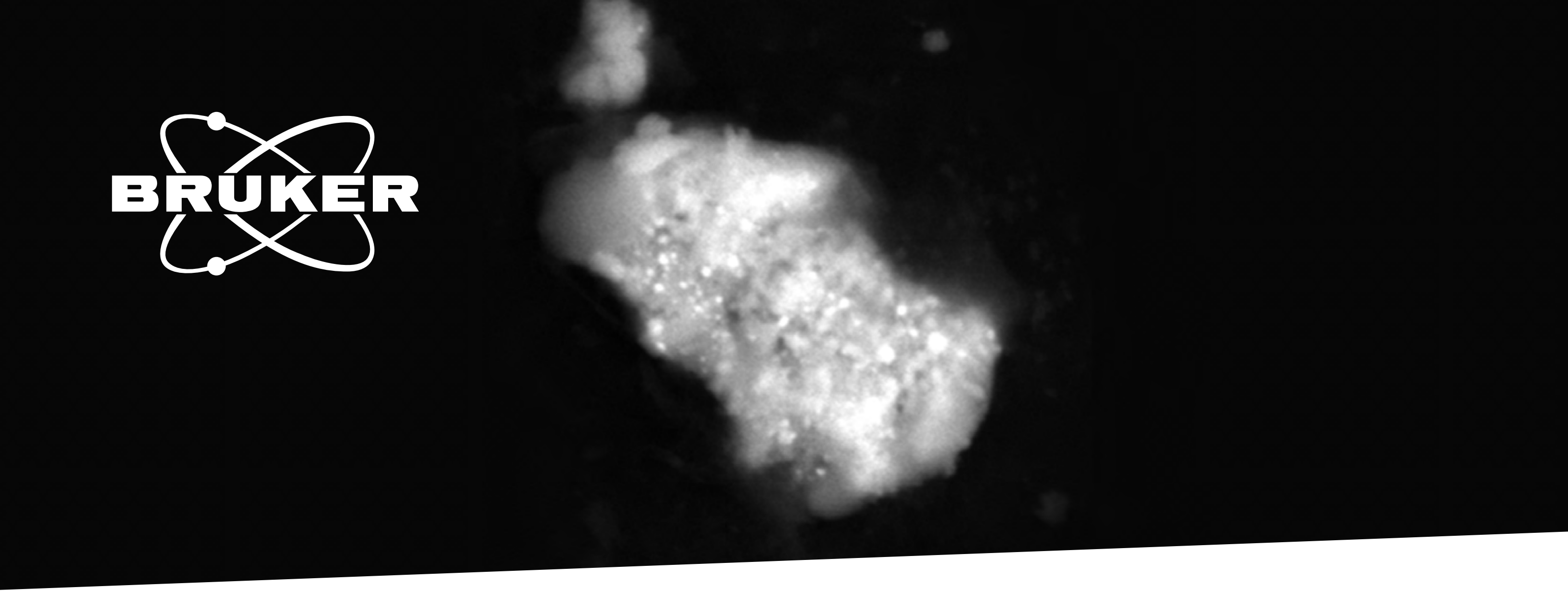

EDS

# Determining gunshot residue using 15 kV acceleration voltage with optimized spectra deconvolution and high resolution XFlash® silicon drift detectors

Application Note # EDS-08

## Introduction

Using an automated scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) to find and positively identify gunshot residue (GSR), has been an accepted method for forensic applications for quite a number of years.

The push to find smaller and smaller GSR particles has become a challenge. This is due to the calibration of the microscope and the required high speed of the analysis on the one hand. On the other hand the industry standard 25 kV acceleration voltage and the insufficient resolution requirements for EDS detectors of currently <150 eV @ Mn Kα prove to be a limitation. The high acceleration voltage due to the fact that until now EDS software relied on the lead L-lines for quantification because of the overlap of the M-lines of lead with sulphur and molybdenum. Additionally there were and still are numerous errors in the M-line positions and intensities with some software solutions.

With the optimized tools available in QUANTAX ESPRIT and the high resolution of 123 eV @ Mn Kα, which Bruker XFlash® detectors provide, this is no longer a limitation, as shows.

We will explain why GSR analyses at 25 kV are suboptimal and describe GSR determination at 15 kV as an alternative. The challenge in this approach is that the lead M-lines have to be used for quantification and one has to deal with the mentioned line overlap with sulphur and possibly molybdenum. This means that a well-functioning peak deconvolution is required for reliable results.

The reason for choosing 15 kV accelerating voltage – apart from the good excitation conditions for the M-lines – is that the interaction volumes at 15 kV are much smaller than those at 25 kV. This can be seen in the Monte Carlo plots below, which compare interaction volumes within a sample consisting of barium, lead and antimony, the typical composition of GSR particles. In fact, the less than half diameter results in an eighth of the interaction volume at 15 kV. This bears the promise that, compared to 25 kV acceleration voltage, relatively more radiation will stem from the particle itself rather than from its surroundings. The smaller the particle the more important this issue becomes, as it has a direct effect on the accuracy of quantification.

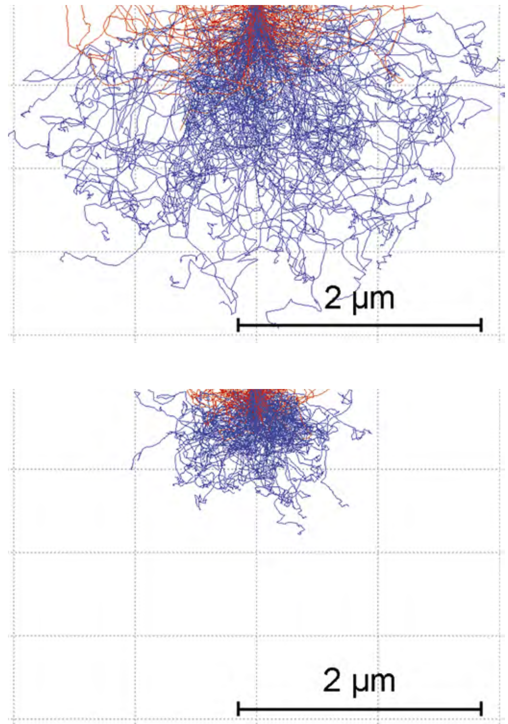


**Figure 1**
Simulated interaction volumes of electrons hitting a sample consisting of barium, lead and antimony with an energy of 25 keV (upper graph) and 15 keV (lower graph).

## Method

A comparison of deconvolution and quantification of the lead L-line at 25 kV with the M-line at 15 kV can be done using a lead containing standard such as Galena. This gives the accuracy of the method based on an absolute standard. However, to simulate real-world conditions, an actual GSR sample was measured as well.

The ESPRIT Feature module was used in conjunction with Jobs and StageControl to automatically scan an area of about 30 mm² of a GSR sample, to detect, measure and classify all potential GSR candidates. The feature detection was set to a single phase binarization of the brightest particles (between 150 and 255 grey scale) and to reject any particles smaller than 3 pixels. Chemical classification was set to acquire the spectra as shown below, and quantify automatically and classify according to common GSR particle compositions (containing Ba, Pb and Sb).

The following conditions for the unattended run were set for image resolution and not speed:

- Detector: XFlash® 5010 Premium Plus 123 eV
- Solid angle: ~ 0.006 sr
- Spectra statistics: 50,000 counts between 0.5 and 15.0 keV
- Imaging: 1024 x 768 pixel, 16 µs / pixel dwell time, overlap of 8%
- Magnification: 500 x, ~0.26 µm / pixel
- Acceleration voltage: 25 kV
- Probe current: ~ 2 nA
- Input count rate: ~ 20 kcps on Cu

Once the run had been completed, the five particles containing over 10 weight % each of barium, lead and antimony – and therefore unambiguously identified as GSR – were reanalyzed with a 1,000,000 count statistic and interactive quantification. This was then repeated for 15 kV. Finally the 5 particles were analyzed with 50,000 counts in the region between 0.5 and 15.0 keV and quantified automatically with the same method as used in the unattended analysis run.

## Results

The results for the automated analysis were ready to be reviewed after four and a half hours. 1603 particles were measured by EDS and just shy of 1000 hits were classified. The hits were divided into the following classes:

- GSR: Ba > 10 weight % and Pb > 10 weight % and Sb > 10 weight %
- GSR 1: Ba > 15 weight %
- GSR 2: Pb > 15 weight %
- GSR 3: Sb > 15 weight %

Particles the classes GSR 1 - 3 are likely to be GSR but do not fulfill the most stringent requirements regarding composition.

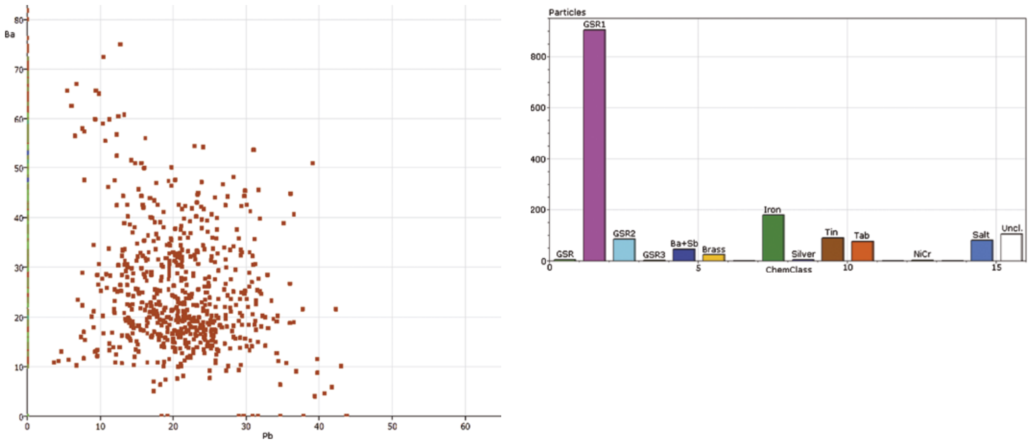


**Figure 2**
Scatter plot showing the distribution of particles according to their Ba content vs. their Pb content (left graph) and histogram showing the chemical classes and numbers of particles that were binned to them (right graph).

The number of particles binned to the particle classes were:

- GSR: 5
- GSR 1: 905
- GSR 2: 85
- GSR 3: 2

Other measured particles were classified as:

- Ba + Sb: 45
- Brass: 24
- Iron: 180
- Silver: 5
- Tin: 89
- Tab: 76
- Ni Cr: 1
- Salt: 81
- Unclassified : 105

Using the "drive to particle" function in the particle review form, each of the 5 definite GSR particles (class GSR) were revisited and reanalyzed using the Objects analysis mode provided by the ESPRIT software and performing a point analysis to confirm the hit.

In this report only two particles are described in detail, but the summary in the tables below contains results for all 5. Note that there was only a deconvolution and no quantification perfomed for carbon due to the fact that the sample is based on a carbon tab.

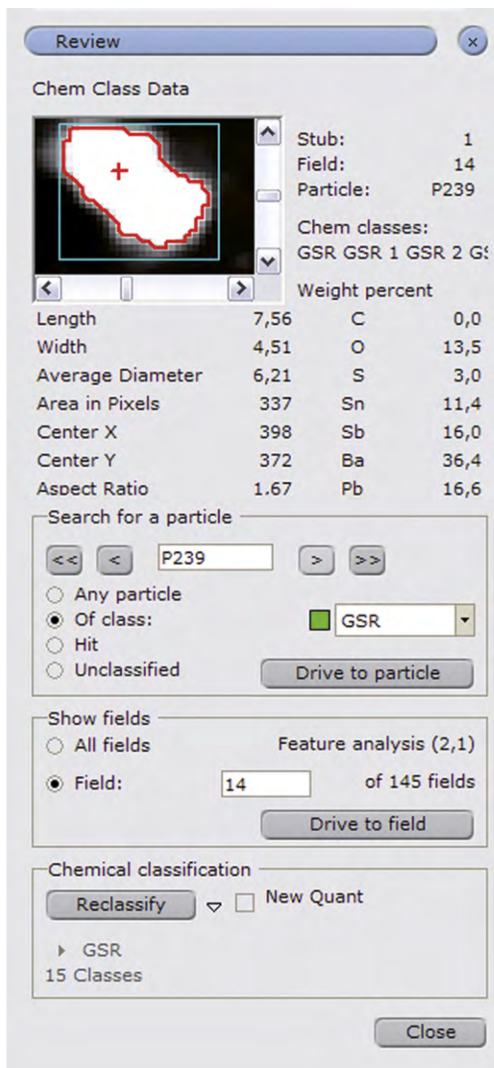


**Figure 3**
The review function provides comfortable options for measurement control, including revisiting particles for post measurement analysis.

## Particle P63

The morphological measurements of this particle show that it has a low aspect ratio (see also particle morphological properties table below), as expected from a GSR particle, and is of a typical size. It is at the spatial resolution limits of EDS at 25 kV as shown in the Monte Carlo simulation above.

Note how the summation spectrum (grey) of the deconvolution peaks (in individual colors) in the graph on the right show an extremely good match to the acquired spectrum (black line).

When comparing the results for the quantification, there are only very minor discrepancies, with lead having a slightly decreased concentration in the 15 kV quantification.

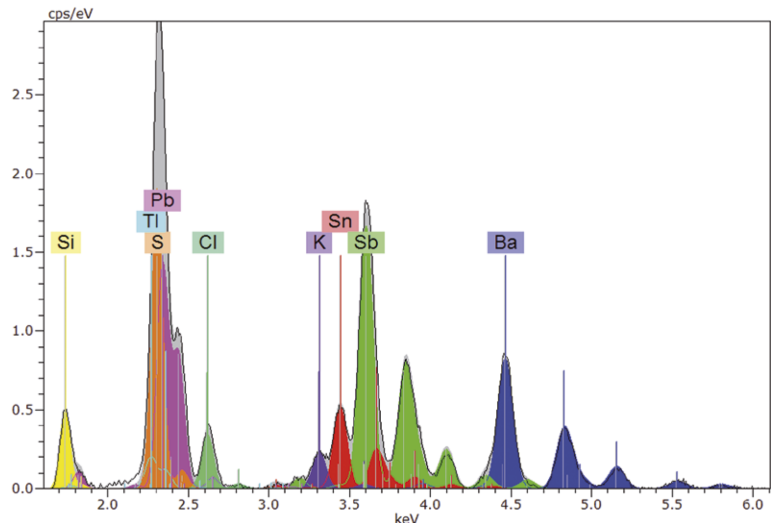


**Figure 4**
Deconvolution results for particle P63 at 15 kV

| | AN | Series | nor. C [wt.%] |
|---|---|---|---|
| Carbon | 6 | K series | 0,00 |
| Oxygen | 8 | K series | 5,96 |
| Sodium | 11 | K series | 1,97 |
| Magnesium | 12 | K series | 0,84 |
| Aluminium | 13 | K series | 0,66 |
| Silicon | 14 | K series | 0,76 |
| Sulfur | 16 | K series | 6,04 |
| Chlorine | 17 | K series | 1,30 |
| Potassium | 19 | K series | 0,74 |
| Iron | 26 | K series | 1,13 |
| Copper | 29 | K series | 1,73 |
| Tin | 50 | L series | 7,24 |
| Antimony | 51 | L series | 26,82 |
| Barium | 56 | L series | 24,13 |
| Lead | 82 | L series | 20,64 |
| | | Total | 100,00 |

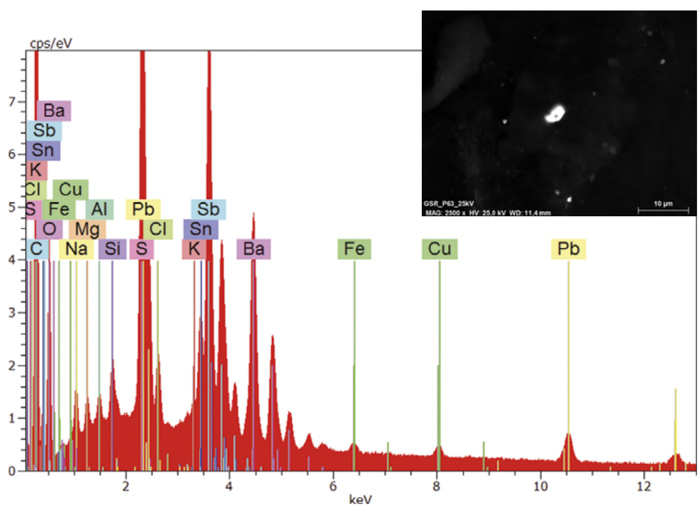


**Figure 5**
Interactive EDS analysis results of particle P63. Analysis at 25 kV, 1,000,000 count spectrum statistic

| | AN | Series | nor. C [wt.%] |
|---|---|---|---|
| Carbon | 6 | K series | 0,00 |
| Oxygen | 8 | K series | 5,36 |
| Sodium | 11 | K series | 2,37 |
| Magnesium | 12 | K series | 0,46 |
| Aluminium | 13 | K series | 1,07 |
| Silicon | 14 | K series | 1,41 |
| Sulfur | 16 | K series | 6,36 |
| Chlorine | 17 | K series | 1,46 |
| Potassium | 19 | K series | 1,40 |
| Cobalt | 27 | K series | 0,03 |
| Copper | 29 | K series | 1,06 |
| Tin | 50 | L series | 8,24 |
| Antimony | 51 | L series | 28,83 |
| Barium | 56 | L series | 24,26 |
| Thallium | 81 | M series | 2,68 |
| Lead | 82 | M series | 15,00 |
| | | Total | 100,00 |

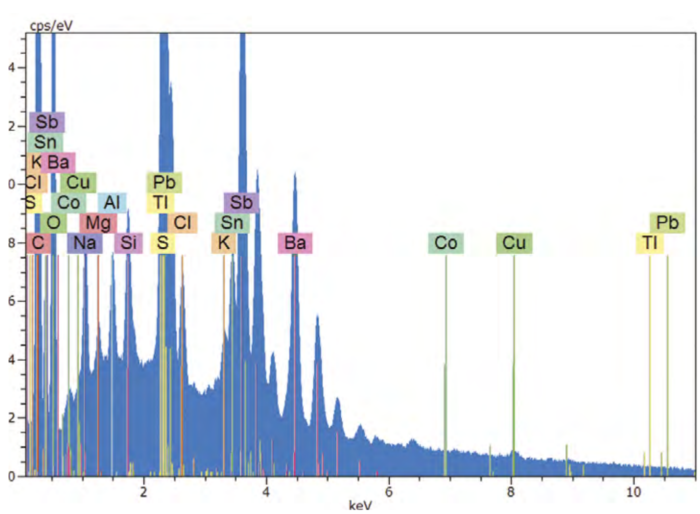


**Figure 6**
Interactive EDS analysis results of particle P63. Analysis at 15 kV, 1,000,000 count spectrum statistic

## Particle P239

The morphological measurements of this particle show that it also has a low aspect ratio (see particle morphological properties table below), as expected from a GSR particle. The spatial resolution of EDS at 25 kV is sufficient for this particle. However, as the depth or thickness (or hollowness) of the particle is not known, there could be some electron transmission at 25 kV, resulting in loss of signal of the particle.

When comparing the quantification results, there are the expected differences especially with respect to the lighter elements. The concentration of lead has increased while barium has decreased and antimony stayed about the same.

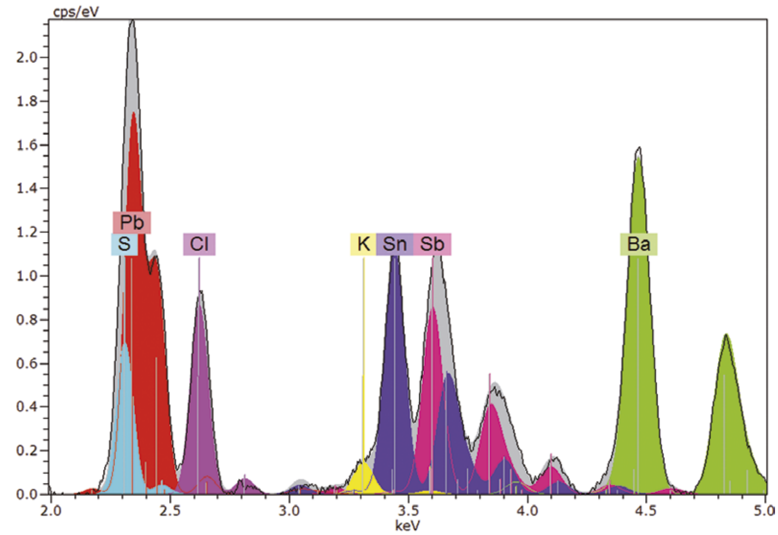


**Figure 7**
Deconvolution results for particle P239 at 15 kV

| | AN | Series | nor. C [wt.%] |
|---|---|---|---|
| Carbon | 6 | K series | 0,00 |
| Oxygen | 8 | K series | 7,40 |
| Aluminium | 13 | K series | 0,19 |
| Chlorine | 17 | K series | 0,85 |
| Iron | 26 | K series | 0,71 |
| Copper | 29 | K series | 1,79 |
| Zinc | 30 | K series | 1,28 |
| Tin | 50 | L series | 23,66 |
| Antimony | 51 | L series | 11,35 |
| Barium | 56 | L series | 44,67 |
| Lead | 82 | L series | 8,10 |
| | | **Total** | **100,00** |

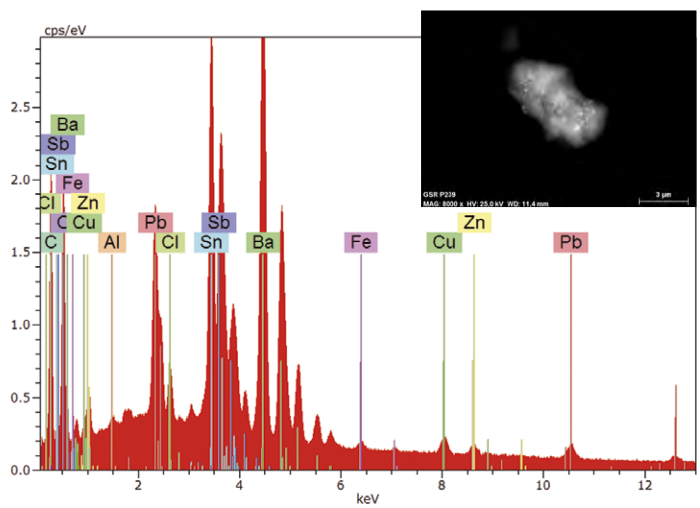


**Figure 8**
Interactive EDS analysis results of particle P239. Analysis at 25 kV, 1,000,000 count spectrum statistic

| | AN | Series | nor. C [wt.%] |
|---|---|---|---|
| Carbon | 6 | K series | 0,00 |
| Oxygen | 8 | K series | 6,65 |
| Magnesium | 12 | K series | 0,05 |
| Aluminium | 13 | K series | 0,14 |
| Silicon | 14 | K series | 0,11 |
| Phosphorus | 15 | K series | 0,17 |
| Sulfur | 16 | K series | 1,65 |
| Chlorine | 17 | K series | 3,29 |
| Potassium | 19 | K series | 0,80 |
| Iron | 26 | K series | 0,24 |
| Cobalt | 27 | K series | 0,00 |
| Copper | 29 | K series | 2,17 |
| Zinc | 30 | K series | 5,23 |
| Tin | 50 | L series | 14,91 |
| Antimony | 51 | L series | 12,18 |
| Barium | 56 | L series | 33,43 |
| Thallium | 81 | M series | 1,31 |
| Lead | 82 | M series | 17,66 |
| | | **Total** | **100,00** |

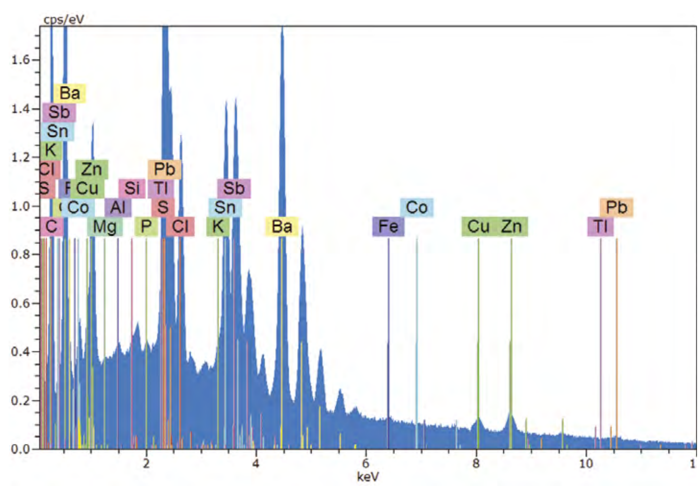


**Figure 9**
Interactive EDS analysis results of particle P239. Analysis at 15 kV, 1,000,000 count spectrum statistic

| Particle | Field | Length | Width | Aspect ratio | Area in pixels | Center X | Center Y |
|---|---|---|---|---|---|---|---|
| P63 | 6 | 4.42 | 2.44 | 1.81 | 104.00 | 301.01 | 589.95 |
| P239 | 13 | 7.56 | 4.51 | 1.67 | 337.00 | 397.72 | 372.40 |
| P604 | 58 | 1.50 | 1.06 | 1.41 | 13.00 | 95.62 | 285.54 |
| P750 | 71 | 3.46 | 1.70 | 2.03 | 54.00 | 242.15 | 651.11 |
| P918 | 91 | 2.14 | 1.60 | 1.34 | 35.00 | 762.89 | 4.09 |

**Table 1**
Particle morphological properties

| Spectrum | O | Na | S | Cl | Fe | Cu | Sn | Sb | Ba | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| P63 | 10.59 | 4.24 | 6.04 | 4.96 | – | – | 7.80 | 23.27 | 18.93 | 24.17 |
| P239 | 13.46 | – | 3.04 | – | – | 3.08 | 11.35 | 16.02 | 36.40 | 16.66 |
| P604 | 22.94 | – | 7.02 | – | – | – | – | 25.72 | 18.72 | 25.60 |
| P750 | 20.19 | – | 6.61 | – | – | – | 5.20 | 22.70 | 17.13 | 28.18 |
| P918 | 26.40 | – | 11.46 | 4.65 | 2.24 | – | – | 24.41 | 11.52 | 19.52 |
| Mean value: | 23.25 | 4.24 | 6.83 | 4.53 | 2.24 | 3.08 | 8.11 | 22.38 | 21.23 | 22.82 |
| Sigma: | 12.57 | 0.00 | 3.02 | 0.50 | 0.00 | 0.00 | 3.09 | 3.74 | 8.54 | 4.17 |
| Sigma mean: | 5.13 | 0.00 | 1.23 | 0.21 | 0.00 | 0.00 | 1.26 | 1.53 | 3.49 | 1.70 |

**Table 2**
Composition of GSR particles [mass %] (automatic quantification of 25 kV spectra)

| Spectrum | O | Na | Si | S | Cl | Sn | Sb | Ba | Pb |
|---|---|---|---|---|---|---|---|---|---|
| P63 | 5.19 | 3.33 | 1.33 | 8.38 | 2.27 | 7.52 | 26.75 | 22.75 | 22.48 |
| P239 | 6.53 | 2.04 | – | – | – | 21.45 | 9.47 | 42.97 | 17.55 |
| P604 | 5.05 | – | – | 11.98 | – | 7.80 | 33.81 | 23.86 | 17.50 |
| P750 | 2.71 | – | – | 14.06 | – | 7.38 | 29.90 | 14.67 | 31.28 |
| P918 | 2.64 | – | – | 11.90 | 2.38 | 7.39 | 38.72 | 18.12 | 18.85 |
| Mean value: | 4.42 | 2.68 | 1.33 | 11.58 | 2.33 | 10.31 | 27.73 | 24.47 | 21.53 |
| Sigma: | 1.70 | 0.91 | 0.00 | 2.36 | 0.08 | 6.23 | 11.15 | 10.97 | 5.82 |
| Sigma mean: | 0.76 | 0.41 | 0.00 | 1.05 | 0.04 | 2.79 | 4.98 | 4.91 | 2.60 |

**Table 3**
Composition of GSR particles [mass %] (automatic quantification of 15 kV spectra)

## Comparison of GSR Particles at 15 and 25 kV

Note the similarity of the result for each particle for lead, barium and antimony. There are some deviations between particles, especially between the smaller ones due to the signal loss and the larger ones, as they are likely to be hollow, skewing the result a little.

However, it is also quite clear that the mean values of these particles vary only a few percent for lead, antimony and barium when comparing 15 and 25 kV. Individual results vary a little more, but these are strongly dependant on the 3 dimensional structure of the particle as well as on its homogeneity. This is because particles smaller than 2 µm in any dimension or ones that are hollow, will display a stronger variation due to the amount of material interacting with the electrons and thus producing X-ray photon emission.

One thing that can be concluded is that an acceleration voltage of 15 kV will excite a much smaller volume of a GSR particle, giving a higher level of confidence that the spectra are produced entirely from within the particles. Hence to absolutely compare the quantitative results obtained at 15 and 25 kV, free from influences of geometry and size, bulk Galena and Crocoite standards were analyzed.

## Comparison Galena and Crocoite standards

| S | Pb | Sum |
|---|---|---|
| 13.40 % | 86.60 % | 100.00 % |

**Table 4**
Certified composition of Galena (PbS) ASTIMEX standard.

| O | Cr | Pb | Sum |
|---|---|---|---|
| 19.80 % | 16.09 % | 64.11 % | 100.00 % |

**Table 5**
Certified composition of Crocoite ($PbCrO_4$) ASTIMEX standard.

Acquiring both low and high count EDS spectra on the Galena and the Crocoite standard first at 25 kV followed by 15 kV, the standardless PB-ZAF quantification results are then compared to each other by count statistics and afterwards to the certified results.

Using Bruker's new Opti-Series-Fit Deconvolution and considering carbon for deconvolution only (due to the samples being carbon-coated), the results of the automatic quantification are as follows:

| Spectrum | S | Pb |
|---|---|---|
| 15 kV, 1,000,000 counts | 13.60 | 86.40 |
| 15 kV, 50,000 counts | 13.53 | 86.47 |
| 25 kV, 1,000,000 counts | 12.23 | 87.77 |
| 25 kV, 50,000 counts | 13.42 | 86.58 |

**Table 6**
Results of Galena analysis [mass %]

| Spectrum | O | Cr | Pb |
|---|---|---|---|
| 15 kV, 1,000,000 counts | 21.04 | 17.67 | 61.29 |
| 15 kV, 50,000 counts | 20.95 | 17.54 | 61.51 |
| 25 kV, 1,000,000 counts | 20.64 | 17.16 | 62.20 |
| 25 kV, 50,000 counts | 20.35 | 16.79 | 62.86 |

**Table 7**
Results of Crocoite analysis [mass %]

As can be seen, the results obtained on the bulk standards at 15 and 25 kV are quite similar. All together the deviation from certified values are negligible. In fact the quantification results of the 15 kV excitation are so close, that it is reasonable to suggest that the 15 kV quantification based on the lead M-lines is reliable, even overlaps with sulphur occur.

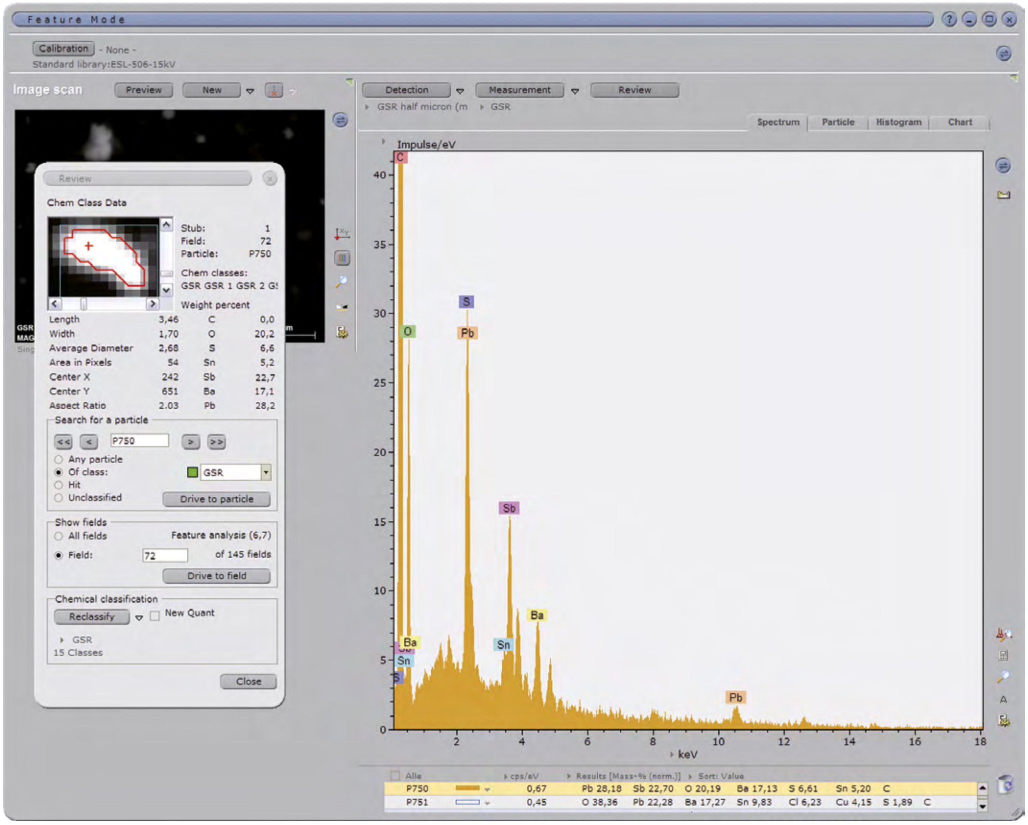


**Figure 10**
Particle review function in detail. In this case the spectra tab is selected which provides access to all particle spectra. Quantification results can be reviewed here and if required a particle can be reclassified including requantification.

## Conclusion

It has been demonstrated that due to the spatial resolution of EDS, it would be favorable to use 15 kV acceleration voltage instead of 25 kV for GSR analysis. It has also been shown that the results of low count spectra of real GSR particles yield similar results when using 15 kV compared to 25 kV. High count spectra also show comparable results for these particles. However, the differences in 25 kV and 15 kV can be attributed to the structure of the particles, such as flat, hollow or small particles affecting results. Furthermore, the inhomogeneous nature of GSR particles adds to the complexity of result interpretation. The much larger excitation volume when analyzing with 25 kV can skew results of these particles even further.

Also, it has been shown, that when using a bulk sample or standard with a known concentration, the new Opti-Series-Fit Deconvolution and the standardless PB-ZAF quantification in conjunction with a high resolution XFlash® detector, can in fact produce very reliable results at 15 kV, matching the certified values.

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