DETAILED XRF ANALYSIS OF Tobia Howell's Ceramic Materials

THE ACCIDENTAL GLAZE PROJECT

"Name the greatest of all inventors. Accident."
Mark Twain

Has this happened to you? Out of the kiln comes a new set of glaze tests. One of the tests is incredibly beautiful!! It's a blood red at cone 6 or a green glaze with only cobalt as a colorant or maybe it's just the best glaze you've seen. You want to share it with the world! But then you realize:
a) That was the test you tossed in 10 grams of… (oh gosh what was that) just to see what would happen.
b) It's the garbage (scrap) glaze
c) You know what's in it then try to reproduce it and it doesn't work. It could be the firing cycle but you can't be sure.
d) You were sure you would remember that formulation

Usually when we design glazes we do just that. There is a huge amount of information out there to help you guide your testing process. What we don't do often enough is go outside those guidelines. Over 30% of great discoveries are accidental. Scrap or garbage glazes are a perfect example, rarely are they just 5 or 6 ingredients in intelligent well thought out proportions. Likely you will have upwards of 15 different ingredients. This large number of variables can have the most amazing results. Remember how hard it was to reproduce "Albany Slip"?

Enter "The Accidental Glaze Project"

Project goals:

The goal of this project is to gather a very large number of accidental glazes (any glaze with an accidental component to them). Through the efficiencies of numbers and the donations of volunteers (testing and administration) we reduce the cost of a full spectrum mineralogical analysis from $100 USD to less than $15 USD (The goal is $10 USD)

From this we make a publication and you or your studio can get full credit for its discovery.

PS (This is a green project encouraging potters to keep their cast away glazes instead of discarding them.)

There are many roles to take in this project. You can be a partner, participant or something in between. If you are interested in finding out what your accidental glaze is, or you want to be published or you just can't wait to see what everyone's accidental glaze contains, or you're a glaze intellectual and want to see what new discoveries this project can uncover.

Let me know if you would like to participate and what role you would like to play. This is definitely a group project.

Tobia's Samples as Received

When and how to use xrf to measure ceramics?

The answers to this question are simple and based on fundamental physics, which we have not yet found a way to violate:

- One can never determine the weight percent of a non-uniform material because it is non-uniform UNLESS you covert it to a uniform material.
- Nor can one ever use xrf to report content it cannot measure like C and O and H. So the content listed in this calibration is only the weight percent of the elements that are measured. It does not add up to 100 percent.
- The Tracer spot size is 3 by 4 mm, if your substance has a mixture of particles smaller than 0.2 mm and they are well mixed then you will get a reasonable answer relative to wt %
- A detailed calibration with the ceramic materials that were provided was done after using the raw Spectra from the Tracer to verify the given values validity.
- If you material is a conglomerate then it is ***not*** uniform and the only way to get a reasonable estimate of its average elemental content is to take a large quantity of it grind it up and then press it into a pellet, there is no other method that will work.
- How did Bruker check / corrected for any matrix effect due to material containing heterogeneous particles with size larger than mud (silt/clay)? Actually you have to do this by grinding your material up and pressing it to pellets. See item 5 ☺
- A calibration that is very accurate on uniform ceramics without preparation and non-uniform material ground and pressed in to pellets.
- Note ceramics or other material with paint, slip, and glaze or any covering like dirt on them are VERY non-uniform!
- Your sample also has to be infinitely thick relative to the range of the emitted photon from each element of interest. See table on next page, you sample must be thicker than the values list for each element noted.

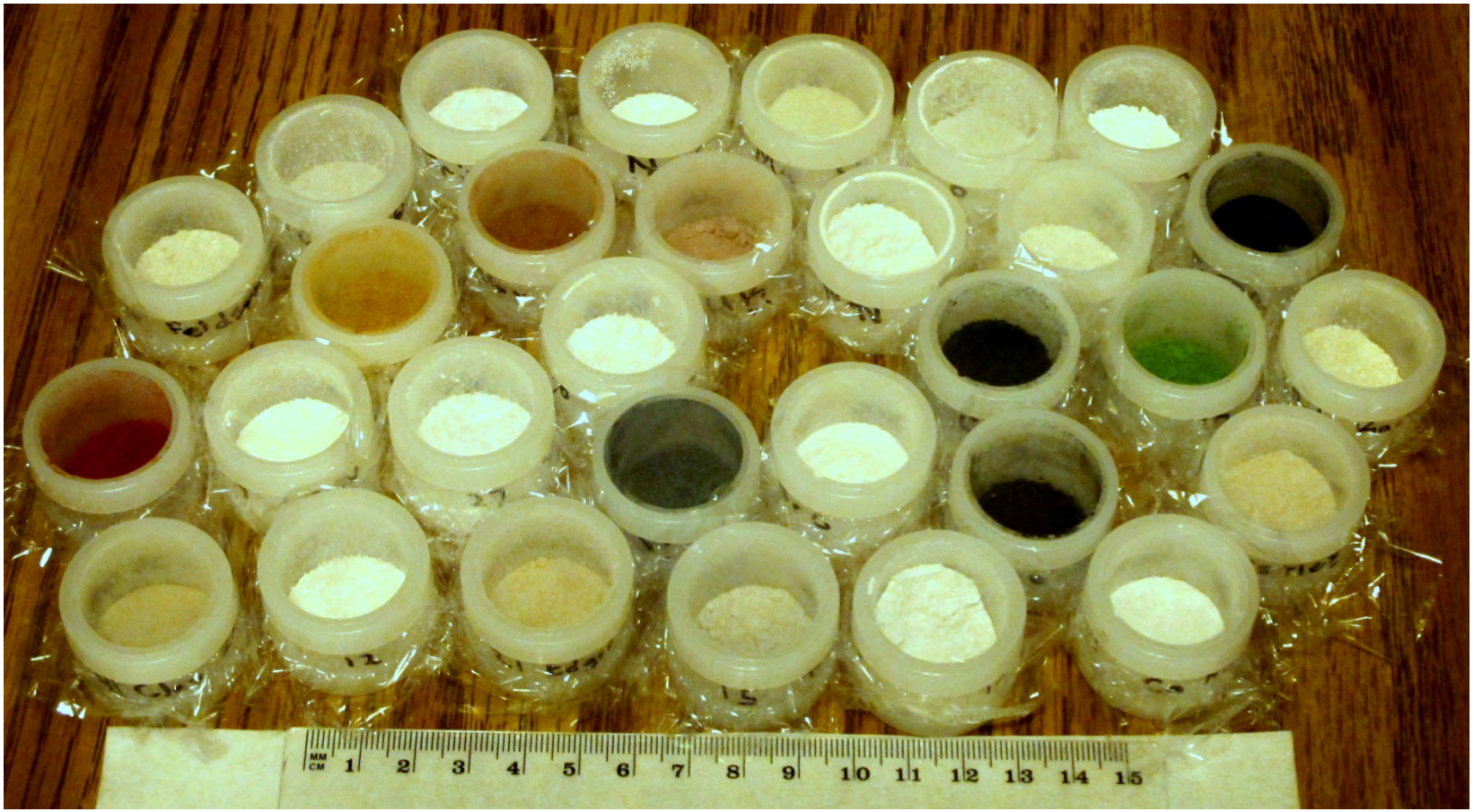
Element	Photon Emitted energy (keV)	Analysis depth in Ceramic(cm)
O	0.53	0.000001
Na	1.04	0.0007
Mg	1.2	0.00096
Al	1.47	0.0017
Si	1.74	0.0027
P	2.01	0.0013
Ca	3.69	0.0064
Cr	5.41	0.0192
Fe	6.4	0.03
Cu	8.01	0.058
Zn	8.64	0.077
Pb	10.55	0.113
Zr	15.78	0.384

System and settings

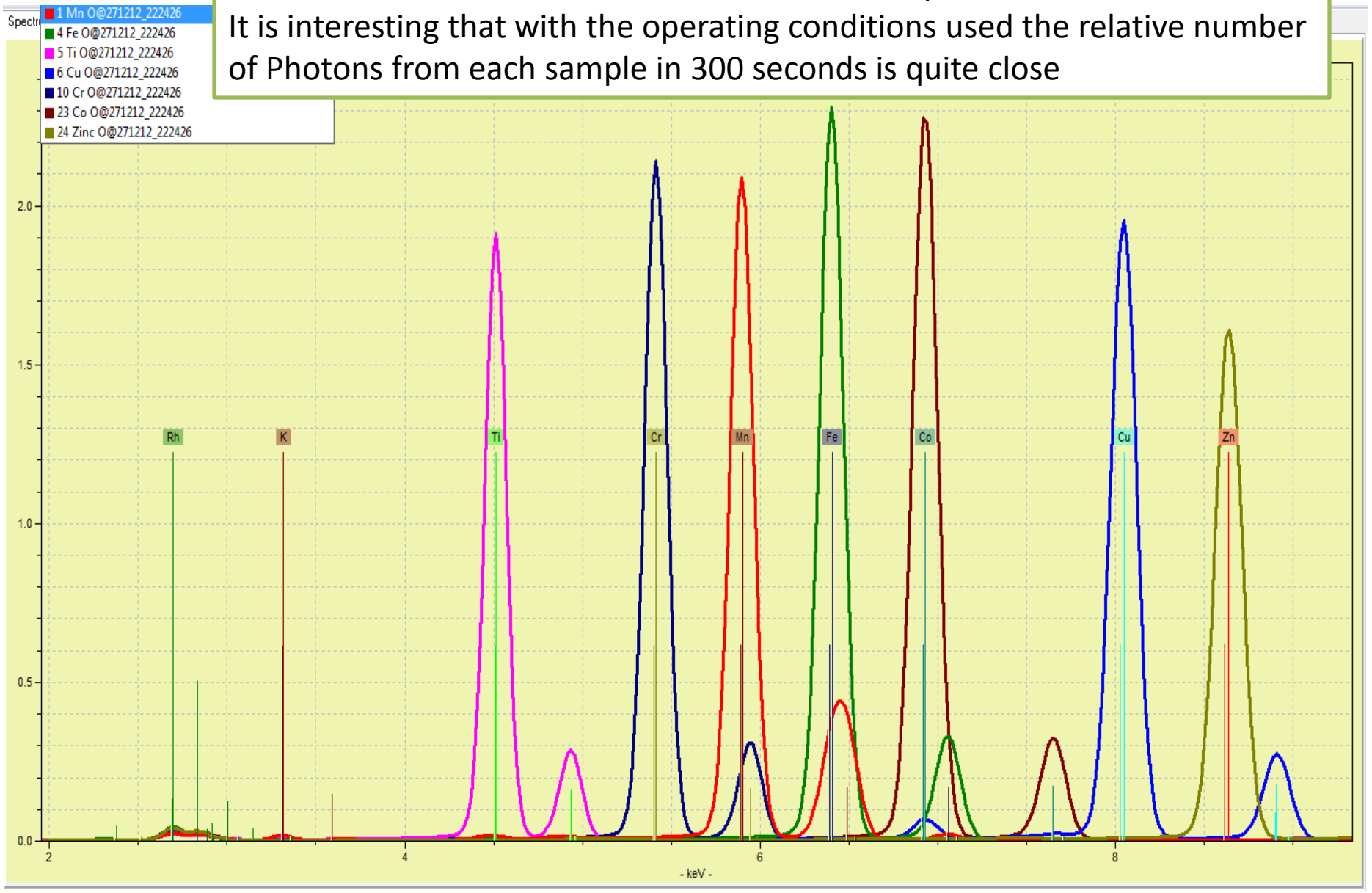
A Bruker Tracer IV SD system was used

1. No beam filter
2. Tube voltage was 15 kV
3. Tube current was 44 micro amps
4. Vacuum at 4 Torr
5. Each sample was placed 3 mm thick in a 1.25” sample cup
6. Each analysis was done for 300 sec

THE SAMPLES AS ANLYZED IN XRF ANALYSIS CUPS WITH 4 MICRON POLY WINDOWS



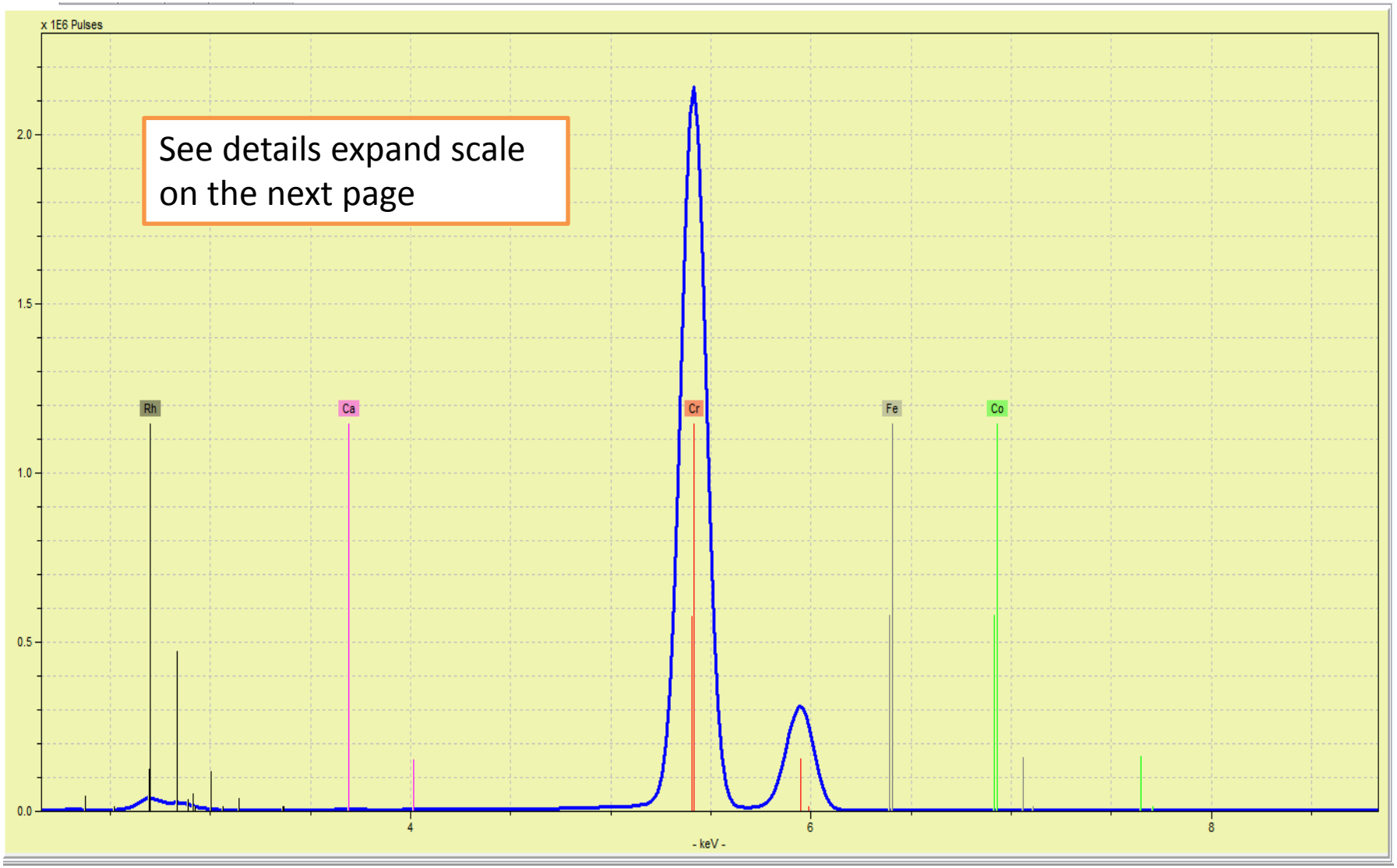
This is a plot of the raw spectral data of several “pure “oxides of Ti, Cr, Mn, Fe, Co, Cu and Zn overlaid to see the relative response of the Tracer.
It is interesting that with the operating conditions used the relative number of Photons from each sample in 300 seconds is quite close



The following is a quick look at some of the “pure” oxides.

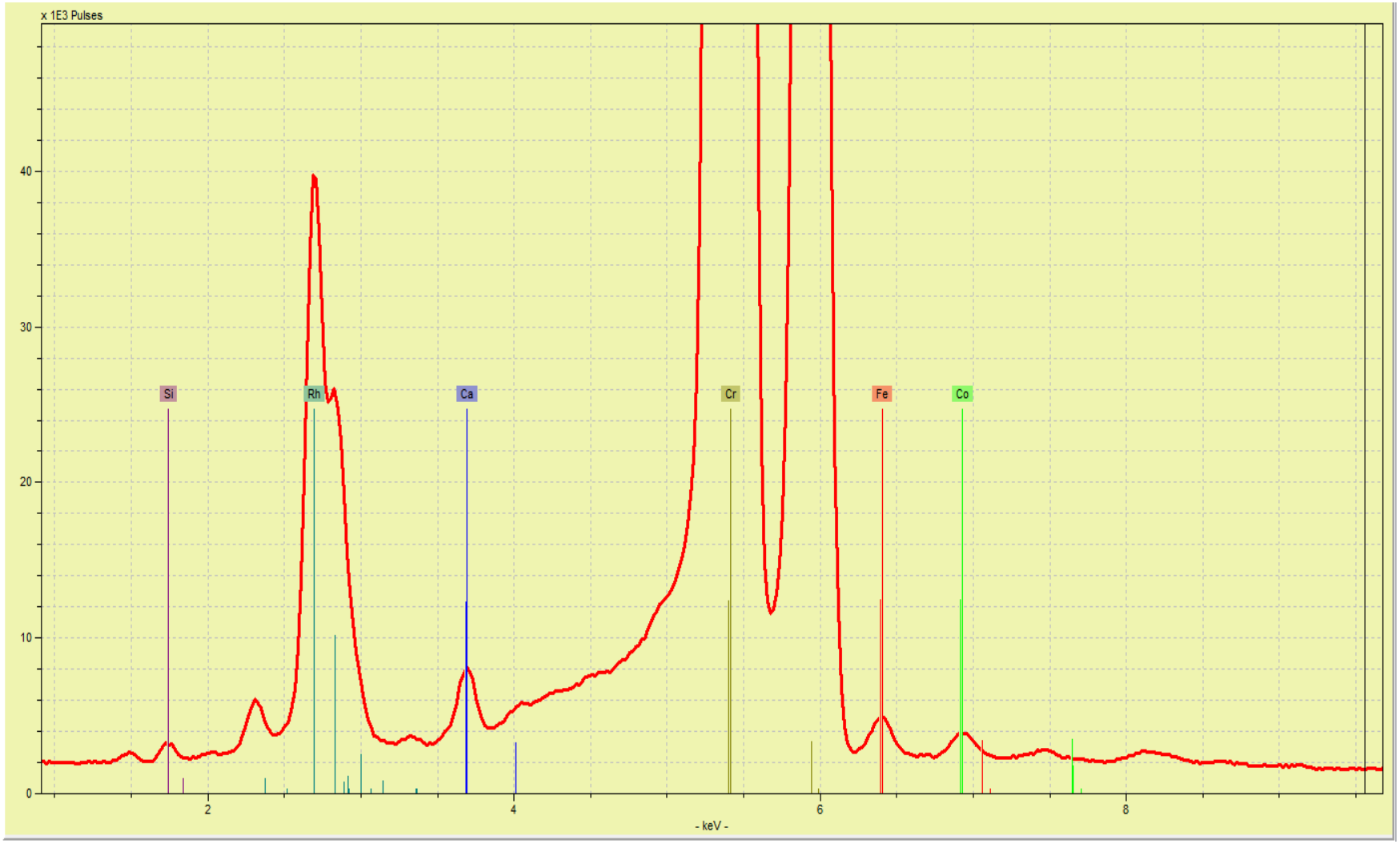
Note the Tracer detected trace elements as noted, these were not indicated in the given material content!

Cr oxide: trace elements are Si , Ca, Fe and Co these are at around 0.01 weight percent

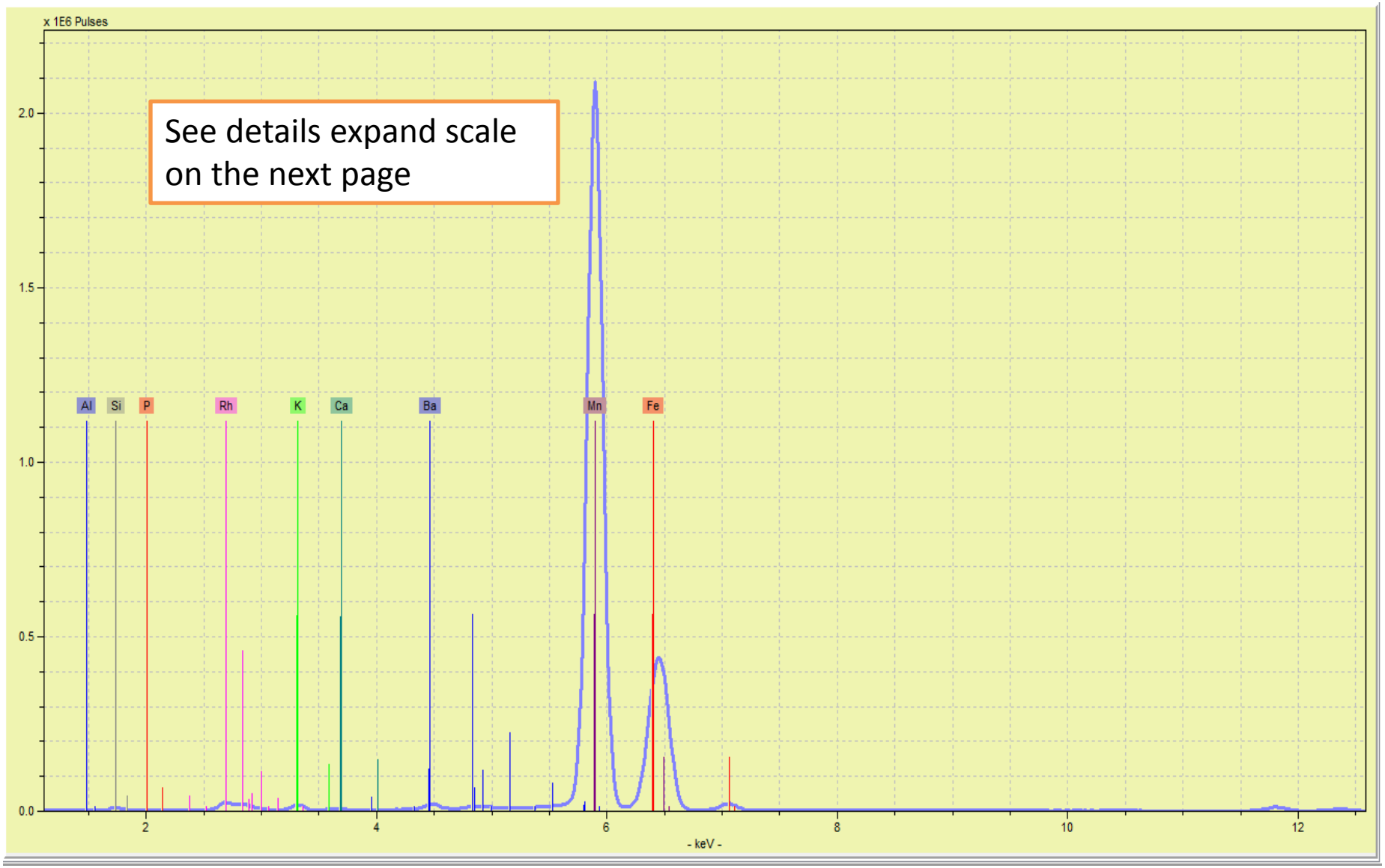


See details expand scale on the next page

Cr oxide: trace elements are Si , Ca, Fe and Co these are at around 0.01 weight percent

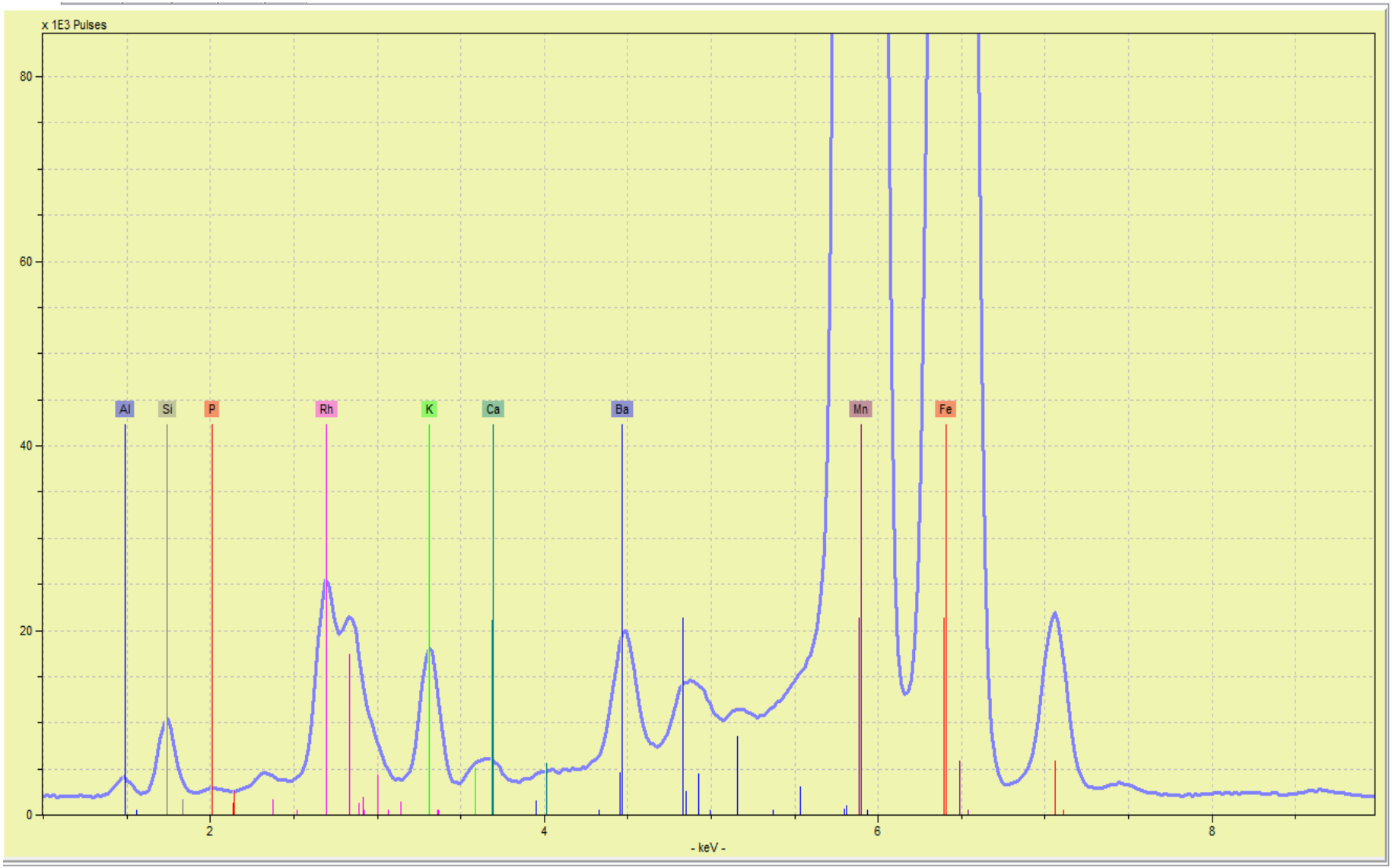


Mn oxide: trace elements are Al, Si , P, K, Ca, and Fe these are at around 0.01 weight percent or less

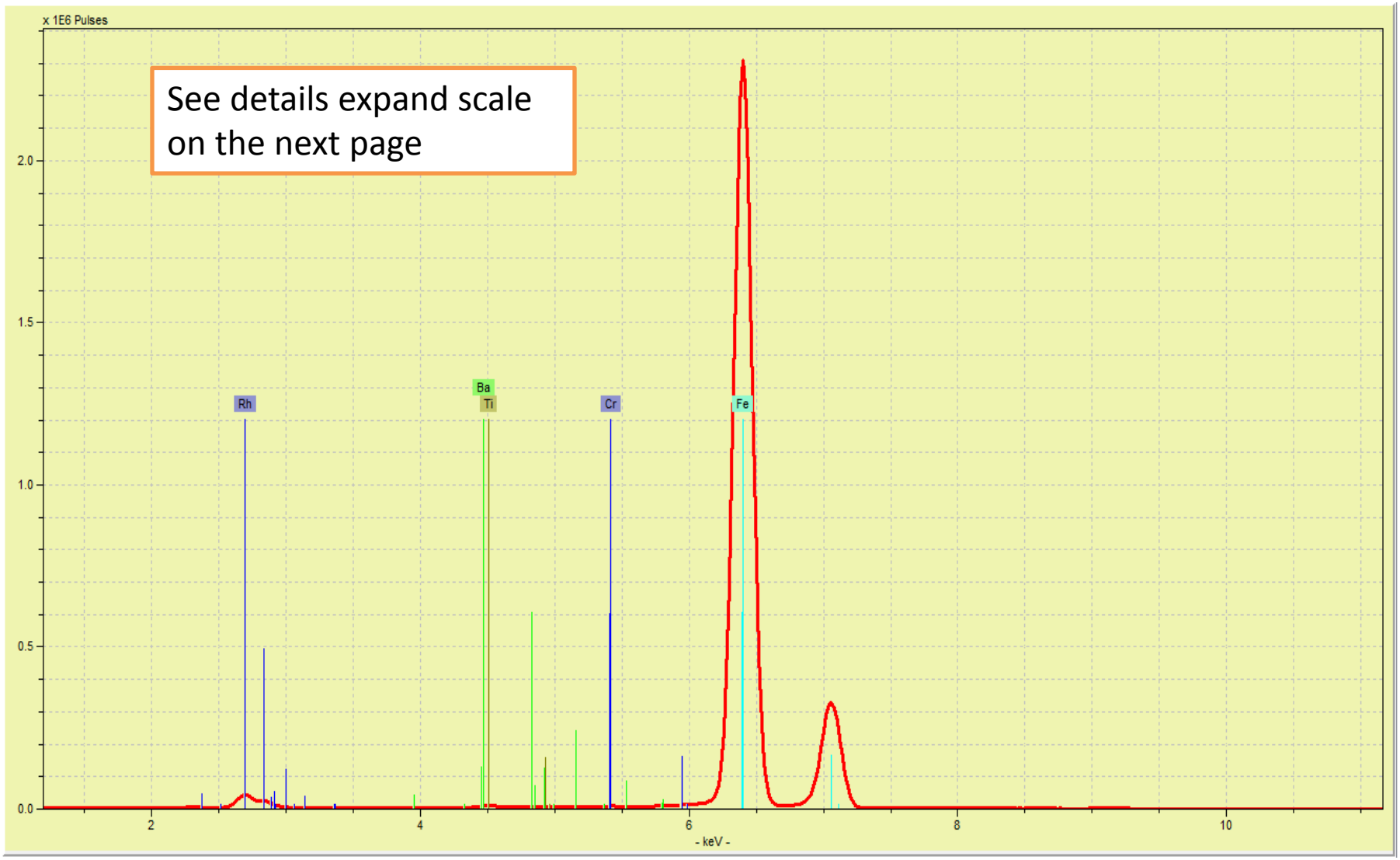


See details expand scale on the next page

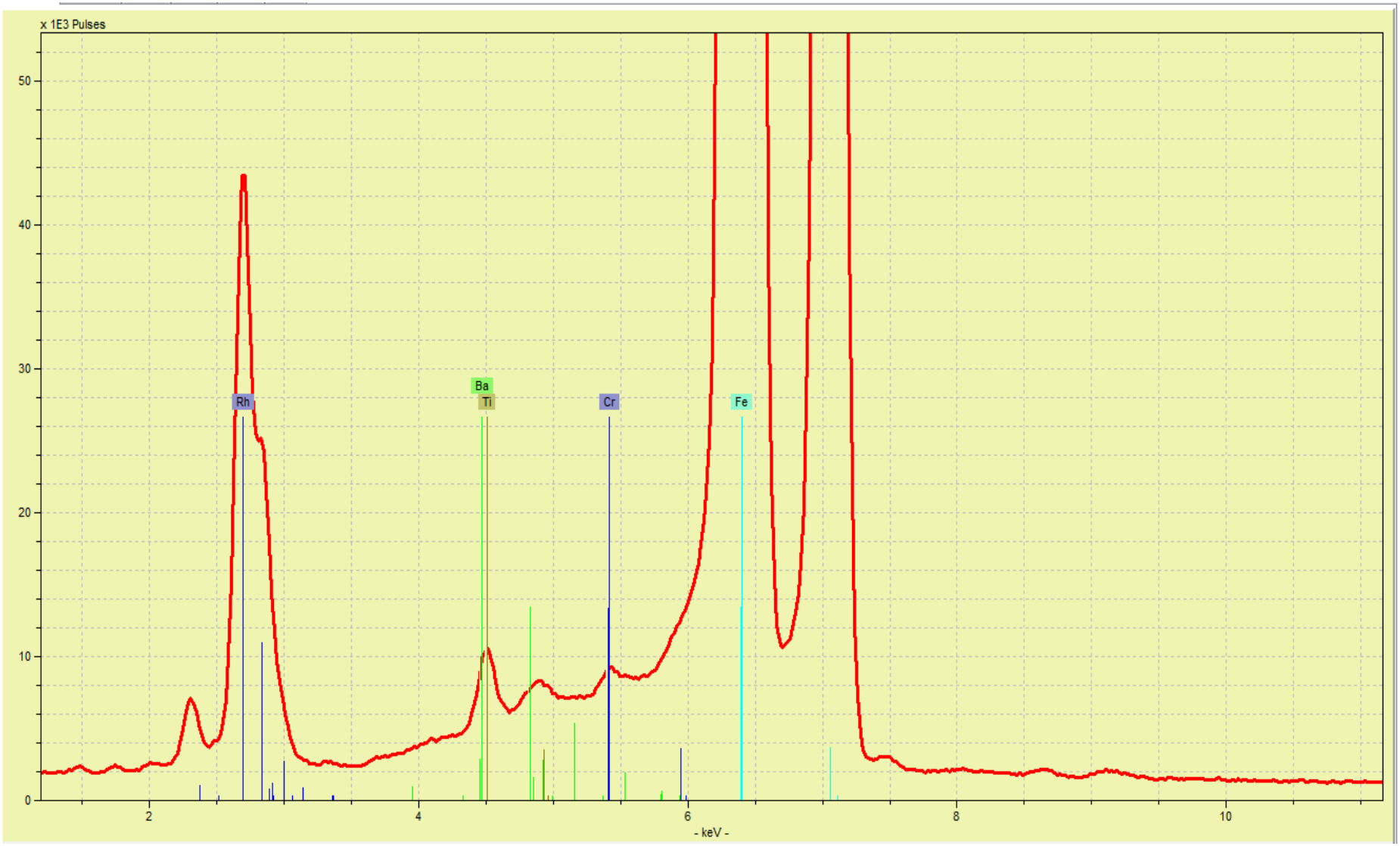
Mn oxide: trace elements are Al, Si , P, K, Ca, and Fe these are at around 0.01 weight percent or less



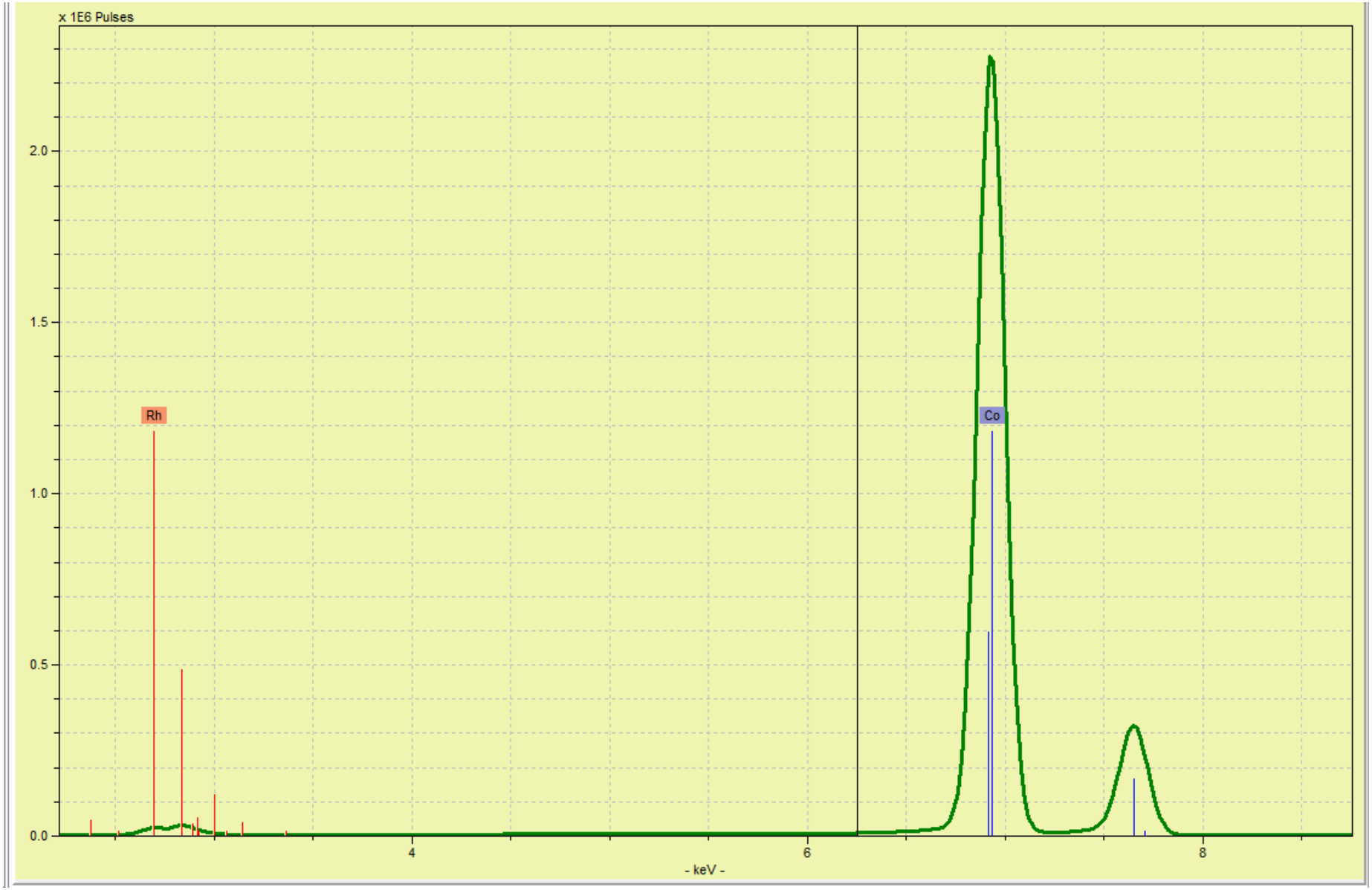
Fe oxide: trace elements are Ba, Ti and Cr these are at around 0.01 weight percent or less



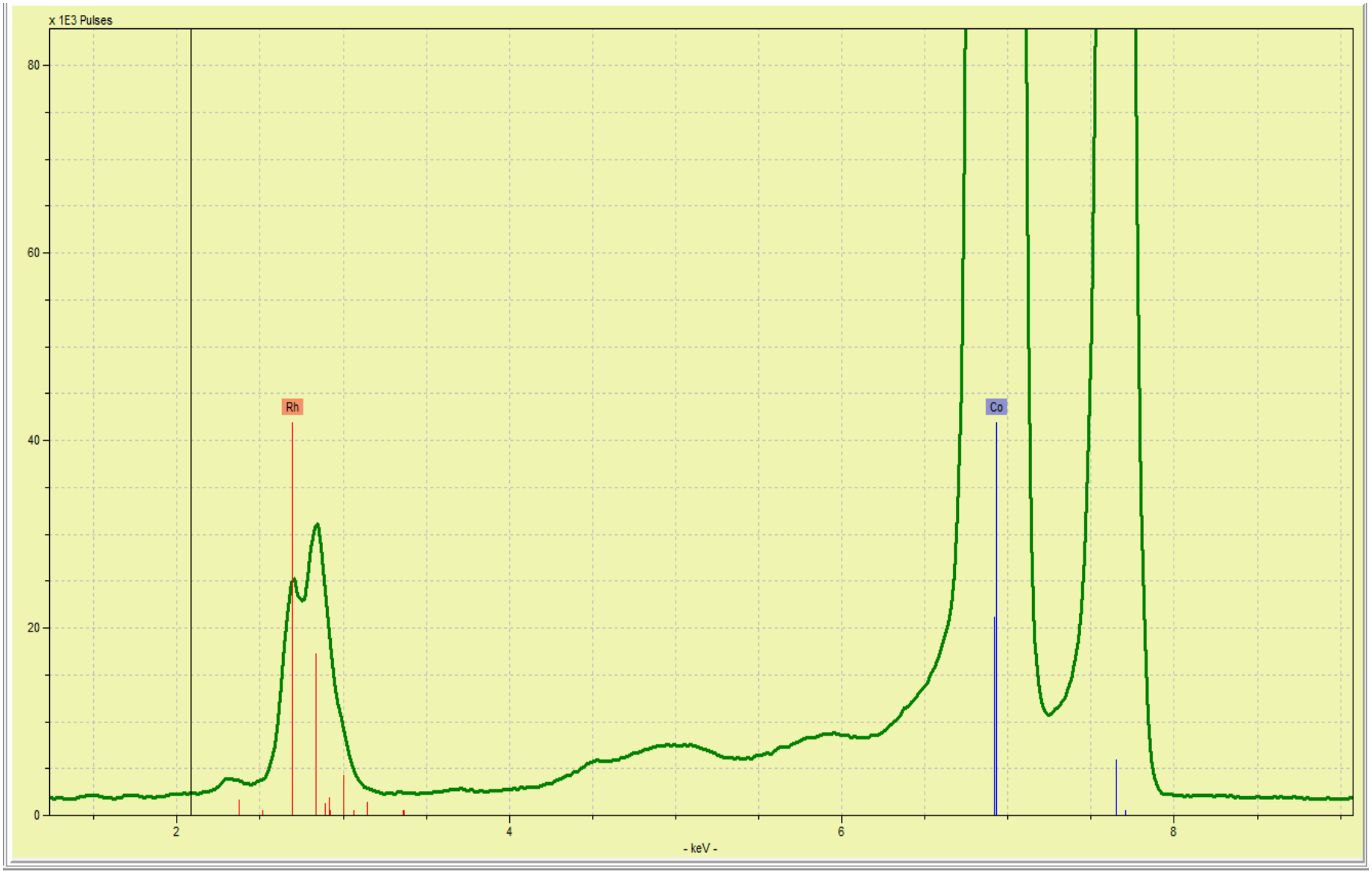
Fe oxide: trace elements are Ba, Ti and Cr these are at around 0.01 weight percent or less



Co oxide: there are no trace elements above 0.01 weight percent

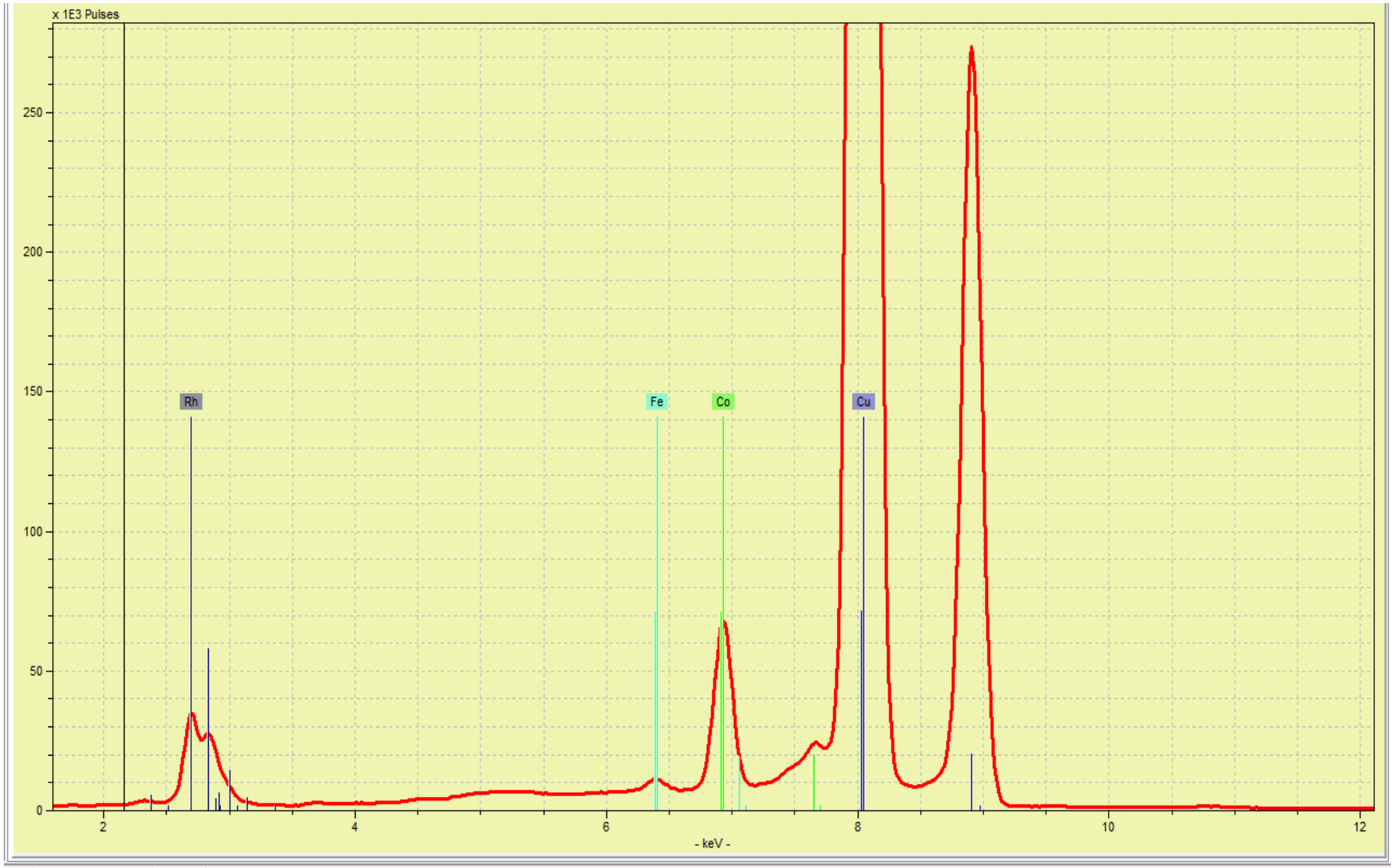


Co oxide there are no trace elements above 0.01 weight percent

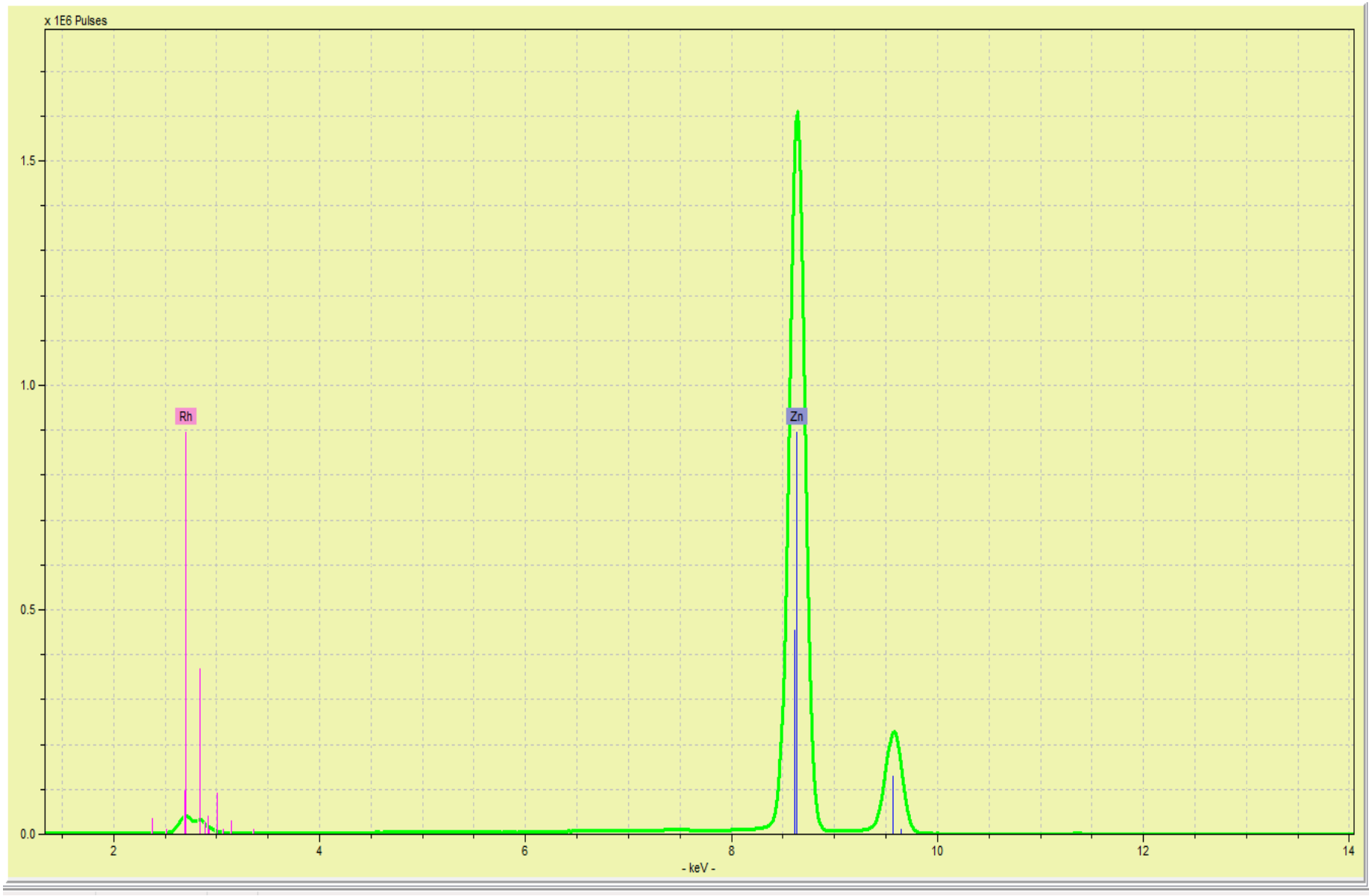


Cu oxide with Co above at about 2.0 weight percent and a trace of Fe.

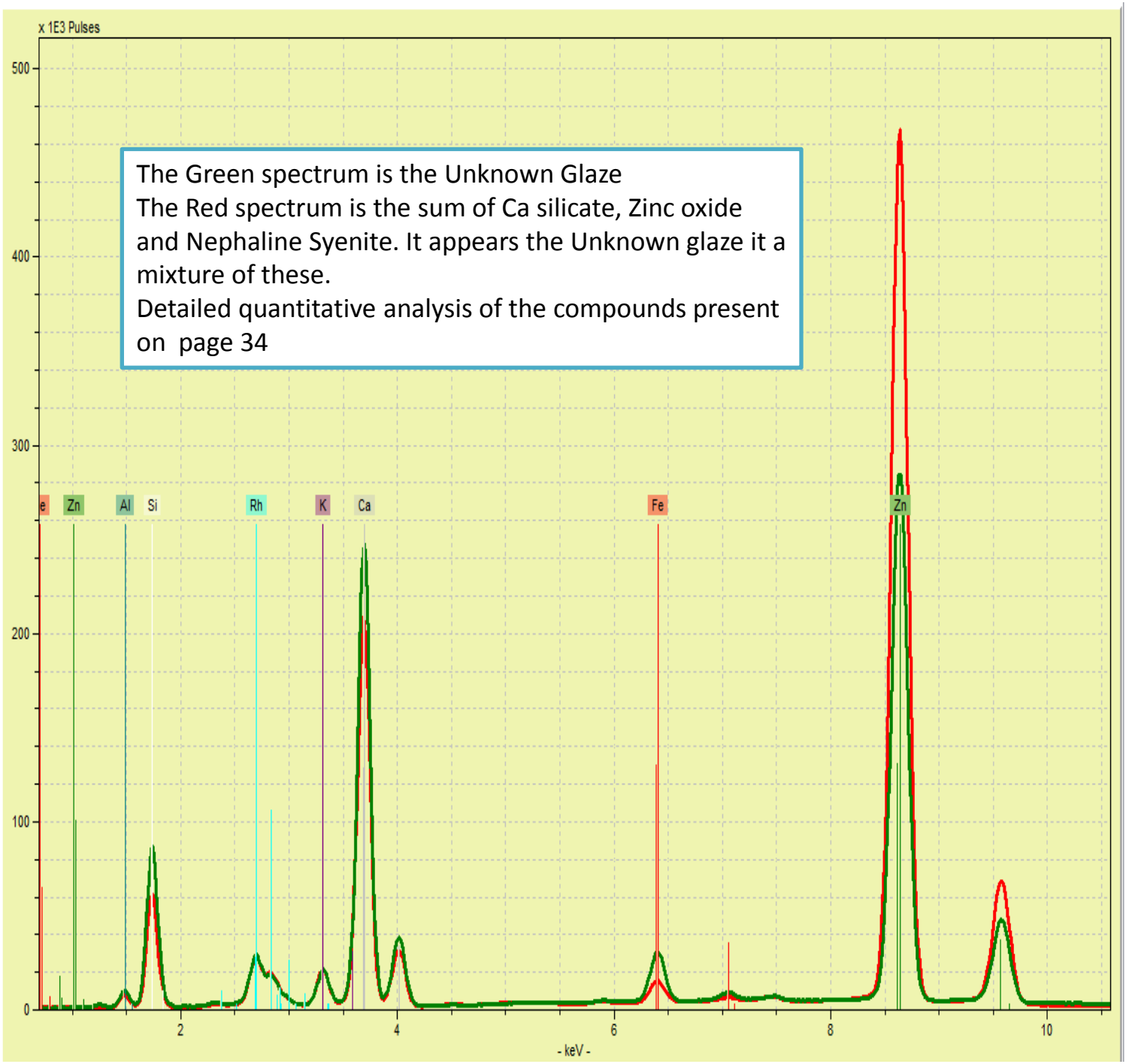
Cu oxide with Co above at about 2.0 weight percent and a trace of Fe.



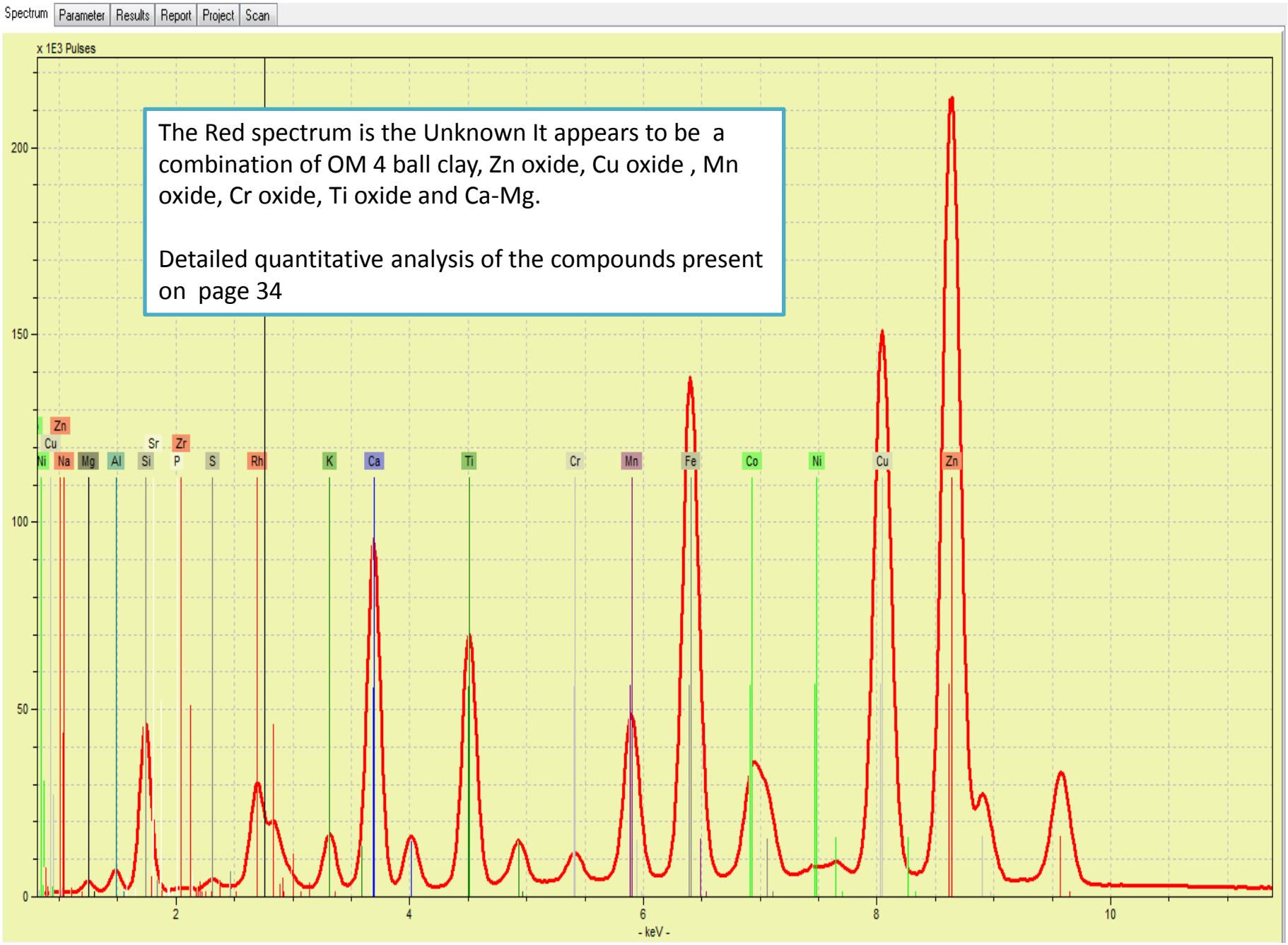
Zn oxide: there are no trace elements above 0.01 weight percent



Project
- Objects
  - Points Ceramic
  - Points glaze
    - 12 Ca Si@301212_235141
    - 24 Zinc O@301212_235141
    - 18 Nepheline Syenite@311212_000434
  - Accu_Points glaze



The Green spectrum is the Unknown Glaze
The Red spectrum is the sum of Ca silicate, Zinc oxide and Nephaline Syenite. It appears the Unknown glaze it a mixture of these.
Detailed quantitative analysis of the compounds present on page 34


Spectrum
Parameter
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Project
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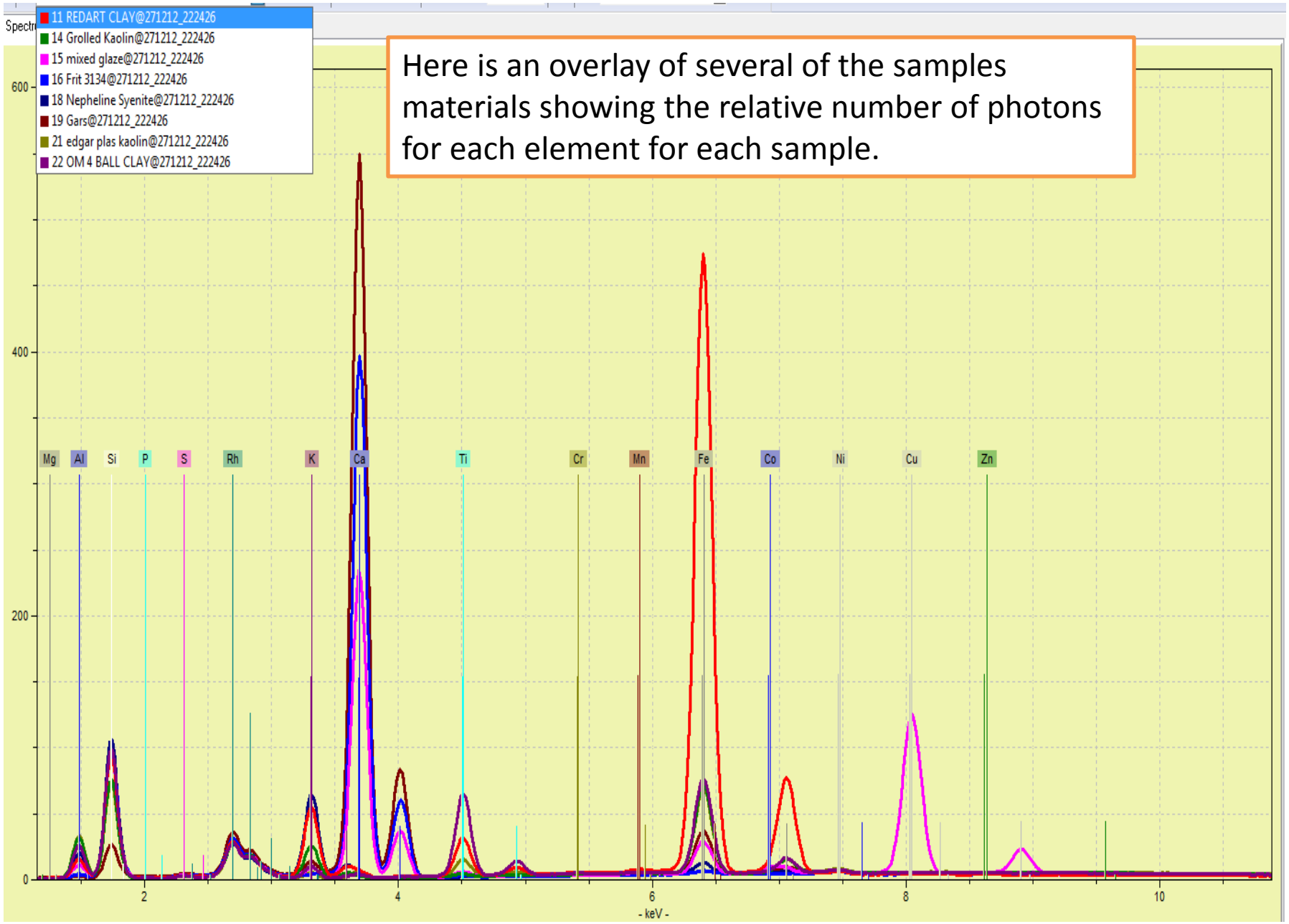
x 1E3 Pulses
200
150
100
50
0
Zn
Cu
Sr
Zr
Ni
Na
Mg
Al
Si
P
S
Rh
K
Ca
Ti
Cr
Mn
Fe
Co
Ni
Cu
Zn
2
4
6
8
10
- keV -
The Red spectrum is the Unknown It appears to be a combination of OM 4 ball clay, Zn oxide, Cu oxide , Mn oxide, Cr oxide, Ti oxide and Ca-Mg.
Detailed quantitative analysis of the compounds present on page 34

Bruker has software that can quickly give one the net number of photons from each element in a given spectra. This allows one to quickly compare the relative concentration of any element in any material, uniform or non-uniform. One can do up to 50000 spectra at once. The software is called ARTAX. This was done to all the data that was taken on the samples sent. Direction and the result of this analysis follows.


11 REDART CLAY@271212_222426
14 Grolled Kaolin@271212_222426
15 mixed glaze@271212_222426
16 Frit 3134@271212_222426
18 Nepheline Syenite@271212_222426
19 Gars@271212_222426
21 edgar plas kaolin@271212_222426
22 OM 4 BALL CLAY@271212_222426
Here is an overlay of several of the samples materials showing the relative number of photons for each element for each sample.
600
400
200
0
Mg
Al
Si
P
S
Rh
K
Ca
Ti
Cr
Mn
Fe
Co
Ni
Cu
Zn
2
4
6
8
10
- keV -

STEPS REQUIRED TO DO SPECTRA ANALYSIS USING ARTAX SOFTWARE provided with the Tracer

This gives the net number of photons form each element for each spectrum analyzed

Net area analysis in Artax 7

1. In ARTAX, click on 'File', click on "open spectrum", file the folder that has all your txt spectrum files, highlight them all and click open
2. Click on "project", click on "new project", right click on "object", click on "add node", enter "Points" in name box. Highlight this folder.
3. Go back to "Project" tab. click on "Add spectrum".
4. Click on "File", click on "save project", give a name (.rtx), click on "save"
5. Click on "spectrum" tab
6. Go to method list and pick your method! See below
7. Highlight the Points folder
8. Click on “Analyze” and then on “Evaluate Results”, a progress bar should appear as all the spectra are being evaluated with “your named method”
9. Then click on “Export” and then on” Results to Excel” Then a box will appear so you name the excel file and put it in a folder that you want the results to be in!
10. Now immediately resave your project file because it now contains your spectra and your results. Use the same name you did before and save on top of the old version of the rtx file.
11. Now go to the folder you saved your results in and open the file and got to the Points tab to see all your net area data. You then edit out the area that gives you no information.

Method Creation

- To create a method open a spectrum that is typical of the spectra you want to analysis, get the periodic table and LABEL ALL THE ELEMENTS THAT ARE IN THE SPECTRUM, YOU CAN NOT SKIP ONE JUST BECAUSE YOU ARE NOT INTERESTED IN IT, YOU MUST LABEL ALL THE ELEMENTS THAT THE SYSTEM HAS DETECTED IN YOUR SAMPLE.
- Then click on the Method editor that is to the left of the method name.
- Click on Identification and make sure the dot is in the Preset list option to the left of the periodic table
- Then click Get elements
- Then go to the Name box and type in whatever name you would like for your method
- Click on Corrections then set cycles at 9 and then pick your energy range for fitting, typically the range of analysis.
- Then click on add

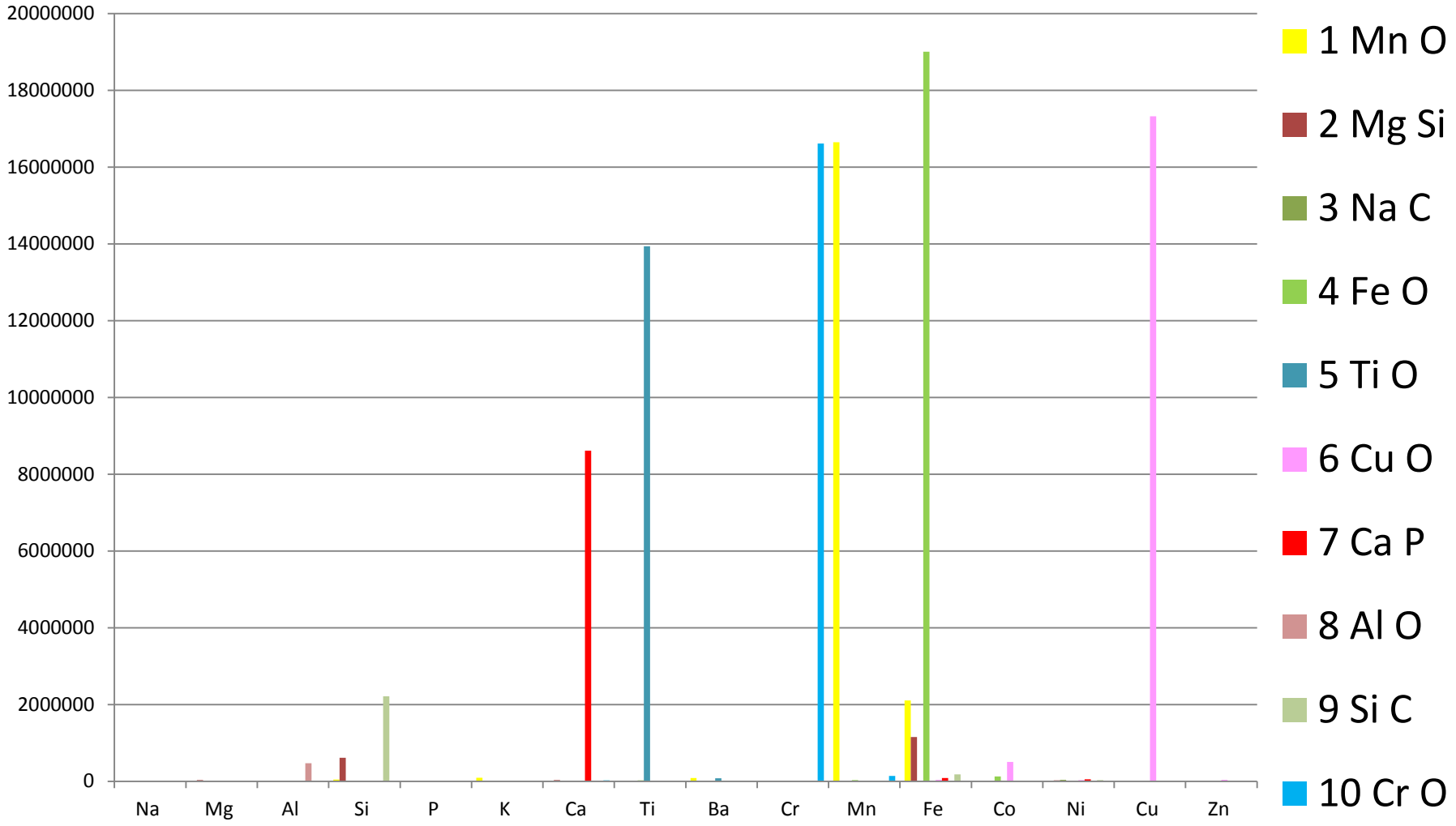
Then click on ok at the bottom of the popup method editor window. Your method should now be in the method window at the top of the Artax screen

Net number of photons for each element in each sample in 60 seconds
This is proportional to the concentration of each element in each sample

	Na	Mg	Al	Si	P	K	Ca	Ti	Ba	Cr	Mn	Fe	Co	Ni	Cu	Zn
1 Mn O	1	177	10578	46353	1879	92855	13107	19216	87534	7888	16643255	2110582	2	8867	2387	7963
2 Mg Si	1	31508	3732	613291	179	1	32112	530	2725	9108	7534	1154827	21423	26041	2727	3163
3 Na C	4153	198	943	1788	1238	1	2529	2772	3729	1	3210	13474	10450	41865	863	1206
4 Fe O	1	96	2301	1800	1246	1	862	28687	12852	9565	35148	19005647	124631	3112	2449	3900
5 Ti O	1	428	3011	955	5159	14014	2019	13937706	78256	288	1703	2372	75	15729	4945	29
6 Cu O	1	1	1388	1352	1038	0	6256	1	4851	13052	1	37749	504050	31395	17324804	40118
7 Ca P	272	1469	2639	14025	2699	12276	8614015	2155	834	1	13711	89004	6252	52747	264	2581
8 Al O	66	3387	474538	1002	1245	1	4535	1531	11821	5447	326	16987	10223	18353	10577	15868
9 Si C	1	261	18005	2216848	62	0	6235	14153	12355	17018	3615	180016	13228	35668	9012	5024
10 Cr O	1	142	3273	5460	602	402	29834	0	3395	16611361	143817	11645	12403	6006	6025	2183
11 REDART CLAY	1	755	82892	546175	538	347937	28250	203553	7048	5874	21966	3846650	31933	15781	4332	6149
12 Ca Si	1	256	11691	605750	1561	4255	4929616	17040	2792	3019	38754	248444	4381	22179	780	490
13 Si O	23	357	11218	1382275	1	1	1703	274	4175	5285	10533	23601	3883	24898	191	2634
14 Grolled Kaolin	1	527	176041	441419	1034	153298	8899	6504	8707	3498	11148	545805	5193	26102	6952	5190
15 mixed glaze	1	1	57710	569915	1042	37902	1609432	23813	3479	3386	20083	204692	39443	19971	1069684	9120
16 Frit 3134	647	49	16605	555550	965	2746	2726678	10229	417	1723	3475	27214	3158	22506	1139	1646
17 custer fledspar	38	1	80264	808351	1150	631258	24335	1	1317	2444	9152	99903	2184	20199	1981	1009
18 Nepheline Syenite	620	1	110665	622034	257	416283	23369	0	767	3460	5830	67885	2586	25517	1542	1999
19 Gars	1	3326	6032	150224	1089	54798	3779967	12835	3019	719	14766	268801	5786	26566	1146	1796
20 Ca Mg	1	19155	1138	15556	1255	3204	5418443	0	766	710	11872	303621	5016	40708	784	624
21 edgar plas kaolin	1	105	188014	434889	2405	22898	35339	79169	12720	7574	8894	523936	4731	29791	4031	4967
22 OM 4 BALL CLAY	1	166	145542	575809	922	50793	17736	446150	14085	8403	6537	594267	6660	26246	2697	5378
23 Co O	1	31	2132	1008	598	0	2761	4757	13864	1	14415	21644	19379759	117669	248	1055
24 Zinc O	1782	1	1601	941	678	1	2438	1	8589	14575	-92	16432	25072	38794	4955	14725926
25 Sr C	1	1	8347	536313	73729	1	6825	1	123630	1690	11134	4716	5228	42816	193	5843
26 rutile	1	196	3901	9889	20622	2650	8278	14509075	81718	13926	4681	345027	5866	8214	9662	2611
27 Li C	1	176	1333	1447	1343	7284	12681	12058	9146	1117	3	9714	12784	67175	6943	792
28 Zr Si	678	135	1561	309379	806030	1	1497	9738	16846	3419	507	34875	24060	19282	148283	7638
Unknown glaze	1	7062	46846	506829	650	116217	1696162	1	2439	3885	6369	216702	4631	25123	558	2561620
Unknown	1	14515	30779	262413	2685	88351	631435	487784	5304	55900	339637	1074097	218790	15184	1273513	1895135

Note the raw spectral data is never wrong.

This is a plot of the net number of photons for the Oxides indicated

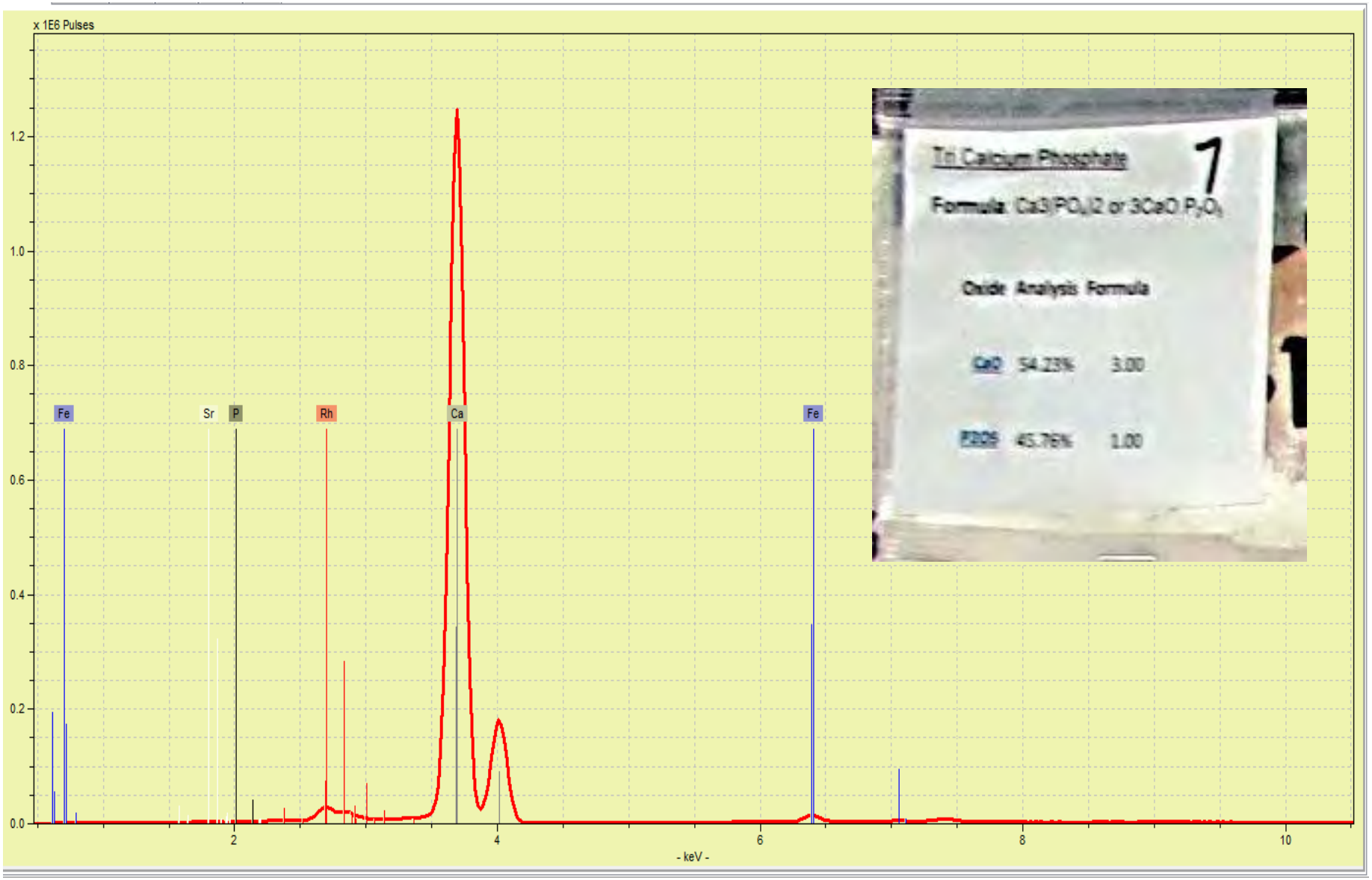


Note the raw spectral data is never wrong.

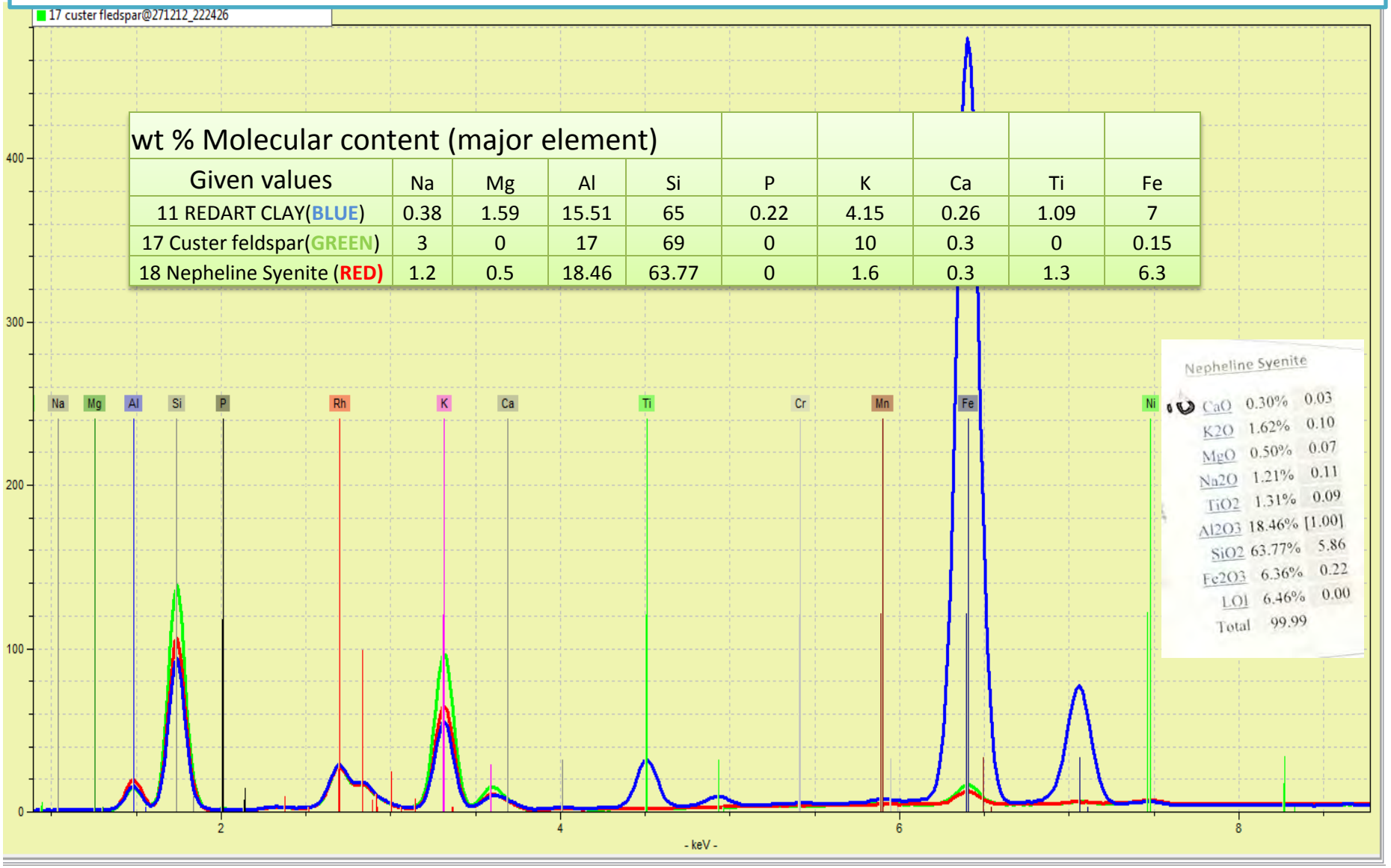
The samples shown in the following slides have raw spectra that are inconsistent with the given content.

Note the raw spectral data is never wrong.

There a problem with the Ca Phosphate: There is no Phosphorous!



There is a problem with the Nepheline Syenite (RED): The raw spectrum shows too much K and way to little Ti and Fe relative to the given concentrations in the table. Note the raw elemental spectrum comparing it to Redart (BLUE) and Custer(GREEN) and the table of given values. I suspect this is not Nep Sy (RED)!



wt % Molecular content (major element)

Given values	Na	Mg	Al	Si	P	K	Ca	Ti	Fe
11 REDART CLAY(BLUE)	0.38	1.59	15.51	65	0.22	4.15	0.26	1.09	7
17 Custer feldspar(GREEN)	3	0	17	69	0	10	0.3	0	0.15
18 Nepheline Syenite (RED)	1.2	0.5	18.46	63.77	0	1.6	0.3	1.3	6.3

Nepheline Syenite

CaO	0.30%	0.03
K2O	1.62%	0.10
MgO	0.50%	0.07
Na2O	1.21%	0.11
TiO2	1.31%	0.09
Al2O3	18.46%	[1.00]
SiO2	63.77%	5.86
Fe2O3	6.36%	0.22
LOI	6.46%	0.00
Total	99.99	

The samples shown in the following slides have raw spectra that the major element contents appear correct but the trace elements apparent in the raw spectra are not in the given content.

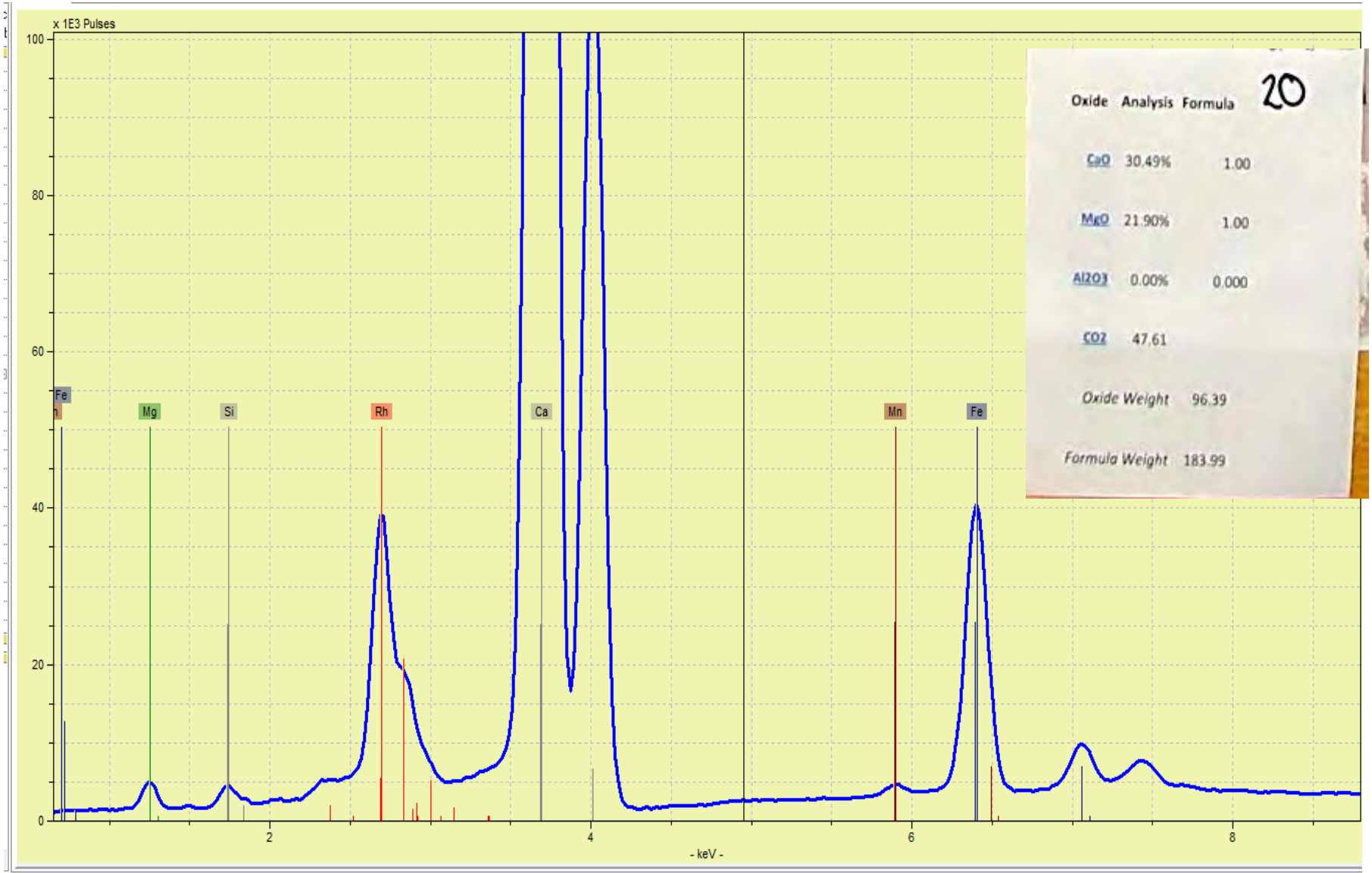
Note the raw spectral data is never wrong.

Gerstley Borate

This is and example of the major element content looking correct but the Trace elements in Gerstley Borate of P, Ti and Mn are not listed.

Ca /Mg

This is and example of the major elements being correct but the Tracer elements in Ca /Mg of Si, Mn and Fe are not listed. Note Fe is about 0.5% and the Si is about 3%.



The next 2 slides shows you how you can use the raw spectra between 2 samples to determine the accuracy of the given values.

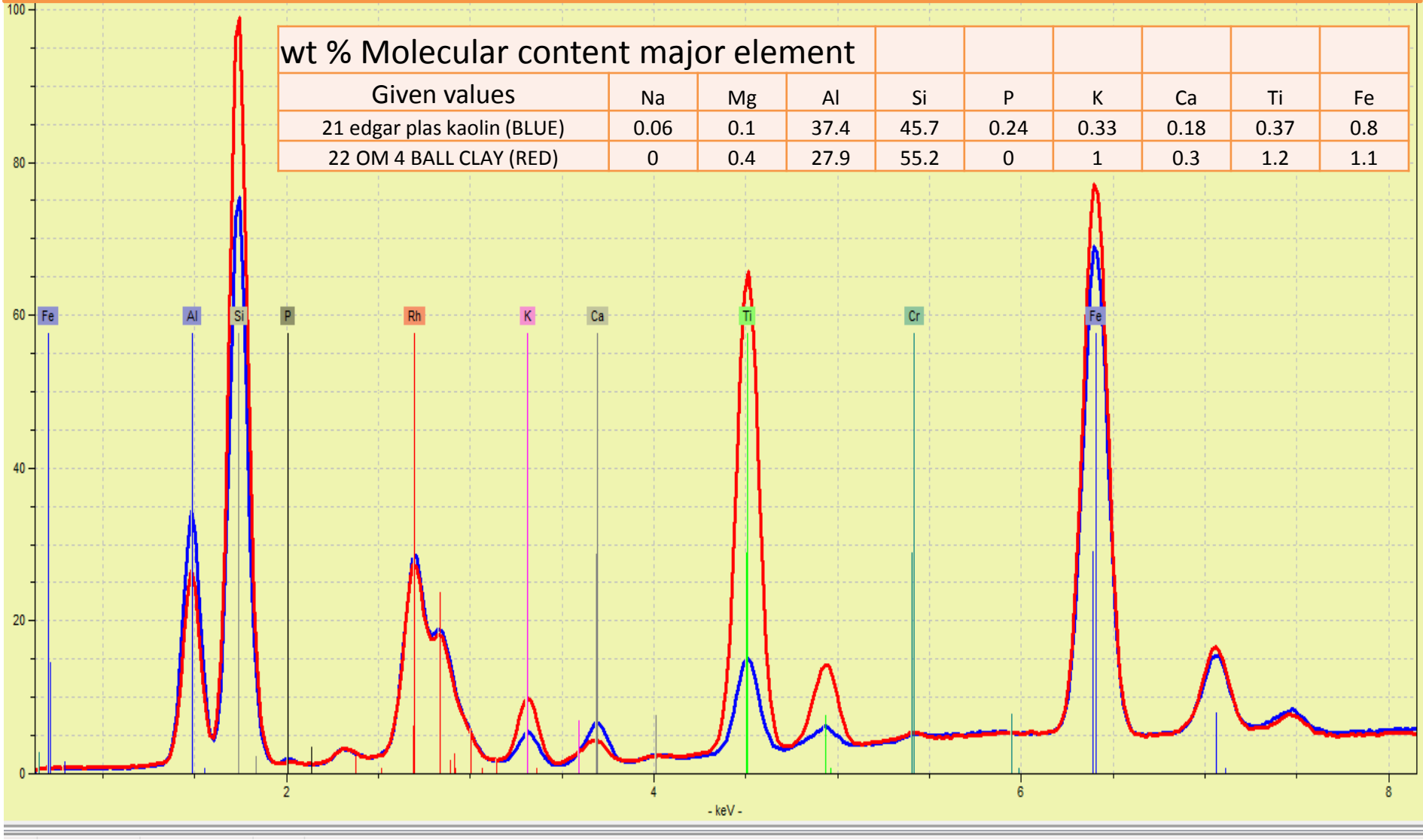
Raw spectra are never wrong. If an element has twice the number of photons from one spectra to an other then there are twice as many atoms for that element present in the sample with twice the photons.

21 edgar plas kaolin@271212_222426
22 OM 4 BALL CLAY@271212_222426

This is and example of the some of major elements between two samples not agreeing. The Al, Si, K and Fe ratios look ok when comparing the given concentration and the raw spectra. The Ca is NOT; the OM 4 Ball (RED) is suppose to be roughly twice the EDGAR (BLUE) according to the given numbers. It looks like the given value of the Ca concentration for EDGAR (blue) is low. If the OM BALL 4 given value for Ca is correct at 0.3 then the correct value for EDGAR is about 0.6 when looking at the relative raw spectrum, which is never wrong!

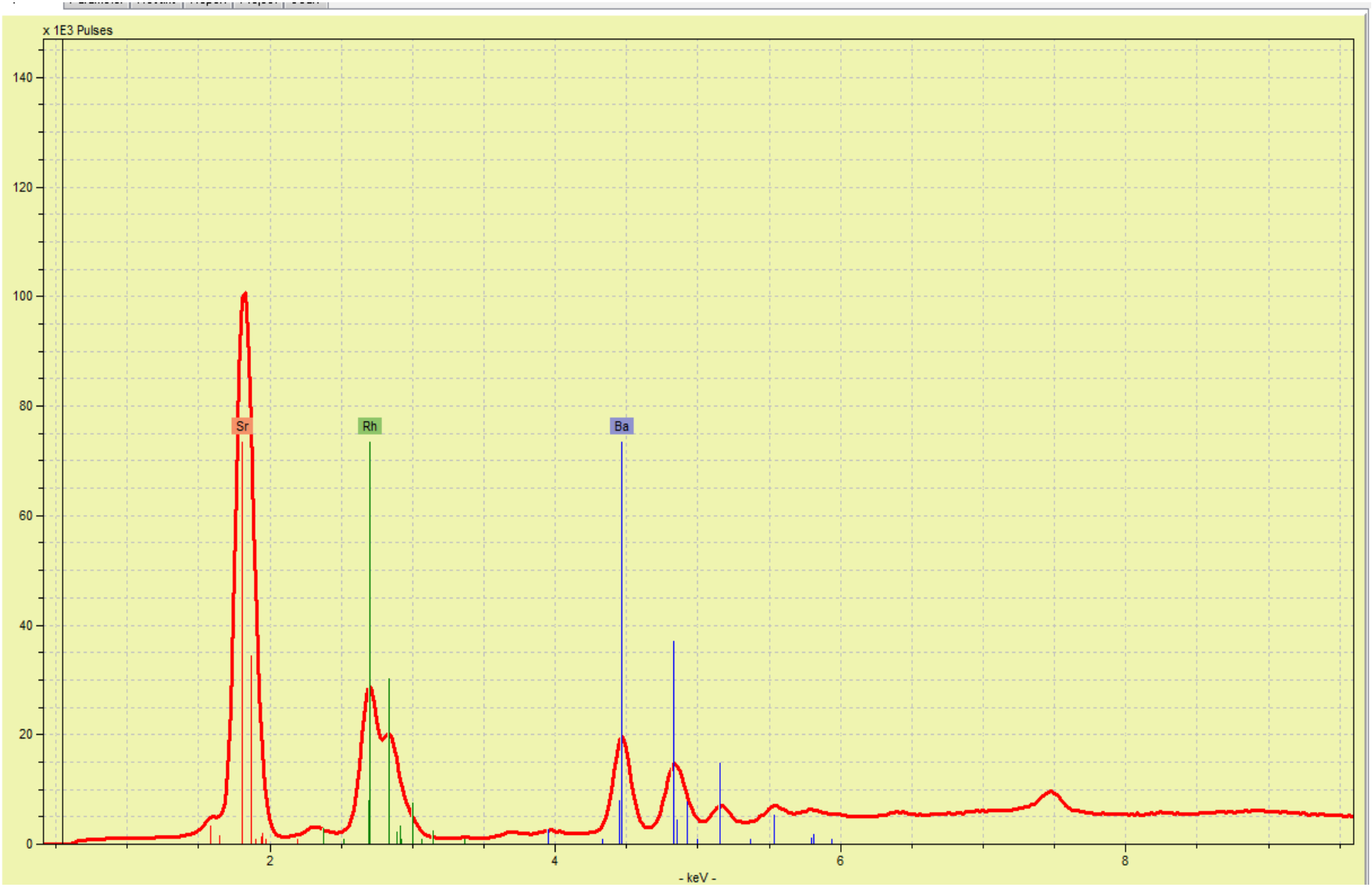
wt % Molecular content major element

Given values	Na	Mg	Al	Si	P	K	Ca	Ti	Fe
21 edgar plas kaolin (BLUE)	0.06	0.1	37.4	45.7	0.24	0.33	0.18	0.37	0.8
22 OM 4 BALL CLAY (RED)	0	0.4	27.9	55.2	0	1	0.3	1.2	1.1



Sr C

It is apparent from the Raw spectrum that the Sr C has a lot of Ba in it! This is not listed on the concentration sheet.



Quantitative analysis

The following weight percent analysis was done by calibrating the Tracer with the know samples given. Only those references that had spectra that appeared to be consistent with the given values were used (see table below) to do the calibration. The calibration was done by analyzing each sample 300 SECONDS, reading the raw spectra into the calibration software and typing in the given values and then creating a calibration response matrix. That was then used to "calibrate" the Tracer response to a given elemental concentration . The calibration matrix was then used to determine the content shown in the next charts. Note the calibration is only as good as the references values used to do the calibration.

Given wt % Molecular content (major element) values and Samples used in the calibration

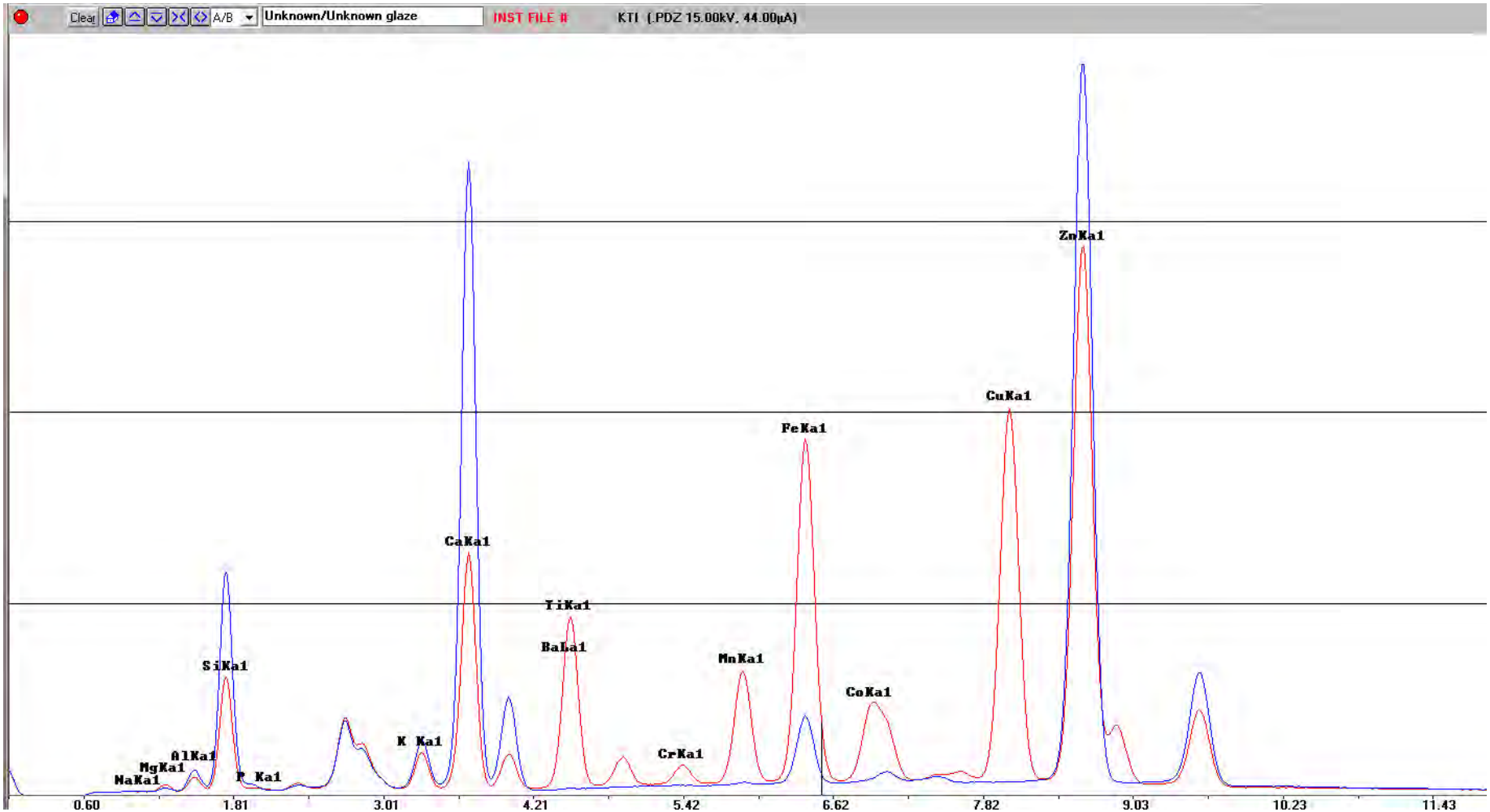
Only those references that had spectra consistent with the given values were used (see table below)

	NaKa1	MgKa1	AlKa1	SiKa1	P Ka1	K Ka1	CaKa1	BaLa1	TiKa1	CrKa1	MnKa1	FeKa1	CoKa1	CuKa1	ZnKa1
1 Mn O	0	0	0.2	0.4	0	0.1	0.05	0.01	0.03	0	100	0.08	0	0	0
2 Mg Si	0	31.67	0	63.38	0	0	0.08	0	0	0	0	0.8	0	0	0
3 Na C	49	0	2	0.5	0	0	0	0	0	0	0	0	0	0	0
4 Fe O	0	0	0	0	0	0	0	0	0.2	0.05	0	99.75	0	0	0
5 Ti O	0	0	0	0	0	0.1	0	0	99.9	0	0	0	0	0	0
6 Cu O	0	0	0	0	0	0	0	0	0	0	0	0.05	2	97.95	0
8 Al O	0	0	99.7	0	0	0	0	0	0	0	0	0	0	0	0
9 Si C	0	0	0	99	0	0	0.03	0	0.03	0	0	0.1	0	0	0
10 Cr O	0	0	0	0	0	0	0	0	0	99.9	0	0.05	0.05	0	0
11 REDART CLAY	0.38	1.59	15.51	65	0.22	4.15	0.26	0	1.09	0	0	7	0	0	0
12 Ca Si	0	0	0.5	50	0	0	47	0	0.3	0	0.3	1.5	0	0	0
13 Si O	0	0	0	99.9	0	0	0	0	0	0	0	0	0	0	0
14 Grolled Kaolin	0.1	0.3	37	48	0	1.9	0	0	0	0	0	0.7	0	0	0
16 Frit 3134	10	0	2	46	0	0	20	0	0	0	0	0	0	0	0
17 custer fledspar	3	0	17	69	0	10	0.3	0	0	0	0	0.15	0	0	0
19 Gars	4.5	3.5	1	10	0.02	0.25	22	0	0.02	0	0.02	0.2	0	0	0
20 Ca Mg	0	21.9	0	3	0	0	30.5	0	0	0	0.05	0.5	0	0	0
21 edgar plas kaolin	0.06	0.1	37.4	45.7	0.24	0.33	0.6	0	0.37	0	0	0.8	0	0	0
22 OM 4 BALL CLAY	0	0.4	27.9	55.2	0	1	0.3	0	1.2	0	0	1.1	0	0	0
23 Co O	0	0	0	0	0	0	0	0	0	0	0	0	99.9	0	0
24 Zinc O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	99.9
26 rutile	0	0	0	0	0	0	0	0	90	0.5	0.5	10	0	0	0

Note the NUMBERS ARE THE GIVEN WEIGHT PERCENT OF THE COMPOUND OF THE ELEMENT NOTED

Calculated
wt % Molecular content (major element) indicated Using Tracer IV SD calibration done with references provided

Samples	Na	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Co	Cu	Zn
Unknown glaze (BLUE)	2.954	9.558	11.164	47.285	0.020	0.736	12.951	0.000	0.000	0.000	0.792	0.078	0.049	25.779
Unknown (RED)	3.452	13.844	6.661	24.698	0.020	0.675	3.403	5.061	0.061	0.166	0.791	0.906	9.018	18.184



Calculated
wt % Molecular content (major element) indicated
Using Tracer IV SD calibration
done with references provided

wt % Molecular content (major element)

	Na	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Co	Cu	Zn
11 REDART CLAY	3.431	1.892	16.240	52.446	0.027	4.163	0.360	1.955	0.013	0.016	7.585	0.151	0.000	0.000
14 Grolled Kaolin	5.430	0.819	35.931	46.520	0.027	1.722	0.083	0.000	0.000	0.000	0.741	0.083	0.000	0.000
15 mixed glaze	3.577	2.069	10.789	53.757	0.022	0.257	13.203	0.210	0.000	0.000	0.789	0.214	0.692	0.000
16 Frit 3134	3.254	1.782	1.963	47.145	0.018	0.019	20.854	0.000	0.000	0.009	0.889	0.018	0.000	0.000
17 custer fledspar	3.984	0.536	15.867	75.460	0.029	9.995	0.667	0.000	0.000	0.000	0.830	0.065	0.000	0.000
18 Nepheline Syenite	4.076	0.000	22.191	62.089	0.029	6.078	0.414	0.000	0.000	0.000	0.848	0.079	0.000	0.000
21 edgar plas kaolin	5.596	0.335	37.755	45.332	0.026	0.243	0.166	0.685	0.002	0.005	0.739	0.084	0.000	0.000
22 OM 4 BALL CLAY	5.011	0.859	28.819	57.802	0.028	0.554	0.115	4.524	0.030	0.054	0.747	0.090	0.000	0.000
26 rutile	1.380	0.908	0.324	0.900	0.010	0.050	0.052	89.673	0.321	0.492	0.808	0.000	0.000	0.000

wt % Molecular content (major element)

Samples	Na	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Co	Cu	Zn
Unknown glaze	2.954	9.558	11.164	47.285	0.020	0.736	12.951	0.000	0.000	0.000	0.792	0.078	0.049	25.779
Unknown	3.452	13.844	6.661	24.698	0.020	0.675	3.403	5.061	0.061	0.166	0.791	0.906	9.018	18.184

Note the NUMBERS ARE THE CALCUALTED WEIGHT PERCENT OF THE COMPOUND OF THE ELEMENT NOTED

The Accidental Glaze is perhaps the unknown glaze and not accidental but because the material used was not what it was said to be.
To remove all accidents one must actually do a detailed elemental analysis of all the materials used. Glazes are like special artistic glasses, the devil is very much in the details, Including the traces elements!
It is clear from the Tracer elemental analysis of this material; what was said of these materials does not always match what is actually there!

Much more could be determined concerning THE materials using the Tracer.....

But the above should give one a glimpse of it capabilities

THE END