**Appendix A: Element Guide** 

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#### <u>ABSTRACT</u>

This chapter provides reference material for XRF analysis starting from the most general (depth of analysis) to the most particular (individual element information). The tables and summaries provided here are intended to help guide the interpretation of spectra on an as-needed basis.

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#### 1. Fluorescence Parameters

#### 1.1 Depth of Analysis

Photons are quanta of energy - in the standard model of physics they are known as gauge bosons. They interact with particles which, unlike them, contain mass. For the majority of physical phenomena humans interact with, these photon interactions occur with electrons in the outermost shells of molecules. XRF simply uses higher energy photons to interact with electron shells in the innermost layers. But as is the case with all energy-matter interactions, there is a terminal depth at which these interactions will no longer be detectable. In XRF, this is commonly known as 'infinite thickness', the depth at which the sample is practically infinitely thick from the perspective of a photon with a given energy.

Infinite thickness in turn can be through of as a reframing of the concept of mass attenuation - that is to stay, the degree to which a mass with a given density can attenuate a photon of a given energy. While it is true that there are thicknesses in which returned photons become negligible, this does not mean that all photons which interact closer to the surface are not themselves attenuated. Instead, attenuation occurs at all depths, with infinite thickness simply being the depth at which the probability a photon with a given energy returns becomes negligible.

The concept originates from Pierre Bouguer observing sunlight fading through a column of wine while on vacation in southern Portugal in the early 18th century<sup>1</sup>. From this, he formulated what would later become known as the inverse square law: that for each unit of distance light travels through a medium, its brightness diminishes by the square of the distance, known today as the Beer-Lambert Law<sup>2</sup>. Mathematically, this can be expressed as follows:

$$I = I_0 e^{-(\mu/\rho_m)\rho_m \ell}$$
<sup>[1]</sup>

Where *I* represents the intensity of light remaining,  $I_0$  represents the initial input of light,  $\mu$  represents the attenuation coefficient,  $\rho_m$  is the mass density, and  $\ell$  is the distance. This equation represents the probabilistic nature of the inverse square law. Not that the outcome is uncertain - it is called a law for good reason - but because it is probabilistic as it represents the chance that a given photon has of making it from point a to point b in a medium with a given mass density. However, for most working in XRF, the key interest isn't the attenuation at 1mm, but instead the maximum attenuation for a photon with a given energy; i.e. the distance of infinite thickness. To calculate this, we can set a defined ratio of *I*, the intensity of the returning photons and  $I_0$ , the intensity of the initial photons. If we set this to 99%, then Beer-Lambert's law can be made more intuitive:

$$\ell = \frac{43.6}{(-\mu/\rho_m)\rho_m}$$
[2]

With this equation, there are only two unknowns in calculating infinite thickness for an x-ray; the density of the material and the mass attenuation coefficient for a photon traveling for that a given density. For example. The k-alpha line of Fe is emitted at 6.4 keV. If we assume the material Fe is in is close to pure silicate (SiO<sub>2</sub>), then our density will be 2.65 gcm<sup>-3</sup>. The mass attenuation coefficient for silicon dioxide can be acquired at nist.gov<sup>3</sup>. Here, the chemical equation can be put in, mass attenuation selected as the data type, and then the result can be calculated. In this case, the mass attenuation for Fe K-alpha at 6.4 keV is about 64.76. Our equation can then be calculated as follows:

$$0.25(mm) = \frac{43.6}{64.76x^{2.65}}$$
[3]

The distance is then 0.25 mm, or about 250 microns. Note that this distance is not, strictly speaking, from the perspective of the photon entering the sample, but rather the photon

exiting the sample. This perspective comes from the following two factors: 1) for XRF, it is only the photons returning from the sample that we are interested in, and 2) the absorption edge is always higher than the fluorescence line being measured, thus by definition there will be photons of a higher energy capable of initiating fluorescence at the emission line's infinite thickness. However, this equation remains valid for the photons emitted from the element in question - it does not factor in the number of photons which make it from the xray tube through the matrix itself.

The infinite thickness for a given photon has important ramifications for XRF analysis. These can be broken down into the following categories:

- 1) Sensitivity to Surface Conditions: Light elements ranging from F to Ca are measured within the first 100 micrometers in most cases; as a result, surface tarnishes, patinas and other oxides can strongly influence these measurements. As an example; when measuring salts, KCI or NaCI are possibilities. It is not impossible to have a small NaCI crystal atop a KCI crystal - thus leading to a perplexing > 100% sum of concentrations; yet from the XRFs perspective it can measure 100% NaCI within 6 micrometers and close to 100% KCI at 50 micrometers at the same time.
- 2) Sample Selection: With both calibration and sample assays, there are two basic rules to follow: aim for samples which are infinitely thick for the intended voltage, or samples which are uniformly thin. The latter approach is often taken in WD-XRF, where fused glass pellets are produced with the same spatial dimensions to mitigate. In many handheld XRF applications this isn't an option, so infinite thickness (when practicable) is the recommended approach.
- 3) In cases where infinite thickness varies (e.g. non-destructive applications in art conservation, archaeology, semiconductors, manuscripts, etc.), the user must be mindful of uncontrollable changes in thickness, and ideally use a reference point in the spectrum

(most easily Raleigh or Compton scattering) to identify changes in thickness, assuming samples being compared are of the same mass.

A table of depths (mm and  $\mu$ m) and mass attenuation coefficients can be found for silicon dioxide (density = 2.65 g/cm<sup>3</sup>) (Table 1). Figures for molded depth of penetration can be found for a variety of common substrates, metals, and pigments in Figures 1 – 39. Note that given the large differences in penetration depth, the y axis may range from micrometers to meters.



Figure 1: Infinite thickness for X-ray penetration into air



Figure 2: Infinite thickness for X-ray penetration into water



Figure 3: Infinite thickness for X-ray penetration into salt



Figure 4: Infinite thickness for X-ray penetration into silicate



Figure 5: Infinite thickness for X-ray penetration into lead glass



Figure 6: Infinite thickness for X-ray penetration into alumina



Figure 7: Infinite thickness for X-ray penetration into calcium oxide



Figure 8: Infinite thickness for X-ray penetration into gypsum



Figure 9: Infinite thickness for X-ray penetration into cortical bone



Figure 10: Infinite thickness for X-ray penetration into enamel



Figure 11: Infinite thickness for X-ray penetration into cellulose



Figure 12: Infinite thickness for X-ray penetration into fructose



Figure 13: Infinite thickness for X-ray penetration into aluminum



Figure 14: Infinite thickness for X-ray penetration into iron



Figure 15: Infinite thickness for X-ray penetration into copper



Figure 16: Infinite thickness for X-ray penetration into silver



Figure 17: Infinite thickness for X-ray penetration into tin



Figure 18: Infinite thickness for X-ray penetration into gold



Figure 19: Infinite thickness for X-ray penetration into lead



Figure 20: Infinite thickness for X-ray penetration into polybutyrene terephthalate



Figure 21: Infinite thickness for X-ray penetration into fluorinated ethylene propylene



Figure 22: Infinite thickness for X-ray penetration into polyethylene



Figure 23: Infinite thickness for X-ray penetration into flexible polyvinyl chloride



Figure 24: Infinite thickness for X-ray penetration into rigid polyvinyl chloride



Figure 25: Infinite thickness for X-ray penetration into polypropylene



Figure 26: Infinite thickness for X-ray penetration into mylar



Figure 27: Infinite thickness for X-ray penetration into Teflon



Figure 28: Infinite thickness for X-ray penetration into lead white



Figure 29: Infinite thickness for X-ray penetration into lead red/minium



Figure 30: Infinite thickness for X-ray penetration into chrome yellow



Figure 31: Infinite thickness for X-ray penetration into vermilion/cinnabar



Figure 32: Infinite thickness for X-ray penetration into hematite



Figure 33: Infinite thickness for X-ray penetration into malachite



Figure 34: Infinite thickness for X-ray penetration into Paris green



Figure 35: Infinite thickness for X-ray penetration into Prussian blue



Figure 36: Infinite thickness for X-ray penetration into ultramarine



Figure 37: Infinite thickness for X-ray penetration into cobalt blue



Figure 38: Infinite thickness for X-ray penetration into zinc oxide



Figure 39: Infinite thickness for X-ray penetration into titanium dioxide

Energy (keV)	$\mu/\rho \ (cm^2 \ g^{-1})$	Depth (µm)	Depth (mm)
0.0107	407,620.00	0.04	0.00004
0.0530	86,616.86	0.19	0.00019
0.1012	77,995.75	0.21	0.00021
0.2014	36,724.46	0.45	0.00045
0.3005	15,620.45	1.05	0.00105
0.4195	7,145.06	2.30	0.0023

Energy (keV)	$\mu/\rho \ (cm^2 \ g^{-1})$	Depth (µm)	Depth (mm)
0.5125	4,377.93	3.76	0.00376
0.6261	9,870.79	1.67	0.00167
0.7154	7,137.53	2.31	0.00231
0.8176	5,103.75	3.22	0.00322
0.9343	3,629.96	4.53	0.00453
1.0677	2,543.47	6.47	0.00647
1.1413	2,119.68	7.76	0.00776
1.2201	1,766.26	9.32	0.00932
1.3043	1,471.61	11.18	0.01118
1.3943	1,226.03	13.42	0.01342
1.4905	1,021.48	16.11	0.01611
1.5933	851.01	19.33	0.01933
1.7033	709.11	23.20	0.0232
1.8021	609.25	27.01	0.02701
1.8208	590.89	27.84	0.02784
1.8297	583.71	28.19	0.02819
1.8371	577.82	28.47	0.02847
1.8481	1,987.53	8.28	0.00828
1.8757	1,928.71	8.53	0.00853
1.9464	1,780.17	9.24	0.00924
2.0807	1,504.38	10.94	0.01094
2.2243	1,257.72	13.08	0.01308
2.3778	1,047.99	15.70	0.0157
2.5418	876.81	76	0.01876
2.7172	734.59	22.40	0.0224
2.9047	615.57	26.73	0.02673
3.1052	513.86	32.02	0.03202

Energy (keV)	$\mu/\rho \ (cm^2 \ g^{-1})$	Depth (µm)	Depth (mm)
3.3194	427.64	38.47	0.03847
3.5484	355.95	46.22	0.04622
3.7933	295.36	55.71	0.05571
4.0550	244.17	67.38	0.06738
4.3348	201.89	81.50	0.0815
4.6339	166.95	98.55	0.09855
4.9537	138.09	119.14	0.11914
5.2955	114.24	144.02	0.14402
5.6609	94.53	174.06	0.17406
6.0515	78.23	210.32	0.21032
6.4690	64.76	254.05	0.25405
6.9154	53.63	306.80	0.3068
7.3925	44.42	370.40	0.3704
7.9026	36.80	447.04	0.44704
8.4479	30.37	541.81	0.54181
9.0308	25.01	657.90	0.6579
9.6539	20.48	803.18	0.80318
10.3200	16.78	980.26	0.98026
11.0321	13.76	1,195.94	1.19594
11.7933	11.29	1,457.81	1.45781
12.6071	9.27	1,775.40	1.7754
13.4770	7.62	2,159.72	2.15972
14.4069	6.27	2,623.79	2.62379
15.4010	5.17	3,182.82	3.18282
16.4636	4.27	3,854.14	3.85414
17.5996	3.53	4,657.64	4.65764
8140	2.93	5,615.55	5.61555

Energy (keV)	$\mu/\rho \ (cm^2 \ g^{-1})$	Depth (µm)	Depth (mm)
20.1122	2.44	6,752.25	6.75225
21.4999	2.03	8,093.63	8.09363
22.9834	1.70	9,667.33	9.66733
24.5692	1.43	11,500.72	11.50072
26.2645	1.21	13,619.48	13.61948
28.0768	1.02	16,104.84	16.10484
30.0141	0.87	18,952.65	95265
32.0850	0.74	22,153.97	22.15397
34.2989	0.64	25,706.45	25.70645
36.6655	0.56	29,598.17	29.59817
39.1954	0.49	33,797.93	33.79793
41.8999	0.43	38,339.14	38.33914
44.7910	0.38	43,096.52	43.09652
47.8816	0.34	48,005.20	48.0052

Table 1: Idealized depth of penetration in a SiO2 matrix (density 2.65 g/cm3)

Basic reference information for XRF spectral interpretation is provided in this section.

- Table 2: Element Information and Abundance
- Table 3: XRF nomenclature
- Table 4: K line emissions
- Table 5: L line emissions
- Table 6 M line emissions
- Table 7 Absorption edges
- Table 8 Fluorescence efficiency

In addition to these tables, a description of the elements commonly studied using XRF, briefly highlighting their implications in geology, archaeology, agriculture, and art conservation. This is not meant to be a full description for each element, but will simply touch on the highlights of their implications when present in a sample. In addition, a companion table for each element will highlight the most likely overlaps and excitations for each peak. This is to allow for quick and convenient investigation to identify unexpected peaks. In addition, absorption edge, fluorescence efficiency, and earth crustal abundance are provided to help provide additional context to these overlaps. This will help readers assess the probability of an overlap, and also potentially how to minimize it with future assays. Lastly, common intercepts and slopes for each element are provided for each elements K, L, and M line in the comments column, though it should be noted these are only very general guides that focus on direct (and common) elemental interferences. For example, no slope is suggested for Si K-alpha, however in geological calibrations it may be advantageous to add either AI or Ca as slope corrections not because of interference, but because it captures matrix variance that can improve gualitative models. However in metallurgical examples (e.g. low ppm Si in steel) such corrections would be highly ill advised.

#### **1.2 Elemental Abundance**

The Earth was formed from gas and dust left over from an earlier star whose explosion created a solar nebula. The elements from which Earth is composed were created both through nuclear fusion in that former star during its life and extreme compression during its explosion. The gradual accretion of material from these elements both small (dust) and large (Theia) created terrestrial planets such as Earth. This process set the basic abundance of elements on Earth. However, crustal abundance (e.g. those elements present in the surface layers of the Earth) is a product both of plate tectonics and (later) biological processes which increased oxidization. The crustal abundance of elements today is the product of 4.5+ billion years of multiple interacting processes, but it forms a singular underlying reality: some elements are more likely to appear in an XRF spectrum than others. These are provided both in Table 2 generally and Tables 9 - 90 for particular elements. Note that milligrams/Liter (mg/L) is equivalent to 1 part per million (ppm) by volume.

Symbol	Element Name	Atomic #	Atomic Weight	Earth Crustal Abundance (mg/L)	Cl Chondrites Abundance (mg/L)
Н	Hydrogen	1	1.00	1400	19700
Не	Helium	2	4.00	0	0.00917
Li	Lithium	3	6.94	20	1.45
Be	Beryllium	4	9.01	2.8	0.0219
В	Boron	5	10.81	10	0.775
С	Carbon	6	12.01	200	34800
Ν	Nitrogen	7	14.00	19	2950
0	Oxygen	8	15.99	461000	459000
F	Fluorine	9	99	585	58.2
Ne	Neon	10	20.18	0	0.00018
Na	Sodium	11	22.99	23600	4692
Mg	Magnesium	12	24.30	23300	95400
Al	Aluminum	13	36.98	82300	8400
Si	Silicon	14	28.08	282000	107000
Р	Phosphorus	15	30.97	1050	985
S	Sulfur	16	32.06	350	53500
Cl	Chlorine	17	35.45	145	698
Ar	Argon	18	39.94	3.5	0.00133
K	Potassium	19	39.09	20900	546
Ca	Calcium	20	40.08	41500	9110
Sc	Scandium	21	44.95	22	5.81
Ti	Titanium	22	47.88	5560	447
V	Vanadium	23	50.94	120	54.6
Cr	Chromium	24	51.99	102	2623
Mn	Manganese	25	54.93	950	1916
Fe	Iron	26	55.84	56300	66
Со	Cobalt	27	58.93	25	513
Ni	Nickel	28	58.70	84	10910
Cu	Copper	29	63.54	60	133
Zn	Zinc	30	65.39	70	309
Ga	Gallium	31	69.72	19	9.62

Symbol	Element Name	Atomic #	Atomic Weight	Earth Crustal Abundance (mg/L)	Cl Chondrites Abundance (mg/L)
	Germaniu				32.6
Ge	m	32	72.61	1.5	
As	Arsenic	33	74.92	1.8	1.74
Se	Selenium	34	78.96	0.05	20.3
Br	Bromine	35	79.90	2.4	3.26
Kr	Krypton	36	83.80	0.0001	0.0000522
Rb	Rubidium	37	85.46	90	2.32
Sr	Strontium	38	87.62	370	7.79
Y	Yttrium	39	88.90	33	1.46
Zr	Zirconium	40	91.22	165	3.63
Nb	Niobium	41	92.90	20	0.283
Мо	Molybdenu m	42	95.94	1.2	0.961
Тс	Technetiu m	43	98.00		
Ru	Ruthenium	44	101.07	0.001	0.690
Rh	Rhodium	45	102.90	0.001	0.132
Pd	Palladium	46	106.42	0.02	0.560
Ag	Silver	47	107.86	0.075	0.201
Cd	Cadmium	48	112.41	0.15	0.674
In	Indium	49	114.82	0.25	0.0778
Sn	Tin	50	171	2.3	1.63
Sb	Antimony	51	121.76	0.2	0.145
Те	Tellurium	52	127.60	0.001	2.28
Ι	Iodine	53	126.90	0.45	0.53
Xe	Xenon	54	131.29	0.00003	0.000174
Cs	Cesium	55	132.90	3	0.188
Ba	Barium	56	137.33	425	2.42
La	Lanthanum	57	139.90	39	0.2414
Ce	Cerium	58	140.12	66.5	0.6194
Pr	Praseodymi um	59	140.90	9.2	0.09390

Symbol	Element Name	Atomic #	Atomic Weight	Earth Crustal Abundance (mg/L)	Cl Chondrites Abundance (mg/L)
271	Neodymiu	(0)	144.24	41.5	0.4737
Nd	m	60	144.24	41.5	
Pm	Promethiu m	61	145.00		
Sm	Samarium	62	150.36	7.05	0.1536
Eu	Europium	63	151.97	2.0	0.05883
Gd	Gadoliniu m	64	157.25	6.2	0.2069
Tb	Terbium	65	158.92	1.2	0.03797
Dy	Dysprosiu m	66	162.50	5.2	0.2558
Но	Holmium	67	164.93	1.3	0.05644
Er	Erbium	68	167.26	3.5	0.1655
Tm	Thulium	69	168.93	0.52	0.02609
Yb	Ytterbium	70	173.04	3.2	0.1687
Lu	Lutetium	71	174.96	0.8	0.02503
Hf	Hafnium	72	178.49	3.0	0.1065
Та	Tantalum	73	180.94	2.0	0.015
W	Tungsten	74	183.85	1.25	0.096
Re	Rhenium	75	186.20	0.0007	0.0400
Os	Osmium	76	190.20	0.0015	0.469
Ir	Iridium	77	192.22	0.001	0.469
Pt	Platinium	78	195.08	0.005	0.925
Au	Gold	79	196.96	0.004	0.148
Hg	Mercury	80	200.59	0.085	0.35
Tl	Thallium	81	204.38	0.85	0.140
Pb	Lead	82	207.20	14	2.62
Bi	Bismuth	83	208.98	0.009	0.110
Ро	Polonium	84	209.00	0.000000002	
At	Astatine	85	210.00		
Rn	Radon	86	222.00	0.00000000004	
Fr	Francium	87	223.00		
Ra	Radium	88	226.02	0.0000007	

Symbol	Element Name	Atomic #	Atomic Weight	Earth Crustal Abundance (mg/L)	Cl Chondrites Abundance (mg/L)
Ac	Actinium	89	227.02	0.0000000055	
Th	Thorium	90	232.03	9.6	0.0300
Ра	Protoactini um	91	231.04	0.0000014	
U	Uranium	92	0.00	2.7	0.0081
Np	Neptunium	93	0.00		
Pu	Plutonium	94	0.00		
Am	Americium	95	0.00		
Cm	Californiu m	96	0.00		

Table 2: Natural elemental abundance<sup>4,5</sup>

#### **1.3 Fluorescence Nomenclature**

XRF nomenclature has evolved with our understanding of the atom. As the latter has become more complex, so too has the detail of XRF nomenclature. Most terminology used by portable XRF community today is a simplification of the Siegbahn nomenclature. As such, it overlaps with other terms such as the International Union of Pure and Applied Chemistry (IUPAC). All are detailed in Table 4, along with descriptions of the electron transitions they describe.

The Sigbahn nomenclature refers to the destination (e.g. K) orbital in the context of the highest peak (e.g.  $\alpha$ ). The succeeding greek letter, and number, were based on the intensity of the emission. As such, most of the nomenclature was not relevant to systematic physics principles, but rather observation in a spectrum. The IUPAC terminology, however, is much more precise and systematic, and therefore more detailed and less easy to remember (most practitioners of XRF will continue to say "K-alpha" as opposed to "K-L3/K-L2"). The more general "K-alpha" terminology is not necessarily a product of terminological sloppiness, but rather a statement of what is actually observed for the majority of XRF spectrometers. Almost all detectors used in ED-XRF today cannot easily resolve the K $\alpha$ 1/K $\alpha$ 2 (K-L3/K-L2) lines themselves for most elements, and instead create a shared Gaussian peak with variance from both contributing. As such, for most elements there aren't distinguishable K $\alpha$ 1/K $\alpha$ 2 (K-L3/K-L2) peaks, but instead shared (in common parlance) "K-alpha peak". This is why, for much of the volume, we use the more general than specific terminology because we cannot yet talk about the K $\alpha$ 1 (K-L3) peak in isolation for all but a select few elements. Though Barium (Ba), at 32 keV, can sometimes have these individual lines differentiable.

Simple Nomenclature	Siegbahn Nomenclature	Recipient		Donor		
		IUPAC Nomenclature	Electron Transition	IUPAC Nomenclature	Electron Transition	
K-alpha	Ka1	К	1s <sup>-1</sup>	L3	$2p_{3/2}^{-1}$	
Simple	Siegbahn	Recipient		Donor		
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Nomenclature	Nomenclature	IUPAC Nomenclature	Electron Transition	IUPAC Nomenclature	Electron Transition	
	Κα2	K	1s <sup>-1</sup>	L2	$2p_{1/2}^{-1}$	
	Κβ1	К	1s <sup>-1</sup>	M3	3p <sub>3/2</sub> -1	
	K <sup>1</sup> β2	K	1s <sup>-1</sup>	N3	$4d_{5/2}^{-1}$	
	Κ <sup>Π</sup> β2	К	1s <sup>-1</sup>	N2	$4p_{1/2}^{-1}$	
	КβЗ	К	1s <sup>-1</sup>	M2	$3p_{1}/^{2-1}$	
	Κ <sup>ι</sup> β4	К	1s <sup>-1</sup>	N5	$4d_{5/2}^{-1}$	
	Κ <sup>Π</sup> β4	Κ	1s <sup>-1</sup>	N4	$4d_{3/2}^{-1}$	
	Κβχ	Κ	1s <sup>-1</sup>	N4	$4d_{3/2}^{-1}$	
	Κ <sup>ι</sup> β5	Κ	1s <sup>-1</sup>	M5	$3d_{5/2}^{-1}$	
K-beta	Κ <sup>Π</sup> β5	Κ	1s <sup>-1</sup>	M4	$3d_{3/2}^{-1}$	
	La1	L3	$2P_{3/2}^{-1}$	M5	$3d_{5/2}^{-1}$	
L-alpha	La2	L3	$2P_{3/2}^{-1}$	M4	$3d_{3/2}^{-1}$	
	Lβ1	L2	$2p_{1/2}^{-1}$	M4	$3d_{3/2}^{-1}$	
	Lβ2	L3	$2P_{3/2}^{-1}$	N5	$4d_{5/2}^{-1}$	
	Lβ3	L1	2s <sup>-1</sup>	M3	$3p_{3/2}^{-1}$	
	Lβ4	L1	2s <sup>-1</sup>	M2	3p <sub>1/2</sub> -1	
	Lβ5	L3	2P <sub>3/2</sub> <sup>-1</sup>	04	5d <sub>3/2</sub> -1	
	Lβ5	L3	2P <sub>3/2</sub> <sup>-1</sup>	05	5d <sub>5/2</sub> -1	
	Lβ6	L3	2P <sub>3/2</sub> -1	N1	4s <sup>-1</sup>	
	Lβ7	L3	2P <sub>3/2</sub> <sup>-1</sup>	01	5s <sup>-1</sup>	
	Lβ7'	L3	2P <sub>3/2</sub> <sup>-1</sup>	N6	4f <sub>5/2</sub> <sup>-1</sup>	
	Lβ7'	L3	2P <sub>3/2</sub> <sup>-1</sup>	N7	4f <sub>7/2</sub> <sup>-1</sup>	
	Lβ9	L1	2s <sup>-1</sup>	M5	3d <sub>5/2</sub> -1	
	Lβ10	L1	2s <sup>-1</sup>	M4	$3d_{3/2}^{-1}$	
	Lβ15	L3	$2P_{3/2}^{-1}$	N4	4d <sub>3/2</sub> -1	
L-beta	Lβ17	L2	$2p_{1/2}^{-1}$	M3	3p <sub>3/2</sub> <sup>-1</sup>	
	Lγ1	L2	$2p_{1/2}^{-1}$	N4	$4d_{3/2}^{-1}$	
	Lγ2	L1	2s <sup>-1</sup>	N2	$4p_{1/2}^{-1}$	
	Lγ3	L1	2s <sup>-1</sup>	N3	$4p_{3/2}^{-1}$	
L-gamma	Lγ4	L1	2s <sup>-1</sup>	O3	$5p_{3/2}^{-1}$	

Simple	Siegbahn	Recipient		Donor	
Nomenclature	Nomenclature	IUPAC Nomenclature	Electron Transition	IUPAC Nomenclature	Electron Transition
	Lγ4'	L1	2s <sup>-1</sup>	O2	$5p_{1/2}^{-1}$
	Lγ5	L2	$2p_{1/2}^{-1}$	N1	4s <sup>-1</sup>
	Lγ6	L2	$2p_{1/2}^{-1}$	O4	$5d_{3/2}^{-1}$
	Lγ8	L2	$2p_{1/2}^{-1}$	01	5s <sup>-1</sup>
	Lγ8'	L2	$2p_{1/2}^{-1}$	N6	$4f_{5/2}^{-1}$
	Lγ8'	L2	$2p_{1/2}^{-1}$	N7	$4f_{7/2}^{-1}$
L-eta	Lη	L2	$2p_{1/2}^{-1}$	M1	3s <sup>-1</sup>
L-l	LI	L3	$2p_{3/2}^{-1}$	M1	3s <sup>-1</sup>
	Ls	L3	$2p_{3/2}^{-1}$	M3	$3p_{3/2}^{-1}$
	Lt	L3	2p <sub>3/2</sub> <sup>-1</sup>	M2	3p <sub>1/2</sub> <sup>-1</sup>
	Lu	L3	$2p_{3/2}^{-1}$	N6	$4f_{5/2}^{-1}$
	Lu	L3	2P <sub>3/2</sub> <sup>-1</sup>	N7	$4f_{7/2}^{-1}$
	Lv	L2	$2p_{1/2}^{-1}$	N6	$4f_{5/2}^{-1}$
	Lv	L2	$2p_{1/2}^{-1}$	N7	$4f_{7/2}^{-1}$
M-alpha	Μα1	M5	3d <sub>5/2</sub> -1	N7	$4f_{7/2}^{-1}$
	Μα2	M5	3d <sub>5/2</sub> -1	N6	$4f_{5/2}^{-1}$
M-beta	Μβ	M4	3d <sub>3/2</sub> -1	N6	$4f_{5/2}^{-1}$
M-gamma	Μγ	M3	3p <sub>3/2</sub> <sup>-1</sup>	N5	$4d_{5/2}^{-1}$
M-zeta	Μζ1	M5	$3d_{5/2}^{-1}$	N3	$4p_{3/2}^{-1}$
	Μζ2	M4	3d <sub>3/2</sub> -1	N2	$4p_{1/2}^{-1}$

Table 3: XRF line nomenclature6,7

## **1.4 XRF Fluorescence Lines**

The following tables (4-6) present the energies of emission for the most common observed electron transitions during XRF, in the simple, Siegbahn and IUPAC nomenclatures.

	K-alpha		K-beta			
	Ka1	Κα2	Kβ1 Kβ2		КβЗ	
Symbol	K-L3	K-L2	K-M3	K-N2	K-M2	
Н	0.01					

	K-alpha		K-beta				
	Κα1	Κα2	Kβ1	Кβ2	Кβ3		
Symbol	K-L3	K-L2	K-M3	K-N2	K-M2		
Не	0.02						
Li	0.05						
Be	0.11						
В	0.18						
С	0.28						
Ν	0.39						
0	0.52						
F	0.68						
Ne	0.85	0.85					
Na	1.04	1.04					
Mg	1.25	1.25	1.30		1.30		
Al	1.49	1.49	1.56		1.56		
Si	1.74	1.74	1.84		1.84		
Р	2.01	2.01	2.14		2.14		
S	2.31	2.31	2.47		2.47		
Cl	2.62	2.62	2.82		2.82		
Ar	2.96	2.96	3.19		3.19		
K	3.31	3.31	3.59		3.59		
Са	3.69	3.69	4.01		4.01		
Sc	4.09	4.09	4.46		4.46		
Ti	4.51	4.50	4.93		4.93		
V	4.95	4.94	5.43		5.42		
Cr	5.41	5.40	5.95		5.94		
Mn	5.90	5.89	6.49		6.49		
Fe	6.40	6.39	7.06		7.05		
Со	6.93	6.91	7.65		7.65		
Ni	7.48	7.46	8.27		8.26		
Cu	8.05	8.03	8.91		8.90		

	K-alpha		K-beta		
	Ka1	Κα2	Kβ1	<b>Kβ2</b>	Кβ3
Symbol	K-L3	K-L2	K-M3	K-N2	K-M2
Zn	8.64	8.62	9.57		9.57
Ga	9.25	9.23	10.27	10.37	10.26
Ge	9.89	9.86	10.98	11.11	10.98
As	10.54	10.51	11.73	11.87	11.72
Se	11.22	11.18	12.50	12.66	12.49
Br	11.92	11.88	13.29	13.47	13.28
Kr	12.65	12.60	14.11	14.31	14.11
Rb	13.40	13.34	14.96	15.19	14.95
Sr	14.16	14.10	15.84	16.09	15.83
Y	14.96	14.88	16.74	17.01	16.73
Zr	15.77	15.69	17.67	17.97	17.65
Nb	16.62	16.52	62	95	61
Мо	17.48	17.37	19.61	19.96	19.59
Тс	37	25	20.62	21.00	20.60
Ru	19.28	19.15	21.66	22.07	21.64
Rh	20.22	20.07	22.72	23.17	22.70
Pd	21.18	21.02	23.82	24.30	23.79
Ag	22.16	21.99	24.94	25.46	24.91
Cd	23.17	22.98	26.10	26.64	26.06
In	24.21	24.00	27.28	27.86	27.24
Sn	25.27	25.04	28.49	29.10	28.44
Sb	26.36	26.11	29.73	30.39	29.68
Те	27.47	27.20	31.00	31.70	30.94
Ι	28.61	28.32	32.30	33.04	32.24
Xe	29.78	29.46	33.62	34.41	33.56
Cs	30.97	30.62	34.99	35.81	34.92
Ва	32.19	31.82	36.38	37.25	36.30
La	33.44	33.03	37.80	38.72	37.72
Ce	34.72	34.28	39.26	40.22	39.17
Pr	36.03	35.55	40.75	41.75	40.65

	K-alpha		K-beta		
	Ka1	Κα2	<b>K</b> β1	<b>Kβ2</b>	Кβ3
Symbol	K-L3	K-L2	K-M3	K-N2	K-M2
Nd	37.36	36.85	42.27	43.32	42.17
Pm	38.73	38.17	43.83	44.92	43.71
Sm	40.12	39.52	45.42		45.29
Eu	41.54	40.90	47.04		46.91
Gd	43.00	42.31	48.70		48.55
Tb	44.48	43.75	50.39	51.68	50.23
Dy	46.00	45.21	52.12	53.45	51.95
Но	47.55	46.70	53.88	55.27	53.70
Er	49.13	48.22	55.68	57.12	55.48
Tm	50.74	49.77	57.51	59.01	57.30
Yb	52.39	51.35	59.38	60.94	59.16
Lu	54.07	52.97	61.29	62.90	61.05
Hf	55.78	54.61	63.24	64.91	62.98
Та	57.53	56.28	65.22	66.97	64.95
W	59.32	57.98	67.25	69.04	66.95
Re	61.14	59.72	69.31	71.16	69.00
Os	63.00	61.49	71.42	73.33	71.08
Ir	64.90	63.29	73.56	75.53	73.20
Pt	66.83	65.12	75.75	77.79	75.37
Au	68.81	66.99	77.98	80.08	77.58
Hg	70.82	68.89	80.26	82.43	79.82
T1	72.87	70.83	82.58	84.81	82.12
Pb	74.97	72.81	84.94	87.24	84.45
Bi	77.11	74.82	87.35	89.72	86.83
Ро	79.29	76.86	89.81	92.25	89.26
At	81.52	78.95	92.32	94.83	91.73
Rn	83.79	81.07	94.87	97.46	94.25
Fr	86.11	83.23	97.48	100.13	96.82
Ra	88.47	85.44	100.13	102.86	99.43
Ac	90.89	87.68	102.84	105.65	102.10

	K-alpha		K-beta				
	Κα1	Κα2	Kβ1	Κβ2	<b>Kβ3</b>		
Symbol	K-L3	K-L2	K-M3	K-N2	K-M2		
Th	93.35	89.96	105.60	108.48	104.82		
Pa	95.86	92.28	108.42	111.39	107.59		
U	98.43	94.65	111.30	114.33	110.42		
Np	101.06	97.07	114.23	117.34	113.30		
Pu	103.73	99.53	117.23	120.41	116.24		
Am	106.47	102.03	120.28	123.54	119.24		
Cm	109.26	104.58	123.39	126.74	122.29		

Table 4: K-line emissions for elements<sup>8</sup>.

	L-alph	a	L-beta				L-gamma		L-eta	L-iota	
	La1	La2	Lß1	Lβ2	Lβ3	Lβ4	Lγ1	Lγ2	Lγ3	Lη	Ll
Symb ol	L3- M5	L3- M4	L2- M4	L3- N5	L1- M3	L1- M2	L2- N4	L1- N2	L1- N3	L2- M1	L3- M1
Na										0.03	0.04
Mg										0.05	
Al						0.12				0.07	0.07
Si						0.16				0.10	0.09
Р					0.19	0.19				0.12	0.12
S					0.22	0.23				0.15	0.15
Cl					0.27	0.27				0.19	0.18
Ar					0.31	0.31				0.22	0.22
Κ					0.36	0.36				0.26	0.26
Ca					0.42	0.42				0.31	0.30
Sc		0.40	0.41		0.47	0.47				0.35	0.35
Ti		0.46	0.46		0.53	0.53				0.40	0.40
V		0.51	0.52		0.59	0.59				0.46	0.45
Cr	0.58	0.57	0.58		0.65	0.65				0.51	0.50
Mn	0.64	0.64	0.65		0.72	0.72				0.57	0.56

	L-alph	a	L-beta				L-gamma		L-eta	L-iota	
	La1	La2	Lß1	Lβ2	Lβ3	Lß4	Ly1	Lγ2	Ly3	Lη	Ll
Symb ol	L3- M5	L3- M4	L2- M4	L3- N5	L1- M3	L1- M2	L2- N4	L1- N2	L1- N3	L2- M1	L3- M1
Fe	0.71	0.71	0.72		0.79	0.79				0.63	0.62
Co	0.78	0.78	0.79		0.87	0.86				0.69	0.68
Ni	0.85	0.85	0.87		0.94	0.94				0.76	0.74
Cu	0.93	0.93	0.95		1.02	1.02				0.83	0.81
Zn	1.01	1.01	1.03		1.11	1.11				0.91	0.88
Ga	1.10	1.10	1.12		1.20	1.19		1.30		0.99	0.96
Ge	1.19	1.19	1.22		1.29	1.29		1.41		1.07	1.04
As	1.28	1.28	1.32		1.39	1.38		1.53	1.53	1.16	1.12
Se	1.38	1.38	1.42		1.49	1.49		1.65	1.65	1.25	1.21
Br	1.48	1.48	1.53		1.60	1.59		1.78	1.78	1.34	1.29
Kr	1.59	1.58	1.64		1.71	1.70		1.91	1.91	1.44	1.39
Rb	1.69	1.69	1.75		1.83	1.82		2.05	2.05	1.54	1.48
Sr	1.81	1.81	1.87		1.95	1.94		2.20	2.20	1.65	1.58
Y	1.92	1.92	2.00		2.07	2.06	2.16	2.35	2.35	1.76	1.69
Zr	2.04	2.04	2.12		2.20	2.19	2.31	2.50	2.50	1.88	1.79
Nb	2.17	2.16	2.26		2.33	2.32	2.46	2.66	2.67	2.00	1.90
Мо	2.29	2.29	2.39	2.52	2.47	2.45	2.63	2.83	2.83	2.12	2.02
Tc	2.42	2.42	2.54	2.68	2.61	2.60	2.79	3.00	3.00	2.25	2.13
Ru	2.56	2.55	2.68	2.84	2.76	2.74	2.97	3.18	3.18	2.38	2.25
Rh	2.70	2.69	2.83	3.00	2.91	2.89	3.15	3.36	3.37	2.51	2.37
Pd	2.84	2.83	2.99	3.17	3.07	3.04	3.33	3.55	3.55	2.66	2.50
Ag	2.98	2.98	3.15	3.35	3.23	3.20	3.52	3.75	3.75	2.81	2.63
Cd	3.13	3.13	3.32	3.53	3.40	3.37	3.72	3.95	3.95	2.96	2.77
In	3.29	3.28	3.49	3.71	3.57	3.54	3.92	4.16	4.16	3.11	2.90
Sn	3.44	3.44	3.66	3.91	3.75	3.71	4.13	4.36	4.37	3.27	3.04
Sb	3.61	3.60	3.84	4.10	3.93	3.89	4.35	4.59	4.59	3.44	3.19
Te	3.77	3.76	4.03	4.30	4.12	4.07	4.57	4.82	4.82	3.61	3.33

	L-alpha		L-beta				L-gamma			L-eta	L-iota
	La1	La2	Lß1	Lβ2	Lß3	Lß4	Ly1	Lγ2	Ly3	Lη	Ll
Symb ol	L3- M5	L3- M4	L2- M4	L3- N5	L1- M3	L1- M2	L2- N4	L1- N2	L1- N3	L2- M1	L3- M1
Ι	3.94	3.93	4.22	4.51	4.31	4.26	4.80	5.06	5.06	3.78	3.48
Xe	4.11	4.10	4.42	4.72	4.51	4.45	5.04	5.30	5.29	3.96	3.64
Cs	4.29	4.27	4.62	4.94	4.72	4.65	5.28	5.54	5.55	4.14	3.79
Ba	4.47	4.45	4.83	5.16	4.93	4.85	5.53	5.80	5.81	4.33	3.95
La	4.65	4.63	5.04	5.38	5.14	5.06	5.79	6.06	6.07	4.52	4.12
Ce	4.84	4.82	5.26	5.61	5.36	5.28	6.05	6.32	6.34	4.73	4.29
Pr	5.03	5.01	5.49	5.85	5.59	5.50	6.32	6.60	6.62	4.93	4.46
Nd	5.23	5.21	5.72	6.09	5.83	5.72	6.60	6.88	6.90	5.15	4.63
Pm	5.43	5.41	5.96	6.34	6.07	5.96	6.89	7.16	7.19	5.36	4.81
Sm	5.64	5.61	6.20	6.59	6.32	6.19	7.18	7.43	7.49	5.59	4.99
Eu	5.85	5.82	6.45	6.84	6.57	6.44	7.48	7.76	7.79	5.81	5.18
Gd	6.06	6.02	6.71	7.10	6.83	6.68	7.79	8.07	8.10	6.05	5.36
Tb	6.28	6.24	6.98	7.36	7.10	6.94	8.10	8.39	8.42	6.29	5.55
Dy	6.50	6.46	7.25	7.63	7.37	7.20	8.42	8.72	8.74	6.54	5.75
Но	6.72	6.68	7.53	7.91	7.65	7.47	8.75	9.05	9.09	6.79	5.94
Er	6.95	6.91	7.81	8.18	7.94	7.75	9.09	9.39	9.43	7.05	6.14
Tm	7.18	7.14	8.10	8.47	8.23	8.03	9.43	9.74	9.78	7.31	6.34
Yb	7.42	7.37	8.40	8.76	8.54	8.31	9.78	10.09	10.14	7.58	6.55
Lu	7.66	7.61	8.71	9.05	8.85	8.61	10.14	10.46	10.51	7.86	6.75
Hf	7.90	7.84	9.02	9.35	9.16	8.91	10.51	10.83	10.89	8.14	6.96
Та	8.15	8.09	9.34	9.67	9.49	9.21	10.96	11.23	11.29	8.43	7.17
W	8.40	8.34	9.67	9.96	9.82	9.53	11.29	11.61	11.68	8.73	7.39
Re	8.65	8.59	10.01	10.28	10.16	9.85	11.68	12.01	12.08	9.03	7.60
Os	8.91	8.84	10.35	10.60	10.51	10.17	12.09	12.42	12.50	9.34	7.82
Ir	9.18	9.10	10.71	10.92	10.87	10.51	12.51	12.84	12.92	9.65	8.04
Pt	9.44	9.36	11.07	11.25	11.23	10.85	12.94	13.27	13.36	9.98	8.27
Au	9.71	9.63	11.44	11.58	11.61	11.20	13.38	13.71	13.81	10.31	8.49
Hg	9.99	9.90	11.82	11.93	12.00	11.56	13.83	14.16	14.27	10.65	8.72

	L-alph	a	L-beta				L-gam	ma		L-eta	L-iota
	La1	La2	Lß1	Lβ2	Lß3	Lβ4	Ly1	Lγ2	Ly3	Lη	Ll
Symb ol	L3- M5	L3- M4	L2- M4	L3- N5	L1- M3	L1- M2	L2- N4	L1- N2	L1- N3	L2- M1	L3- M1
Tl	10.27	10.17	12.21	12.27	12.39	11.93	14.29	14.63	14.74	10.99	8.95
Pb	10.55	10.45	12.61	12.62	12.80	12.31	14.76	15.10	15.22	11.35	9.19
Bi	10.84	10.73	13.02	12.98	13.21	12.69	15.25	15.58	15.71	11.71	9.42
Ро	11.13	11.02	13.44	13.34	13.64	13.08	15.74	16.08	16.21	12.08	9.66
At	11.43	11.31	13.87	13.71	14.07	13.49	16.25	16.59	16.73	12.47	9.90
Rn	11.73	11.60	14.32	14.08	14.52	13.90	16.77	17.10	17.26	12.86	10.14
Fr	12.03	11.90	14.77	14.46	14.98	14.32	17.30	17.64	17.80	13.25	10.38
Ra	12.34	12.20	15.23	14.84	15.45	14.75	17.85	18	35	13.66	10.62
Ac	12.65	12.50	15.71	15.23	15.93	15.19	41	74	92	14.08	10.87
Th	12.97	12.81	16.20	15.62	16.43	15.64	98	19.30	19.50	14.51	11.12
Ра	13.29	13.12	16.70	16.04	16.93	16.10	19.58	19.90	20.11	14.95	11.37
U	13.61	13.44	17.22	16.43	17.46	16.58	20.17	20.49	20.71	15.40	11.62
Np	13.94	13.76	17.75	16.84	17.99	17.06	20.78	21.10	21.34	15.86	11.87
Pu	14.28	14.08	29	17.26	54	17.56	21.42	21.73	21.98	16.33	12.12
Am	14.62	14.41	85	17.68	19.11	07	22.07	22.37	22.64	16.82	12.38
Cm	14.96	14.74	19.43	10	19.69	59	22.73	23.03	23.32	17.32	12.63

Table 5: L-line emissions for elements<sup>9</sup>

Symbol	M-alpha		M-beta	M-gamma	M-zeta	
	Μα1	Μα2	Μβ	Μγ	Μζ1	Μζ2
	M5-N7	M5-N6	M4-N6	M3-N5	M5-N3	M4-N2
Zn						0.01
Ga						0.02
Ge						0.03
As						0.04
Se					0.0538	0.05
Br					0.0644	0.07

Symbol	M-alpha		M-beta	M-gamma	M-zeta	
	Μα1	Μα2	Μβ	Μγ	Μζ1	Μζ2
	M5-N7	M5-N6	M4-N6	M3-N5	M5-N3	M4-N2
Kr						0.08
Rb					0.0964	0.10
Sr					0.114	0.11
Y					0.13	0.13
Zr				0.323	0.1526	0.1526
Nb				0.349	0.1724	0.1724
Мо				0.379	0.1935	0.1935
Тс				0.412	0.2153	0.2153
Ru				0.448	0.2379	0.2379
Rh				0.485	0.2614	0.2614
Pd				0.522	0.2848	0.2848
Ag				0.562	0.3103	0.3103
Cd				0.603	0.337	0.337
In				0.646	0.366	0.366
Sn				0.684	0.397	0.397
Sb				0.735	0.429	0.429
Те				0.779	0.464	0.464

Symbol	M-alpha		M-beta	M-gamma	M-zeta	
	Μα1	Μα2	Μβ	Μγ	Μζ1	Μζ2
	M5-N7	M5-N6	M4-N6	M3-N5	M5-N3	M4-N2
Ι				0.826	0.497	0.497
Xe				0.874	0.525	0.525
Cs				0.924	0.5681	0.5681
Ва				0.974	0.6037	0.6037
La	0.833	0.833	0.854	1.025	0.64	0.64
Ce	0.883	0.883	0.902	1.079	0.6792	0.6792
Pr	0.929	0.929	0.950	1.131	0.712	0.712
Nd	0.978	0.978	0.997	1.180	0.753	0.753
Pm				1.234	0.79	0.79
Sm	1.081	1.081	1.100	1.287	0.831	0.831
Eu	1.131	1.131	1.153	1.341	0.8746	0.8746
Gd	1.185	1.185	1.209	1.334	0.914	0.914
Tb	1.240	1.240	1.266	1.457	0.9545	0.9545
Dy	1.293	1.293	1.325	1.507	0.9995	0.9995
Но	1.348	1.348	1.383	1.570	1.049	1.049

Symbol	M-alpha		M-beta	M-gamma	M-zeta	
	Μα1	Μα2	Μβ	Μγ	Μζ1	Μζ2
	M5-N7	M5-N6	M4-N6	M3-N5	M5-N3	M4-N2
Er	1.406	1.406	1.443	1.627	1.0868	1.0868
Tm	1.462	1.462	1.503	1.694	1.1291	1.1291
Yb	1.521	1.521	1.568	1.770	1.187	1.187
Lu	1.572	1.572	1.623	1.833	1.2266	1.2266
Hf	1.646	1.646	1.700	1.902	1.2778	1.2778
Та	1.702	1.702	1.760	1.961	1.3308	1.3296
W	1.776	1.774	1.835	2.033	1.3835	1.3787
Re	1.845	1.843	1.910	2.104	1.4368	1.431
Os	1.921	1.918	1.988	2.177	1.4919	1.4831
Ir	1.988	1.983	2.062	2.255	1.5458	1.5373
Pt	2.065	2.059	2.134	2.332	1.6022	1.592
Au	2.142	2.133	2.220	2.404	1.6605	1.648
Hg	2.195	2.184	2.285	2.485	1.724	1.712
T1	2.270	2.266	2.360	2.569	1.778	1.763
Pb	2.345	2.340	2.442	2.658	1.84	1.823

Symbol	M-alpha		M-beta	M-gamma	M-zeta	
	Μα1	Μα2	Μβ	Μγ	Μζ1	Μζ2
	M5-N7	M5-N6	M4-N6	M3-N5	M5-N3	M4-N2
Bi	2.422	2.426	2.534	2.745	1.901	1.883
Ро	2.501	2.503	2.620	2.842	1.947	
At	2.581	2.582	2.707	2.929	2.023	
Rn	2.663	2.662	2.794	3.006	2.093	
Fr	2.746	2.742	2.881	3.093	2.156	
Ra	2.829	2.823	2.967	3.185	2.19	
Ac	2.913	2.904	3.054	3.265	2.29	
Th	2.996	2.984	3.145	3.369	2.364	2.322
Ра	3.083	3.070	3.251	3.470	2.387	
U	3.171	3.161	3.337	3.566	2.507	2.4548
Pu	3.339	3.332	3.534	3.765	2.663	2.601
Am	3.438	3.424	3.646	3.869	2.751	2.68
Cm	3.525		3.74	3.976	2.726	

Table 6: M-line emissions for elements<sup>10</sup>

## **1.5 Absorption Edges**

The fluorescence of each element is a probability density function with unequal tails - at higher energies is a diminishing possibility of excitement, while at lower energies there is a

sharp drop to 0 as the highest probability of excitement is reached. This point of the lowest excitation energy (but highest probability) is known as the absorption edge for the element. This can be thought of as the minimum energy needed to solicit a fluorescence response from a given element. For those with instruments with customizable parameters, it can be used to optimize voltage and filter settings for specific elements. All else being equal, the more photons with the energies provided in Table 7 will solicit the largest fluorescence response from each target element.

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Н									
Не									
Li	0.05	0.01							
Be	0.11	0.01	0.00	0.00					
В	0.19	0.01	0.00	0.00					
С	0.28	0.02	0.01	0.01					
N	0.41	0.04	0.01	0.01					
0	0.54	0.04	0.01	0.01					
F	0.70	0.05	0.01	0.01					
Ne	0.87	0.05	0.02	0.02	0.00	0.00	0.00		
Na	1.07	0.06	0.03	0.03	0.00	0.00	0.00		
Mg	1.30	0.09	0.05	0.05	0.01	0.00	0.00		
Al	1.56	0.12	0.07	0.07	0.01	0.01	0.01		
Si	1.84	0.15	0.10	0.10	0.01	0.01	0.01		
Р	2.15	0.19	0.14	0.14	0.02	0.01	0.01		
S	2.47	0.23	0.16	0.16	0.03	0.02	0.02		
Cl	2.82	0.27	0.20	0.20	0.03	0.02	0.02		
Ar	3.21	0.33	0.25	0.25	0.04	0.03	0.03		
K	3.61	0.38	0.30	0.29	0.05	0.03	0.03		
Са	4.04	0.44	0.35	0.35	0.06	0.03	0.03	0.00	0.00
Sc	4.49	0.50	0.40	0.40	0.07	0.04	0.04	0.00	0.00
Ti	5.00	0.56	0.46	0.45	0.07	0.04	0.04	0.00	0.00
V	5.47	0.63	0.52	0.51	0.08	0.05	0.05	0.00	0.00
Cr	5.99	0.70	0.58	0.57	0.09	0.05	0.05	0.00	0.00
Mn	6.54	0.77	0.65	0.64	0.10	0.06	0.06	0.00	0.00
Fe	7.11	0.84	0.72	0.71	0.11	0.07	0.07	0.00	0.00

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Co	7.71	0.93	0.79	0.78	0.12	0.08	0.08	0.01	0.01
Ni	8.33	1.01	0.87	0.85	0.14	0.09	0.09	0.01	0.01
Cu	8.98	1.10	0.95	0.93	0.16	0.10	0.10	0.02	0.02
Zn	9.66	1.19	1.04	1.02	0.18	0.12	0.12	0.03	0.03
Ga	10.37	1.30	1.14	1.12	0.20	0.15	0.14	0.04	0.04
Ge	11.10	1.41	1.25	1.22	0.23	0.17	0.16	0.06	0.05
As	11.87	1.53	1.36	1.32	0.26	0.19	0.18	0.07	0.07
Se	12.66	1.65	1.47	1.43	0.29	0.22	0.21	0.10	0.09
Br	13.47	1.78	1.60	1.55	0.33	0.25	0.24	0.11	0.11
Kr	14.33	1.92	1.73	1.68	0.36	0.28	0.27	0.14	0.13
Rb	15.20	2.07	1.86	1.80	0.39	0.31	0.30	0.16	0.16
Sr	16.11	2.22	2.01	1.94	0.43	0.34	0.33	0.18	0.18
Y	17.04	2.37	2.16	2.08	0.47	0.38	0.36	0.21	0.20
Zr	00	2.53	2.31	2.22	0.51	0.41	0.39	0.23	0.23
Nb	99	2.70	2.47	2.37	0.54	0.45	0.42	0.26	0.25
Мо	20.00	2.87	2.63	2.52	0.59	0.48	0.46	0.28	0.28
Tc	21.04	3.04	2.79	2.68	0.63	0.52	0.50	0.31	0.31
Ru	22.12	3.22	2.97	2.84	0.67	0.56	0.53	0.34	0.34
Rh	23.22	3.41	3.15	3.00	0.72	0.60	0.57	0.37	0.37
Pd	24.35	3.60	3.33	3.17	0.77	0.65	0.62	0.41	0.41
Ag	25.51	3.81	3.52	3.35	0.83	0.70	0.67	0.45	0.44
Cd	26.71	4.02	3.73	3.54	0.88	0.76	0.71	0.49	0.48
In	27.94	4.24	3.94	3.73	0.94	0.81	0.77	0.54	0.53
Sn	29.20	4.47	4.16	3.94	1.01	0.87	0.82	0.58	0.57
Sb	30.49	4.70	4.38	4.13	1.07	0.93	0.88	0.63	0.62
Te	31.81	4.94	4.61	4.34	1.15	1.00	0.94	0.69	0.68
Ι	33.17	5.19	4.85	4.56	1.21	1.07	1.00	0.74	0.73
Xe	34.56	5.45	5.11	4.79	1.29	1.14	1.06	0.80	0.78
Cs	35.99	5.71	5.36	5.01	1.36	1.21	1.13	0.85	0.84
Ba	37.44	5.99	5.62	5.25	1.44	1.27	1.19	0.90	0.88
La	38.93	6.27	5.89	5.48	1.51	1.34	1.24	0.95	0.93
Ce	40.44	6.55	6.16	5.72	1.58	1.40	1.30	1.00	0.98

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Pr	41.99	6.84	6.44	5.96	1.65	1.47	1.65	1.05	1.03
Nd	43.57	7.13	6.72	6.21	1.72	1.54	1.42	1.11	1.08
Pm	45.18	7.43	7.01	6.46	1.80	1.61	1.48	1.16	1.13
Sm	46.83	7.74	7.31	6.72	1.88	1.69	1.54	1.22	1.19
Eu	48.52	8.05	7.62	6.98	1.97	1.77	1.61	1.28	1.24
Gd	50.24	8.38	7.93	7.24	2.05	1.84	1.68	1.33	1.29
Tb	52.00	8.71	8.25	7.51	2.13	1.92	1.74	1.39	1.35
Dy	53.79	9.05	8.58	7.79	2.21	2.01	1.81	1.45	1.41
Но	55.62	9.39	8.92	8.07	2.31	2.09	1.89	1.52	1.47
Er	57.49	9.75	9.26	8.36	2.40	2.17	1.95	1.58	1.53
Tm	59.39	10.12	9.62	8.65	2.49	2.26	2.02	1.64	1.59
Yb	61.33	10.49	9.98	8.94	2.60	2.37	2.11	1.72	1.66
Lu	63.31	10.87	10.35	9.24	2.71	2.47	2.19	1.79	1.74
Hf	65.35	11.27	10.74	9.56	2.82	2.58	2.28	1.87	1.81
Та	67.42	11.68	1.14	9.88	2.93	2.68	2.37	1.95	1.83
W	69.53	12.10	11.54	10.21	3.05	2.79	2.46	2.03	1.96
Re	71.68	12.53	11.96	10.54	3.17	2.91	2.55	2.12	2.04
Os	73.87	12.97	12.39	10.87	3.30	3.03	2.65	2.20	2.12
Ir	73.87	13.42	12.82	11.22	3.43	3.15	2.74	2.29	2.21
Pt	78.40	13.88	13.27	11.56	3.56	3.28	2.85	2.69	2.30
Au	80.73	14.35	13.73	11.92	3.70	3.42	2.96	2.49	2.39
Hg	83.10	14.84	14.84	12.28	3.85	3.55	3.07	2.59	2.48
Tl	85.53	15.35	14.70	12.66	4.00	3.70	3.18	2.69	2.58
Pb	88.01	15.86	15.20	13.04	4.15	3.85	3.30	2.80	2.68
Bi	90.53	16.39	15.71	13.42	4.32	4.01	3.43	2.91	2.79
Ро	93.11	16.94	16.24	13.81	4.48	4.16	3.36	3.02	2.89
At	95.73	17.49	16.79	14.21	4.65	4.33	3.66	3.14	3.00
Rn	98.40	05	17.34	14.62	4.82	4.49	3.79	3.25	3.11
Fr	101.14	64	17.91	15.03	5.00	4.66	3.91	3.37	3.22
Ra	103.92	19.24	48	15.44	5.18	4.83	4.05	3.49	3.33
Ac	106.76	19.84	19.08	15.87	5.64	5.00	4.17	3.61	3.44
Th	109.65	20.47	19.64	16.30	5.55	5.18	4.30	3.73	3.55

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Pa	112.60	21.11	20.31	16.73	5.74	5.37	4.44	3.85	3.66
U	115.61	21.76	20.95	17.17	5.93	5.55	4.56	3.97	3.78
Np	167	22.43	21.60	17.61	6.13	5.74	4.70	4.10	3.89
Pu	121.79	23.10	22.27	60	6.34	5.94	4.84	4.22	4.01
Am	124.98	23.81	22.95	51	6.13	5.74	4.70	4.10	3.89
Cm	128.24	24.53	23.65	97	6.34	5.94	4.84	4.22	4.01

Table 7: Absorption edges<sup>11</sup>

### **1.6 Fluorescence Efficiency**

Earlier in this section (Table 1) the depth of analysis was discussed. Put simply, each photon has diminishing odds of making it successfully through a given material (matrix) in a process known as attenuation. At a certain point, the probability of element escaping the matrix becomes vanishingly small, and this forms the maximum depth of analysis for which an element can be seen in the material.

Fluorescence efficiency can be thought of as the same phenomenon, but from within the atom itself. In other words, what percentage of photons escape its original atom's electron cloud? Because each element has a (generally) fixed number of electrons, this property is very consistent, and can be expressed by the following formula:

 $\phi = \frac{Photonsemitted}{Photonsabsorbed}$ 

This equation represents the quantum yield of a given fluorescence reaction. In general, lower energy photons are more likely to be absorbed than emitted. Despite the name quantum yield, the underlying phenomenon can be described quite simply: what proportion of fluoresced photons actually make it out of the atom? For sodium K-line emissions that number is just over 2%, and for silver K-line emissions that number is just over 82%. Thus lower Z elements tend to have weaker signals than their higher Z counterparts. Table 8 presents these quantum yields (fluorescence efficiency) for each element.

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Н									
He									
Li	0.0001								
Be	0.0003								
В	0.0007								
С	0.0014								

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
N	0.0031								
0	0.0058								
F	0.0092								
Ne	0.0160				0.0000				
Na	0.0210				0.0000				
Mg	0.0257	0.0000	0.0012	0.0000	0.0000				
Al	0.0330	0.0000	0.0008	0.0008	0.0000				
Si	0.0429	0.0000	0.0004	0.0004	0.0000				
Р	0.0555	0.0000	0.0000	0.0000	0.0000				
S	0.0707	0.0001	0.0003	0.0003	0.0000				
Cl	0.0885	0.0001	0.0002	0.0002	0.0000				
Ar	0.1090	0.0002	0.0002	0.0002	0.0000				
K	0.1321	0.0002	0.0003	0.0003	0.0000	0.0000			
Са	0.1468	0.0003	0.0003	0.0003	0.0000	0.0000		0.0019	
Sc	0.1831	0.0004	0.0008	0.0008	0.0000	0.0000		0.0019	
Ti	0.2184	0.0005	0.0011	0.0015	0.0000	0.0000		0.0020	
V	0.2529	0.0006	0.0018	0.0026	0.0000	0.0000		0.0021	
Cr	0.2865	0.0007	0.0023	0.0037	0.0000	0.0000		0.0022	
Mn	0.3192	0.0008	0.0031	0.0050	0.0000	0.0000		0.0023	
Fe	0.3510	0.0010	0.0036	0.0063	0.0000	0.0000		0.0024	
Co	0.3819	0.0012	0.0044	0.0077	0.0000	0.0000		0.0024	
Ni	0.4119	0.0014	0.0051	0.0093	0.0000	0.0000		0.0025	
Cu	0.4411	0.0016	0.0057	0.0110	0.0000	0.0000		0.0026	
Zn	0.4694	0.0018	0.0000	0.0120	0.0000	0.0000		0.0027	
Ga	0.4968	0.0005	0.0120	0.0130	0.0000	0.0000	0.0000	0.0027	
Ge	0.5233	0.0004	0.0130	0.0150	0.0000	0.0000	0.0000	0.0027	
As	0.5490	0.0028	0.0140	0.0160	0.0000	0.0001	0.0000	0.0027	
Se	0.5738	0.0032	0.0160	0.0180	0.0000	0.0001	0.0001	0.0027	
Br	0.5978	0.0036	0.0180	0.0200	0.0001	0.0000	0.0001	0.0027	

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Kr	0.6209	0.0041	0.0200	0.0200	0.0001	0.0000	0.0001	0.0027	
Rb	0.6432	0.0046	0.0220	0.0240	0.0001	0.0000	0.0001	0.0027	
Sr	0.6647	0.0051	0.0240	0.0260	0.0001	0.0000	0.0002	0.0027	
Y	0.6853	0.0059	0.0260	0.0280	0.0001	0.0001	0.0002	0.0028	
Zr	0.7051	0.0068	0.0000	0.0310	0.0001	0.0001	0.0002	0.0028	
Nb	0.7241	0.0094	0.0320	0.0340	0.0001	0.0002	0.0002	0.0029	
Мо	0.7424	0.0100	0.0348	0.0370	0.0001	0.0003	0.0002	0.0029	
Tc	0.7598	0.0110	0.0370	0.0400	0.0001	0.0003	0.0003	0.0028	
Ru	0.7765	0.0210	0.0400	0.0430	0.0002	0.0003	0.0003	0.0028	
Rh	0.7924	0.0130	0.0430	0.0460	0.0002	0.0004	0.0003	0.0027	
Pd	0.8075	0.0140	0.0470	0.0490	0.0002	0.0005	0.0004	0.0027	
Ag	0.8219	0.0120	0.0510	0.0520	0.0002	0.0006	0.0005	0.0027	
Cd	0.8356	0.0180	0.0560	0.0560	0.0003	0.0007	0.0005	0.0027	
In	0.8485	0.0200	0.0610	0.0600	0.0003	0.0008	0.0006	0.0027	
Sn	0.8607	0.0390	0.0690	0.0690	0.0004	0.0001	0.0006	0.0027	
Sb	0.8723	0.0390	0.0690	0.0690	0.0004	0.0009	0.0006	0.0027	
Те	0.8832	0.0410	0.0740	0.0740	0.0005	0.0009	0.0007	0.0027	
Ι	0.8934	0.0440	0.0790	0.0790	0.0006	0.0010	0.0008	0.0027	
Xe	0.9029	0.0460	0.0830	0.0850	0.0007	0.0010	0.0009	0.0027	0.0003
Cs	0.9118	0.0490	0.0900	0.0910	0.0008	0.0011	0.0010	0.0027	0.0011
Ba	0.9201	0.0520	0.0960	0.0970	0.0008	0.0012	0.0010	0.0027	0.0011
La	0.9278	0.0550	0.1030	0.1040	0.0008	0.0012	0.0010	0.0026	0.0021
Ce	0.9349	0.0580	0.1100	0.1100	0.0008	0.0013	0.0011	0.0026	0.0032
Pr	0.9414	0.0610	0.1170	0.1180	0.0008	0.0014	0.0011	0.0031	0.0041
Nd	0.9474	0.0640	0.1240	0.1250	0.0009	0.0014	0.0012	0.0036	0.0050
Pm	0.9528	0.0660	0.1320	0.1320	0.0009	0.0015	0.0013	0.0041	0.0059
Sm	0.9577	0.0710	0.1400	0.1390	0.0009	0.0016	0.0013	0.0048	0.0071
Eu	0.9621	0.0750	0.1490	0.1470	0.0010	0.0017	0.0014	0.0054	0.0083
Gd	0.9660	0.0790	0.1580	0.1550	0.0010	0.0018	0.0014	0.0061	0.0094
Tb	0.9695	0.0830	0.1670	0.1640	0.0011	0.0019	0.0015	0.0067	0.0106

Symbol	K	L1	L2	L3	M1	M2	M3	M4	M5
Dy	0.9725	0.0890	0.1780	0.1740	0.0011	0.0019	0.0015	0.0073	0.0120
Но	0.9751	0.0940	0.1890	0.1820	0.0011	0.0019	0.0016	0.0080	0.0135
Er	0.9772	0.1000	0.2000	0.1920	0.0012	0.0020	0.0017	0.0086	0.0149
Tm	0.9790	0.1060	0.2110	0.2010	0.0013	0.0022	0.0018	0.0101	0.0168
Yb		0.1120	0.2220	0.2180	0.0014	0.0024	0.0020	0.0115	0.0186
Lu	0.9816	0.1200	0.2340	0.2200	0.0015	0.0026	0.0021	0.0130	0.0205
Hf	0.9823	0.1300	0.2430	0.2420	0.0015	0.0028	0.0025	0.0132	0.0214
Та	0.9828	0.1370	0.2580	0.2430	0.0016	0.0030	0.0028	0.0135	0.0223
W	0.9830	0.1470	0.2700	0.2550	0.0017	0.0033	0.0032	0.0137	0.0232
Re	0.9830	0.1440	0.2830	0.2680	0.0018	0.0036	0.0030	0.0179	0.0240
Os	0.9827	0.1300	0.2950	0.2810	0.0020	0.0039	0.0032	0.0222	0.0248
Ir	0.9822	0.1200	0.3080	0.2940	0.0005	0.0016	0.0042	0.0264	0.0256
Pt	0.9816	0.1140	0.3210	0.3060	0.0023	0.0048	0.0034	0.0281	0.0273
Au	0.9808	0.1070	0.3340	0.3200	0.0025	0.0054	0.0036	0.0297	0.0291
Hg	0.9790	0.1070	0.3470	0.3330	0.0008	0.0020	0.0061	0.0314	0.0308
Tl	0.9789	0.1070	0.3600	0.3470	0.0029	0.0065	0.0035	0.0033	0.0235
Pb	0.9778	0.1120	0.3730	0.3600	0.0032	0.0076	0.0057	0.0338	0.0337
Bi	0.9778	0.1170	0.3870	0.3730	0.0036	0.0087	0.0060	0.0347	0.0350
Ро	0.9755	0.1220	0.4010	0.3860	0.0040	0.0098	0.0063	0.0355	0.0362
At	0.9744	0.1280	0.4150	0.3990	0.0041	0.0108	0.0068	0.0413	0.0396
Rn	0.9733	0.1340	0.4290	0.4110	0.0042	0.0119	0.0072	0.0472	0.0430
Fr	0.9723	0.1390	0.4430	0.4240	0.0044	0.0129	0.0077	0.0530	0.0463
Ra	0.9713	0.1460	0.4560	0.4370	0.0013	0.0079	0.0132	0.0588	0.0497
Ac	0.9201	0.1530	0.4680	0.4500	0.0047	0.0151	0.0200	0.0646	0.0531
Th	0.9699	0.1610	0.4790	0.4630	0.0013	0.0079	0.0132	0.0676	0.0565
Pa	0.9694	0.1620	0.4720	0.4760	0.0013	0.0079	0.0132	0.0676	0.0565
U	0.9692	0.1760	0.4670	0.4890	0.0013	0.0079	0.0132	0.0676	0.0565
Np	0.9692	0.1870	0.4660	0.5020	0.0013	0.0079	0.0132	0.0676	0.0565
Pu	0.9696	0.2050	0.4640	0.5140	0.0054	0.0204	0.0108	0.0938	0.0700
Am	0.9701	0.2180	0.4710	0.5260	0.0013	0.0079	0.0132	0.0676	0.0565
Cm	0.9711	0.2280	0.4790	0.5390	0.0054	0.0204	0.0108	0.0938	0.0700

Table 8: Fluorescence efficiency/fluorescent yield<sup>12</sup>

#### 2 The Elements

#### 2.1 Fluorine, F (9)

Fluorine is the lowest Z element detectable using handheld XRF. This is only possible when using graphene detector windows (thickness ~1  $\mu$ m) vs. traditional beryllium windows (thickness ~8  $\mu$ m) on silicon-drift detectors. These thinner windows create less attenuation for all light elements making fluorine a possibility; but it is worth laying out the limitations. First, this application requires a helium flush with an open path for x-rays (e.g. no window), since even a 4-8  $\mu$ m polypropylene window on the nose of the instrument will add too much attenuation to resolve the fluorine K-alpha peak. But the challenges to identifying fluorine go further. Some instruments do not record energies below 1 keV. Additionally, because most detectors have only 2048 channels, only 4-5 channels will be dedicated to these low energies. If the sample is a mineral (e.g. fluorite or cryolite) then every effort should be made to increase the fluorescence of Si and Al, as these will act as a secondary target for fluorine. In synthetic materials, the anode (if Rh or Ag) will be the primary excitation source, and thus increasing this scatter is essential.

Fluorine will be most visible in synthetic materials such as Teflon, principally due to the much lower density and thus deeper penetration of very low-energy x-rays.

Fluorine has an almost exhaustive list of applications, and not all can be mentioned here. A significant percentage of all fluorine used today is as a gas to produce nuclear fuel<sup>13</sup>. It is also used to create inert dielectric material for transformers and circuit breakers in high-voltage uses<sup>14</sup>. It can be used in some iron alloys. It is still used in refrigerants<sup>15</sup>, although international treaties since the 1980's have sharply curtailed its use due to its highly negative impact on the ozone layer. As noted earlier in this section, it is used in polymers such as Teflon. Biological applications include fluorosurfactants which repel water<sup>16</sup>. About one-third of all agrichemicals include fluorine in some form<sup>17</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
F	0.68 keV	K-line	0.70 keV	0.009	585 ppm	
Fe	0.71 keV	L-alpha Overlap	0.71 keV	0.001	5.63 %	Fe L-alpha is a concern due to abundance, but the fluorescence efficiency of its L-line mitigates this problem to some degree
Mn	0.64 keV	L-alpha Overlap	0.64 keV	0.005	950 ppm	Mn L-alpha is less likely to be an overlap for F K-alpha

Table 9: Observable emission lines for fluorine and its most common fluorescence interactions.

#### 2.2 Neon, Ne (10)

Neon, element #10, is the second lightest element that can be measured with handheld XRF. As a noble gas, neon is not typically encountered in typical XRF activities. However, under specific circumstances, this element is detectible. The only way to do so is to flow the analyte (neon gas) through the handheld unit and seal the nose using a mask. This application requires a vacuum seal in the handheld itself, though it is not impossible for a chamber to be built to house an XRF unit with this capability.

Neon is principally used in lighting, as it is the gas which is ionized. This property of neon lends itself to extreme flexibility in glass tubing, leading to the characteristic storefront signs. It is also an inexpensive refrigerant

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ne	0.85 keV	K-alpha	0.87 keV	0.016		
Ni	0.85 keV	L-alpha Overlap	0.85 keV	0.009	84 ppm	Ni is unlikely to be present in gas measurements of Ne

Table 10: Observable emission lines for neon and its most common fluorescence interactions.

#### 2.3 Sodium, Na (11)

Sodium is one of the most difficult elements to analyze by handheld XRF, and this is particularly acute for non-destructive applications. As just one example, the analytical depth for sodium is 7 µm in silicates. For this reason, atmospheric modification is often necessary to resolve this peak, typically a vacuum or flow of helium. This is why the analysis of sodium is generally restricted to laboratory equipment. It is possible to use helium in conjunction with a handheld unit, but that only surmounts one challenge - the window of an XRF unit will still attenuate its signal. In some limited cases, sodium can be detected if a vacuum is introduced into the nose of an instrument. However, this is only possible in extreme cases (in either NaCl salts or soda glasses where the concentration of sodium is above 5%).

For portable instrumentation, there are two options for detection of sodium in quantities above 0.5% when the atmosphere can be controlled. Both require an open nose (e.g. no barrier between the detector and the sample). The first option is to contain the unit within a vacuum, effectively turning it into a laboratory unit. The disadvantage for using this approach is that there is a limit to the size dimensions of a sample. The second option is to flow helium between the sample and the detector. This is not as difficult as it sounds. Units capable of vacuum control are by default capable of helium use. Helium purges the atmosphere between the detector and sample of N<sub>2</sub>, O<sub>2</sub>, and Ar. It has the secondary effect of desiccating the surface of the sample, enabling the detection of sodium to a deeper depth. However, this can be a negative since it has the potential of altering the sample. For most glasses and ceramics this is not a problem, although for soils it can dry out the sample.

As with all elements, sodium is influenced by the fluorescence of other elements present in the spectrum; these can excite sodium above and beyond what would normally be expected. The most significant of these is aluminum (1.4 keV), most prevalent in geologic materials. This secondary excitation from Al can make its detection and even quantification possible. For

silicate samples, a much lower limit of detection of sodium is possible. The best measurement conditions for sodium are: helium flow or vacuum chamber, 9-15 keV voltage, 50+ µA current.

Soda glasses can be archaeologically important, and are verified by high concentrations of sodium (10-14%  $Na_2O$ ). However, even when present in lesser quantities (1 - 10%  $Na_2O$ ), it can provide information about how the glass was made.

In soils, sodium can indicate formation processes in lacustrian deposits. It can also indicate the presence of salt as well, which can be important for paleoenvironmental reconstructions. It can also indicate the risk of salt development, as free CI anions can react with NaO to precipitate out as salt.

Sodium can also be measured in liquids down to 1% with a helium flow. This allows for the determination of NaCl in water.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Na	1.04 keV	K-alpha	1.07 keV	0.210	2.36 %	Intercepts: Cl K- alpha, Rh L-alpha (depends on tube anode) Slopes: Al K-alpha
Cl	0.92 keV	K-line Escape Peak (silicon)	2.82 keV	0.090	145 ppm	Can make Na detection difficult in salts
Rh	1 keV	L-line Escape Peak (silicon)	3.0 keV	0.046	1 ppb	Common problem in Rh tube instruments
Cu	0.93 keV	L-alpha Overlap	0.93 keV	0.011	60	
Zn	1.01 keV	L-alpha Overlap	1.02 keV	0.012	70 ppm	
Ga	1.10 keV	L-alpha Overlap	1.12 keV	0.013	19 ppm	
Sm	1.10 keV	M-Line Ovelrap	1.97 keV	0.001	7.05 ppm	Very rare

Eu	1.13 keV	M-Lines Overlap	2.05 keV	0.001	2 ppm	Very rare
Al	1.49 keV	K-alpha Excitatio n	1.56 keV	0.033	8.23 %	Common effect in silicates
Si	1.74 keV	K-alpha Excitatio n	1.84 keV	0.043	28.2 %	Common effect in silicates

Table 11: Observable emission lines for sodium and its most common fluorescence interactions.

#### 2.4 Magnesium, Mg (12)

Magnesium used to be the problem element for most XRF analyses, but with increasingly sophisticated tubes and detectors it is possible to analyze at small concentrations with portable instrumentation, in some cases without atmospheric modification. As with sodium, the best results still occur when using either helium or vacuum. Unlike sodium, a helium purge is not necessary to see it in low quantities. Even ~0.7% Mg is detectable in silicates when taken with a vacuum inside the instrument (Figure X). As such, in-situ analysis of low quantities of magnesium is possible even in fieldwork conditions. However, the shallow depth of analysis (9.6  $\mu$ m in silicates) means that the success for analyzing magnesium will depend very much upon the sample matrix.

Successful measurement of magnesium, like sodium, tends to depend upon the fluorescence of aluminum and silicon. Higher aluminum and silicon typically mean higher sensitivity for magnesium, while correspondingly lower amounts of aluminum and silicon mean that fewer photons are available. As such, the detection limits for magnesium can vary considerably.

Magnesium is abundant on Earth, but its distribution is highly uneven. For igneous rocks, the deeper the source of magma, the more magnesium tends to be present. Magnesium reaches its peak concentration in materials that are mafic (>2% MgO) and ultramafic (>18% MgO), although the specific definitions also depend upon iron. Some ultramafic rocks have as much as 40% MgO. The transition from magic to felsic materials on Earth's crust is a product of plate tectonics<sup>19</sup>. In metamorphic rocks, magnesium can substitute for calcium when it is

subjected to heat and pressure forming dolomite<sup>20</sup>. In fact, plate tectonics are not needed to cause increases in magnesium. In calcium-carbonate forming organisms present in the sea, magnesium increases in concentration with temperature, making it a useful paleothermometer<sup>21</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Mg	1.25 keV	K-alpha	1.30 keV	0.026	2.33 %	Slopes: Si K-alpha
	1.30 keV	K-beta				
Rh	1 keV	L-line Escape Peak (silicon)	3.0 keV	0.046	1 ppb	Common problem in Rh tube instruments
As	1.28 keV	L-alpha Overlap	1.32 keV	0.016	1.8 ppm	
Gd	1.185 keV	M-Line Overlap	2.13 keV	0.001	6.2 ppm	Very rare
Тb	1.24 keV	M-Line Overlap	2.21 keV	0.001	1.2 ppm	Very rare
Al	1.49 keV	K-alpha Excitati on	1.56 keV	0.033	8.23 %	Common effect in silicates
Si	1.74 keV	K-alpha Excitati on	1.84 keV	0.043	28.2 %	Common effect in silicates

Table 12: Observable emission lines for magnesium and its most common fluorescence interactions.

#### 2.5 Aluminum, AI (13)

Aluminum is the first element that can be reliably measured in portable instruments without atmospheric modification, although that certainly helps. Its comparative ease of measurement is not just because it fluoresces at a higher energy, but also because it tends to occur in high quantities in materials such as clays where 7-15% (elemental, not oxide) of the composition

is common. It is still highly influenced by the adjacent, and almost always larger, silicon Kalpha peak. In general, excitation of aluminum depends on the excitation of silicon.

At several times in human history, aluminum was considered to be more valuable than gold. Napoleon Bonaparte traded in his silverware for aluminum. There was even a proposal to coat the US capitol rotunda with aluminum (it proved to be too expensive). In the early 19th century, aluminum was thought to be the metal of the future. But while nobility thought it was a luxury good, it was destined to become a ubiquitous household item. As energy became cheaper, so too did aluminum. Today, it is used to wrap half-eaten sandwiches.

Despite our proclivity to store beer and sandwiches in it, aluminum is a critical alloy. It does not corrode easily, and it is surprisingly strong for its density. Satellites and space shuttles alike are dependent on it to maintain their weight balance. In nature, aluminum is ubiquitous as well. It forms about 8% of the Earth's crust by weight, and is the third most common element. Typically, aluminum is most commonly found as alumina, or Al<sub>2</sub>O<sub>3</sub>. When at high purity, the oxide mineral can form the gemstone sapphire, or when less pure, a ruby.

Aluminum is not common in pigments for paintings, though it can be a major component of some, such as ultramarine. In general, any material derived from the earth's crust will have trace concentrations of aluminum. Alumina, the most common oxide, is not reactive and as such it can be used to infer geologic weathering processes. For example, in carbonitic soils, MgO and CaO will leach out with rain, while Al<sub>2</sub>O<sub>3</sub> stays the same<sup>22</sup>. Their relative abundance along with Al can indicate the amount of precipitation. Al<sub>2</sub>O<sub>3</sub> can also indicate clay fraction if it has strong correlations with iron, potassium, and titanium<sup>23</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Al	1.49 keV	K-alpha	1.56 keV	0.033	8.23 %	Slopes: Si K-alpha

	1.56 keV	K-beta				
К	1.6 keV	K-line Escape Peak (silicon)	3.61 keV	0.132	2.09 %	K is highly likely to co-occur with Al in many earth materials.
Br	1.48 keV	L-alpha Ovelrap	1.55 keV	0.020	2.4 ppm	Very rare
Yb	1.52 keV	M-alpha Ovelrap	2.71 keV	0.001	3.2 ppm	Very rare
Si	1.74 keV	K-alpha Excitatio n	1.56 keV	0.033	28.2 %	Common effect in silicates

Table 13: Observable emission lines for aluminum and its most common fluorescence interactions.

#### 2.6 Silicon, Si (14)

After oxygen (46%), silicon (28%) is the second most abundant element in Earth's crust. Its measurement is thus common, even without atmospheric aid. As with all low Z elements measured by XRF, silicon is hampered by a shallow depth of measurement (for example, its characteristic X-rays can only travel about 27 µm through a silica matrix). Yet, its abundance makes measuring it easier despite this limitation. If the voltage and current are adjusted to maximize the scattering of a rhodium or silver anode L-lines, then measuring silicon is well within the capabilities of non-destructive XRF.

Silicon is present in almost all geologic materials. However, its ubiquity does not mean it cannot convey useful information. Silicon, along with aluminum, titanium, potassium, and iron, can convey information about clay fraction. Relative to elements such as calcium it can be informative about biogenic activity in lakes, for instance in diatom species that metabolize silicon instead of calcium carbonate in building their shells<sup>24</sup>.

In iron alloys, silicon prevents oxidization and helps control the amount of all-important carbon<sup>25</sup>. Its most celebrated modern application is as a semiconductor material, forming the majority composition for most computer chips and solar panels as a monocrystalline

material<sup>26</sup>. This same function is crucial for XRF devices, where silicon is used for silicon-drift

detectors,	silicon	pin-diode	detectors,	or silicon-lithium	detectors.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Si	1.74 keV	K-alpha	1.56 keV	0.033	28.2 %	
	1.84 keV	K-beta				
Rb	1.69 keV	L-alpha Ovelrap	1.80 keV	0.024	90 ppm	Unlikely to be high enough in concentration
Та	1.70 keV	M-alpha Overlap	3.05 keV	0.002	2 ppm	Very rare
W	1.78 keV	M-Line Overlap	3.17 keV	0.002	1.25 ppm	Potentially significant in some metals
Rh	2.70 keV	L-alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Si
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Si

Table 14: Observable emission lines for silicon and its most common fluorescence interactions.

#### 2.7 Phosphorous, P (15)

Phosphorous is a challenging element to measure for two reasons. First, it typically occurs in low quantities in most materials. Second, it is affected by the escape peak of the fifth most common element on Earth, calcium (4.2%). Between these two effects, phosphorous is often missed. The typically low quantity of phosphorus in most samples contrasts with the quantity of its neighbor in the spectrum, silicon. As such, the much higher silicon concentrations will almost always interfere with the detection of phosphorus in its normal abundance. Reliable quantification for low levels of phosphorus is as dependent on that element as it is on silicon.

As phosphorus concentrations begin to increase above 0.25%, it is much easier to confidently quantify the element.

Phosphorous provides a look, first and foremost, into biological activity in sedimentary geology and soil science. Its presence in soils in particular can be a key indicator for crop growth. It is often the limiting factor, and thus is highly in demand as a fertilizer. However, its high demand has resulted in overuse, and it is chiefly responsible for creating toxic dead zones, for example, where rivers wash excess into the sea<sup>27</sup>.

In pigments, the analysis of phosphorus can indicate biological elements used to produce composite paints. The most salient example is in the case of bone black, in which the key mineral is calcium phosphate (CaPO<sub>4</sub>). There are of course exceptions. One example is cobalt-based pigments being roasted with other phosphates in their preparation. Another example can be found when mineral phosphate can coincide with uranium in natural deposits<sup>28</sup>.

The high reactivity of phosphorus is one of the reasons for its essential role in biology. It also makes for many key applications in industry. In alloys, phosphorus, like silicon, can help control the negative effects of oxygen. Its high reactivity has led to its use in munitions as well.

An unusual, but ultimately significant role for phosphorus begins in our bodies and ends in nuclear weapons. Calcium phosphate is the material most vertebrates produce to harden their skeletons. In rare cases, when this material is buried it can fossilize and lead to the trove of information we have about the natural history of earth. The process of permineralization of phosphorus can attract elements like uranium, particularly when fossilization occurs in anoxic zones such as the Morrison formation of North America. This led to the preservation of uranium in dinosaur bones from Grants, New Mexico used by scientists in the Manhattan project as the source of uranium for the first nuclear weapons<sup>29</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Р	2.01 keV	K-alpha K-beta	2.15 keV	0.056	1,050 ppm	Intercepts: Ca K-alpha Slopes: Si K-alpha, Ca K-alpha
	keV	11 0000				
Ca	1.99 keV 3.69 keV	Escape Peak / Excitati on	4.04 keV	0.147	4.15 %	Very common interference with P measurements, but can also excite P
Y	1.92 keV	L-alpha Overlap	2.37 keV	0.028	33 ppm	Very rare
Zr	2.04 keV	L-alpha Overlap	2.53 keV	0.031	165 ppm	
Ir	1.99 keV	M-Line Overlap	3.56 keV	0.001	1 ppb	Exceptionally rare
Pt	2.07 keV	M-Line Overlap	3.70 keV	0.002	5 ppb	Exceptionally rare
Rh	2.70 keV	L-alpha Excitati on	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of P
Ag	2.98 keV	L-alpha Excitati on	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of P

Table 15: Observable emission lines for phosphorous and its most common fluorescence interactions.

#### 2.8 Sulfur, S (16)

Sulfur is easy to identify, provided a molybdenum tube is not used or the sample does not contain lead or mercury. The L-lines of molybdenum overlap directly and M-lines of lead and mercury to the right and left of the sulfur K-alpha line, respectively. The greatest challenge occurs with rhodium anode tubes, where L lines overlap on either side can impair low-level quantification.

Sulfur is an important paleoenvironmental indicator in geologic deposits. Its presence often indicates the presence of anoxic environments in ocean basins. This is the result of heightened competition for oxygen, where metals that are normally soluble in water (MO<sub>4</sub>, UO<sub>3</sub>, VO<sub>2</sub>, etc.)

begin to precipitate out of solution and deposit on the seafloor<sup>30</sup>. These anoxic conditions can lead to increases in sulfate reducing bacteria, which can further harm the ecosystems due to the production of hydrogen sulfide<sup>31</sup>. For petroleum exploration, these elements are important for identifying the prospect and extent of hydrocarbon deposits. It can also be used to assess risk. The same conditions that preserve carbon also attract sulfur which can have a negative effect on the surviving deposits. Foremost of these is the presence of gypsum (CaSO<sub>4</sub>). These deposits can be extensive and they risk sulfur contamination in oil. Gypsum is also dangerous for hydro technical construction, where its ability to absorb water can undermine dams<sup>32</sup>.

Gypsum is a threat to oil and hydrotechnical constructions, but a potential boon to agriculture. Calcium sulfate represents a potent fertilizer that provides two critical nutrients, calcium and sulfur<sup>33</sup>. Calcium helps form plant cell walls (among many other functions) while sulfur has an essential role in protein formation. Methionine is distinguished from the other essential amino acids because: a) it is the only one which contains sulfur, and b) it is least common in plants but is abundant in animal tissue, despite plants having the ability to synthesize it<sup>34</sup>. There are, however, a few plants that are rich in methionine, chief among them soybeans<sup>35</sup>. The amount of sulfur in the ground can be a limiting factor in the amount of usable protein humans can access. XRF can be used at three stages to improve protein availability: first by analyzing the soil, second by evaluating the fertilizer intended to replenish it, and third by analyzing the final plant itself.

Industrial applications for sulfur vary greatly, but the most financially important application for sulfur is its presence as a pollutant. For example, in Canada, pollution regulations prohibit more than 0.25% sulfur in fuel for transport shipping vessels approaching port<sup>36</sup>. This is because sulfur dioxide contributes to acid rain<sup>37</sup>. XRF enables on-site determination of the sulfur content in fuel. Measurement of sulfur at 0.25% is an effortless analytical task for the equipment.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
S	2.31 keV 2.47 keV	K-alpha K-beta	2.47 keV	0.071	350 ppm	Intercepts: Rh L-alpha (depends on tube anode)
Мо	2.29 keV	L-alpha Overlap	2.52 keV	0.037	1.2 ppm	Can be significant in some industrial materials
Hg	2.2 keV	M-Line Overlap	4.00 keV	0.003	85 ppb	Common in oil-based paints
Pb	2.35 keV	M-Line Overlap	4.32 keV	0.003	14 ppm	Almost universal in oil-based paints
TI	2.27 keV	M-Line Overlap	4.15 keV	0.003	850 ppb	Very rare
Ca	3.69 keV	K-alpha Excitatio n	4.04 keV	0.147	4.15 %	
Rh	2.70 keV	L-Alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of S
Ag	2.98 keV	L-Alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of S

Table 16: Observable emission lines for sulfur and its most common fluorescence interactions.

#### 2.9 Chlorine, Cl (17)

In now-ubiquitous rhodium anode instruments the L-lines of rhodium overlap with the K-alpha line of chlorine. This makes qualitative analysis of chlorine difficult, but it can improve the quantitative analysis of chlorine as the rhodium L-beta lines, along with argon K-alpha line, have the potential to excite chlorine. If the overlap with rhodium can be subtracted, the data for chlorine is nonetheless quite good. In the event that this cannot be done, or if qualitative analysis is preferred, a thin filter can help. Filters with a thickness of 25 µm titanium or 50 µm aluminum are commonly used. Alternatively, one can use a Teflon membrane - simply 3-6 layers of Teflon tape atop each other. This preserves a high- count rate while preventing absorption of the L-lines from either rhodium or silver.

The presence of the rhodium L-lines is not simply an inconvenience. It is the product of Rayleigh scattering due to an elastic interaction with the electrons in the sample. As a consequence, changes in the density of the sample will affect the elastic scattering and make rhodium a moving target. Combine this with rhodium L-beta's ability to excite chlorine, and you have a difficult-to-control variable.

Chlorine is a highly reactive element and quite common in nature. It has a tendency of being bad news when it is found unexpectedly. In paintings, it can induce reactions that degrade existing chemical bonds. This leads to corrosion, and is evident by how close an object is to the sea in coastal areas<sup>38</sup>. At archaeological sites it can cause degradation of structures, particularly those made of mud brick. In agriculture, it can threaten salinification of soil resulting in lost productivity. But for your food, it makes it that much more delicious. And for your body, it is essential to life. When you read these words, it is in part due to chlorine anions moving between the synapses of nerves<sup>39</sup>.

The analysis of chlorine with handheld XRF tends to be mostly qualitative. Effective calibrations for chlorine tend to be rare owing to its difficulty in analysis using ICP-OES. However, as a qualitative indicator it is typically sufficient to answer questions.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Cl	2.62 keV 2.82 keV	K-alpha K-beta	2.82 keV	0.089	145 ppm	Intercepts: Rh L- alpha Slopes: Rh L-alpha, Ag L-alpha (depends on tube anode)
Rh	2.70 keV	L-alpha overlap / Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Cl, but will overlap with them as well.
Ru	2.56 keV	L-alpha Overlap	2.84 keV	0.043	1 ppb	Very rare

Rn	2.66 keV	M-alpha Overlap	5.00 keV	0.004		This is a rare, dangerous gas, unlikely to affect the measurement of Cl
Ca	3.69 keV	K-alpha Excitatio n	4.04 keV	0.147	4.15 %	
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Cl

Table 17: Observable emission lines for chlorine and its most common fluorescence interactions.

#### 2.10 Argon, Ar (18)

Analysis of argon is unlikely to be the goal of a given project, but nonetheless it will almost always be present in analysis without atmospheric modification. However, argon will overlap with both rhodium and silver L-lines, thus affecting normalization by these lines in many calibrations.

Argon forms a little over 0.9% of the gaseous composition of Earth's atmosphere. For this reason, it is the most common element in handheld XRF spectrum by a technicality. Argon has no practical use, but it can be used as a weak indicator for porosity in the studied material. This can be particularly important if a vacuum is used within the nose of the instrument. However, this use would be primarily qualitative.

It is possible, however, to analyze argon in gas. One can flow gas through an XRF instrument to analyze the purity of the gas itself. When used in this way, neon is also detectable since the matrix is so light. However, argon can be difficult to observe due to a partial overlap with either the rhodium or silver L-lines. In this case, the same Teflon filter that works for chlorine will work here as well.

Elen	ıent	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
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Ar	2.96 keV 3.19 keV	K-alpha K-beta	3.21 keV	0.109	3.5 ppm	While Ar is rare in Earth's crust, it forms 0.98% of the Earth's atmosphere. Intercepts: Ag L- alpha, Rh L-alpha (depends on tube anode)
Ag	2.98 keV	L-alpha Overlap	3.35 keV	0.052	75 ppb	Can be common in painting or metals, and will occur in Ag anode instruments.
Th	2.99 keV	M-Line Overlap	5.74 keV	0.001	9.6 ppm	Rarely in concentrations large enough to cause overlap.
Rh	3.00 keV	L-beta Overlap	3.00 keV	0.046	1 ppb	This overlap should be expected in Rh anode instruments

Table 18: Observable emission lines for argon and its most common fluorescence interactions.

#### 2.11 Potassium, K (19)

For silver anode instruments, the analysis of potassium can be difficult, especially at low concentrations. The L-line emissions from silver overlap with potassium and may complicate the analysis. The use of a filter can remediate this, but it will result in reduced total counts for potassium. However, a rhodium tube is not a complete solution to the problem because the rhodium  $L\gamma$ 2 line overlaps with the potassium K-lines as well. This is not a concern in geologic samples, but in low-density samples that cause anode scattering and with lower potassium concentrations, the overlap should not be taken for granted.

Like chlorine, potassium is essential for nervous system functionality<sup>40</sup>. It is also essential for plants because it opens and closes their stomata, allowing them to take in  $CO_2^{41}$ , though open stomata can also cause water loss. Spreading potassium where it is needed is big business. It is one of the chief fertilizers<sup>42</sup> needed around the world to ensure a sustained food supply.
It is no wonder that life has such an affinity for potassium as it can be found almost everywhere. Along with aluminum, titanium, and iron, it can be used to determine the clay fraction in soils<sup>43</sup>. It is unusual to find any soil without some amount of potassium. The main question is whether potassium is available to the plants growing there, as some oxidization forms preclude plant uptake<sup>44</sup>. This is why analysis of soils should be complemented with measurements of the plants themselves. This can help strengthen inferences as to whether additional potassium in the form of potash (K<sub>2</sub>O<sub>3</sub>) is needed in the soil.

In paintings, the presence of potassium can indicate either a green earth (alongside iron in the fourth oxidization state)<sup>45</sup> or a plant-based pigment (as K is common in them)<sup>46</sup>. In neither case is its presence diagnostic, only helpful.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
К	3.31 keV 3.59 keV	K-alpha K-beta	3.61 keV	0.132	2.09 %	Intercepts: Ag L- alpha, Rh L-alpha (depends on tube anode)
Ag	3.35 keV	L-beta Overlap	3.35 keV	0.052	75 ppb	Can be common in painting or metals, and is guaranteed in Ag anode instruments.
In	3.29 keV	L-alpha Overlap	3.73 keV	0.060	250 ppb	Rarely in concentrations large enough to cause overlap.
Rh	3.36 keV	L- gamma Overlap	3.81 keV	0.013	1 ppb	In Rh anode instruments, a filter will be needed.

Table 19: Observable emission lines for potassium and its most common fluorescence interactions.

#### 2.12 Calcium, Ca (20)

As was the case with aluminum and silicon, potassium and calcium are bound elements that influence one another. The K-beta line of potassium can overlap with the K-alpha line of

calcium, while increased calcium increases the fluorescence of potassium. And because of this, more potassium can potentially steal photons that would have otherwise manifested in the calcium K-alpha line. While both elements are qualitatively visible, quantification often requires corrections of one to the other.

Also, as a cautionary note, calcium can be a common contaminant in mylar film. As such, a distinct calcium peak may be present when using this film. If the instrument was not calibrated using mylar, a systematic offset in calcium could be reported.

In humans, calcium is present in the form of hydroxyapatite in our bones. Calcium forms an important structural fiber in plants<sup>47</sup>. When you get a bruised or bitter fruit, it is a deficiency in calcium that led to the weakness. It is structurally important to mollusks and protists, but in a different chemical form, CaCO<sub>3</sub>. When these animals die en masse in the ocean, their calcium carbonate shells deposit over each other for hundreds of thousands of years, forming limestone bed formations. Should these limestone deposits be subjected to heat and pressure beneath the Earth, they will form marble. Michelangelo's David is one-part artists' vision, another part ancient ocean, and a third part from the heat of the Earth.

Calcium can be found in diverse forms, including CaO, CaCO<sub>3</sub>, CaSO<sub>4</sub>, and CaPO<sub>5</sub>, among many others. It is common in laboratory ICP and XRF systems to report Ca as CaO, regardless of what true chemical form Ca is in. This is misleading at best, and invalid at worst. It is a reminder that convention is not always based on sound scientific practice.

Calcium can be found prominent with phosphorus in bone black. However, many grounds use gypsum (CaSO<sub>4</sub>), both calcium and sulfur may appear in these cases. Many reversible restorations also use CaSO<sub>4</sub> to form a base, as such a clear signal for both calcium and sulfur may indicate just that.

In the analysis of pigments, calcium can be a part of the ground (i.e. gesso) used on the canvas. It can also be used in restoration - when UV light is used to identify portions of restoration on a mounted painting, it is often calcium-based compounds that fluoresce. The

pigments bone black and ivory black all are burned, ground up bone. As such, the association of calcium with phosphorus is a significant identifier for these pigments. That said, the escape peak of calcium is near phosphorus (3.69 keV - 1.74 keV = 1.95 keV), while phosphorus has its K-alpha line at 2.01 keV. Because of this, it is necessary to confirm that the highest point of the peak is higher than 2 keV to prevent misidentification. Fortunately, software is increasingly better at auto-removing escape peaks.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ca	3.69 keV	K-alpha	4.04 keV	0.147	4.15 %	Intercepts: K K-
	4.01 keV	K-beta				alpha Slopes: K K-alpha
К	3.59 keV	K-beta Overlap	3.61 keV	0.132	2.09%	K co-occurs with Ca in most contexts, this should be an expected overlap
Sb	3.60 keV	L-alpha Overlap	4.13 keV	0.069	200 ppb	Can be common in painting or metals
Sn	3.66 keV keV	L-beta Overlap	4.16 keV	0.069	2.3 ppm	Can be common in painting or metals
Fe	6.39 keV	K-alpha Excitatio n	7.11 keV	0.351	5.63 %	High Fe presence in many materials excites Ca.
Cr	3.7 keV	K-alpha Escape Peak	5.99 keV	0.287	102 ppm	Unlikely to influence Ca, but could be a factor in some pigments, metals, and ores.

Table 20: Observable emission lines for calcium and its most common fluorescence interactions.

## 2.13 Scandium, Sc (21)

The analysis of scandium directly using XRF is close to impossible for most purposes. First, it typically exists in single digit ppm concentrations, far below the limits of detection for most XRF geometries. Second, it overlaps with the K-beta line of calcium, a much more

ubiquitous element. As a result, scandium will almost never exhibit a fluorescence line, even

if it is present in moderate quantities.

Scandium, being a rare earth, will occur with other elements in that group in geologic materials. This usually means the most reliable indicators of Sc will be yttrium (Y), lanthanum (La), cerium (Ce), and neodymium (Nd), although all but yttrium are difficult to measure with XRF.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Sc	4.09 keV	K-alpha	4.49 keV	0.183	22 ppm	Intercepts: Ca K- alpha
	4.46 kev	K-beta				
Са	4.01 keV	K-beta Overlap	4.04 keV	0.147	4.15 %	Ca is much more common than Sc, and will almost always obscure its fluorescence.
I	3.93 keV	L-alpha Overlap	4.56 keV	0.079	450 ppb	I is less rare than Sc, but nonetheless would overlap with it.

Table 21: Observable emission lines for scandium and its most common fluorescence interactions.

# 2.14 Titanium, Ti (22)

Titanium wears many hats. To those new to XRF, its ubiquity will be quite surprising as titanium metal is marketed as new and rare. In reality titanium makes up 0.4% of the Earth's crust. While highly localized concentrations may be rare, it is a pigment that will be seen frequently in commercial paints that post-date 1920<sup>48</sup>, with the singular exception of a white pigment used in the pre-contact Andes region of South America<sup>49</sup>. The primary direct overlap that can cause confusion in the analysis of titanium is the presence of high quantities of barium, whose L-lines overlap with both the K-alpha and -beta peaks of titanium. Further complicating matters is the fact that the vanadium K-alpha line falls directly on top of the K-beta line of titanium. Situations in which all overlap each other are not rare.

Fortunately, the L-lines of barium fall just to the left of titanium. A skilled eye should be able to spot the difference. A second common overlap is the iron escape peak from silicon-based detectors.

The ubiquity of titanium underlies its importance in many fields. It is (arguably) most significant in the analysis of pigments. Titanium dioxide (TiO<sub>2</sub>) was commercially introduced around 1920; it forms a brilliant white that is purer than its predecessors zinc oxide (ZnO) and lead white (2PbCO<sub>3</sub>,Pb(OH)<sub>2</sub>). By adding a coloring element to it, you can turn it into just about any color imaginable. This has made it a popular pigment for paintings. The problem? Many paintings are forgeries made with the intent of being passed for the original. As such, its presence in the spectrum of any painting (presumably) older than 100 years means one of two things: either the painting has been modified/restored by an art conservator, or it is a recent creation. These are relevant from both a commercial perspective and from a restoration perspective. However, the ubiquity of natural TiO<sub>2</sub> in soil has caused confusion on this matter. Many historical pigments contain trace amounts of TiO<sub>2</sub>, particularly those which are not synthetic. The presence of this natural and expected titanium has led to the misidentification of historical paintings as modern.

Problems measuring titanium can also be caused by the presence of barium. Barium sulfate (BaSO<sub>4</sub>) can be common in the gesso used in the priming layers of paintings. Because it overlaps so heavily with titanium, barium can also be misidentified as titanium leading to misattribution and an incorrect appraisal of the history of an object. Great care should be taken in this area of the spectrum (4.5 - 5 keV). It is recommended to separately examine both the K-lines for titanium and L-lines for barium before making any important decisions regarding an object.

Titanium is also an important clay forming element, and it can be used along with magnesium, aluminum, silicon, potassium, calcium, and iron to help characterize a clay<sup>50</sup>. It

has a secondary role as a trace element in certain contexts. For example, limestone deposits typically have abundant CaCO<sub>3</sub> formed as plankton die and fall to the bottom of the ocean. These deposits can also include titanium typically deposited by silt transported by alluvial processes into deltas or via aeolian processes (e.g. air-blown sand). For example, the Amazon Basin watershed transports a tremendous quantity of titanium into the Atlantic Ocean, while at the same time aeolian dust originating from the Sahara Desert is deposited as well. These sources will contribute small amounts of titanium relative to calcium, but nonetheless are still detectable. In the Cariaco basin, the deposits of titanium are due to fluctuations from local rivers in Venezuela. The rivers discharge more silt when the Inter-Tropical convergence zone drifts south<sup>51</sup>. Titanium thus forms a proxy record for this effect; more titanium is seen when the ITCZ is low.

Titanium also forms many modern alloys; while it is a common element, its utility in metallurgy has only been realized in the past century<sup>52</sup>. It has the highest strength to density ratio of any other metal, and is often alloyed with other metals such as aluminum.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ti	4.50 keV	K-alpha	5.00 keV	0.218	5,560 ppm	Intercepts: Ba L-alpha
	4.93 keV	K-beta				
Ba	4.45 keV	L-alpha Overlap	5.25 keV	0.097	425 ppm	Can be common in painting and geologic samples
La	4.63 keV	L-alpha Overlap	5.48 keV	0.104	39 ppm	Not as common, but in some geologic deposits can be considered

Fe	4.7 keV	K-alpha Escape Peak	7.11 keV	0.351	5.63 %	As Fe is almost always one of the dominant elements in the spectrum, this effect can be challenging in silicon-based detectors
						detectors

Table 22: Observable emission lines for titanium and its most common fluorescence interactions.

## 2.15 Vanadium, V (23)

Vanadium overlaps completely with the K-beta line of the much more common titanium, and as a result it can rarely be positively identified visually. It also overlaps with barium L-beta, which again is a more common element. While a calibration can adjust for these factors, deconvolution will be needed for any spectral analysis in most cases.

Vanadium can also form an alloy, but generally as a trace or minor component. Vanadium can be a tracer as well. It indicates reduction-oxidization reactions in anoxic environments<sup>53</sup>, making it useful to petroleum exploration. Some crystals can also be high in vanadium as well.

Vanadium's primary use today is as an additive to steel, most often in steels which operate at high speeds. Vanadium increases the tensile strength of steel while simultaneously reducing its weight<sup>54</sup>. For this reason, vanadium's first major production use was in the metal chassis of the Model T Ford<sup>55</sup>. Vanadium is also used in aluminum alloys in jet engines.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
V	4.94 keV	K-alpha	5.47 keV	0.253	120 ppm	Intercepts: Ti K-alpha
	5.43 keV	K-beta				

Ti	4.93 keV	K-beta overlap	5.00 keV	0.218	5,560 ppm	Ti will almost always obscure the V K-alpha line
Ba	4.83 keV	L-beta overlap	5.62 keV	0.096	425 ppm	Ba will likely obscure the V K-alpha line if present.
La	5.04 keV	L-beta overlap	5.89 keV	0.103	39 ppm	La, in REE-bearing geologic materials, can obscure the V K-alpha line

Table 23: Observable emission lines for vanadium and its most common fluorescence interactions.

### 2.16 Chromium, Cr (24)

Chromium lies in an area of the spectrum relatively clear of overlapping lines. In principle chromium is easy to measure. This is certainly the case in metals, but in geologic samples the concentrations are so low that it is often difficult to get a well resolved K-alpha line even with lots of analysis time. As a result, chromium is one of the lowest-Z elements to require some kind of filtration of the spectra to improve its signal-to-noise ratio.

Chromium, like titanium, is present in most soils, but in far smaller amounts. Like vanadium, it can indicate reduction-oxidization reactions in the deep ocean<sup>56</sup>. As a metal, it has tremendous value. When alloyed with iron, it helps make stainless steel<sup>57</sup>. As an element in the soil, it forms a dangerous toxin. This property of chromium makes it (almost) universally used as a treatment for leather. When combined with lead, chromium can make a brilliant yellow pigment. As a stand-alone oxide, it can form a brilliant green. The name of the element comes from the Greek  $\chi \rho \omega \mu \alpha$ , as its color properties were immediately apparent when the element was first discovered in 1797<sup>58</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Cr	5.40 keV	K-alpha	5.99 keV	0.287	102 ppm	Intercepts: V K-alpha
	5.95 keV	K-beta				

V	5.43 keV	K-beta Overlap	5.47 keV	0.253	120 ppm	
Ba	5.53 keV	L- gamma Overlap	5.62 keV	0.096	425 ppm	The overlap is the Lγ1 line.
La	5.38 keV	L-beta Overlap	5.48 keV	0.104	39 ppm	La, in REE-bearing geologic materials, can obscure the V K- alpha line
Pm	5.41 keV	L-alpha	5.96 keV	0.118		Pm is rare and unlikely to be detectable.

Table 24: Observable emission lines for chromium and its most common fluorescence interactions.

#### 2.17 Manganese, Mn (25)

Manganese has very few spectral overlaps, though its proximity to the ubiquitous Iron K-alpha peak can sometimes obscure it. The elements which do overlap with manganese tend to be rare, whereas it is abundant. As a result, manganese is one of the easier elements to analyze both qualitatively and quantitatively. Though it is important to note that its close proximity to Fe can amplify and also obscure Mn's contribution to the spectrum. As Mn and Fe can often correlate in their abundance in some geologic deposits, this effect should be important to note.

Manganese is almost always found with iron, with the exception of modern processes which can purge Mn out to undetectable levels. The most common manganese oxide mineral forms have black or purple hues when ground down into fine powders, which were used as colorants in some of the earliest glass manufactured<sup>59</sup>. The Ulubrun shipwreck, which occurred 3,000 years ago and was excavated by the Institute for Nautical Archaeology, managed to pull up purple glass ingots with the diameter of a foot from the bottom of the Mediterranean<sup>60</sup>. This high-valued material was traded over long distances. Somewhat less glamorously, manganese is common in mineral pigments used around the world<sup>61</sup>. Manganese oxides, along with iron oxides, are the main mineral pigments used to create some of the oldest cave paintings in Europe and South East Asia, dating to the Late Pleistocene, some over 25 thousand years ago<sup>62</sup>.

Manganese cations (Mn<sup>2+</sup>) precipitate out of well-oxygenated waters. As a result, manganese can be a proxy for oxygen levels of water systems<sup>63</sup>, although it usually needs to be normalized to a more ubiquitous element like iron as a control for proper interpretation<sup>64</sup>. Manganese oxide reactions make it useful in lithium batteries<sup>65</sup>.

Manganese is a common micronutrient for plants, though it may not always be essential it can make a critical difference in the health of the plant<sup>66</sup>. While good for plants, these elements can be bad for those companies using plants for biofuel<sup>67</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Mn	5.89 keV	K-alpha	6.54 keV	0.391	950 ppm	Intercepts: Cr K- alpha, Fe K-alpha
	6.49 keV	K-beta				
Cr	5.95 keV	K-beta Overlap	5.99 keV	0.287	102 ppm	Cr K-beta overlaps strongly with Mn K- alpha, but this is normally not
Fe	6.39 keV	K-alpha Overlap	7.11 keV	0.351	5.63 %	Fe, which is more abundant, can overlap if in sufficient quantities.
Nd	5.83 keV	L-beta Overlap	7.13 keV	0.064	38 ppm	Some Nd lines overlap with Mn
La	5.79 keV	L- gamma Overlap	5.89 keV	0.104	39 ppm	La slightly overlaps in it's L-emissions, but is unlikely to be in higher concentrations than Mn.

Table 25: Observable emission lines for manganese and its most common fluorescence interactions.

# 2.18 Iron, Fe (26)

There is no element more ubiquitous than iron when it comes to XRF analysis. It is both in an ideal portion of the spectrum and abundance just about everywhere. Iron is the fourth most common element on Earth. The only challenge, and it is a minor one, is that the K-alpha peak

of iron overlaps with the K-beta of manganese. However, because iron is so common this is rarely a problem. Some rocks, such as jade, have so little iron that the contribution of manganese to the peak should not be taken for granted.

Iron forms one of the most important elements to civilization, life, and geology. It takes many diverse forms. The core of our Earth is filled with iron, and its hot metallic churn generates a powerful magnetic field around the Earth shielding us from the majority of dangerous cosmic radiation. Iron forms an essential nutrient for life, whether you are a plant or a human. Iron forms the metal that makes most tools, vehicles, and machines possible. The earliest expressions of art were with red and yellow iron oxide pigments made from ground ochre 100,000 years ago<sup>68</sup>. Critically, the versatility of iron comes from its complex mixtures with other elements. It is formed from supernova explosions, when unstable nickel 56 is produced and quickly decays into iron<sup>69</sup>.

Iron tools first emerged about 3,000 years ago, however they were not common. Many early tools were simply meteorites found in the Saharan desert and hammered into shape<sup>70</sup>. It wasn't until the very Late Bronze Age that iron tools of any kind emerge, and not until the aptly named Iron Age that their use becomes widespread<sup>71</sup>. It was most frequently alloyed with carbon to increase its strength. In recent times, elements such as chromium, nickel, and molybdenum<sup>72</sup> have been added to give it greater strength and durability.

Iron is an essential nutrient to many plants. For animals, it is essential for its oxidization properties<sup>73</sup> – the same process that led your bike to rust is the same one carrying oxygen from lungs in the blood stream<sup>74</sup>. In some agricultural applications, iron in ash can be used to estimate the previous plant biomass prior to burning.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Fe	6.39 keV	K-alpha	7.11 keV	0.351	5.63 %	Intercepts: Mn K- alpha

	7.06 keV	K-beta				
Mn	6.49 keV	K-beta Overlap	6.54 keV	0.391	950 ppm	Mn K-beta overlaps with Fe K-alpha, but Fe K-alpha tends to be more abundant. However, the two elements are often found together.
ТЬ	6.24 keV	L-alpha Overlap	7.51 keV	0.164	1.2 ppm	Tb L-lines overlap with both Fe K-alpha and K-beta, but are much less common.
Dy	6.46 keV	L-alpha Overlap	7.79	0.174	5.2 ppm	Dy L-lines overlap with both Fe K-alpha and K-beta, but are much less common.

Table 26: Observable emission lines for iron and its most common fluorescence interactions.

## 2.19 Cobalt, Co (27)

Cobalt shares a significant overlap with Iron's K-beta peak. As Fe is an order more common in Earth's crust, the cobalt peak is often buried and difficult to measure either qualitatively or quantitatively. A calibration or deconvolution can often pull out its contribution to the K-beta peak of iron, allowing detection to the ppm level.

Cobalt gets its name from the German word kobald, meaning goblin. This comes from its occurrence in highly toxic ores<sup>75</sup>. Cobalt has its oldest use as a blue and/or black pigment which is frequently found in historical paintings<sup>76</sup>, glazes<sup>77</sup>, and glass<sup>78</sup>. However, most of the properties of cobalt were mistakenly attributed to bismuth throughout much of the pre-modern era<sup>79</sup>. Its discovery as a unique element in the early 18th century changed that, and also changed the history of the study of elements - cobalt was the first scientific discovery of an element<sup>80</sup>, but not the last.

In the modern era cobalt also makes an excellent alloy for jet engines and wind turbines due to its strength and resistance to wear<sup>81</sup>. It is also a key component in lithium ion batteries<sup>82</sup>,

which has led to exploration of miners in developing countries and cobalt being listed as a conflict mineral<sup>83</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Со	6.91 keV	K-alpha	7.71 keV	0.382	25 ppm	Intercepts: Fe K-alpha Slopes: Fe K-alpha
	7.65 keV	K-beta				
Fe	7.06 keV	K-beta Overlap	7.11 keV	0.351	5.63 %	Fe K-beta dominates Co K-alpha in almost all cases
Zn	6.9 keV	Escape Peak	9.66 keV	0.469	70 ppm	In brass alloys measured with an Is- based detector, the high concentration of Zn can leave an escape peak.
Er	6.91 keV	L-alpha Overlap	8.36 keV	0.192	3.5 ppm	Er L lines overlap with Co, but are unlikely to be in high enough concentrations to be detectable.
Eu	6.84 keV	L-beta Overlap	6.98 keV	0.147	2 ppm	Eu L lines overlap with Co, but are unlikely to be in high enough concentrations to be detectable.

Table 27: Observable emission lines for cobalt and its most common fluorescence interactions.

## 2.20 Nickel, Ni (28)

Nickel is relatively isolated in the spectrum with few probable overlaps. As a result, it should be easy to measure. In practice, however, its use as a component in the construction of XRF systems makes it significantly more difficult to measure. The chief offender is beryllium windows on detectors. These necessitate Ni-based detector cans due to their temperature expansion. Other detector windows, such as graphene-based ones, will avoid this potential contaminant in the spectrum.

Nickel is one of the most common elements around today, and one may be forgiven for thinking it was as common in the past. In a geologic sense it was. Nickel, along with iron, forms the core of the Earth<sup>84</sup>, and is an abundant trace metal. Humans however did not begin using it in large amounts until after its discovery in the 18th century<sup>85</sup>. There is one exception: early instances of iron use were scattered throughout the Bronze Age when meteorites were used as a source of iron<sup>86</sup>. Many of these meteorites contained up to 10% Ni by weight.

Nickel is used in many steel and copper alloys today due to its elasticity and resistance to corrosion<sup>87</sup>. It alloys very well with precious metals and thus can be found with them. Most notably, when alloyed with gold it can form white gold.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ni	7.46 keV	K- alpha	8.33 keV	0.412	84 ppm	Intercepts: Co K- alpha
	8.27 keV	K-beta				
Со	7.65 keV	K-beta Overla p	7.71 keV	0.382	25 ppm	Co is less likely to be present than Ni in most materials, but nonetheless this can be a useful correction for metal calibrations.
Tb	7.36 keV	L-beta Overla p	7.51 keV	0.164	1.2 ppm	Tb is unlikely to be confused with Ni.

Table 28: Observable emission lines for nickel and its most common fluorescence interactions.

## 2.21 Copper, Cu (29)

Copper, like nickel, is relatively easy to measure with XRF. There are few overlapping lines and when properly filtered, low concentrations of copper can be detected. Unfortunately, like nickel, copper is likely to be used as a component in the construction of many XRF instruments, and thus can be present as a contaminant in the spectrum.

Copper is the oldest known metal regularly used by human societies<sup>88</sup>. It was discovered independently multiple times in Eurasia<sup>89</sup>, the Americas<sup>90</sup>, and Africa<sup>91</sup>. Copper was alloyed with other metals (arsenic, lead, tin, zinc, etc.) to create different kinds of tools<sup>92</sup>. Its use stretches back thousands of years, although early forms were all almost entirely pure elemental copper and later as alloys. The Bronze Age saw the use of copper alloys, most famously between copper and tin to form a strong bronze alloy<sup>93</sup>. However, there were many alternate alloys that were confused with bronze (then and now), including many copper-lead alloys. In the Americas, the use of metallic copper occurred later, the majority of which was in the past 2,000 years. In Peru, some populations made arsenical copper alloys<sup>94</sup> while others experimented with copper-lead mixtures<sup>95</sup>. Andean Highland metallurgy features arguably the only development of tin bronze alloys outside Eurasia<sup>96</sup>.

In pigments, copper tends to be associated with green colors<sup>97</sup>. Most commonly this is malachite<sup>98</sup>, named after a type of copper ore. However, there are many different green pigments which were historically used, including verdigris green, a copper carbonate and chloride<sup>99</sup>. Copper is also present in Egyptian Blue<sup>100</sup>, a pigment which was in use for thousands of years in ancient Egypt and not-as-ancient Rome, though it is no longer commonly used.

Modern applications of copper do not differ as much from ancient applications as one might imagine. It is still used in metal alloys for its flexibility and strength in both utilitarian and ornamental alloys<sup>101</sup>. One use that would not have been anticipated is electricity<sup>102</sup>. Copper's excellent conductivity leads to its use in both wiring and motors.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Cu	8.03 keV	K-alpha	8.98 keV	0.441	60 ppm	Intercepts: Ni K-alpha
	8.91 keV	K-beta				

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Ni	8.26 keV	K-beta Overlap	8.33 keV	0.412	84 ppm	Ni K-beta overlap should not often be a serious obstacle to measuring Cu, but in some metals it should be considered.
Hf	7.90 keV	L-alpha Overlap	9.56 keV	0.242	3 ppm	Hf is unlikely to be present in high enough quantities to interfere with Cu, but if it is, the leading indicator will be a large Zr signal at ~15 keV, as Hf is almost without exception always bound to Zr.
Та	8.15 keV	L-alpha Overlap	9.88 keV	0.243	2 ppm	Ta is very unlikely to exist in quantities large enough to contribute to this fluorescence.
Ir	8.04 keV	L-l Overlap	11.22 keV	0.294	1 ppb	This overlap is highly unlikely due to the rarity of Ir.

Table 29: Observable emission lines for copper and its most common fluorescence interactions.

## 2.22 Zinc, Zn (30)

Zinc is similar to both copper and nickel in that it appears in a relatively clear portion of the spectrum, and in that it is often used as a component in the manufacture of devices containing both elements. These three elements are often visible, but the highest signal-to-noise ratio can be attained by using a 25  $\mu$ m titanium and 300  $\mu$ m aluminum filter. This will cause the spectrum to reach its minima at about 9.5 keV.

Zinc represents the middle point between nickel and copper. While nickel is one of the newest metals and copper the oldest, zinc is the quintessential medieval metal<sup>103</sup>. While produced in India since the Bronze Age<sup>104</sup>, it didn't see wide use in Europe until the Iron Age<sup>105</sup>, and saw continued use throughout the medieval and modern period. It was most typically alloyed with copper to form a type of brass, although the precise ratio varied by period and by culture. As

brass was less likely to tarnish, it formed the base metal for Astrolabes<sup>106</sup> for both Arabic and European populations.

Geologically, these three metals are common, with copper and zinc considerably more abundant than Ni. They are common enough to not be very useful for sourcing, although such a broad statement may not hold true everywhere. Copper gives turquoise its blue-green color<sup>107</sup>.

Zinc oxide, ZnO, while known since 1780 AD, wasn't widely available until after 1840<sup>108</sup>, and thus is a key element in identifying the time of either a painting or restoration. ZnO forms a white color, and displaced lead white as it was less poisonous and accessible. ZnO could easily change color based on dyes, and thus ushered in a new era of painting.

Zinc is also an essential	micronutrient for	plants whose absence	can inhibit	photosynthesis <sup>109</sup> .

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Zn	8.62 keV	K-alpha	9.66 keV	0.469	70 ppm	Intercepts: Cu K- beta
	9.57 keV	K-beta				
Cu	8.91 keV	K-beta Overlap	8.98 keV	0.441	60 ppm	Cu K-beta can overlap with Zn K- alpha
Re	8.59 keV	L-alpha Overlap	10.54 keV	0.268	0.7 ppb	Re overlaps heavily with Zn, but is very rare and shouldn't be an influence on most analyses
Au	8.49 keV	L-l Overlap	13.73 keV	0.334	4 ppb	High amounts of Au can cause an L-peak to overlap heavily with Zn

Table 30: Observable emission lines for zinc and its most common fluorescence interactions.

## 2.23 Gallium, Ga (31)

Gallium's ease of measurement contrasts with the rarity of getting a well-defined peak in most materials, although it is easiest to see when present in aluminum metals. More often, the K-line for gallium will be confused for another element, such as an L-gamma peak of Pb. In many calibrations, high gallium is an indicator that something is amiss.

Gallium has the same number of outer valence electrons as aluminum (3). As a result, it will follow with AI almost universally, regardless if AI is present as an oxide in soil, in an alloy, or as a gem. Gallium for this reason can be used as a tracer element to identify geochemical provenance, although it is not as useful as most others.

Gallium's primary, and almost exclusive, use is as a semiconductor<sup>110</sup> with applications in integrated circuits. It can also be used in photovoltaic materials such as solar panels<sup>111</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ga	9.23 keV 10.27 keV	K-alpha K-beta	10.37 keV	0.497	19 ppm	Intercepts: Zn K- alpha, Pb L-alpha
Zn	9.57 keV	K-beta Overlap	9.66 keV	0.469	70 ppm	While Zn is more common than Ga, in high enough concentrations its K- beta emission will overlap.
Pb	9.19 keV	L-l Overlap	15.2 keV	0.373	14 ppm	High amounts of Pb can cause an L-peak to overlap heavily with Ga
Ir	9.18 keV	L-alpha Overlap	11.215 keV	0.294	1 ppb	Ir is unlikely to be present in high enough concentrations to be confused with Ga.

Hf	9.16 keV	L-beta Overlap	11.27 keV	0.130	3 ppm	Hf is unlikely to be present in high enough quantities to interfere with Ga, but if it is, the leading indicator will be a large Zr signal at ~15 keV, as Hf is almost without exception always
						bound to Zr.

Table 31: Observable emission lines for gallium and its most common fluorescence interactions.

# 2.24 Germanium, Ge (32)

Typically, the parameters that are best for copper and zinc are also the best for gallium and germanium with respect to their K-alpha peaks. The two elements do not suffer from many overlaps with other elements, so they should be relatively easy to spot provided you stumble across a deposit.

Germanium has four outer valence electrons, giving it similar properties to carbon, silicon, tin, and lead. Germanium is as versatile as all of these, but far rarer. As a result, it is prized for many applications. Germanium can form a detector and semiconductor much like silicon for x-rays, but be useful for a greater energy range given its greater density, including gamma rays<sup>112</sup>. This makes it important for computing applications in lower temperatures<sup>113</sup>.

Finding germanium when analyzing samples is unlikely, but if you do it will likely happen measuring geologic deposits of plant material such as coal or petrified wood<sup>114</sup>. The concentration of cellulose seems to attract germanium over long periods of time.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ge	9.86 keV	K-alpha	11.10 keV	0.523	1.5 ppm	Intercepts: Zn K-
	10.98 keV	K-beta				alpha

Zn	9.57 keV	K-alpha	9.66 keV	0.469	70 ppm	Zn is much more common than Ge, and a large enough K-beta can overwhelm Ge K- alpha.
W	9.82 keV	L-beta Overlap	12.10 keV	0.147	1.25 ppm	W L-beta can be confused with Ge K-alpha
Au	9.71 keV	L-alpha Overlap	11.92 keV	0.320	4 ppb	Au L-alpha can be confused with Ge K-alpha
Cr	~9.90 keV	K-alpha Sum Peak	5.99 keV	0.286	102 ppm	In alloys, pigments, and ores, the Cr sum peak could be an issue.

Table 32: Observable emission lines for germanium and its most common fluorescence interactions.

#### 2.25 Arsenic, As (33)

Arsenic is, in isolation, quite easy to measure. But it has one of the most challenging overlaps in XRF. The K-alpha line of arsenic overlaps almost completely with the L-alpha line of lead. This is one of the most common sources of confusion for XRF users, both in qualitative and quantitative domains. Confirmation of arsenic generally requires identifying the K-beta peak. Low-level detection is possible with proper filtration.

Due to its highly toxic nature, the presence of arsenic is uncommon in most human-made objects. Its first major application was in copper alloys, where arsenic dramatically strengthened copper. Arsenical bronze can be found in both the Old<sup>115</sup> and New<sup>116</sup> Worlds. Arsenic also strengthens glass<sup>117</sup>, and as such can be a trace or even minor component, depending on how strong the glass needs to be.

Arsenic is not uncommon in pigments; its most famous use is in Scheele's Green developed in the late 18th century<sup>118</sup>, which saw widespread use<sup>119</sup>. However, copper arsenate pigments in general were common, and have been found, among other places, in the preserved wall paintings in Pompei<sup>120</sup>. Arsenic sulfide pigments are also common, realgar is an orange-red pigment which includes arsenic, and orpiment a yellow pigment<sup>121</sup>.

Arsenic can be a powerful toxin in environments, and tends to indicate depositional settings

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
As	10.51 keV 11.73 keV	K-alpha K-beta	11.87 keV	0.549	1.8 ppm	Intercepts: Pb L-beta Slopes: Pb L-beta
Pb	10.55 keV	L-alpha Overlap	13.04 keV	0.360	14 ppm	Pb L-alpha overlaps with As K-alpha, and other peaks must be used to clarify what is in the sample

where oxygen was not present in high quantities<sup>122</sup>.

Table 33: Observable emission lines for arsenic and its most common fluorescence interactions.

## 2.26 Selenium, Se (34)

Selenium is one of the first elements in the periodic table to be almost completely clear of any overlapping element lines. Unfortunately, its rarity prevents many from taking advantage of the clarity of its measurement. Seeing it will almost always require significant filtration of the X-ray beam.

Selenium appears in some modern art pieces as an element alongside the use of titanium dioxide and zinc oxide pigments. It can also be present as a trace element in ancient bronze alloys. Selenium is used commercially as a decolorizing agent in glasses<sup>123</sup>, though it can also be used to give a slight pink complexion.

Selenium has the same number of outer valence electrons as oxygen and sulfur, and it shares some of their properties. However, it is only a fraction as common as the other two elements. For this reason, it can be a significant toxin to plants<sup>124</sup> and animals<sup>125</sup> in even low quantities, although it is essential in very small quantities for the latter<sup>126</sup>. Efforts to qualitatively identify it even in the low ppm can identify potential hazards. This can be useful in applications ranging from home gardening to habitat restoration.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Se	11.18 keV	K-alpha	12.66 keV	0.574	50 ppb	
	12.50 keV	K-beta				
Pt	11.07 keV	L-beta Overlap	13.27 keV	0.321	5 ppb	Pt L-beta overlaps with Se K-alpha, but will also be much less common.
Au	11.20 keV	L-beta Overlap	14.35 keV	0.107	4 ppb	Au L-beta lines can overlap with Se K- alpha, but are unlikely to be confused
Th	11.12 keV	L-l Overlap	16.30 keV	0.463	9.6 ppm	Th is unlikely to be in high enough concentrations to cause this overlap, but the possibility should be in mind.

Table 34: Observable emission lines for selenium and its most common fluorescence interactions.

#### 2.27 Bromine, Br (35)

Bromine, like selenium, is relatively free from overlaps. However, the L-beta line of mercury will overlap with it, so verification with the K-beta peak will be important. Bromine is almost entirely absent from all available calibrations. For this reason, it is often neglected in XRF analysis.

Bromine is a relatively common halogen, although its presence can indicate either a former saline presence or volcanic ash in normal soil in geologic deposits<sup>127</sup>. At archaeological sites, bromine is attracted to silver and builds up over time if it is available in the soil<sup>128</sup>. In some cases, this effect can be used to verify that a silver object was buried for a long period of time.

Interestingly, bromine can be an indicator of biological productivity in lacustrine and marine ecosystems<sup>129</sup>. It is unclear why, but bromine aggregation in sediments can indicate a previously productive environment<sup>130</sup>.

Today, bromine is an effective and widely used flame retardant<sup>131</sup>, albeit with unsubstantiated concerns regarding toxicity<sup>132</sup>. Bromine can be found in your clothes, the furniture you sit on, and many other cloths and plastics. It was previously used as a gasoline additive<sup>133</sup> and as a pesticide<sup>134</sup> although both have been phased out due to environmental concerns.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Br	11.88 keV	K-alpha	13.47 keV	0.598	2.4 ppm	
	13.29 keV	K-beta				
Hg	11.82 keV	L-beta Overlap	14.21 keV	0.333	85 ppb	Hg L-beta overlaps with Br K-alpha, and thus Hg L-alpha should be checked.
TI	11.93 keV	L-beta Overlap	15.35 keV	0.360	850 ppb	Tl L-beta lines can also overlap with Br, but are unlikely to be a problem.
U	11.62 keV	L-1 Overlap	17.17 keV	0.489	2.7 ppm	This overlap should not be discounted should U be present in high quantities.

Table 35: Observable emission lines for bromine and its most common fluorescence interactions.

#### 2.28 Krypton, Kr (36)

Krypton is unlikely to be measured by a handheld XRF, except in cases where the gas is in a low-density container (such as a plastic bag) or flowing through the instrument. The key overlaps of concern are the lead L-beta and selenium K-beta lines, but these are unlikely given the limitations of measuring Kr.

Krypton, like neon, can be used as an ionized gas to produce lamps<sup>135</sup>. Krypton fluoride lasers are used in energy research<sup>136</sup>. It can be used in magnetic resonance imaging. The

radioisotope <sup>85</sup>Kr can indicate evidence of nuclear activity, and has been used to remotely identify the development of nuclear weapons<sup>137</sup>. The decay of that isotope can also be a dating system for groundwater<sup>138</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Kr	12.60 keV 14.11 keV	K-alpha K-beta	14.33 keV	0.621		
Pb	12.62 keV	L-beta Overlap	13.04 keV	0.360	14 ppm	Pb L-beta completely overlaps with Kr K- alpha
Se	12.50 keV	K-beta Overlap	12.66 keV	0.574	50 ppb	Sr K-beta can also overlap with Kr K- alpha

Table 36: Observable emission lines for krypton and its most common fluorescence interactions.

#### 2.29 Rubidium, Rb (37)

For most XRF instruments (those using a rhodium or silver tube), rubidium will occur in an area of maximum excitation potential and, with the proper filter, minimal background interference. As a result, rubidium and its neighbors in the spectrum enjoy low detection limits.

For most XRF users, rubidium is a trace element useful in determining provenance for ceramics<sup>139</sup>, obsidian<sup>140</sup>, and sediments<sup>141</sup>. To physicists, rubidium is a playground element. The isotope <sup>87</sup>Rb at near absolute zero temperature begins to behave like a boson<sup>142</sup> (just like a photon) and stops respecting space and time, earning experimenters a Nobel prize in 2001. The isotope is also slightly radioactive and decays into <sup>87</sup>Sr slowly over time<sup>143</sup>. This can be used to roughly date geologic materials<sup>144</sup> and also forms the basis of strontium radiogenic isotope ratio sourcing<sup>145</sup> and tracing<sup>146</sup>. Rubidium has another interesting use. It is

the basis for atomic clocks due to its hyperfine structure<sup>147</sup>, which in turn supports the global satellite communications<sup>148</sup>.

Rubidium has properties quite similar to potassium, and tends to be found in nature with it<sup>149</sup>. For example, in your morning coffee and the occasional banana. Even though the element itself is more common than copper, it is rarely found in ores and is harder to extract, most of it is produced as a byproduct of lithium mining<sup>150</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Rb	13.34 keV	K-alpha	15.20 keV	0.643	90 ppm	
	14.96 keV	K-beta				
Ро	13.34 keV	L-beta Overlap	13.81 keV	0.386		Polonium's L-beta line overlaps exactly over Rb K-alpha, however this will almost certainly not be observed by most users.
Au	13.38 keV	L- gamma Overlap	13.73 keV	0.334	4 ppb	Au L-gamma can also overlap with Rb K-alpha, but other gold peaks will be more pronounced
U	13.61 keV	L-alpha overlap	17.17 keV	0.489	2.7 ppm	U L-alpha is unlikely to be a common problem for Rb K-alpha

Table 37: Observable emission lines for rubidium and its most common fluorescence interactions.

## 2.30 Strontium, Sr (38)

Strontium, like rubidium, is easy to measure with the most common (rhodium and silver) anode materials, again with proper filtration.

Strontium follows calcium almost everywhere it goes<sup>151</sup>, from sea shells to plaster to bones. The isotopes of strontium found in bone and plants can be used as a provenance indicator<sup>152</sup>. Like trace elements rubidium, zirconium, and others, it can be used to determine provenance for some geologic materials<sup>153</sup>. However, while it is reliable in obsidian it is unreliable in most other contexts. In groundwater, it is mobile like calcium, virtually guaranteeing heterogeneous dispersion in chert. In ceramics, the strontium in the clay may be useful, but ceramics are often tempered with sea shells, sand, organics, and other sediments. The surfaces of vessels can be either glazed, slipped, or painted which make accurate measurement even more difficult without the destructive, mechanical removal of exterior surfaces. In all of these cases, strontium will be the trace element most affected, and this should be considered when attempting to determine sources. Strontium in some marine organisms can be a paleothermometer<sup>154</sup>.

Strontium has limited uses today. In cathode monitors (old computer and tv screens) it was used to block X-rays from being emitted<sup>155</sup>, which incidentally was the real reason you shouldn't have sat so close to the (cathode ray tube) TV.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Sr	14.1 keV	K-alpha	16.11 keV	0.665	370 ppm	
	15.84 keV	K-beta				
Pu	14.28 keV	L-alpha Overlap	06 keV	0.514		Plutonium's L- alpha lines will overlap with Sr K- alpha, however this is highly unlikely to occur for almost all XRF users.
Kr	14.11 keV	K-beta Overlap	14.33 keV	0.621		As Kr is a gas, it is unlikely to overlap with Sr K-alpha

Со	~13.80	K-alpha	7.71 keV	0.382	25 ppm	In alloys, ores, and
	keV	Sum				some pigments the
		Peak				sum peak of Co
						could overlap.

Table 38: Observable emission lines for strontium and its most common fluorescence interactions.

#### 2.31 Yttrium, Y (39)

Yttrium, like rubidium, is likely to be maximally excited by the rhodium and silver anode materials with good filtration. Unfortunately, it also overlaps with the K-beta line for the more common rubidium. As a result, qualitative and quantitative analysis of yttrium need to be considered carefully.

This rare earth element behaves like its lanthanide counterparts, but unlike them it is readily visible in most handheld XRF units. As the name would apply, it is a trace element that can be used for sourcing obsidian<sup>156</sup>, ceramics<sup>157</sup>, sediments<sup>158</sup>, and other volcanic materials<sup>159</sup>. It is also intentionally added to many consumer products such as glass, plastic, and currency for the same reason. Almost without exception, yttrium indicates the presence of other rare earth elements. It can be a valuable tracer element for this reason.

Yttrium fluoresces red with phosphorous<sup>160</sup>, and is used in cathode ray monitors and LED lights. Interestingly, lunar rocks recovered from the Apollo space missions found a surprising amount of vttrium<sup>161</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Y	14.88 keV 16.74 keV	K-alpha K-beta	17.04 keV	0.685	33 ppm	Intercepts: Rb K- alpha
Rb	14.96 keV	K-beta Overlap	15.20 keV	0.643	90 ppm	Rb K-beta overlaps completely with Y K-alpha, and is more common. As a result, overlap will be almost universal

Ni	~15.00 keV	K-alpha Sum Peak	8.33 keV	0.412	84 ppm	In alloys or ores, the Ni sum peak could interfere with Y.

Table 39: Observable emission lines for zirconium and its most common fluorescence interactions.

### 2.32 Zirconium, Zr (40)

Zirconium, like rubidium, strontium, and yttrium, is in an area of the spectrum that is maximally excited by silver and rhodium anodes. It also overlaps with the strontium K-beta line, but with the exception of calcium-rich materials, zirconium is clearly resolved for both qualitative and quantitative analysis. The zirconium K-alpha line is easily identifiable, and only hampered by the common overlap with the strontium K-beta line. In minerals with lots of uranium or thorium, there is potential overlap.

Zirconium crystals are the quintessential survival compounds. The very last remnants of rocks from the creation (or shortly thereafter) of the Earth are preserved in the form of zircon (ZrO<sub>2</sub>) crystals<sup>162</sup>. Trace amounts of uranium in these crystals slowly decay to lead over 4.4 billion years<sup>163</sup>. As such, these crystals serve as the last surviving clocks from both the Earth and achondrite meteors.

The survival of zirconium is thanks to its fracture resistance, the same thing which makes it an attractive substitute for diamonds. In its metallic form, as zircaloy, its strength and corrosion resistance are used as cladding for nuclear fuel<sup>164</sup>. In its elemental form, zirconium is very susceptible to oxidization in an explosive manner<sup>165</sup>. Pouring water on a zirconium fire is akin to pouring gasoline over a campfire<sup>166</sup>. A far more benign use of zirconium is as a glaze on ceramics<sup>167</sup>, it pairs the strength and translucence of lead oxide with its harmlessness.

In its oxidized form, zirconium is not reactive. This forms the basis for its stability over billions of years. It also makes it an inert trace element, used for determining the source of obsidian<sup>168</sup>, ceramics<sup>169</sup>, and sediments<sup>170</sup>. For geochemical purposes, it can also be used to identify changes in sedimentation across a stratigraphic section<sup>171</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Zr	15.69 keV 17.67	K-alpha K-beta	17.99 keV	0.705	165 ppm	Intercepts: Sr K- alpha
	keV					
Sr	15.84 keV	K-beta Overlap	16.11 keV	0.665	370 ppm	Sr K-beta overlaps with Zr K-alpha, the strength of this overlaps is material- dependent. It should always be considered
Bi	15.58 keV	L- gamma Overlap	16.39 keV	0.387	8.5 ppb	Bi L-gamma is near Zr K-alpha, but is unlikely to be in large enough quantities to influence it.
Ро	15.74 keV	L- gamma Overlap	16.24 keV	0.401		Po L-gamma is near Zr K-alpha, but is highly unlikely to be in large enough quantities to influence it.

Table 40: Observable emission lines for zirconium and its most common fluorescence interactions.

#### 2.33 Niobium, Nb (41)

Niobium, like rubidium, strontium, yttrium and zirconium, is in an area of the spectrum that is likely to be excited by common anode materials like silver and rhodium. However, it overlaps with the K-beta line from yttrium, and tends to be present in small quantities. Thus, while it may be qualitatively visible, it can be difficult to quantify.

In geologic contests, niobium can be used as an indicator for provenance<sup>172</sup>, as it is used in obsidian<sup>173</sup>. Niobium can also be used as a tracer for ores to verify conflict minerals<sup>174</sup>.

When present at small concentrations in steel alloys, niobium can improve strength<sup>175</sup> and formability<sup>176</sup>. In larger concentrations, it can form superalloys<sup>177</sup> used in wind turbines and space shuttles. When used with germanium, tin, or titanium, niobium can be used to form superconducting magnets<sup>178</sup> such as those used in particle accelerators.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Nb	16.52 keV	K-alpha	97 keV	0.724	20 ppm	Intercepts: Y K- alpha, Cu K-alpha (if sum peak present)
	62 keV	K-beta				sum peux present)
Y	16.74 keV	K-beta Overlap	17.04 keV	0.685	33 ppm	Y K-beta overlaps completely with Nb K-alpha, and may be more common.
U	16.58 keV	L-beta Overlap	21.76 keV	0.176	2.7 ppm	U L-beta lines overlap with Nb K- alpha, and can be significant in some materials.
Cu	~16.10 keV	K-alpha Sum Peak	8.98 keV	0.441	60 ppm	In ores, pigments, or metals, the sum peak of Cu may obscure Nb.

Table 41: Observable emission lines for niobium and its most common fluorescence interactions.

#### 2.34 Molybdenum, Mo (42)

Molybdenum is readily excited by both silver and rhodium anodes, but unfortunately it falls close to the inelastic (Compton) peak of rhodium anode instruments which makes its detection much more difficult. Also making its quantification more difficult is its presence at low amounts in geologic materials. However, in metals, a lower Compton facilitates much easier detection. The K-alpha peak of molybdenum also falls in close proximity to the K-beta peak of Zr. While

it is relatively easy to distinguish the two, it nonetheless can present a challenge if qualitativeonly analysis is employed. Molybdenum is best detected using an aggressively thick filter such as one with 150  $\mu$ m copper, 25  $\mu$ m titanium, and 300  $\mu$ m aluminum. Although a thicker filter with 250  $\mu$ m copper, 25  $\mu$ m titanium, and 300  $\mu$ m aluminum can provide more sensitivity at the cost of excitation photons.

In geologic samples, molybdenum can be used as a key element in paleoenvironmental reconstruction when reduction-oxidization processes occur<sup>179</sup>. A key example is in ocean basins. MoO<sub>4</sub> is a common soluble oxide spread out in world oceans. However, in anoxic basins, the oxygen is lost due to downhill chemical reactions, and the Mo<sup>4-</sup> anion readily binds with sulfur. The result is MoS<sub>4</sub>, which is not soluble and precipitates out<sup>180</sup>. The anoxic conditions in which this reaction takes place can be the same as those in which carbon is preserved due to lack of bacteria. As a result, molybdenum can be used to indicate the extent of hydrocarbon deposits<sup>181</sup>. In deeper time, the same effect helps date the beginning of photosynthesis. The early Earth would have been unrecognizable to most people living today due to a lack of oxygen. The ocean waters from between four to two billion years ago were anoxic, and thus MoS<sub>4</sub> is common in their deposits<sup>182</sup>. The evolution of cyanobacteria and introduction of photosynthesis meant that oxygen was introduced to oceans, leading to MoO<sub>4</sub> which was soluble<sup>183</sup>. Molybdenum is thus a valuable tracer of biological activity. Fitting enough, molybdenum is an important micronutrient for almost all plants due to the same reduction-oxidization reactions, as it is critical for nitrogen fixation<sup>184</sup> and other functions. At the same time, without molybdenum in the water, photosynthetic algae lacked an essential nutrient<sup>185</sup>. This element is also essential to animals, though admittedly in trace quantities for the reduction of sulfur in the body<sup>186</sup>. Molybdenum is one of the many elements that our lives depend on, but it is rarely recognized for this.

Humans were late to recognize molybdenum. In the ancient world it was often confused with galena, or PbS<sup>187</sup>. Today, molybdenum is more frequently encountered in steel alloys as it

increases both strength and thermal resistance<sup>188</sup>. Molybdenum can substitute for platinum in

some alumina-supported catalysts<sup>189</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Мо	17.37 keV	K-alpha	20.00 keV	0.742	1.2 ppm	Intercepts: Zr K- alpha
	19.61 keV	K-beta				
Zr	17.67 keV	K-beta Overlap	17.99 keV	0.705	165 ppm	Zr K-beta doesn't quite overlap with Mo K-alpha, but low concentrations of Mo can make identification difficult.
U	17.22 keV	L-beta Overlap	20.95 keV	0.467	2.7 ppm	U L-beta lines overlap with Mo K- alpha, and can be significant in some materials.
Zn	~17.30 keV	K-alpha Sum Peak	9.66 keV	0.469	70 ppm	In pigments, ores, or alloys, the Zn sum peak could interfere with Mo.
Мо	2.29 keV 2.39 keV	L-alpha L-beta	2.52 keV	0.037	1.2 ppm	Intercepts: S K- alpha, Pb M-lines
S	2.31 keV	K-alpha Overlap	2.47 keV	0.071	350 ppm	S K-alpha will be more common than Mo L-alpha in most circumstances.
Pb	2.35 keV	M-Line Overlap	4.32 keV	0.001	14 ppm	Pb M lines will be more common than Mo L-alpha in most circumstances.

Table 42: Observable emission lines for molybdenum and its most common fluorescence interactions.

## 2.35 Technetium, Tc (43)

Detecting Tc will depend heavily on the context of the application – as the element is extremely rare naturally (and always radioactive) it will be hard to distinguish. In medical and some industrial applications it may produce a pronounced peak. When an Rh anode peak is used, it is likely that the Compton (inelastic scattering) peak will overwhelm any signal. Depending on the geometry, an Ag anode could produce similar concerns.

Technetium is radioactive in all its isotopes; in nature it is found as a fission product of uranium and/or thorium. It is used in nuclear medicine due to its detectable gamma rays and relatively short half-life.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Тс	25 keV	K- alpha	21.04 keV	0.760		
	20.62 keV	K-beta				
Nb	62 keV	K-beta Overla p	97 keV	0.724	20 ppm	Nb K-beta will be much more common, though it is unlikely XRF would be used in any context besides industrial applications for Tc.
Ри	29 keV	L-beta Overla p	22.27 keV	0.464		Pu L-beta lines overlap with Tc K-alpha, though neither is likely to be seen.
Tc	2.42 keV	L-alpha	2.68 keV	0.040		
	2.54 keV	L-beta				
S	2.31 keV	K- alpha Overla p	2.47 keV	0.071	350 ppm	S K-alpha will be more common than Tc L-alpha in almost all circumstances

Pb	2.35 keV	M-Line Overla p	4.32 keV	0.001	14 ppm	Pb M lines will be more common than Tc L-alpha in almost all
		P				circumstances.

Table 43: Observable emission lines for technetium and its most common fluorescence interactions.

### 2.36 Ruthenium, Ru (44)

Ruthenium's K-alpha peak is close to the inelastic (Compton) scattering from silver anodes and is immersed in it with rhodium anodes. As a result, ruthenium detection is difficult without customized filtration of the x-ray beam.

Ruthenium, due to its rarity, wasn't discovered until the modern era, though it can be found as a trace element in some ancient gold-based alloys<sup>190</sup>. It hardens palladium and platinum, and can be used in catalytic converters<sup>191</sup>. With lead and bismuth, it can make thick filmed chip resistors<sup>192</sup>. In superalloys, it can help with heat resistance<sup>193</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ru	19.15 keV 21.66 keV	K-alpha K-beta	22.12 keV	0.777	1 ppb	Intercepts: Rh K- alpha, Ag K-alpha (depends on tube anode)
Мо	19.61 keV	K-beta Overlap	20.00 keV	0.742	1.2 ppm	Mo K-beta overlap with Ru K-alpha, however both elements are not common in spectra.
Rh	~19 keV	Compton	23.22 keV	0.792	1 ppb	The inelastic scattering from Rh anode devices is significant and often precludes any analysis of Ru.
Ru	2.56 keV	L-alpha	2.84 keV	0.043	1 ppb	Intercepts: Cl K-
	2.68 keV	L-beta				alpha

Cl	2.62 keV	K-alpha Overlap	2.82 keV	0.089	145 ppm	In most samples, even small amounts of Cl will overwhelm Ru L- alpha emissions.
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Table 44: Observable emission lines for ruthenium and its most common fluorescence interactions.

## 2.37 Rhodium, Rh (45)

Rhodium is one of the most common elements used for x-ray tube anodes in handheld XRF devices. As a result, rhodium can be both the rarest and most common observation in spectra from handheld XRF instruments. However, its use in the x-ray tube often precludes its identification in samples due to elastic (Rayleigh) scattering. If the tube anode is silver, measurement of rhodium can paradoxically become more difficult. In this case, it will often interfere with inelastic (Compton) scattering.

Rhodium is extraordinarily rare, one of the rarest elements in earth's crust<sup>194</sup>. With few exceptions, you will not see these elements in natural materials. They are on occasion found in jewelry. Rhodium can be found in precious metal bands. Both rhodium and palladium form critical components of catalytic converters<sup>195</sup>, Rhodium for reduction and palladium for oxidization. Dipping these precious metals in gasoline may not seem to be the best use of such rare elements, but they have a tremendously beneficial effect on reducing pollution when used. Fortunately, they can be recycled after use. While existing in extremely low quantities, rhodium can be a proxy for past volcanic activity in ice cores<sup>196</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Rh	20.07 keV	K-alpha	23.22 keV	0.792	1 ppb	
	22.72 keV	K-beta				

U	20.17 keV	L- gamma Overlap	20.95 keV	0.489	2.7 ppm	A U L-gamma line overlaps with Rh K- alpha, but this will only be an issue with large amounts of U
Rh	2.70 keV	L-alpha	3.00 keV	0.046	1 ppb	
	2.83 keV	L-beta				
CI	2.62 keV	K-alpha Overlap	2.82 keV	0.089	145 ppm	In most samples, even small amounts of Cl will overwhelm Rh L- alpha emissions. The major exception is Rh anode tubes.

Table 45: Observable emission lines for rhodium and its most common fluorescence interactions.

#### 2.38 Palladium, Pd (46)

The K-line emissions for palladium overlap with the high-energy Compton peak for Rh-tube instruments, making it difficult to detect in most handheld systems. Its close proximity to the K-line emission of Ag also inhibits its detection. In both cases, significant filtration will be needed to block the K-alpha fluorescence from both of these elements (and thus inhibiting incoherent scattering).

Palladium is most commonly thought of as a precious metal. It is however most frequently used to minimize air pollution from cars<sup>197</sup>. As a catalytic converter, it can convert 90% of the nasty gaseous emissions from cars into harmless water and short-term harmless (but long-term concern) CO<sub>2</sub>. A small percentage of palladium exists in car exhaust and is subsequently taken up by plants<sup>198</sup>.

In electronics, palladium can be used as an electrode<sup>199</sup>, plating<sup>200</sup>, and conductor<sup>201</sup>. It is often alloyed with nickel in these contexts. For jewelry, it can be alloyed with gold to produce white gold, just like nickel and platinum, though it has been associated with allergic reactions<sup>202</sup>.
Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Pd	21.02 keV	K-alpha	24.35 keV	0.808	15 ppb	
	23.82 keV	K-beta				
Ag	~21 keV	Compto n	25.51 keV	0.822	75 ppb	The inelastic scattering from Ag anode devices is significant and often precludes any analysis of Pd.
Pd	2.84 keV	L-alpha	3.17 keV	0.049	15 ppb	Intercepts: Rh L- alpha, Ar K-alpha
	2.99 keV	L-beta				
Rh	2.83 keV	L-beta Overlap	3.00 keV	0.046	1 ppb	Rh L-beta will overlap with Pd K- alpha, though this is primarily a concern for Rh anode tubes.
Ar	2.96 keV	K-alpha Overlap	3.21 keV	0.109	3.5 ppm	Ar is much more common and likely to overlap.

Table 46: Observable emission lines for palladium and its most common fluorescence interactions.

#### 2.39 Silver, Ag (47)

While the gold L-lines are difficult to see and complicated by the presence of zinc and lead, the silver peak has no overlaps. As such, silver can be used as an indicator element for these deposits when the other elements are too difficult. This does not mean that Ag is a perfect predictor for the presence of precious metals like gold, but it is a safer bet to rely upon this element compared to others.

Silver is a frequent component of electronics due to its electrical conductivity<sup>203</sup>. Silver foil was often used in religious iconography<sup>204</sup>, particularly in Eastern Orthodox art. It is also an almost constant contaminant in any gold alloys<sup>205</sup> and occasionally visible in copper alloys.

Archaeologically, silver was typically used in prestige luxury items and, in the form of electrum, a gold-silver alloy, as currency<sup>206</sup>. In fact, when buried, silver will react with chlorine, bromine, and other halides, a chemical reaction that forms the basis of traditional photographic methods<sup>207</sup>. The presence of these elements in a silver alloy can indicate that it was buried for some time.

Today silver is typically found in the form of sterling silver, 92.5% Ag and 7.5% Cu. it can also be alloyed with germanium to form Argentium<sup>208</sup>. A concern of many however is silver plated materials used in producing forgeries and cheap replicas<sup>209</sup>. An unusual property of silver is that it readily absorbs neutrons. As such, silver is sometimes used in control rods for fission reactions in nuclear reactors<sup>210</sup>.

In photography, silver nitrate is commonly used in gelatin to produce prints. Its sensitivity to light is also employed in solar panels. It can also be sputtered onto windows to form a sheen layer. It has catalytic properties which can be used in oxide reactions.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ag	21.99 keV	K-alpha	25.51 keV	0.822	75 ppb	Intercepts: Cd K- alpha
	24.94 keV	K-beta				Slopes: Cd K-alpha, Sn K-alpha
Ru	22.07 keV	K-beta	22.12 keV	0.777	1 ppb	Ru K-beta overlaps with Ag K-alpha, but the concurrence of the two is unlikely.
Ag	2.98 keV	L-alpha	3.35 keV	0.052	75 ppb	
	3.15 keV	L-beta				

Ar	2.96 keV	K-alpha Overlap	3.21 keV	0.109	3.5 ppm	Argon forms 0.93% of the Earth's atmosphere, meaning without atmospheric control it will likely obscure Ag L-alpha unless Ag is in the tube or an Ag alloy is being analyzed.
Rh	2.83 keV	L-beta Overlap	3.15 keV	0.043	1 ppb	In Rh anode instruments, Rh L- lines will overlap with Ag.

Table 47: Observable emission lines for silver and its most common fluorescence interactions.

#### 2.40 Cadmium, Cd (48)

The analysis of silver and cadmium is somewhat complicated by the type of x-ray tube used. If a rhodium or molybdenum tube is used these elements will be on the other side of the spectrum, making both more difficult to determine in smaller concentrations. This is particularly true when a light-element matrix is analyzed, particularly those containing mostly carbon or oxygen. This leads to greater backscatter and thus makes detection more difficult. If a silver tube is present, then the analysis of either element is greatly complicated.

There is, however, a relatively simple solution, which is to use a filter. The tube can be blocked out using a very thick copper filter, such as 200 µm copper, 25 µm titanium, and 200 µm aluminum. This will reduce the backscatter for both elements. Once this is controlled, very small variations can be seen for these both elements, often breaking the 1 ppm barrier common for handheld XRF instruments.

Cadmium has been in the limelight recently due to Restriction of Hazardous Substances (ROHS) regulations on the toxic metals that may be present in consumer materials<sup>211</sup>. For plastics, the knowledge of the presence of cadmium is extremely important due to environmental effects<sup>212</sup>. For the same reason, cadmium can be critical to identify in soil

deposits as well<sup>213</sup>. In both cases, cadmium is being identified in a mostly light element matrix

(primarily O with some C), thus backscatter will get in the way of trace detections.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Cd	22.98 keV	K-alpha Overlap	26.71 keV	0.836	150 ppb	Intercepts: Pb L- alpha, Rh K-alpha (depends on tube
	26.10 keV	K-beta				anode)
Rh	22.72 keV	K-beta Overlap	23.22 keV	0.792	1 ppb	Rh K-beta overlaps with Cd K-alpha, and this effect will be common in Rh anode instruments.
Рb	~23 keV	Sum Peak	15.86 keV	0.373	14 ppm	The sum peak of Pb L-alpha and L-beta lines can result in a confusing overlap near Cd K-alpha - though this will require lots of Pb and no Cd K-beta peak will be present. This will appear in almost all oil paintings.
Cd	3.13 keV	L-alpha	3.54 keV	0.056	150 ррь	Intercepts: K K- alpha, Ar K-alpha
	3.32 keV	L-beta				
К	3.31 keV	K-alpha Overlap	3.61 keV	0.132	2.09 %	K is more common than Cd, so any identification based on Cd L-alpha requires controlling for this element.
Ar	3.19 keV	K-beta Overlap	3.21 keV	0.109	3.5 ppm	Ar is 0.93% of the atmosphere, without atmospheric control it will likely overlap with Cd L-alpha
Pd	3.07 keV	L-beta Overlap	3.60 keV	0.014	15 ppb	Pd is more rare than Cd, this overlap is less likely to be a concern.

Table 48: Observable emission lines for cadmium and its most common fluorescence interactions.

## 2.41 Indium, In (49)

Indium's rarity makes its appearance in XRF spectra unlikely. One of its only overlap is the K-beta line for palladium, so if indium is present it is unlikely to be encumbered by spectral interference from other elements, although it requires heavy filtration to be seen at low concentrations. Some XRF instruments use detector shields with an indium coating which manifests as an artifact. Unfortunately, because this will be a detector-side contaminant, it cannot be filtered out.

Indium's major uses following the decades after its discovery were as a stabilizing agent in non-ferrous metals<sup>214</sup> and as coatings for aircraft bearings<sup>215</sup>. Indium phosphate is a common semiconductor<sup>216</sup> used in LCD and LED displays for electronics. It can be a safe substitute for mercury in alkaline batteries<sup>217</sup>. As a neutron absorber, it can be used in nuclear control rods<sup>2</sup> Since 2009, it has been used in fade-resistant blue pigments (YInMn)<sup>219</sup>, arguably one of few modern pigments developed in two centuries.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
In	24.00 keV	K-alpha	27.94 keV	0.849	250 ppb	
	27.28 keV	K-beta				
Pd	23.82 keV	K-beta Overlap	24.35 keV	0.808	15 ppb	Pd K-beta overlaps with In K-alpha
In	3.29 keV	L-alpha	3.73 keV	0.060	250 ppb	Intercepts: K K- alpha, Ag L-alpha
	3.49 keV	L-beta				

К	3.31 keV	K-alpha Overlap	3.61 keV	0.132	2.09 %	The much more common K K-alpha line will likely overwhelm any L- line emission from In. Though it may be detectable if In concentrations are high enough.
Ag	3.35 keV	L-beta Overlap	3.35 keV	0.052	75 ppb	In Ag anode tubes, this overlap will likely occur.
Cd	3.32 keV	L-beta	3.72 keV	0.056	150 ppb	Cd is more common than In, this overlap should not be discounted

Table 49: Observable emission lines for indium and its most common fluorescence interactions.

#### 2.42 Tin, Sn (50)

In principle, tin is not difficult to measure as its only expected spectral overlap is with the Kbeta line from silver, although this is obviously a concern for silver anode instruments. However, tin is a common soldering agent and radiation shield. As a result, it has a reasonable likelihood of being a contaminant in many instruments. It will also produce a high backscatter. For any application requiring low detection limits, one should use very heavy filtration of the beam.

A one point in history, tin was the most consequential element to human societies, even more so than gold. Alloyed with copper, it formed strong bronze alloys which were more effective for both work and war. This element became one of the first global strategic resources<sup>220</sup>, driving ancient politics to a degree not seen again until the gold rush of the Spaniards in the Americas and our own pursuit of fossil fuels today. In the Bronze Age, sophisticated networks for tin connected distant places such as Cornwall, England<sup>221</sup> to Afghanistan through trade centralized in modern-day Turkey, Egypt, and Greece. The mercantile kings of this world alternatively warred and traded with each other. Around the 12th century BC, most of the cities across the Eastern Mediterranean were burned and depopulated, and the region entered a

long economic depression that saw the loss of writing in many areas. Some have argued that this was connected to the drop in the tin trade, others to climate change, but no one knows for sure.

Tin is still an important alloying metal today, thanks to the same properties which fueled its utility to ancient societies. Due to the presence of four valence electrons in the outer- shell like carbon, silicon, and lead, it readily binds with elements at high temperature and produces a strong, durable alloy. Today, tin is primarily used for solder when combined with lead or Ag and Cu<sup>222</sup>.

Tin has other uses outside metal alloys. Lead-tin yellow was a pigment in oil paintings<sup>223</sup>. Tin is often found as a opacifier in historic glass<sup>224</sup>. Tin can also find itself in modern glasses with indium tin oxide to provide conduction in some touch screen technologies<sup>225</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Sn	25.04 keV 28.49 keV	K-alpha K-beta	29.20 keV	0.861	2.3 ppm	Intercepts: Ag K- alpha
Ag	24.94 keV	K-beta Overlap	25.51 keV	0.822	75 ppb	Ag K-beta overlaps with Sn K-alpha, and this effect will be common in Ag anode instruments. Moreover, this can be a significant obstacle in measuring some early archaeological bronzes
Sn	3.44 keV 3.66 keV	L-alpha L-beta	3.94 keV	0.069	2.3 ppm	Intercepts: K K- alpha, Ag L-alpha

К	3.31 keV	K-line	3.61 keV	0.132	2.09 %	The much more common K K-alpha line will likely overwhelm any L- line emission from Sn. Though it may be detectable in artificial materials (e.g. paintings)
Ag	3.35 keV	L-beta Overlap	3.35 keV	0.052	75 ppb	In Ag anode tubes, this overlap will likely occur.
Cd	3.32 keV	L-beta	3.72 keV	0.056	150 ppb	Cd is less common than Sn, this overlap is not as likely.

Table 50: Observable emission lines for tin and its most common fluorescence interactions.

## 2.43 Antimony, Sb (51)

Antimony occurs directly adjacent to tin on the Periodic Table (K-line of 36.4 keV), thus its measurement is similarly constrained by backscatter and Si detector thickness. With a natural abundance of 200 ppb, antimony is unlikely to show up in many assays.

The use of antimony extends to the earliest complex societies; it was used as a cosmetic pigment in ancient Egypt<sup>226</sup>. Pliny the Elder mentions antimony sulfide for medical uses<sup>227</sup>. In historical pigments, it is present in Naples yellow, Pb3(SbO4)2 and other lead-antimony-tin yellows<sup>228</sup>. It was also used as an opacifier in glasses throughout history<sup>229</sup>.

The primary use for antimony today is as a fire retardant in a trioxide form<sup>230</sup>. Its second and third most common uses are as anodes in batteries<sup>231</sup> and metal alloys. Antimony strengthens lead, so is used in applications where heavy but strong alloys are needed (such as boat keels)<sup>232</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Sb	26.11 keV	K-alpha	30.49 keV	0.872	200 ppb	Intercepts: Cd K-
	29.73 keV	K-beta				aipna

Cd	26.10 keV	K-beta Overlap	26.71 keV	0.836	150 ppb	Cd K-beta overlaps with Sb K-alpha, though as both are unlikely to appear in most materials, the Cd K-alpha peak should always be referenced before making a qualitative interpretation.
Sb	3.61 keV 3.84 keV	L-alpha L-beta	4.38 keV	0.069	200 ppb	Intercepts: Ca K- alpha, Sn L-alpha
Ca	3.69 keV	K-alpha	4.04 keV	0.147	4.15 %	The much more common Ca K- alpha line will likely overwhelm any L-line emission from Sb. Though it may be detectable in artificial materials (e.g. paintings)
Sn	3.66 keV	L-alpha	3.94 keV	0.069	2.3 ppm	Sn is more common, this overlap is to be expected.

Table 51: Observable emission lines for antimony and its most common fluorescence interactions.

#### 2.44 Tellurium, Te (52)

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Tellurium occurs in an otherwise ideal portion of the XRF spectrum for detection with minimal chance of an overlap. Provided 50 kV x-rays are emitted with very heavy filtration, it is detectable in small quantities even when factoring in detector inefficiency.

Tellurium is primarily used in iron<sup>233</sup> and copper<sup>234</sup> alloys to make them more amenable to machining. Cadmium telluride is the semiconductor used in solar panels<sup>235</sup>. The anticipated growth of the solar industry in the 21st century is expected to increase demand for this element. Cadmium-telluride semiconductors can also be used for high energy x-ray

applications<sup>236</sup>, including XRF. Tellurium suboxide was used as the writable media in rewritable compact disks<sup>237</sup>.

Element	Energy	Туре	Absorptio n Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Те	27.20 keV	K-alpha	31.81 keV	0.883	1 ppb	Intercepts: In K-alpha
	31.00 keV	K-beta				
In	27.28 keV	K-beta Overlap	27.94 keV	0.849	250 ppb	In K-beta can overlap with Te K-alpha, but the peaks should be distinct.
Te	3.77 keV	L-alpha	4.34 keV	0.074	1 ppb	Intercepts: Ca K-
	4.03 keV	L-beta				alpha
Ca	4.01 keV	K-beta Overlap	4.04 keV	0.147	4.15 %	The much more common Ca K-alpha line will likely overwhelm any L-line emission from Te.
Sn	3.91 keV	L-beta Overlap	3.94 keV	0.069	2.3 ppm	Sn is more common
Sb	3.93 keV	L-beta Overlap	4.70 keV	0.039	200 ppb	Sb is more common than Te.

Table 52: Observable emission lines for tellurium and its most common fluorescence interactions.

#### 2.45 lodine, I (53)

lodine, like tellurium, is clearly identifiable in theory but with some greater difficulty in practice due to minimal overlaps but high backscatter.

lodine can concentrate in some seaweeds<sup>238</sup>, sometimes concentrations that are visible without filtration. Cultures which used seaweed in agriculture or metalworking, such as in Scandinavia<sup>239</sup>, may have detectable iodine on archaeological artifacts. It can be consumed by humans as potassium iodide<sup>240</sup>. Iodine is also an excellent disinfectant and antimicrobial agent, and traditionally has been used as an agent for water treatment<sup>241</sup> in both industrial and individual use. It is also added to salt for health benefits, and is important in the mental

development of children<sup>242</sup>. One of the most bioavailable forms of nuclear waste is a radioactive isotope of iodine<sup>243</sup>. Consumption of stable iodine can prevent biological accumulation<sup>244</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
I	28.32 keV 32.30 keV	K-alpha K-beta	33.17 keV	0.893	450 ppb	Intercepts: Sn K- alpha
Sn	28.49 keV	K-beta Overlap	29.20 keV	0.861	2.3 ppm	Sn K-beta is generally far enough away on the spectrum to avoid confusion.
I	3.94 keV 4.22 keV	L-alpha L-beta	4.56 keV	0.079	450 ppb	Intercepts: Ca K- alpha
Ca	4.01 keV	K-beta Overlap	4.04 keV	0.147	4.15 %	The much more common Ca K-alpha line will likely overwhelm any L- line emission from I.
Sn	3.91 keV	L-beta Overlap	3.94 keV	0.069	2.3 ppm	Sn is more common
Sb	3.93 keV	L-beta Overlap	4.70 keV	0.039	200 ppb	Sb is more common

Table 53: Observable emission lines for iodine and its most common fluorescence interactions.

#### 2.46 Xenon, Xe (54)

Xenon, as a noble gas, is unlikely to be measured using handheld XRF. However, it enjoys one of the unique advantages in the event it is measured because there are almost no possible overlaps with the K-alpha from xenon. The chief obstacles to measuring this element are backscatter and detector inefficiency.

Like other noble gases, Xenon can be ionized to produce light<sup>245</sup>, though it is often done in high-tech settings to produce lasers<sup>246</sup>. In high pressure settings xenon produces a spectrum

of light similar to the sun, thus making it useful in both photography<sup>247</sup> and filming. It is also used in some automobile headlights<sup>248</sup>. Interestingly, xenon can be used as a very cost-inefficient anesthetic<sup>249</sup> and neuroprotectant<sup>250</sup>, although this has also led to its use as a doping agent in sports<sup>251</sup>.

Element	Energy	Туре	Absorptio n Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Xe	29.46 keV	K-alpha	34.56 keV	0.903		Intercepts: Sb K-
	33.62 keV	K-beta				aipiia
Sb	29.73 keV	K-beta Overlap	30.49 keV	0.872	200 ррb	It is unlikely the circumstance would emerge where Sb K-beta overlaps with Xe K-alpha, but it may happen if Sb is present in the glass containing Xe
Xe	4.11 keV	L-alpha	4.79 keV	0.085		Intercepts: Ca K-
	4.42 keV	L-beta				aipiia
Ca	4.01 keV	K-beta Overlap	4.04 keV	0.147	4.15 %	Ca's ubiquity will likely hinder the identification of Xe L-alpha
Sc	4.09 keV	K-alpha Overlap	4.49 keV	0.183	22 ppm	The Sc K-alpha peak will be more likely to be identified than Xe L-alpha, though both are obscured by Ca
Sb	4.10 keV	L-beta Overlap	4.13 keV	0.069	200 ppb	It is unlikely for Sb and Xe to occur in the same material
Sn	4.13 keV	L-gamma Overlap	4.16 keV	0.069	2.3 ppm	It is unlikely for Sn and Xe to occur in the same material

 Table 54: Observable emission lines for xenon and its most common fluorescence interactions.

## 2.47 Cesium, Cs (55)

Cesium is an uncommon element to observe in the course of XRF assays, but there are almost no overlaps with other elements that could cause confusion for its K-line emission.

It behaves chemically like other Class I elements potassium and rubidium. But, because of its rarity, it had no known application until its discovery in the late 19th century. Cesium holds the unique distinction of being discovered via spectrometry<sup>252</sup>.

Cesium's most important application is in atomic clocks<sup>253</sup>, where its hyperfine structure allows for extreme precision in time. In fact, all present-day cell-phones, computers and other networked systems base their time on cesium atomic clocks<sup>254</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Cs	30.62 keV	K-alpha	35.99 keV	0.912	3 ppm	
	34.99 keV	K-beta				
Те	31.00 keV	K-beta Overlap	31.81 keV	0.883	1 ppb	Te is unlikely to overlap due to its rarity.
Cs	4.29 keV	L-alpha	5.01 keV	0.091	3 ppm	
	4.62 keV	L-beta				
Sb	4.35 keV	L-beta Overlap	4.38 keV	0.069	200 ppb	
Те	4.30 keV	L-beta Overlap	4.34 keV	0.074	1 ppb	

Table 55: Observable emission lines for cesium and its most common fluorescence interactions.

# 2.48 Barium, Ba (56)

In handheld XRF, both the K- and L-line emissions of barium are usually visible. The K-line can be identified at 32 keV, with minimal overlapping lines, though it is more visible if x-rays of 50-keV or greater are sent. Fortunately, there are no overlaps with this emission line to

cause any confusion in its identification. However, overlaps are not the primary concern. At this high of an energy range in the spectra, there are three challenges to getting an effective K-line emission: 1) detector efficiency for silicon-drift detectors declines with increased energy, 2) there are fewer available photons for excitation, and 3) high backscatter that is difficult to filter. Identification of the L-line emissions are more challenging as they overlap with the K-line emissions for titanium. Therefore, in cases where barium is abundant, it will be detectable in the corresponding lower energy ranges at 4.45 keV.

Barium tends to follow where calcium leads, and is found in similar places. The easiest place to find it is in barium sulfate mineral barite (BaSO<sub>4</sub>)<sup>255</sup>. Barite can be a common component of grounding or underlayers as heavy spar in canvas paintings<sup>256</sup>. And, somewhat less prestigiously, it is a heavy additive to drilling fluid for petroleum extraction<sup>257</sup>. Barium can be found in ancient glass, particularly those from East Asia<sup>258</sup>. While it is not necessarily rare, it is uncommon and can be used as a trace indicator for the provenance studies in both ceramics and obsidian. It tends to precipitate in oxic-anoxic boundaries in marine systems<sup>259</sup>. However, it can be highly mobile in saturated sediments leading to taphonomic deposition in porous materials over time, therefore should be interpreted with caution.

The use of barium in both pigments and glass is common, provided we look to China. There, the use of Han Blue (BaCuSi<sub>4</sub>O<sub>10</sub>) and purple (BaCuSi<sub>2</sub>O<sub>5</sub>)<sup>260</sup> was common following the Qin (221 - 206 BC) and Han (207 BC - 219 A.D.) dynasties. It is an analogue of Egyptian Blue<sup>261</sup>, with barium taking the place of calcium. Like Egyptian blue, Han blue was a synthetic pigment produced through firing silica, copper, and alkali with witherite (BaCO<sub>3</sub>) in place of lime (CaCO<sub>3</sub>). Barium was also key to glass production in China, its presence can be diagnostic for identifying East Asian glass work<sup>262</sup>. Barium oxide glass was also used more recently in cathode ray tubes<sup>263</sup>, where it could both attenuate x-rays owing to its density and lower the dispersion pressure relative to lead glass.

Barium does have one moment of geopolitical importance. Two refugees from Nazi rule in Euorpe, Lise Meitner and Oto Frischt, recognized the unexpected presence of barium following the bombardment of uranium with neutrons could be explained by a more rapid half life than the one then known. While it had been speculated that this was a fission process, Meitner and her nephew realized the tremendous energy that would be released by the decay of uranium into barium and (they correctly guessed) the noble gas krypton. They spoke to Einstein about this finding, since his equation E=mc<sup>2</sup> predicted that, among other things, tremendous energy was stored in the form of mass. Einstein, after collecting input from scientists such as Meitner and Frischt, wrote to then-president Franklin Roosevelt about this, and urged him to focus America's research on this momentous discovery before the Germans found out. Within days, the groundwork for the Manhattan project was laid out.

For most handheld XRF instruments, these elements will be visible in both the K- and Lemission lines, with the latter being more reliable in most cases. To identify them using the Kshell, a very strong filter is needed along with long acquisition times. In this case, a direct copper filter would be preferable to ensure that the material fits within the instrument. In addition to this, the infinite thickness of the sample will range from 3 cm to 4 cm, depending upon the light elements present. The more sample mass presented to the unit, the better the quantitative analysis of the rare elements will be.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ba	31.82 keV	K-alpha	37.44 keV	0.920	425 ppm	
	36.38 keV	K-beta				

Te	31.70 keV	K-beta Overlap	31.84 keV	0.883	1 ppb	The K-beta for Te will come close to the K-alpha for Ba, but it is unlikely to ever reach high enough concentrations to present a serious concern.
Ba	4.47 keV	L-alpha	5.25 keV	0.097	450 ppm	Intercepts: Ti K- alpha
	4.83 keV	L-beta				
Ti	4.50 keV	K-alpha Overlap	4.99 keV	0.218	5,560 ppm	Ti will almost always overwhelm the signal of Ba L- alpha due to its higher abundance in geologic materials.
Sc	4.46 keV	K-beta Overlap	4.49 keV	0.183	22 ppm	It is highly unlikely that Sc will ever exist in detectable concentrations for XRF analysis, let alone enough to interfere with either Ti or Ba.
La	4.63 keV	L-alpha Overlap	5.48 keV	0.104	39 ppm	The L-alpha of La can come near the L- line of Ba, but there would be other REE elements present that would indicate the problem.

Table 56: Observable emission lines for barium and its most common fluorescence interactions.

#### 2.49 Lanthanum, La (57)

Lanthanum, like barium, has no common interferences in its K-line emissions. However, for most handheld XRF systems, detecting the La K-line emissions will only occur when it is present in high concentrations. It is also subject to the same detection limitations as barium; low detector counting efficiency, fewer excitation photons, and high backscatter.

Unfortunately, the L-line limitations for lanthanum are even more severe due to overlap with

the K-alpha line for titanium. Compounding this problem is the fact that in most substrates Lanthanum will likely be present in small quantities which makes its identification obscure.

Like all other REEs, Lanthanum has no known pre-industrial uses. In classical Greek, lanthanum's name literally means "to lie hidden". Because of its larger ionic radius, it is more reactive than most other REEs besides europium. Its reactivity led to its first major application in lantern mantles<sup>264</sup>. Its reactivity also makes it an attractive element for nickelmetal hydride batteries<sup>265</sup> in some hybrid vehicles, even when diluted. And occasionally, it can be found in copper alloys as a strengthening agent<sup>266</sup>. In very small amounts, it can stimulate hormesis in plants<sup>267</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
La	33.03 keV	K-alpha	38.93 keV	0.928	39 ppm	
	37.80 keV	K-beta				
I	33.04 keV	K-beta Overlap	33.17 keV	0.893	450 ppb	The K-beta line for I overlaps slightly with the K-line for La, but it's median will be a lower energy.
La	4.65 keV	L-alpha	5.48 keV	0.104	39 ppm	Intercepts: Ti K-
	5.04 keV	L-beta				alpha
Ti	4.50 keV	K-alpha Overlap	4.99 keV	0.218	5,560 ppm	Ti will almost always overwhelm the signal of La L-alpha due to its higher abundance in geologic materials.
Cs	4.62 keV	L-beta Overlap	5.36 keV	0.091	3 ppm	The L-beta line of Cs overlaps almost completely with the L-alpha line for Ce.

Table 57: Observable emission lines for lanthanum and its most common fluorescence interactions.

## 2.50 Cerium, Ce (58)

Of all REE elements, cerium is the most abundant at 66 ppm in Earth's crust. As a result, it has the highest probability of being observed by XRF. Its K-line is a possible point of detection, but 50 keV x-rays will likely be needed to excite it when paired with heavy filtration. However, the L-line emission of Ce is a more likely way to identify the presence of this element. It has fewer overlaps than La, although it will still require some filtration to be detected.

Like lanthanum, cerium was used in lantern mantles. It can also be used in trace amounts in some aluminum alloys<sup>268</sup>. It is also used in some fluorescent lamps<sup>269</sup>. Silica fibers doped with cerium can be used as detectors in particle physics<sup>270</sup> and wavelength shifters<sup>271</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ce	34.28 keV	K-alpha	40.44 keV	0.935	66.5 ppm	
	39.26 keV	K-beta				
Ce	4.84 keV	L-alpha	5.72 keV	0.110	66.5 ppm	Intercepts: Ba L-
	5.26 keV	L-beta				alpha
Ba	4.83 keV	L-beta Overlap	5.62 keV	0.096	450 ppm	The L-beta of the more common Ba overlaps directly with Ce L-alpha
Cs	4.72 keV	L-beta Overlap	5.71 keV	0.049	3 ppm	The L-beta line of Cs overlaps almost completely with the L-alpha line for Ce.
Ti	4.93 keV	K-beta Overlap	4.99 keV	0.218	5,560 ppm	The K-beta of the more abundant Ti comes close to Ce L- alpha.
V	4.95 keV	K-alpha Overlap	5.47 keV	0.253	120 ppm	The K-alpha of V is also more likely to overlap, its effects are additive to Ti

Table 58: Observable emission lines for cerium and its most common fluorescence interactions.

### 2.51 Praseodymium, Pr (59)

Like cerium, this rare earth has few overlaps in its L-line emissions, but it is about one-sixth as common as cerium and unlikely to be seen even in REE-rich materials.

Along with neodymium, praseodymium can create powerful magnets<sup>272</sup> that are widely used in electronics. It strengthens some magnesium alloys, leading to its use in aircraft. Its interesting uses in physics aside, it can be used as a yellow colorant in glasses<sup>273</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Pr	35.55 keV	K-alpha	41.99 keV	0.941	9.2 ppm	
	40.75 keV	K-beta				
Cs	35.83 keV	K-beta Overlap	35.99 keV	0.912	3 ppm	The K-beta of Cs overlaps with the K- alpha of Pr
Pr	5.03 keV	L-alpha	5.69 keV	0.118	9.2 ppm	Intercepts: Ti K-
	5.49 keV	L-beta				Slopes: La L-alpha
Ti	4.93 keV	K-beta Overlap	4.99 keV	0.218	5,560 ppm	The K-beta of the much more abundant Ti overlaps, and likely overwhelms, any L-alpha signal from Pr.
V	4.94 keV	K-alpha Overlap	5.47 keV	0.253	120 ppm	The K-alpha of the more abundant (and higher fluorescence efficiency) V overlaps with Pr L- alpha
Ba	4.93 keV	L-beta Overlap	5.99 keV	0.052	450 ppm	The L-beta of the more common Ba can overlap directly with Pr L-alpha

La	5.04 keV	L-beta Overlap	6.27 keV	0.055	39 ppm	The L-beta of La overlaps with the L- alpha of Pr, and this overlap is predicted for any occurrence of Pr outside of specialized industrial
						specialized industrial activity.

Table 59: Observable emission lines for praseodymium and its most common fluorescence interactions.

## 2.52 Neodymium, Nd (60)

This is the second most abundant REE, and is the last possible K-line emission to be observed on current-generation handheld XRF analyzers, whose detectors are typically limited to a maximum energy of 40 keV. It is possible to adjust gain settings on detectors to capture higher energies, but the efficiency of silicon crystals to capture all of their photon emissions declines rapidly as energy increases. For the same reason, the quantity of neodymium must be appreciable to be identified using this line, even with an excitation voltage of 50 kV. Its L-line emission, like that of cerium, is the likelier means to detect its presence, although overlap from the Ce L-beta is a concern. It benefits from light filtration.

Neodymium isotopes can be used to trace past ocean currents<sup>274</sup> and plate tectonics<sup>275</sup>. Its principle application, like praseodymium, is in powerful neodymium magnets<sup>276</sup> used widely in electronics. Even small amounts of neodymium can exert a magnetic force strong enough to lift hundreds of times its original weight. Recent research has used the unusual genetic properties of Nd to identify its north and south poles on individual atoms<sup>277</sup>. It can also be used in glass as a component for infrared lasers, though it is also useful for higher energy lasers as well in applications such as eye surgery<sup>278</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Nd	36.85 keV	K-alpha	43.57 keV	0.947	41.5 ppm	Intercepts: Ba K- alpha

	42.27 keV	K-beta				
Ba	36.38 keV	K-beta Overlap	37.44 keV	0.920	450 ppm	The K-beta of Ba overlaps with the K- alpha of Nd
Nd	5.23 keV	L-alpha	6.21 keV	0.125	41.5 ppm	Intercepts: Cr K-
	5.72 keV	L-beta				Slopes: Ce L-alpha
Cr	5.40 keV	K-alpha Overlap	5.99 keV	0.287	102 ppm	The Cr K-alpha comes close enough to the L-alpha line of Nd to obscure it in many cases
V	5.43 keV	K-beta Overlap	5.47 keV	0.253	120 ppm	The K-beta of V overlaps with Nd L- alpha
Ba	5.16 keV	L-beta Overlap	5.25 keV	0.097	450 ppm	The L-beta of the more common Ba can overlap directly with Nd L-alpha
Се	5.26 keV	L-beta Overlap	6.16 keV	0.110	66.5 ppm	Because Ce will often correlate with Nd, this overlap should be expected. This also means that ~5.2 keV is the best spot to identify rare earths in a normal XRF spectrum.

Table 60: Observable emission lines for neodymium and its most common fluorescence interactions.

# 2.53 Promethium, Pr (61)

Promethium is both highly rare and very unstable; it is unlikely to be observed using XRF.

Some isotopes are long-lived enough to be functional in atomic batteries<sup>279</sup>, though these are typically used only in research.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
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Pm	5.43 keV 5.96 keV	L-alpha L-beta	6.46 keV	0.132		Intercepts: Cr K- alpha, La L-alpha Slopes: La L-alpha
Cr	5.4 keV	K-alpha Overlap	5.99 keV	0.287	102 ppm	Cr is much more common than Pm, this overlap should be anticipated.
V	5.43 keV	K-beta Overlap	5.47 keV	0.253	120 ppm	The K-beta line of V would overlap with Pm if it were present.
La	5.38 keV	L-beta Overlap	5.48 keV	0.104	39 ppm	The L-beta of La overlaps with the L- alpha of Pm

 Table 61: Observable emission lines for promethium and its most common fluorescence interactions.

#### 2.54 Samarium, Sm (62)

Samarium is difficult to identify in XRF spectra, and will likely be only secondary to other REE's. It is the first K-line to be beyond the range of identification for silicon-drift detectors, although the gain on these detectors can be manipulated to record those energies. The L-line emission is difficult to see due to overlaps with much more common transition metals.

When alloyed with cobalt, samarium can produce a strong magnet<sup>280</sup>. Although weaker than neodymium magnets, they can operate at much higher temperatures<sup>281</sup>. Radioactive isotopes of samarium can be used to treat cancer. Some isotopes can be used as control rods in nuclear reactors<sup>282</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Sm	5.64 keV 6.20 keV	L-alpha L-beta	6.72 keV	0.139	7.1 ppm	Intercepts: Ce L-alpha, Nd L-alpha Slopes: Ce L-alpha
Ce	5.61 keV	L-beta Overlap	5.96 keV	0.110	66.5 ppm	The L-beta line of Ce overlaps with Sm, and this is to be expected if Sm is present.

Nd	5.72 keV	L-beta Overlap	6.72 keV	0.125	41.5 ppm	The L-beta line of Nd comes close to overlapping with Sm, and this is to be expected if Sm is present
						present.

Table 62: Observable emission lines for samarium and its most common fluorescence interactions.

# 2.55 Europium, Eu (63)

Due to an overlapping L-line emission with the vastly more common manganese K-alpha emission lines, Europium is highly unlikely to be detected using XRF.

It can be used sometimes in phosphors, but its applications are limited<sup>283</sup>. It is a by-product of some nuclear reactions.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Eu	5.85 keV 6.45 keV	L-alpha L-beta	6.98 keV	0.147	2 ppm	Intercepts: Mn K-alpha, Cr K- alpha, Pr L- alpha Slopes: Mn K- alpha
Mn	5.89 keV	K-alpha Overlap	6.54 keV	0.391	950 ppm	The K-alpha line of the vastly more abundant Mn will almost certainly obscure Eu's fluorescence in most cases.
Cr	5.95 keV	K-beta Overlap	5.99 keV	0.287	102 ppm	The K-beta line of Cr would overlap with the L- alpha of Eu.

Pr	5.85 keV	L-beta Overlap	5.96 keV	0.118	9.2 ppm	The L-beta line of Pr
		_				comes close to
						overlapping
						with Eu, and
						this is to be
						expected if Eu
						is present.

Table 63: Observable emission lines for europium and its most common fluorescence interactions.

### 2.56 Gadolinium, Gd (64)

As with other REEs, the overlap with manganese K-alpha lines eliminates the ability to identify its L-line emissions.

Gadolinium produces a green color in phosphors<sup>284</sup>, and is sometimes used in electronic displays. It has some use as a superconductor when oxidized with barium and copper<sup>285</sup>. In medical usage, gadolinium's room-temperature paramagnetic properties can be used to identify the location of tumors<sup>286</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Gd	6.06 keV	L-alpha	7.24 keV	0.155	6.2 ppm	Intercepts: Mn K- alpha, Cr K-alpha Slopes: Mn K-alpha
	6.71 keV	L-beta				
Mn	5.89 keV	K-alpha Overlap	6.54 keV	0.391	950 ppm	The K-alpha line of the vaslty more abundant Mn will almost certainly obscure Eu's fluorescence in most cases.
Cr	5.95 keV	K-beta Overlap	5.99 keV	0.287	102 ppm	The K-beta line of Cr would overlap with the L-alpha of Eu.

Nd	6.09 keV	L-beta Overlap	6.21 keV	0.125	41.5 ppm	The L-beta line of Nd comes close to
						overlapping with Eu, and this is to be expected if Eu is present.

Table 64: Observable emission lines for gadolinium and its most common fluorescence interactions.

# 2.57 Terbium, Tb (65)

Like other REEs, its L-line emissions are obscured by the K-alpha emissions of much more common transition metals.

Terbium can be used in fuel cells<sup>287</sup> and green phosphors<sup>288</sup>. When used to make the alloy Terfenol-D<sup>289</sup>, it can expand and contract in magnetic fields. This makes it useful in sonar systems<sup>290</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Tb	6.28 keV	L-alpha	7.51 keV	0.174	1.2 ppm	Intercepts: Fe K-alpha, Mn K-alpha
	6.98 keV	L-beta				Slopes: Fe K-alpha
Fe	6.39 keV	K-alpha Overlap	7.11 keV	0.351	5.63 %	The K-alpha line of the vastly more abundant Fe will prevent identification of Tb in almost all cases.
Mn	6.49 keV	K-beta Overlap	6.54 keV	0.391	950 ppm	The K-alpha line of the vaslty more abundant Mn will almost certainly obscure Tb's fluorescence in most cases.
Sm	6.20 keV	L-beta Overlap	7.74 keV	0.139	7.1 ppm	The L-beta line of Sm comes close to overlapping with Tb, and this is to be expected if Tb is present.

Table 65: Observable emission lines for terbium and its most common fluorescence interactions.

## 2.58 Dysprosium, Dy (66)

Like most REEs, the L-line emissions of dysprosium are difficult-to-impossible to detect due to more common transition metals.

Dysprosium has one of the highest magnetic strengths of any element at the single ion level<sup>291</sup>. In neodymium magnets, small amounts of dysprosium increase coercivity<sup>292</sup> and make these magnets useful for motors that expend energy (electric cars) or generate energy (wind turbines)<sup>293</sup>. It is also used in Terfonal-D<sup>294</sup> in sonar applications.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Dy	6.50 keV 7.25 keV	L-alpha L-beta	7.79 keV	0.174	5.2 ppm	Intercepts: Fe K- alpha, Mn K-alpha Slopes: Fe K-alpha
Fe	6.39 keV	K-alpha Overlap	7.11 keV	0.351	5.63 %	The K-alpha line of the vastly more abundant Fe will prevent identification of Dy in almost all cases.
Mn	6.49 keV	K-beta Overlap	6.54 keV	0.391	950 ppm	The K-beta line of the vastly more abundant Mn will almost certainly obscure Dy's fluorescence in most cases.
Eu	6.45 keV	L-beta Overlap	7.62 keV	0.149	2 ppm	The L-beta line of Eu completely overlaps with Dy, and this is to be expected if Dy is present.

Table 66: Observable emission lines for dysprosium and its most common fluorescence interactions.

#### 2.59 Holmium, Ho (67)

Holmium has L-line emissions that are obscured by K-alpha emissions of transition metals.

Like dysprosium, holmium has one of the highest magnetic strengths of any element<sup>295</sup>. It can be used to generate very strong magnetic fields<sup>296</sup>. In magnesium oxide, a single holmium atom can represent a bit of data<sup>297</sup> - providing a possibility for atomic hard drives. It can also be used as a yellow/red colorant in glass<sup>298</sup> and cubic zirconia<sup>299</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Но	6.72 keV	L-alpha	8.07 keV	0.182	1.3 ppm	Intercepts: Fe K- alpha, Mn K-alpha
	7.53 keV	L-beta				Slopes: Fe K-alpha
Fe	6.39 keV	K-alpha Overlap	7.11 keV	0.351	5.63 %	The K-alpha line of the vastly more abundant Fe will prevent identification of Ho in almost all cases.
Mn	6.49 keV	K-beta Overlap	6.54 keV	0.391	950 ppm	The K-beta line of the vastly more abundant Mn will almost certainly obscure Ho's fluorescence in most cases.
Sm	6.59 keV	L-beta Overlap	6.72 keV	0.139	7.1 ppm	The L-beta line of Sm comes close to overlapping with Ho, and this is to be expected if Ho is present.
Eu	6.46 keV	L-beta Overlap	7.62 keV	0.149	2 ppm	The L-beta line of Eu comes close to overlapping with Ho, and this is to be expected if Ho is present.

Table 67: Observable emission lines for holmium and its most common fluorescence interactions.

# 2.60 Erbium, Er (68)

The L-line emission of Erbium is difficult to detect due to overlap with K-line emissions from more common transition metals.

Erbium has wide use in lasers used for surgery<sup>300</sup>. In glass fibers<sup>301</sup>, it is widely used for optical communications. It can strengthen titanium alloys<sup>302</sup>. It can be used as a pink colorant in glass<sup>303</sup>. Erbium mixed with uranium in nuclear fuel can provide increased reliability and increased economic performance<sup>304</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Er	6.95 keV	L-alpha	8.36 keV	0.192	3.5 ppm	Intercepts: Fe K- alpha, Co K-alpha
	7.81 keV	L-beta				
Fe	7.06 keV	K-beta Overlap	7.11 keV	0.351	5.63 %	The K-beta line of the vastly more abundant Fe will prevent identification of Er in almost all cases.
Со	6.91 keV	K-alpha Overlap	7.71 keV	0.382	25 ppm	The K-alpha line of Co will likely obscure Er's fluorescence in most cases.
ТЪ	6.98 keV	L-beta Overlap	8.25 keV	0.167	1.2 ppm	The L-beta line of Tb comes close to overlapping with Er, and this is to be expected if Er is present.
Eu	6.84 keV	L-beta Overlap	6.98 keV	0.147	2 ppm	The L-beta line of Eu comes close to overlapping with Er, and this is to be expected if Er is present.

Table 68: Observable emission lines for erbium and its most common fluorescence interactions.

# 2.61 Thulium, Tm (69)

Thulium, like most REEs, is difficult to detect due to the overlap of its L-lines with the K-lines of more common transition metals.

Thulium is widely used to generate infrared lasers<sup>305</sup>. It can be used as a radiation source in some medical applications<sup>306</sup>. It is used in some currency due to its blue fluorescence under UV light<sup>307</sup>. It is also used in high-temperature superconductors<sup>308</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Tm	7.18 keV	L-alpha	8.65 keV	0.201	520 ppb	Intercepts: Fe K-alpha, Gd L-alpha
	8.10 keV	L-beta				Slopes: Gd L-alpha
Fe	7.06 keV	K-beta Overlap	7.11 keV	0.351	5.63 %	The K-beta line of the vastly more abundant Fe will prevent identification of Er in almost all cases.
Gd	7.10 keV	L-beta Overlap	7.24 keV	0.155	7.1 ppm	The L-beta line of Gd comes close to overlapping with Tm, and this is to be expected if Gd is present.
Dy	7.20 keV	L-beta Overlap	9.05 keV	0.089	5.2 ppm	The L-beta line of Dy comes close to overlapping with Tm, and this is to be expected if Tm is present.
Тb	7.10 keV	L-beta Overlap	8.71 keV	0.083	1.2 ppm	This overlap should be expected in REE materials where Tm fluoresces

Table 69: Observable emission lines for thulium and its most common fluorescence interactions.

# 2.62 Ytterbium, Yb (70)

The L-line emissions of ytterbium are difficult to detect due to overlap with the K-line emissions of more common transition metals.

Ytterbium can be used in atomic clocks<sup>309</sup>, and is used by the National Institute of Standards and Technology (NIST) for this purpose<sup>310</sup> with other REEs. It is sometimes included in

stainless steel for thermal stability<sup>311</sup>. It is also used in lasers due to its long lifetime and short pulse length<sup>312</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Yb	7.42 keV 8.40 keV	L-alpha L-beta	8.94 keV	0.218	3.2 ppm	Intercepts: Ni K-alpha
Ni	7.46 keV	K-alpha Overlap	8.33 keV	0.412	84 ppm	The K-alpha line of the more abundant Ni will be a challenge in the identification of Yb in most cases.
Тb	7.36 keV	L-beta Overlap	7.51 keV	0.164	1.2 ppm	This overlap should be expected in REE materials where Yb fluoresces
Dу	7.37 keV	L-beta Overlap	9.05 keV	0.089	5.2 ppm	The L-beta line of Dy comes close to overlapping with Yb, and this is to be expected if Yb is present.

Table 70: Observable emission lines for ytterbium and its most common fluorescence interactions.

# 2.63 Lutetium, Lu (71)

Lutetium, with the highest Z of the REEs, is difficult to detect due to its L-line emission

overlapping with more common K-line emissions from transition metals.

Due to its extreme rarity, it is uncommonly used. Its similar properties to other lanthanides indicate that it can be used in atomic clocks<sup>313</sup> and lasers<sup>314</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Lu	7.66 keV	L-alpha	9.24 keV	0.220	800 ppb	Intercepts: Ni K-
	8.71 keV	L-beta				alpha

Ni	7.46 keV	K-alpha Overlap	8.33 keV	0.412	84 ppm	The K-alpha line of the more abundant Ni will be a challenge in the identification of Lu in almost all cases.
Но	7.53 keV	L-beta Overlap	8.92 keV	0.189	1.3 ppm	The L-beta line of Ho comes close to overlapping with Lu, and this is to be expected if Lu is present at all.
Dу	7.63 keV	L-beta	7.79	0.174	5.2 ppm	The L-beta line of Dy comes close to overlapping with Lu, and this is to be expected if Lu is present at all.

Table 71: Observable emission lines for lutetium and its most common fluorescence interactions.

#### 2.64 Hafnium, Hf (72)

The L-line emissions of hafnium fluoresce amidst the most abundant transition metals. Therefore, it faces many of the same identification problems that the REEs face in handheld XRF. However, hafnium benefits from being abundant in areas where transition metal abundance will be lessened due to its correlation with zirconium. Additionally, hafnium is just far enough from the copper K-alpha line that when the latter is in small quantities hafnium is still visible. Detecting it still requires filtration of the beam, as it is unlikely to occur in high ppm levels.

Hafnium was one of the elements predicted to exist by Dmitri Mendeleev based on his organization of the elements<sup>315</sup> and understanding of titanium and zirconium. It would take over half a century to find it. At the time of its discovery in 1923<sup>316</sup>, it would be the last stable element discovered by scientists.

Hafnium's principal use today is in control rods<sup>317</sup> for nuclear reactors as many of its isotopes are neutron absorbers. It can be alloyed with niobium (famously used on the Apollo Lunar Module<sup>318</sup>), iron<sup>319</sup>, titanium<sup>320</sup>, nickel<sup>321</sup>, and tantalum<sup>322</sup>. It is also used in microprocessors<sup>323</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Hf	7.90 keV	L-alpha	9.56 keV	0.242	3 ppm	Intercepts: Cu K-alpha
	9.02 keV	L-beta				
Cu	8.03 keV	K-alpha Overlap	8.98 keV	0.441	60 ppm	The K-alpha line of the more abundant Cu will be a challenge in the identification of Hf, but Zr can be used to identify the probability of an overlap.
Но	7.91 keV	L-beta Overlap	8.07 keV	0.182	1.3 ppm	The L-beta line of Ho comes close to overlapping with Hf, but Zr or an REE can be used to identify which is present.
Er	7.81 keV	L-beta Overlap	9.26 keV	0.200	3.5 ppm	The L-beta line of Er comes close to overlapping with Hf, but Zr or an REE can be used to identify which is present.

Table 72: Observable emission lines for hafnium and its most common fluorescence interactions.

#### 2.65 Tantalum, Ta (73)

Tantalum fluoresces amidst more common transition metals that are both more abundant and have higher fluorescence efficiencies, making its identification challenging, although not impossible. The L-alpha lines are too close to the K-lines of copper to be easily identifiable, but its L-beta lines are a more promising identifier due to fewer overlaps with common

elements. As is the case with other transition metals, filtration is needed to detect low quantities of this element.

Tantalum is a key component in capacitors<sup>324</sup> and resistors<sup>325</sup>; the growth of computers in general and smartphones in particular have caused increased demand for this element<sup>326</sup>, which unfortunately has led to its status as a major conflict mineral and major human rights concerns<sup>327</sup>. It is occasionally used in specialized applications for alloys - such as in nuclear reactors<sup>328</sup> and jet engine components<sup>329</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Та	8.15 keV	L-alpha	9.88 keV	0.243	2 ppm	Intercepts: Cu K- alpha
	9.34 keV	L-beta				
Cu	8.05 keV	K-alpha Overlap	8.98 keV	0.441	60 ppm	The K-alpha line of the more abundant Cu will be a challenge in the identification of Ta
Tm	8.10 keV	L-beta Overlap	9.62 keV	0.211	520 ppb	Tm is less abundant than Ta, so this overlap is less likely to be of concern.
Тя	1.70	M-alpha	1.74 keV	0.021		Intercepts: Si K-
	keV					alpha
	1.76 keV	M-beta	1.79 keV	0.013		
Si	1.74 keV	K-alpha	1.56 keV	0.033	28.2 %	Si is much more common, and is a key component in almost all detectors. It will certainly interfere.
Rb	1.69 keV	L-alpha Overlap	1.80 keV	0.024	90 ppm	Rb is unlikely to be present in high enough quantities to leave a detectable L line.

Rh	2.70 keV	L-alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Ta
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Ta

Table 73: Observable emission lines for tantalum and its most common fluorescence interactions.

#### 2.66 Tungsten, W (74)

Like many heavier elements, the L-line overlaps with many more common transition metals. However, it is spaced between the copper and zinc K-alpha lines, and thus it is a little less challenging to identify than tantalum. Filtration is still necessary to see its L-lines. However, some XRF devices use a tungsten anode, so the user should verify their x-ray tube target isn't tungsten when using it to identify this element.

The most widely known tungsten application was as a filament in incandescent lamps<sup>330</sup>, but these are becoming increasingly rare as they produce more heat than light. For different reasons, tungsten is used in fluorescent lighting<sup>331</sup>. Most tungsten today is used to make tungsten carbide, an ideal strong metal used in high temperature applications<sup>332</sup>. For example. tungsten is used in the equipment used to make synthetic diamonds<sup>333</sup>. It is frequently used in alloys such as steel<sup>334</sup>. It can be used as an alternative to depleted uranium in armor-piercing weapons<sup>335</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
W	8.40 keV	L-alpha	10.21 keV	0.255	1.3 ppm	Intercepts: Zn K- alpha
	9.67 keV	L-beta				

1					1	
Cu	8.05 keV	K-alpha Overlap	8.98 keV	0.441	60 ppm	The K-alpha line of the more abundant Cu will be a challenge in the identification of W
Zn	8.62 keV	K-alpha Overlap	9.66 keV	0.469	70 ppm	The K-alpha line of the more abundant Zn will be a challenge in the identification of W
Tm	8.47 keV	L-beta Overlap	8.65 keV	0.201	520 ppb	Tm is less abundant than W, so this overlap is less likely to be of concern.
Yb	8.40 keV	L-beta Overlap	9.98 keV	0.222	3.2 ppm	Yb is not likely to interfere with W in most circumstances
W	1 78	M-alpha	1.81 keV	0.021		Intercents: Si K-
••	keV	Wi-aipila	1.01 KC V	0.021		alpha
	1.84 keV	M-beta	1.87 keV	0.013		
Si	1.74 keV	K-alpha	1.56 keV	0.033	28.2 %	Si is much more common, and is a key component in almost all detectors. It will certainly interfere.
Sr	1.81 keV	L-alpha Overlap	1.94 keV	0.026	370 ppm	Sr is much more common, and can have high enough concentrations in some deposits. Ca may also be an issue at the same time.
Rb	1.83 keV	L-beta Overlap	2.07 keV	0.005	90 ppm	Rb is unlikely to be present in high enough quantities to leave a detectable L line.
Rh	2.70 keV	L-alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of W

Ag	2.98	L-alpha	3.35 keV	0.052	75 ppb	The L-emission from
	keV	Excitatio				Ag tubes improves
		n				the fluorescence of
						W

Table 74: Observable emission lines for tungsten and its most common fluorescence interactions.

#### 2.67 Rhenium, Re (75)

Rhenium is one of the rarer elements, and is thus unlikely to be identified by handheld XRF. Its L-lines fluoresce amidst the transition metals, which further complicates its identification even in the unlikely event it is present. Some degree of filtration is needed to verify its presence.

Rhenium can be used in jet engines to increase maximum stress that will result in creep over a given time at a given temperature (i.e. creep strength)<sup>336</sup>. It lowers the temperature of tungsten and molybdenum alloys to make them more workable<sup>337</sup>. It can also be used in catalyst reforming<sup>338</sup>. Radioactive isotopes of rhenium can be used to treat liver cancer<sup>339</sup>, and they can also be used as a substitute for technetium<sup>340</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Re	8.65 keV	L-alpha	10.54 keV	0.268	0.7 ppb	Intercepts: Zn K-
	10.01 keV	L-beta				alpha
Zn	8.62 keV	K-alpha Overlap	9.66 keV	0.469	70 ppm	The K-alpha line of the more abundant Zn will absolutely be a challenge in the identification of Re
Cu	8.91 keV	K-beta Overlap	8.98 keV	0.441	60 ppm	In Cu rich materials, the K- beta peak may be enough to overwhelm the signal for Re
Yb	8.54 keV	L-beta Overlap	10.49 keV	0.112	3.2 ppm	Yb, while rare, is almost a magnitude of order more common than Re and an overlap should not be discounted
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Lu	8.71 keV	L-beta Overlap	10.35 keV	0.234	800 ppb	This interaction is unlikely to occur
Re	1.85 keV	M-alpha	1.88 keV	0.022		
	1.91 keV	M-beta	2.03 keV	0.013		
Sr	1.87 keV	L-beta Overlap	2.01 keV	0.024	370 ppm	Sr is much more common, and can have high enough concentrations in some deposits. Ca may also be an issue at the same time.
W	1.84 keV	M-beta Overlap	1.87 keV	0.013	1.25 ppm	Potentially significant in some metals
Rh	2.70 keV	L-alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Re
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Re

Table 75: Observable emission lines for rhenium and its most common fluorescence interactions.

## 2.68 Osmium, Os (76)

Osmium is yet another rare element with L-line fluorescence buried amidst more common transition metals. Its L-alpha overlaps with the much more common copper K-beta line, and thus L-beta will be the more likely identifier for this element. Some filtration will be necessary to see it in the unlikely event it is present.

As Osmium is one of the rarest stable elements in Earth's crust<sup>341</sup>, it is highly unlikely to be present in any handheld XRF assays. It is also highly toxic<sup>342</sup>, though this opens up applications as a potential cancer treatment<sup>343</sup>. In its tetroxide form it has been used to identify fingerprints<sup>344</sup> and as a stain in scanning electron<sup>345</sup> and transmission electron microscopy (TEM)<sup>346</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Os	8.91 keV	L-alpha	10.87 keV	0.281	1.5 ppb	Intercepts: Cu K-
	10.35 keV	L-beta				агрпа
Cu	8.91 keV	K-beta Overlap	8.98 keV	0.441	60 ppm	The K-alpha line of the more abundant Cu will be a challenge in the identification of Os
Hf	9.02 keV	L-beta Overlap	10.74 keV	0.243	3 ppm	Hf, while rare, is almost a magnitude of order more common than Os and an overlap should not be discounted
Os	1.92 keV	M-alpha	1.96 keV	0.023		Intercepts: P K-
	1.99 keV	M-beta	2.03 keV	0.014		aipna, Ca K-aipna
Р	2.01 keV	K-alpha Overlap	2.15 keV	0.056	1,050 ppm	P is much more common, its interference is likely.
Y	1.92 keV	L-alpha Overlap	2.22 keV	0.028	33 ppm	As an REE, Y is unlikely to occur in large enough quantities to have visible L lines.
Sr	1.93 keV	L-beta Overlap	2.22 keV	0.005	370 ppm	Sr is much more common, and can have high enough concentrations in some deposits. Ca may also be an

						issue at the same time.
Са	1.99 keV 3.69 keV	K-alpha Escape Peak / Excitation	4.04 keV	0.147	4.15 %	Very common interference if high Ca concentrations are present.
Rh	2.70 keV	L-alpha Excitation	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Os
Ag	2.98 keV	L-alpha Excitation	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Os

Table 76: Observable emission lines for osmium and its most common fluorescence interactions.

#### 2.69 Iridium, Ir (77)

Iridium is another highly rare element, but it has fewer overlaps with the common transition metals. The main obstacle is the K-line of gallium. It will require filtration to be visible.

Iridium is famously the element used to identify the signature of a meteor impact which led to the K-Pg extinction event in which dinosaurs, pterosaurs, and marine reptiles went extinct<sup>347</sup>. Iridium's corrosion resistance<sup>348</sup> leads to its use in some alloys for aircraft parts<sup>349</sup> and deepwater pipelines<sup>350</sup>. A radioactive isotope is used as an energy source in some gamma radiation devices<sup>351</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ir	9.18 keV 10.71 keV	L-alpha L-beta	11.22 keV	0.294	1 ppb	Intercepts: Cu K- alpha

Ga	9.23 keV	K-alpha Overlap	10.37 keV	0.497	19 ppm	The K-alpha line of the more abundant Ga will be a challenge in the identification of Ir
Cu	8.91 keV	K-beta Overlap	8.98 keV	0.441	60 ppm	The K-alpha line of the more abundant Cu will be a challenge in the identification of Ir
Hf	9.16 keV	L-beta Overlap	11.27 keV	0.130	3 ppm	Hf, while rare, is almost a magnitude of order more common than Ir and an overlap should not be discounted
Ir	1.99 keV	M-alpha	2.04 keV	0.024	1 ppb	Intercepts: P K-
	2.06 keV	M-beta	2.12 keV	0.018		aipiia, Ca K-aipiia
Р	2.01 keV	K-alpha	2.15 keV	0.056	1,050 ppm	P is much more common, its interference is likely.
Zr	2.04 keV	L-alpha Overlap	2.31 keV	0.031	165 ppm	Zr is more common than Ir, but may not necessarily be common when they co-occur
Ca	1.99 keV 3.69 keV	K-alpha Escape Peak / Excitatio n	4.04 keV	0.147	4.15 %	Ca can play a duel role exiting Ir M lines and also obscuring them with an escape peak.
Rh	2.70 keV	L-alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Ir
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Ir

Table 77: Observable emission lines for iridium and its most common fluorescence interactions.

## 2.70 Platinum, Pt (78)

Platinum is comparably easy to identify using handheld XRF compared to many other platinum group metals due to fewer (but not entirely discountable) overlaps of the L-line with major K-lines. It will require filtration to be visible unless it is highly abundant.

Platinum has a long history of use in jewelry in both the old world  $(Egypt)^{352}$  and the new  $(Peru)^{353}$ . However, its most common use today is not in jewelry, but instead in catalytic converters<sup>354</sup> in automobiles to finalize combustion of hydrocarbons into CO<sub>2</sub> and water. It can be alloyed with cobalt to make long-lasting magnets<sup>355</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Pt	9.44 keV	L-alpha	11.56 keV	0.306	5 ppb	
	11.07 keV	L-beta				
Ga	9.23 keV	K-alpha Overlap	10.37 keV	0.497	19 ppm	The K-alpha line of the more abundant Ga will be a challenge in the identification of Ir
Hf	9.35 keV	L-beta Overlap	9.56 keV	0.242	3 ppm	Hf, while rare, is almost a magnitude of order more common than Ir and an overlap should not be discounted
Та	9.34 keV	L-beta Overlap	11.14 keV	0.258	2 ppm	Ta is as rare as Pt, so verification using either the L- beta of Pt or L- alpha of Ta will be helpful
Pt	2.07 keV	M-alpha	2.12 keV	0.025	5 ppb	Intercepts: P K-
	2.13 keV	M-beta	2.20 keV	0.022		aipiia, Ca K-aipiia

Р	2.01 keV	K-beta Overlap	2.15 keV	0.056	1,050 ppm	P can be more common, an in large enough quantities can overwhelm Pt M.
Y	2.08 keV	L-beta Overlap	2.22 keV	0.028	33 ppm	As an REE, Y is unlikely to occur in large enough quantities to have visible L lines.
Zr	2.04 keV	L-alpha Overlap	2.31 keV	0.031	165 ppm	Zr is more common than Hg, but may not necessarily be common when they co-occur
Y	2.07 keV	L-beta Overlap	2.22 keV	0.028	33 ppm	As an REE, Y is unlikely to occur in large enough quantities to have visible L lines.
Ca	3.69 keV 1.99 keV	K-alpha Excitation / Escape Peak	4.04 keV	0.147	4.15 %	Ca can play a duel role exiting Pt M lines and also obscuring them with an escape peak.
Rh	2.70 keV	L-alpha Excitation	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Pt
Ag	2.98 keV	L-alpha Excitation	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Pt

Table 78: Observable emission lines for platinum and its most common fluorescence interactions.

#### 2.71 Gold, Au (79)

It is difficult to estimate how many XRF units have been sold for the purpose of identifying gold, but it is a challenging measurement to make by XRF. The gold L-alpha lines fluoresces too near to the zinc K-beta lines to be easily identifiable, leading many to use the L-beta emission. However, gold's use in the electronic components within the instrument can lead it to appear as a contaminant in the XRF spectrum. The L-beta line of tungsten also overlaps

with gold, which also makes gold difficult to observe and can result in unusual behavior in some calibrations which do not anticipate either W or Au. Gold is thus very challenging to measure below 3 ppm. It requires strong filtration to observe in low quantities.

Gold has had an outsized impact on human civilization, and you would be forgiven for thinking it was similarly relevant to natural processes<sup>356</sup>. However, this inert element plays very little role in chemical processes and simply accumulates passively in ether veins<sup>357</sup> or alluvial<sup>358</sup> deposits. When gold is common, it is only common at the ppm level, unless someone is very, very lucky.

Civilizations which developed in isolation of each other from South America to China assigned value to gold<sup>359</sup>, although with varying levels of obsession. Some have speculated that because of its shine it triggers our instinctive attraction to water - essentially gold serves as a subversive perpetual mirage<sup>360</sup>. It serves almost universally as a decorative element not only because of its luster, but also because of its malleability<sup>361</sup>. Because gold is inert, it does not tarnish. Gold can be functionally deployed in electronics when alloyed with other metals such as nickel<sup>362</sup>, and can be used as a catalyst with palladium<sup>363</sup>. Gold is often used to store value in areas with unstable economies<sup>364</sup>. It can be alloyed with elements like nickel and palladium to produce a white colored alloy<sup>365</sup>. Its value across the world has led it to be widely used in currency<sup>366</sup>.

Gold in the computer age has proven to be critical<sup>367</sup>. It is highly conductive<sup>368</sup> and does not corrode<sup>369</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Au	9.71 keV 11.44 keV	L-alpha L-beta	11.92 keV	0.320	4 ppb	Intercepts: Zn K- alpha, W L-alpha

Zn	9.57 keV	K-beta Overlap	9.66 keV	0.469	70 ppm	The K-beta line of Zn overlaps with the Au L- alpha line, and is a major hurdle to the identification of low quantities of Au.
Ge	9.86 keV	K-alpha Overlap	11.10 keV	0.523	1.5 ppm	This overlap is unlikely to occur, but sufficient Ge could overwhelm the signal for Au.
W	9.67 keV	L-beta Overlap	11.54 keV	0.270	1.3 ppm	W L-beta also overlaps with Au L-alpha, which complicates many calibrations
Та	9.67 keV	L-beta Overlap	9.89 keV	0.243	2 ppm	The Ta L-line overlap with Au is less common, but not to be discounted in unusual geologic contexts
Au	2.14 keV 2.22 keV	M-alpha M-beta	2.21 keV 2.29 keV	0.026 0.026	4 ppb	Intercepts: P K- alpha, Ca K- alpha
Р	2.14 keV	K-beta Overlap	2.15 keV	0.056	1,050 ppm	P can be more common, an in large enough quantities can overwhelm Au M.
Ca	3.69 keV 1.99 keV	Excitation / Escape Peak	4.04 keV	0.147	4.15 %	Ca can play a duel role exiting Au M lines and also obscuring them with an escape peak.
Zr	2.20 keV	L-beta Overlap	2.31 keV	0.031	165 ppm	Zr is more common than Hg, but may not necessarily be common when they co-occur

Nb	2.17 keV	L-alpha Overlap	2.37 keV	0.034	20 ppm	Nb is unlikely to occur in high enough concentrations to create a visible L line.
Мо	2.29 keV	L-alpha Overlap	2.52 keV	0.037	1.2 ppm	Can be significant in some industrial materials and in hard rock mining contexts.
Hg	2.2 keV	M-Line Overlap	4.00 keV	0.003	85 ppb	Common in oil- based paints
Rh	2.70 keV	L-Alpha Excitation	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Au
Ag	2.98 keV	L-Alpha Excitation	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Au

 Table 79: Observable emission lines for gold and its most common fluorescence interactions.

#### 2.72 Mercury, Hg (80)

The identification of mercury is easier than most other L-line emissions due to few K-line overlaps. Although it will still need heavy filtration to be visible in small quantities.

As a pigment, mercury is found in cinnabar and its synthesized variant, vermillion. This makes a bright red that has commonly been used by painters for centuries across the world. In Çatalhöyük in south-central Turkey, a Neolithic village occupied 9,000 years ago, cinnabar was painted across the skulls of the dead when they were buried beneath houses<sup>370</sup>. In historical paintings, it is often used to form skin tones<sup>371</sup>. Artists would deposit mercury first and then layer it with lead white<sup>372</sup> creating a dimensional effect similar to looking at a person's face. Just as blood fluoresces red beneath your cheeks, mercury fluoresces beneath the lead cheeks of paintings. It can also be used more passively simply by mixing with lead white.

Mercury is a less fortunate element to find in other circumstances. It forms a potent environmental pollutant, though one detectable by XRF<sup>373</sup>. In gold mining it is used to form an amalgam with minute portions of gold (and subsequently removed via vaporization) this has made it a dangerous follower of the precious metals industry<sup>374</sup>, creating long-term risk long after mining as ended<sup>375</sup> if the land is not properly reclaimed.

Mercury is a liquid at standard temperature and pressure; it is the only metal which behaves this way<sup>376</sup>. Its sensitivity to heat made it useful in thermometers, though this also made it a household toxin<sup>377</sup>. Today, it is commonly used in fluorescent light bulbs as the target for electrons, which makes it both a household and workplace toxin<sup>378</sup>.

In the ancient world it was used ineffectively for medicine<sup>379</sup>. China's first emperor poisoned himself with it believing it would make him immortal, incidentally making him the first recorded death of mercury poisoning<sup>380</sup>. It was even used in makeup in Egypt<sup>381</sup>.

While we encounter it frequently as a liquid, mercury can still be used in metal alloys. When alloyed with gold or silver, it forms an amalgam<sup>382</sup> used to fill dental cavities, although its use for this purpose has been in sharp decline for over twenty years. It was used to help bind gold to copper and silver alloys<sup>383</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Hg	9.99 keV 11.82 keV	L-alpha L-beta	12.28 keV	0.333	85 ppb	
Ge	9.86 keV	K-alpha Overlap	11.10 keV	0.523	1.5 ppm	The K-alpha line of Ge overlaps with Hg, but Hg will be more likely in manufactured objects.
W	9.96 keV	L-beta Overlap	10.21 keV	0.255	1.3 ppm	W L-beta also overlaps with Hg L- alpha,

Hg	2.20 keV	M-alpha	2.30 keV	0.027	85 ppb	Intercepts: S K-
	2.29 keV	M-beta	2.39 keV	0.028		alpha, Mo L-alpha
S	2.31 keV	K-alpha Overlap	2.47 keV	0.071	350 ppm	S in even low concentrations will see overlap with Hg M.
Zr	2.20 keV	L-beta Overlap	2.31 keV	0.031	165 ppm	Zr is more common than Hg, but may not necessarily be common when they co-occur
Мо	2.29 keV	L-alpha Overlap	2.52 keV	0.037	1.2 ppm	Can be significant in some industrial materials and in hard rock mining contexts
Ca	3.69 keV	K-alpha Excitatio n	4.04 keV	0.147	4.15 %	Ca in normal concentrations may excite Hg M.
Rh	2.70 keV	L-Alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Hg
Ag	2.98 keV	L-Alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Hg

Table 80: Observable emission lines for mercury and its most common fluorescence interactions.

#### 2.73 Thallium, TI (81)

Most XRF users are unlikely to encounter thallium, but it has few overlaps and would not be a challenging element to measure. It would nonetheless require filtration to be observable in most cases.

Thallium was used in pesticides<sup>384</sup> before its prohibition in the 1970's in many countries. Because of conductivity with infrared light in some compounds<sup>385</sup>. Radioactive thallium has been used in some cases as a replacement for technetium in medical applications<sup>386</sup>. It is currently being researched as a potential superconductor<sup>387</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
TI	10.27 keV	L-alpha	12.66 keV	0.347	850 ppb	
	12.21 keV	L-beta				
Ga	10.27 keV	K-beta Overlap	10.37 keV	0.497	19 ppm	The K-alpha line of the more abundant Ga will be a challenge in the identification of Tl
Re	10.28 keV	L-beta Overlap	10.54 keV	0.268	0.7 ppb	Re L-beta also overlaps with Tl L- alpha, but is much less common
Tl	2.27 keV	M-alpha	2.39 keV	0.029	850 ppb	Intercepts: S K-
	2.36 keV	M-beta	2.49 keV	0.030		aipiia, Nio L-aipiia
S	2.31 keV	K-alpha Overlap	2.47 keV	0.071	350 ppm	S is much more common, and will almost certainly overlap without sample preparation.
Мо	2.29 keV	L-alpha Overlap	2.52 keV	0.037	1.2 ppm	Can be significant in some industrial materials and in mining contexts
Hg	2.2 keV	M-Line Overlap	4.00 keV	0.003	85 ppb	Common in oil- based paints
Ca	3.69 keV	K-alpha Excitatio n	4.04 keV	0.147	4.15 %	Large concentrations of Ca could influence the fluorescence of this element
Rh	2.70 keV	L-Alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Tl
Ag	2.98 keV	L-Alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Tl

Table 81: Observable emission lines for thulium and its most common fluorescence interactions.

#### 2.74 Lead, Pb (82)

The identification of lead is generally unambiguous in the XRF spectrum. While its L-alpha overlap with the As K-alpha is a widely understood challenge, its L-beta emission is almost always unmistakable. If minute portions of lead are to be identified, filtration is needed. Lead is quite common and a filter is not always needed. The challenge with lead is not how it is impacted by other elements, but rather how it influences them. Lead L-lines can overwhelm other elements with their intensity. There are many direct overlaps, including lead M with sulfur K-alpha, lead-L-I with gallium-K-alpha, lead-L-alpha with arsenic-K-alpha, lead-L-beta with krypton-K-alpha, and lead-L-delta with yttrium-K-alpha. But the problems don't end there. The sum peak of lead-L-alpha and lead-L-beta overlap with the cadmium-K-alpha. This latter overlap can substantially affect the interpretation of the spectra. Any identification of cadmium in a painting should employ both K-alpha and K-beta.

Lead is the heaviest stable element, almost all elements below it in atomic number are stable, all above it are radioactive. It is the final product of radioactive decay for the three most common radioactive isotopes on Earth, <sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th. The radiation generated from the decay of 238U and 232Th generates 20.0+/-8.7 terrawats of energy to Earth's heat flux<sup>388</sup>. This heat not only makes continental drift possible<sup>389</sup>, but also creates the magnetic shield protecting the Earth from cosmic radiation<sup>390</sup>. Life on Earth is ultimately a byproduct of this lead production.

Lead has a deep relationship with humanity, often not for the better. Lead is very common across the Earth, though often in small concentrations less than 30 ppm. It was used relatively early in the Bronze Age as an alloy with copper due to its ability to lower the melting temperature of the resulting mixture<sup>391</sup>. As a raw elemental metal, it is also highly malleable, leading to its common use for a variety of purposes. For these reasons lead crept into people's lives and began manifesting its toxic effects. Lead can substitute for metals your body needs

such as zinc<sup>392</sup>. Because it has four valence electrons, like carbon it can combine into multiple compounds. In humans, it can cause cognitive impairment<sup>393</sup>. Up until the 1970s, lead was used as an additive to gasoline<sup>394</sup>, following the termination of its use, blood lead levels tended to drop<sup>395</sup>. Its use in paint provided a particularly potent path to the human body. Because lead carbonate has a somewhat sweet taste, young children would occasionally consume the chips which came off the walls of their homes, resulting in the presence of lead paint at home being a significant predictor of lead toxicity in children<sup>396</sup>. While today this is considered to be dangerous, this sweetening effect was embraced by the Romans, who used lead acetate as a sweetener<sup>397</sup>. This can also be a modern problem, as lead poisoning due to adulterating marijuana with lead has been documented<sup>398</sup>.

For XRF users, lead will frequently accompany art. It was frequently used as a priming agent for canvases<sup>399</sup>. Lead white (PbCO<sub>3</sub>)<sup>400</sup> and lead red (PbO)<sup>401</sup> were the most prominent pigments used, with lead white being used as a mix for many other pigments. It was used in combination with other metals in pigments as well, including Chrome Yellow (CrPbO<sub>4</sub>)<sup>402</sup> among others. Lead was also used widely in both glass<sup>403</sup> and glazes<sup>404</sup>, forming bright colors. Analyzing these materials can be a challenge; a pure lead oxide will not allow photons at 40 keV to escape past half a millimeter. As such, lead begins to absorb its own signal. Quantifying lead in these circumstances becomes very difficult. There is a further problem with lead in these circumstances, with an atomic weight of over 200, variations in this element can overwhelm others when the unit of weight % is used.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Pb	10.55 keV	L-alpha	13.04 keV	0.360	14 ppm	Intercepts: As K- beta
	12.62 keV	L-beta				

As	10.51 keV	K-alpha Overlap	11.87 keV	0.549	1.8 ppm	As K-alpha is a widely understood overlap, which generally requires Pb L-beta for confirmation
Os	10.35 keV	L-beta Overlap	12.39 keV	0.295	1.5 ppb	Os L-beta also overlaps with Pb L- alpha, but its rarity precludes this as a serious concern
Pb	2.35 keV	M-alpha	2.48 keV	0.031	14 ppm	Intercepts: S K-
	2.44 keV	M-beta	2.57 keV	0.031		alpha, Mo L-alpha
S	2.31 keV	K-alpha	2.47 keV	0.071	350 ppm	S is much more common, and will likely overlap.
Мо	2.39 keV	L-alpha Overlap	2.63 keV	0.035	1.2 ppm	Can be significant in some industrial materials
Hg	2.49 keV	M-gamma Overlap	2.85 keV	0.003	85 ppb	If Hg signal is large enough, this can overlap partially. Common in oil- based paints
Ca	3.69 keV	K-alpha Excitation	4.04 keV	0.147	4.15 %	In Ca rich materials, this can provide additional excitation.
Rh	2.70 keV	L-Alpha Excitation	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Pb
Ag	2.98 keV	L-Alpha Excitation	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Pb

Table 82: Observable emission lines for lead and its most common fluorescence interactions.

# 2.75 Bismuth, Bi (83)

The detection of bismuth L-lines is often difficult due to its proximity to the more common lead L-lines. Filtration will be necessary.

Bismuth was once thought to be the heaviest stable isotope - it is now known to be radioactive, albeit with a half-life that is over 4 billion times longer than the known age of the universe<sup>405</sup>. Adding to its strangeness, bismuth has the lowest thermal conductivity of any metal. Bismuth, like ice, expands when it is frozen. For this reason, it is useful in printing presses. As a non-toxic heavy metal, it has some medicinal applications. It is the 'bismol' in Pepto-Bismol as it can act as an anti-diarrheal<sup>406</sup>.

Intentional use of bismuth dates almost exclusively to the modern era, though it can occur in both pigments and ancient alloys. Toward the end of the Inca Empire bismuth was alloyed with copper to form an unusual bronze alloy<sup>407</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Bi	10.84 keV	L-alpha	13.42 keV	0.373	8.5 ppb	Intercepts: Pb L- alpha
	13.02 keV	L-beta				
Pb	10.55 keV	L-alpha Overlap	13.04 keV	0.360	14 ppm	
As	10.51 keV	K-alpha Overlap	11.87 keV	0.549	1.8 ppm	As K-alpha is a widely understood overlap, which generally requires Pb L-beta for confirmation
Hg	11.82 keV	L-beta Overlap	14.21 keV	0.347	8.5 ppb	Hg L-beta occurs near Bi L-alpha as well.
Bi	2.42 keV	M-alpha	2.58 keV	0.024	8.5 ppb	Intercepts: S K- alpha
	2.53 keV	M-beta	2.69 keV	0.033		
S	2.46 keV	K-beta Overlap	2.47 keV	0.071	350 ppm	S is much more common and interference should be expected.

Мо	2.52 keV	L-beta Overlap	2.52 keV	0.037	1.2 ppm	Can be significant in some industrial materials
Pb	2.44 keV	M-beta	2.57 keV	0.031	14 ppm	Pb is more common, and can be in concentrations large enough to have an M line.
Rh	2.70 keV	L-Alpha Excitatio n	3.0 keV	0.046	1 ppb	The L-emission from Rh tubes improves the fluorescence of Bi
Ag	2.98 keV	L-Alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Bi

Table 83: Observable emission lines for bismuth and its most common fluorescence interactions.

## 2.76 Polonium, Po (84)

While polonium is rare, it has few L-line overlaps, and those are with elements that are themselves rare as well. However, it is unlikely to be found unless uranium deposits are analyzed.

Polonium can be used in nuclear reactors, though they were more commonly used in the former Soviet Union.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ро	11.13 keV	L-alpha	13.81 keV	0.386		
	13.44 keV	L-beta				
Pt	11.07 keV	L-beta Overlap	13.27 keV	0.321	5 ppb	Pt is rare; this overlap is unlikely
Ge	10.98 keV	K-beta Overlap	11.10 keV	0.523	1.5 ppm	Ge is rare; this overlap is unlikely
Ir	10.92 keV	L-beta Overlap	11.22 keV	0.294	1 ppb	Ir is unlikely to be observable with handheld XRF.

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Ро	2.50 keV	M-alpha	2.68 keV	0.034		
	2.62 keV	M-beta	2.80 keV	0.034		
Cl	2.62 keV	K-alpha	2.82 keV	0.089	145 ppm	Cl is much more common and overlap should be expected.
S	2.46 keV	K-beta Overlap	2.47 keV	0.071	350 ppm	S, if in high enough quantities, will also overwhelm any signal from Po M.
Rh	2.70 keV	L-alpha Overlap/ Excitatio n	3.0 keV	0.046	1 ppb	Rh anode instruments may excite Po M lines, but they will also likely obscure them.
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Po if in detectable quantities.

Table 84: Observable emission lines for polonium and its most common fluorescence interactions.

## 2.77 Radon, Rn (86)

Rn features few overlaps, though those that exist occur among elements more common than it. As with all noble gases, it doesn't react with other elements. However, unlike most other noble gases, Rn is radioactive in all of its isotopic forms. Because it is a decay product for uranium, it is naturally produced and emitted from the Earth. In some areas, underground structures can be at risk of radon poisoning. In the past, it was used in radiation therapy.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Rn	11.73 keV	L-alpha	14.62 keV	0.411		
	14.32 keV	L-beta				

Au	11.61 keV	L-beta overlap	14.35 keV	0.320	4 ppb	Au is rare, but a portion of its L-beta emissions overlap
As	11.73 keV	K-beta overlap	11.87 keV	0.549	1.8 ppm	As is more common, and it's K-beta line is close to Rn's L-alpha
Rn	2.66 keV	M-alpha	2.89 keV	0.036		
	2.79 keV	M-beta	3.02 keV	0.036		
Cl	2.62 keV	K-alpha Overlap	2.82 keV	0.089	145 ppm	Cl should be expected to overwhelm any detection of Rn M lines unless Rn is in exceptionally high quantities.
Rh	2.70 keV	L-alpha Overlap	3.0 keV	0.046	1 ppb	In Rh tubes, filtration will be needed to remove interference if Rn M is a goal.
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Rn M if it is detectable.

 Table 85: Observable emission lines for radon and its most common fluorescence interactions.

### 2.78 Radium, Rn (88)

Few elements overlap with Rn making it comparatively easy to identify in an XRF spectra should it be present. However, it is highly rare, and only found in uranium and thorium ore deposits. In the past, it was used as a luminescent pigment and as a very dangerous natural supplement. Some of its isotopes are long lived; they will continue to irradiate the notebooks of the element's discoverer, Marie Curie, for millennia to come<sup>408</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Ra	12.34 keV	L-alpha	15.44 keV	0.437		

	15.23 keV	L-beta				
TI	12.27 keV	L-beta overlap	12.66 keV	0.347	850 ppb	
Ra	2.83 keV	M-alpha	3.11 keV	0.048		
	2.97 keV	M-beta	3.25 keV	0.047		
Cl	2.82 keV	K-beta Overlap	2.82 keV	0.089	145 ppm	Cl is more common, and this overlap should be anticipated
Ar	2.96 keV	K-alpha Overlap	3.21 keV	0.109	3.5 ppm	While Ar is rare in Earth's crust, it forms 0.98% of the Earth's atmosphere.
Rh	2.83 keV	L-alpha overlap / Excitatio n	3.15 keV	0.043	1 ppb	In Rh tubes, filtration will be needed to remove interference if Ra M is a goal.
Ag	2.98 keV	L-alpha Excitatio n	3.35 keV	0.052	75 ppb	The L-emission from Ag tubes improves the fluorescence of Ra M. However, it will also overlap with the right tail of the peak.

Table 86: Observable emission lines for radon and its most common fluorescence interactions.

#### 2.79 Thorium, Th (90)

Analysis of thorium is comparatively easy compared to most other L-line emissions. Its main overlaps are proximity to the L-beta line of bismuth and the K-alpha of rubidium, though it is sufficiently far from both to be clear. Occasionally, with large quantities of lead, it can be obscured. The most common overlap will be the sum peak of iron K-alpha. For this reason, heavy filtration is needed to identify thorium in low quantities to reduce backscatter and to reduce the influence of the iron sum peak.

The L-lines of thorium are identifiable more often than not when one analyzes soils or other geologic materials. Archaeologists and geologists can use this element when sourcing objects such as obsidian, ceramics, or rocks.

In modern contexts, thorium was used in lantern mantles<sup>409</sup> due to its brilliance during combustion. Due to its radioactivity, other elements such as yttrium have been substituted in its place<sup>410</sup>. It has the potential of providing a cleaner fuel for nuclear reactors<sup>411</sup>, but as of this writing still rarely used for this purpose.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Th	12.97 keV 16.20 keV	L-alpha L-beta	16.30 keV	0.463	9.6 ppm	Intercepts: Fe K- alpha, Rb K- alpha
Fe	~12.8 keV	Sum Peak	7.11 keV	0.351	5.63 %	The sum peak of Fe K-alpha is the highest likelihood overlap for Th L- alpha
Bi	12.98 keV	L-beta Overlap	13.42 keV	0.373	8.5 ppb	The Bi L-beta comes close to the Th L-alpha line
Pb	12.80 keV	L-beta Overlap	15.86 keV	0.112	14 ppm	In large quantities, Pb L- beta can become a non-trivial concern
Rb	13.34 keV	K-alpha Overlap	15.20 keV	0.643	90 ppm	Rb is generally more abundant than Th, but not abundant enough to normally overlap.
Th	3.00 keV	M-alpha	3.33 keV	0.050	9.6 ppm	Intercepts: Ar K-
	3.15 keV	M-beta	3.49 keV	0.059		alpha

Ar	2.96 keV	K-alpha Overlap	3.21 keV	0.109	3.5 ppm	While Ar is rare in Earth's crust, it forms 0.98% of the Earth's atmosphere.
Ag	2.98 keV	L-alpha Overlap	3.35 keV	0.052	75 ppb	Can be common in painting or metals. In Ag anode instruments, a filter will be needed.
Rh	3.00 keV	L-beta Overlap	3.00 keV	0.046	1 ppb	In Rh anode instruments, a filter will be needed.
Pd	3.04 keV	L-beta Overlap	3.60 keV	0.047	15 ppb	Pd is unlikely to be more common than Th.

Table 87: Observable emission lines for thorium and its most common fluorescence interactions.

#### 2.80 Uranium, U (92)

Uranium, like thorium, is also relatively common, but it is often dwarfed in the spectrum by the rubidium K-line, which fluoresces next to it at a lower energy. As such, you will typically only see it in natural abundance when using a deconvolution method to remove the effects of rubidium. In most sediments, the uranium signal will be difficult to identify.

Uranium is a key element in nuclear energy<sup>412</sup>, but it is not restricted to human activity. A deposit of <sup>235</sup>U went critical some two billion years ago in present day Gabon<sup>413</sup>. Thus, even humans were late to the fission game.

Uranium is not unknown in art objects. In the mid-20<sup>th</sup> century, artists were swept by the novelty of radioactive materials. Following their discovery by Marie Curie, they were briefly incorporated as pigments and patinas, typically in yellow to yellow-green shades<sup>414</sup>. In a ceramic glaze, it can be made into an orange color see in in some Fiestaware<sup>TM415</sup>. It is also present in glasses as well<sup>416</sup>, giving them a yellow-green color.

Today, most uranium is used in military contexts. In its depleted form (<sup>238</sup>U) it is used as shielding and armor. This causes long-term concerns of its health effects in former areas of conflict<sup>417</sup>. Its enriched form (<sup>235</sup>U) is used in fissile nuclear weapons, beginning with the Trinity blast in Alamagordo, New Mexico and the Hiroshima and Nagasaki bombings<sup>4</sup> Uranium can be common in phosphate deposits, which can be a concern in some mineral fertilizers<sup>419</sup>.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
U	13.61 keV	L-alpha	17.17 keV	0.489	2.7 ppm	Intercepts: Rb K- alpha
	17.22 keV	L-beta				
Rb	13.34 keV	K-alpha Overlap	15.20 keV	0.643	90 ppm	Rb is much more abundant and it's K- line generally overlaps with U L- alpha
Br	13.47 keV	K-beta Overlap	13.47 keV	0.598	2.4 ppm	Br K-beta is unlikely to be in high enough quantities to overlap with U L-alpha
Со	~13.80 keV	K-alpha Sum Peak	7.71 keV	0.382	25 ppm	In alloys, ores, and some pigments the sum peak of Co could overlap.
U	3.17 keV	M-alpha	3.55 keV	0.565	2.7 ppm	Intercepts: K K-alpha
	3.34 keV	M-beta	3.73 keV	0.676		
K	3.31 keV	K-alpha Overlap	3.61 keV	0.132	2.09 %	K is much more common and it's overlap should be anticipated.
Cd	3.13 keV	L-alpha Overlap	3.54 keV	0.056	150 ppb	Cd is unlikely to overlap, but can in some manufactured materials.
Ag	3.15 keV	L-beta Overlap	3.52 keV	0.051	75 ppb	In Ag anode instruments, this overlap should be anticipated and a filter used.

Rh	3.15 keV	L-gamma Overlap	3.15 keV	0.043	1 ppb	In Rh anode instruments, this overlap should be anticipated and a
						filter used.

Table 88: Observable emission lines for uranium and its most common fluorescence interactions.

## 2.81 Plutonium, Pu (94)

The measurement of plutonium is comparatively difficult compared to uranium. Its L-alpha emission overlaps with the much more common element strontium's K-alpha line, while its L-beta line overlaps with the Compton (inelastic) scattering peak for Rh anode instruments.

Plutonium occurs naturally in uranium deposits as a result of the decay of U238. U238 gains a neutron, becoming U239. It then emits and electron and anti-neutrino, which in turn produce neptunium and then the more stable (but still radioactive) plutonium. It is much more commonly produced as a consequence of fission during nuclear power generation.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Pu	14.28 keV 29 keV	L-alpha L-beta	06 keV	0.514		Intercepts: Sr K- alpha Slopes: Rh K-alpha, Ag K-alpha (depends on tube anode)
Sr	14.10 keV	K-alpha Overlap	16.11 keV	0.665	370 ppm	Sr is much more abundant and it's K- line generally overlaps with Pu L- alpha
Br	13.47 keV	K-beta Overlap	13.47 keV	0.598	2.4 ppm	Br K-beta is unlikely to be in high enough quantities to overlap with U L-alpha
Pu	3.34 keV	M-alpha	3.78 keV	0.565		Intercepts: K K- alpha

	3.53 keV	M-beta	3.97 keV	0.068		
К	3.31 keV	K-alpha	3.61 keV	0.132	2.09 %	K is much more common and it's overlap should be anticipated.
Ag	3.35 keV	L-beta Overlap	3.35 keV	0.052	75 ppb	In Ag anode instruments, this overlap should be anticipated and a filter used.
Cd	3.32 keV	L-beta Overlap	3.73 keV	0.056	150 ppb	Cd is unlikely to overlap, but can in some manufactured materials.
Rh	3.36 keV	L- gamma Overlap	3.81 keV	0.013	1 ррb	In Rh anode instruments, this overlap should be anticipated and a filter used.

 Table 89: Observable emission lines for plutonium and its most common fluorescence interactions.

#### 2.82 Americium, Am (95)

The measurement of americium will be relatively unimpeded - the Sr K-alpha line is close, but not so close to overwhelm the L-lines for americium. Heavy filtration paired with high voltage will be necessary.

Though Am is itself a synthetic element, it is often used in smoke detectors due to its low gamma radiation. It can also be used to remove impurities from diamonds.

Element	Energy	Туре	Absorption Edge	Fluorescence Efficiency	Earth Crustal Abundance	Comments
Am	14.62 keV	L-alpha	1 51 keV	0.526		Intercepts: Sr K-alpha Slopes: Rh K-alpha, Ag K-alpha (depends
	85 keV	L-beta				on tube anode)

Sr	14.10 keV	K-alpha Overlap	16.11 keV	0.665	370 ppm	Sr is much more abundant and it's K- line generally overlaps with Am L- alpha
Rn	14.52 keV	L-beta Overlap	05 keV	0.134		Rn will be a gas, so it is unlikely to interfere
Am	3.44 keV	M-alpha	3.89 keV	0.565		Intercepts: Ca K-
	3.646 keV	M-beta	4.096	0.068		агрпа
Са	3.69 keV	K-alpha	4.04 keV	0.147	4.15 %	Ca is much more common and its overlap should be anticipated.
Sb	3.60 keV	L-alpha Overlap	4.13 keV	0.069	200 ppb	Can be common in painting or metals
Sn	3.44 keV keV	L-alpha Overlap	3.94 keV	0.069	2.3 ppm	Can be common in painting or metals
Cr	3.7 keV	K-alpha Escape Peak	5.99 keV	0.287	102 ppm	Unlikely to influence Am, but could be a factor in some pigments, metals, and ores.

Table 90: Observable emission lines for americium and its most common fluorescence interactions.

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