Assessment of the Capacity of XRF Analysis as a Tool for the Screening of Brake Pad Friction Materials

Summary Report

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1. ABSTRACT:

Six samples of brake pad fiction materials with known formulations were analyzed for 7 metals (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) both qualitatively and quantitatively by X-ray fluorescence to determine if the technique would be suitable for use as a screening tool for future monitoring of brake pads in the field. Both solid pads and powdered friction material were analyzed. Qualitative scanning of the samples showed the presence of six of the seven metals (Cr, Cu, Ni, Pb, Sb, and Zn; Cd was not present in the samples) at some concentration. As expected based on the known formulation of the samples, three of the metals (Cu, Sb, and Zn) were major components while the other three (Cr, Ni, and Pb) were only present in trace amounts that were visible above the background signal but not quantifiable. The precision of multiple scans of different regions on the same sample varied from metal to metal and appeared to be dependent on the form in which the metal had been added to the original friction material; forms that were distributed homogeneously had very good precision while forms that had heterogeneous distributions in the samples typically had poor precision.

Quantitative XRF analysis was able to determine the concentrations of Cu, Sb, and Zn in the samples. This analysis was done using both the internal calibration of an Innov-X XRF field analyzer and a separate external calibration based on independent metal standards and scans from a Bruker Tracer-IIISD field analyzer for comparative purposes. The problems with precision seen during qualitative analysis were confirmed with single scans for Cu resulting in concentrations as low as 21.4% and as high as 258% of the expected Cu content. This appears to be the result of heterogeneity in the friction material resulting from the form in which the Cu was added, with fibrous materials resulting in poorer precision than powdered materials. However, both instruments were generally able to determine the Cu content to within ±30% of the expected value based on the average measurement for five scans of separate regions of the same solid sample. The Innov-X instrument generally under predicted Cu values while the external calibration of the Bruker instrument was much closer to the expected value (±10%); however in the samples that contained CuS as a source for Cu, both the Innov-X (to a lesser degree) and the Bruker (to a much greater degree) over predicted the amount of Cu present in the solid sample. In contrast, the Innov-X over predicted the concentrations of both Sb and Zn by close to 200%. Scans of the powdered samples were much less accurate than those of the corresponding solid samples.

While XRF analysis is more than sensitive enough to detect the metals of concern in friction materials at well below the regulatory limits, the associated issues with accuracy and precision (as well as with the differences between internal and external calibrations) severely restrict the capacity for use as a field screening technique. Field screening would likely result in a significant number of false negatives. It would also be difficult (if not impossible) to distinguish between Cu content at the lower levels (0.5% and 2%). In addition, much of the interpretation of data relied upon knowledge and confirmation of the design intent and ingredients used to prepare the samples, none of which could be expected for field testing. Further research into both the development of useable standards for external calibration and refine the accuracy and precision issues is essential before XRF could reasonably be used as a screening tool. Given the current state of knowledge and standardization, XRF screening is not recommended for use with brake pads.

2. INTRODUCTION

X-ray fluorescence (XRF) analysis is a powerful analytical tool that, under the correct conditions, can be used to pre-screen products for the presence of regulated metals. The Environmental Chemistry Laboratory (ECL) was asked to assess the capacity for XRF analysis to accurately screen the friction material portion of automobile brake pads for the presence (and possibly amount) of copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), zinc (Zn), cadmium (Cd), and antimony (Sb), all of which are common components of friction materials. To do this, ECL analyzed six friction materials (Authorization #10EC0224) of different but known composition provided by Greg Vyletel of Meritor, Inc. (Table 1).

Table 1. ***Known formulation for Materials 1 through 6 based on design specifications***

Component	Material 1 (wt %)	Material 2 (wt %)	Material 3 (wt %)	Material 4 (wt %)	Material 5 (wt %)	Material 6 (wt %)
Zinc Powder	2.00	0.00	2.00	4.00	2.00	4.00
Antimony Trisulfide	3.60	3.60	3.60	3.60	3.60	3.60
Copper Fiber	0.00	5.00	6.00	0.00	5.00	2.00
Copper Powder	0.00	3.00	0.00	0.00	0.00	0.00
Brass Fiber	7.35	0.00	0.00	0.00	0.00	0.00
Copper Sulfide	0.00	0.00	3.00	0.75	0.00	0.00
Total expected Cu content	**5.00**	**8.00**	**8.00**	**0.50**	**5.00**	**2.00**
Total expected Zn content	**4.35**	**0.00**	**2.00**	**4.00**	**2.00**	**2.00**
Total expected Sb content	**2.00**	**2.00**	**2.00**	**2.00**	**2.00**	**2.00**

The XRF analyses were completed using two different x-ray fluorescence instruments: a Bruker Tracer III-SD portable XRF and an Innov-X Systems α-6500 portable XRF. The unaltered surface of the friction materials were scanned using both the Bruker and the Innov-X. Similarly, powdered samples of the same material were also scanned using the Bruker III-SD. Attempts were made to collect both qualitative data (from the Bruker instrument only) and quantitative data (from both instruments) about the presence or absence of the listed metals in the friction material. In addition, the data resulting from the internal calibration of the Innov-X and from the manual calibration of the Bruker was compared.

This XRF analysis was followed by digestion of the powdered samples and subsequent analysis by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) to verify the composition of the samples. These results were reported separately.

3. PROCEDURE

3.1. Sample Preparation

Six different sample materials were received by ECL in both solid pad and powdered form, labeled Material 1 through Material 6. The powdered and solid samples were distinguished using a letter; for example, the solid friction material sample labeled Material 1A corresponded to the powdered sample labeled Material 1C and so on.

Each whole sample was labeled in 5 “randomly” selected places using three-hole punch reinforcement labels to mark the areas to be scanned. This was done to ensure the reproducibility of multiple scans of the same area could be collected on both instruments. Without some sort of indicator, it would be nearly impossible to verify that the same spot had

been scanned by both instruments. Photos of the whole friction materials and the numbered reinforcements can be seen in Appendix A. In addition, the "random" placement of the reinforcements on the surface of the whole pads was meant to replicate the likely field use of the instrument during which a collector might choose to scan the pad in multiple different locations.

The powdered samples were homogenized to the extent possible and carefully transferred into separate sample cups sealed both top and bottom using x-ray transparent film. After sealing in the samples, all efforts were made not to shake or otherwise cause large disturbances to the powdered sample to avoid possible settling due to density differences in particles.

3.2. XRF Calibration

Basic single element calibration of the Innov-X Systems α-6500 portable XRF instrument was performed at the factory by the manufacturer. All measured values from the Innov-X are based on this original calibration.

Internal XRF calibration can be problematic and often can give erroneous results because of the nature of the calibration. For example, concentrations are determined based on the relationship between the signal intensity of a given peak and a pre-set standard intensity for whatever single sample was used to perform the manufacturer calibration. The problem is that there can be large differences in signal intensity for the same concentration of an element in two different matrices. Furthermore, the internal calibration both assumes linearity of the signal-to-concentration relationship across the entire concentration range and relies upon a peak recognition algorithm to identify which elements are present, each of which may or may not be valid depending on the specific elements and interferences present and the matrix being analyzed.

In an attempt to eliminate the issues associated with reliance on the internal calibration, the Bruker Tracer III-SD portable XRF instrument was used to create an external calibration based on measurements made of metal standards with known purities. While this allows a much more customizable and accurate approach than the internal relative calibration (being based on data for each separate element), this process was limited by the lack of availability and quality of known standards. Due to lack of suitable standards, external calibration curves were only developed for Cu and Pb and were limited to two points: a pure standard and a blank. The pure copper standard was used as the blank for the Pb calibration and the pure Pb standard was used as the blank for the Cu curve. The signal intensity was measured for the primary peak of the metal being calibrated for both the standard and the blank. This value was used to create a linear calibration to which other signal intensity measurements for the same peak could be compared. More points would have been preferred in both calibrations, but ECL possessed no suitable alloy standards to introduce additional points between the pure standard and the blank.

One significant downside to the use of external calibration is that it requires more training and effort (before and after the scans to set up the calibration curve and subsequently calculate the concentrations in the sample) on the part of the collector in the field. This may not be desirable and/or feasible in many cases, as it runs counter to the desire to use XRF analysis as a quick and easy field screening technique.

3.3. Analysis

The solid pads were scanned on both the Innov-X and the Bruker instruments. The samples were placed over the XRF window with the open center of the reinforcement centered over the instrument aperture, exposing the uncovered friction material. This was repeated for each of the five locations marked on each sample. It was obvious if the pad was not correctly placed over the aperture as the presence of reinforcement in the aperture during the scan was noticeable by background differences in the scan results. The Innov-X instrument was set to 40 kilovolts (kV) using the default amperage and a 60 second scan time. The Bruker instrument was also set to 40kV at 14 microamperes (μAmp) with a 100 second scan time. No filters were used during the scans.

The powdered samples were scanned using only the Bruker instrument by carefully setting the sample cups containing the powdered friction material over the instrument aperture exposing the sample to the instrument through the bottom layer of x-ray transparent film. Once the bottom side of the sample cup had been scanned, the cup was carefully inverted (attempting to minimize agitation which might result in settling or other density-based changes in the sample) and rescanned to test the homogeneity of the powdered samples. The powder scans used the same instrument settings on the Bruker instrument as previously used for the solid samples.

4. RESULTS

4.1. Visual Inspection

Prior to XRF analysis, visual differences were noted both between the different friction material pads and between the selected scan areas on some of the specific pad samples. Material 1 had the most abundant visible metallic flakes on the surface which had a shiny yellow or brassy color. Materials 2, 3, 5, and 6 each contained visible reddish metallic bits that were larger and more spread out than Material 1. Of these, Material 6 had the least metallic spots, but the difference was minimal. Material 4 had no visible metallic spots on the surface of the friction material. It appeared to be a uniform gray material across the entire surface. Photographs of these samples showing the metallic spots can be found in Appendix A.

Because XRF is, for the most part, a surface measurement, differences in the scanned surface can cause large differences in the measured results for a given sample. Any significant heterogeneity can result in large deviations in scanned results from spot to spot on the sample. For example, if one scan happens to be centered on a visible piece of copper in the pad, the results will indicate a very high concentration of copper relative to an adjacent location without any visible copper. The visible heterogeneity of the solid pads is a strong indicator that XRF will not likely be a good screening technique.

4.2. XRF Analysis of Whole Pads

Each of the whole pad samples were analyzed in the same five locations on the surface of the pad using both XRF instruments. The Bruker instrument produced both qualitative spectra showing the presence or absence of Cd, Cr, Cu, Ni, Pb, Sb, and Zn and quantitative results for Cu based on an external calibration. Attempts were made to produce an external calibration for Pb as well; however, the signal intensities for lead were too low for accurate measurement. The Innov-X instrument was utilized for quantitative purposes only and produced numeric data based solely on the internal calibration. All of the individual XRF

spectra produced for both the whole pads and the powdered samples can be found in Appendix E.

4.2.1. Qualitative Analyses

As expected after the visual inspection of the solid pads, a comparison of the spectra for the whole pads demonstrates the dramatic differences in intensities for the copper peaks. For example, the difference in copper peak heights for the 5 scans of Material 1 can be seen varying from 120,000 pulses to 10,000 pulses, suggesting a large variation in the amount of copper detected in the scan (Figure 1). This is most likely due to variations in the distribution of solid copper particles on or near the surface of the pads. Based on the known formulation (Table 1), solid copper ingredients are commonly mixed in to the friction materials creating a non-homogenous solid, which explains both the visual and XRF scanned variation in copper levels. This lack of reproducibility across five different spots on the surface of the pad was also present in Materials 2, 3, 5, and 6. Appendix B contains spectral overlays for the Cu and Zn peaks for all six materials.

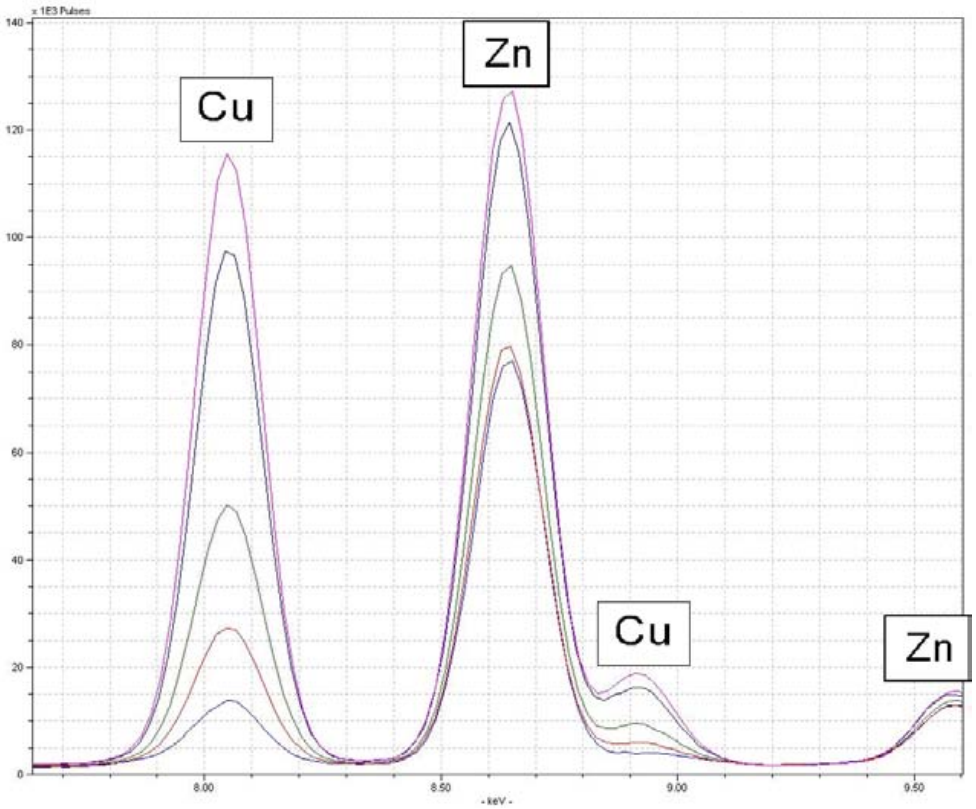

Figure 1*: XRF spectrum overlay for the five scanned areas of Material 1 (whole pad) using the Bruker instrument.*

Of the six samples, only Material 4 (which represents a pad containing Cu at the 0.5% proposed limit that will be implemented in 2025) showed any precision for multiple scan areas on the same sample (Figure 2). This matches both the visual inspection of the pad surface, which showed no visible evidence of solid copper and the known formulation, which used copper sulfide (CuS), which is a very fine crystalline powder that is expected to have a much more homogenous distribution within the solid material than the other forms of solid copper used, such as copper fiber or copper (or brass) powders.

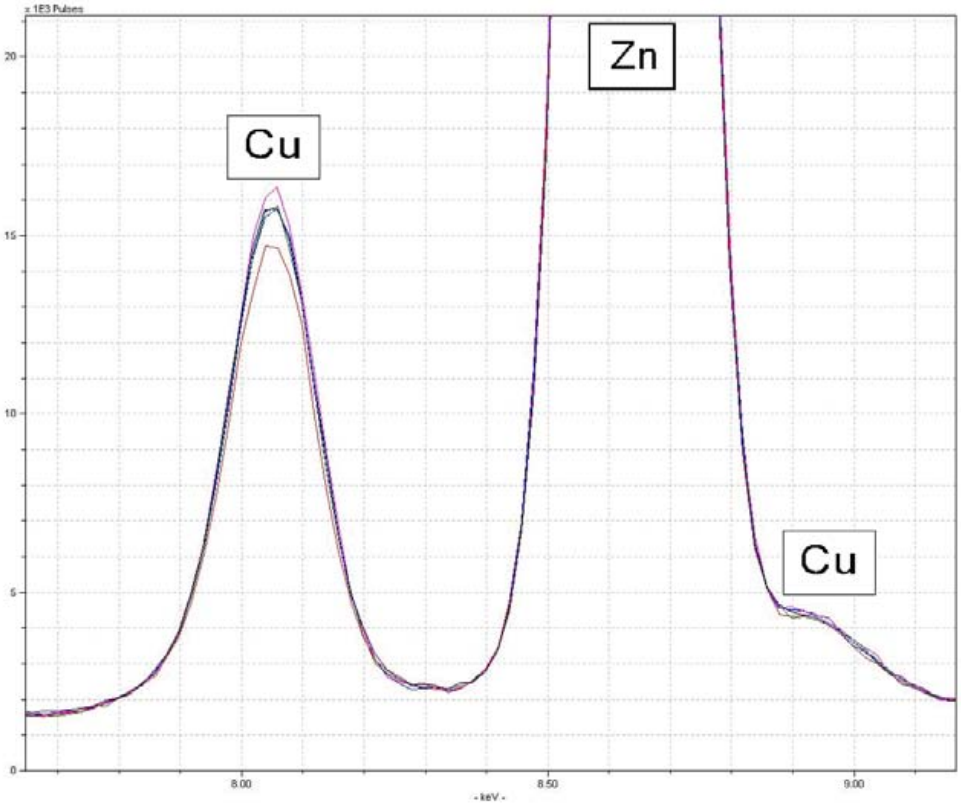

Figure 2*: XRF spectrum overlay for the five scanned areas of Material 4 (whole pad) using the Bruker instrument.*

These results suggest that while XRF may not be a good screening tool for current friction materials (which rely on copper being distributed in a heterogeneous manner), the potential for XRF screening may increase if or when friction material composition becomes based on a more homogenously distributed form of copper such as CuS.

In contrast to Cu, peak reproducibility for Sb and Zn (which were both also expected in percent levels) across the five scanned regions per pad was generally better than for Cu. The Zn peaks for Material 1 showed notable lack of reproducibility, unlike Materials 3 through 6 which were fairly consistent for all five areas scanned (Figure 1; Appendix B). A quick review of the proposed composition reveals that while Materials 1, 3, 4, 5, and 6 all contained Zn powder as an ingredient, Material 1 also contained brass fiber. Unlike the Zn powder, which can reasonably be expected to have a relatively homogenous distribution, the brass fiber (representing an additional source of zinc) would be expected to be distributed in a much more heterogeneous fashion, much like the Cu wire in some of the samples. Material 2 was expected to contain no Zn and no Zn peak was visible in any of the five areas scanned.

Similarly, the Sb peaks were very consistent across all five scans of each pad for all six materials, again most likely due to the fine powdered form of Sb used in the formulation (antimony trisulfide, Sb_2S_3; see Table 1 for the formulation of the samples and Appendix E for the individual sample scans).

Very small peaks for Cr, Ni, and Pb were visible in the scans for all six materials; however, these metals were difficult to distinguish from background signal due to the size

and nature of the peaks and overlap by peaks from other elements (notably barium interference in the Cr peak). No Cd was noted in any scan for any of the samples.

4.2.2. Quantitative Analyses - Innov-X Instrument with Internal Calibration

The initial attempt to measure concentrations of the metals in question by XRF was completed using the Innov-X instrument in the "point-and-shoot" manner commonly used in the field. The Innov-X instrument prints out a list of detected elements and their concentrations based on the internal manufacturer calibration. This calibration assumes linearity and involves preprogrammed algorithms in the software to detect and quantify the peak intensities. As such, there is typically little to no capacity for external correction or adjustment.

The Innov-X instrument was able to report detectable amounts of Cu, Zn, and Sb for all six materials but was unable to detect Cd, Cr, Ni, or Pb above the internally calculated detection limit (Appendix C). There were significant issues with the precision of the Cu measurements. Relative standard deviation (RSD) is a measure of the precision and reproducibility of the scans across the entire pad. For example, in Material 1 the relative standard deviation (RSD) for Cu was 62.8% which is well above acceptable levels (typically less than ±20% RSD) for precision in quantitative measurements (Table 1). These results match the quantitative scans which showed a large deviation between scans of different regions of the same pad. Similarly, the RSD for Zn shows poor precision (20 %), although not nearly as bad as the precision of the Cu measurements. Again, this matches what was seen in the qualitative analysis, as does the excellent precision for the Sb measurements with an RSD of 2.6% (Table 1).

Table 2. ***Concentrations of metals in Material 1 (solid pad) as measured by the internal calibration of the Innov-X instrument. Similar results for Materials 2 through 6 can be found in Appendix C.***

Element	Unit	Material 1 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<158	<160	<149	<161	<159		
Cr	ppm	<670	<679	<636	<652	<684		
Pb	ppm	<39	<40	<46	<43	<35		
Ni	ppm	<254	<251	<239	<271	<236		
Cu	%	3.21	2.03	3.67	6.64	1.14	3.34	62.8%
Zn	%	7.80	5.41	6.15	7.65	4.98	6.40	20.0%
Sb	%	4.06	4.15	3.92	4.04	4.19	4.07	2.6%
Hg	ppm	<41	<36	<35	<36	<33		

Avg: average value over 5 scanned regions
RSD: relative standard deviation

The RSDs for Cu ranged from a low of 5.4% in Material 4 to a high of 73.5% in Material 6, suggesting that both the form and the amount of Cu used in the production of the friction material can have a large impact on the reproducibility of multiple scans of the same solid pad (Table 3). The precision for all five measurements of Materials 2 through 4 were well within acceptable limits (± 20% RSD), with Material 4 having very good precision at under 10% RSD. This matches the qualitative results for precision as determined on the

Bruker instrument. Materials 2 and 3 were both formulated in part using a powdered form of Cu (powdered Cu metal or CuS) in addition to the typical Cu fiber (Table 1). Similarly, the Cu in Material 4 came completely from a powdered source. As a result, more homogeneity should be expected in these three samples. The RSDs for Materials 2 and 3 were greater than for Material 4 due to the presence of Cu fiber which creates regions with more or less Cu depending on the heterogeneous distribution of the fiber in the solid pad.

Table 3. ***Copper content of all six friction materials in solid pad form as measured by the internal calibration of the Innov-X instrument.***

Sample	Design Intent (%)	% Copper in Solid Pad – Innov-X						
		1	2	3	4	5	Avg	RSD
Material 1	5.00	3.21	2.03	3.67	6.64	1.14	3.34	62.8%
Material 2	8.00	7.13	9.62	7.93	6.39	7.74	7.76	15.5%
Material 3	8.00	10.8	10.7	9.54	7.40	10.8	9.85	14.9%
Material 4	0.500	0.602	0.682	0.637	0.631	0.683	0.647	5.4%
Material 5	5.00	5.10	4.62	2.17	4.58	2.99	3.89	32.1%
Material 6	2.00	0.924	0.799	0.648	1.61	3.21	1.44	73.5%

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In contrast, Materials 1, 5 and 6 all had RSDs well outside the acceptable limits (Table 3). The Cu present in Materials 1, 5 and 6 was solely from the Cu fiber (Table 1). Because the Cu fiber is not homogeneously distributed through the entire pad, any spot chosen for a scan may or may not have Cu present. In addition, because XRF measures predominantly the surface characteristics of a sample (or only a shallow depth into the material), if the Cu fiber is not at or near the surface, it may not be detected at all. This can explain the lack of precision in the measurements.

Accuracy of the XRF scans is also a potential issue for screening. The individual scans by the Innov-X were not especially accurate, with measured values as low as 22.8% and as high as 160.5% of the expected Cu content; however, the averaged value of 5 scans for each pad resulted in values generally within ±30% of the expected value for the pad (Table 3). While this is not especially accurate for quantitative purposes, it might be acceptable for use in screening purposes with the caveat that the range of values measured for the lower Cu content pads (Materials 1, 4, 5, and 6) have significant overlap and as such, it may not be possible to distinguish between them based solely on screening scans of this type.

Based on the digestion and ICP-AES analysis (reported previously), the actual Cu content of the friction materials corresponded very closely with the design intent with the average concentration measured by ICP-AES falling within 5% of the expected concentration (Table 4). The one exception was for Material 1; however, upon investigation and further analysis, it was discovered that the brass fiber actually used had a different composition of Cu and Zn than the values used to calculate the theoretical Cu and Zn content. As a result, the actual amount of Cu in the sample is lower and the actual amount of Zn is higher than in the design intent.

Table 4. ***A comparison of the copper content and difference from design intent in friction materials.***

Sample	Design Intent (% Cu)	ICP-AES Analysis		Innov-X XRF Analysis	
		Average % Cu	% Recovery	Average % Cu	% Recovery
Material 1*	5	4.30	86.0%	3.34	66.8%
Material 2	8	8.19	102.4%	7.76	97.0%
Material 3	8	8.30	103.8%	9.85	123.1%
Material 4	0.5	0.499	99.8%	0.647	129.4%
Material 5	5	5.24	104.8%	3.89	77.8%
Material 6	2	2.09	104.5%	1.44	72.0%

Average % Cu for ICP-AES was based on 3 replicate analyses of powdered friction material.
Average % Cu for XRF was based on 5 replicate analyses of the same material in solid pad form.

** Material 1 had less Cu than intended in the actual formulation due to differences in the source of the brass fiber.*

In contrast to the ICP-AES analysis, the Innov-X measurements had a tendency to either under predict or over predict the actual Cu content of the pad by between 20-30% (Table 4). In three of the six samples (Materials 1, 5, and 6) which contained Cu in only fiber form, the average measured value was below the expected value. This is a critical observation because if the intent of screening the friction materials is to ensure they do not contain more than a given threshold amount, under prediction during measurement can lead to a high incidence of false negatives.

Material 1 had a slightly lower recovery (67% versus 72-77%) than the other samples for both the Innov-X analysis and the ICP-AES analysis. This resulted from a difference between the design formulation and the actual Cu and Zn content of the brass fiber used. Assuming the Cu concentration based on the ICP-AES analysis is accurate (based on the accuracy with the other six materials), the recovery for the Innov-X instrument is actually 77.7%, which is well within the range of other two samples (Materials 5 and 6).

Materials 3 and 4 (which both contained CuS) over predicted the Cu content by close to 30%; however, the measured Cu value for Material 2 (made up of a mix of Cu fiber and Cu powder) was very close to the expected value. Based on this, there may or may not be a relationship between the form of Cu used to create the friction material and the ability of XRF to make an accurate, quantitative measurement of the Cu content. Additional research would be needed to investigate this issue.

The Innov-X analysis also greatly over predicted the Sb and Zn content of the friction materials (Table 5). Both metals were measured at close to twice the design value for the samples. Both the Zn and Sb design intents were verified to be accurate by ICP-AES. Therefore, while the internal calibration appears to be fairly accurate for Cu, it is very inaccurate for both Sb and Zn. This result is not unexpected, as the internal calibration of many XRF instruments (including both instruments used in this study) is based on a pure copper standard. As a result, the Cu concentration should be fairly accurate while other metals will be less accurate, as their concentrations are calculated relative to the intensity of the Cu signal. Another complicating aspect is that Cu is in the center of the optimal energy range for both instruments, whereas Sb is out towards the limits of the range. This could explain the differences in Sb and Zn recoveries. These two factors are an unavoidable consequence of relying on the internal calibration of the instrument.

Table 5. ***Antimony and Zinc concentrations in solid friction material samples as measured by the Innov-X instrument.***

Sample	Antimony (wt. %)			Zinc (wt. %)		
	Design Intent	Avg. Measured Value	% Recovery	Design Intent	Avg. Measured Value	% Recovery
Material 1	2.00	4.07	204%	4.00	6.40	160%
Material 2	2.00	3.95	198%	0.00	ND	
Material 3	2.00	4.07	204%	2.00	4.20	210%
Material 4	2.00	3.79	190%	4.00	7.00	175%
Material 5	2.00	3.85	193%	2.00	3.72	186%
Material 6	2.00	4.03	202%	4.00	7.66	192%

ND = not present above the detection limit for the internal calibration.

4.2.3. Quantitative Analyses – Bruker Instrument with External Calibration

The second attempt to measure metal concentrations in the samples by XRF was completed using the Bruker instrument after establishing an external calibration from metallic standards. The Bruker instrument produces a spectrum for the specific scan, from which the signal intensity for each peak can be determined. That peak intensity is compared to the external calibration for each individual element of interest to determine the concentration measured in the scan. Due to lack of acceptable standards, external calibration curves were only created for Cu and Pb. As seen in Section 4.2.1, peaks for Cr, Cu, Ni, Pb, Sb, and Zn were all visible on the scans using the Bruker instrument; however, the Cr, Ni, and Pb peaks were either barely above background levels or were partially obscured by interferences from other elements. Therefore no signal intensities could be determined for Cr, Ni, or Pb. As a result, the only element considered using an external calibration was Cu.

The concentrations measured by the Bruker instrument for each area on each sample differed (sometimes greatly) from the values measured by the Innov-X instrument (Tables 4 and 6). In addition, the average Cu content of each sample are slightly higher when determined using the Bruker external calibration (most likely the result of analysis using two different calibrations). The precision (RSD values) of the two different sets of measurements were very similar both in value and in pattern amongst the five samples. Also much like the Innov-X measurements, the individual scans had a very wide range of recoveries, from 21.4% to 258% of the expected Cu content. Neither instrument nor calibration differences appear to affect the precision assuming the same spot is scanned by both instruments. However, the possibility that there were slight differences in the exact area scanned (and the presence/absence of localized regions of Cu from the Cu fiber) cannot be excluded, as the labeled scan area is larger than the actual beam width used to make the scan.

Table 6. ***Copper content of all six friction materials in solid pad form as measured by external calibration on the Bruker instrument.***

Sample	% Copper in Solid Pad – Bruker							Design Intent	% Recovery
	1	2	3	4	5	Avg	RSD		
Material 1	8.60	2.28	4.29	10.1	1.07	5.27	74.7%	5.00 %	105.4%
Material 2	7.32	8.61	10.7	9.38	7.82	8.76	15.2%	8.00 %	109.5%
Material 3	11.0	9.72	11.6	9.80	13.0	11.0	12.4%	8.00 %	137.5%
Material 4	1.15	1.25	1.29	1.23	1.25	1.23	4.2%	0.500 %	246.0%
Material 5	6.24	7.60	3.35	5.20	3.83	5.24	33.2%	5.00 %	104.8%
Material 6	1.16	1.37	2.20	2.09	1.26	1.62	30.4%	2.00 %	81.0%

While the precision of the two instruments was very similar, the degree of accuracy of the averaged values to the design intent was very different. With the exception of Materials 3 and 4, all of the samples had average values that were within 20% of the design intent, which is a generally acceptable range for most analyses (Table 6). The external calibration had the tendency to over predict slightly for the samples with higher Cu content, but for field screening, false positives are much less of a concern than false negatives, assuming the field screening is followed by a confirmation analysis in a laboratory to find the actual concentration.

Materials 3 and 4 were measured at concentrations much higher than expected (Table 6). This was also noted in the analysis using the Innov-X (Table 4). Both of these materials contained CuS in their formulation and increasing the relative amount of CuS used appears to increase the over prediction of the sample concentration. Approximately 25% of the Cu content of Material 3 is from CuS and the average measured value is greater than the design value at 123% and 138% (Innov-X and Bruker instruments, respectively). The Cu in Material 4 is provided 100% by CuS and the average measured value is greater than the design value at 129% and 246%. This is highly suggestive of a correlation between CuS content and over prediction but insufficient data has been collected to validate this correlation, let alone establish any sort of causation. As mentioned previously, additional research into the effects of the form of Cu added to the friction material on XRF analysis is needed.

It is also notable that the average values tend to get less accurate as the concentration decreases (Table 6). Excluding Material 3 (mentioned above), the average values for the samples with 5% and 8% design intent are within 10% of the expected value, which is considered to be good accuracy for most analyses and well within the acceptance criteria for most standards. However, with the 2% sample and more obviously with the 0.5% sample (even accounting for possible issues with CuS), the accuracy drops off quickly. This is a result of the limited nature of the external calibration (a single standard and a blank), where the lowest values are far enough away from the single standard that the linearity of the calibration becomes questionable. The acquisition of additional standards at lower levels could improve this external calibration and would likely result in improved accuracy for the lowest concentrations.

4.3. XRF Analysis of Powdered Samples

Six powdered friction material samples (each corresponding with one of the whole pad friction material samples) were placed in XRF sample cups and scanned using the Bruker instrument to produce both qualitative spectra and quantitative signal intensities for use in the

external calibration for Cu. In addition, the samples were scanned from both the top and the bottom of the cup to test for any density-based issues in analysis (such as the settling of dense metallic particles of Cu). After XRF analysis, these powdered samples were used for the ICP-AES analysis.

4.3.1. Qualitative Analyses

Data for the powdered friction materials was only collected for the Bruker Tracer III-SD prior to acid digestion and ICP analysis. Because many of the components of the friction material are added in metallic form, the process of generating the powdered sample is likely to create small metallic particles which have a different density than the rest of the bulk powdered material. These particles would have a tendency to sink to the bottom of any sample container. To test this phenomenon, the powdered samples were placed in sample cups sealed top and bottom using x-ray transparent film. Both the top and the bottom of the sample cup were scanned and the resulting spectra were overlaid. Differences between forms of Cu added during the formulation of the friction material were immediately obvious. For example, the powdered form of Material 4 had near perfect precision for both top and bottom scans (Figure 3). In contrast, Material 5 had drastic differences between the two scans for Cu, with lesser differences for Zn. Without even considering the known formulation, this suggests that the Cu in Material 4 was well-homogenized in the pad before the sample was powdered while the Cu in Material 5 was clearly in a metallic form which separated and settled to one side of the cup. This further supports the impact of initial Cu source on the quality of the XRF data. The CuS used to provide the Cu in Material 4 clearly allows for homogenous distribution which, as mentioned previously, results in good reproducibility of scans. The Cu fiber used to provide the Cu in Material 5 is simply ground up in the powdering process to create metallic particles which settle in the sample cups, resulting in poor reproducibility. Similar overlays for all six samples can be seen in Appendix D.

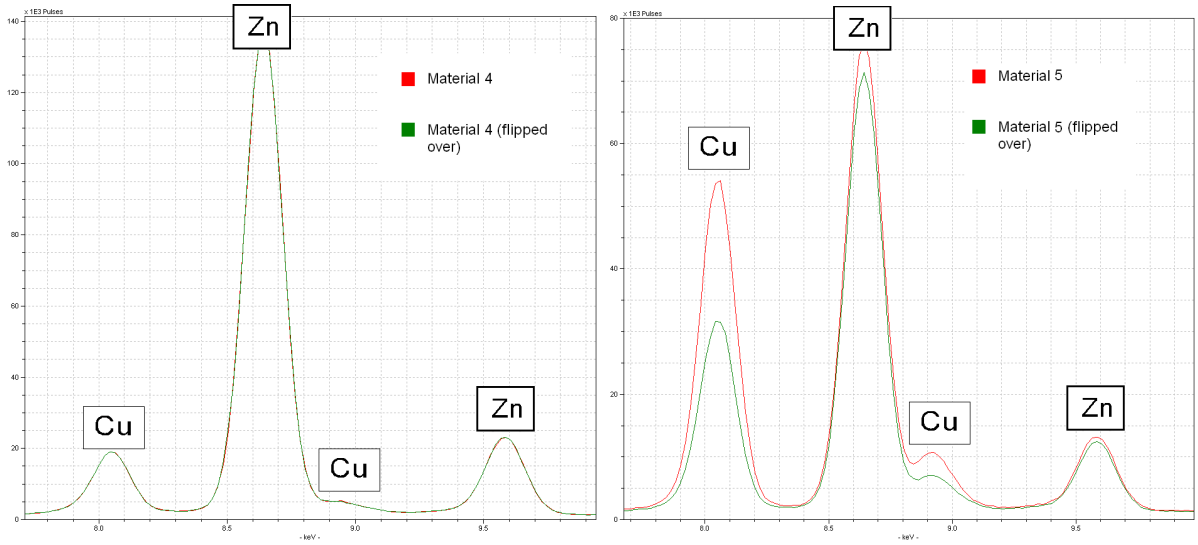


Figure 3. ***XRF spectrum overlay for the top and bottom scans for powdered samples of Materials 4 and 5 to test for the settling of metallic particles due to density differences.***

Outside of noting differences in scan reproducibility based on formulation differences, there was effectively no qualitative difference in the ability to detect the metals

in this matrix outside of a slight increase in precision for samples containing powdered forms of Cu.

4.3.2. Quantitative Analyses – Bruker Instrument with External Calibration

For comparative purposes, the signal intensities for Cu in the scans of the six powdered friction material samples were used to determine the concentration of Cu based on an external calibration from the Bruker instrument. As seen in the qualitative scans, the precision of repeated scans increases for samples with easily homogenized forms of Cu as shown by the <10% RSD values (Materials 2 through 4; Table 7). The precision appeared to improve slightly for the samples with poorly homogenized Cu sources, perhaps because the powdering process increased the homogenization of the samples. However, the accuracy of the analysis was notably decreased, with average recoveries ranging from as low as 51.4% to as high as 296.0% of the design intent. When considering these results, it is important to review the individual scan results, where it becomes obvious that settling and scan location are critical components to these results. All three samples that had very low values relative to the design intent had very high RSDs, indicating that settling of the metallic particles was playing a significant role in the value determined for Cu. It is also important to note that those three samples were also the three samples that used Cu or brass fiber to provide the Cu in the friction material. As expected based on previous results, Materials 3 and 4 had a large degree of over prediction.

Table 7. ***Copper content of all six friction materials in powdered form as measured by external calibration on the Bruker instrument.***

Material	% Copper in Powdered Friction Material – Bruker						Design Intent	% Recovery
	1	2	3	4	Avg	RSD		
Material 1	1.65	0.910	4.50	3.23	2.57	62.4%	5.00 %	51.4%
Material 2	8.67	9.46	10.2	9.84	9.55	6.9%	8.00 %	119.4%
Material 3	11.1	9.94	11.8	11.5	11.1	7.3%	8.00 %	138.8%
Material 4	1.50	1.35	1.53	1.53	1.48	5.9%	0.500 %	296.0%
Material 5	2.83	4.67	2.70		3.40	32.4%	5.00 %	68.0%
Material 6	1.26	1.10	1.07	1.72	1.29	23.4%	2.00 %	64.5%

Contrary to initial expectations, the solid pads appear to be better for the purpose of XRF screening. There was only a slight increase in the reproducibility of the measurements in powdered form which is countered by the decrease in accuracy. The preparation of powdered friction material requires drilling into the solid pad under controlled circumstances. Since there is no real gain to scanning the powdered form over the solid form, it would be easier to simply screen the solid material and only convert those of concern into powdered form for confirmation analysis by digestion and subsequent ICP-AES analysis.

5. SUMMARY AND CONCLUSIONS

X-ray fluorescence analysis was completed on six different brake pad friction materials in both solid (pad) and powdered forms. These samples were created by the same manufacturer and the design intent was sent to ECL along with the samples for verification purposes. By design, the materials had similar amounts of filler material while the amounts of Cu and Zn were varied. In the initial XRF spectra, it was possible to see peaks for metals (Cr,

Ni, and Pb) which were present at levels below the capacity for XRF to make quantitative determinations. Additionally, metals present in significant (% or sub-%) concentrations (Cu, Sb, and Zn) were clearly visible with little to no background interference. The only metal not detected was Cd, which is not present in the samples at measurable concentrations (based on previously reported ICP-AES results). When metals were added in a form that was easily homogenized throughout the material during creation (such as antimony trisulfide or copper sulfide), XRF returned very good precision for multiple scans of the same solid pad or powder but precision dropped off rapidly with the inclusion of copper fiber. Minimal background signal was encountered for these samples; however this may not be true for friction materials from other manufacturers or of different base formulations. More research is needed on a wide range of different brake pads to determine if background signal can interfere with XRF screening of brake pad friction materials.

It was possible to obtain values for the concentration of Cu, Sb, and Zn in the samples using the internal calibration of the Innov-X instrument. The other four metals of concern (Cd, Cr, Ni, and Pb) were non-detectable by this instrument. "Field" scans using the Innov-X were generally accurate to within ±30% for the average of 5 scanned regions, but tended to underestimate the true value of the sample. It was necessary to use an average of multiple scans of each solid sample because individual scans had recoveries ranging from 22.8% to 160.5% of the expected Cu content. Because of the wide range of recoveries in the individual scans, it may not be possible to distinguish between samples with different Cu content at lower concentrations (namely at the 0.5% and 2% levels). More scans incorporated into the average would increase the accuracy of the Cu measurement but would also increase the time needed to analyze a single sample and make the analysis less useful as a screening technique. For samples with significant visual heterogeneity, a limit set of three to five scans may not be sufficient to represent the true concentration and will likely have limited reproducibility. While the Innov-X was able to quantify both Sb and Zn, the recoveries were almost twice the actual metal content in the samples. This alone should call in to question the ability of XRF for use as a screening tool. Further investigation would be needed to understand why these two metals had measured values so far above the actual values and whether or not this same phenomenon is present for other metals of concern which happened to be non-quantifiable in this study (such as Pb or Cr).

Only Cu was quantified on the Bruker instrument because ECL had no appropriate standards to use for the construction of external calibration curves for the other metals except Pb. An external calibration curve was prepared for Pb, but the samples did not have measurable signal intensities in spite of the visible presence of Pb peaks just above background noise. The external calibration appeared to eliminate the under prediction found with the internal calibration, with three of the samples within 10% of the expected value, but its accuracy was limited by the lack of standards. The result of this was a drop-off in accuracy at the lower Cu concentrations. There was no notable improvement in the precision of the Cu measurements by the Bruker instrument, most likely because the poor precision resulted from sample composition and not from analytical sources.

While potentially more accurate, external calibration is more complex than simple field scanning using the internal calibration, requiring the measurement of signal intensities, development of a separate calibration curve, and further data processing. While this is simple to do in a laboratory setting, it is not as simple in the field, and therefore is less useful as a field screening tool. More research is needed both to develop appropriate standards for use in this sort of external calibration and to simplify the process of external calibration. Ideally, a standardized set of solid friction materials could be developed for this use, but this would take time, money, and industry partners to complete the formulation.

Materials 3 and 4 had a consistent problem with significant over prediction in both the Innov-X and especially the Bruker scans. Unlike the other four samples, these used CuS as a source for the Cu content. This may or may not explain the poor accuracy of measurements on these samples and emphasizes, along with the poor reproducibility resulting from the use of Cu or brass fibers, the fact that the specific components used to prepare the friction material can have a significant impact on the ability to obtain useable results from XRF analyses. Without further research into the materials used as a Cu source in friction materials, there is no way to be sure why Materials 3 and 4 behaved in a different manner than the other four samples. That said, of all six samples, Material 4 has the greatest potential for effective XRF screening if the accuracy issue could be solved through further experimentation.

It was expected that the powdered sample, which gave excellent accuracy and precision when analyzed via ICP-AES, would give results at least as good, if not better, than the solid pads, as the distribution of Cu in the powder should theoretically be more homogenous than in the pads. However, the quantitative results for the powdered samples demonstrated poorer precision and accuracy relative to the expected Cu content. This is most likely due to density-based settling of the heavier metallic particles in the powdered material.

One issue not addressed by this study was the variation in friction material matrices from manufacturer to manufacturer. All six of the formulated materials used in this study were produced by a single manufacturer using a single set of source materials; however, manufacturers use a wide range of different materials and even different suppliers and sources of the same materials to formulate their proprietary blend. This variation in matrix could have a very large negative impact on the capacity of XRF as a tool for field screening.

Finally, it is important to note that interpretation of the quantitative results was only possible in this study because the specific design intent and formulations for the friction materials were known; otherwise, the data obtained would be considered of poor quality due to the precision of the measurements and would not be usable for screening purposes. As it currently exists, the XRF analysis of brake pads is not robust enough to adequately screen samples in the field for compliance with regulatory levels. Too many unresolved analytical issues remain to accept the screening data as valid.

In summary, brake pad friction materials generally have highly complex matrices that can vary from manufacturer to manufacturer. If XRF is to be used as a tool for screening brake pads, the issues associated with matrix composition, precision of multiple measurements on single samples, and accuracy of those measurements must be fully understood and overcome in order to obtain the quality results needed from XRF screening. Many of the issues with XRF analysis and screening presented here have the potential for resolution given time, funding, and manpower for further investigation. Research into a wide range of commercially produced (rather than custom-formulated) friction materials and the development of improved standards and calibration is essential before XRF screening is viable for this particular matrix. Therefore, at this time ECL recommends against using XRF screening on brake pads.

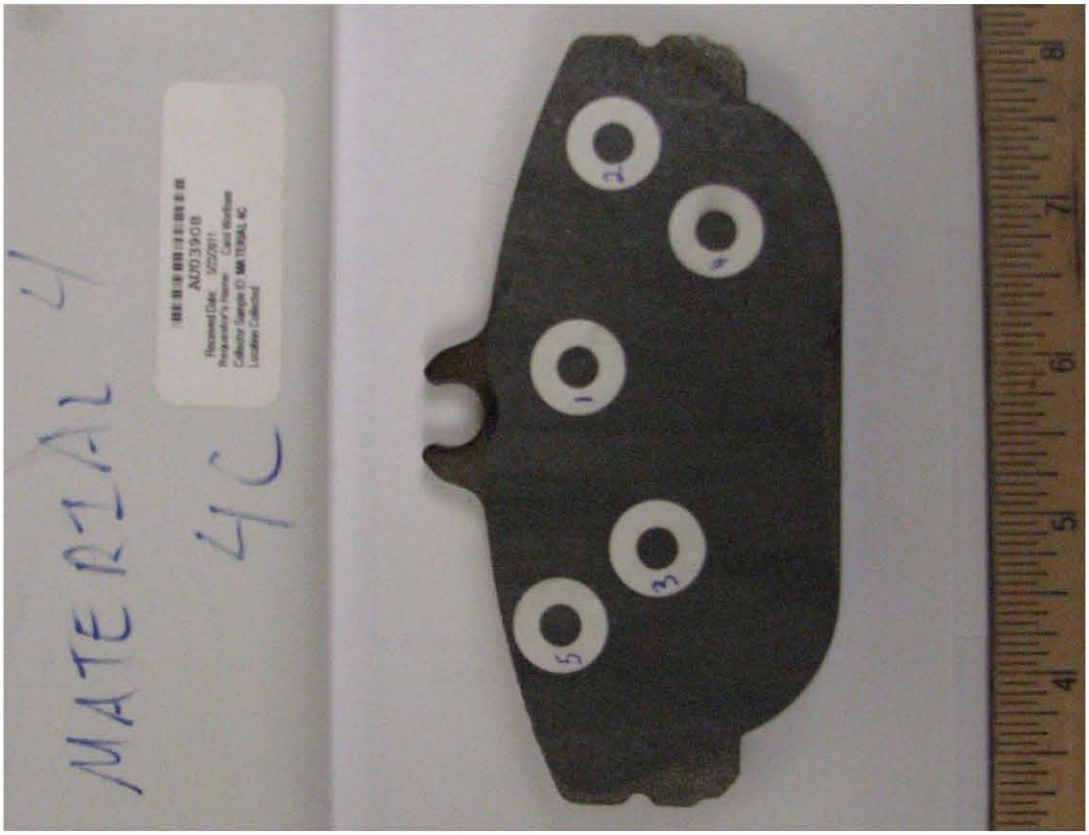
APPENDIX A

Photographs of the solid friction material pads showing the five scan regions on each pad, as indicated by the numbered, white, three-hole punch reinforcements. (Note also the visual heterogeneity of the surface of each pad.)

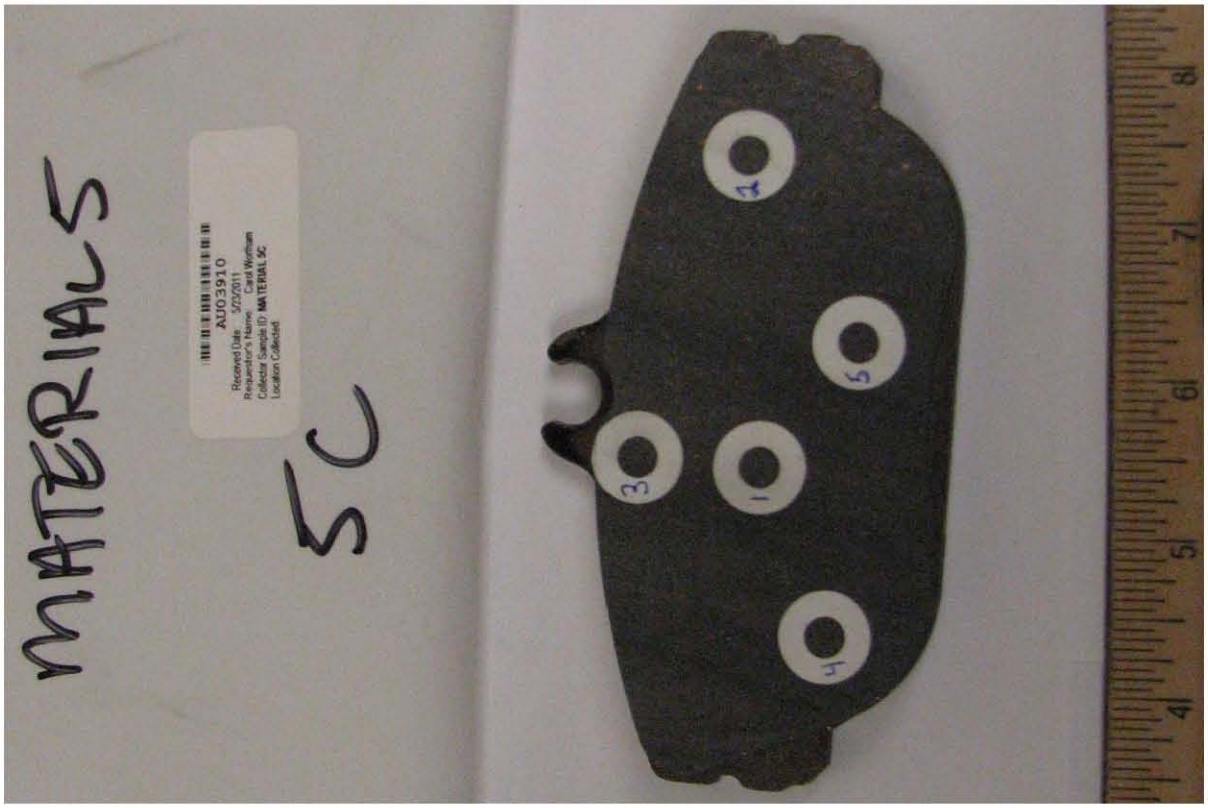
MATERIAL 2A
2A
AU03904
Received Date: 5/23/2011
Requestor's Name: Carol Wortham
Collector Sample ID: MATERIAL 2A
Location Collected:

MATERIAL 1C
AU03902
Received Date: 5/23/2011
Requestor's Name: Carol Wortham
Collector Sample ID: MATERIAL 1C
Location Collected:

MATERIAL 3
AU03906
Received Date: 3/2/2011
Requestor's Name: Carol Wyrtham
Collector Sample ID: MATERIAL 3C
Location Collected:
3C
1
2
3
4
5


MATERIAL 4
AU03908
Received Date: 3/2/2011
Requestor's Name: Carol Wyrtham
Collector Sample ID: MATERIAL 4C
Location Collected:
4C
1
2
3
4
5

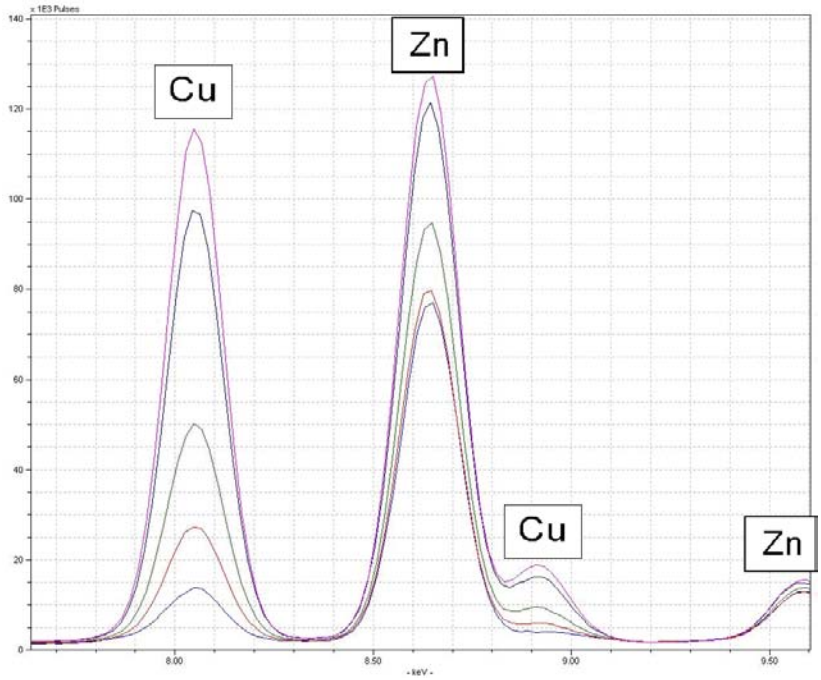
MATERIAL G
6C
AU03912
Received Date: 5/23/2011
Requestor's Name: Carol Wortham
Collector Sample ID: MATERIAL 6C
Location Collected:


MATERIALS
5C
AU03910
Received Date: 5/23/2011
Requestor's Name: Carol Wortham
Collector Sample ID: MATERIAL 5C
Location Collected:

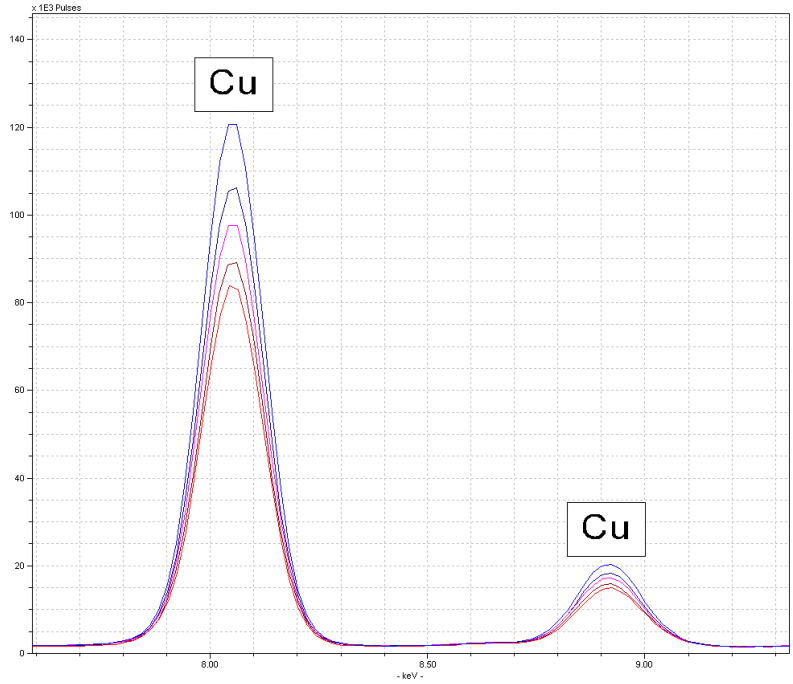
APPENDIX B

XRF Spectral Overlays of All Scan Areas for Copper and Zinc in Each Solid Friction Material Sample

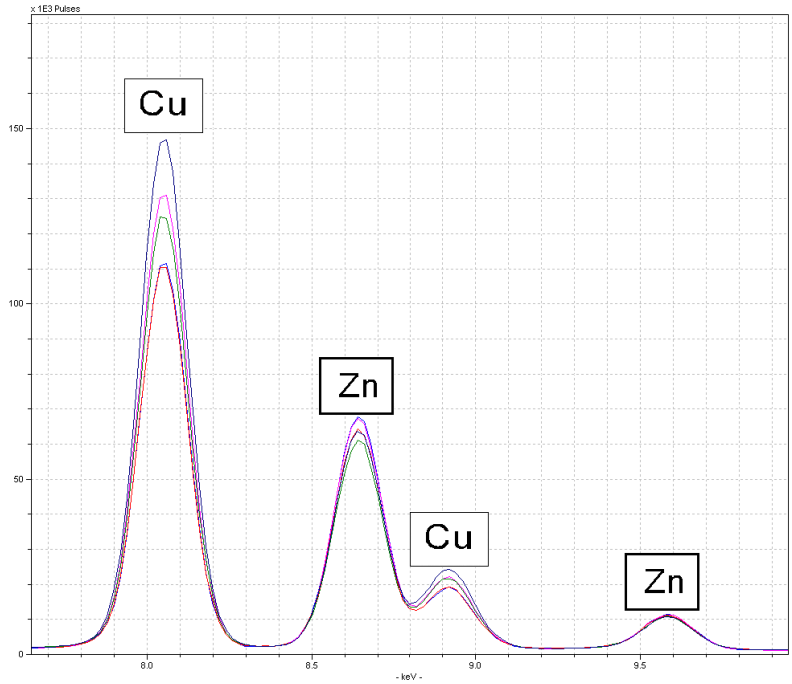
Material 1:



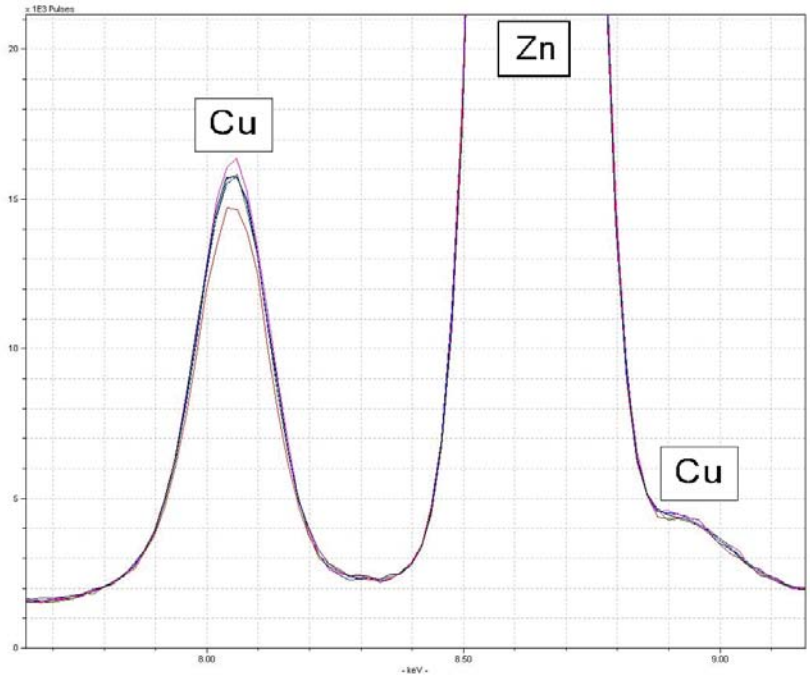
Material 2:



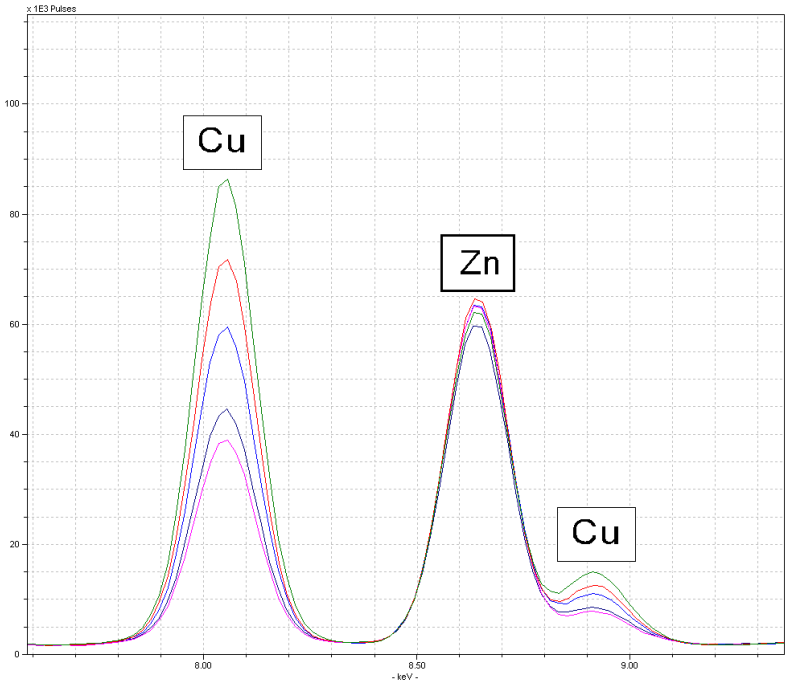
Material 3:



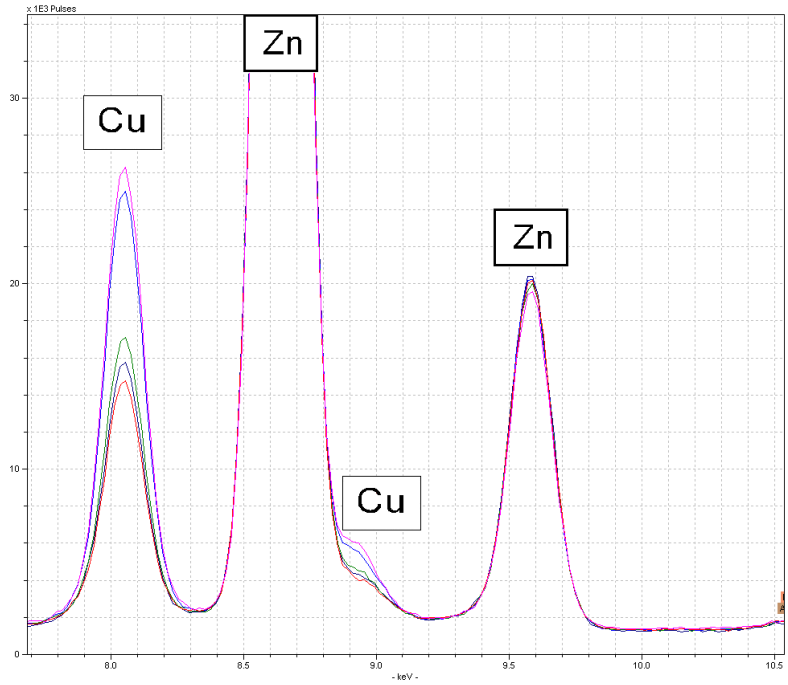
Material 4:



Material 5:



Material 6:



APPENDIX C

Summary Results for All Materials
(Innov-X Systems α-6500 portable XRF)

Element	Unit	Material 1 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<158	<160	<149	<161	<159		
Cr	ppm	<670	<679	<636	<652	<684		
Pb	ppm	<39	<40	<46	<43	<35		
Ni	ppm	<254	<251	<239	<271	<236		
Cu	%	3.21	2.03	3.67	6.64	1.14	3.34	62.8%
Zn	%	7.80	5.41	6.15	7.65	4.98	6.40	20.0%
Sb	%	4.06	4.15	3.92	4.04	4.19	4.07	2.6%
Hg	ppm	<41	<36	<35	<36	<33		

Element	Unit	Material 2 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<133	<154	<157	<134	<147		
Cr	ppm	<626	<711	<687	<610	<668		
Pb	ppm	<34	<38	<40	<35	<36		
Ni	ppm	<214	<236	<239	<212	<232		
Cu	%	7.13	9.62	7.93	6.39	7.74	7.76	15.5%
Zn	%	0.071	<0.0423	0.0642	<0.0313	<0.0374	0.0676	7.1%
Sb	%	3.99	3.99	3.96	3.99	3.80	3.95	2.1%
Hg	ppm	<25	<32	<33	<25	<31		

Element	Unit	Material 3 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<162	<157	<153	<155	<159		
Cr	ppm	<680	<610	<573	<616	<605		
Pb	ppm	<43	<40	<39	<42	<42		
Ni	ppm	<284	<256	<257	<257	<261		
Cu	%	10.8	10.7	9.54	7.40	10.8	9.85	14.9%
Zn	%	4.46	4.21	4.08	4.11	4.15	4.20	3.6%
Sb	%	4.22	4.00	3.99	4.06	4.10	4.07	2.3%
Hg	ppm	<39	<38	<33	<36	<40		

Element	Unit	Material 4 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<127	<152	<127	<133	<135		
Cr	ppm	<554	<702	<546	<563	<576		
Pb	ppm	<31	<39	<32	<34	<35		
Ni	ppm	<199	<232	<183	<198	<213		
Cu	%	0.602	0.682	0.637	0.631	0.683	0.647	5.4%
Zn	%	6.72	7.46	6.79	6.93	7.11	7.00	4.2%
Sb	%	3.66	4.00	3.69	3.77	3.85	3.79	3.6%
Hg	ppm	<35	<39	<33	<35	<34		

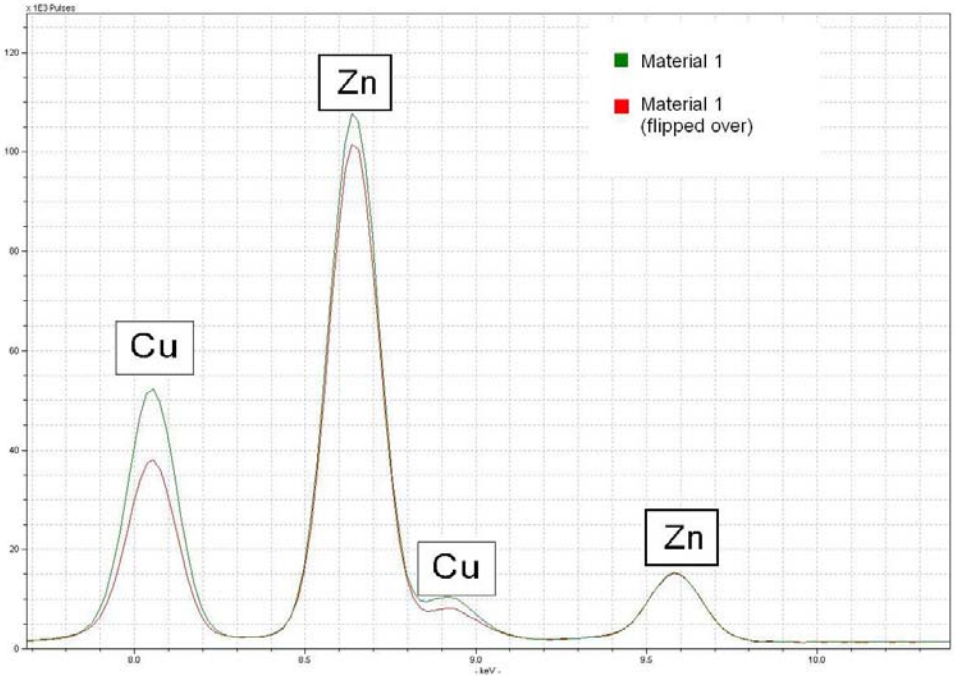
Element	Unit	Material 5 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<148	<155	<130	<134	<127		
Cr	ppm	<684	<713	<588	<604	<556		
Pb	ppm	<40	<38	<35	<36	<33		
Ni	ppm	<245	<241	<191	<207	<192		
Cu	%	5.10	4.62	2.17	4.58	2.99	3.89	32.1%
Zn	%	3.80	3.84	3.67	3.75	3.56	3.72	3.0%
Sb	%	3.79	3.99	3.81	3.89	3.75	3.85	2.5%
Hg	ppm	<34	<37	<31	<36	<33		

Element	Unit	Material 6 – Solid Pad						
		1	2	3	4	5	Avg	RSD
Cd	ppm	<132	<137	<159	<163	<158		
Cr	ppm	<513	<567	<668	<651	<670		
Pb	ppm	<32	<33	<42	<44	<39		
Ni	ppm	<192	<38	<242	<244	<254		
Cu	%	0.924	0.799	0.648	1.61	3.21	1.44	73.5%
Zn	%	7.02	7.67	7.98	7.81	7.80	7.66	4.9%
Sb	%	3.80	3.99	4.20	4.09	4.06	4.03	3.7%
Hg	ppm	<34	<38	<41	<40	<41		

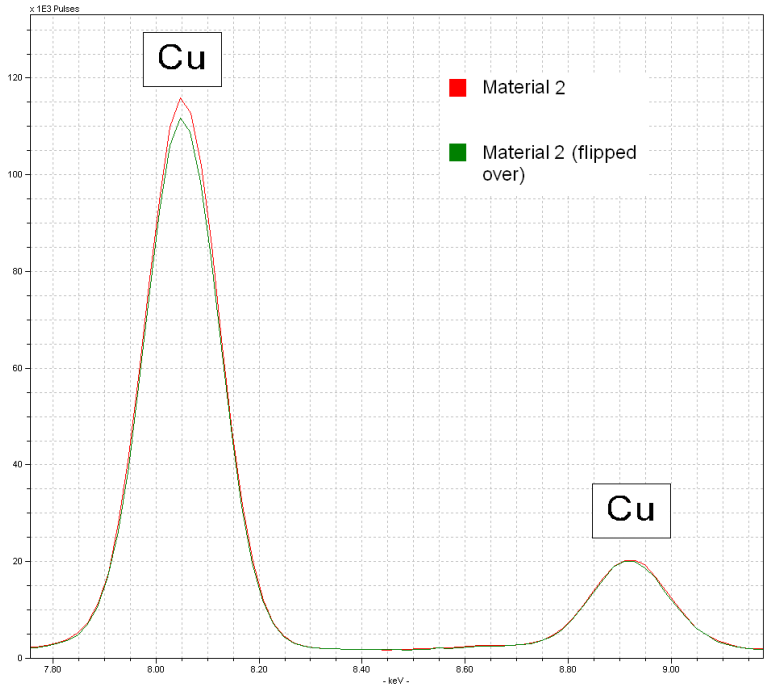
APPENDIX D

XRF Spectral Overlays of Top and Bottom Scans for Powdered Samples
(All scans made using the Bruker Tracer III-SD XRF instrument)

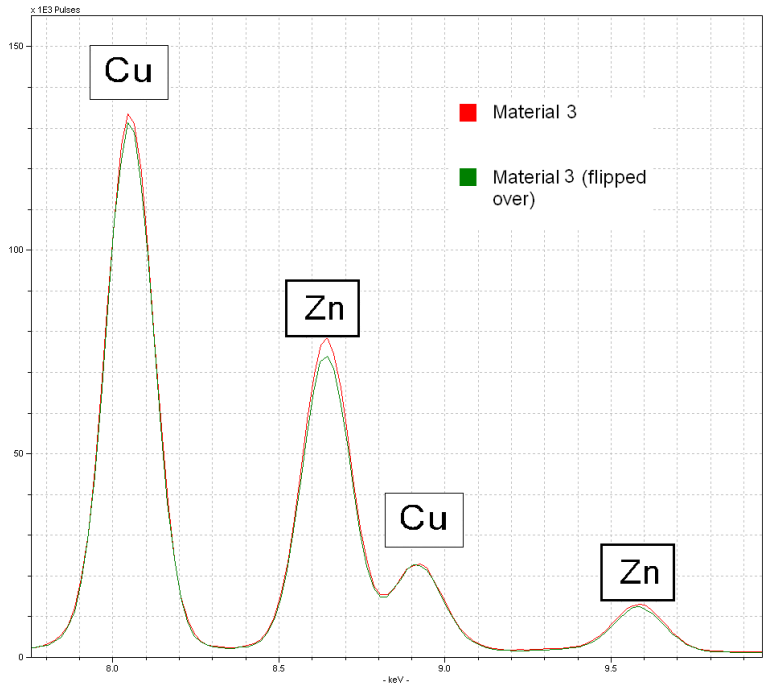
Material 1 (Powdered):



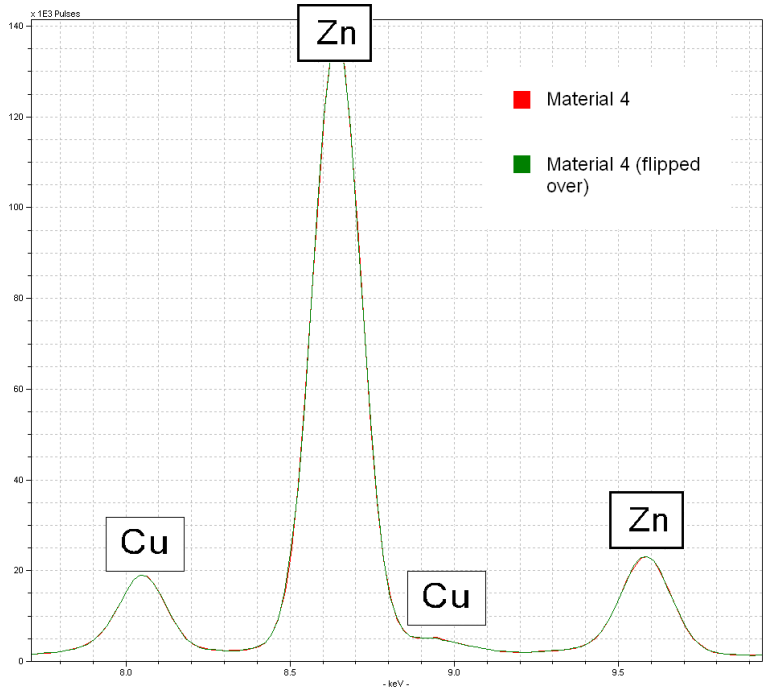
Material 2 (Powdered):



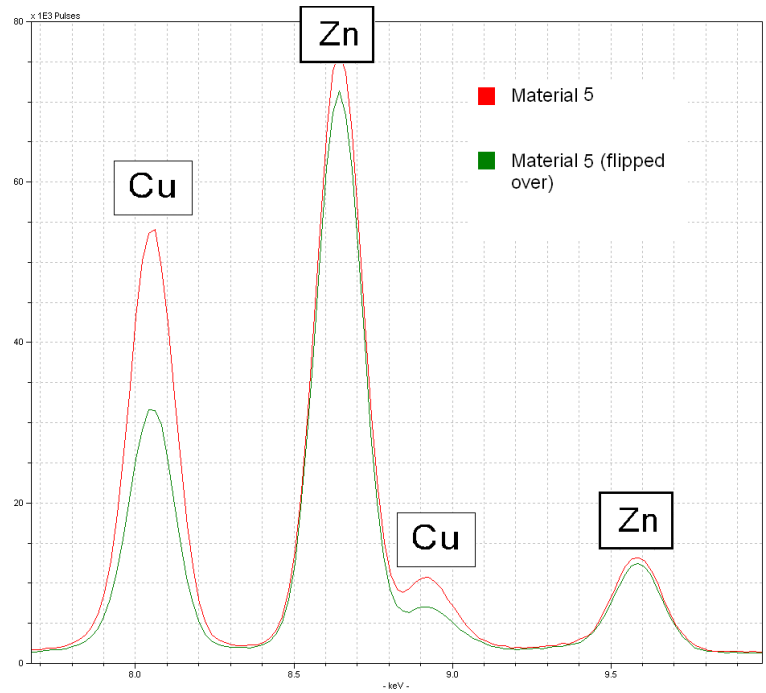
Material 3 (Powdered):



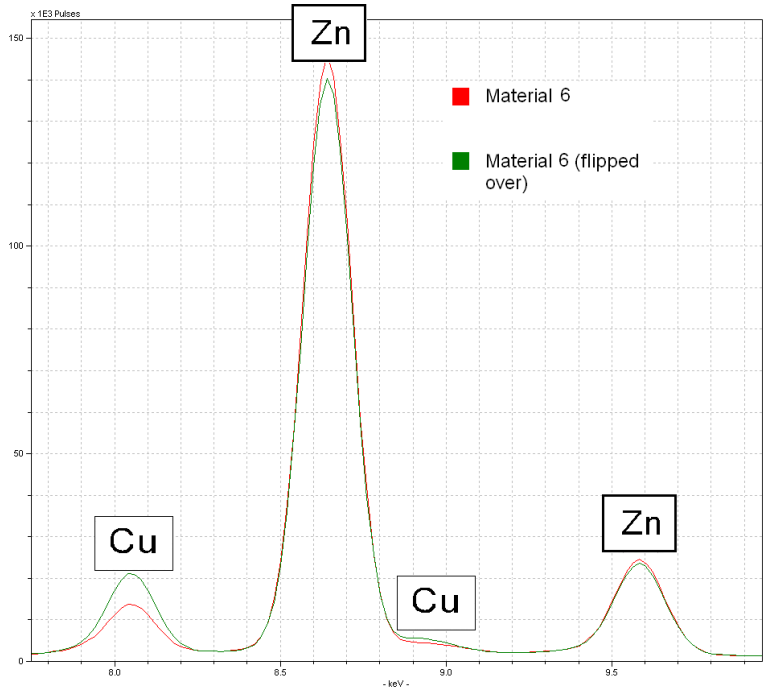
Material 4 (Powdered):



Material 5 (Powdered):



Material 6 (Powdered):

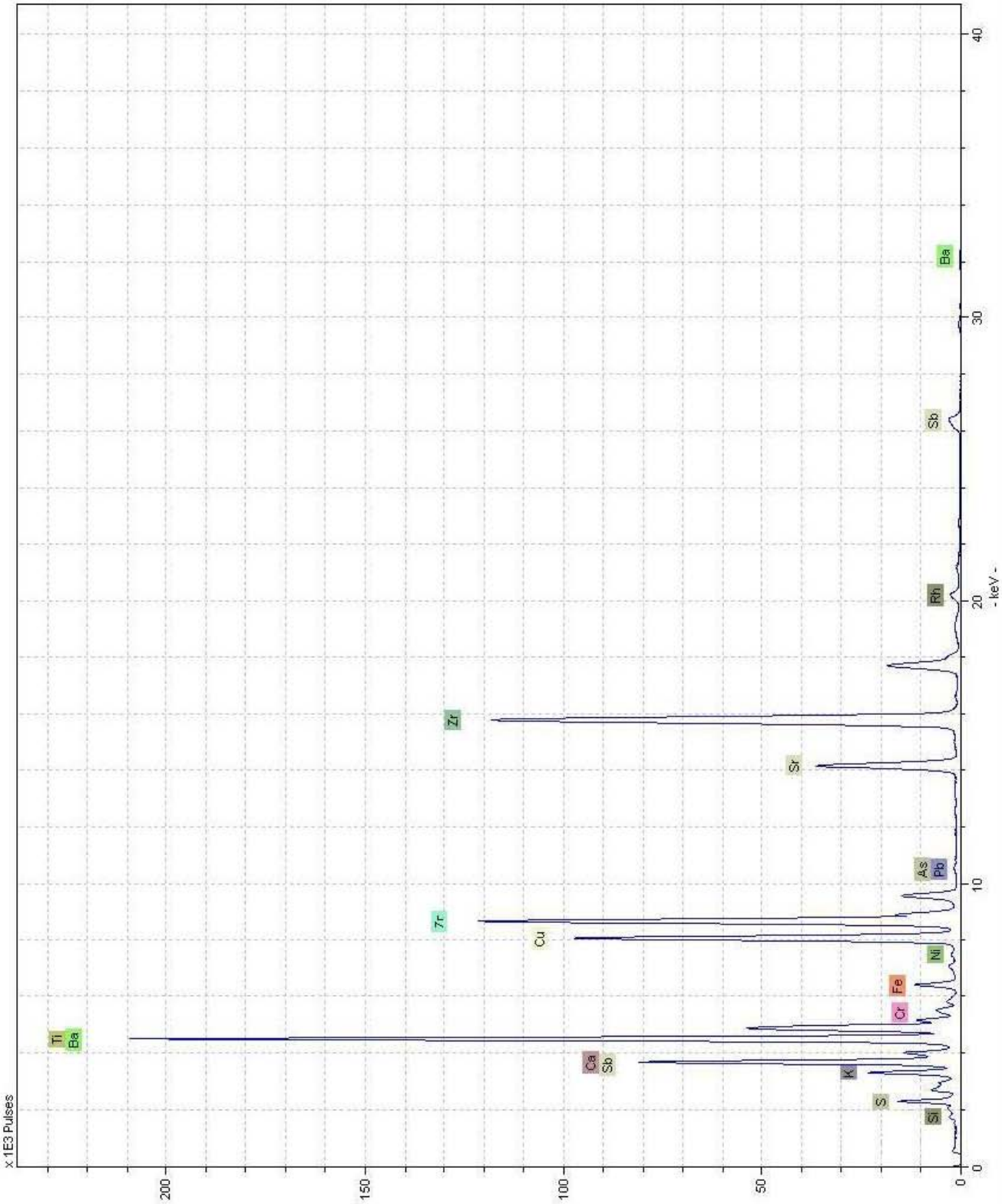


APPENDIX E

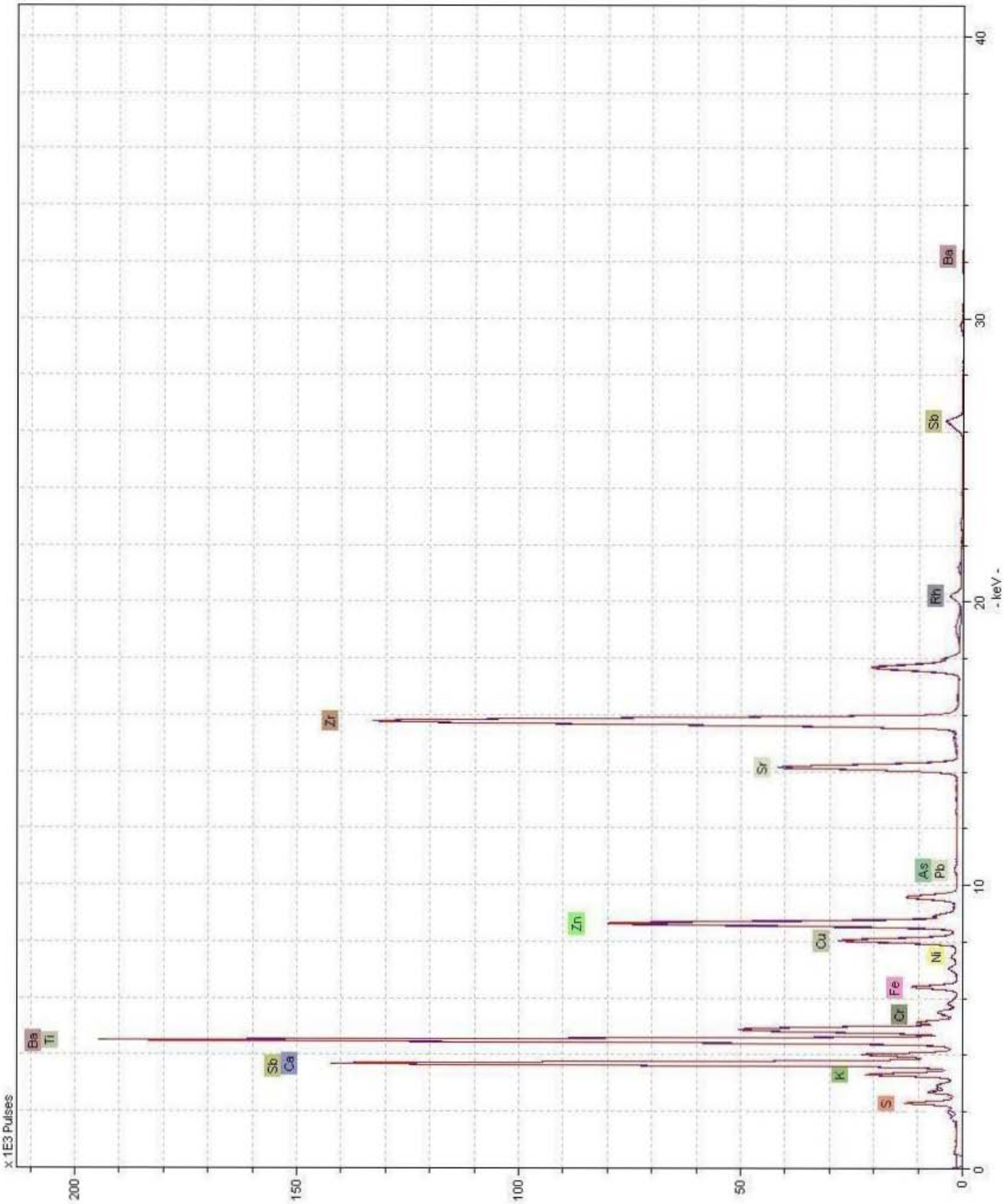
Individual XRF Spectra for All Scans

(All scans made using the Bruker Tracer III-SD XRF instrument; each scan area corresponds to the numbered scan area shown in Appendix A)

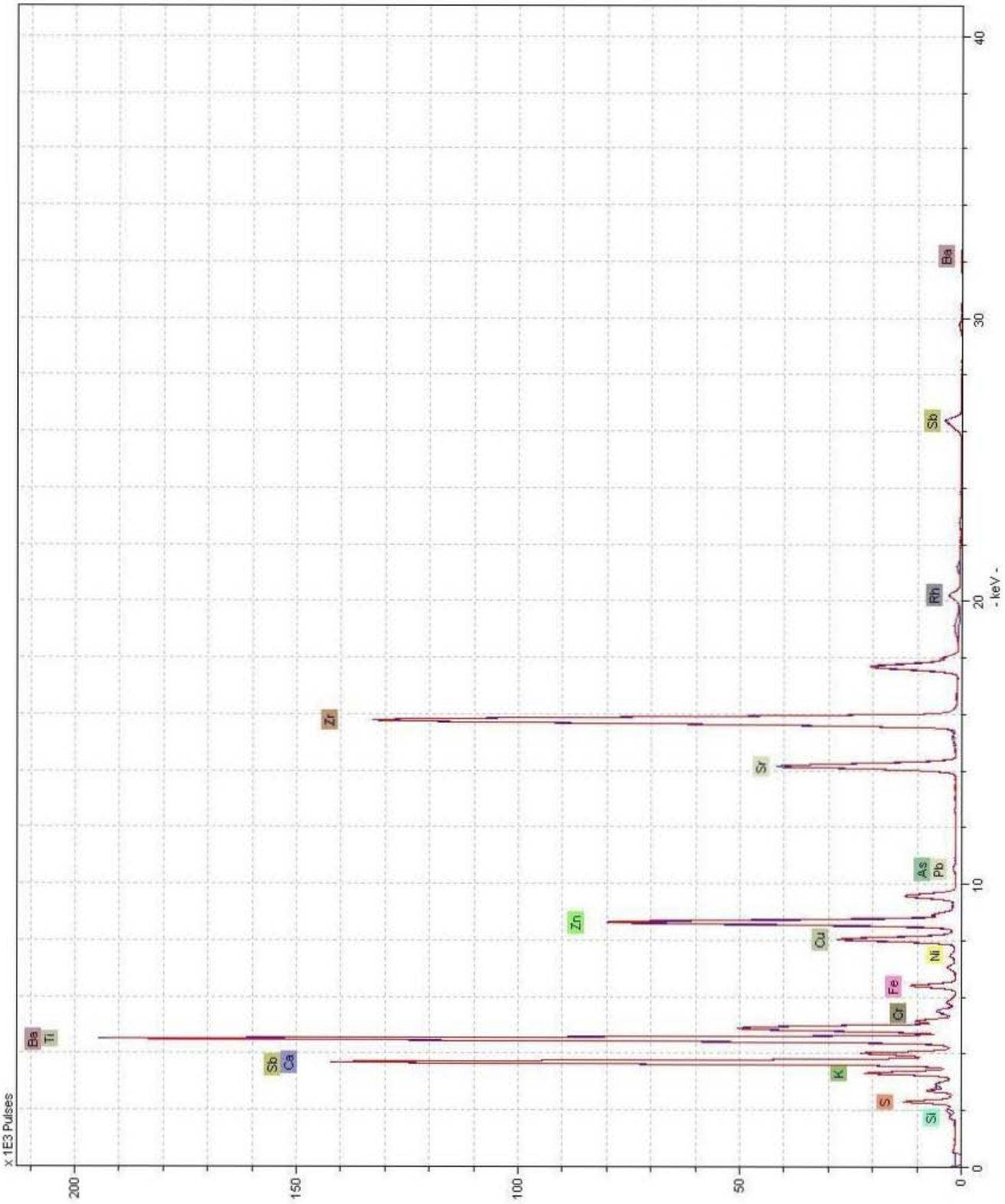
Material 1 (Solid), Scan Area 1



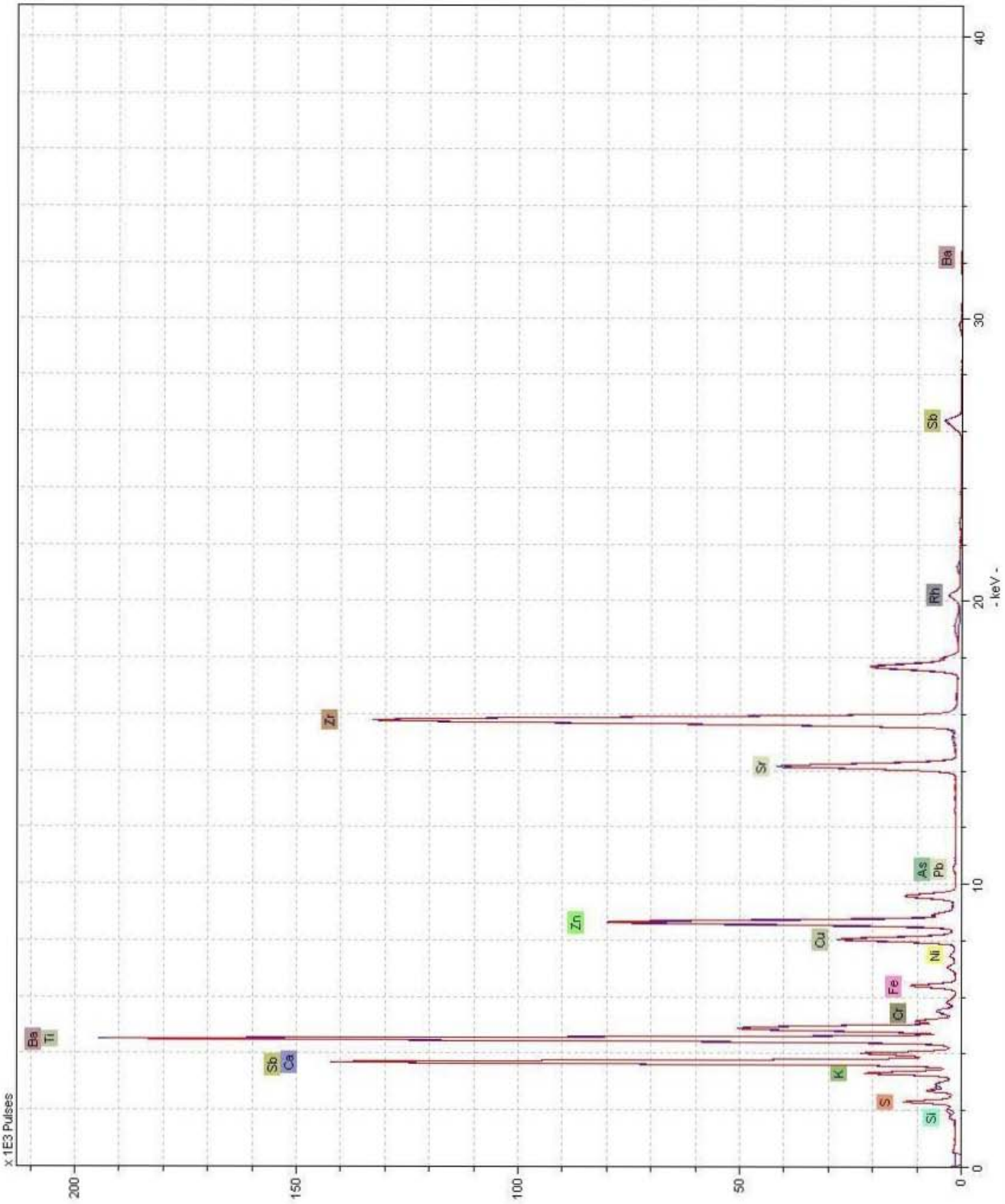
Material 1 (Solid), Scan Area 2



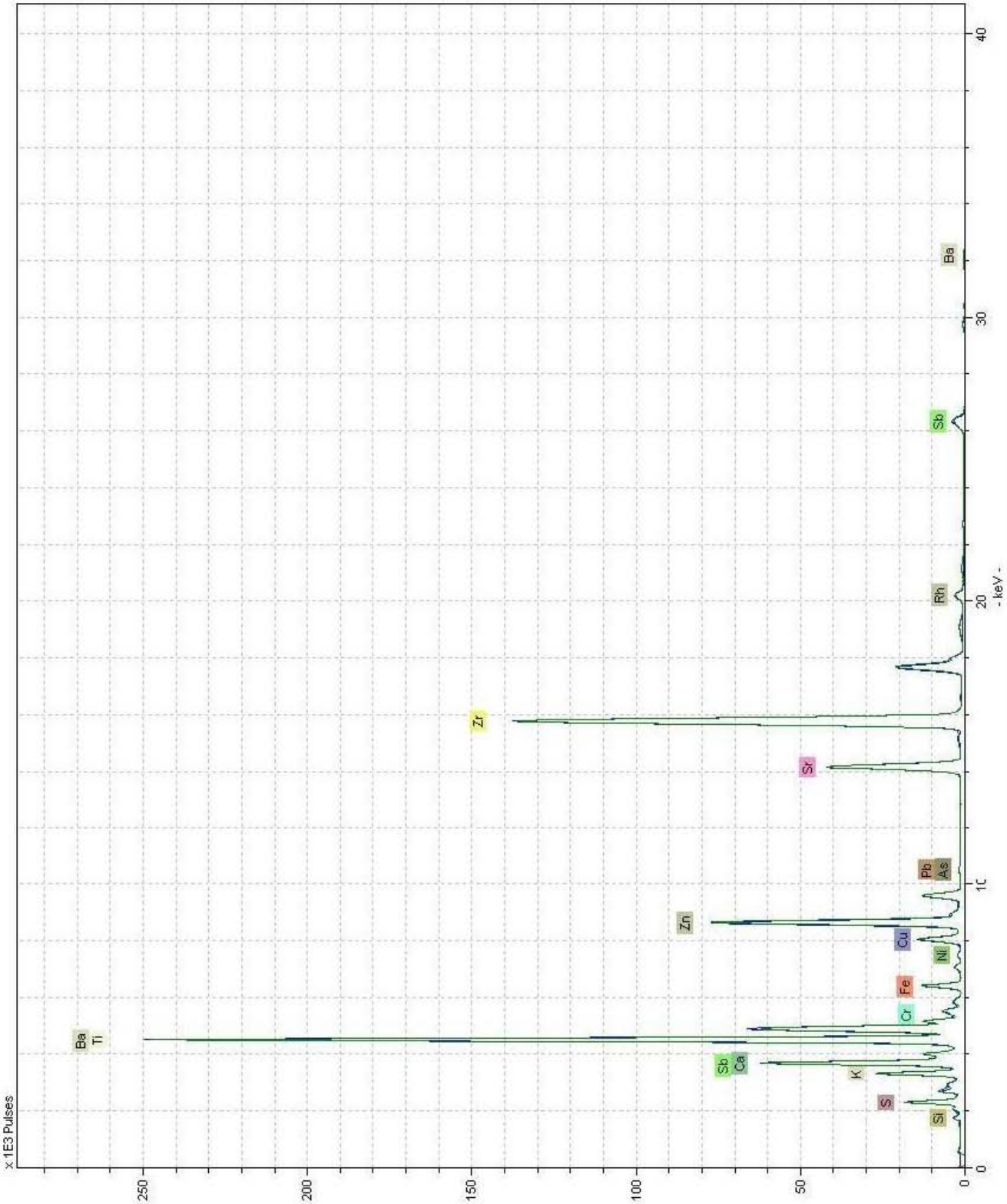
Material 1 (Solid), Scan Area 3



Material 1 (Solid), Scan Area 4

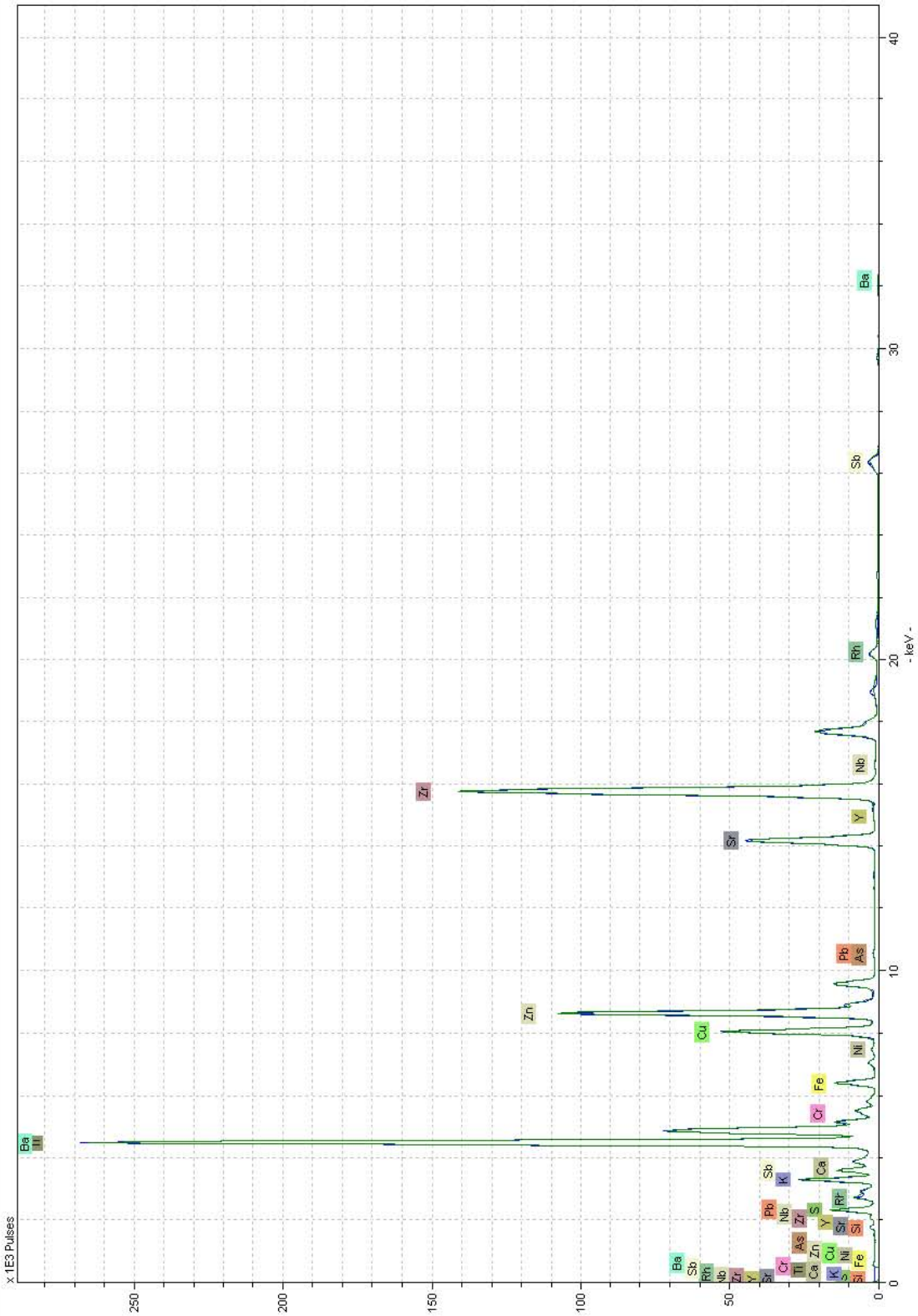


Material 1 (Solid), Scan Area 5

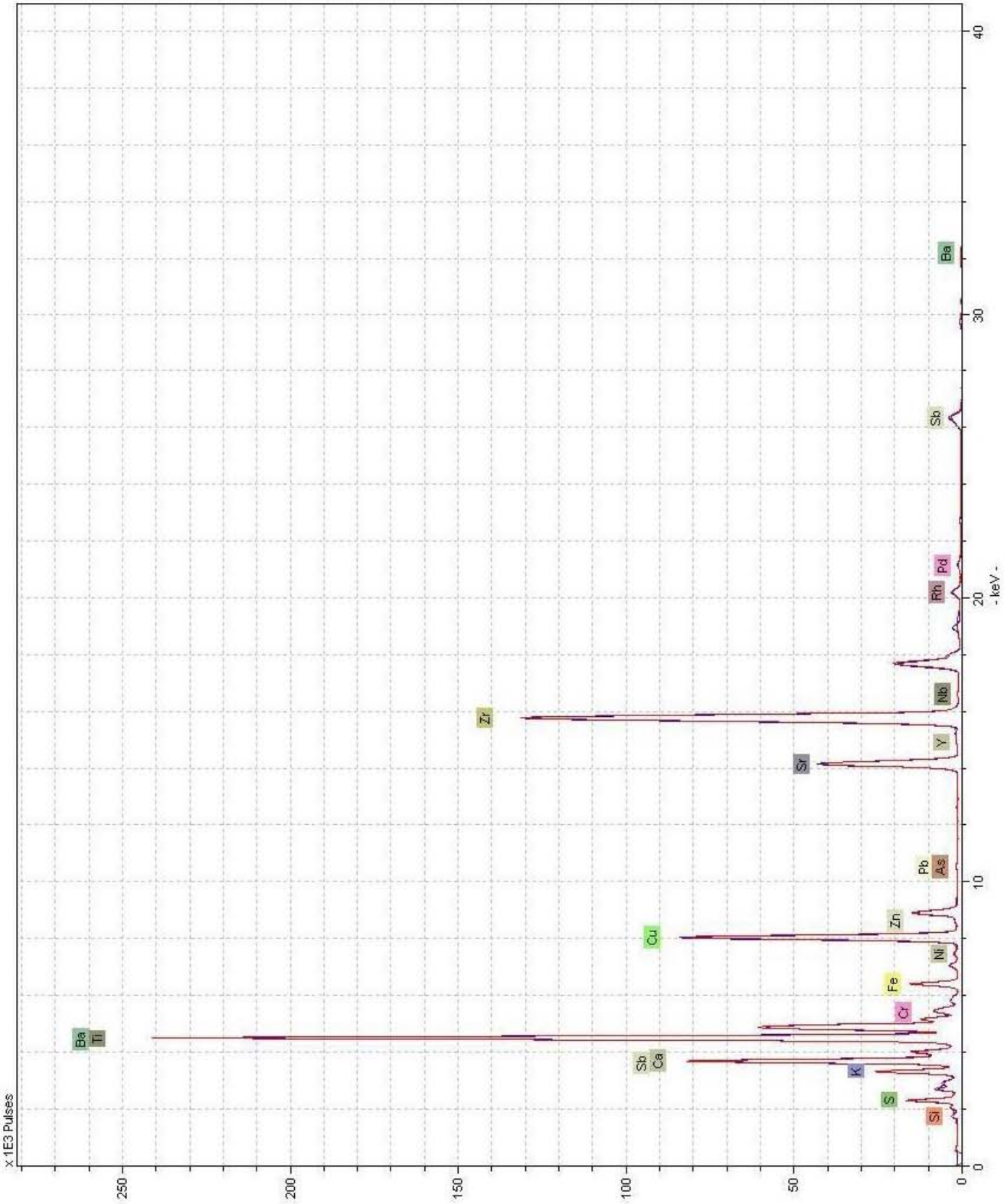


Material 1 (Powder), Bottom

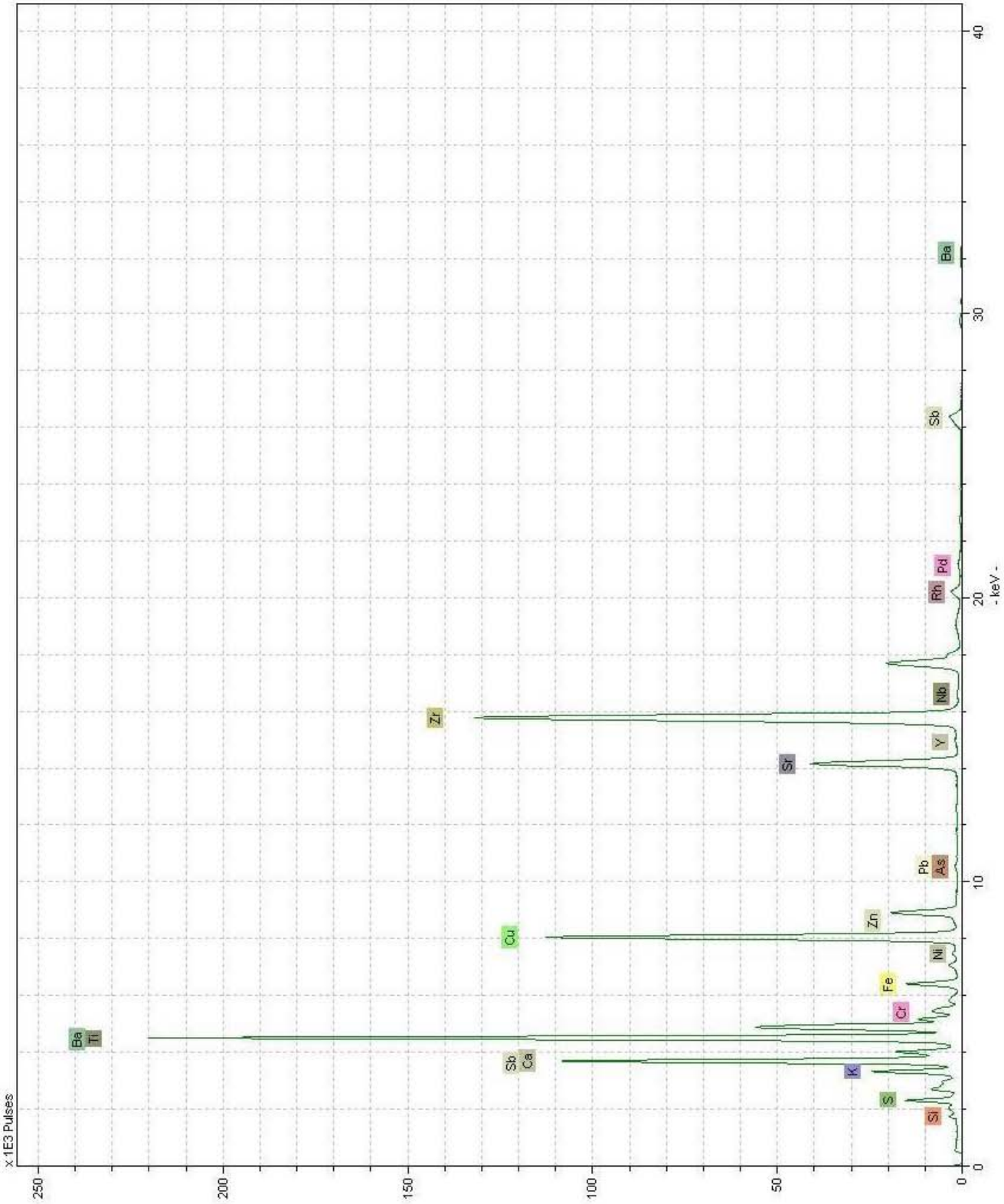
Material 1 (Powder), Top



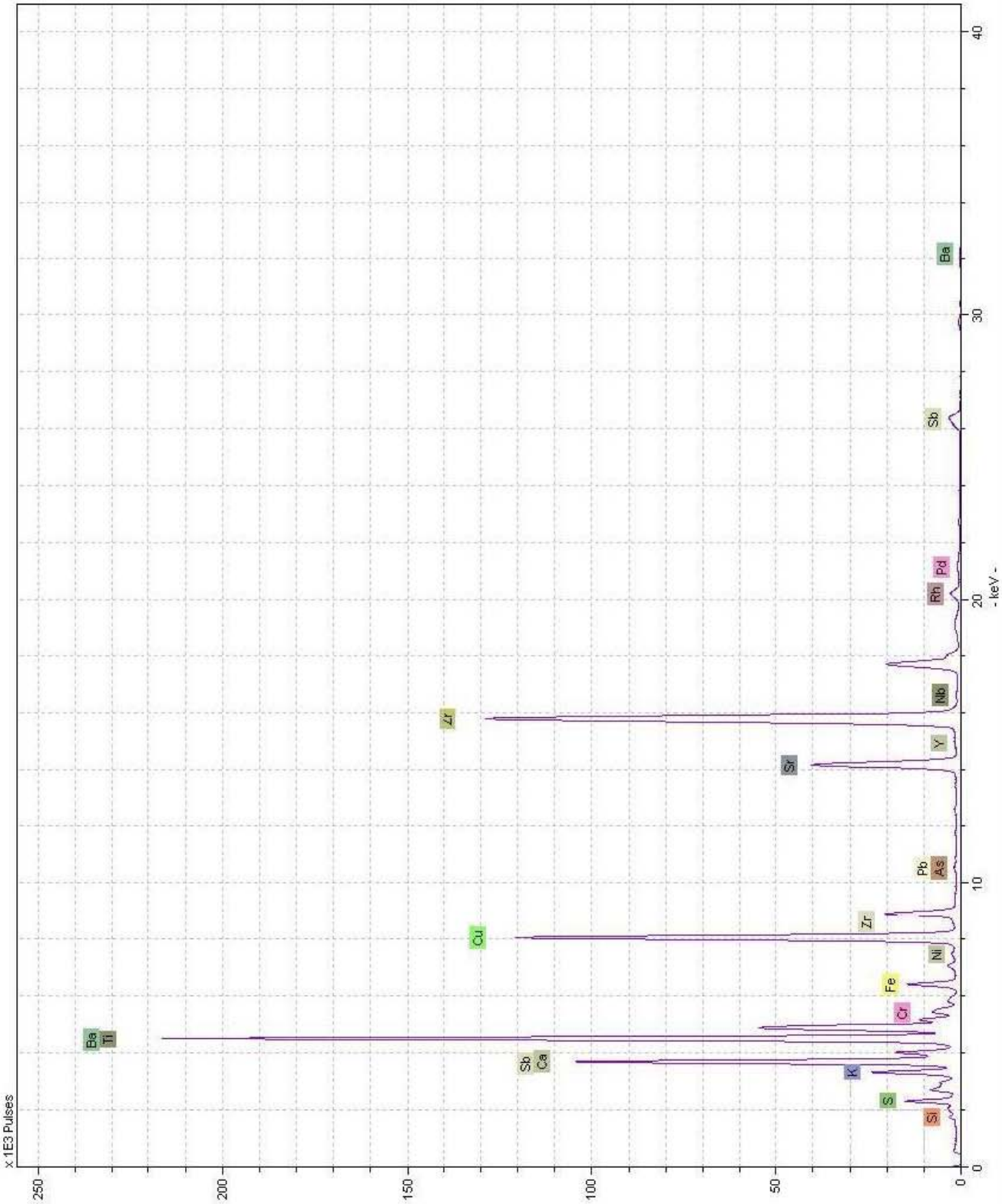
Material 2 (Solid), Scan Area 1



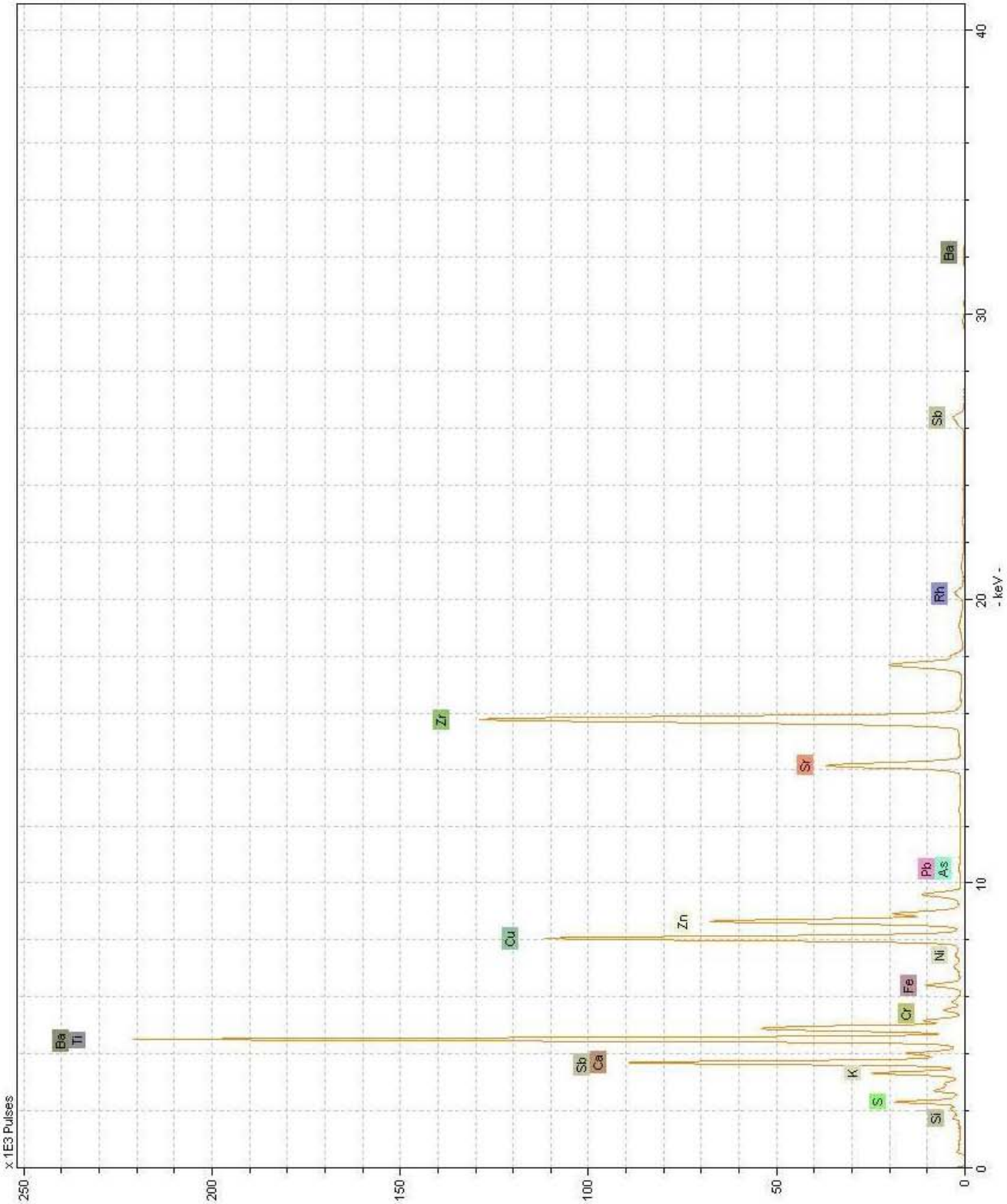
Material 2 (Solid), Scan Area 2



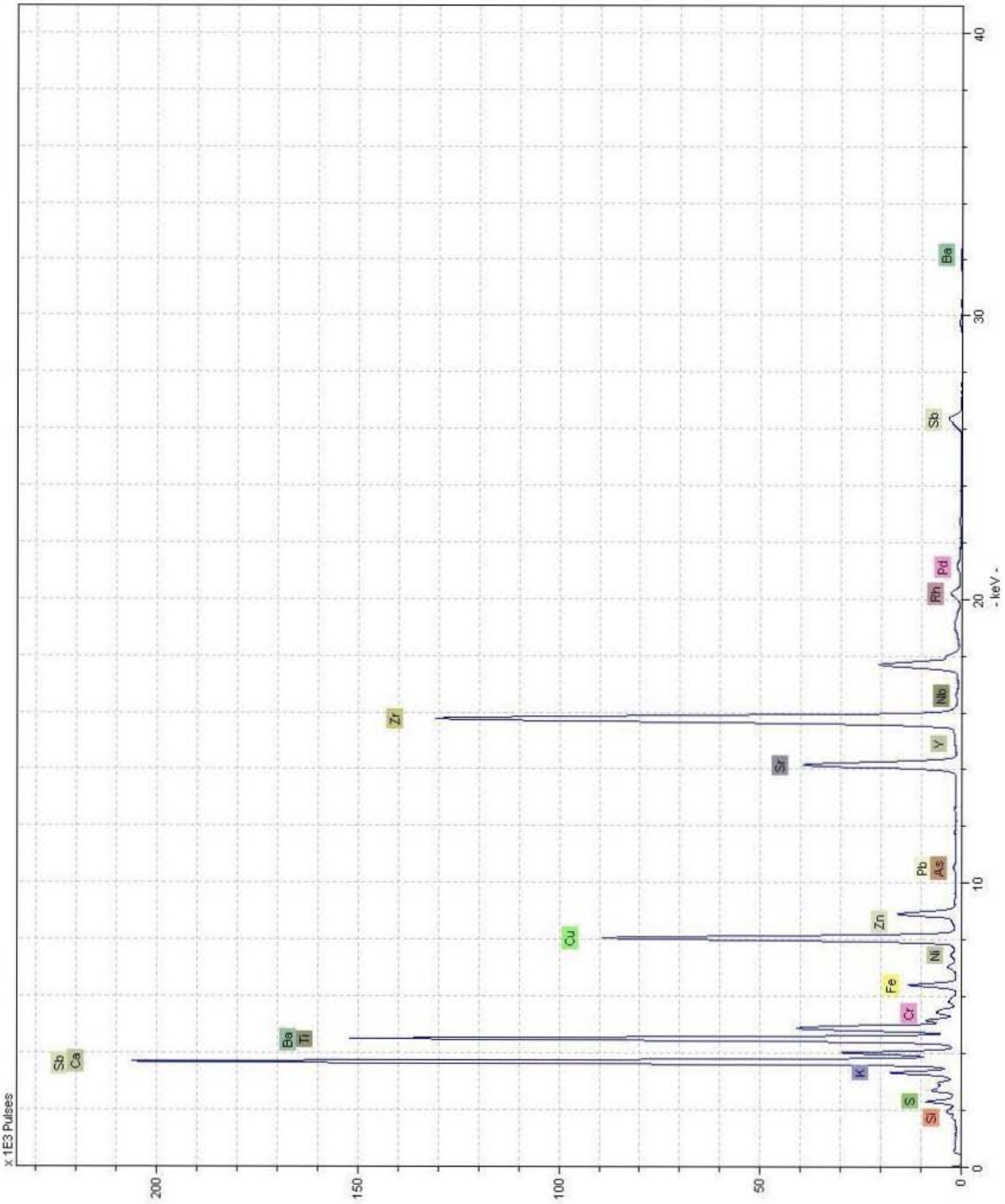
Material 2 (Solid), Scan Area 3



Material 2 (Solid), Scan Area 4



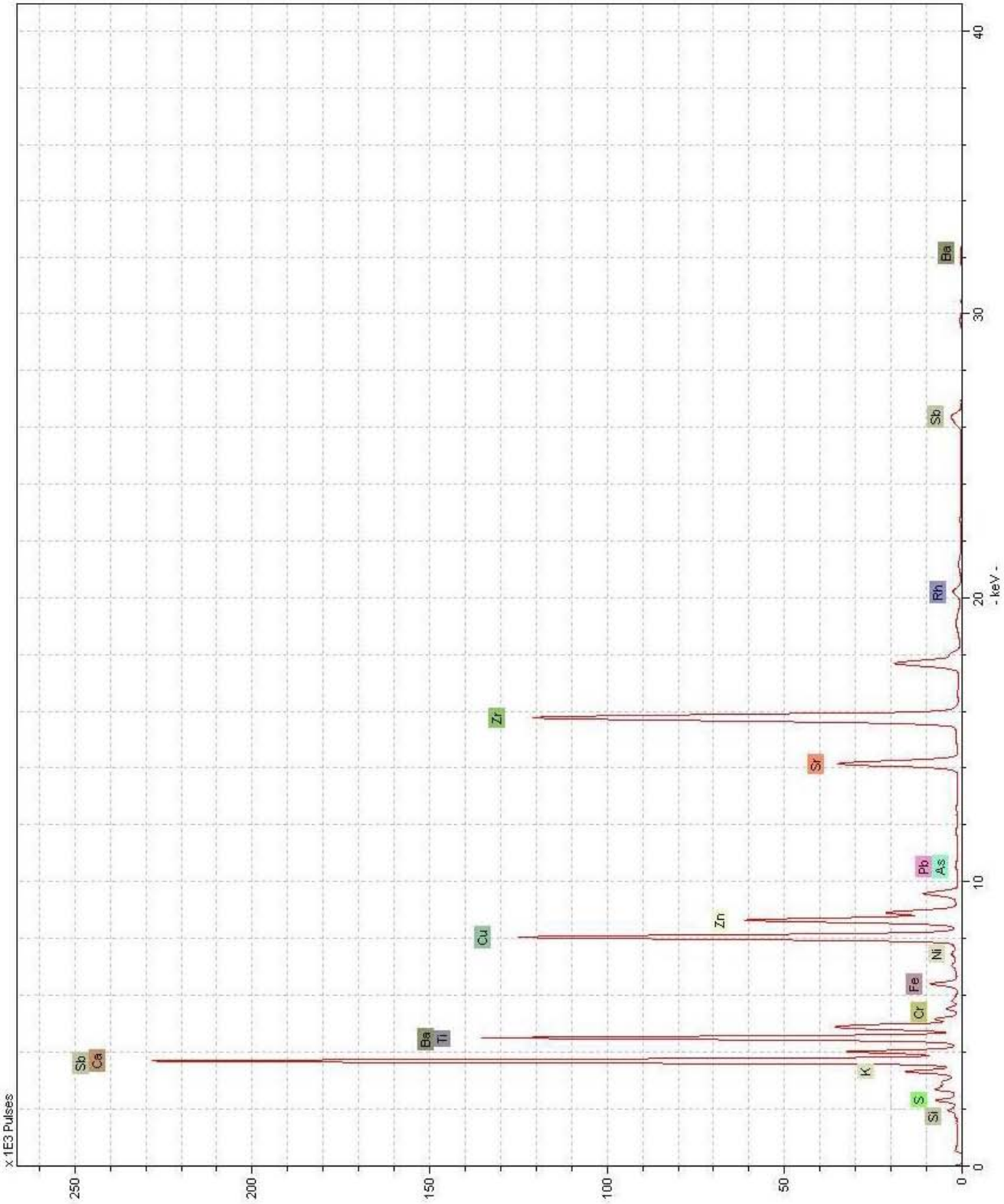
Material 2 (Solid), Scan Area 5



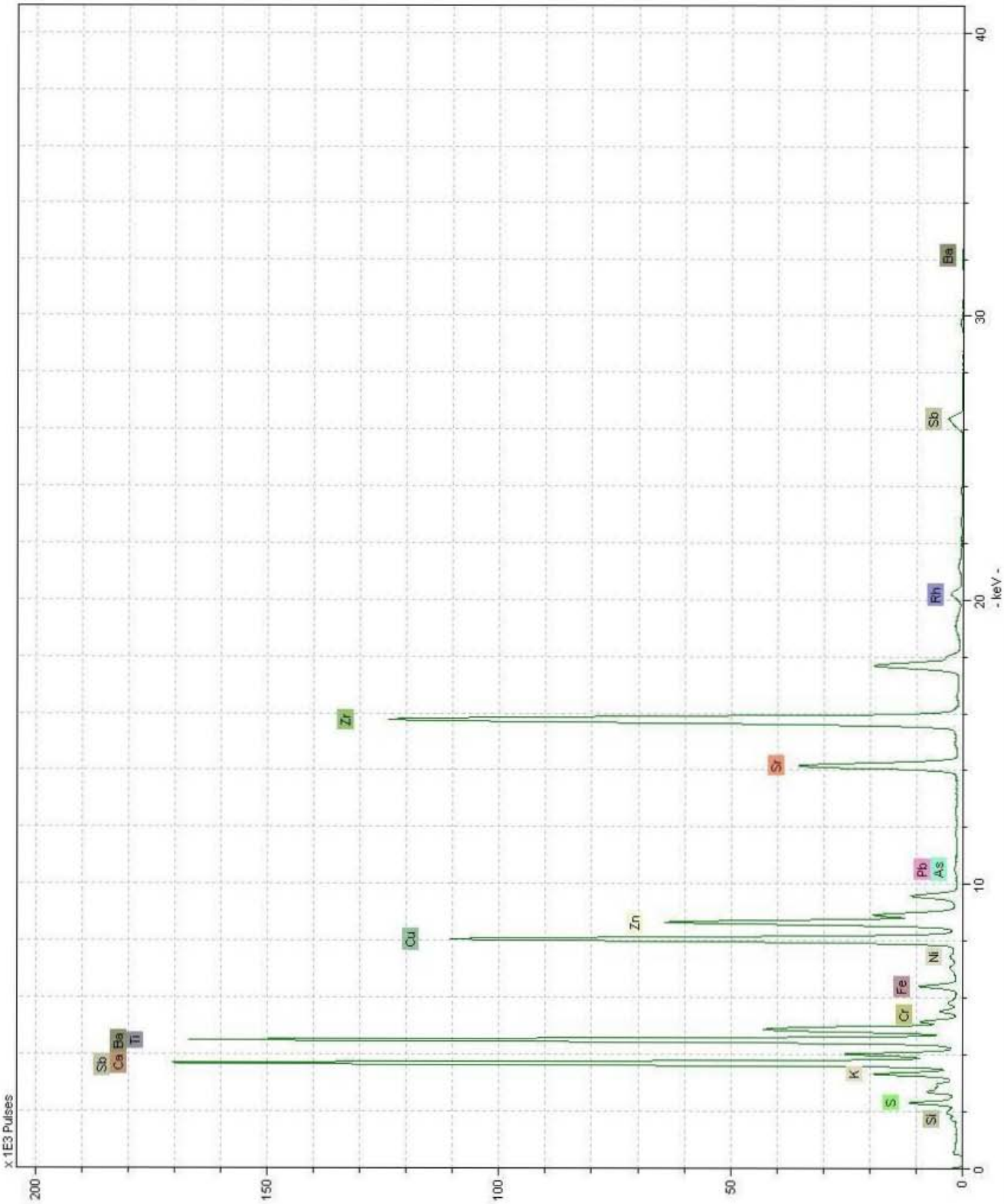
Material 2 (Powder), Bottom

Material 2 (Powder), Top

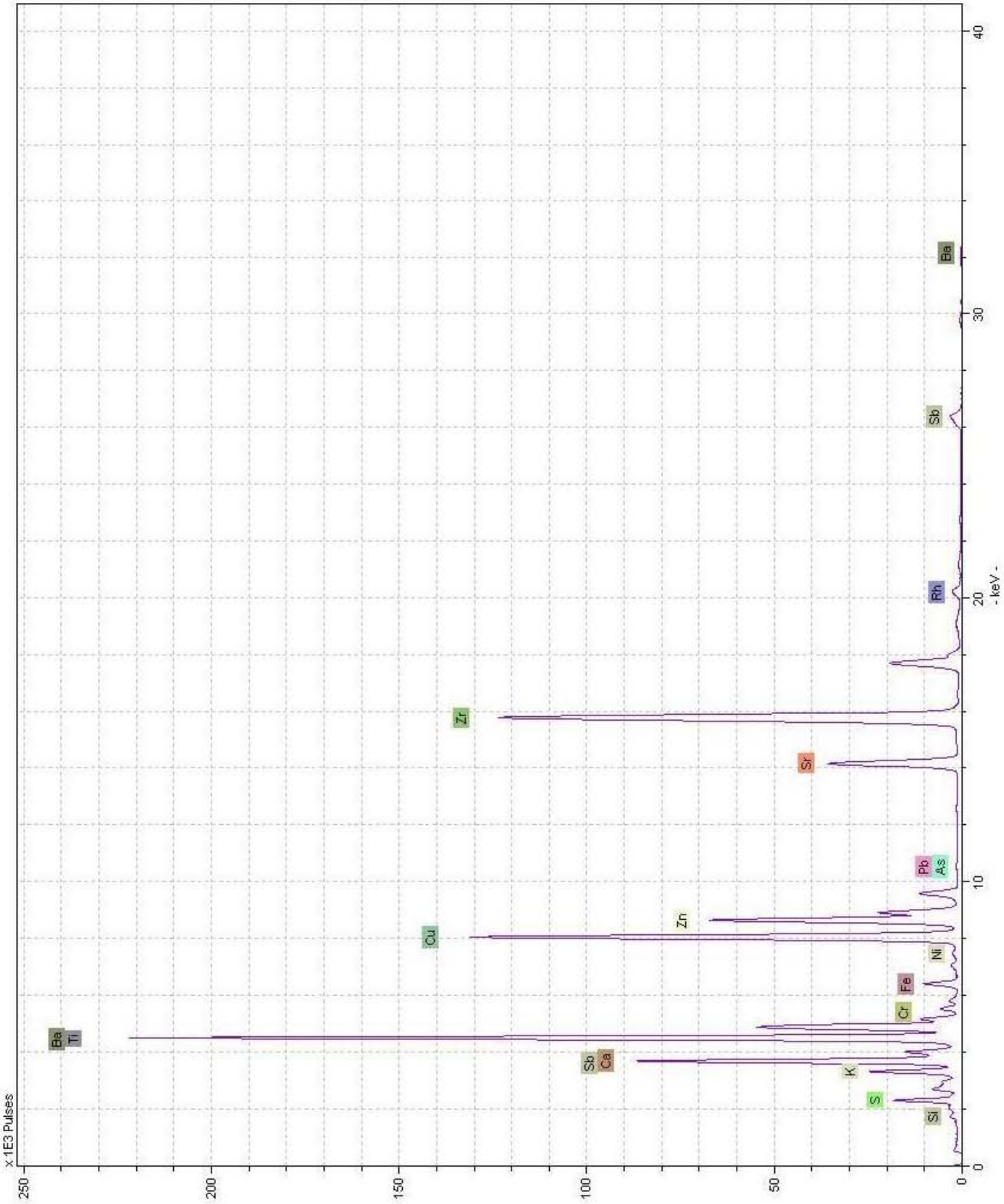
Material 3 (Solid), Scan Area 1



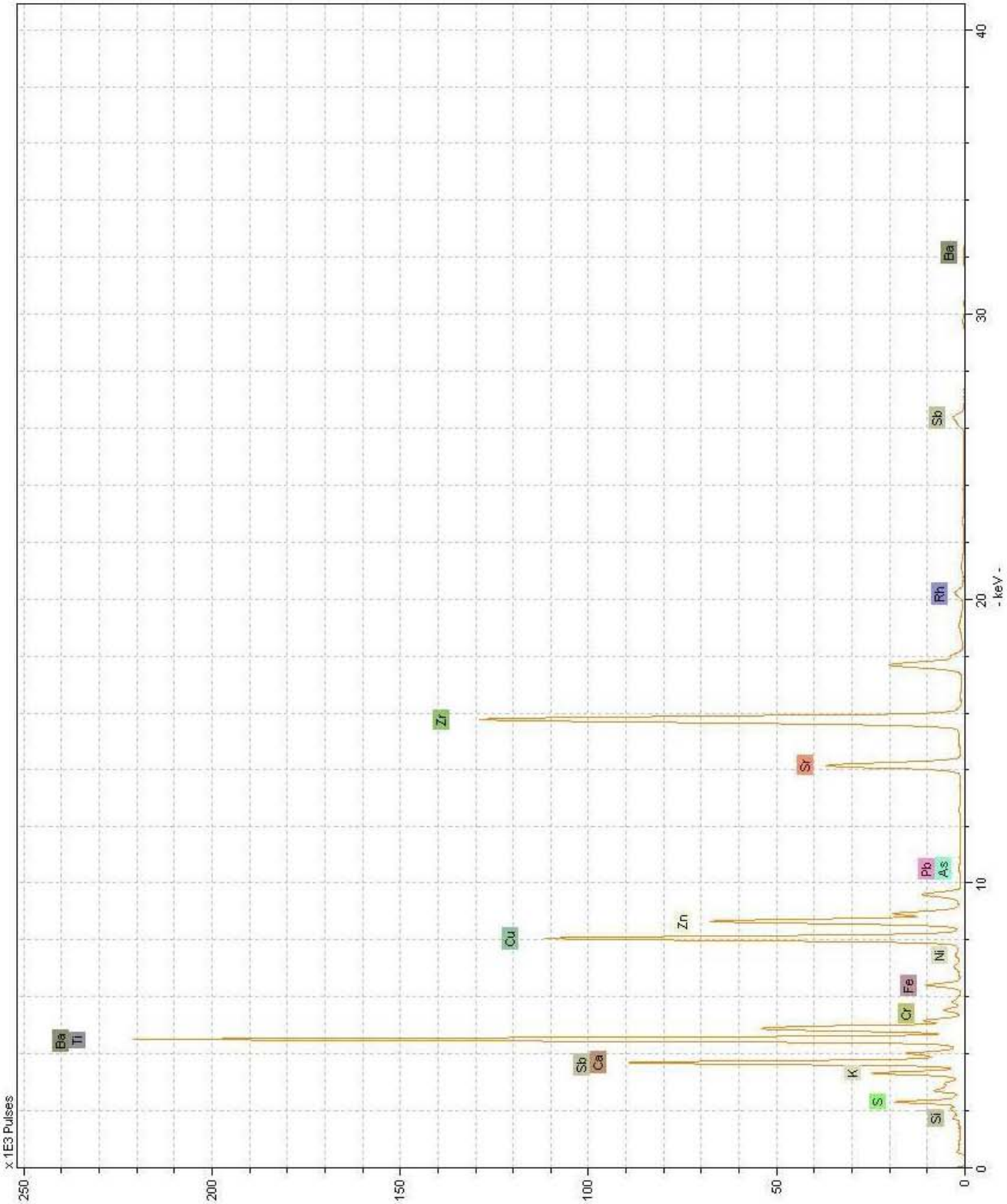
Material 3 (Solid), Scan Area 2



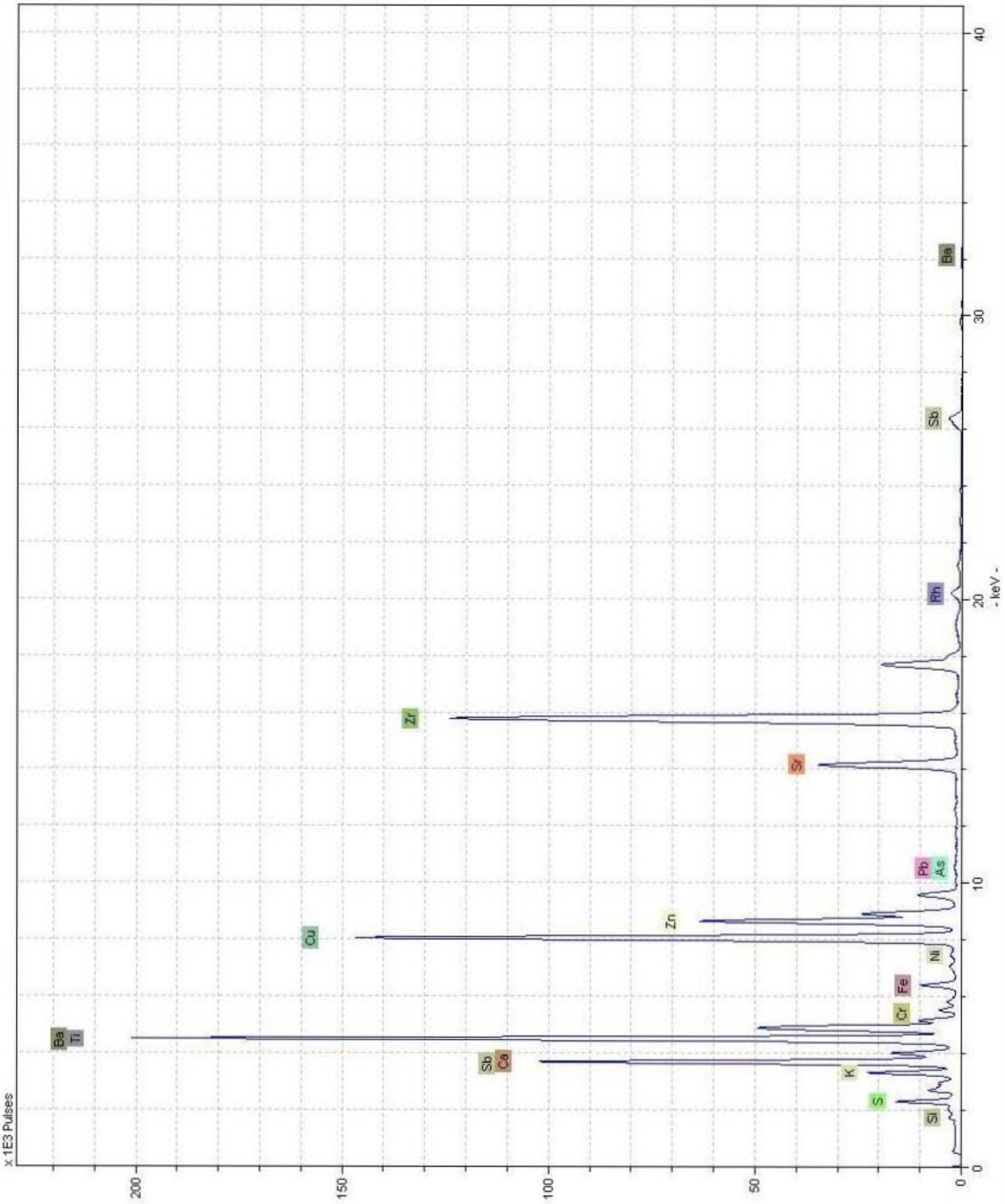
Material 3 (Solid), Scan Area 3



Material 3 (Solid), Scan Area 4

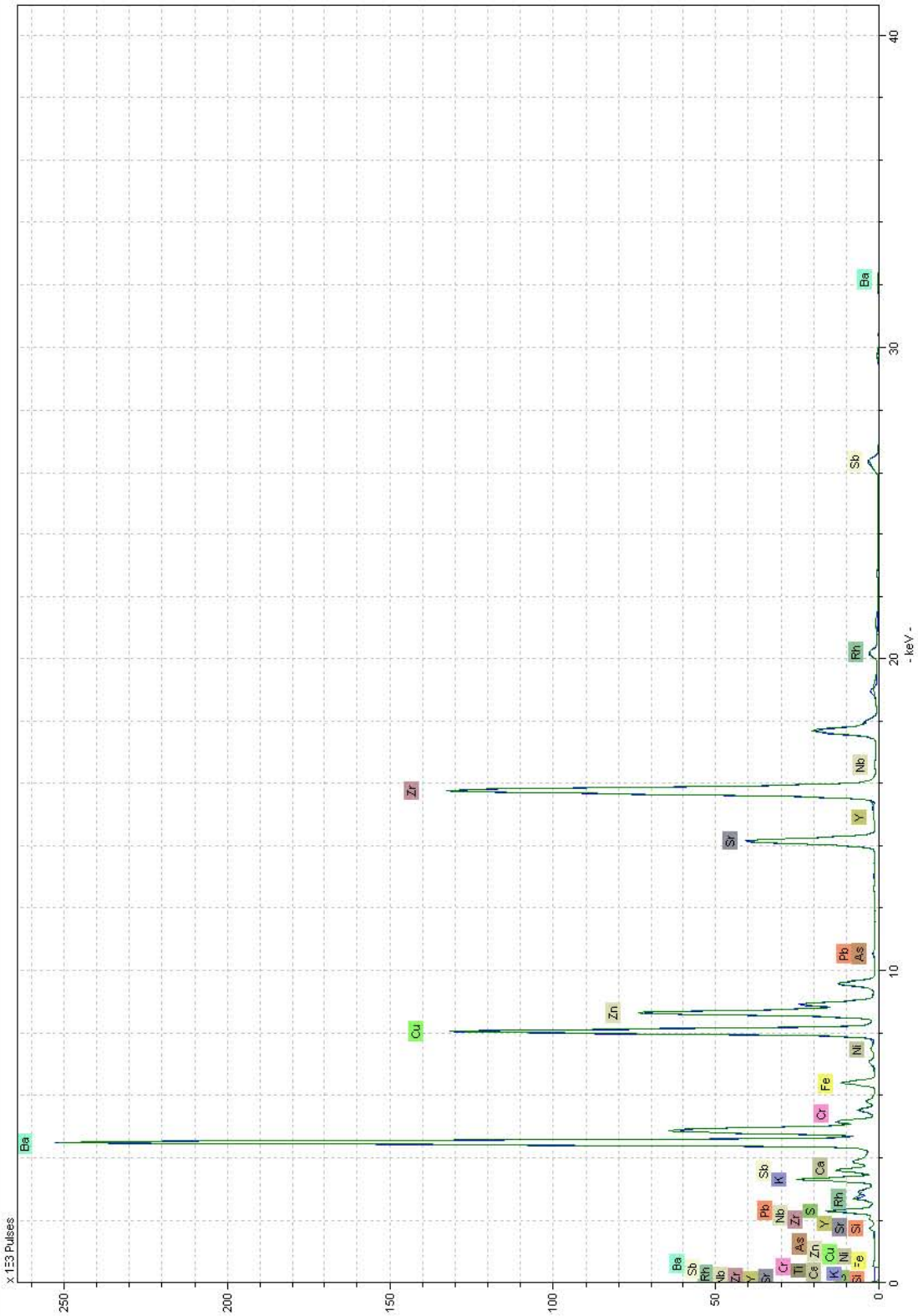


Material 3 (Solid), Scan Area 5

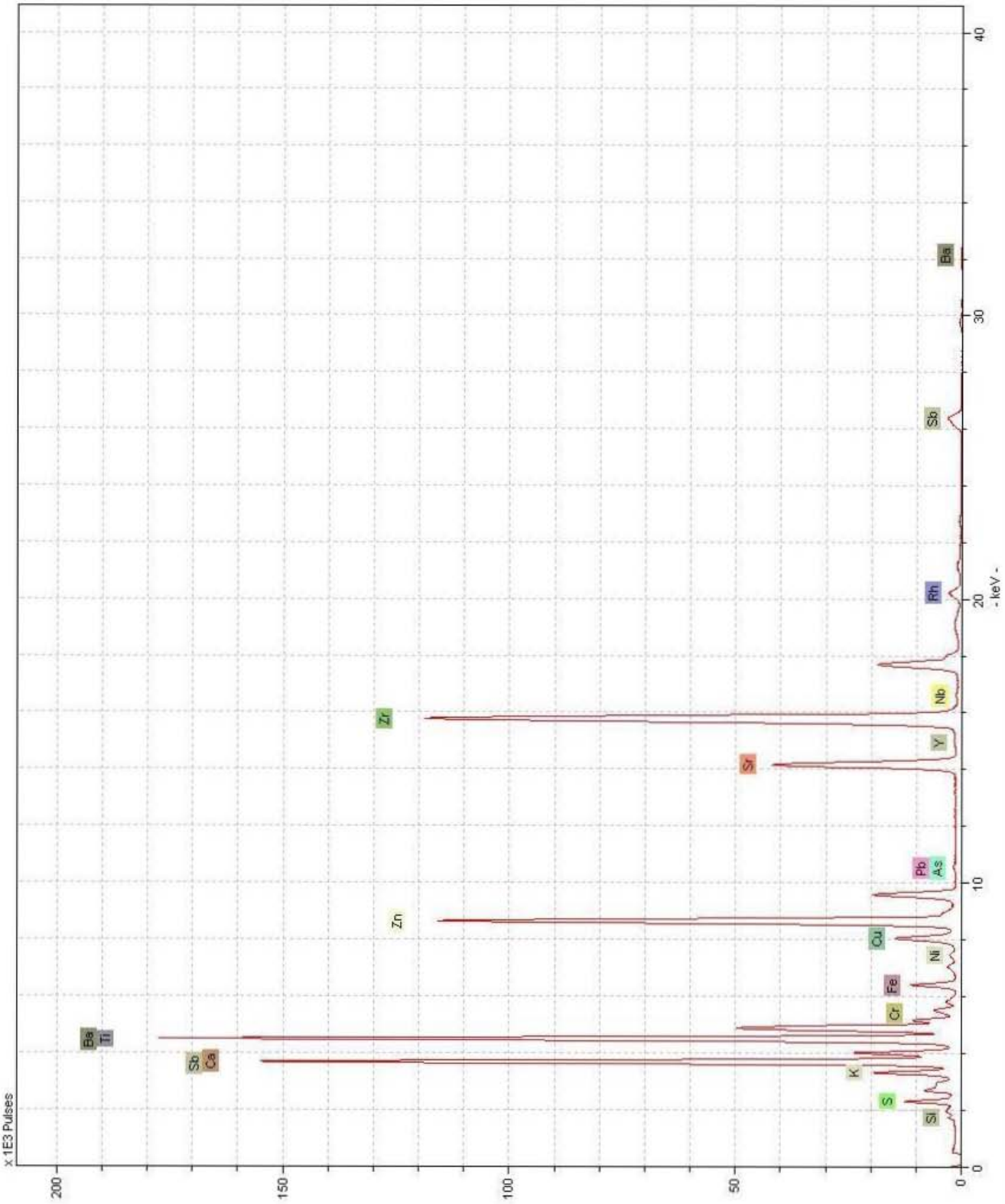


Material 3 (Powder), Bottom

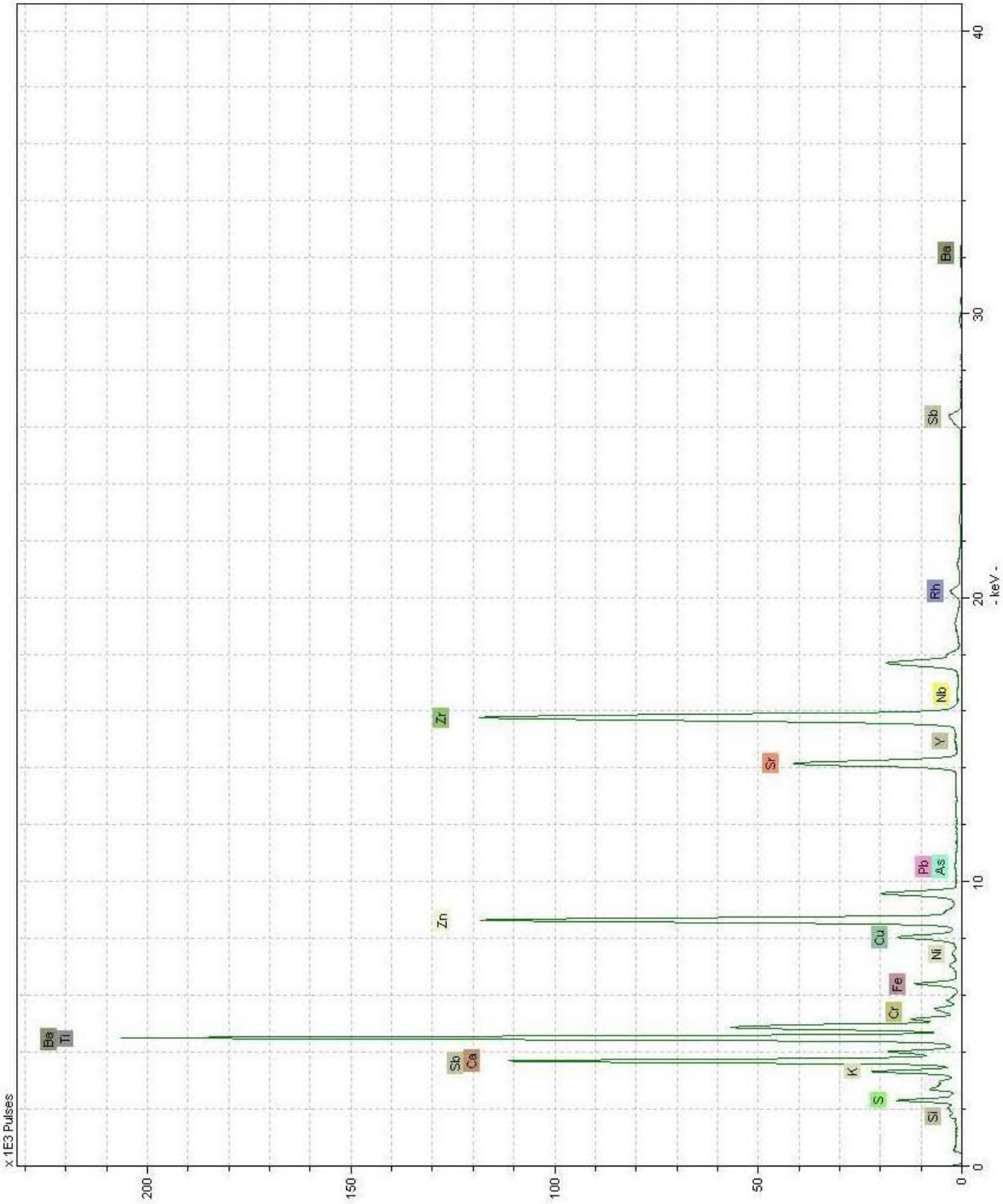
Material 3 (Powder), Top



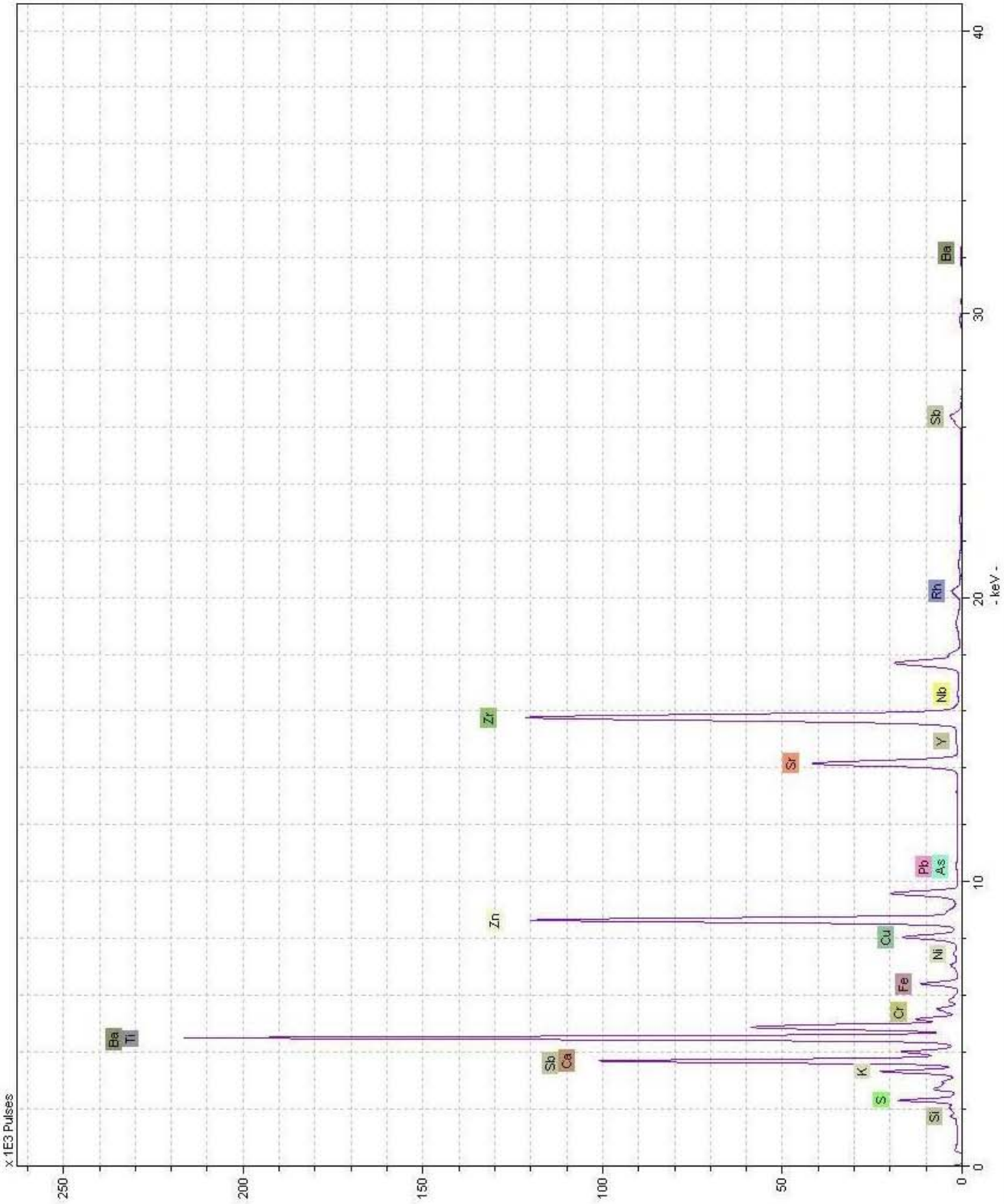
Material 4 (Solid), Scan Area 1



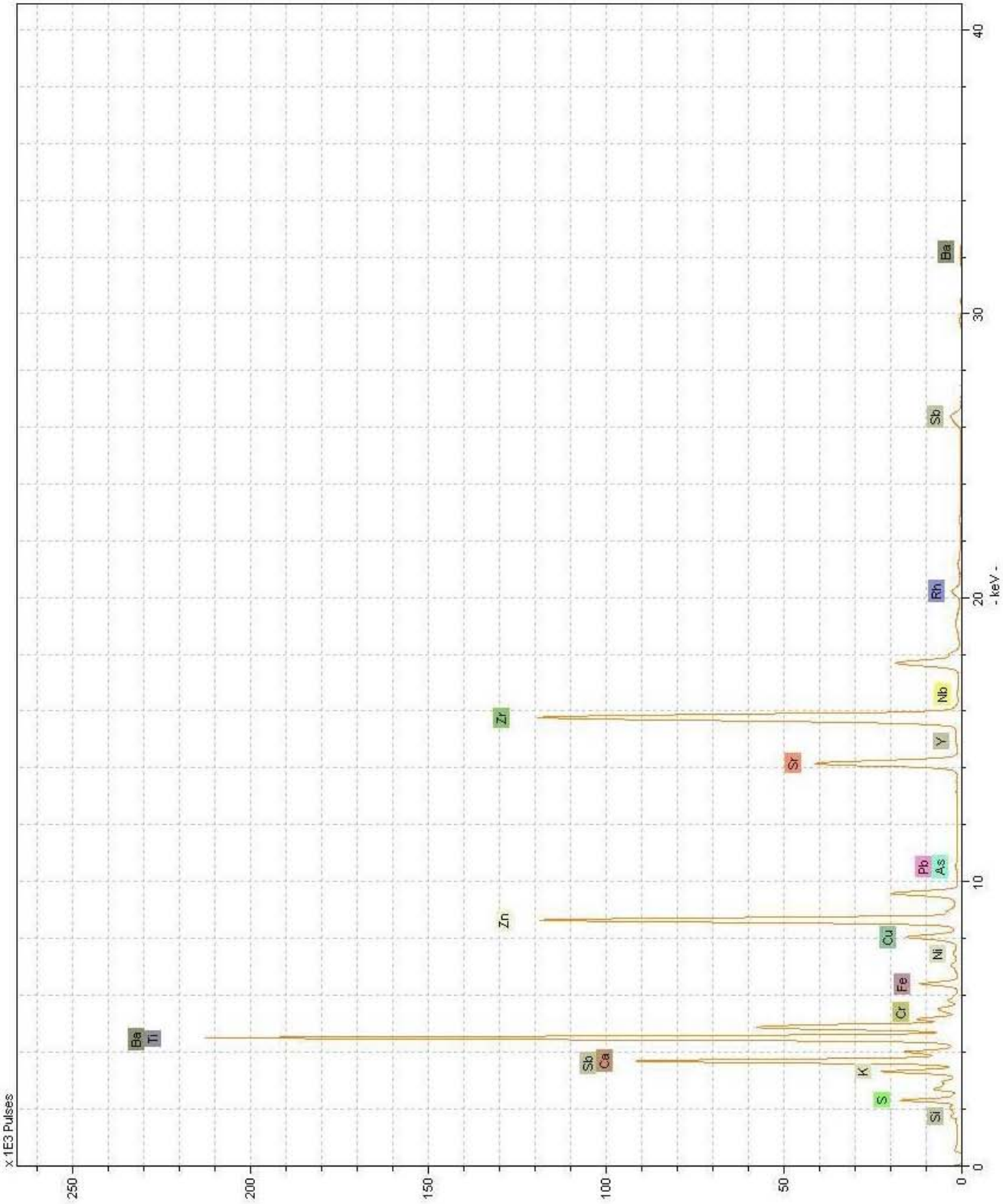
Material 4 (Solid), Scan Area 2



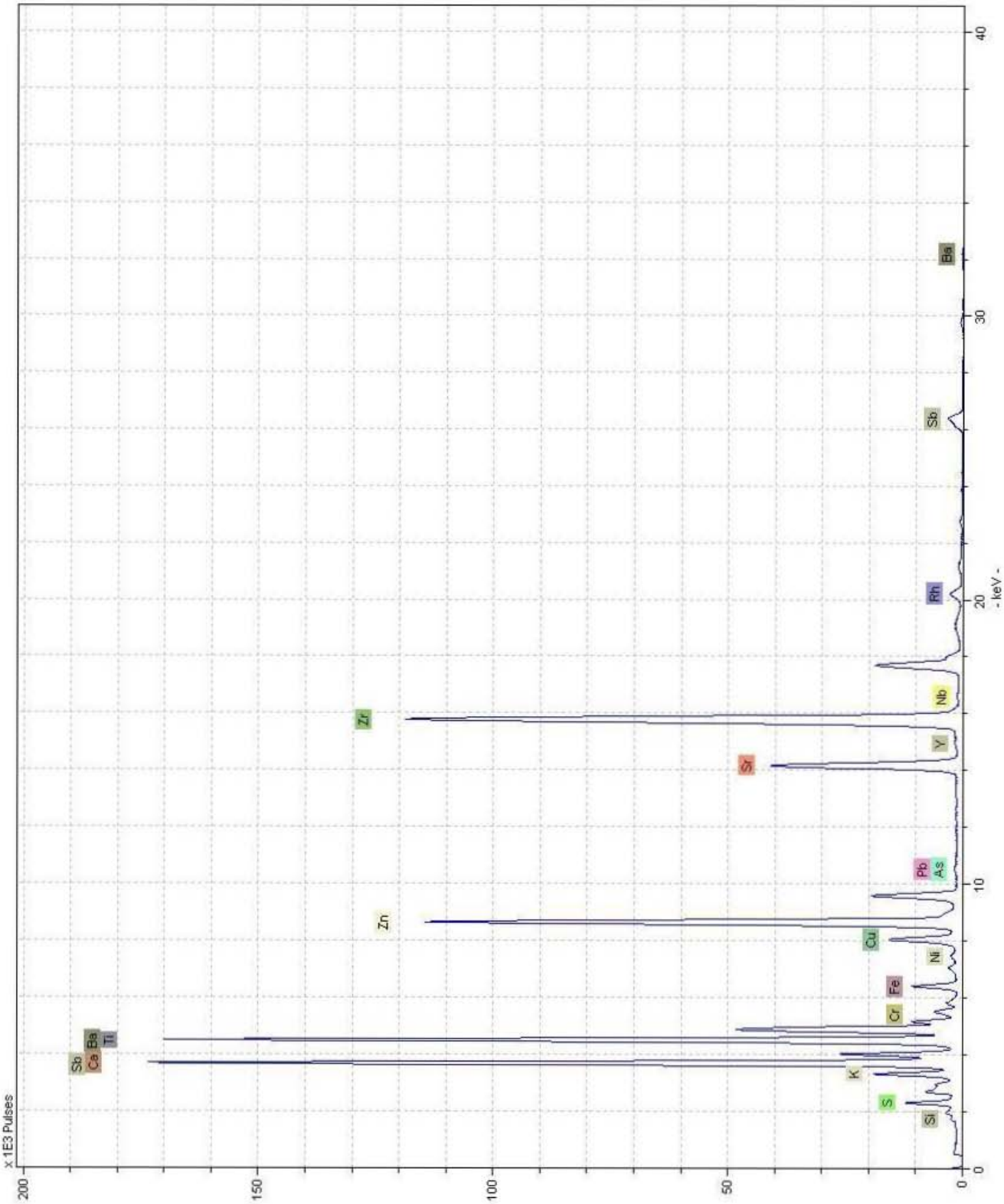
Material 4 (Solid), Scan Area 3



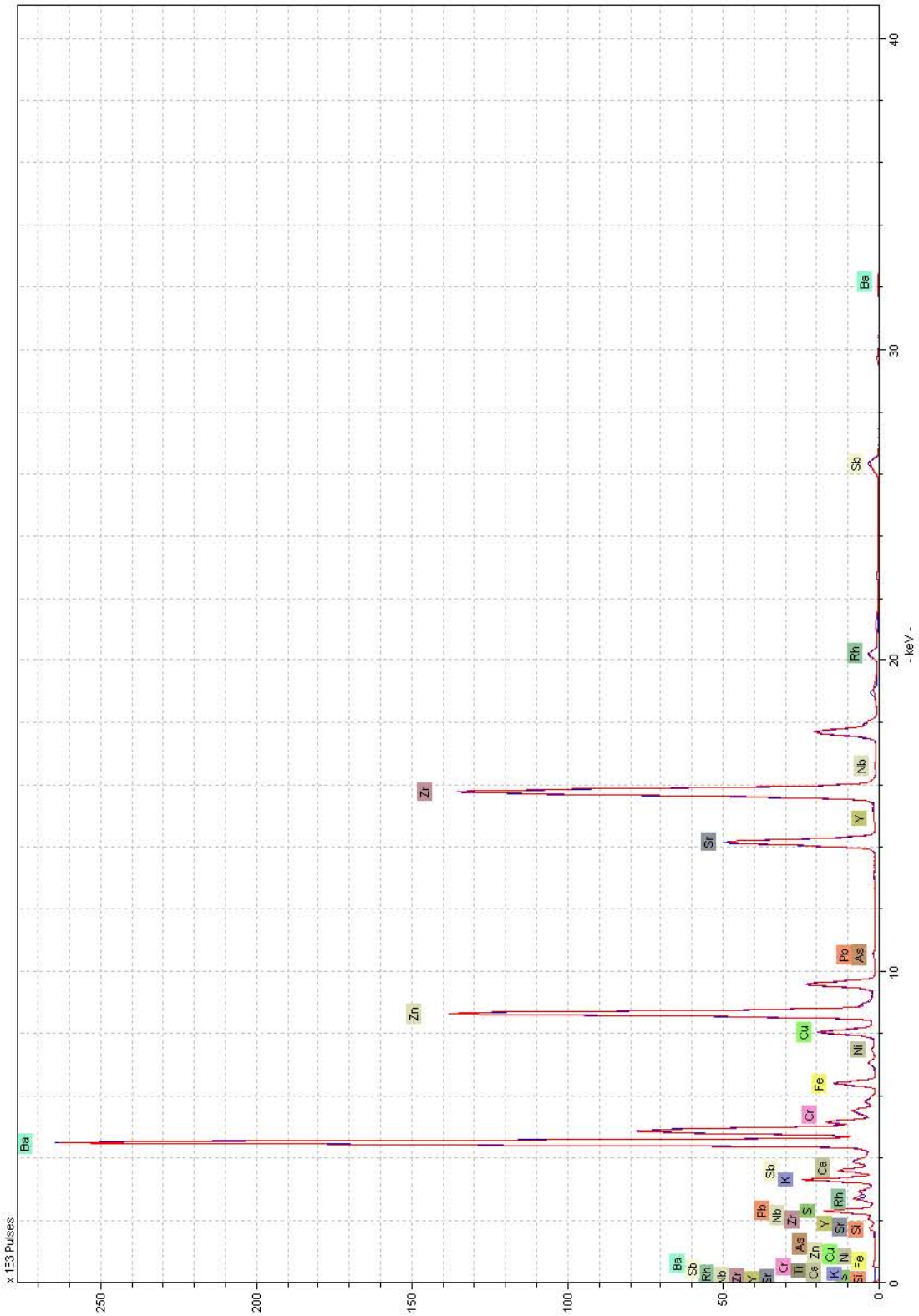
Material 4 (Solid), Scan Area 4



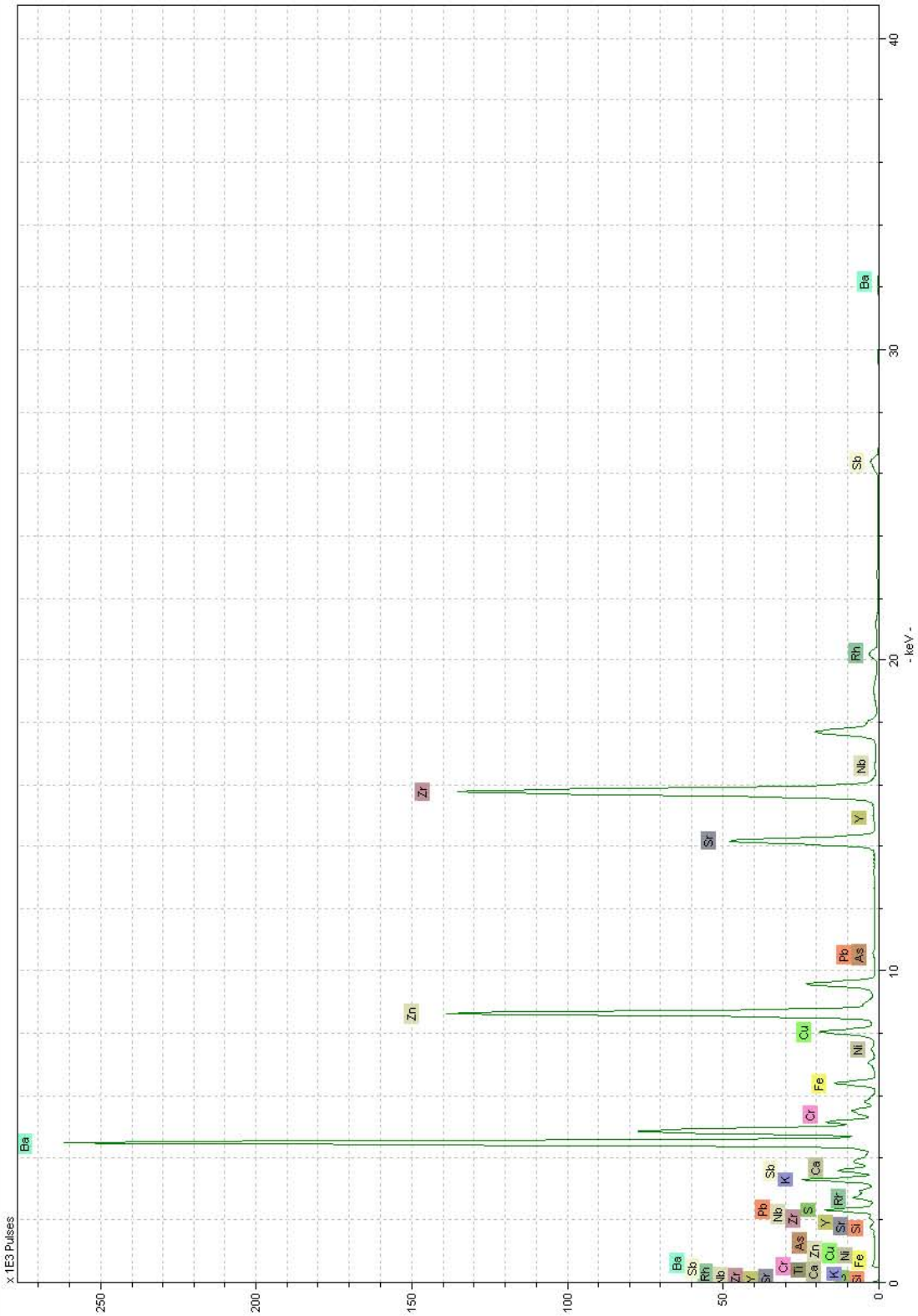
Material 4 (Solid), Scan Area 5



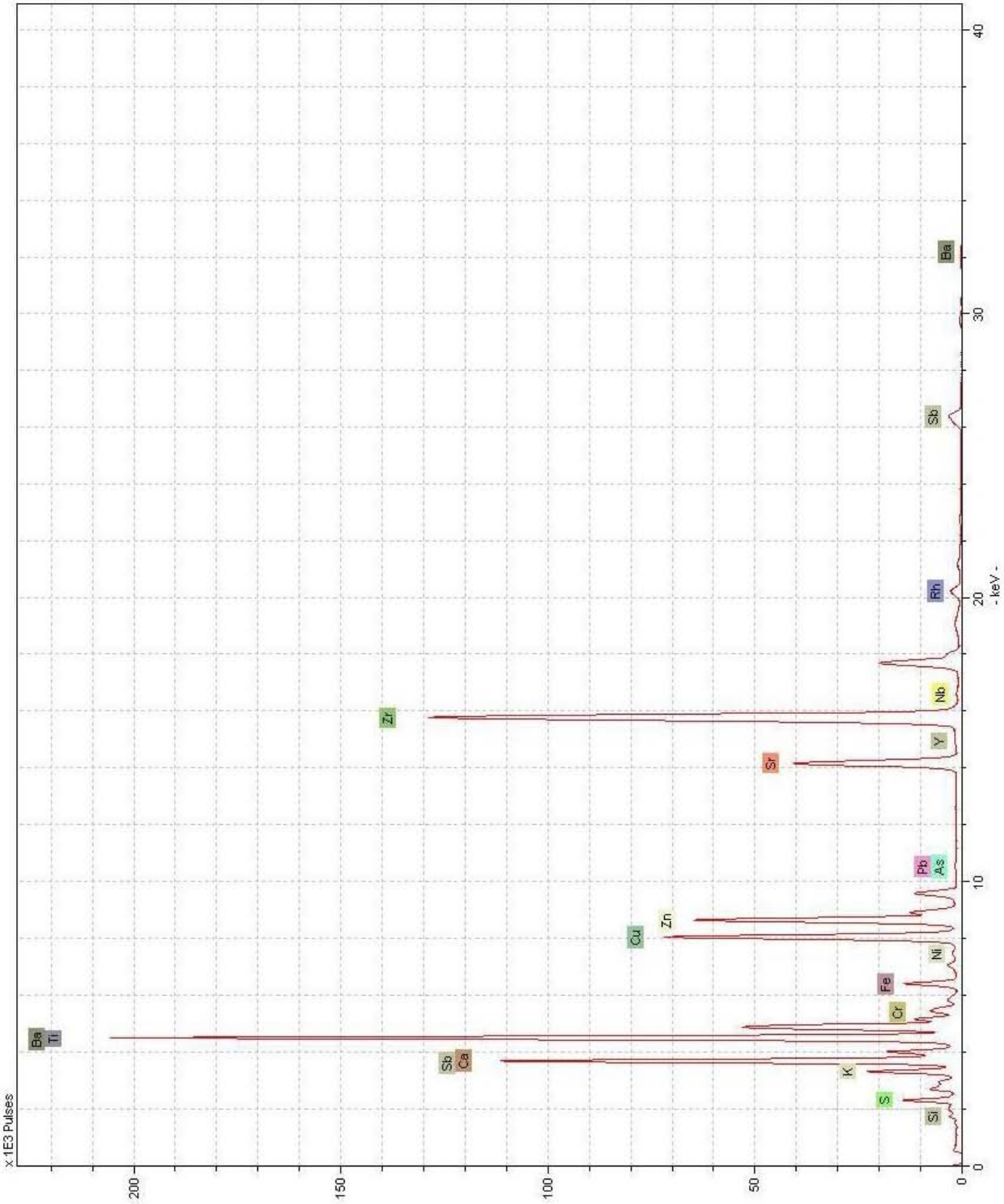
Material 4 (Powder), Bottom



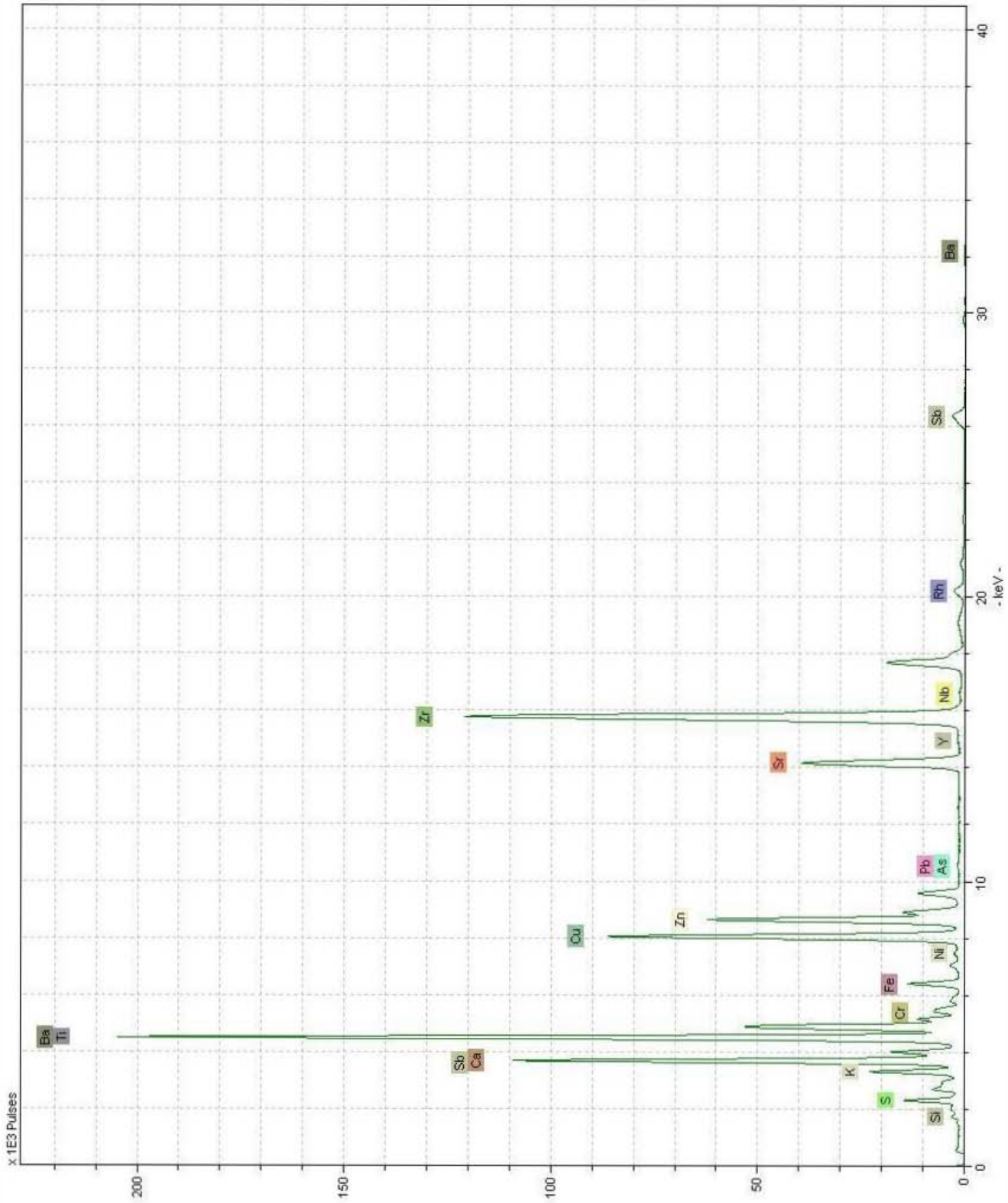
Material 4 (Powder), Top



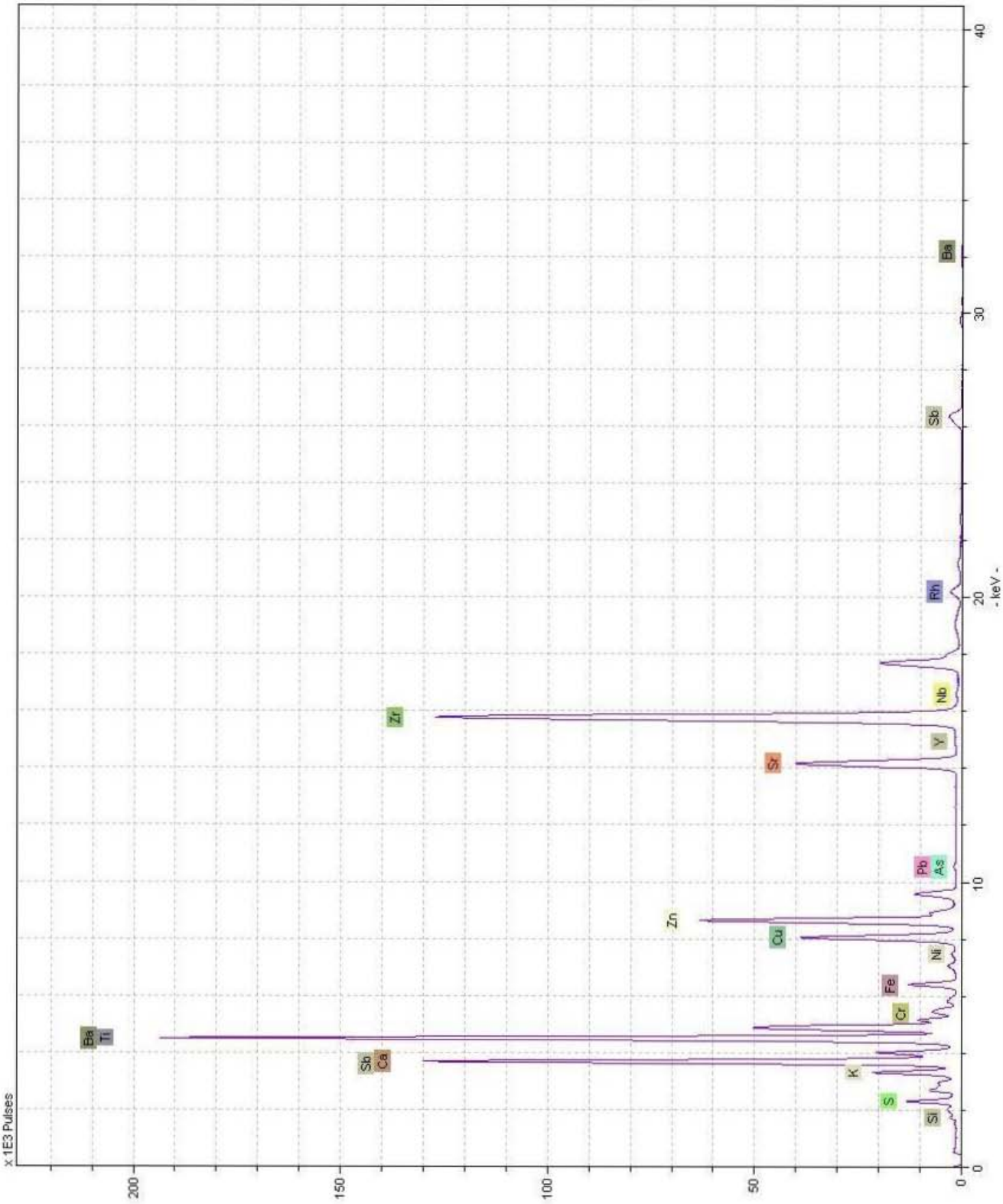
Material 5 (Solid), Scan Area 1



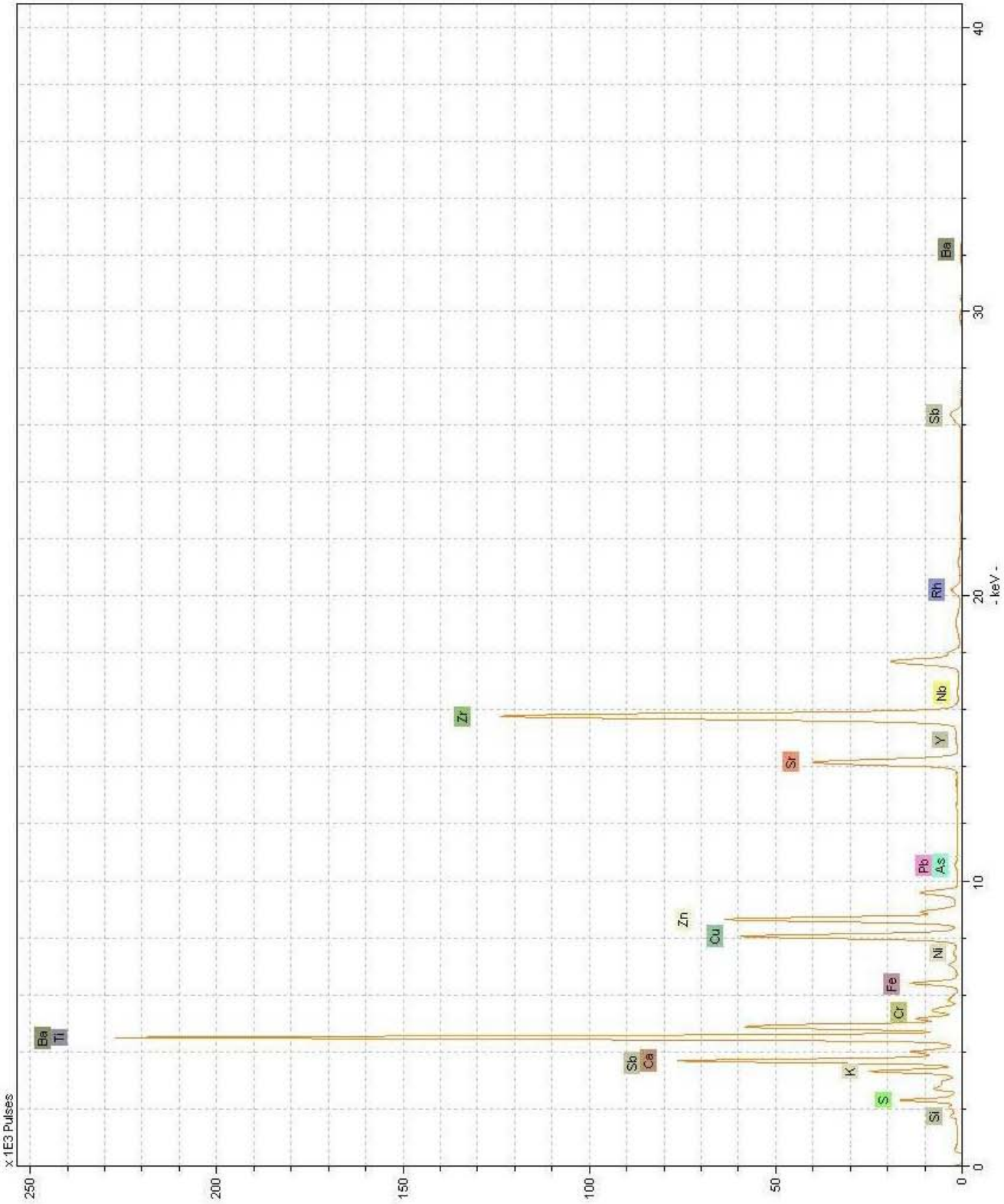
Material 5 (Solid), Scan Area 2



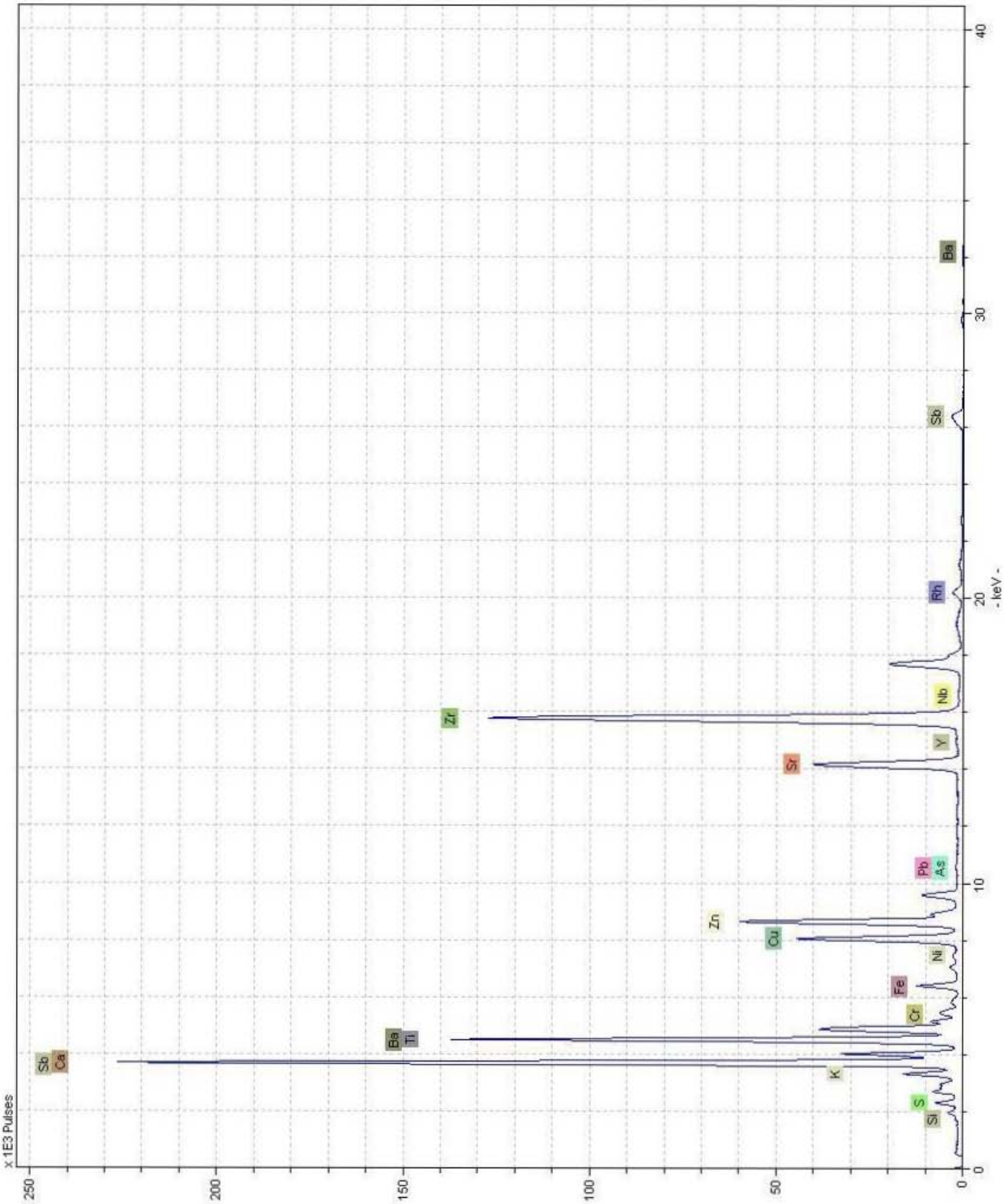
Material 5 (Solid), Scan Area 3



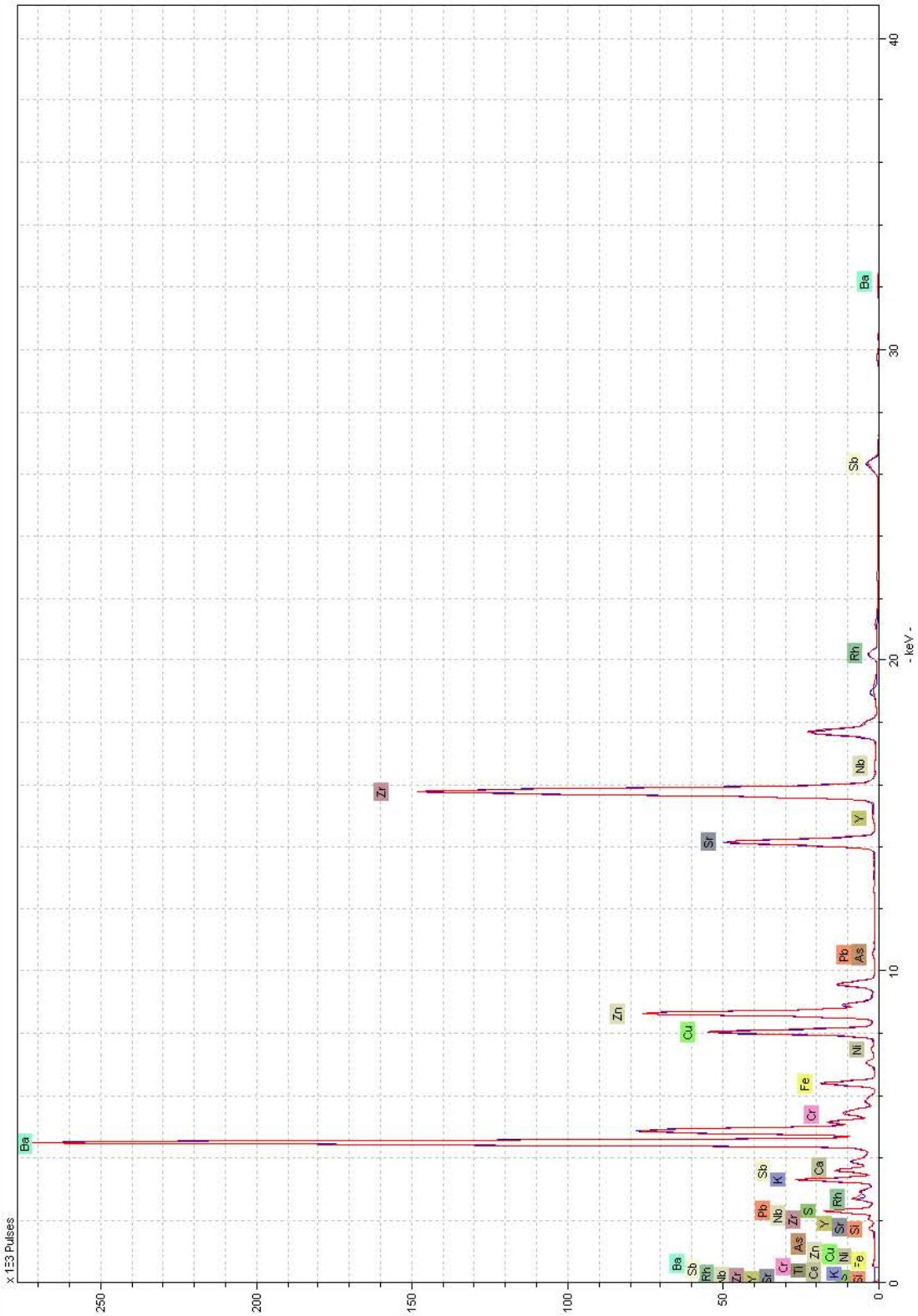
Material 5 (Solid), Scan Area 4



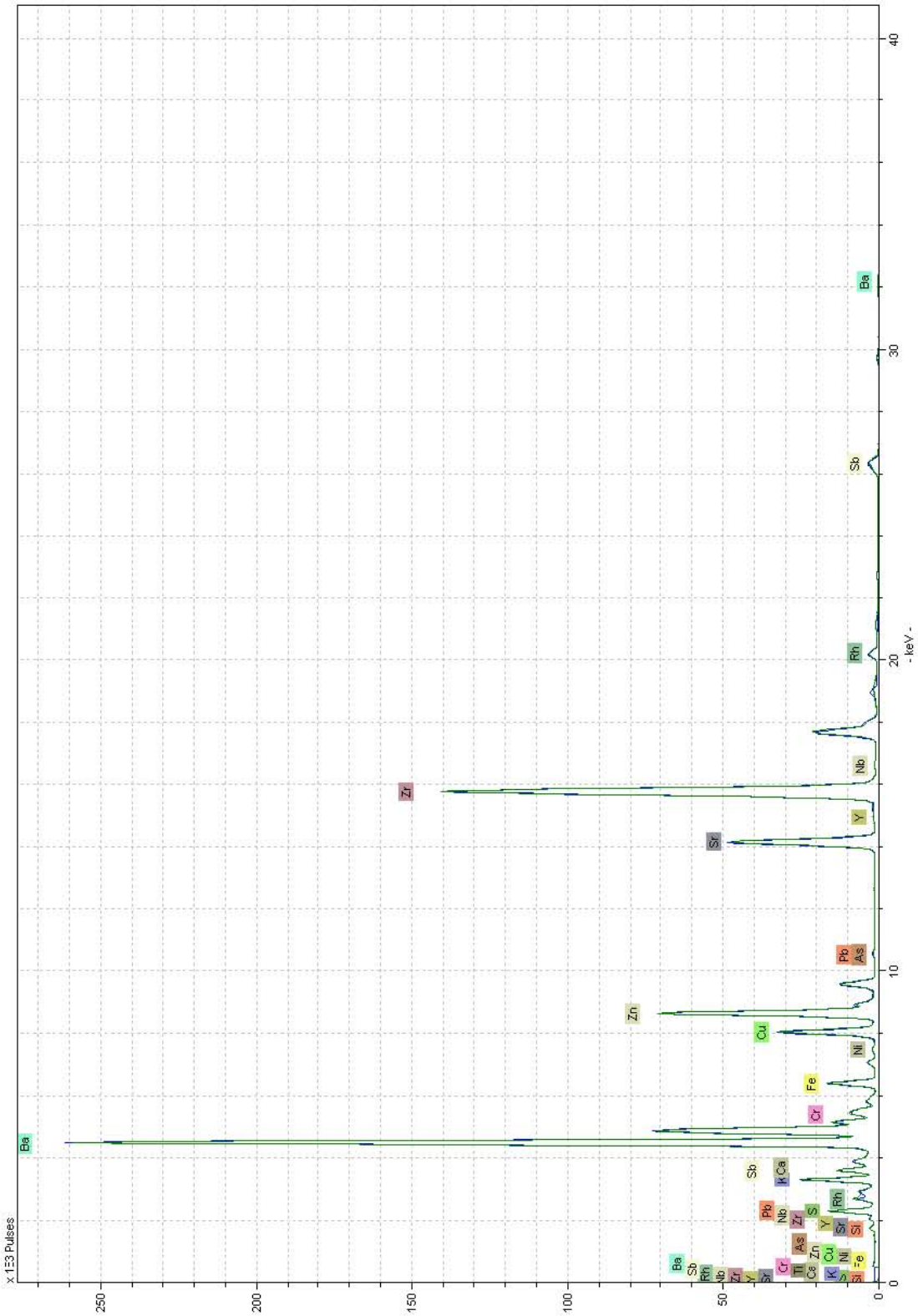
Material 5 (Solid), Scan Area 5



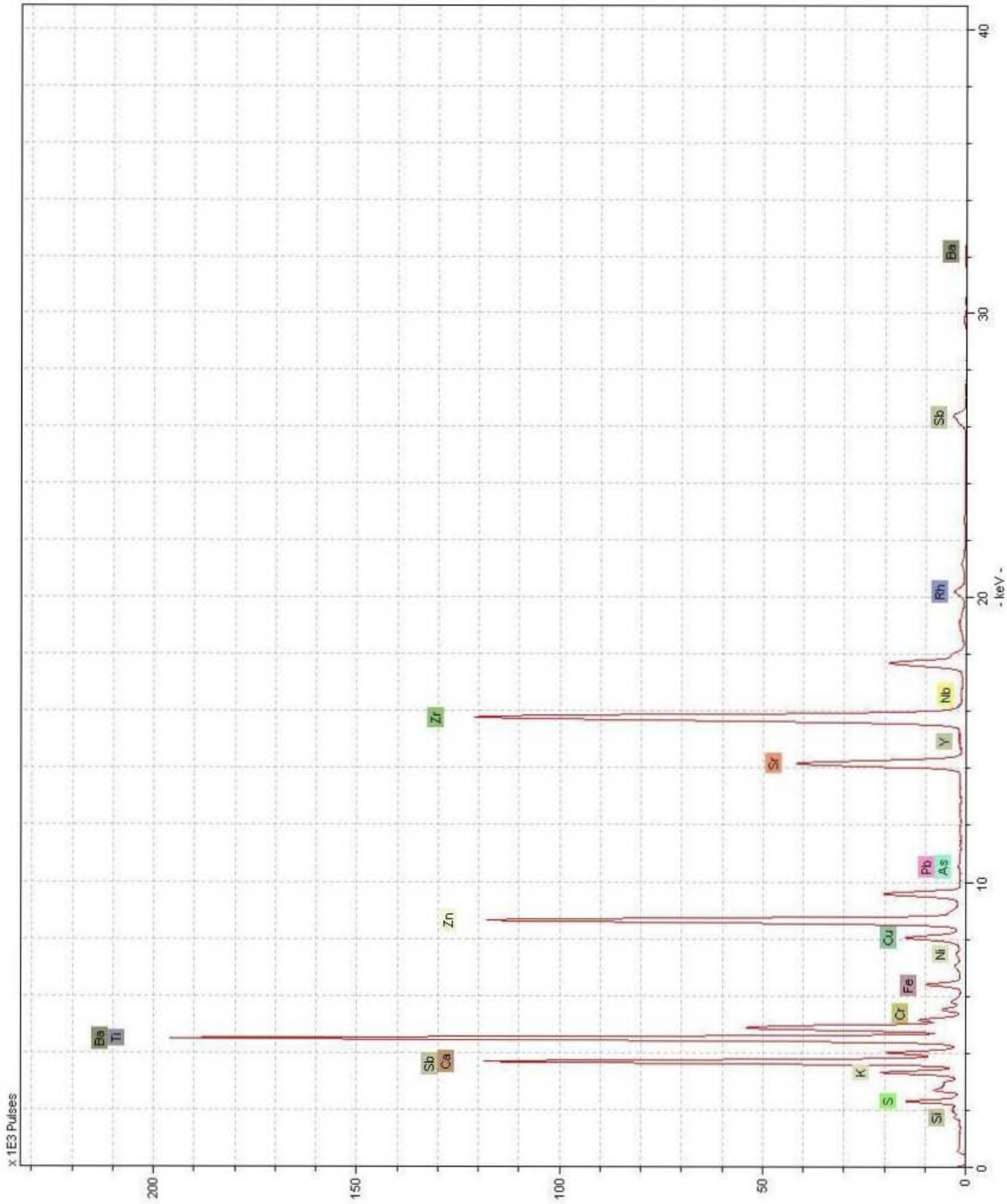
Material 5 (Powder), Bottom



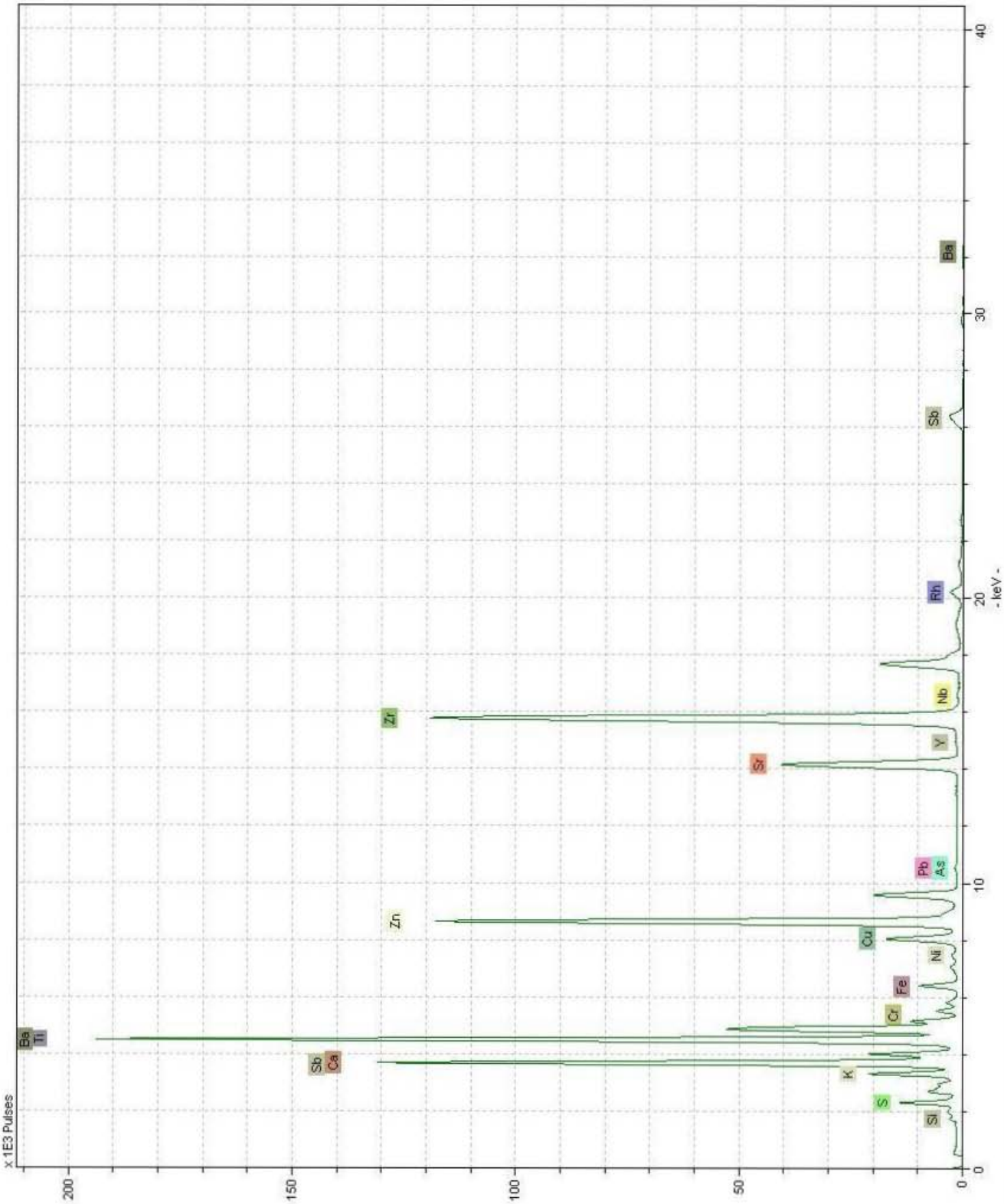
Material 5 (Powder), Top



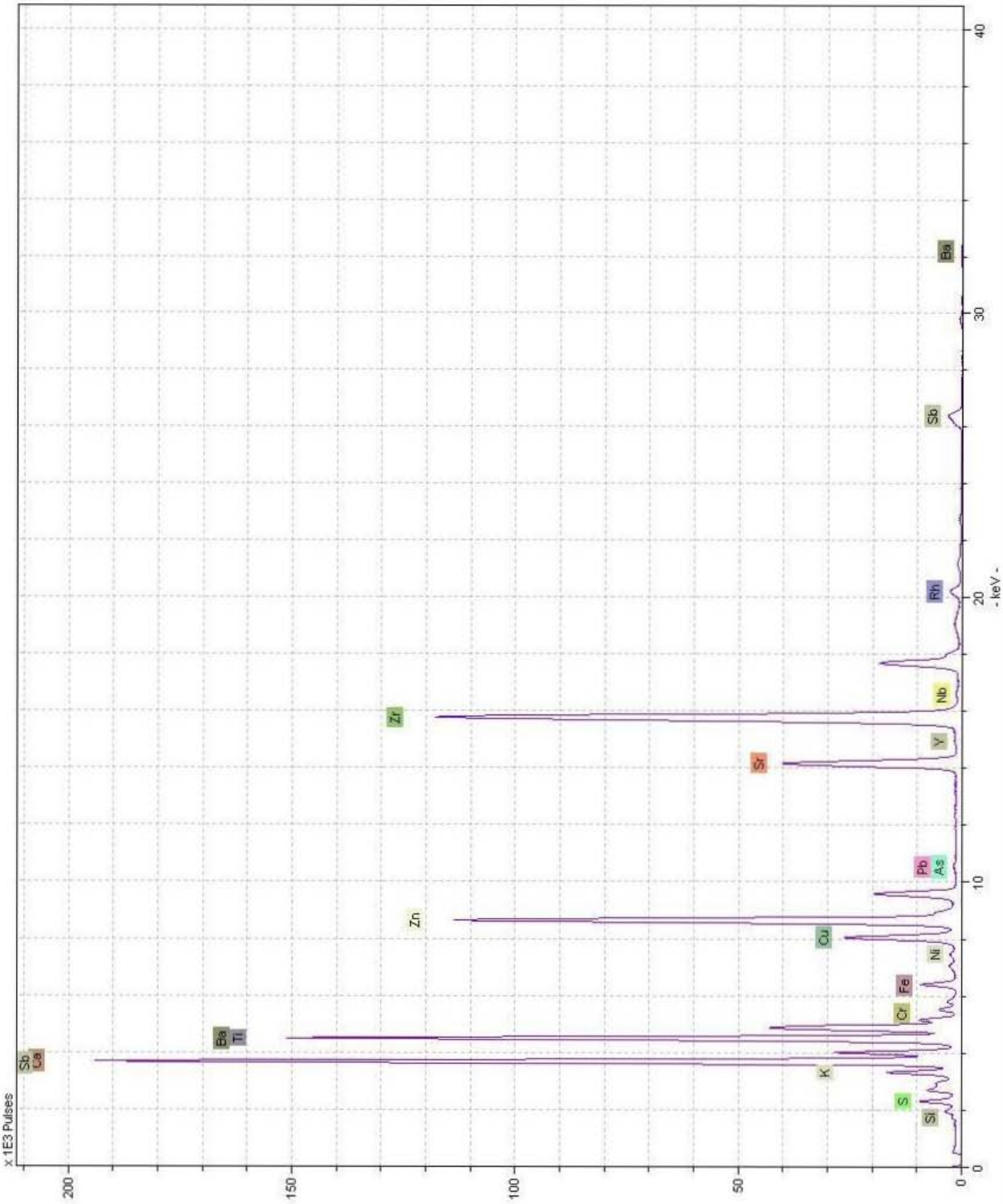
Material 6 (Solid), Scan Area 1



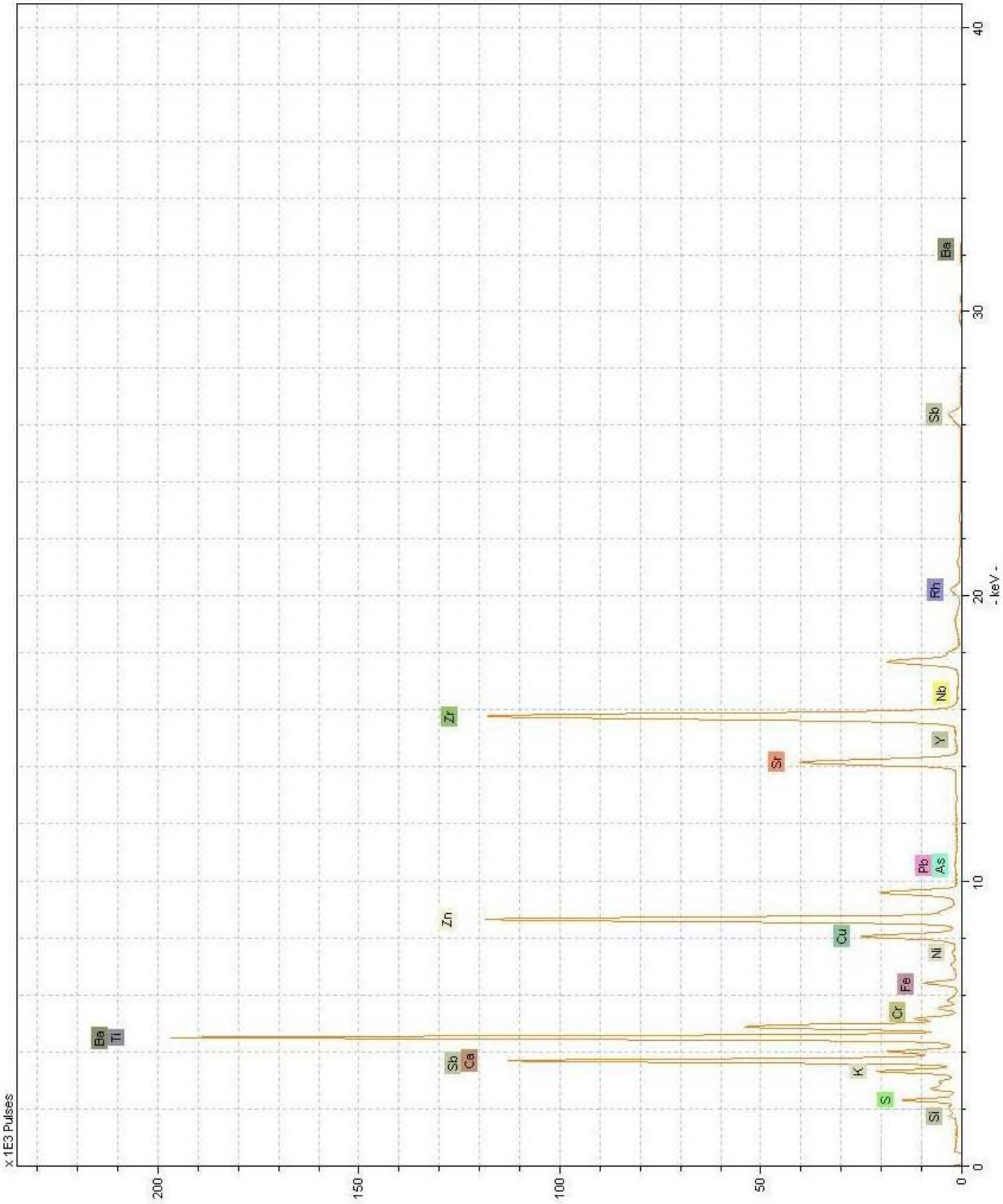
Material 6 (Solid), Scan Area 2



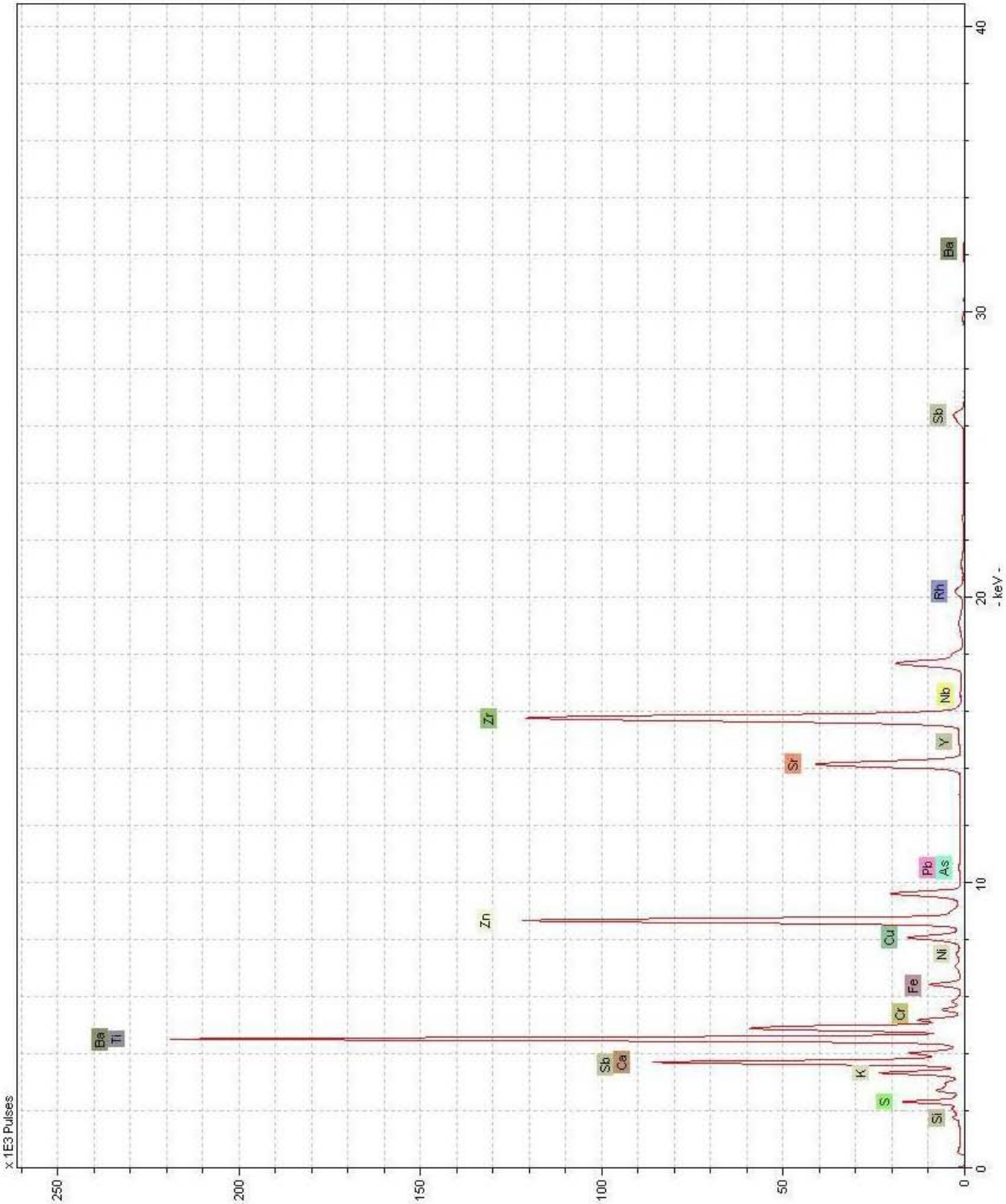
Material 6 (Solid), Scan Area 3



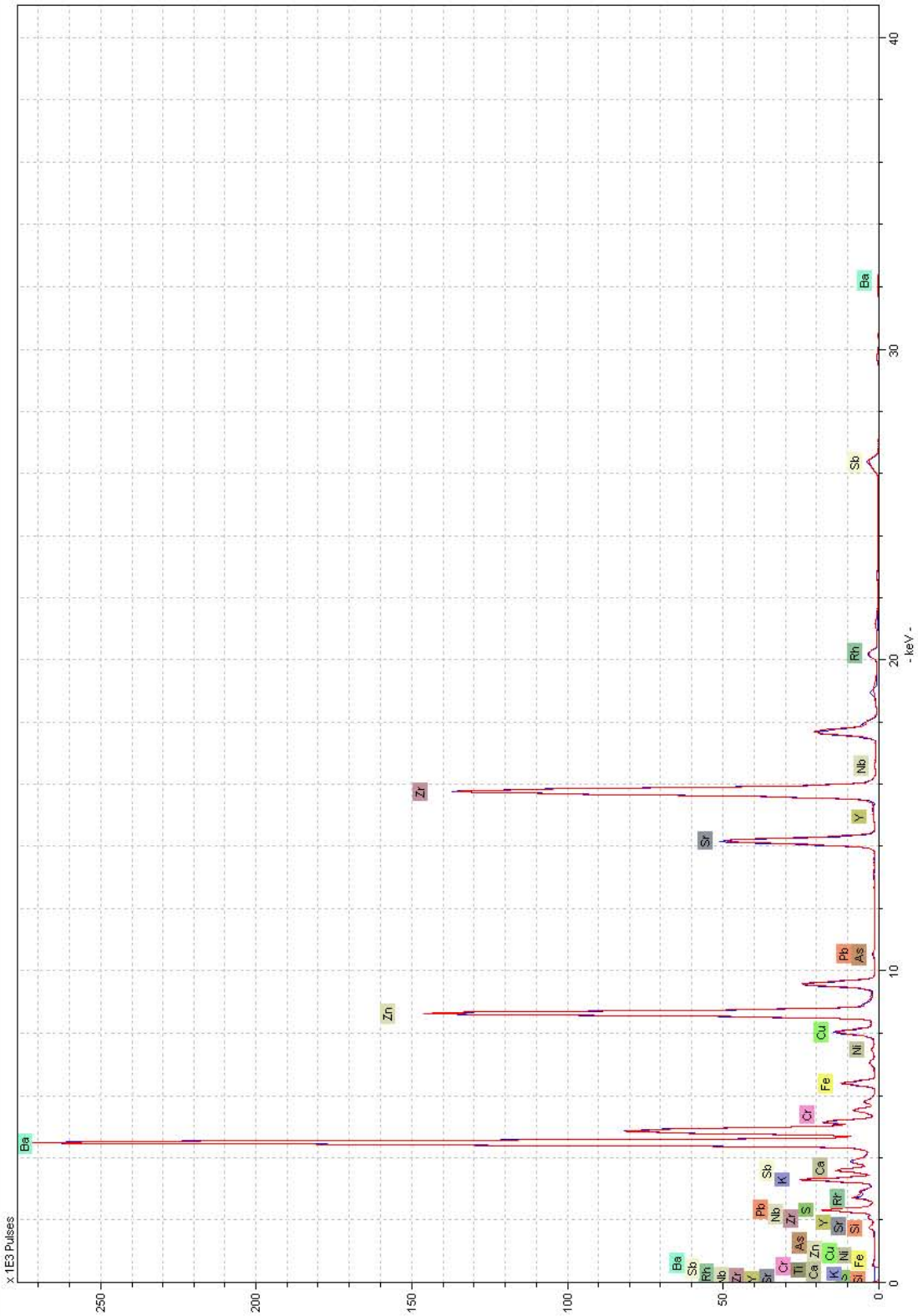
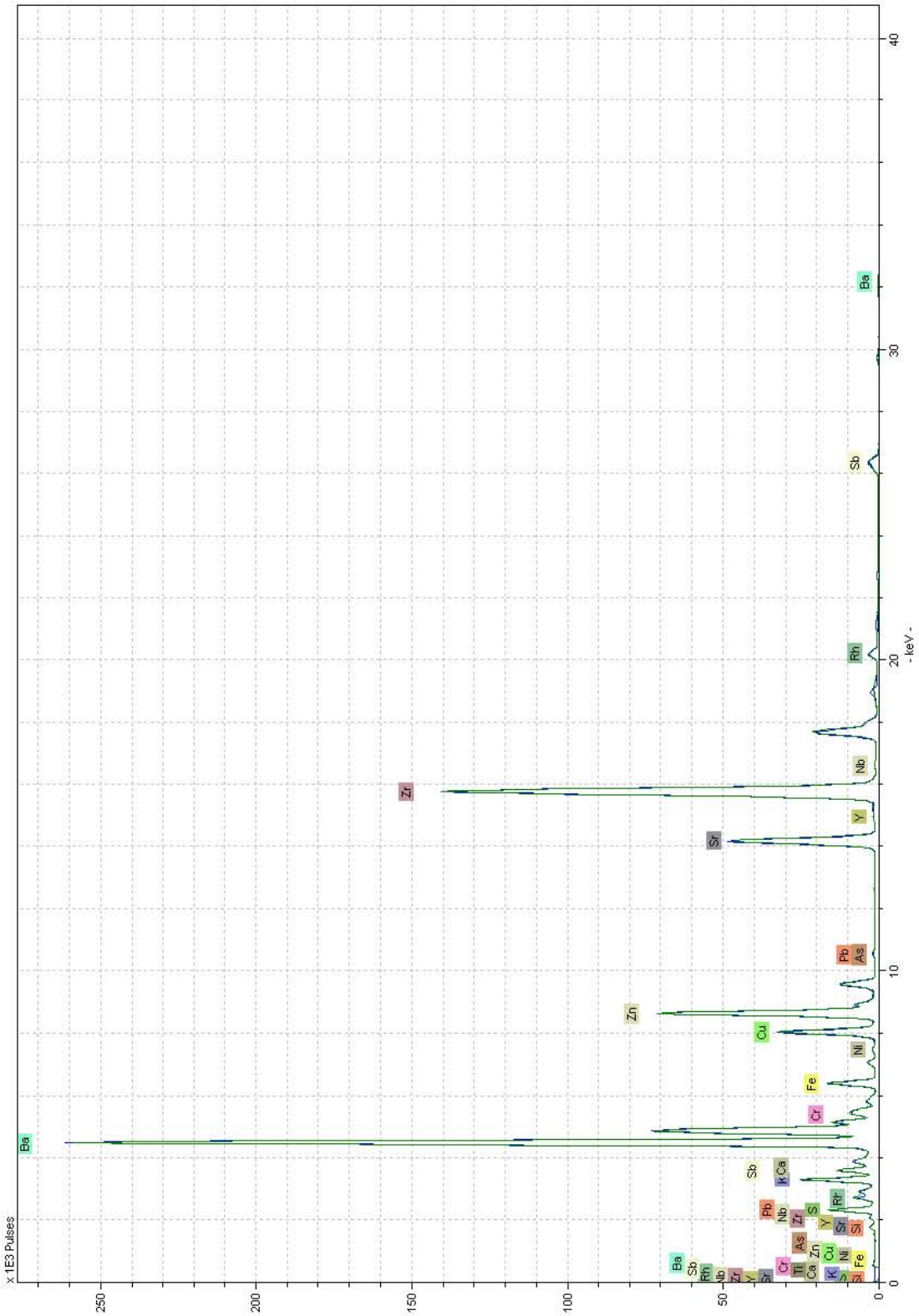
Material 6 (Solid), Scan Area 4



Material 6 (Solid), Scan Area 5



Material 6 (Powder), Bottom



Material 6 (Powder), Top