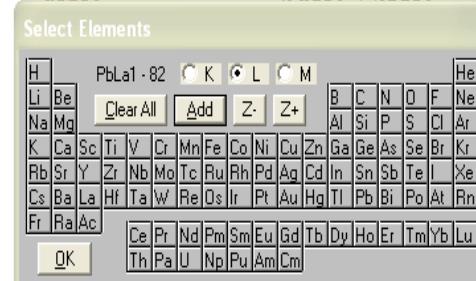
Clear □ △ ▽ ▹ ▻ A/B

BrNL102 a 500 sec Artax 30 NF/BrNL102

INST FILE #

KTI (PDZ 30.00kV, 1.00 $\mu$ A)

## BrNL102 a 500 sec Artax 30 NF/BrNL102 a clean 500 sec Artax 30 NF



## PDZ Preview

Path OK

Name	Date
BrNL104 a	01/16/20
BrNL103 b 500 sec	01/16/20
BrNL103 b	01/16/20
BrNL103 a clean	01/16/20
BrNL103 a	01/16/20
BrNL102 b 500 sec	01/16/20
BrNL102 a clean 500 sec Artax 30 NF	01/23/20
BrNL102 a 500 sec	01/15/20
BrNL102 a 500 sec Artax 30 NF	01/23/20
BrNL102 a 500 sec	01/15/20
BrNL101 b	01/15/20
BrNL101 a clean	01/15/20
BrNL101 a	01/15/20
BrNL098 b	01/15/20
BrNL098 a	01/15/20
BrNL097 b	01/15/20
BrNL097 a	01/15/20

Cnt:28275

LSec:500.00

Chan:427.446

Kev:8.5603

Det:-40.5C

Amb:93.4F

Raw:7.584.00

Valid:5,314.00

evch:20.0266

Vac:651

Shift:0.00000

S1 TRACER

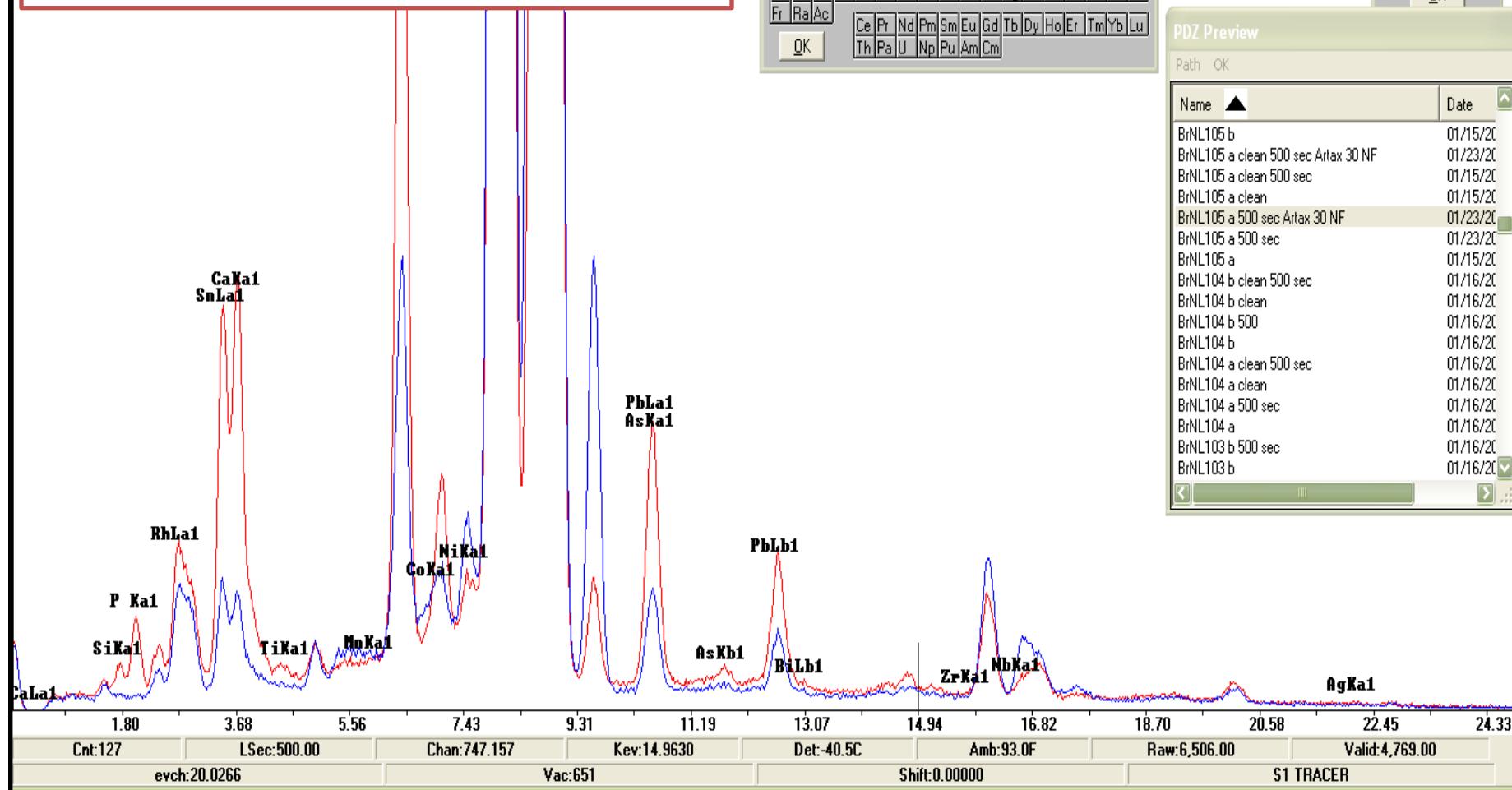
File Setup ID Download Timed Tube Help

Clear A/B **BrNL105 a 500 sec Artax 30 NF/BrNL105**

INST FILE #

KTI (PDZ 30.00kV, 1.00 $\mu$ A)**FeKa1**   **CuKa1**

## BrNL105 a 500 sec Artax 30 NF/BrNL105 a clean 500 sec Artax 30 NF



## Select Elements

H	PbLa1	-82	<input type="radio"/> K	<input checked="" type="radio"/> L	<input type="radio"/> M	He												
Li	Be		<input type="radio"/> K	<input checked="" type="radio"/> L	<input type="radio"/> M													
Na	Mg		<input type="radio"/> K	<input checked="" type="radio"/> L	<input type="radio"/> M													
		Clear All	Add	Z-	Z+													
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Nb	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Pn	
Fr	Ra	Ac	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm									

OK

Spectrum Ove...

-

+

Move A &gt;&gt; B

Clear B

OK

## PDZ Preview

Path OK

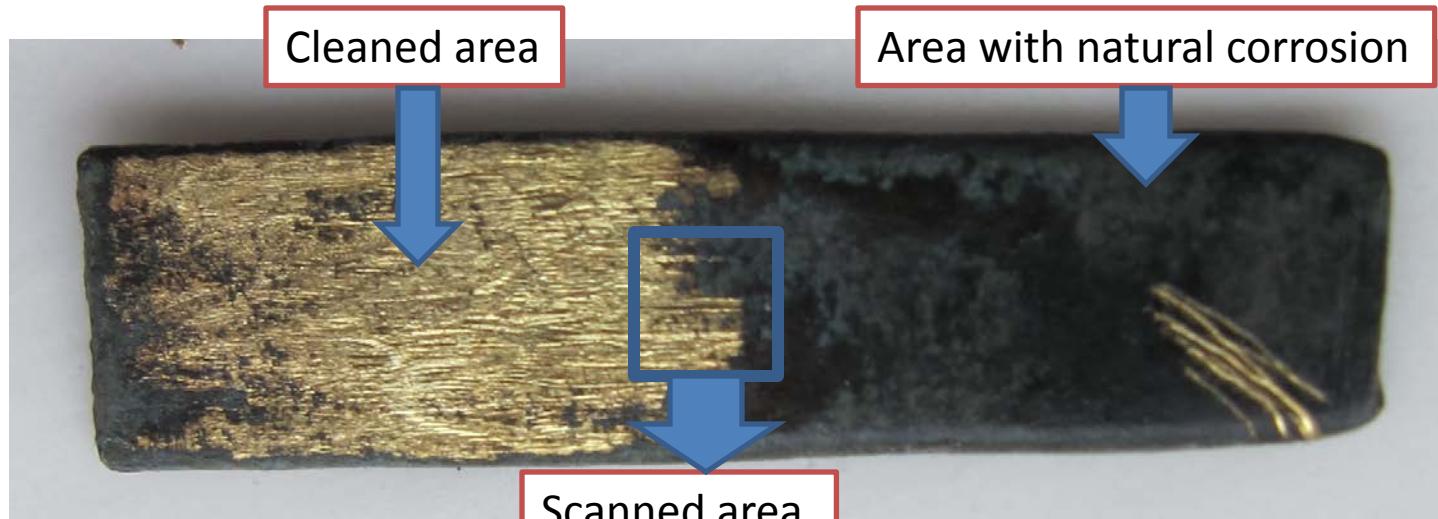
Name	Date
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BrNL105 a clean 500 sec Artax 30 NF	01/23/20
BrNL105 a clean 500 sec	01/15/20
BrNL105 a clean	01/15/20
BrNL105 a 500 sec Artax 30 NF	01/23/20
BrNL105 a 500 sec	01/23/20
BrNL105 a	01/15/20
BrNL104 b clean 500 sec	01/16/20
BrNL104 b clean	01/16/20
BrNL104 b 500	01/16/20
BrNL104 b	01/16/20
BrNL104 a clean 500 sec	01/16/20
BrNL104 a clean	01/16/20
BrNL104 a 500 sec	01/16/20
BrNL104 a	01/16/20
BrNL103 b 500 sec	01/16/20
BrNL103 b	01/16/20



## Tracer III V + quantitative analysis of each analysis

Note that the in all cases for the clean metal analysis the Fe, Cu, As, Pb, Sn, Ag, and Sb are lower and the Zn and Ni are higher. This is also clearly evident in the the Artax scans which follow. **Note only the Clean analysis below is accurate.**

	BrNL011 a 500 sec	BrNL011 a clean 500 sec		BrNL105 a clean 500 sec	BrNL102 a 500 sec	BrNL102 a clean 500 sec
FeKa1	0.90	0.39	1.52	0.49	0.76	0.20
NiKa1	0.15	0.19	0.06	0.17	0.08	0.13
CuKa1	75.96	75.94	77.80	77.16	71.56	70.83
ZnKa1	14.79	17.10	10.10	15.89	22.58	25.01
AsKa1	0.17	0.04	0.62	0.06	0.07	0.01
PbLb1	1.79	1.09	3.37	1.39	2.46	0.84
AgKa1	0.05	0.02	0.08	0.02	0.02	0.01
SnKa1	4.60	3.12	5.57	2.71	0.37	0.28
SbKa1	0.06	0.03	0.13	0.04	0.05	0.00
SUM	98.49	97.92	99.27	97.93	97.95	97.32

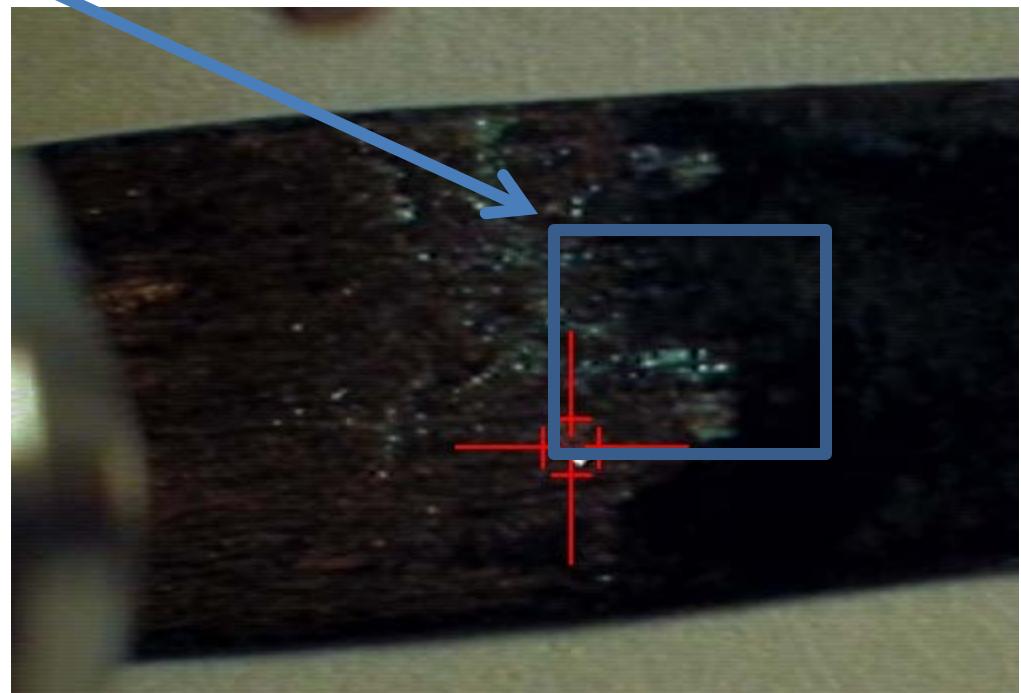


Scanned area

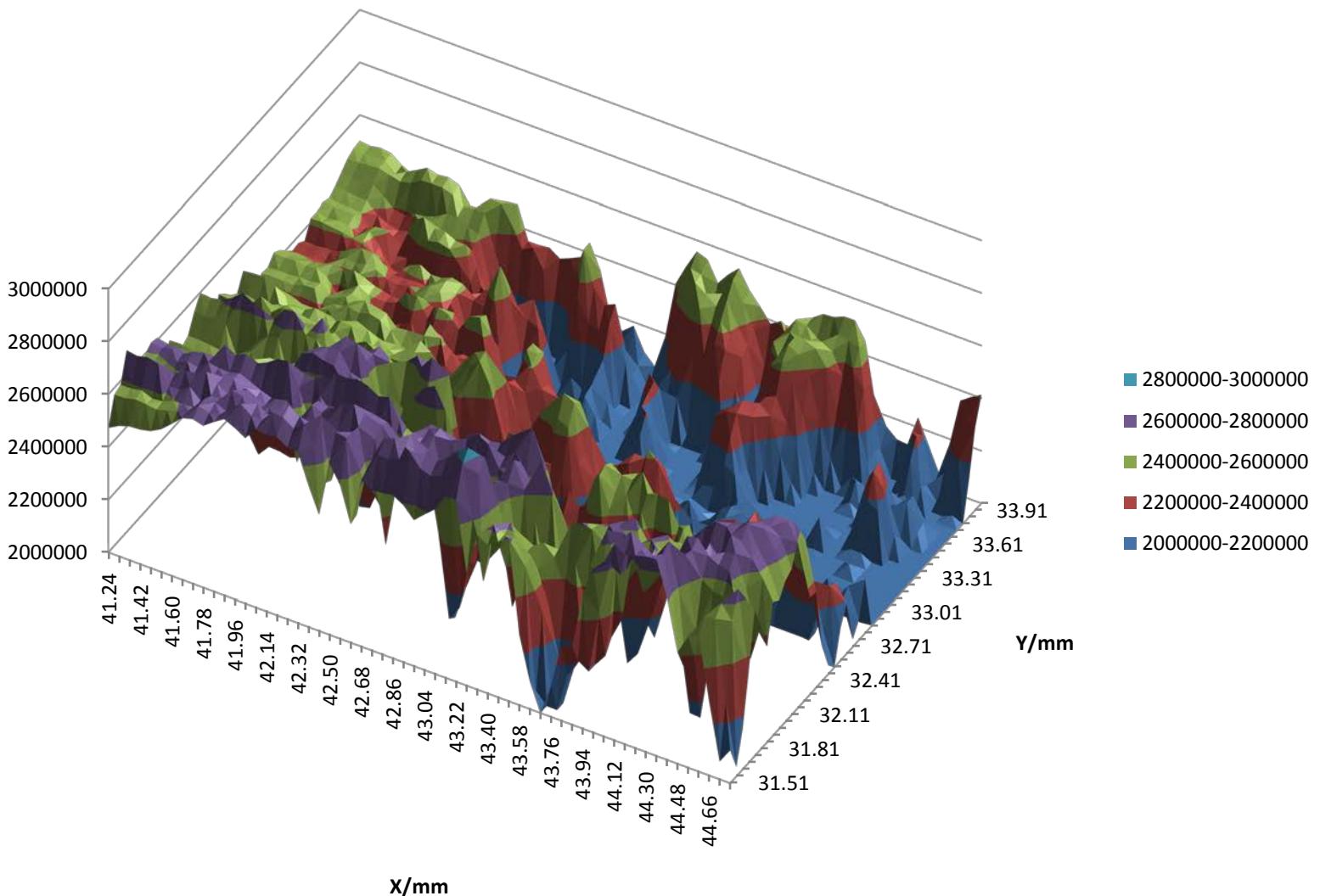
## Sample BrNL011

### Xrf elemental scan

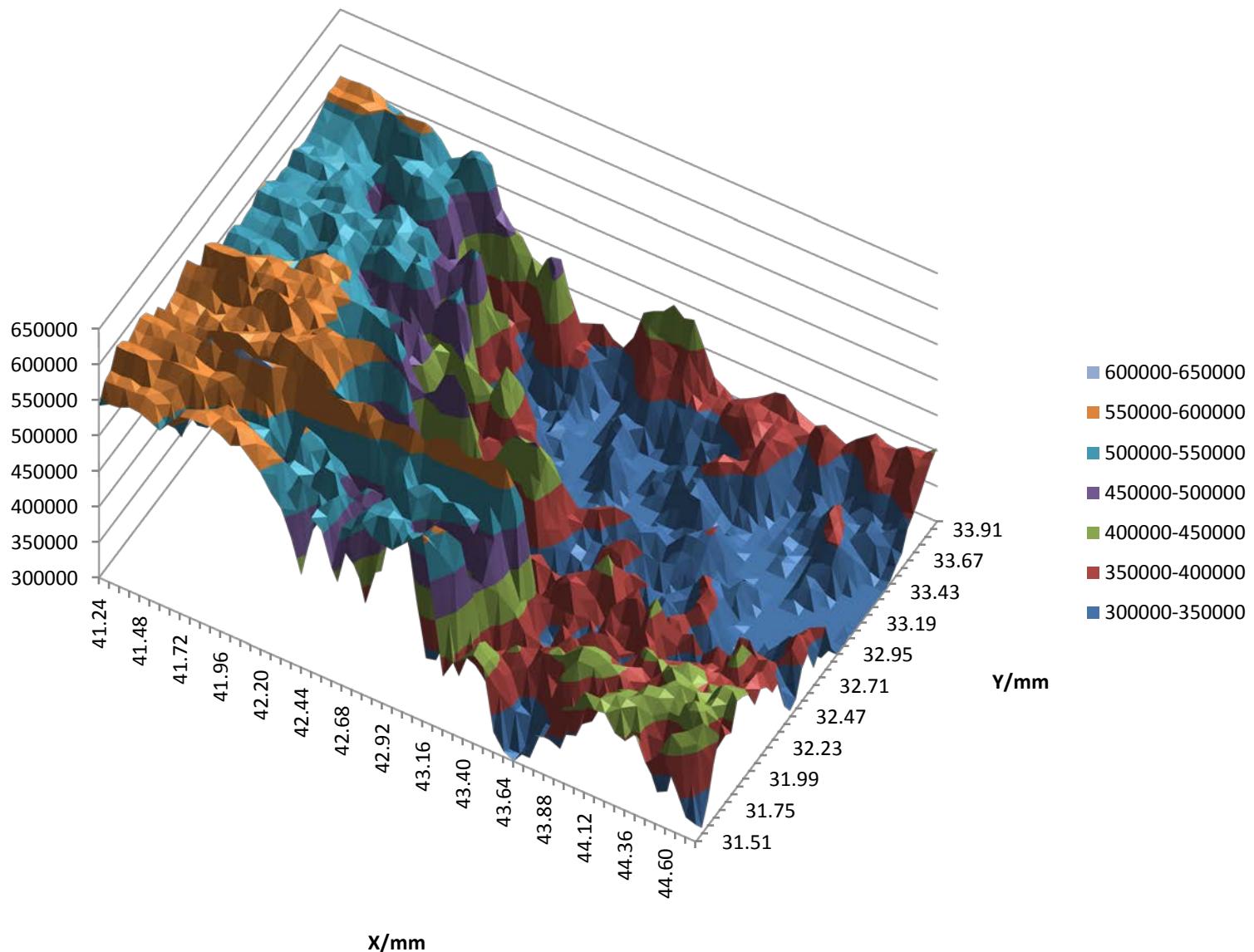
1. 2520 points
2. .065 mm spot size
3. .060 mm spacing
4. 2.5 mm by 3.5 mm area
5. 21 hours
6. 30 sec per analysis



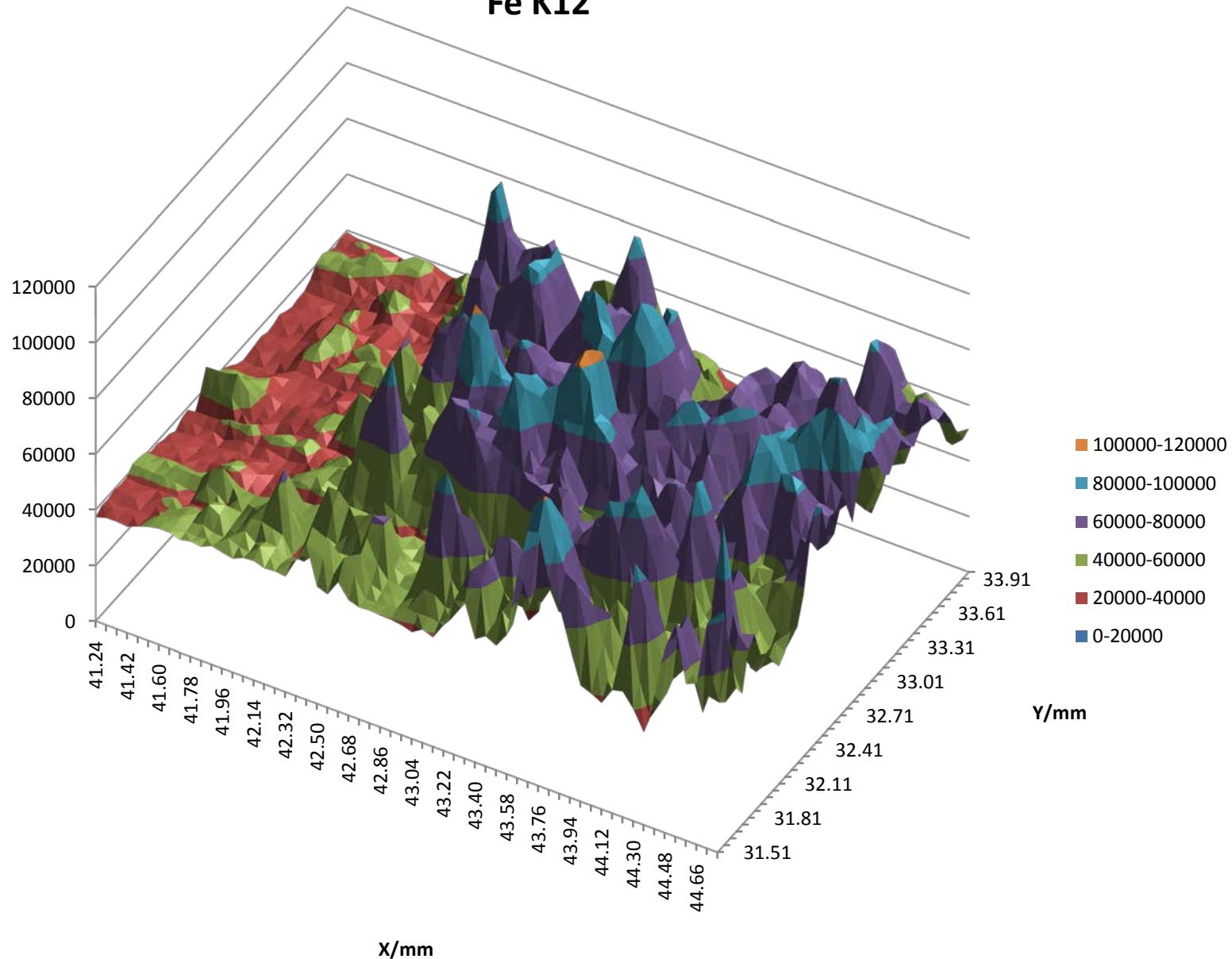
## Cu K12



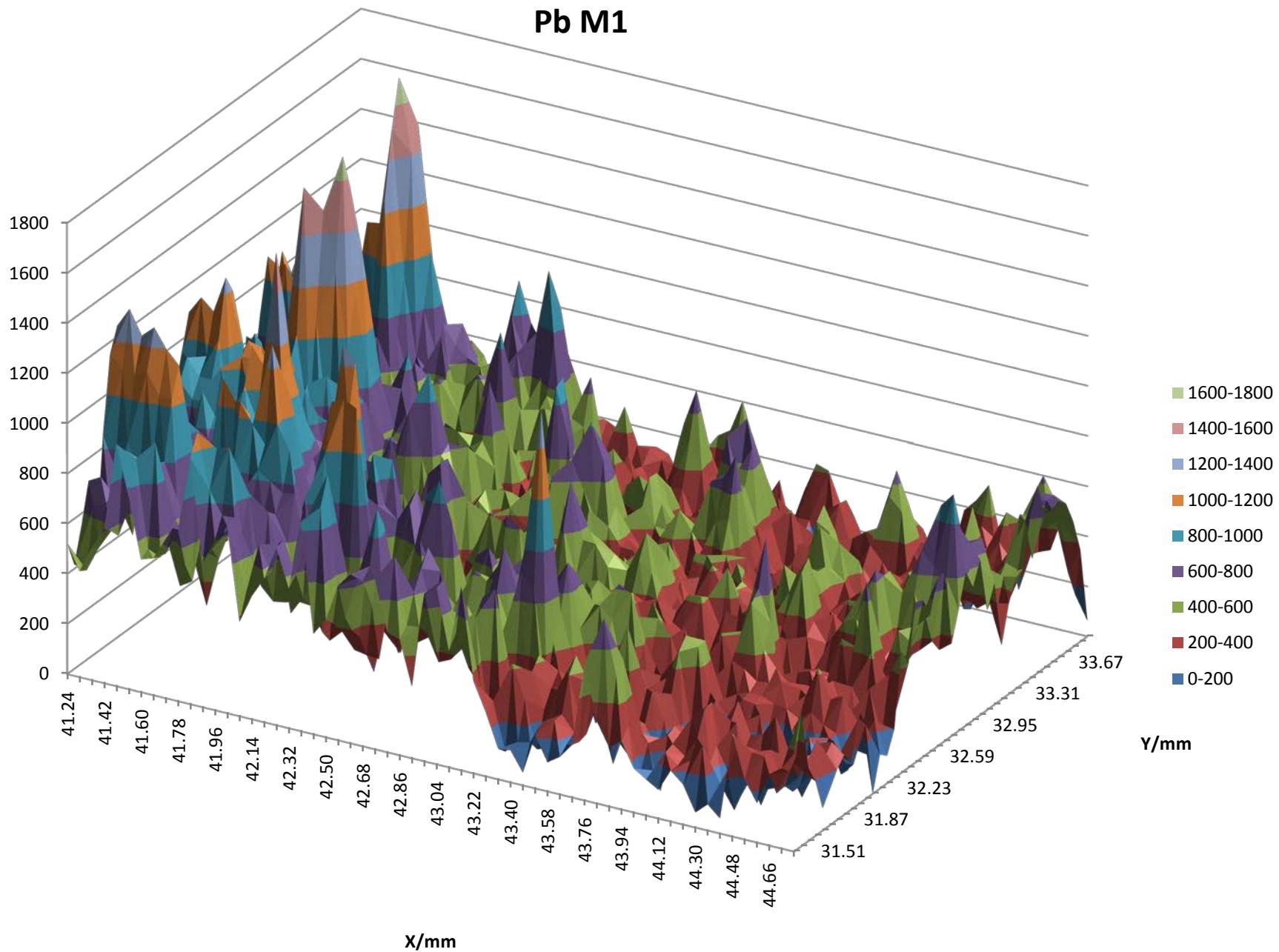
# Zn K12

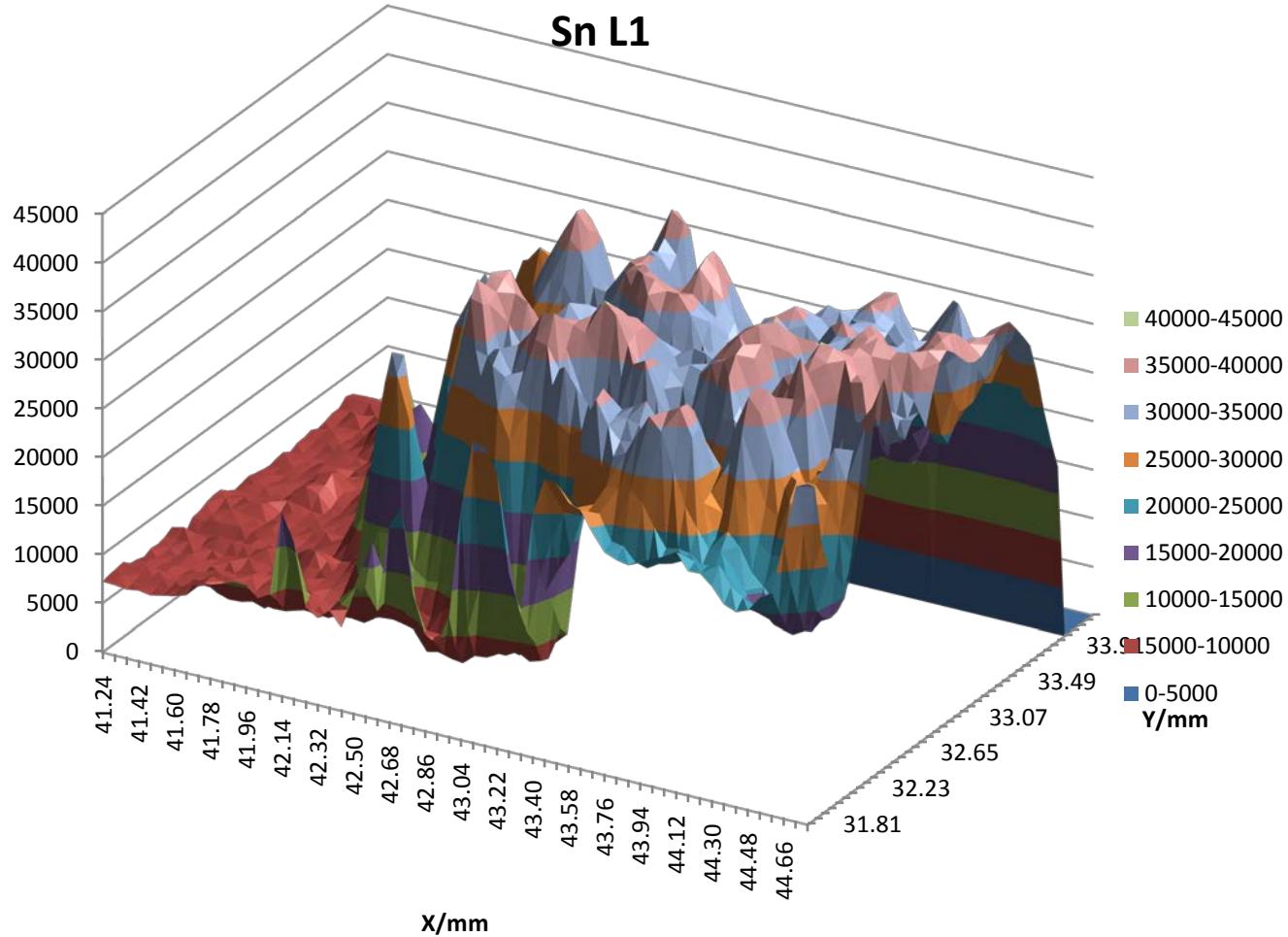


# Fe K12

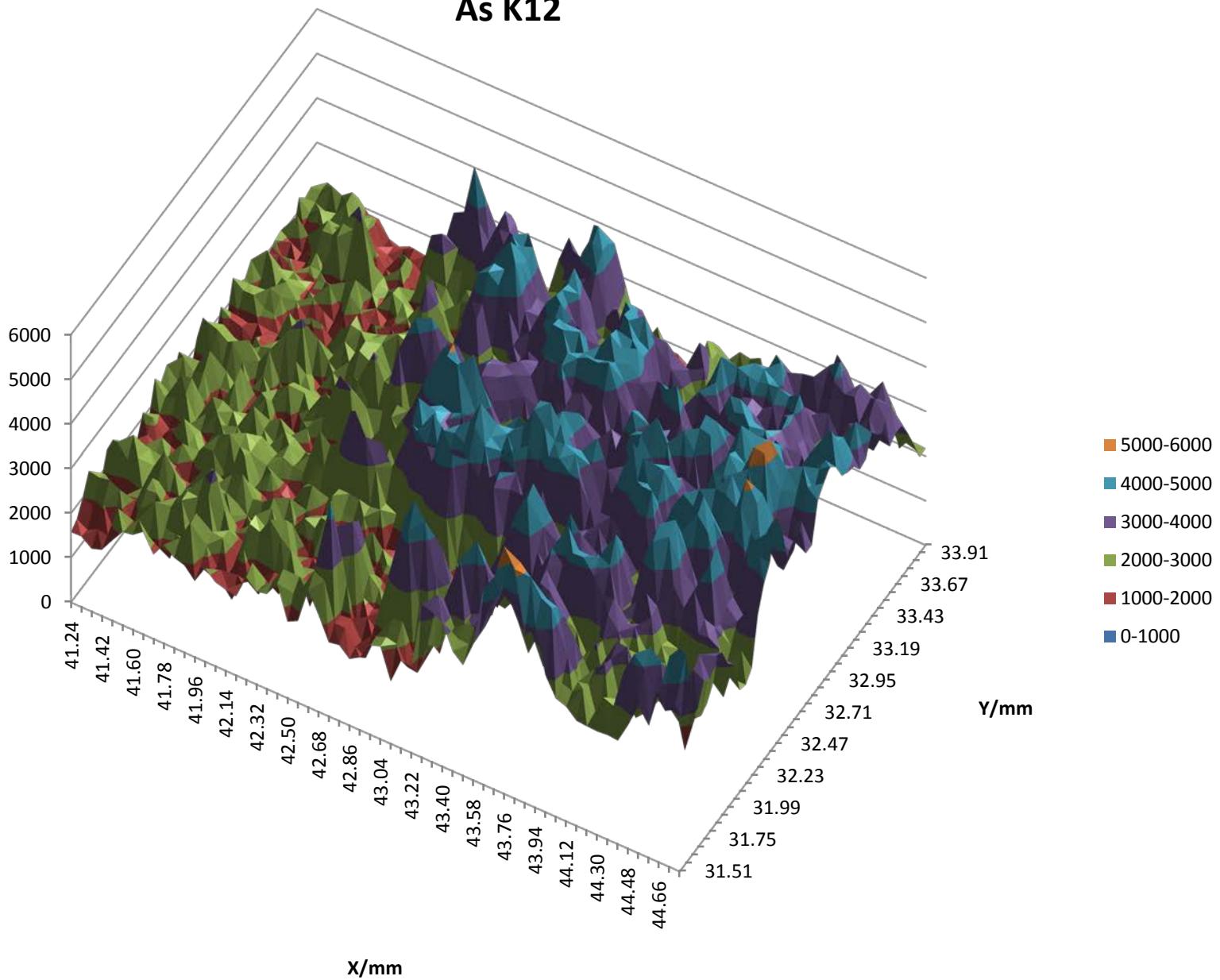


# Pb M1

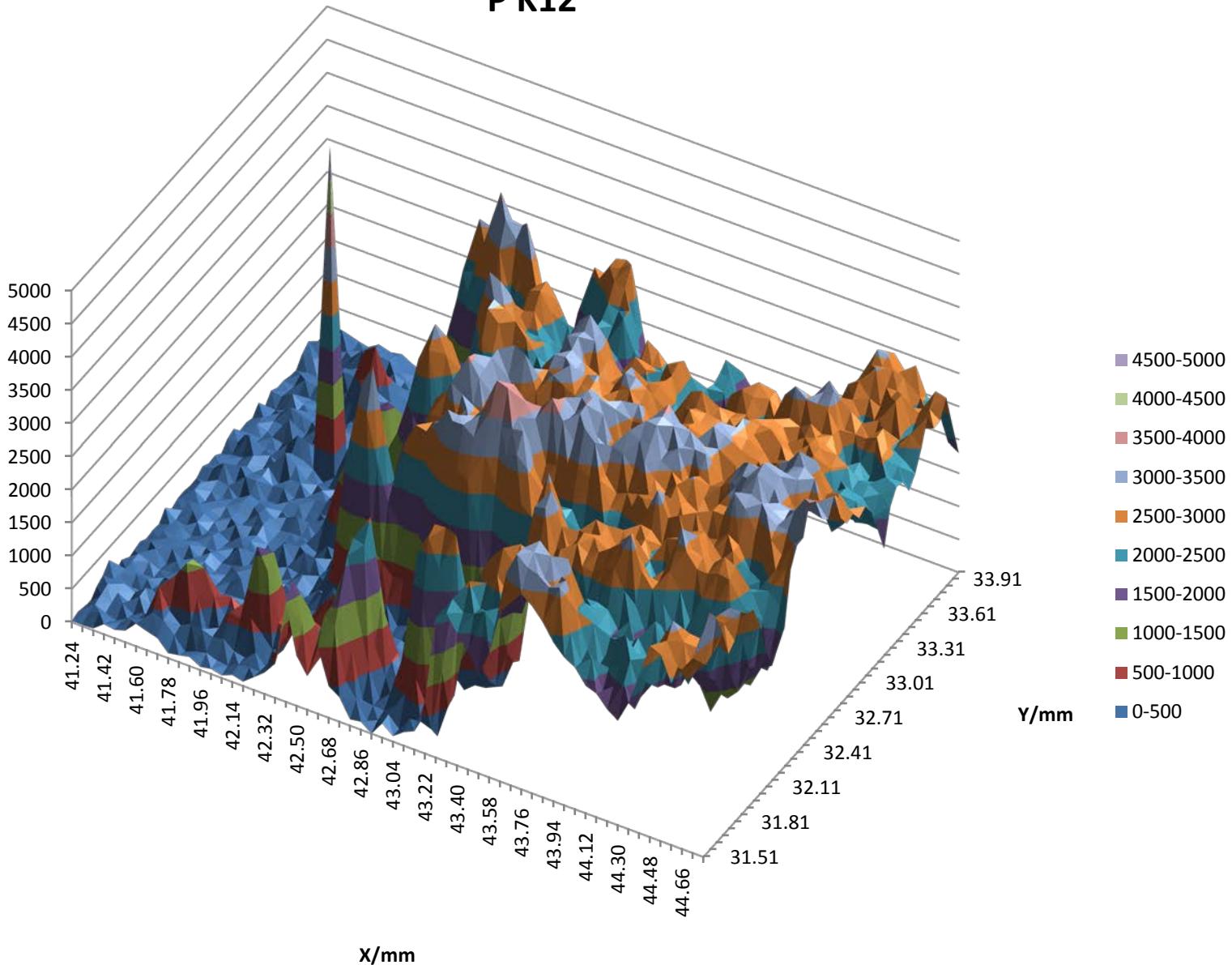




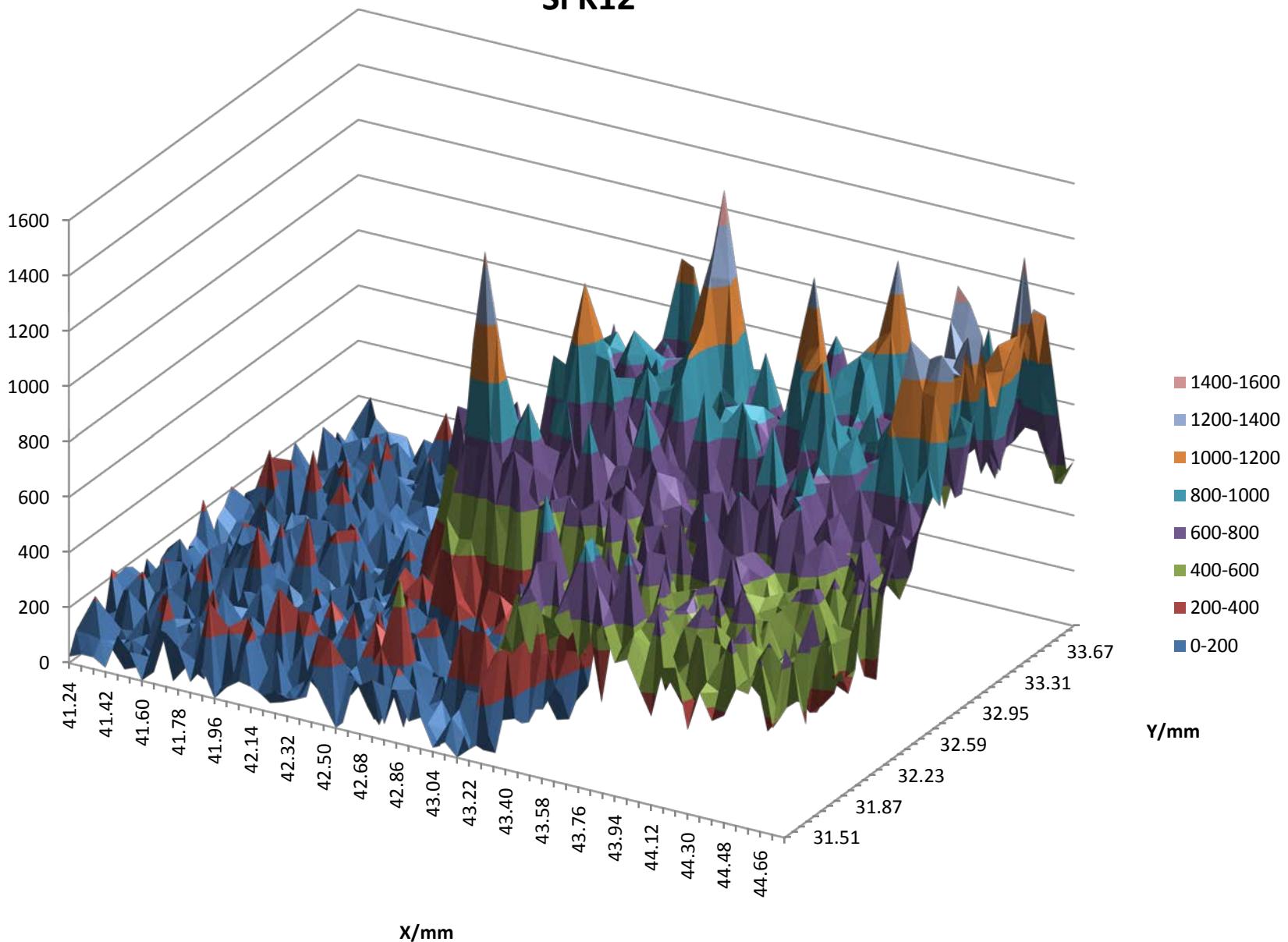
# As K12



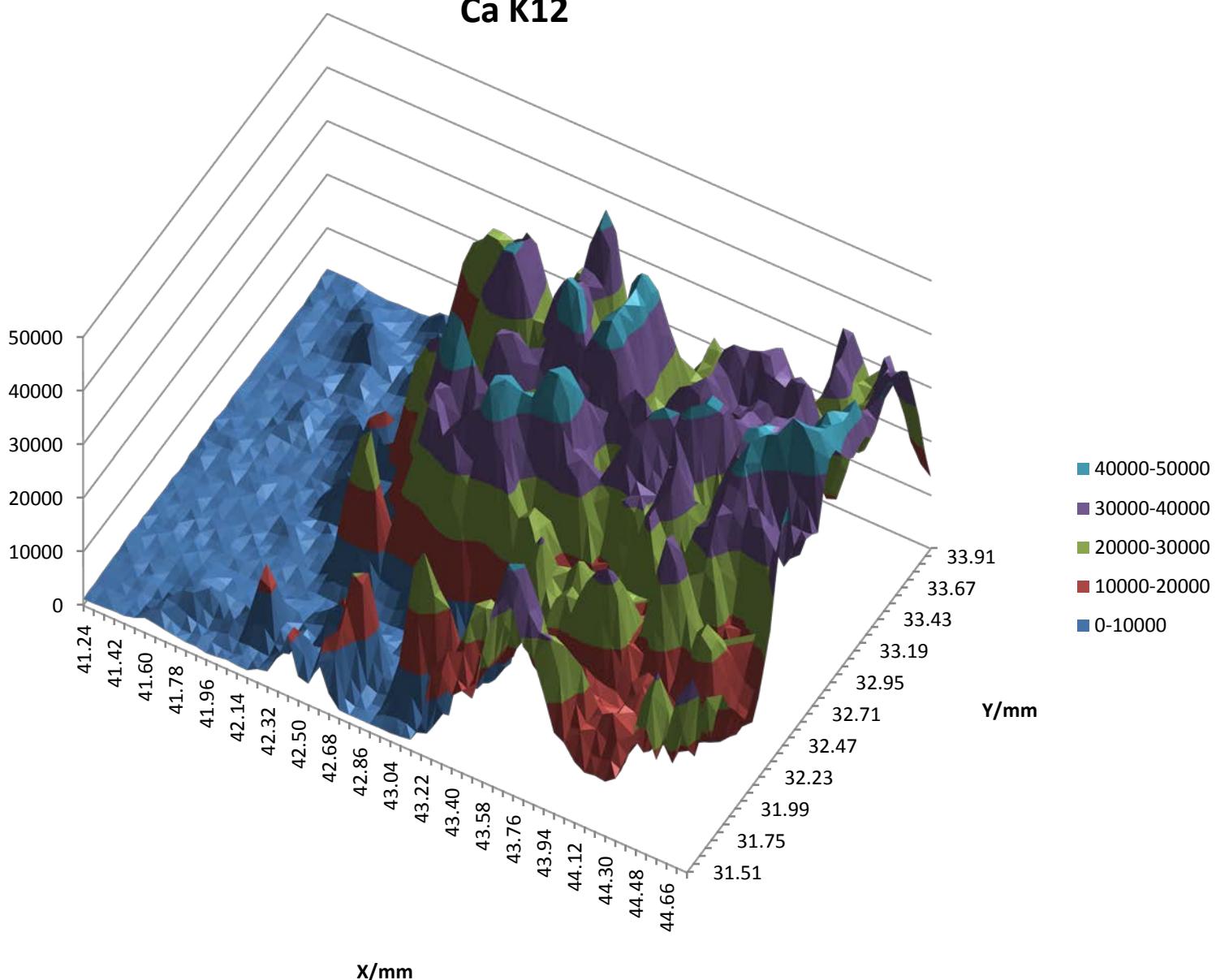
# P K12



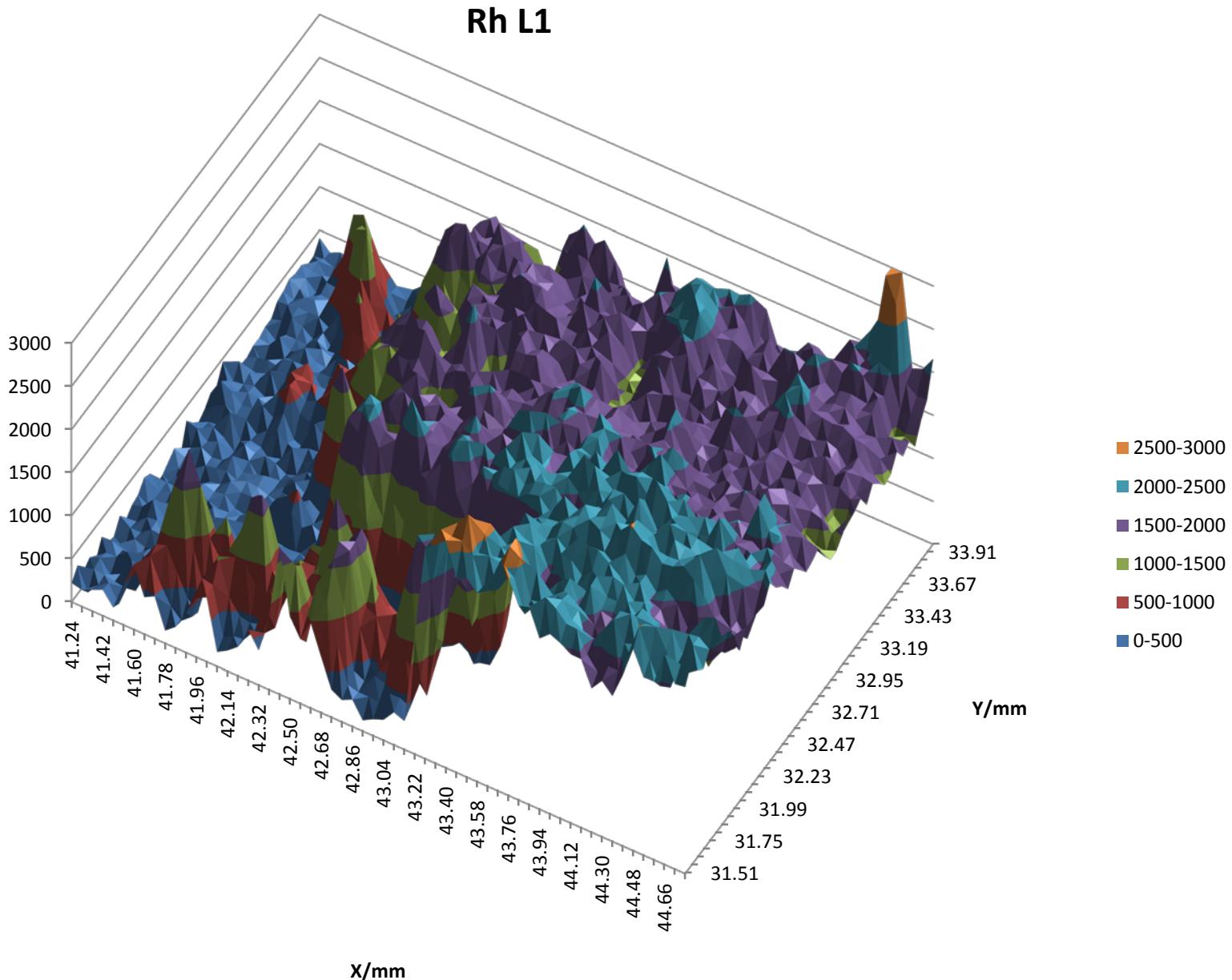
# Si K12



# Ca K12



# Rh L1



XRF 31B107

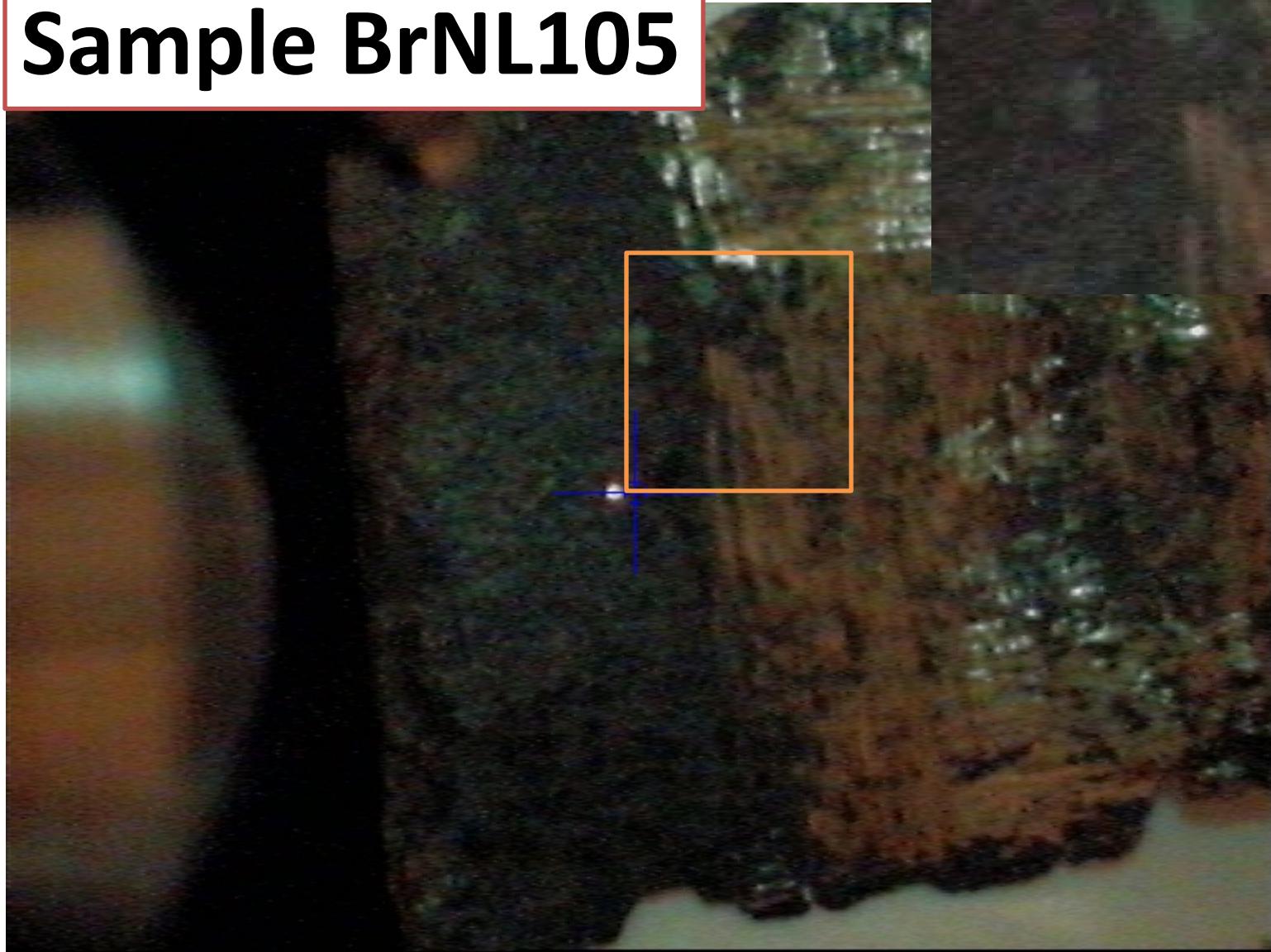
NL6

NL 6b

Br NL105

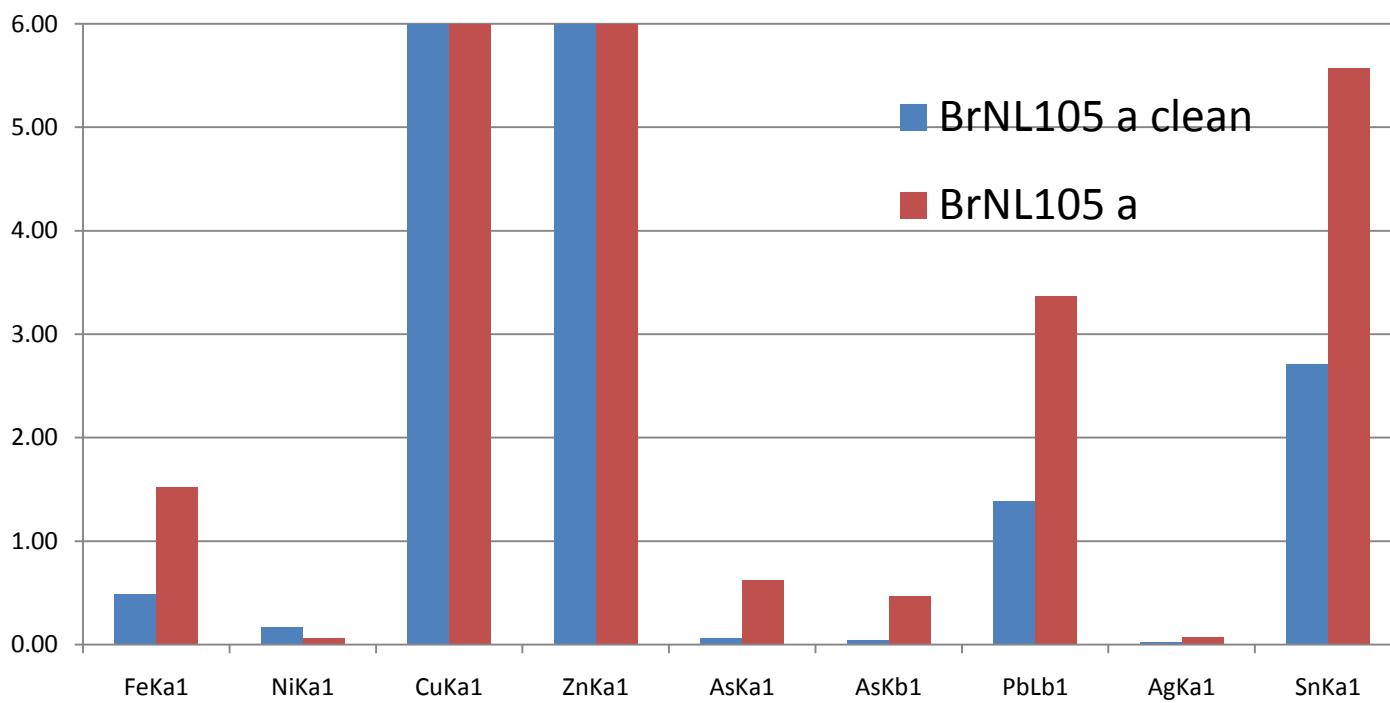
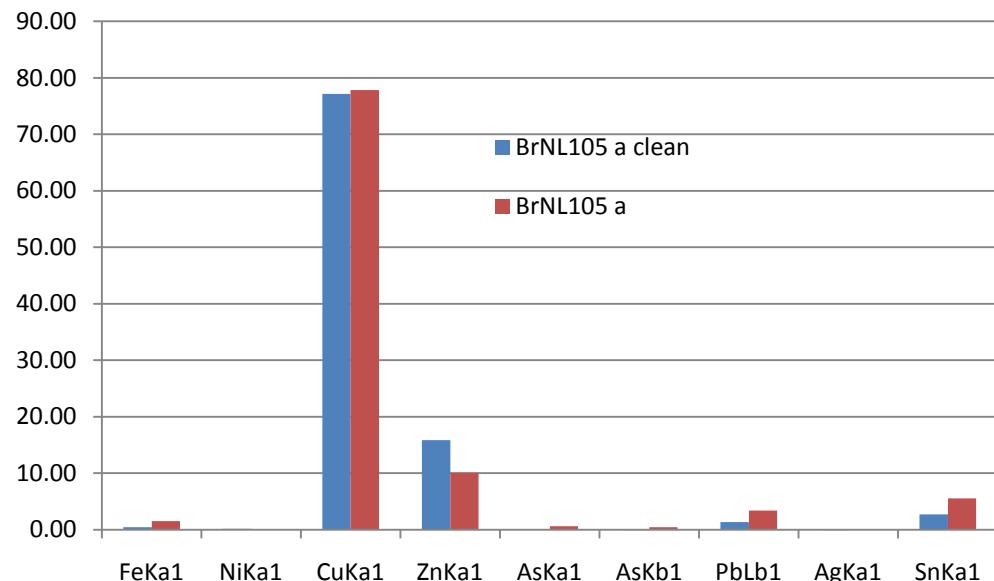


# Sample BrNL105

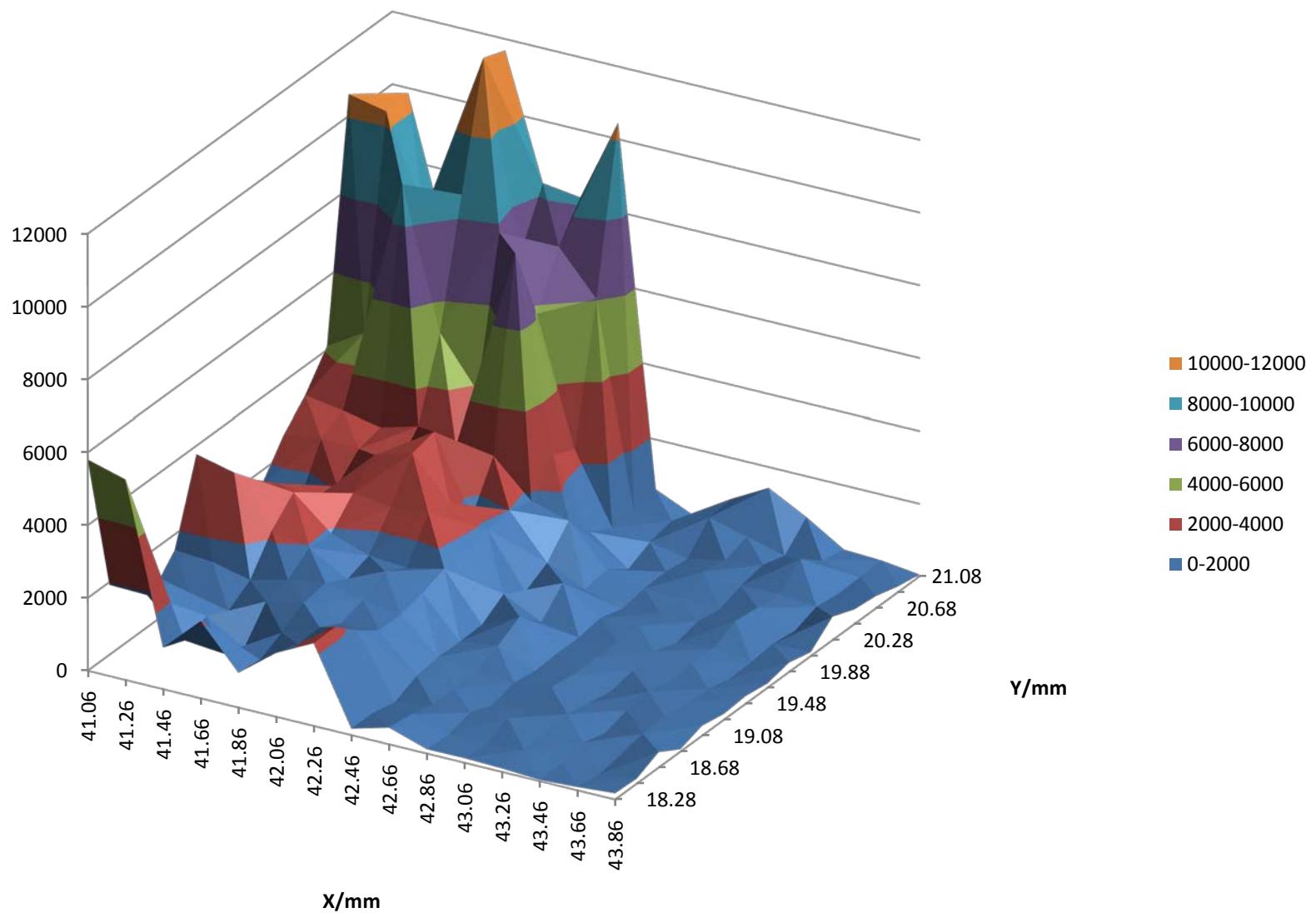


**Quantification done with the Tracer III V +**  
**Area 3 mm 4mm on each surface**

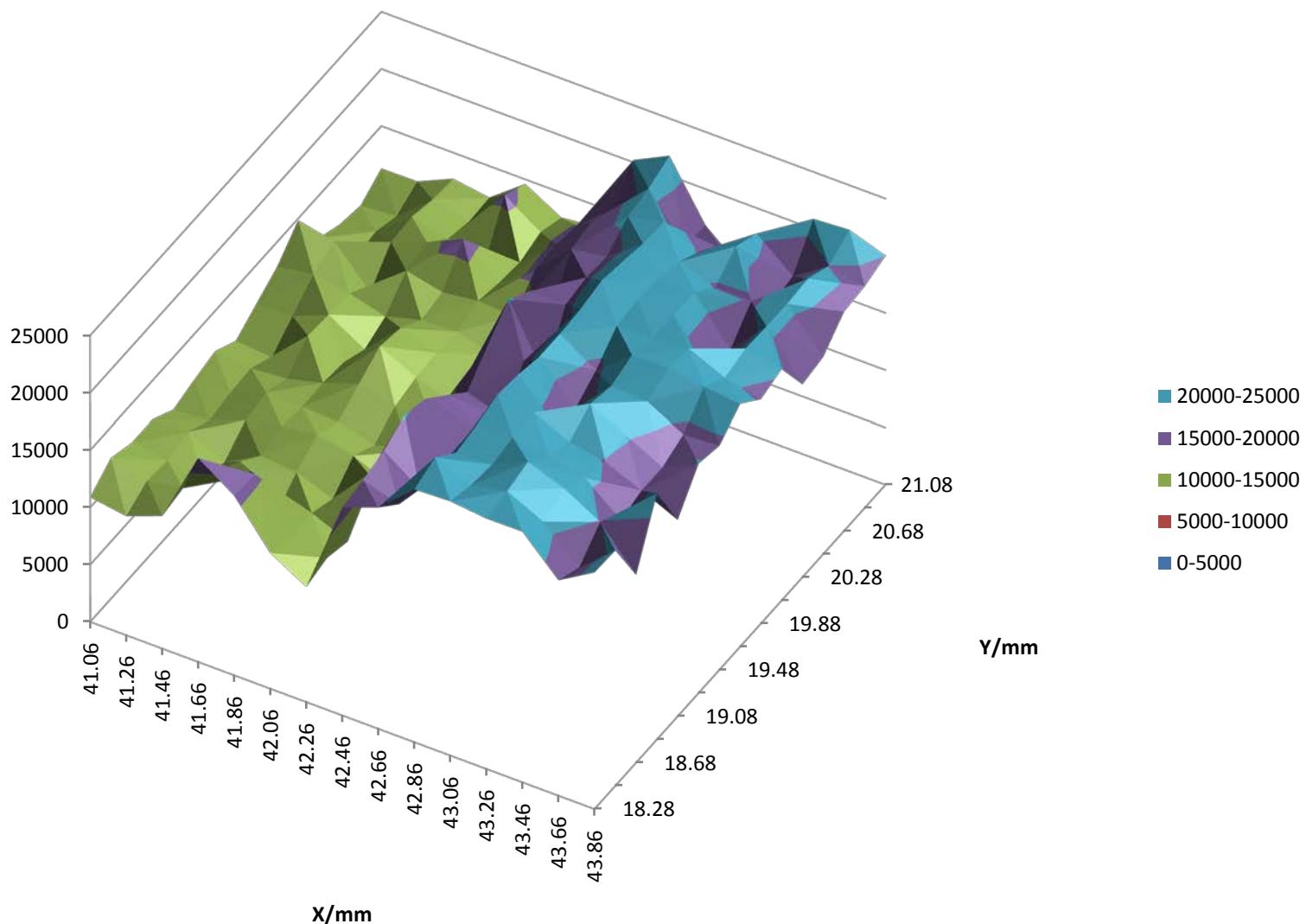
	BrNL105 a clean	BrNL105 a
FeKa1	0.49	1.52
NiKa1	0.17	0.06
CuKa1	77.16	77.80
ZnKa1	15.89	10.10
AsKa1	0.06	0.62
AsKb1	0.04	0.47
PbLb1	1.39	3.37
AgKa1	0.02	0.08
SnKa1	2.71	5.57



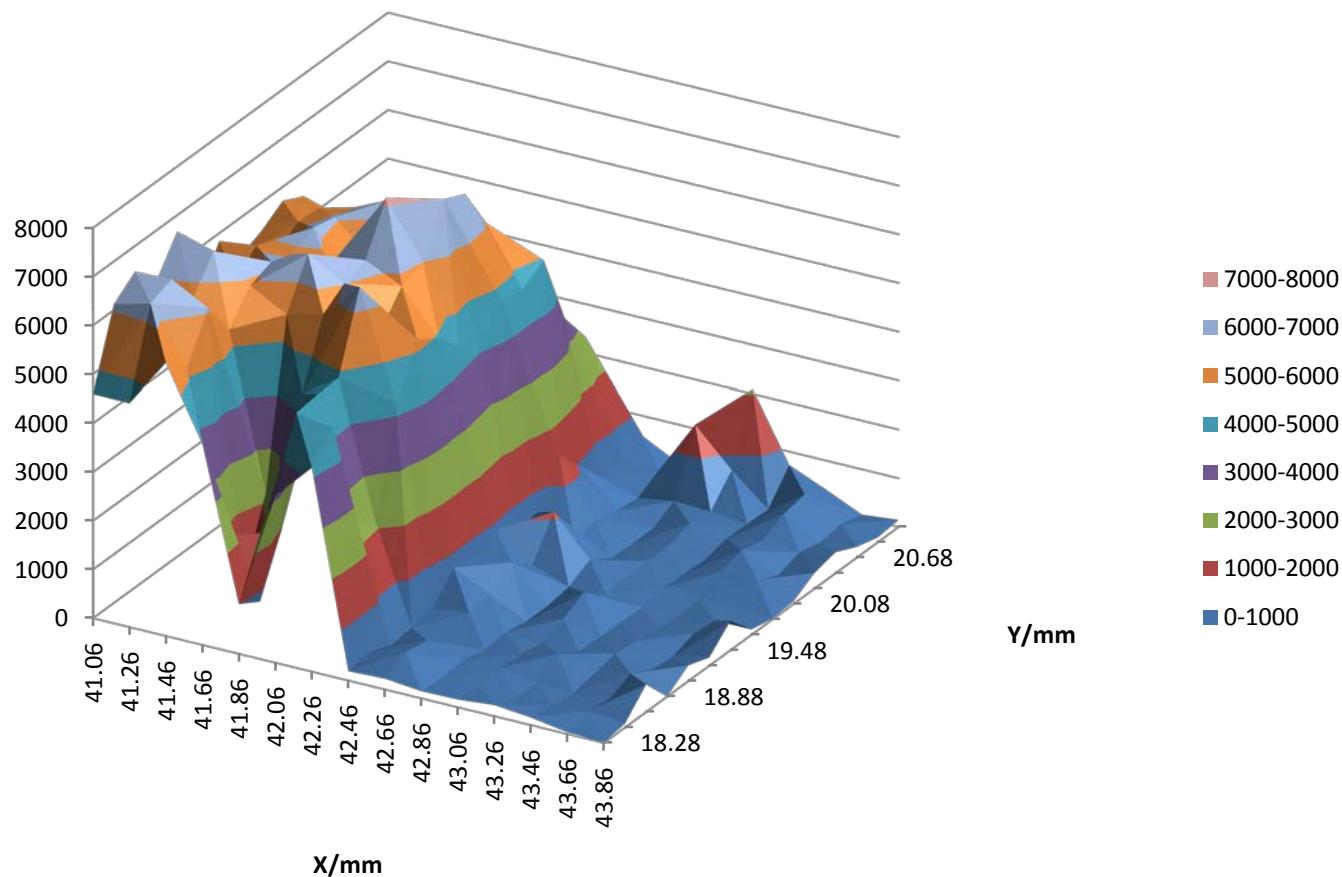
## Si K12



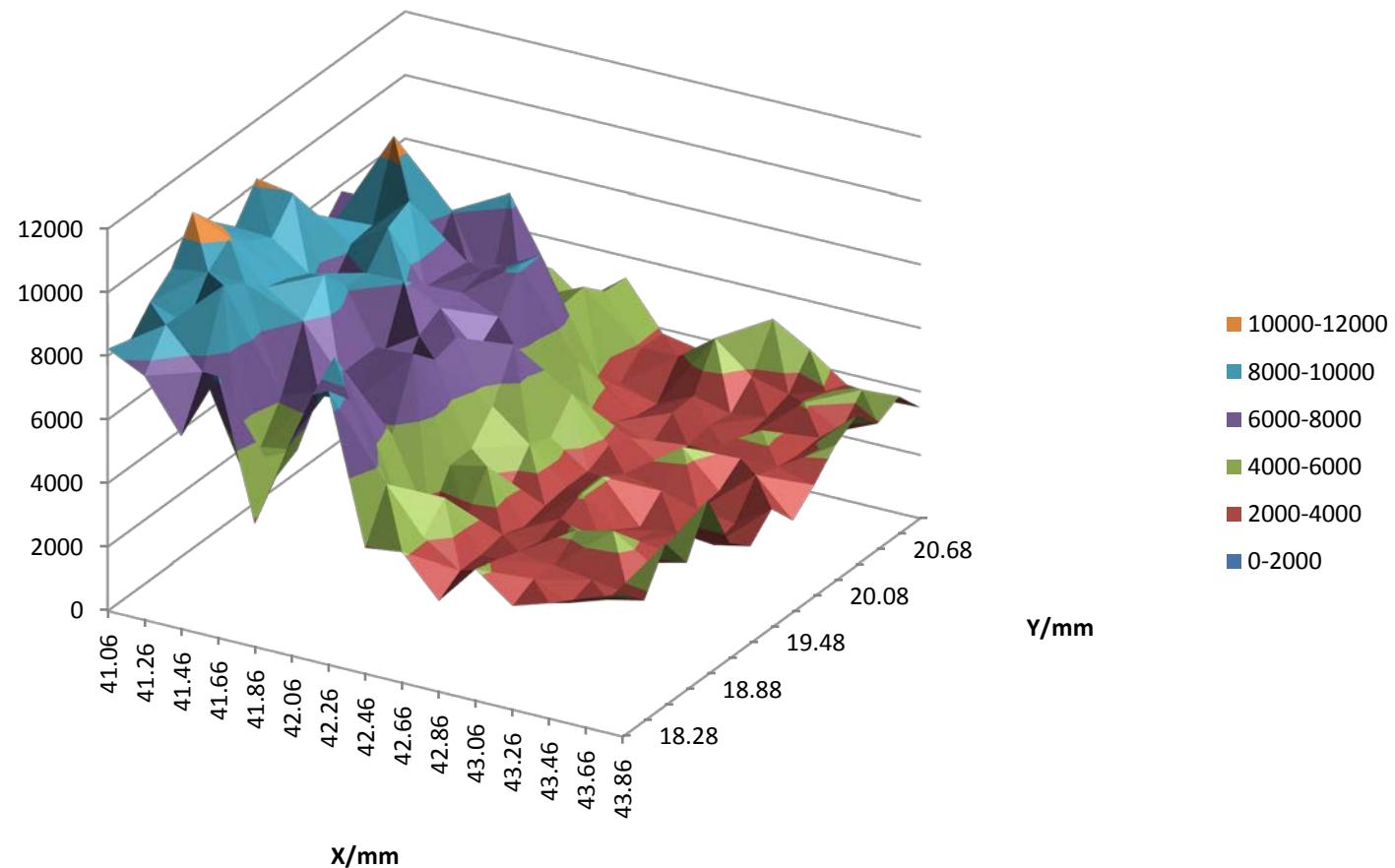
## Ni K12



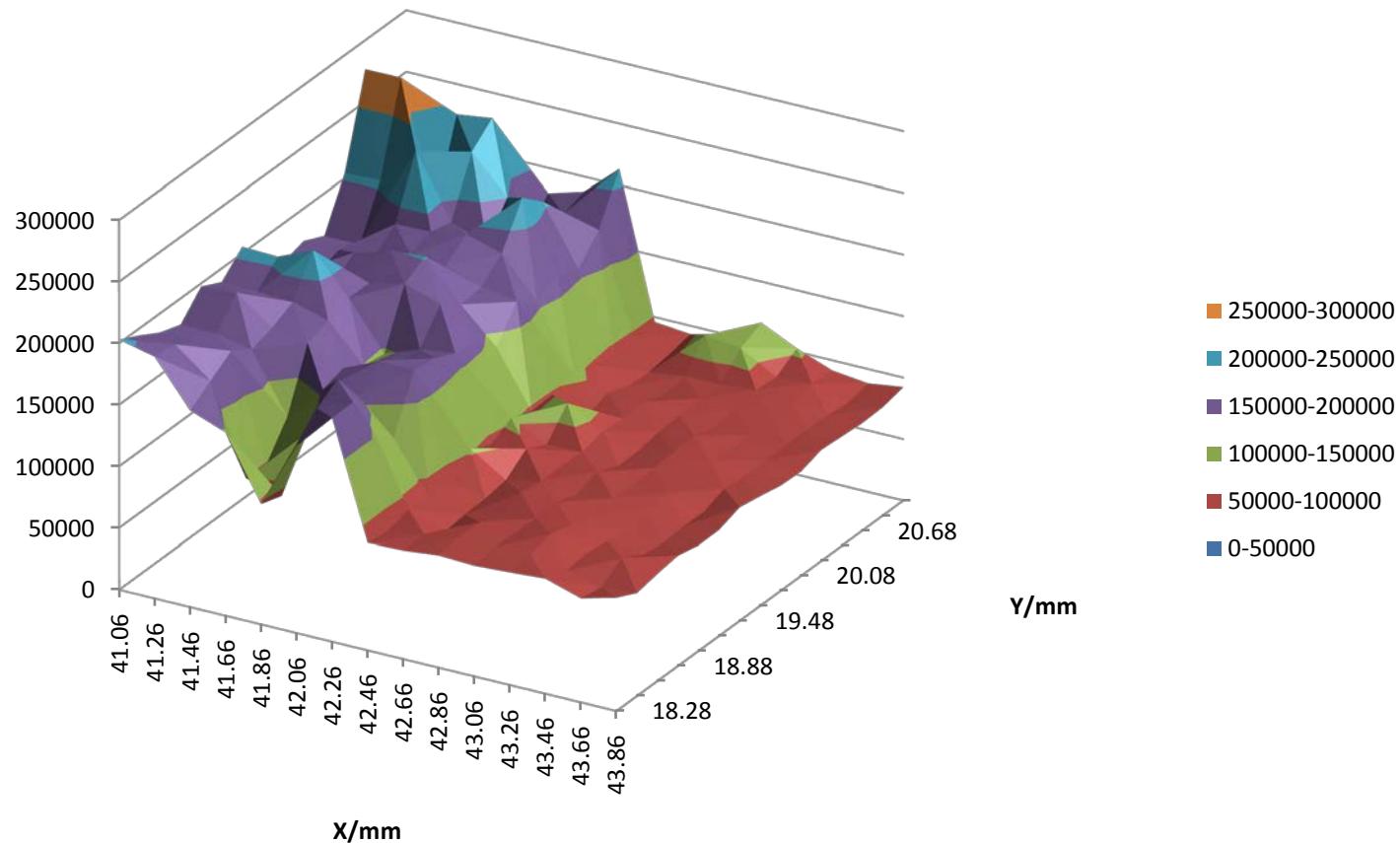
## P K12



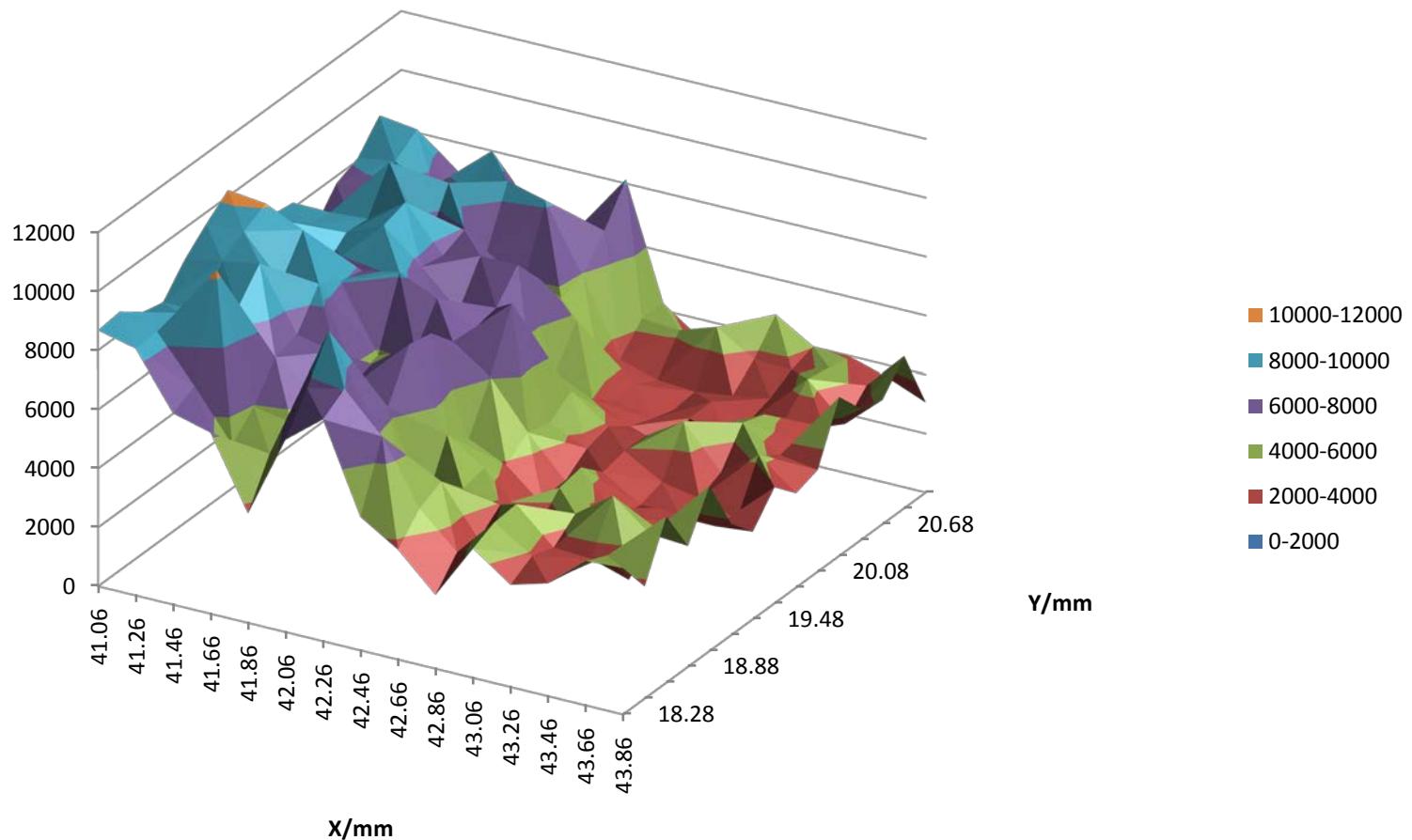
## As K12



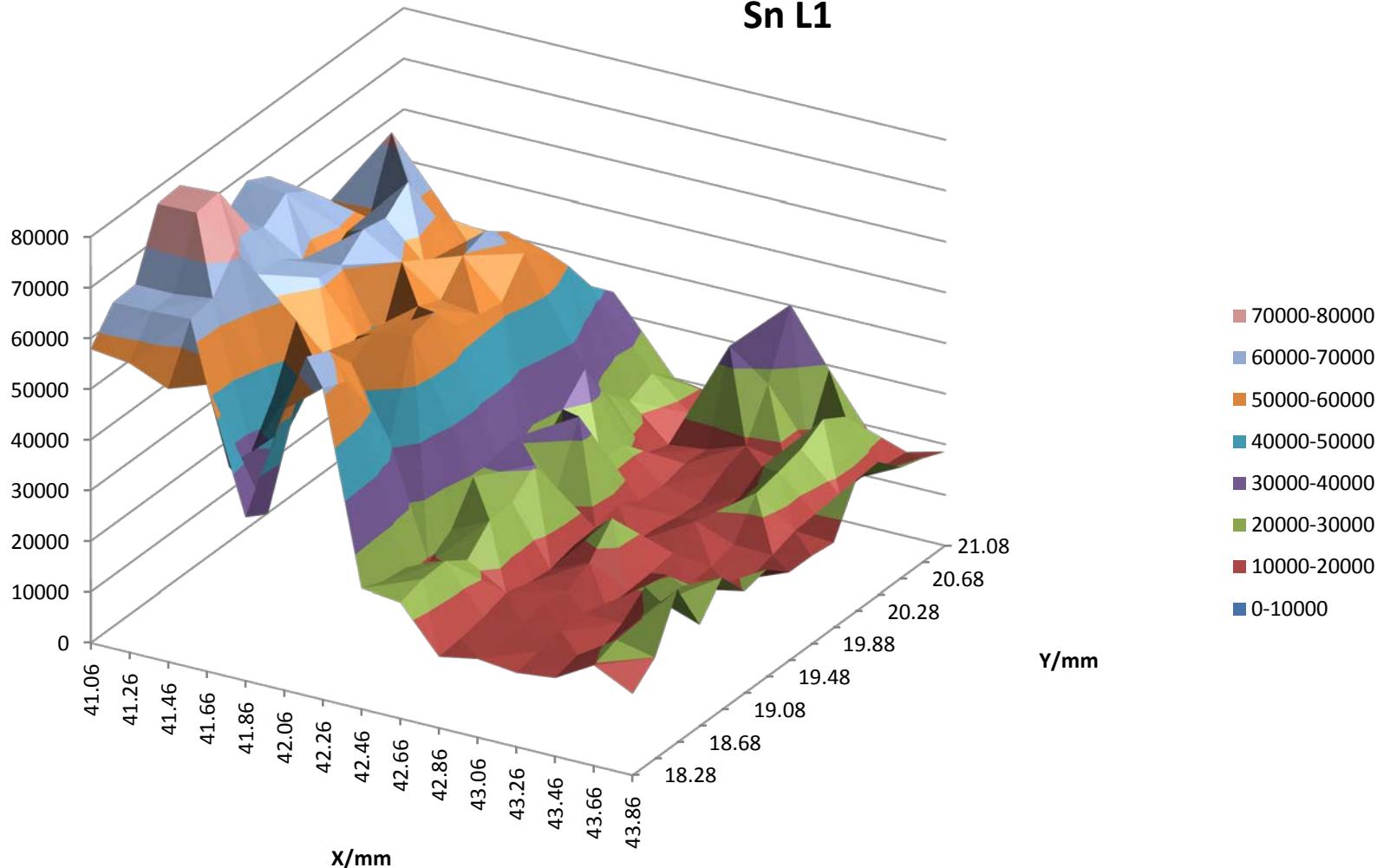
## Fe K12



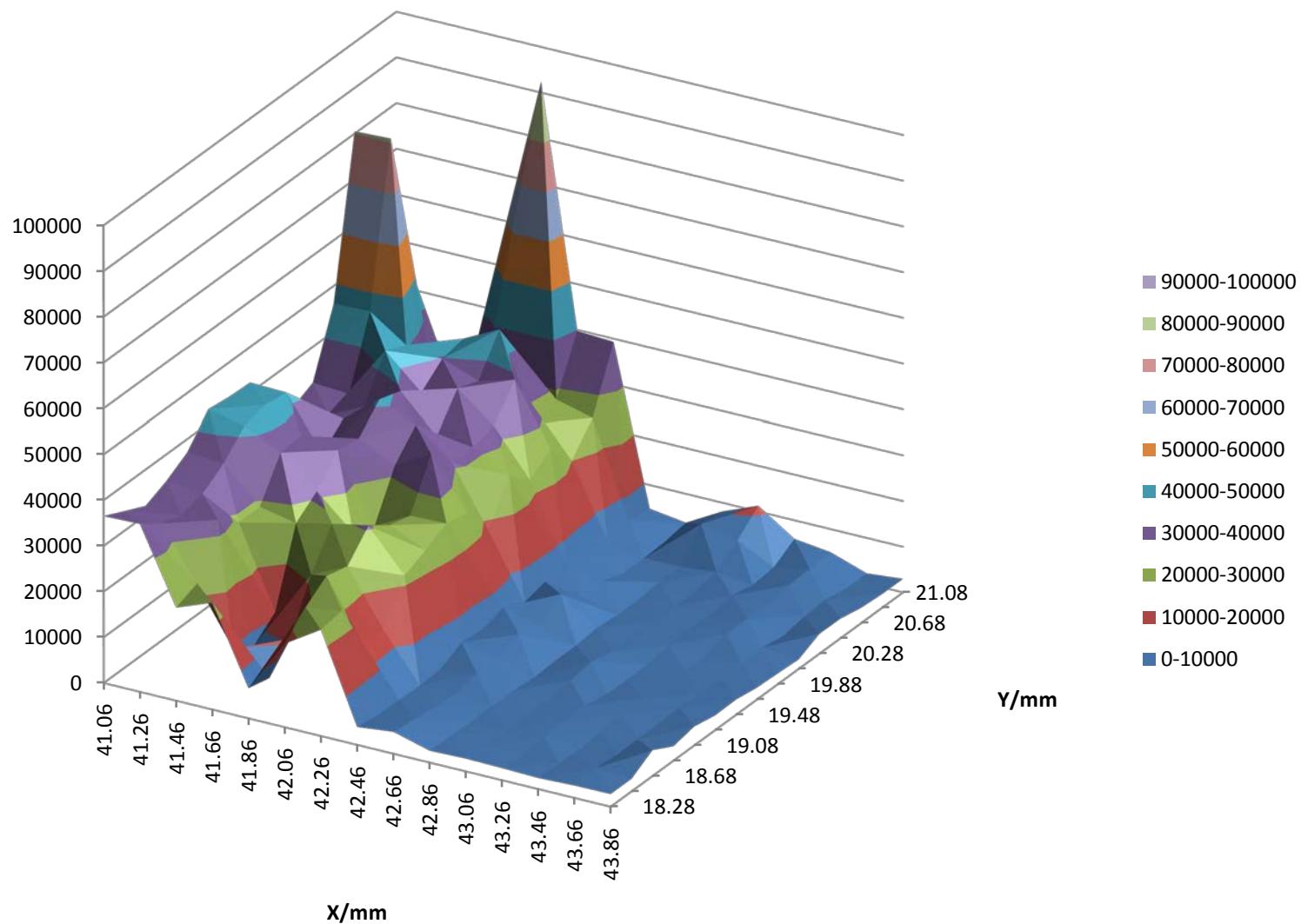
# Pb L1



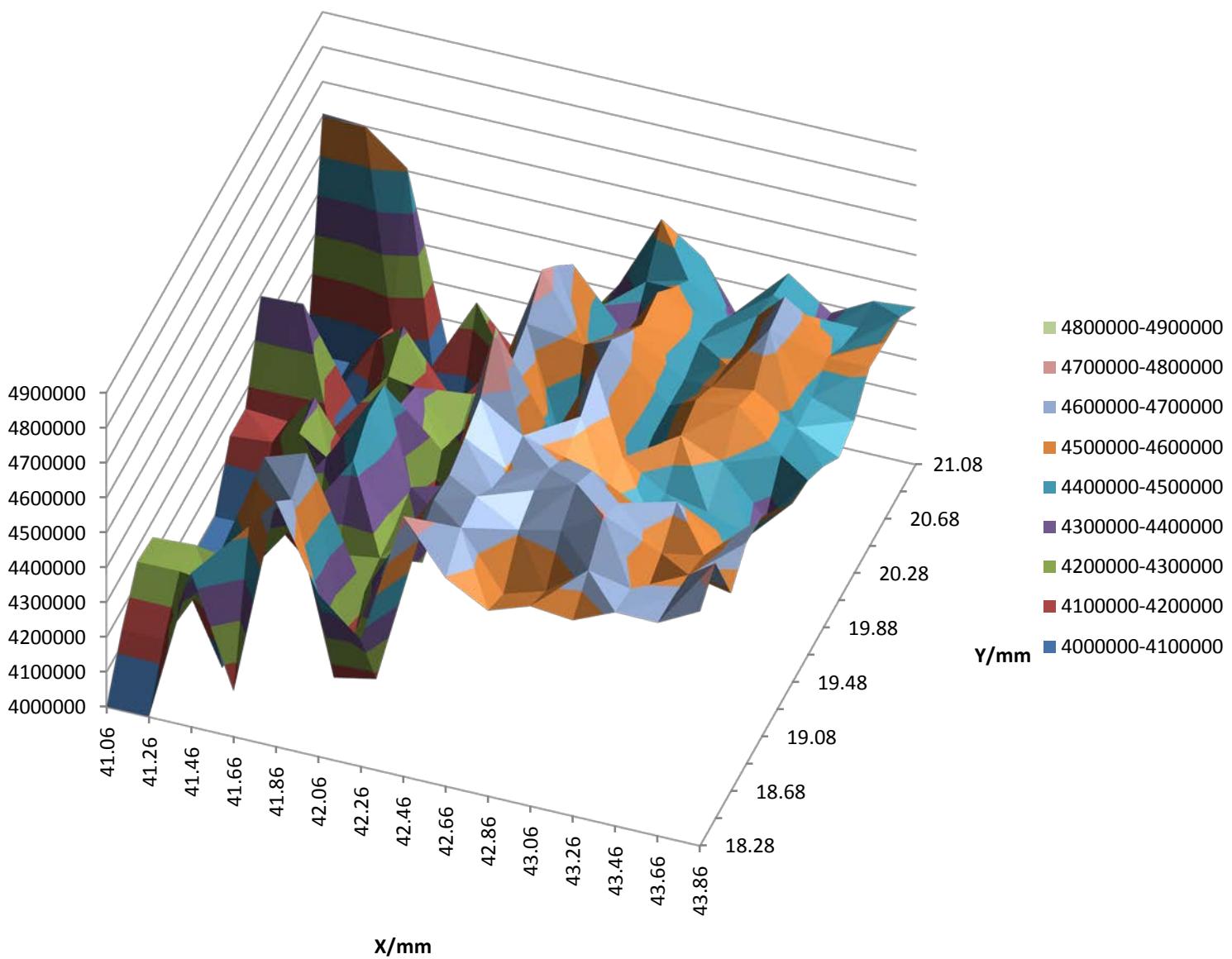
# Sn L1



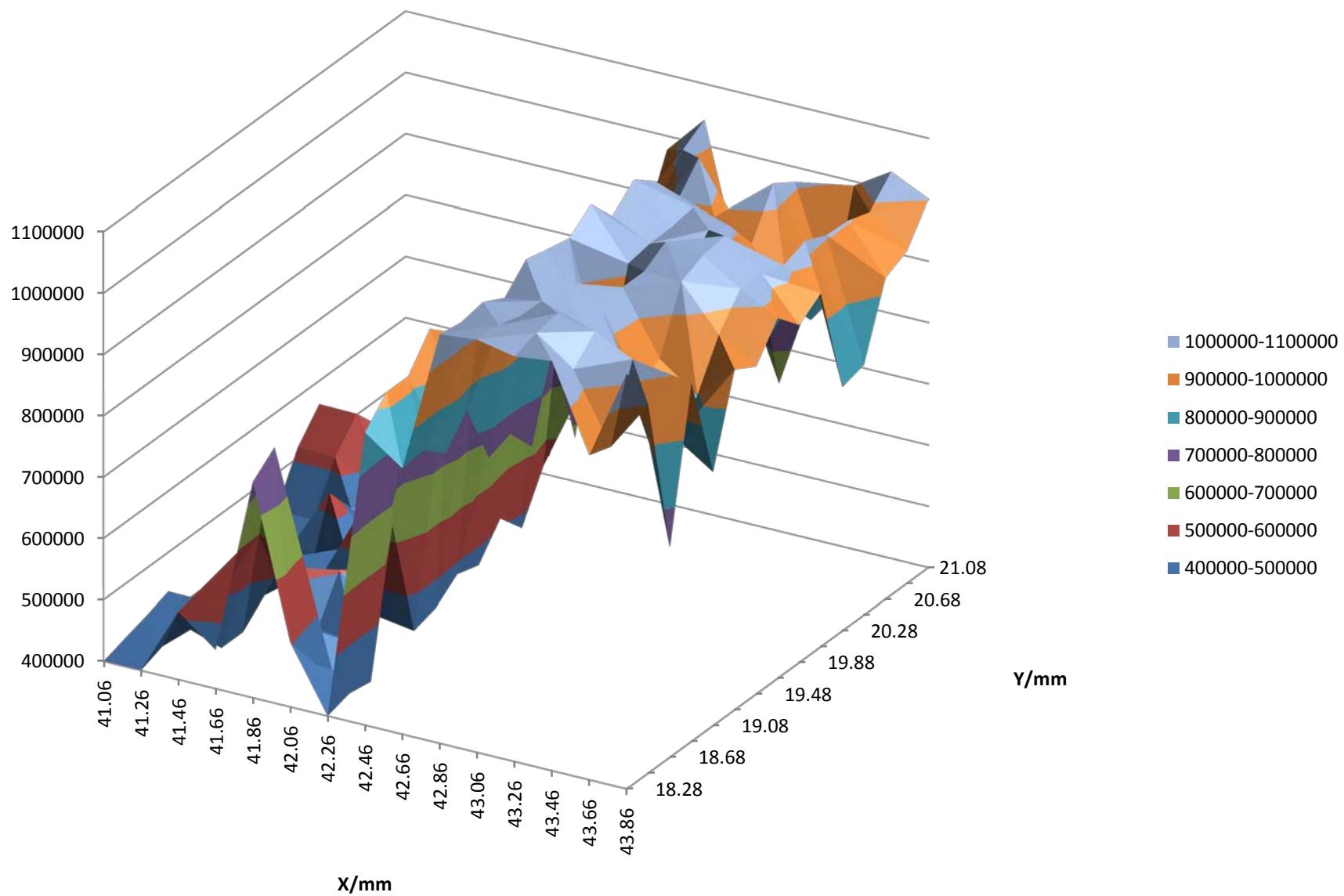
## Ca K12



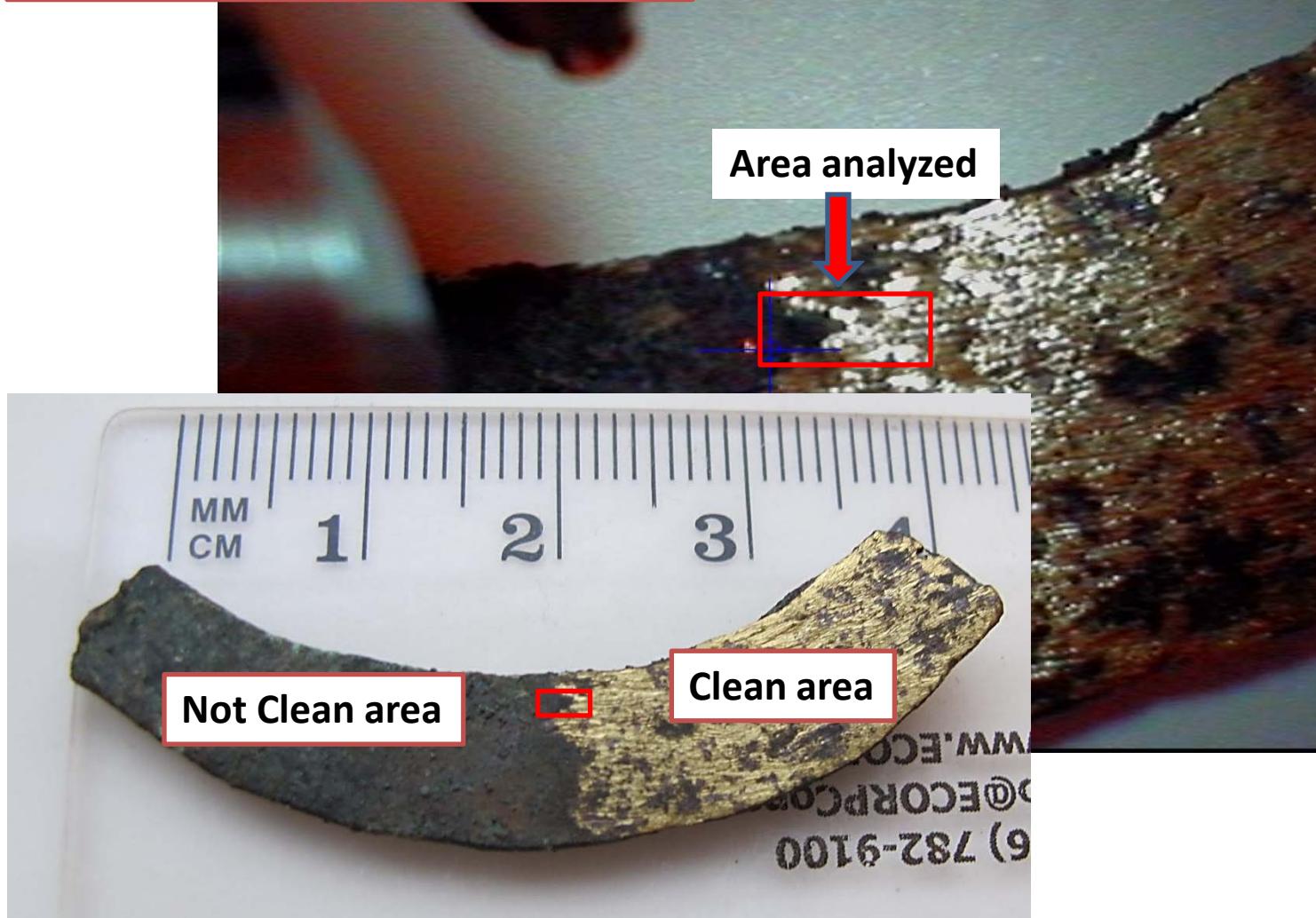
## Cu K12



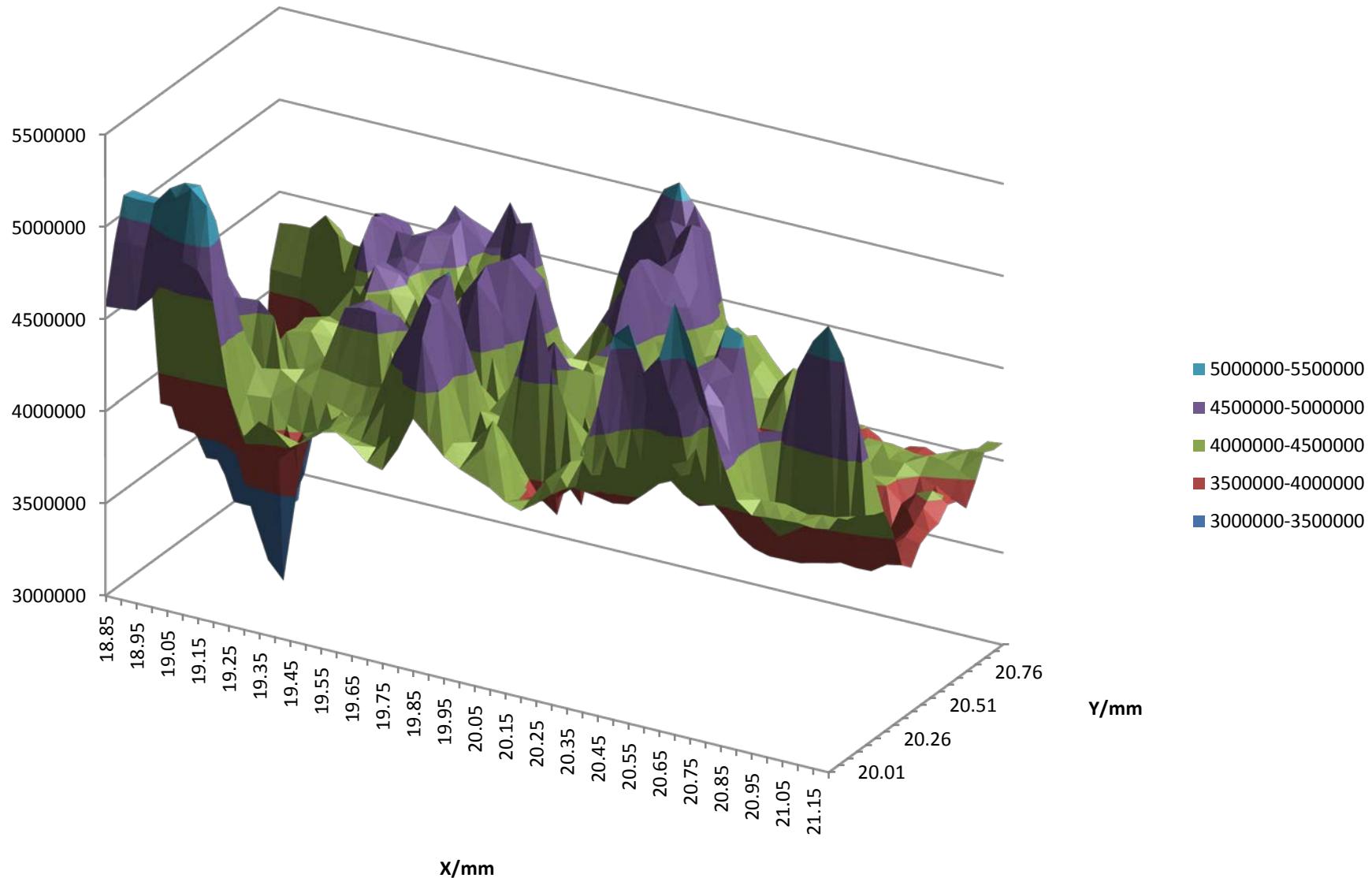
## Zn K12



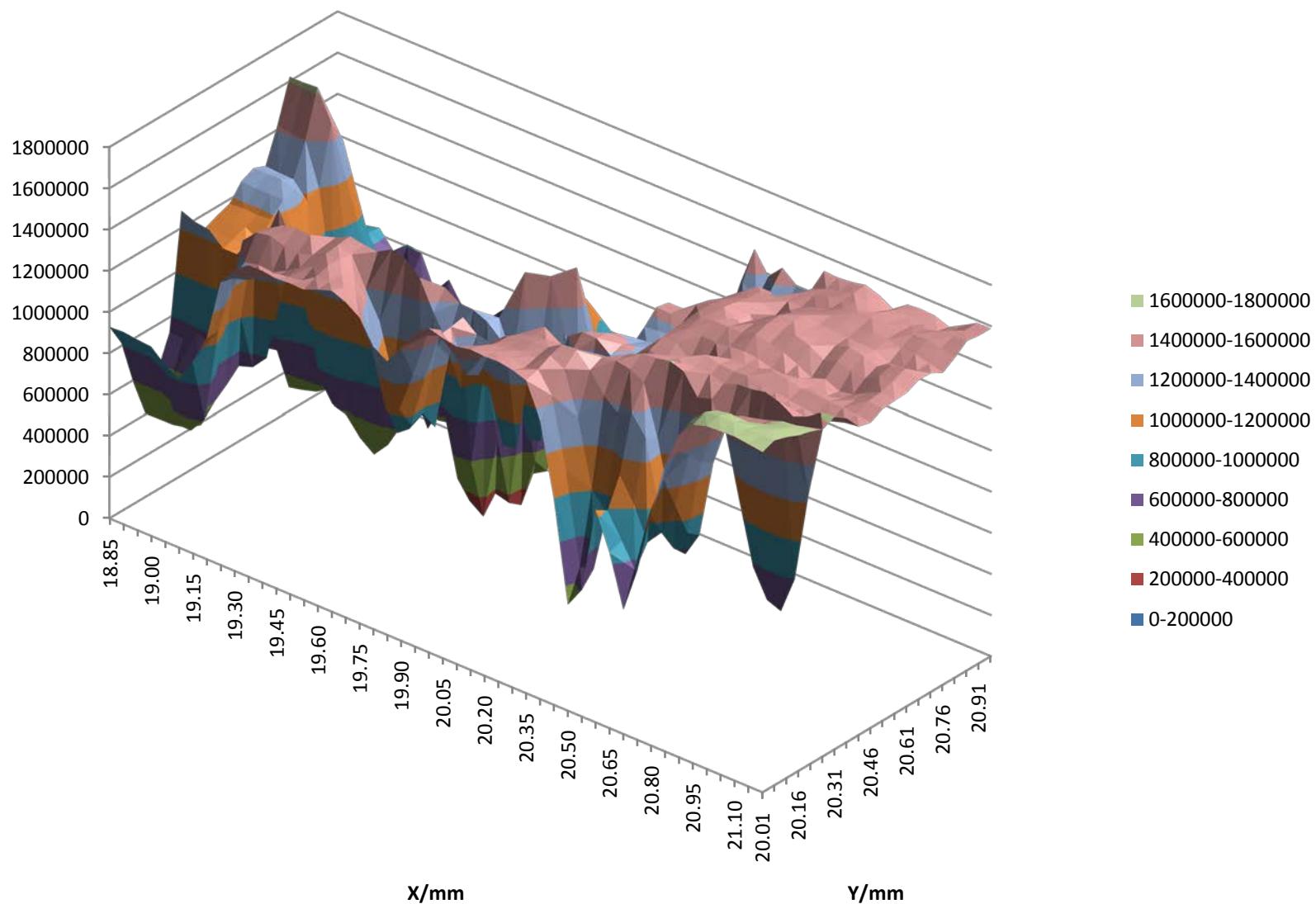
# Sample BrNL102



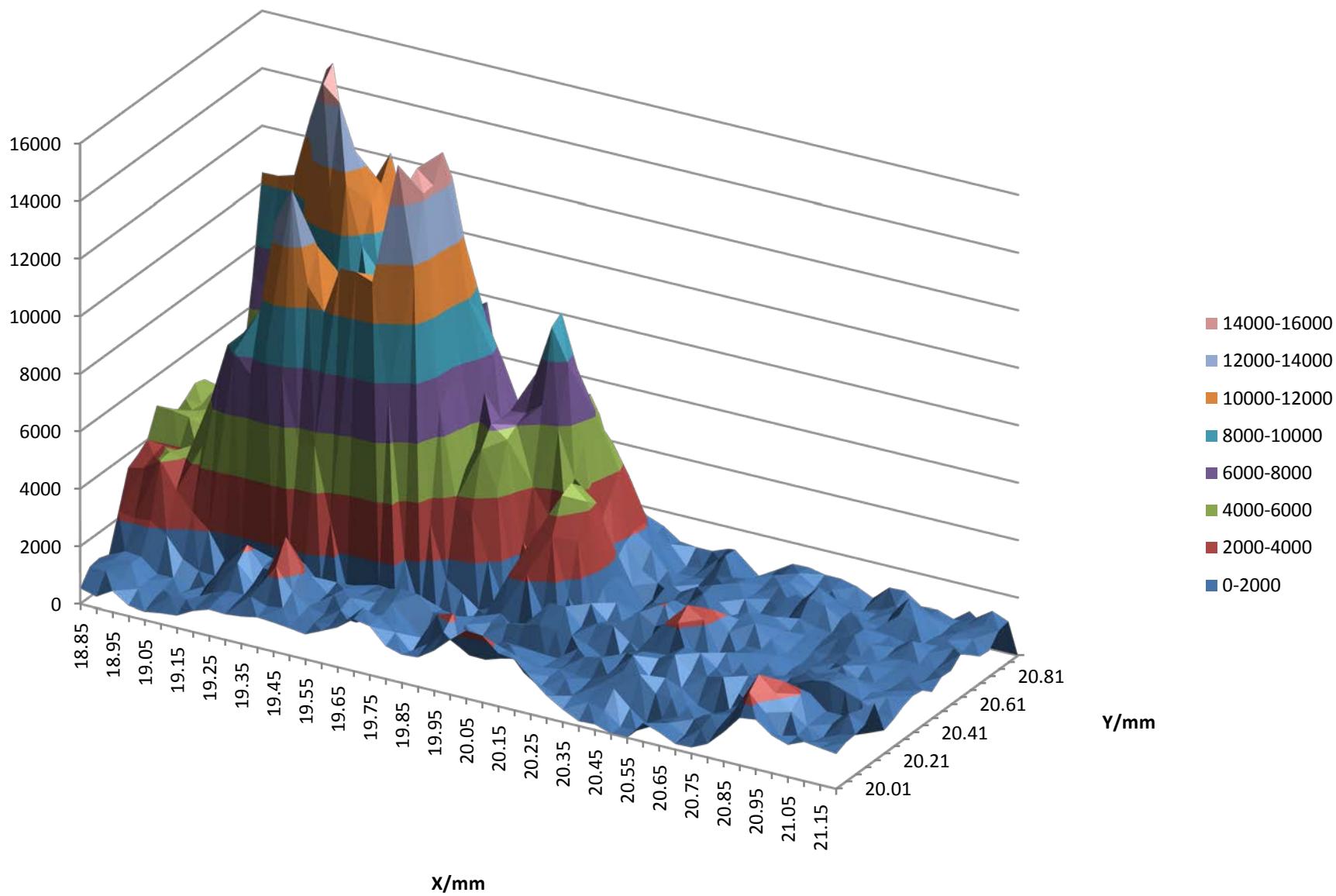
## Cu K12



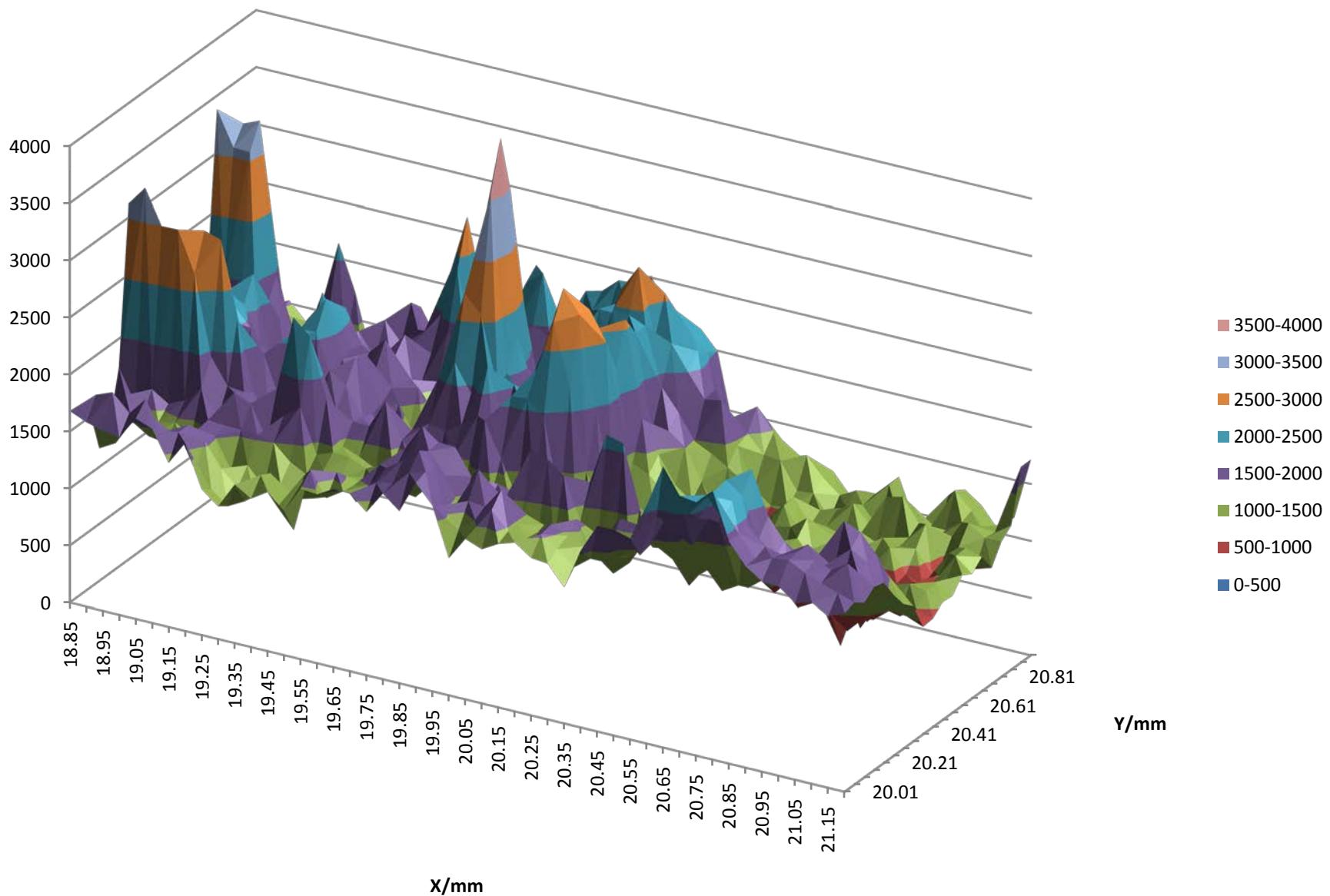
## Zn K12



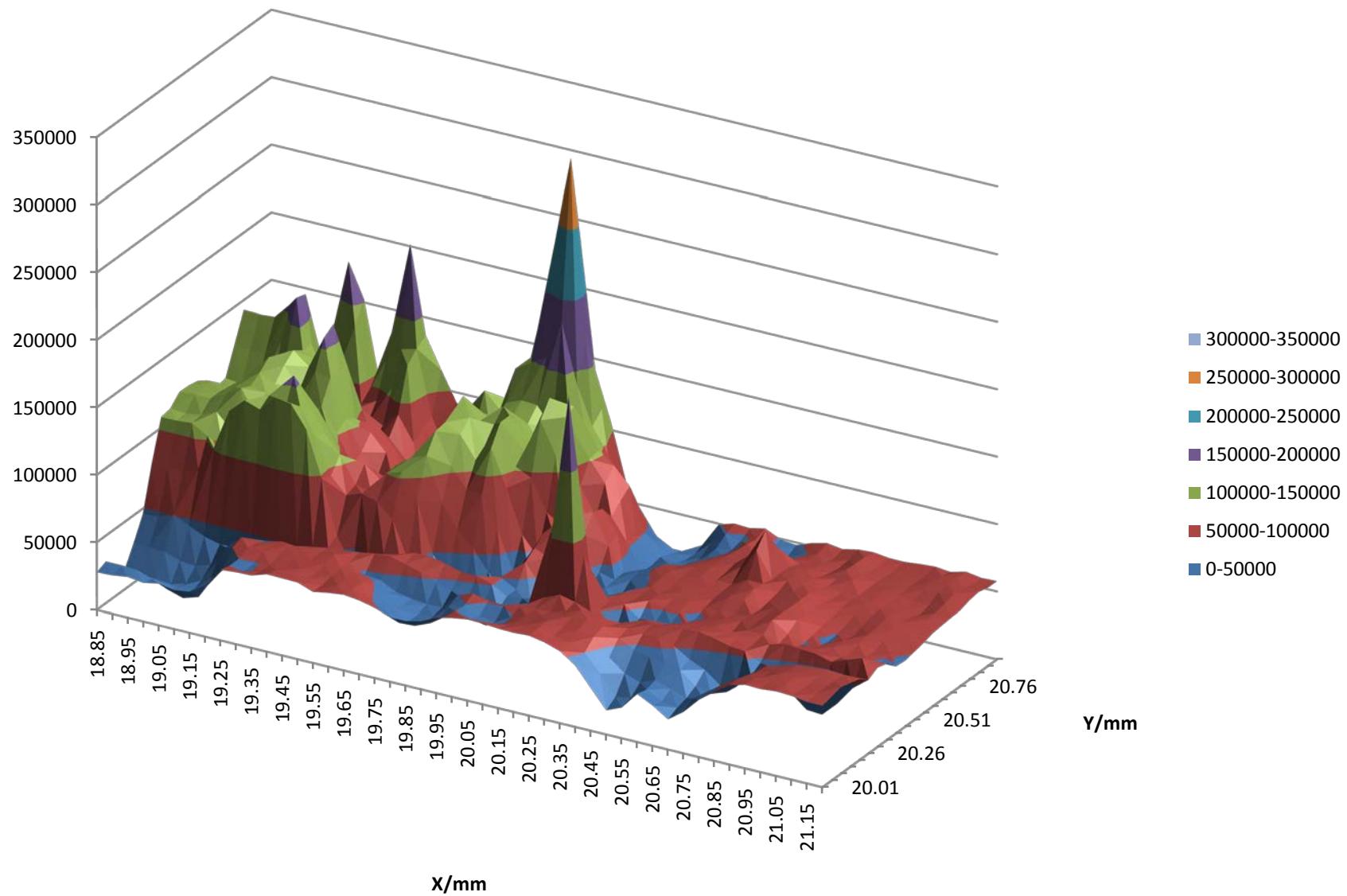
# Pb M1



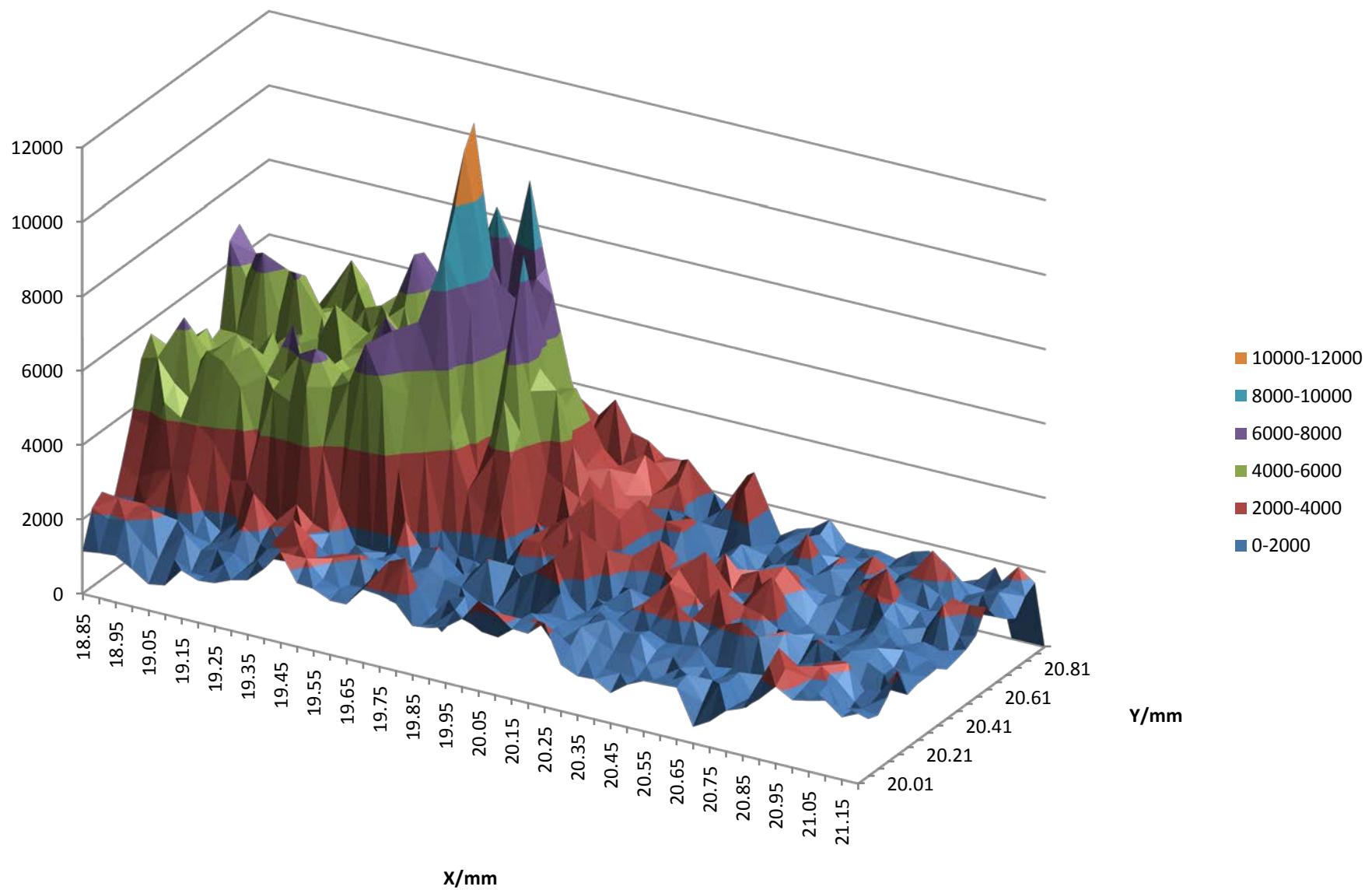
# Sn L1



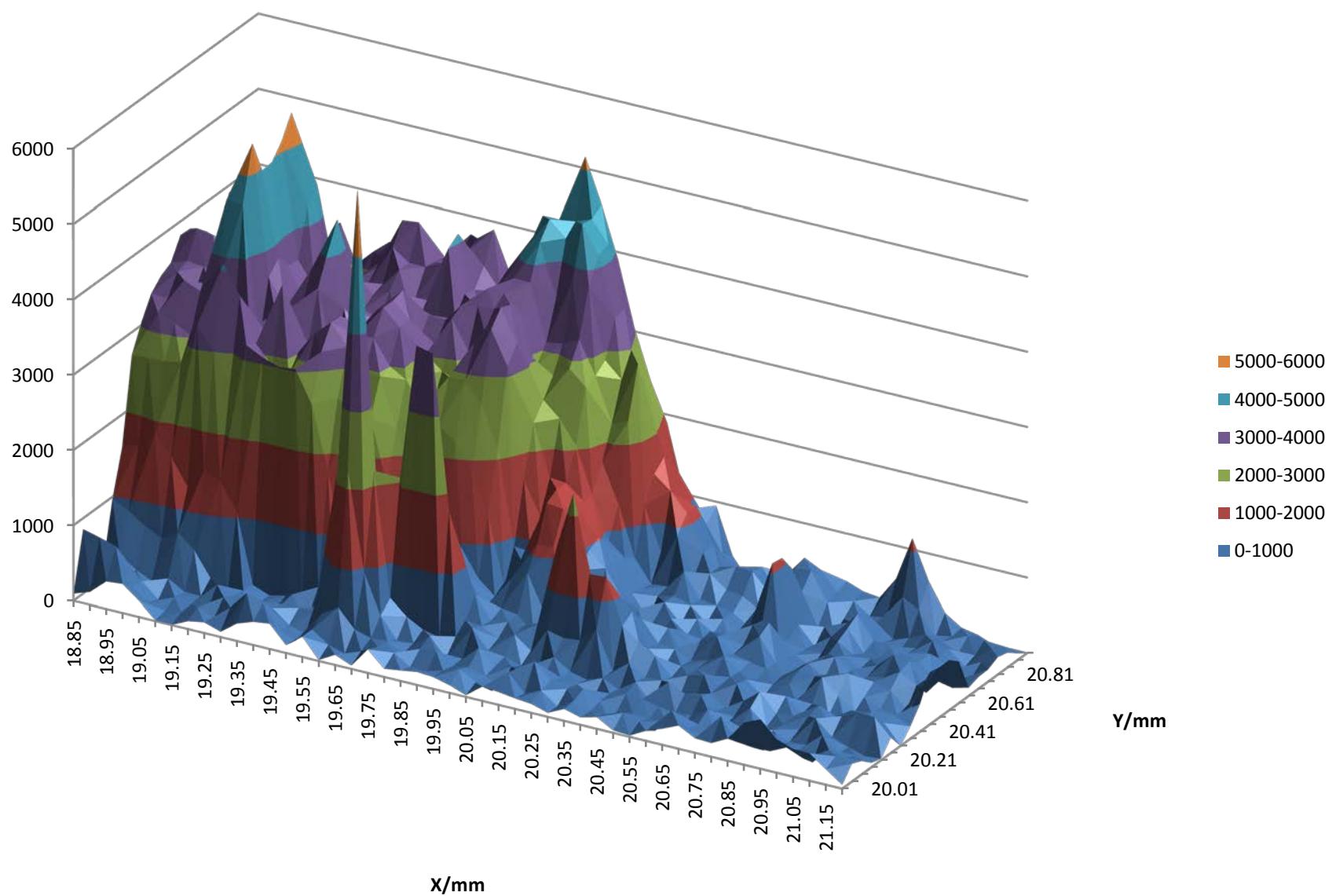
# Fe K12



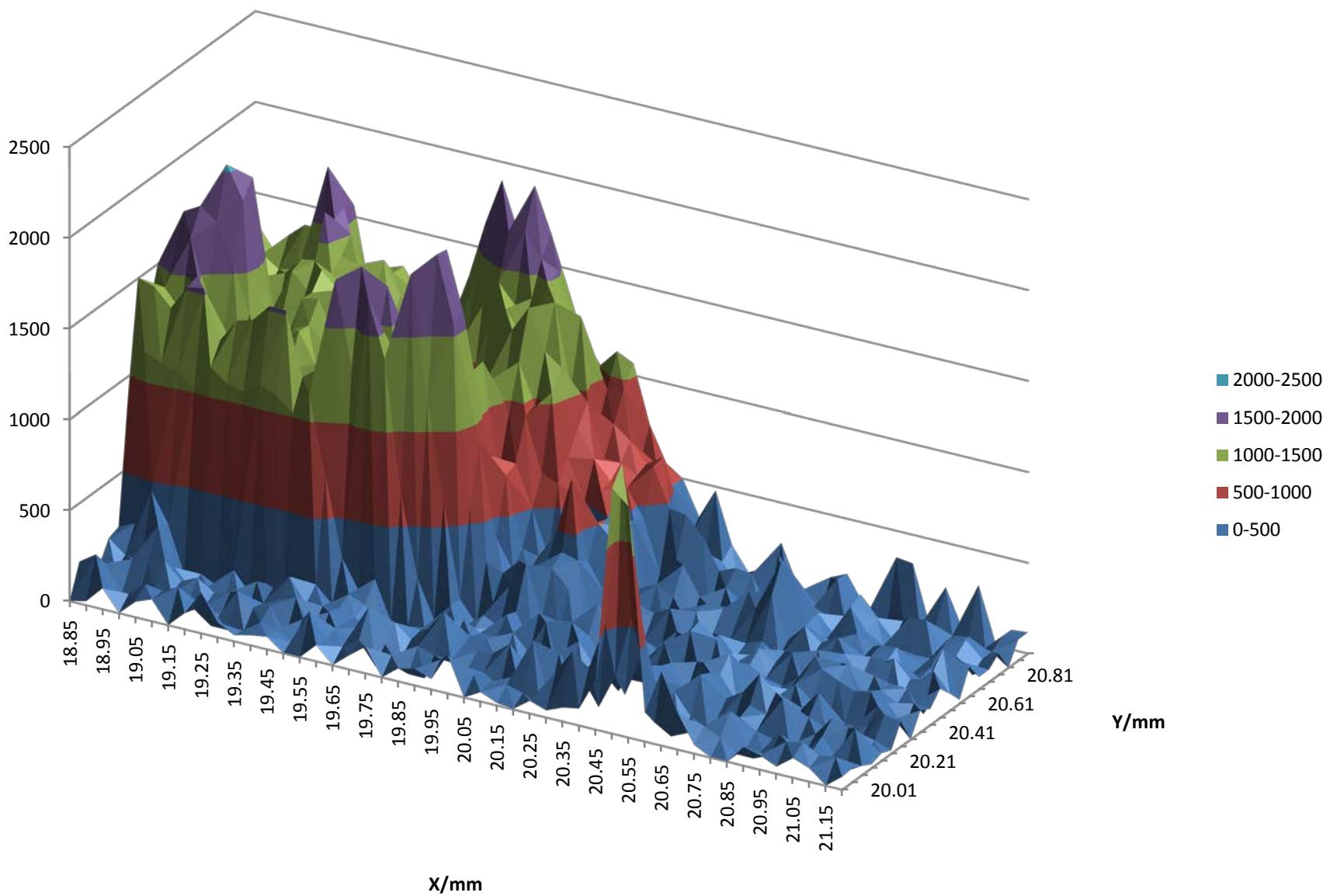
# As K12



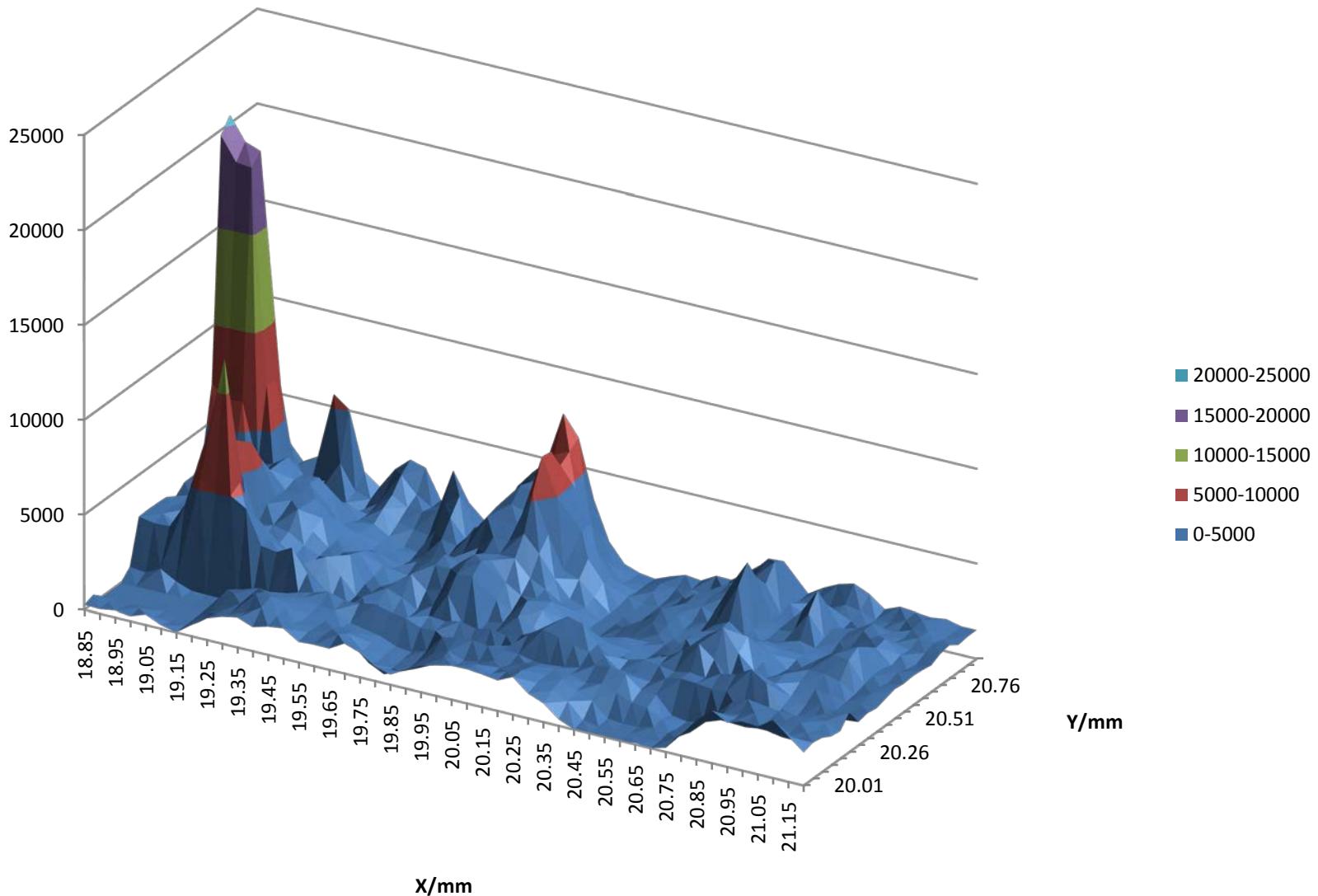
# Si K12



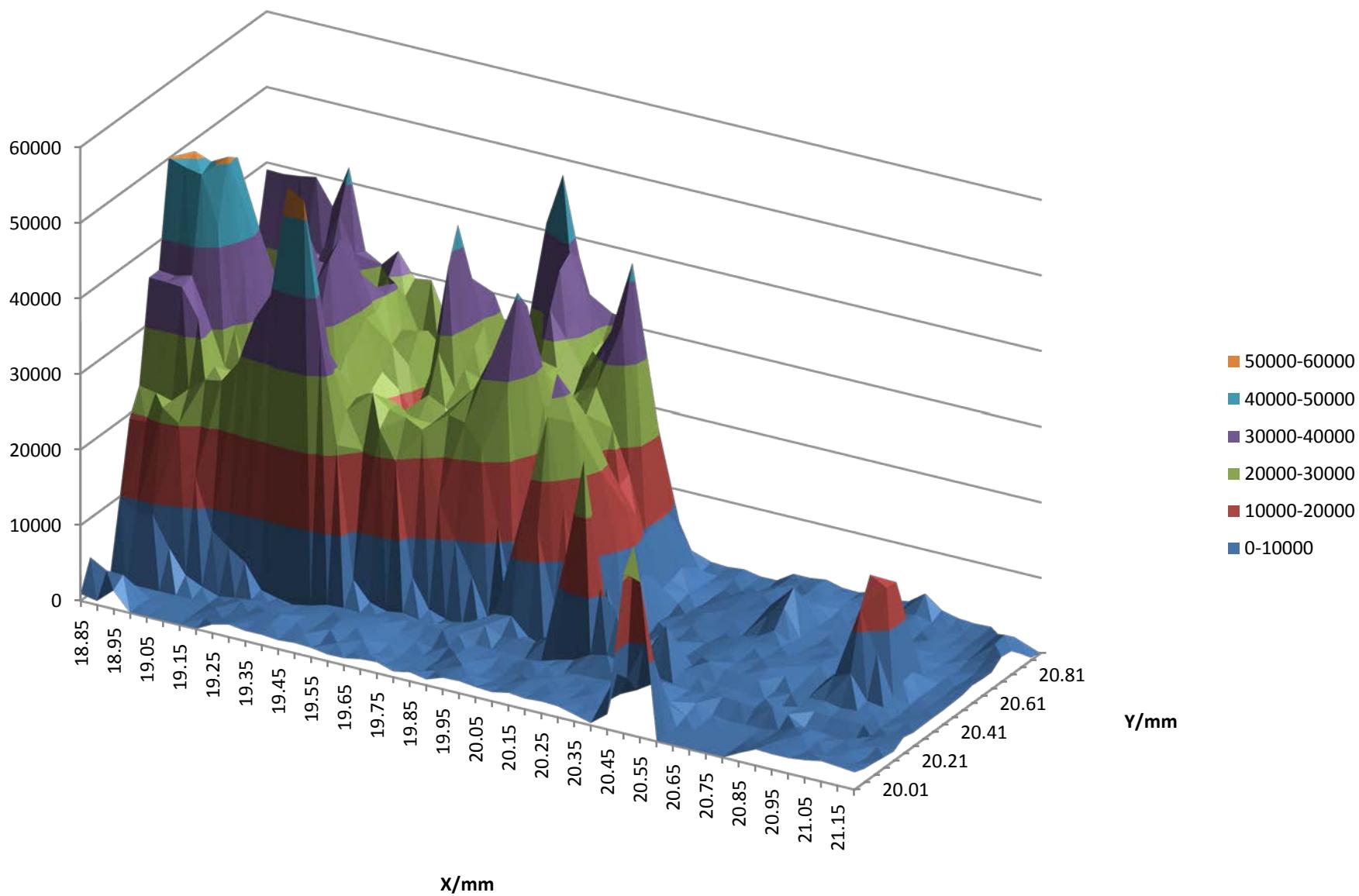
# P K12



# K K12



# Ca K12



## Rh L1

