

EDS on Phenom desktop SEMs

The fastest and most reliable EDS workflow for desktop SEM systems

Introduction

Analytical information with SEM-EDS

Energy dispersive X-ray spectroscopy (EDS) is the analysis of X-rays that are emitted by the atoms of the sample under excitement of the incoming electron beam of the electron microscope. EDS is a commonly used technique in electron microscopy because it is a fast, accurate, and non-destructive technique that provides local information of a microvolume. This makes EDS highly attractive for many research fields such as metallurgy, surface analysis, and mineralogy. Thermo Scientific™ Phenom™ desktop SEMs provide a fully integrated and automated solution for EDS analysis on a wide variety of samples. EDS on Phenom desktop SEMs is the most reliable analytical solution for all kinds of users who want results fast without compromising on quality.

What are SEM signals? Where do they come from?

When the electron beam hits the specimen, an increasing number of interactions take place as the electrons penetrate further into the sample material. In an SEM, the three most important signals come from backscattered electrons, secondary electrons, and X-rays, as schematically shown in Figure 1. There is no sharp distinction between the depths from which certain signals can be detected; it is a matter of probabilities. Low-energy signals that are generated deeper in the sample have a lower probability to reach the surface than high-energy signals. In short, lower-energy signals are more susceptible to absorption in the sample, and higher-energy signals tend to scatter more.

Secondary electrons are relatively low-energy electrons (usually <50 eV) that are generated throughout the sample, but typically detected from the surface of the sample, hence providing topological information. Backscattered electrons originate from the incoming electron beam and escape from the sample via scattering. This scattering process depends highly on the elements the electrons encounter on their paths leaving the sample. This means that, from the backscattered electron signal, compositional information can be deduced. Backscattered electrons can have energies of an order of magnitude higher than secondary electrons and provide information from deeper within the sample.

X-rays are generated in a relatively large volume within the specimen and undergo many interactions as they escape the sample. The energy of these emitted X-rays is not higher than the primary beam energy. Understanding these interactions is crucial for the quantitative interpretation of X-ray spectra. We will elaborate on the most important factors and how the Phenom software models them to achieve accurate and consistent quantitative results.

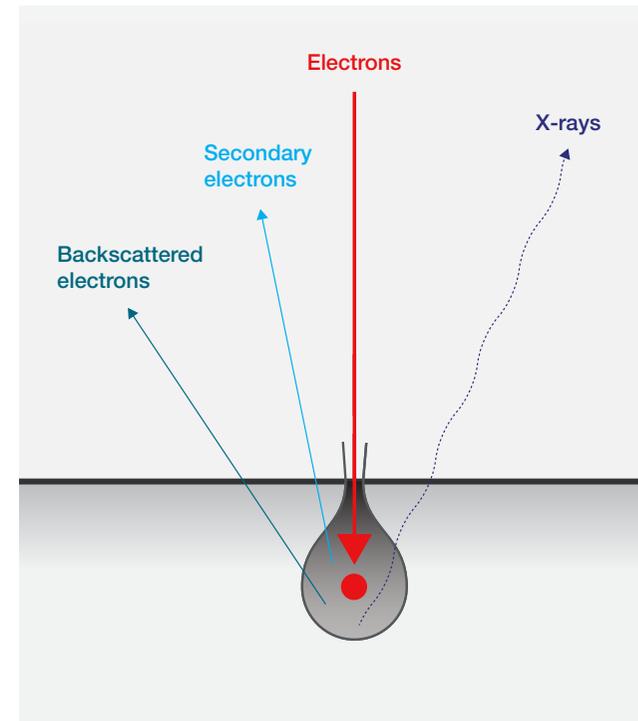


Figure 1: The typical interaction volume of an incoming electron beam is between one and a few hundred cubic micrometers in size. This depends predominantly on the acceleration voltage of the incoming beam. Multiple signals at different depths can be detected; closest to the surface, mostly secondary electrons are generated, while deeper in the sample, mostly X-rays are generated.

X-ray signals

From X-rays to spectrum

The Bohr model is very useful for understanding how X-rays are generated from an incoming electron. The model describes that electrons are present in shells that differ in energy. The shells are labeled alphabetically from K onwards, where the K-shell is the shell closest to the atom's nucleus. The K-shell is the lowest in energy, followed by the L and M shells, and so forth. In general, the first three shells are the most relevant for X-ray analysis on an SEM. The incoming electron beam excites an electron from a lower energy shell towards a higher one. Upon returning to its original, lower energy state shell, the electron emits an X-ray. The energy levels are unique, meaning that the energies of the X-rays are characteristic per atom.

There are several discrete energy gaps between shells, and, except for the K-shell, each shell has more than one energy level. The corresponding energy transitions are named via a two-letter combination. The first letter denotes the shell to which the electron falls back, and the subsequent Greek letter denotes the lines in order of importance (brightness in the spectrum). So, K_{α} and K_{β} lines represent a relaxation to the K shell from the L and the M shell, respectively. The energy of the corresponding (X-ray) photon is the difference between the energy levels, which is schematically shown in Figure 1.

Relaxation to the ground state can happen via one or more intermediate states. Suppose an electron from the K-shell is given enough energy to relocate into the M-shell. Then, relaxation could happen directly via a transition

from this M-shell back to the K-shell. Another possibility is that an electron from the intermediate L-shell could fill the K-shell vacancy, and, subsequently, an electron from the M-shell fills the vacancy the L-shell just created. All these relaxation events result in emission of a photon with energy dependent on the transition; the energy of the photon(s) is equal to the difference in energy levels between the original K-subshell and the M-subshell.

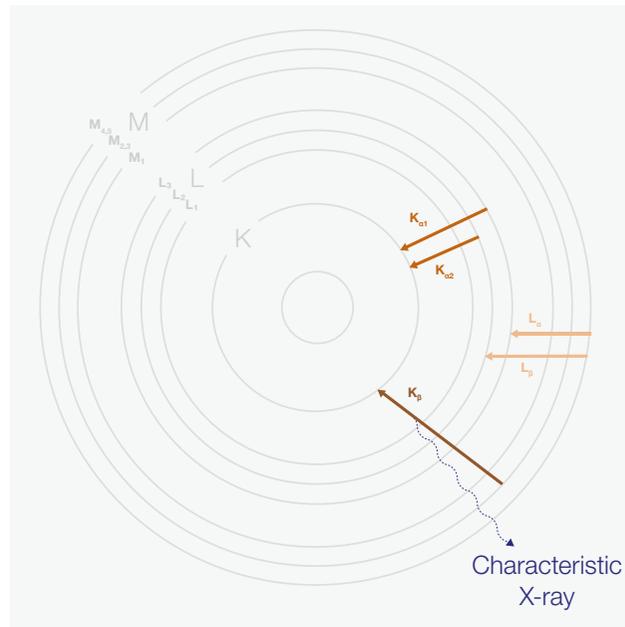


Figure 2: Schematic representation of the energy fallback of electrons after excitement under the electron beam. Note that the scaling in the imaging is arbitrary.

Detecting X-rays

Silicon drift detectors (SDDs) are widely used for detecting X-rays in the SEM due to their improved performance. X-rays hitting the detector window are converted into small electrical currents that are amplified and then measured by the digital pulse processor. SDDs achieve higher performance than older lithium-drifted silicon, or Si(Li), detectors, including higher throughput, better resolution, and improved light element performance. For the accuracy of EDS analysis, it is very important to correct for artifacts arising from the detection process (see Expert Section below). Phenom desktop SEMs have simultaneous control over both the electron beam and the EDS detection electronics, all integrated in a single user interface. This leads to optimized signal analysis and an improved user experience.

The Phenom approach

From data to information

Phenom desktop SEM-EDS analysis is a fully automated workflow that uses a forward modeling approach. This means that a synthetic spectrum is mapped onto the original spectrum to identify and quantify the elements. The process is iterative and convergent; multiple synthetic spectra are created to find the closest possible match with the original spectrum as outlined in Figure 3.

Background correction

An EDS spectrum contains signal originating from electrons that lose energy inside the specimen. The contribution from this background signal must be eliminated so that accurate qualitative and quantitative analyses can be performed. This background signal is emitted over the entire spectrum range, up to the primary beam energy.

However, the intensity of the background signal is not uniform because electrons penetrating the sample decrease energy gradually, emitting a continuum of X-rays along their path.

The shape of this background signal is modeled based on the primary beam energy, sample composition, and detection process.

The Phenom algorithm takes all these factors into account so that the background correction can be modeled with the highest accuracy.

Element identification

Elemental identification from the acquired spectrum is fully automated in Phenom desktop SEMs. For elemental identification, peak positions are checked against a known database of spectral lines. This approach is used by most analytical vendors. The Phenom algorithm uses a [library](#) that encompasses many published and peer-reviewed databases of atomic spectral information.

The use of a data library is a convenient method; however, it is not always possible to assign a single element to a peak at a given position. Several X-ray peaks differ by only a few tens of eV, which is less than the resolution of the EDS detector.

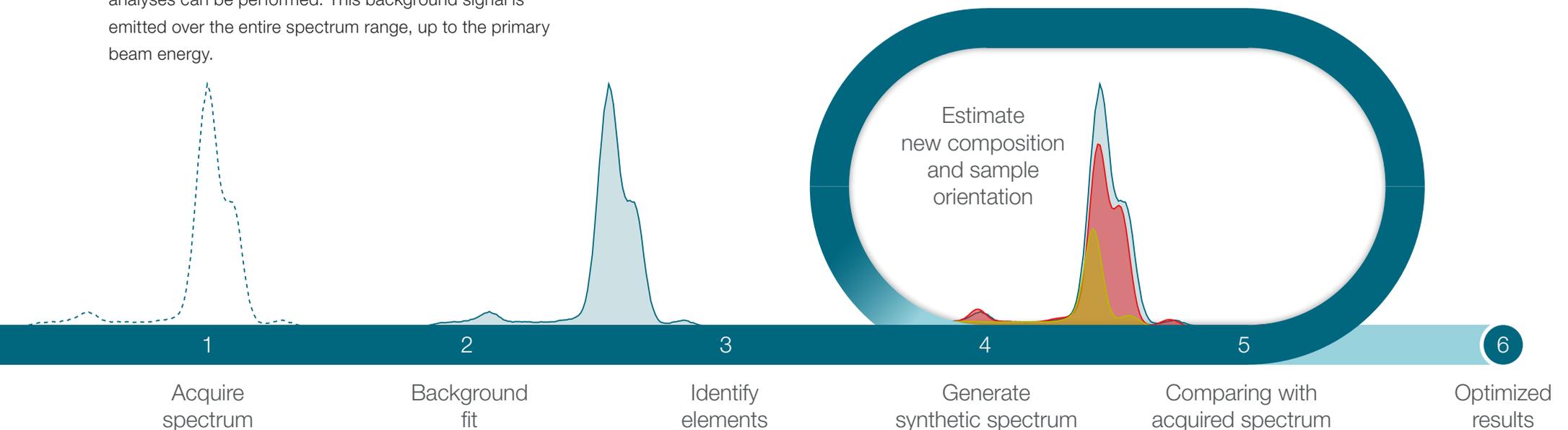


Figure 3: The Phenom EDS workflow uses a forward modeling method that generates a synthetic spectrum that is compared to the original spectrum until the overall best match is found. The algorithm automatically corrects for all detector artifacts and involves physical aspects so that all available information in the data is used. After a few seconds, a final, fully optimized result is available.

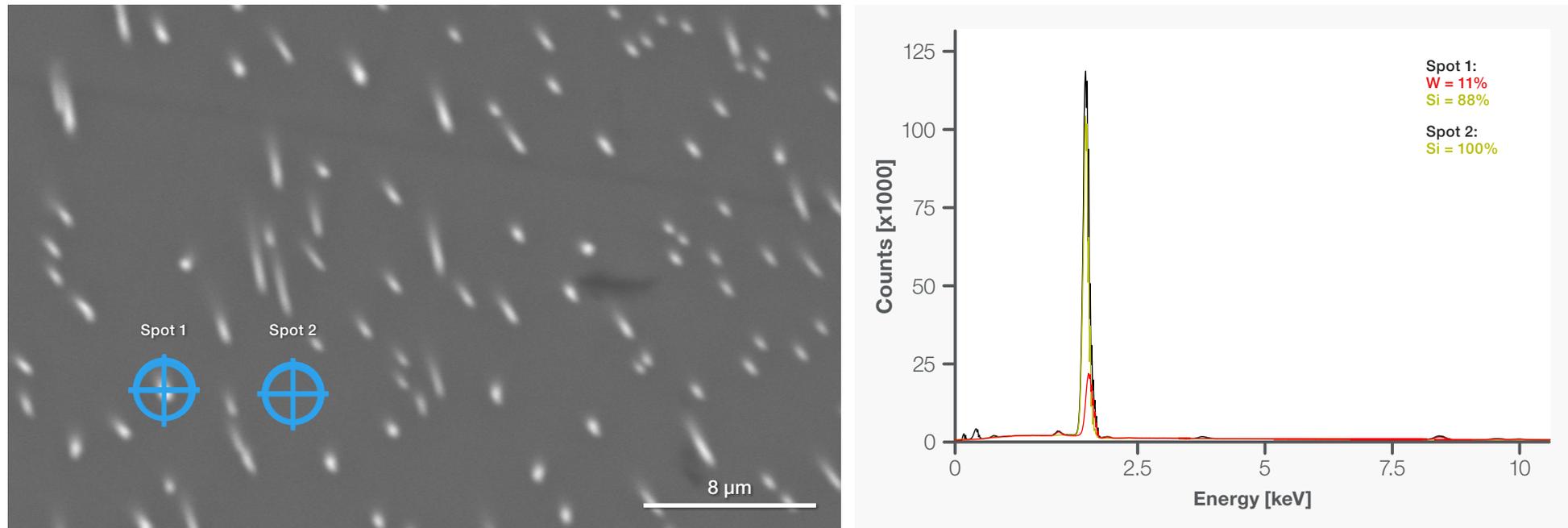


Figure 4: Inhouse sample with W flakes melted in a pure Si matrix. The Phenom algorithm can easily detect the overlapping W $M\alpha_1$ peak at 1.779 keV from the Si $K\alpha_1$ peak at 1.739 keV and quantify them properly. The percentages represent the atomic weights, respectively.

It is therefore important to check for the presence of other energy lines; for example, that a K_β peak has a corresponding K_α peak. The Phenom EDS algorithm compares the obtained spectrum with the synthetic spectrum over the full energy range. Several iterations are run on the spectrum to find an overall best match, guaranteeing the most accurate results.

Handling overlapping elements

There are many known examples in which peaks from different elements will overlap; for example, silicon ($K\alpha_1=1.739$ keV) and tungsten ($M\alpha_1=1.779$) have a separation of 40 eV, which is beyond the resolution of the EDS detector. Peak deconvolution is a mathematical

approach for the separation of overlapping peaks and the determination of the contribution of each individual element to the combined peak shape. As can be seen in Figure 4, the Phenom EDS algorithm easily resolves these overlaps to a correct quantification.

Once a spectrum is acquired, a first-order estimate of the elements and their intensities will be used to generate a new spectrum for the elements and their estimated composition. The concentrations are then varied according to efficient mathematical optimization techniques until their synthetic spectrum matches the observed spectrum as closely as possible, after which, the best match will be reported as the final EDS result. This approach offers the main advantage that physics and

mathematics are now decoupled; the synthetic spectra depend only on the physical process of X-ray formation, while the mathematics are used to determine when the difference is the smallest. To simulate the spectra properly, several effects as described below must be considered, and they are all integrated in the iterative process.

Quantification

Full quantification for the highest accuracy

Peak heights in a spectrum are only loosely related to the concentration of an element in the sample. Consider the example of strontium fluoride (SrF_2). While it may be expected from the stoichiometry that the peak of F is twice as high as the peak of Sr, in fact, the Sr peak contains twice as many counts. There are several factors that must be accounted for by the software in order to provide accurate quantitative information; these are referred to as matrix corrections.

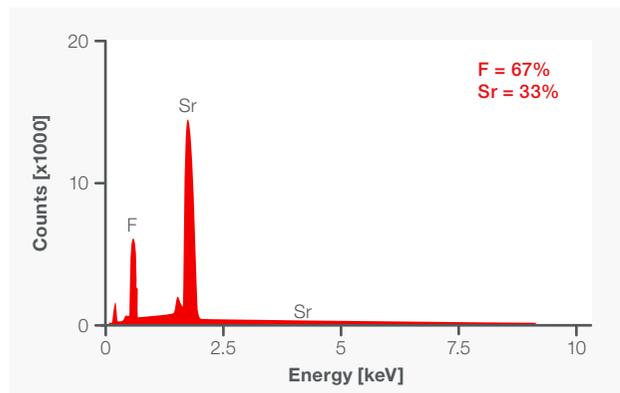


Figure 5: A spot mode measurement of strontium fluoride showing that the intensities of the peaks are not what may be expected from the chemical composition, while the quantification is very accurate.

Correction for atomic number, X-ray absorbance, and fluorescence effects (ZAF corrections)

X-rays generated within the sample travel in all directions, and they are either absorbed within the sample or they pass through it. They do not gradually lose energy as electrons do. Absorption of X-rays is most likely when their energy is equal to or slightly above the ionization

energy of another atom in the sample. When an excited X-ray from one element has an energy greater than the critical ionization energy of an electron shell in another element, this can induce a secondary X-ray. This process is known as secondary fluorescence (or, simply, fluorescence). Both these effects relate to the atomic number Z . High- Z elements tend to be strong absorbers, so large fluorescence corrections are required for low- Z elements in a matrix containing high- Z elements. On the other hand, higher- Z atoms generate more X-rays, while the penetration depth of the electron beam is reduced. The net sum of both effects is often referred to as Z correction. The correction for Z , absorption, and fluorescence is performed automatically in the Phenom software for spot and line scan analysis.

The so-called $\phi(\rho z)$ (Phi-Rho- Z) functions are an extension of the ZAF correction and describe the effect of changes on X-ray transmission through the interaction volume as a function of the accelerating voltage and the matrix it penetrates. The Phenom algorithm uses the extended Pouchou and Pichour algorithm, typically abbreviated as XPP.

Elemental mapping

For larger-area scanning, a full analysis over all pixels is very time-consuming and can take up to one second per pixel. This leads to unacceptable run times, so, often, in mapping modes, a balance is found between accuracy and speed. Phenom desktop SEMs ensure that overlapping signals are properly deconvoluted.

This means that all overlapping signals will appear as different signals in the elemental map. The major advantage to this approach is that the elemental composition of an area can be measured very accurately without compromising on speed. Therefore, you can run the analysis on all pixels and avoid binning strategies that combine pixels, so that the highest EDS resolution remains possible. Considering a realistic SiW case, for example a forensic use case to study molten glass droplets on a tungsten wire, you can now immediately distinguish the W wire from the silicon dioxide droplets (see Figure 6).

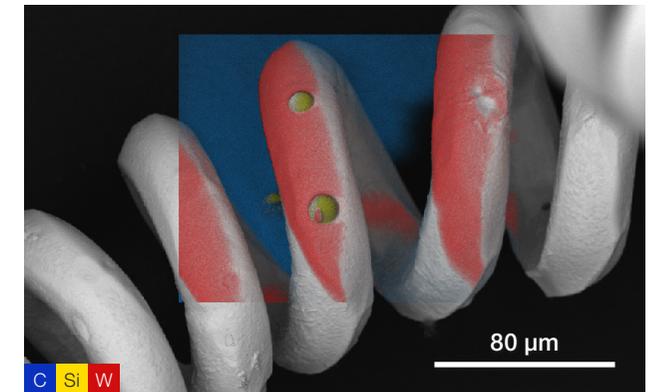


Figure 6: Using EDS, a molten glass droplet (SiO_2) can clearly be distinguished on a tungsten wire for forensic use cases.

Expert section

Typical SDDs consist of an active region composed of fully depleted, high-resistivity silicon, a front contact area, and a collection anode. X-rays incident upon the front contact area are absorbed in the bulk Si region and generate electron-hole pairs. The quantity of charged carriers generated depends on the energy of the incident X-ray. A pre-established electric field between the front contact and the anode causes these electrons and holes to drift along the field lines, i.e., toward the anode. The charge accumulated at the anode is then converted to a voltage by a pre-amplifier. The incident X-ray energy can be determined by monitoring the magnitude of the voltage step after each pulse, i.e., after each incident X-ray is absorbed.

There is a limit to how precisely this voltage step is measured, and this imprecision is one of the reasons that a Gaussian spread for a given energy is processed rather than a discrete peak. The dominant reason for Gaussian peaks, however, is the statistical spread over the electron-hole pairs generated in the detector by the incoming X-ray. This means that the width of these Gaussians is both detector- and energy-dependent. Although many electrical parameters define the overall performance of a detector, the most accepted parameter is the width of these Gaussian peaks. This is often referred to as the resolution of the detector. For practical reasons, manufacturers of EDS detectors report the number for the K α peak of manganese, and this has become a standard specification. For Phenom EDS detectors, the K α value for manganese is ≤ 132 eV.

In addition to the manganese K α peak resolution, several other parameters should be considered when assessing EDS system performance. The elemental range defines the elements in the periodic table that can be analyzed. Since X-ray flux scales linearly with the active sensor area, larger detectors have a higher throughput. When describing throughput, input count rates are often mentioned, defined as X-ray events leaving the detector for processing. Although dependent on the count rate, typically not more than half of these input counts are used for identification and quantification. The count rate leaving the digital pulse processor (DPP) is called the output count rate and is the more relevant parameter, as this reflects the amounts of counts that are useful. The Phenom EDS system uses a 25 mm² (or optional 70 mm²) SDD with a maximum output count rate of 90,000 counts per second with a detection range of boron to americium.

Incomplete charge collection

X-rays that interact near the surface of the detector generate a charge that is not completely measured because these X-rays end up in the inactive layer of the detector. Therefore, their energy is measured a little bit lower than it actually is. This effect is called incomplete charge collection, or simply ICC. Low-energy X-rays, in particular, suffer from this because they do not have the energy to penetrate deep into the detector. Therefore, X-ray lines with an energy of less than 750 eV have a significant shift to the left in the spectrum.

An empirical model is used in which the low-energy part of the spectrum is linearized by doing a carbon calibration so the peaks can be shifted to where one would expect them. However, ICC is not a simple shift, as shown in Figure 7.

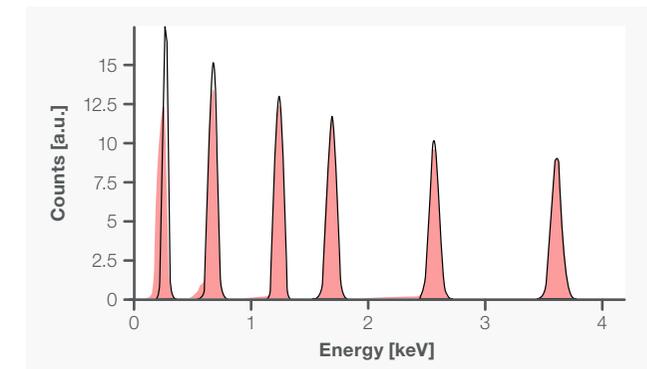


Figure 7: Examples of relevant low-energy K α peaks, from left to right: CK α (279 eV), FK α (675 eV), MgK α (1,252 eV), SiK α (1,739 eV), ClK α (2,623 eV), and CaK α (3,693 eV). The black curve is the Gaussian simulated for identical counts for all peaks; because the FWHM increases with energy, the peaks are smaller at higher energies to keep the area constant. The red curves are the same peaks with ICC applied.

It can be noted that for low energy, the resulting peak appears as a more-or-less Gaussian shape but with a broadening and a shift to the left; in the case of CK α , by as much as ~ 25 eV. From the peak shapes, it is apparent why adding this to the forward model is an important step in reducing false positives. If the black Gaussians are subtracted from the red peaks, a significant residual will remain, which is very likely to be misidentified as the next-lower element. Also, as research moves toward lighter element sensitivity, ICC correction becomes more important.

This ICC-enabled version is present in the Phenom User Interface from version 1.7 onwards and is switched on by default. This also means that there is no need to do a carbon calibration, underlining the strengths of the end-to-end Phenom EDS workflow.

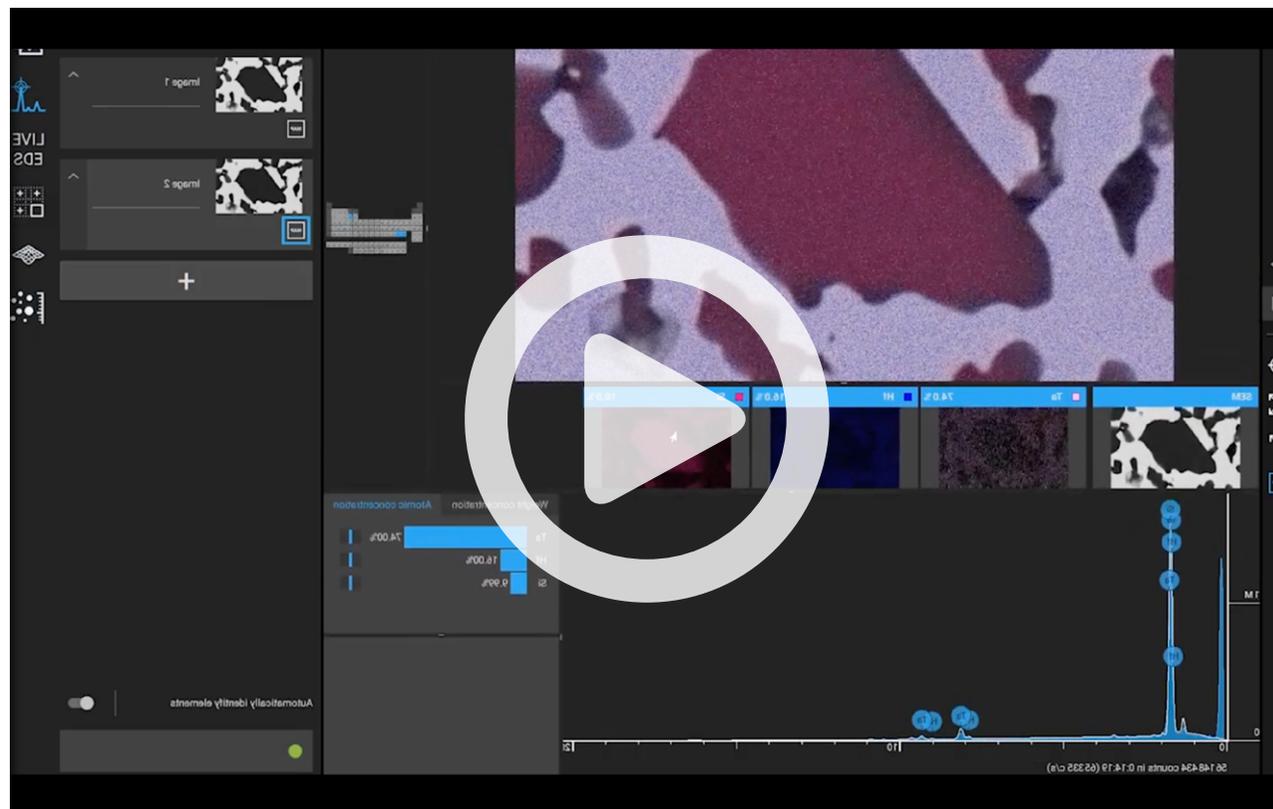
Other electronics related artifacts

There are two more relevant artifacts that may occur during the detection of X-rays: sum peaks and escape peaks. It may happen that two high-intensity peaks arrive in the pulse-processing electronics instantaneously, resulting in a false peak at the sum of the two X-ray energies. The generic effect of being unable to distinguish signals is called pulse pile-up, and the cases where signals are double-counted are referred to as sum peaks. Sum peaks can originate both from the same element and from signals from different elements. Escape peaks are inherent to any type of silicon detector. These occur when an incoming X-ray excites an X-ray from the silicon in the detector. Typically, this is corrected for by reducing the original photon energy with ~ 1.74 keV, as this corresponds to the Si K α peak. Both pulse pile-up and escape peaks are accounted for in the simulated spectra and thus part of the automated signal analysis.

Drift correction

Due to thermal effects or lack of conductivity, samples that are exposed to a high-energy electron beam can start drifting. This effect is usually very small, but when imaging a zoomed-in area of a sample for a longer time (which is exactly what often happens when making an EDS map), the shift can amount to several pixels and can cause a visible mismatch between the BSD or SE image and the EDS map. The drift correction feature in the algorithm compensates for this drift by measuring the image shift

during the mapping and adjusting the beam position on-the-fly to provide the correct results. The map in Figure 6 is the result of an analysis lasting a comparable amount of time on the same sample, with the drift correction option active.



The Phenom EDS Solution Story. Duration 5.74

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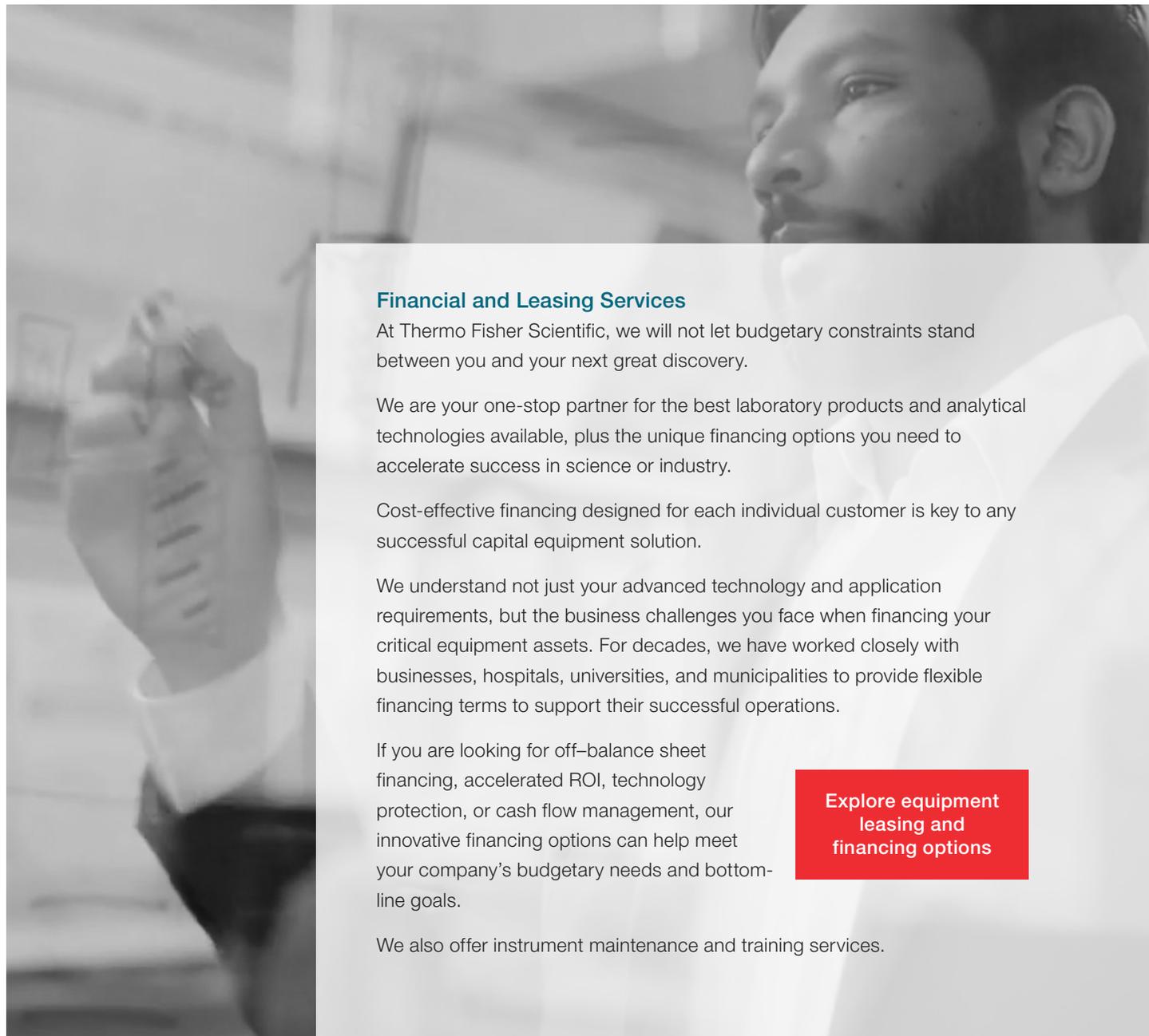
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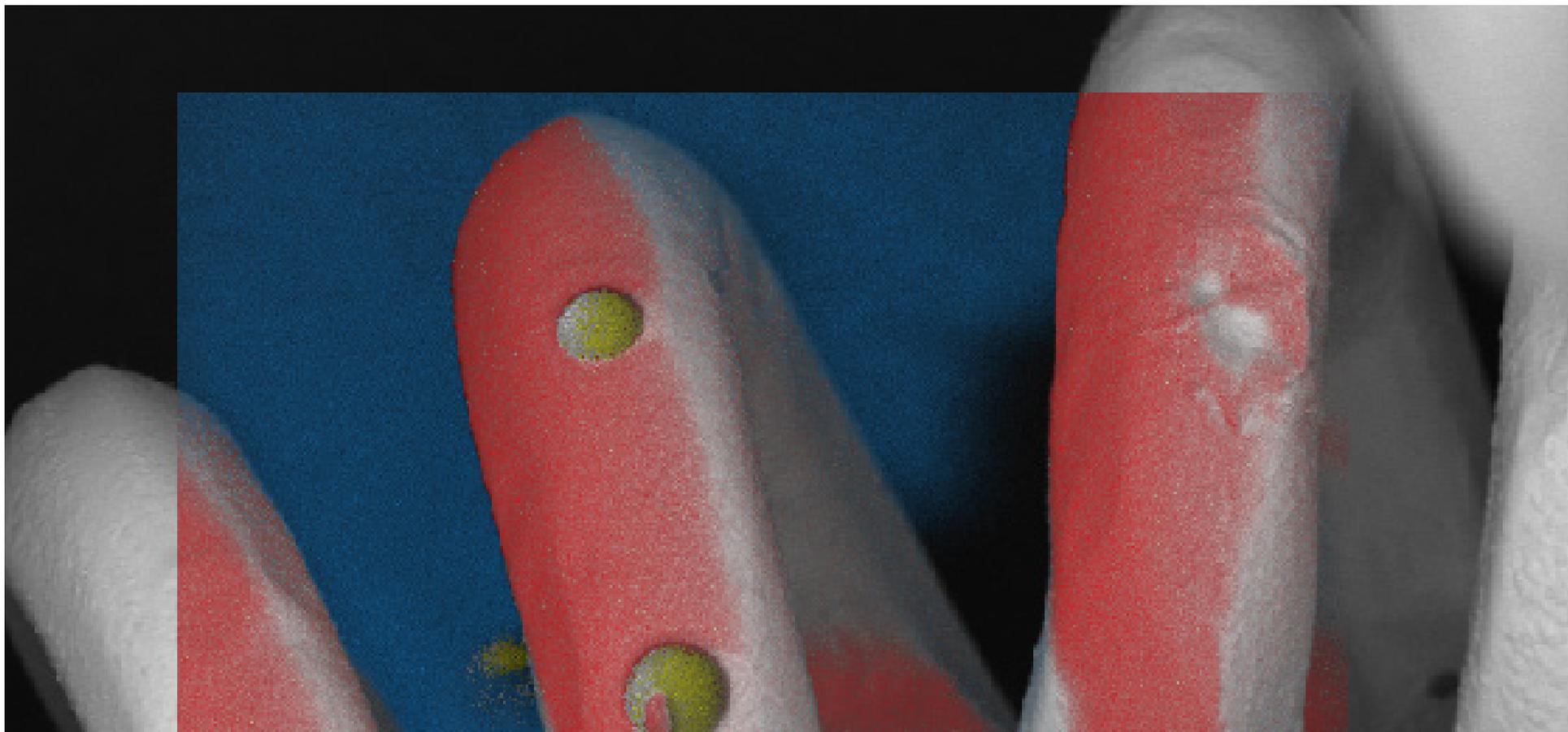


Figure 8: Small glass (SiO_2) droplets on a tungsten wire are a challenging sample for EDS due to overlapping signals. The Phenom mapping algorithm can fully resolve these signals and sometimes be used in forensics to clarify if a car's headlights were turned on during an accident.

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