

thermo scientific

State-of-the-art EDS

An introduction to elemental analysis with ColorSEM Technology

ThermoFisher
SCIENTIFIC

Introduction

Energy dispersive X-ray spectroscopy (EDS) in the scanning electron microscope (SEM) is one of the easiest methods for analyzing the composition of microscopic samples.

EDS:

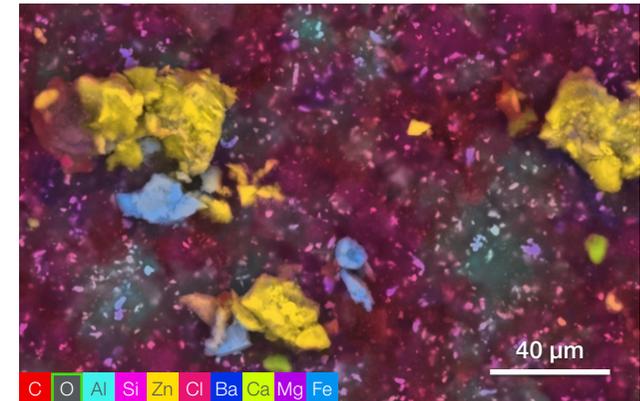
- Is sensitive to low concentrations - minimum detection limits below 0.1% in the best cases
- Affords a high degree of relative precision - typically 2-4%
- Is nondestructive in most situations
- Requires minimal sample preparation effort and time
- Delivers complete analyses of complex samples quickly, often in under a minute

Thermo Scientific™ ColorSEM Technology offers users a leap forward in usability, convenience, and speed of analysis, as it integrates state-of-the-art elemental analysis with the electron image in real time. With one software interface, the analyst can:

- View the sample image from any electron detector
- See areas of different chemical composition on the sample surface
- View point and area compositional analyses with a single click
- Chart compositional changes across the sample
- Create maps of elemental or phase distribution across the sample

Such sophisticated real-time analysis comes about through our unique combination of decades of experience and expertise in both electron microscopy and EDS microanalysis. ColorSEM Technology is made possible by a number of recent advances in the technologies that underpin state-of-the-art EDS.

- Design advances in the silicon drift diode (SDDs) that reduce noise, improve sensitivity, and support faster data processing, enabling:
 - Enhanced light element analysis
 - Ability to maintain excellent resolution even at very high count rates
 - Improved peak resolution, leading to better deconvolution of overlapping peaks and more accurate quantitative analysis
- Faster data computation to process the raw data and performs all the empirical corrections required to turn an X-ray spectrum into an accurate identification and quantitative analysis
- Improved automation that allows faster construction of large area maps stitched together from multiple high magnification images
- Novel data segmentation approaches based on machine learning that provide live color X-ray imaging



Example of ColorSEM Technology image showing fillers with different compositions on paper. Acc voltage 20 kV, beam current 3.6 nA, low vacuum mode (60 Pa).

This paper describes how ColorSEM Technology delivers new levels of speed, convenience, and insight during SEM EDS analysis. The paper begins with the collection process for X-rays generated from the interaction of accelerated electrons with the sample, before discussing the spectral processing steps needed to report accurate and reliable results to the user. Readers with prior knowledge of these processes may wish to jump directly to the section that describes the modes of analysis within the ColorSEM Technology user interface and discuss interesting applications of ColorSEM Technology to the analysis of selected samples.

EDS Hardware

Overview of EDS Analysis

When excited under an electron beam, each element within a sample emits a unique and characteristic X-ray signal. The number of X-rays emitted by each element is loosely related to the concentration of that element and its atomic (Z) number. The role of the EDS system is to capture the X-rays as they are emitted from the sample, convert these X-rays into a series of electrical voltage pulses whose amplitude reflects the energy of the detected X-ray, and pass them to a multichannel analyzer that creates a histogram of the X-ray spectrum as shown in Figure 1. Automated peak identification software determines the elements present in the histogram before quantification routines calculate the relative concentrations present. These quantification routines themselves consist of several steps, including spurious peak removal, background removal, net peak intensity calculation, and matrix corrections for the relative effects of absorption, fluorescence and atomic number variance (Z) of the different elements within the sample. As a final step, the EDS system software coordinates the chemical information from the EDS spectra with the electron beam position, enabling point identification, line-scanning and X-ray elemental mapping.

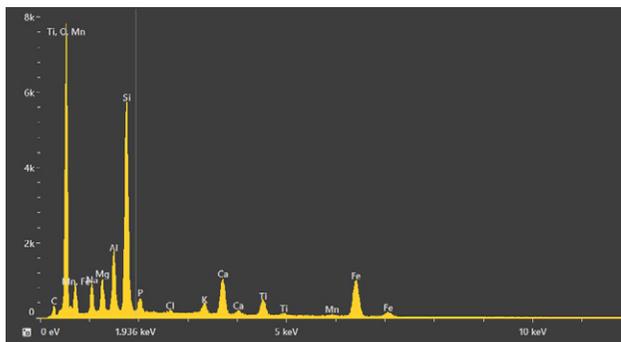


Figure 1: A representative EDS spectrum, showing the identification of peaks acquired for an aluminium rich silicate at 15 keV, 5 seconds live time.

Detector Design

The EDS detector consists of a solid-state silicon drift detector (SDD) module mounted to the end of an insertable tube in order to move as close to the sample as possible and maximize the solid angle of capture. The module is cooled to an operational temperature between -30 and -60 degrees Celsius in order to reduce the noise and improve operational performance. A collimator is typically fitted to the end of the detector to act as an aperture and prevent stray X-rays from the chamber entering the detector. The collimator is usually combined with an electron trap which consists of a strong magnetic field that prevents electrons from reaching the sensor. A vacuum-tight and light-tight, ultrathin window is usually used to protect the detector. Without a window any condensable fluids (pumping fluids, water vapor) present within the microscope chamber can condense on the module when it is running at operational temperature, damaging the detector. For the best low energy X-ray detection, it is possible to use windowless EDS detectors, provided the chamber is sufficiently clean and robust interlocks are in place.

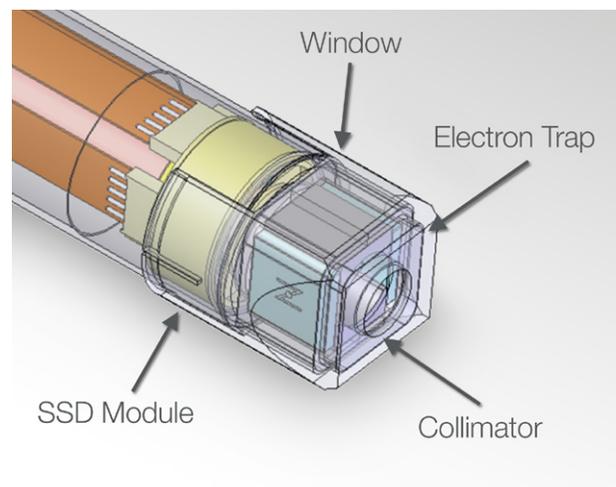


Figure 2: The components of the EDS detector head, including a Peltier cooled SDD module, a light and vacuum tight X-ray window, electron trap and collimator.

The SDD Detector

A full description of the operation of the SDD is listed in Reference 1. Impurities within the detector crystal lead to local shortages or abundances of electrons, and these free electrons or holes serve as charge carriers under the influence of an applied electric field. The silicon atoms within the detector are covalently bonded, sharing electrons amongst the outer orbitals of several neighboring atoms. These electrons are said to occupy the valence band. When an X-ray enters the crystal, it is absorbed upon interactions with the electrons from the silicon atoms, yielding a high energy photoelectron. This photoelectron eventually dissipates its energy through numerous interactions, promoting valence band electrons to the conduction band and leaving holes in the once filled valence bands. The free charge (holes + electrons) created within the SDD module leads to a temporary increase in its conductivity. The resulting current is integrated with respect to time, and the total charge conducted is directly proportional to the energy of the absorbed X-ray.

In an SDD, a series of concentric drift electrodes create a field gradient, along which the charge 'drifts' towards a small anode contact at the center of the back surface of the module (Figure 3). On the front surface, a radiation entrance window is composed of a thin, shallow implanted p-doped region, which provides a homogeneous sensitivity over the whole detector area. A thin, conductive layer is applied on top of this p+ doped region in order to improve radiation hardness. In an SDD, the anode is extremely small relative to the overall active area of the detector, resulting in a low overall device capacitance and, consequently, a low overall electronic noise. Practically, this enables excellent resolution at higher count rates, particularly at low energies where the signal to noise ratio is poorer.

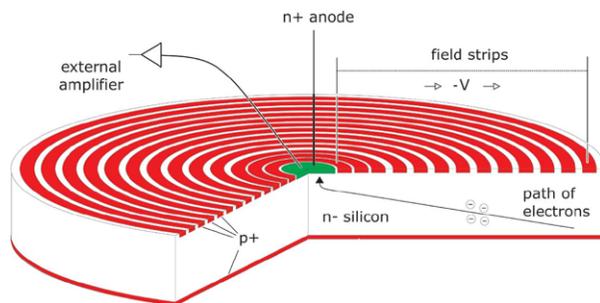


Figure 3: Cross section of the SDD. Concentric rings create a field gradient, along which the charge drifts towards the small collection anode and integrated FET integrated on the back surface. Image courtesy of PN sensor.

Field Effect Transistor

The next step in the signal-processing chain is the preamplifier, where current conducted by the detector crystal is integrated, amplified and converted into a voltage signal. The output of the amplification circuit is a voltage saw tooth comprised of a slowly rising linear ramp representing leakage current from the detector and FET, superimposed with step increases proportional to the energy of each X-ray event. Over time, the circuit is reset to avoid saturation and the process is repeated.

In modern SDD designs, the FET of the amplifying electronics is often integrated directly onto the detector chip, minimizing capacitance between the detector anode and the amplifier FET. Such designs minimize the sources of noise, enabling high resolution spectroscopy at shorter shaping times.

Digital Pulse Processing

ColorSEM Technology incorporates a set of proprietary digital pulse processing algorithms, tailored to provide the best possible performance with the specific hardware used in the Thermo Fisher Scientific detectors and microscopes.

The Role of the Digital Pulse Processor (DPP)

The role of the digital pulse processor (DPP) is to convert the amplified voltage ramp delivered from the FET and analog pre-amplifier into a y-axis “count” at a particular energy when displayed as a histogram. High performance digital pulse processing is at the core of delivering fast and accurate sample analysis because the X-ray spectrum is the starting point for all qualitative and quantitative analysis performed in the software. The most important requirements for effective, high-performance pulse processing are:

- Resolution – measured as a width of the detected peaks; peaks should be as narrow as possible
- Accuracy – X-rays should be reported in the X-ray spectrum at the correct energy
- Stability – X-rays should be reported at the correct and consistent energy over time and regardless of the intensity of X-ray flux on the detector

Optimizing Shaping Time

One of the key variables in the DPP process is the shaping time. This is defined as the time over which the pulse processor averages the input signal to estimate the height of every arriving pulse. Choice of an appropriate shaping time is critical to the outcome of the chemical analysis but is dependent upon several variables:

- The operating conditions of the microscope
 - beam current
 - accelerating voltage
 - stage and detector geometry
- The material of the sample
- Collection efficiency of the EDS detector
- User’s requirements for speed and accuracy in the analysis

Traditionally, users have been required to manually enter or select a shaping time in the software user interface. The value selected should be based on the factors in the list above, but is more frequently chosen as a compromise value based on prior experience, a single value always used by the lab, or through time consuming empirical experimentation where the analyst repeats the experiment at several different shaping times in order to discover what appears to generate the best-looking spectrum for the sample.

ColorSEM Technology eliminates the need for the user to set the shaping time. Instead, an adaptive shaping time is automatically determined in real time for every pulse. The key idea is to use the longest possible measurement time, subject to system-defined constraints (Figure 4). At low count rates, the time between subsequent pulses is sufficient for the most accurate measurements, limited only by the noise characteristics of the system. Higher beam currents used to accelerate map-based or area-based analysis result in increased X-ray count rates on the detector. The system quickly adapts the shaping time to obtain the best possible measurement for every pulse. Where the pulses are close to each other, the shaping time is short; where the pulses are further apart, the shaping time is longer. This gives ColorSEM the best possible throughput and resolution under all conditions, without the need for user interaction. Adaptive shaping times are particularly beneficial when analyzing samples with regions of variable atomic weight.

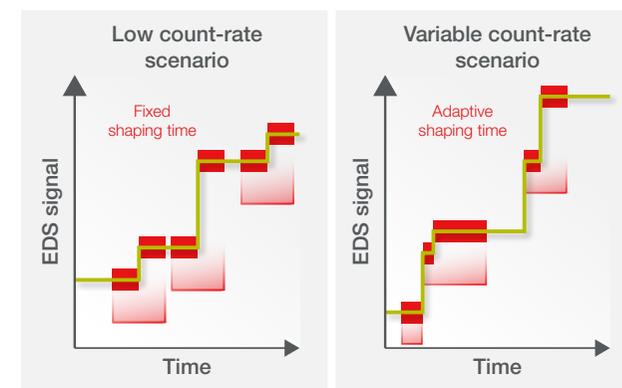


Figure 4: Example of fixed (left) and adaptive (right) shaping times used during digital pulse processing.

Electron beam synchronization and minimum dwell times

For a traditional “discrete” EDS system, the final step of the EDS hardware chain is to correlate the electron beam position with the X-ray spectrum generated at that position. Positioning of the beam is done through an external beam control interface in a support box. This controls the microscope beam position via an analog control interface. Additionally, column, beam and stage parameters must be read through an external digital interface between the support PC running the EDS software and the PC that runs the microscope. Each of these external interfaces adds a time delay to every measurement made, slowing the overall operation of the system in comparison to the full integration of ColorSEM Technology.

ColorSEM Technology integrates the EDS detector directly into the system architecture of the electron microscope, synchronizing with the microscope pixel clock at a 25 ns timing resolution. This enables EDS analysis at an astonishingly short dwell time of 100 ns, one hundred times less than typically achieved using a discrete EDS system. Shorter dwell times allow the user to:

- Reduce beam dose, mitigating possible surface damage
- Achieve substantially faster drift correction

Additionally, ColorSEM provides an electron image that is always current. Due to its ability to control all parameters of the electron image, such as focus, beam shift, and image astigmatism, without connection lags during the EDS analysis, Color SEM Technology centralizes beam control into a single platform.

Spectral Analysis

Introduction

The role of the EDS hardware is to produce a histogram, with energy (eV) on the x-axis and intensity (number of counts) of the y-axis. Each of these histograms (also referred to as “spectra”) are correlated with a precise location in the electron image. The role of the EDS software is to process the histogram and determine which elements are present, and in what concentration.

Qualitative Analysis

Qualitative analysis is the process of identifying which elements are present in a sample above the minimum detection limit. The minimum detection limit arises from the statistical uncertainty of the peak intensity measurements.² Qualitative analysis determines the energies of the peaks present in the spectrum and compares them with the known energies of X-ray emissions. This peak identification process happens automatically with ColorSEM Technology, where sophisticated algorithms check for inconsistencies in the spectrum such as a $k\beta$ peak without corresponding $k\alpha$ peak and also remove both sum peaks (arrival of near simultaneous X-rays) and escape peaks (emission of a silicon $k\alpha$ X-ray). However, the most challenging aspect of automated peak identification comes during the analysis of samples with overlapping peaks; for example, in the cases of S $k\alpha$ (2.31 keV) and Mo $L\alpha_1$ (2.29 keV) as shown in Figure 5.

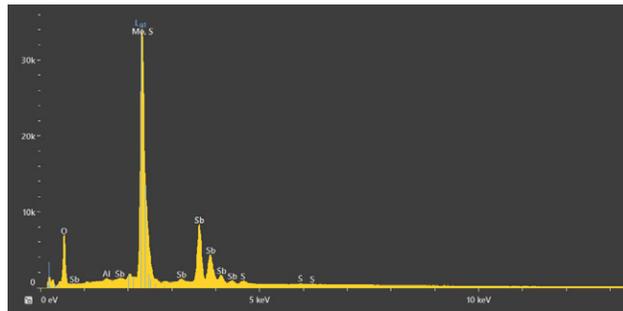


Figure 5: Automatic peak identification of the sample containing sulfur and molybdenum.

Accelerating Voltage Effects

The accelerating voltage used in the electron column influences both the spatial resolution of the X-ray signal and the efficiency with which characteristic X-rays are excited from the sample atoms. Higher voltages produce higher energy electrons, which penetrate more deeply into the sample and spread more widely than low-energy electrons. This results in a degradation of spatial resolution, but also a more efficient X-ray excitation. The overvoltage represents the ratio of the accelerating voltage to the energy of the excited line and is typically between 1.5 and 2. Figure 6 shows a comparison of copper spectra acquired at 5, 10, 15 and 20 keV primary beam energy, showing a large change in ratios of K lines and L lines.

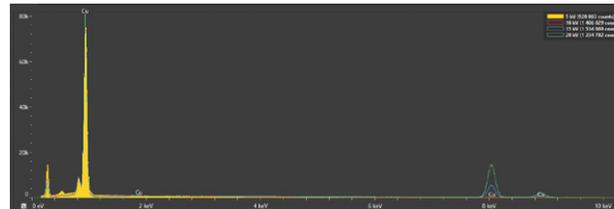


Figure 6: Spectra of pure copper taken at accelerating voltages of 5, 10, 15 and 20 kV.

At least one set of X-ray lines (K, L, or M) can be observed below 10 keV for each element. In ColorSEM Technology, qualitative and quantitative analysis routines adapt automatically to the accelerating voltage, enabling the user to obtain reliable results for any kV (Figure 7).

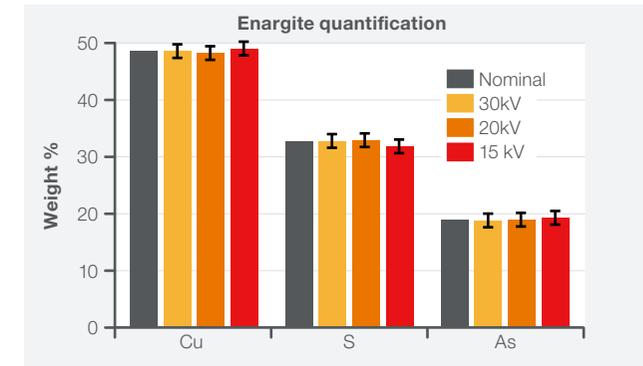


Figure 7: Quantification results of Cu, S and As in an Engnrite (Cu_3AsS_4) reference material at 30, 20 and 15 kV.

The spatial resolution of secondary electrons is much higher than that of X-rays. As a result, a feature large enough to be seen in the secondary electron image may not be large enough to contain the entire interaction volume from which X-rays emanate. Both the accelerating voltage of the electron column and the mean atomic number of the analyzed sample volume influence the spatial resolution of the X-ray signal (Figure 8).

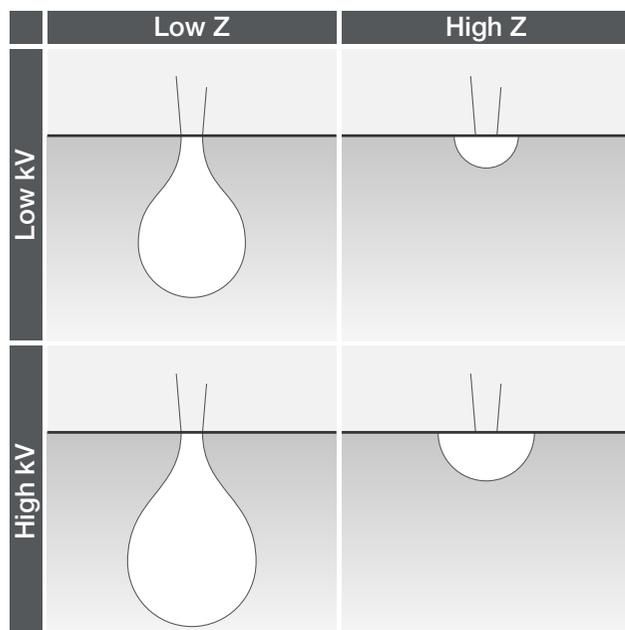


Figure 8: Schematic depiction of the variation of interaction volume shape with average sample atomic number (Z) and electron beam accelerating voltage kV.

By using a lower beam energy, high resolution results can be obtained. In the case of Pt excited at 10 keV, the only X-ray line available is the M-line at 2.05 keV. Combining low-kV excitation with a quantification engine that is capable of reliably handling such signals, even nanoparticles can be analysed with ColorSEM Technology (Figure 9).

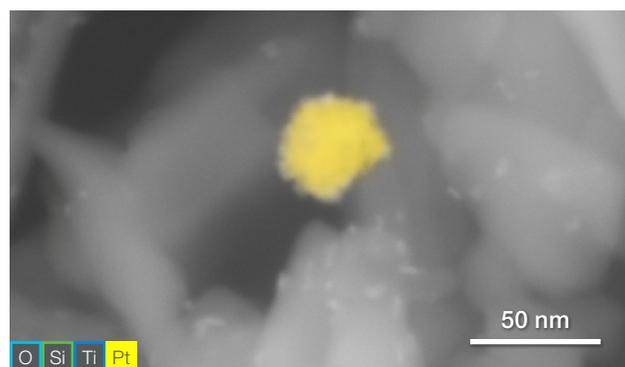


Figure 9: High resolution analysis of Pt nanoparticles on TiO_2 acquired using Thermo Scientific Apreo 2 equipped with ColorSEM Technology. Acquired at 10 kV, 0.4 nA.

Quantitative Analysis

Quantitative analysis seeks to establish not only the identities of the elements present in a sample, but also their concentrations, together with an indication of the confidence that can be placed in the computed results. Quantitative analysis proceeds through several phases: background removal, deconvolution of overlapped peaks, and calculation of elemental concentration. Traditional EDS systems built by third-party suppliers require that, after identifying the feature of interest on the sample with the microscope software, the analyst must switch to a second software application, re-acquire the image, and then perform another, entirely separate, acquisition to collect the EDS data. ColorSEM Technology removes this triplicate data acquisition model, delivering qualitative and quantitative elemental analysis directly in the microscope image.

Background Removal

EDS spectra always contain a background component originating from the Bremsstrahlung radiation emitted as the electrons are decelerated by the nuclei in a sample. The background profile is dependent on the accelerating voltage, take off angle and the elements present in the sample. The background contribution towards the peak intensities must be removed in order to quantify the composition of sample accurately. A background modelling approach calculates a theoretical model of background shape, including absorption edges, then normalizes the theoretical model to areas of the spectrum known not to include characteristic peak information. Whilst this technique can prove reliable for the analysis of peaks above 1 keV, it is highly operator-subjective and is significantly slower than other background removal techniques such as digital peak filtering (Figure 10).

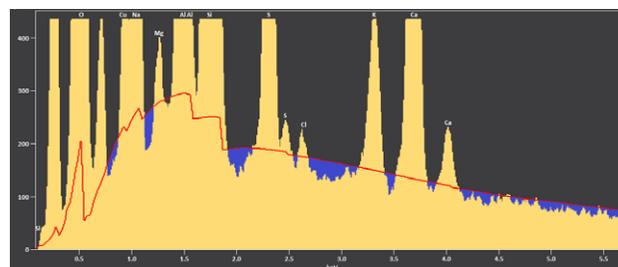


Figure 10: A modeled background for a geological section. Whilst accurate at higher energies, there are shortcomings in determining the background position using this methodology.

Digital peak filtering is an alternate method for extracting the net peak intensities and is independent of the choice of background model. This is particularly beneficial in the determination of low energy peak intensities, which are challenging to determine correctly for even the most accurate background models (Figure 10). Digital peak filtering uses an intelligent filter to remove low- and high-frequency components of the spectrum, corresponding to the background and stochastic noise respectively. Apart from the speed of operation, the principle benefit of using digital filtering is the removal of all operator subjectivity, enabling consistent results over a wide range of operating conditions. Figure 11 shows the result of digital filtering of $\text{Fe } \text{k}\alpha$, $\text{k}\beta$ and $\text{Mn } \text{k}\alpha$ peaks with ColorSEM Technology.

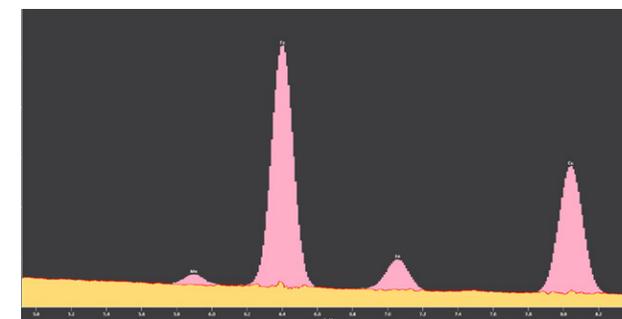


Figure 11: Digital top hat filtering of the $\text{Mn } \text{k}\alpha$, $\text{Fe } \text{k}\alpha$ and $\text{Fe } \text{k}\beta$ peaks.

Peak Deconvolution

Once spectral artefacts have been corrected for and the background removed, the remaining peaks are evaluated for their intensities. This task is straightforward when there are no overlaps, as the operator can simply integrate the area under a region of interest for each element. When there are overlapping peaks, the situation is much more complicated because the peaks must first be separated by means of mathematical peak deconvolution routines. Such routines depend on subtracting a model of the interfering peak from the analyzed composite peak. The reference peak shapes can be computed theoretically or obtained experimentally.

The most reliable procedures add the models together in varying proportions until the result best fits the data. The goodness of this fit is evaluated using a chi-square (χ^2) test, with the idea being that χ^2 is minimized when the proportions in which the peak models are added together reflect the proportions in which the constituent peaks are present in the overlapped data. A good approach is to consider the first and second derivatives of the standards in the least square fit to allow the algorithm to accommodate slight offsets in peak positions and width.

For the most reliable peak-fitting deconvolution routines, it can be beneficial to combine background filtering and reference deconvolution in a single operation, often referred to as filtered least-squares fitting. A major strength of such an approach is in the measurement of severely overlapping peaks such as S, Mo, Pb and Si, Ta, W. Acquired standards spectra are deconvoluted for each element, using real reference peak shapes rather than theoretically generated shapes. This results in an accurate deconvolution, especially for complex higher order lines.

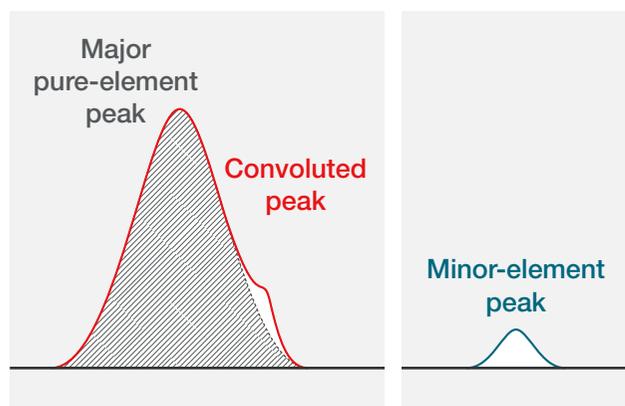


Figure 12: The principles of reference deconvolution. The solid line at the left depicts a pair of overlapped peaks. A pure-element spectrum for the major component (crosshatched area) is acquired, normalized to the sample peak, and subtracted, leaving the minor overlapping peak.

An example of overlapping peak deconvolution is shown in Figure 13, showing the overlap of molybdenum $L\alpha_1$ (2.29 keV) and sulfur $K\alpha_1$ (2.31 keV). X-ray mapping of this sample incorrectly shows an identical distribution of raw counts for S and Mn across the target area.

The erroneous X-ray mapping results are due to S-rich and Mn-rich phases both contributing X-rays from the mapped area. By running a peak deconvolution fit against internal reference peak libraries, the correct elemental distribution can be accurately determined. ColorSEM Technology includes this technology and is able to correctly deconvolve these overlapping elements during data acquisition.

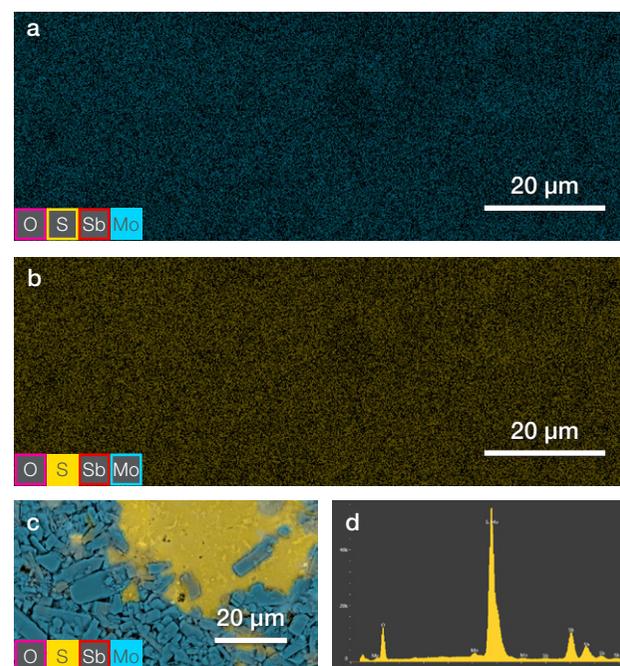


Figure 13: Gross count mapping of a) Mo and b) S, showing an identical chemical distribution. These overlaps can be correctly deconvolved by use of a linear least squares fit peak deconvolution approach as shown in c). d) shows the peak positions of Mn and S.

Matrix Correction

Once the net peak intensities have been determined for each element, the next step is to calculate the sample composition, usually in terms of weight or atomic percent. The relationship between net peak counts and elemental concentrations is complex and at the core of accurate quantitative microanalysis. Such calculations consider the influence that each element exerts on the relative peak intensities of all the other elements, through the application of a matrix correction routine.

Three factors are considered in matrix correction routine:

- Atomic number (Z)
- Absorption within the sample and detector (A)
- X-ray-induced fluorescence (F)

The Z correction accounts for the effects of atomic number on excitation efficiency, fluorescent yield, and detector efficiency. The A correction represents the likelihood of a generated X-ray becoming reabsorbed before detection. The F correction corrects for the secondary fluorescence induced within the sample due to excitation from characteristic X-rays or Bremsstrahlung. X-rays generated by secondary fluorescence can be fluoresced several microns away from the interaction volume depending on the energy of the X-ray absorbed. ColorSEM Technology uses the PROZA algorithm for EDS quantification, which is an evolution from the standard ZAF approach. This algorithm considers how the matrix corrections vary with the depth distribution function (Φ), mass density (ρ) and mean atomic number (Z) and enable a more accurate quantification, particularly for light elements.

The Z, A and F correction terms depend on the geometry of both the sample and the EDS detector. Each of these terms is integrated along the path that the X-ray travels through the sample and to the detector. Miscalculations in the X-ray pathway, for example due to sample topography, represent a significant source of uncertainty Figure 14.

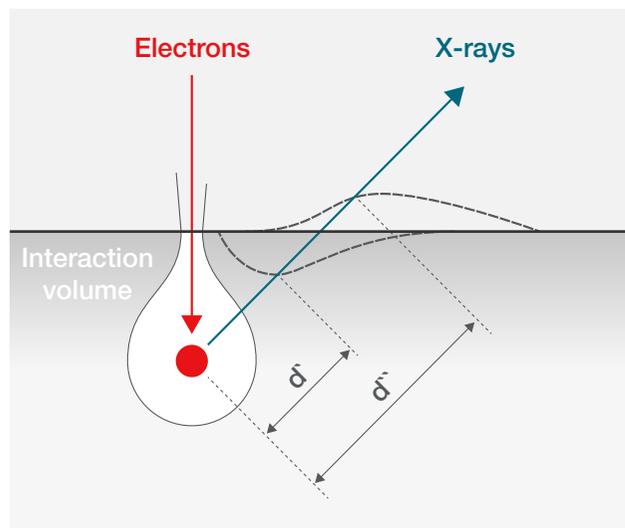


Figure 14: Illustration of the dependence of the absorption path length (d' and d'') as a function of sample topography.

Pathlength calculations are automatic in most modern SEM-EDS systems and consider beam conditions (kV, beam deceleration), stage position (working distance, tilt) and EDS detector position to provide accurate quantification over a range of operating conditions (Figure 15). However, the operator should remain aware of the sources of relative error in the measurements and the impact these will have on the final quantitative results.

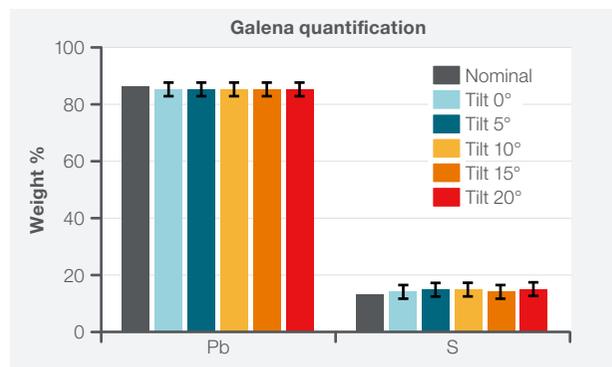


Figure 15: Quantification of Galena (PbS) at a sample tilt of 0-20 degrees using ColorSEM Technology.

K-ratio calculation

For determination the concentrations of the elements in the sample, it is necessary to apply matrix corrections to the raw intensities to allow for differences in composition between the sample and the standard. These Z, A and F corrections are applied to each element in the sample through use of a k ratio.

The k-ratio is defined as the ratio between the number of X-rays in the net peak for the element of interest and the number of X-rays counted for the same element, under the same conditions, in a sample of known concentration.

$$k\text{-ratio} = \frac{\text{unknown peak counts}}{\text{std counts}}$$

Standardless Analysis

ColorSEM Technology utilizes a standardless analysis approach to quantitative analysis and delivers highly accurate quantitative results, provided sufficient care is taken to understand and minimize the sources of uncertainty. An internal database contains characteristic peak intensities from a set of experimental standards measured under a range of measurement conditions, including accelerating voltage, take off angle and detector type. Net peak intensities are interpolated mathematically from the database values and used to determine k-ratios, which are then used to calculate the concentration of the elements present. The key to successful standardless analysis lies in the completeness of the system database, the interpolation methodology and in minimizing the difference in acquisition conditions between that of the reference standards and the sample of interest. Using this approach, ColorSEM Technology is able to return excellent quantitative analysis for compounds, alloys, and minerals, even in the presence of elements with overlapping X-ray peaks (Figure 16).

	Limiting chemical composition (%)	Measured values with 1.2 nA beam current		Measured values with 4.5 nA beam current	
		AVERAGE	STD DEV	AVERAGE	STD DEV
Ni	50-55%	52.975	0.404	52.915	0.329
Cr	17-21%	20.095	0.354	19.925	0.579
Nb	4.75-5.5%	5.39	0.597	5.995	0.952
Mo	2.8-3.3%	3.215	0.057	3.315	0.057
Ti	0.65-1.15%	0.92	0.108	0.915	0.073
Al	0.2-0.8%	0.505	0.038	0.495	0.022
Co	Max 1%	0.09	0.062	0.16	0.092
Si	Max 0.35%	0.1	0	0.1	0
Mn	Max 0.35%	0.175	0.07	0.32	0.04
Fe	Balance	16.58	0.5	16.6	0.5

Figure 16: Quantitative analysis of an Inconel 718 reference material, acquired with 20 measurements per sample, at 20 kV accelerating voltage.

Modes of Analysis

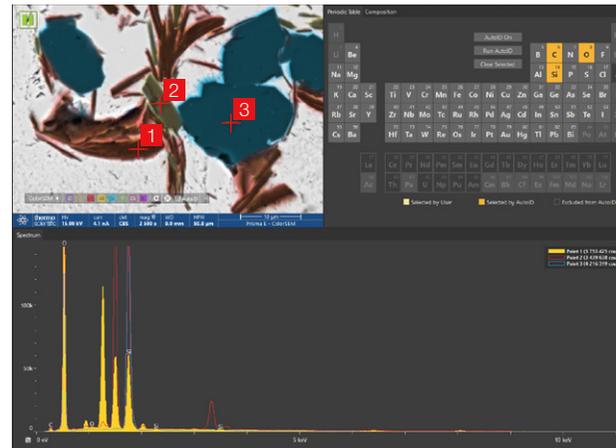
Introduction

In SEM EDS, qualitative and quantitative information from EDS is usually combined with the electron beam position to provide insight into compositional variation across the sample. There are three principle modes for combining spatial and spectral information: point mode, linescan and X-ray mapping. The X-ray mapping itself starts with simple region-of-interest gross count mapping and ends with full quantitative information for each and every pixel. ColorSEM Technology goes one step further and combines progressive electron image segmentation with fully quantitative X-ray processing routines to provide live time chemical imaging.

The most appropriate choice of analysis mode depends on the nature of the problem that the analyst is seeking to solve. Since ColorSEM Technology is built upon the principle of tightest possible integration of the electron microscope and EDS system, it is possible to seamlessly combine information between each of these modes, providing the analyst with an extremely natural workflow for arriving at the correct answer.

X-ray point & ID

X-ray point & ID drives the electron beam to position on the sample and acquires a spectrum. Termination criteria for that acquisition are based on either an acquisition live time or on a statistical number of X-rays in the spectrum. Point analyses are completed either in a survey mode or as a batched acquisition mode, to compare information across a range of points and shapes on the sample. Point & ID is typically the first analysis used as it provides the shortest time to data. Figure 17 shows a three point analysis of a Malachite mineral sample, showing the live color electron image, the full spectrum at each point and the full compositional information within the SEM user interface.



Element	Point 1 (Atomic %)	Point 2 (Atomic %)	Point 3 (Atomic %)
C	1.7	2.6	2.3
O	63.4	62.8	65.8
Mg	16.1	-	-
Al	8.6	14.1	-
Si	9.5	16.5	31.9
P	0.7	0.9	-
K	-	4	-

Figure 17: Top: SEM user interface showing three point analysis of the mineral malachite. Bottom: quantification results from the three points. Sample courtesy of Unidad de Microscopía Electrónica de Barrido. URJC.Dr. G. del Rosario H., R. García-quismondo C.

X-ray Linescan

X-ray linescans show how the elemental composition varies in one dimension across the sample. The analyst typically specifies the length and number of points in the line, as well as the dwell time per point and the number of passes across the sample. Similar to X-ray point mode analyses, X-ray linescans provide full quantitative information per point, although typically take longer to acquire due to a larger number of analysis points.

Figure 18 shows a somewhat typical X-ray linescan application for the analysis of contaminants within a glass fiber-reinforced polymer. The exact concentrations of the elements Al, Si, Ca, and Fe are shown as they vary across the sample. Using ColorSEM Technology, it is a straightforward operation to combine different modalities of information with a single image.

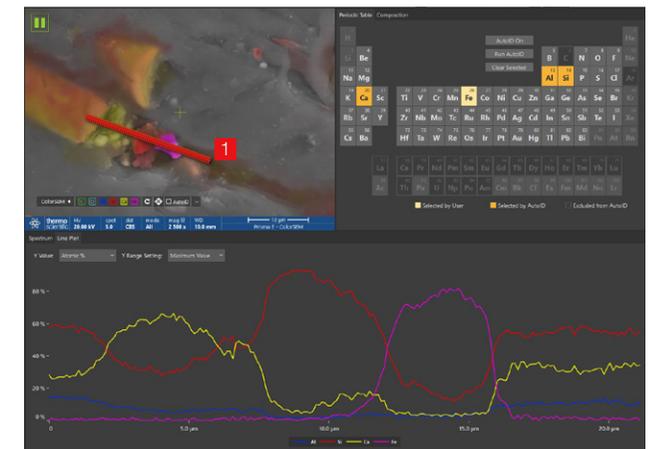


Figure 18: X-ray linescan for contaminants within a PCB. (Acquisition parameters: Acc. voltage 20 kV, beam current 1.2 nA, average count rate 4000 cps, total acquisition time \approx 350 s, total points in the linescan 200).

X-ray Elemental Mapping

X-ray maps show how the elemental composition varies in two dimensions across the sample. During X-ray mapping a full spectrum is acquired for each pixel in the image, and for this reason X-ray mapping is often referred to as spectral imaging.

Spectral images are the extremely rich datasets; for example, a spectral image with 1024 x 1024 pixels contains one million distinct spectra and over two billion unique data points, assuming 2048 channels per spectrum (corresponding to a 10 eV channel width over 20 keV). By acquiring a full spectral image, the operator is able to perform full offline image processing, extracting any number of points or lines from within an X-ray elemental map. The drawback with X-ray spectral imaging is the long acquisition time needed to get statistically sufficient data, notwithstanding that modern EDS detectors offer very high output count rates. Whilst qualitative analysis of a simple compound might need as few as 500 counts per pixel, quantitative analysis of a transition metal and ligand complexes could require over 50,000 counts per pixel to obtain accurate results. To accelerate analysis, a range of strategies is commonly used, including pixel binning and multivariate statistical techniques.

Gross Count X-ray Mapping

The simplest mapping strategy is gross count mapping, also referred to as raw count mapping or region of interest mapping. Gross count mapping allocates an energy window for each element of interest in the sample and assigns all peaks within that energy window to that element. For well-isolated peaks, gross count mapping can provide adequate results; however, the lack of background removal and peak deconvolution frequently leads to artefacts.

Figure 19 shows an example of gross count X-ray mapping for a geological sample. The elements aluminum (1410-1682 eV), calcium (3562-3818 eV), potassium (3187-3437 eV) and oxygen (468-582 eV) are well isolated, and the gross count maps provide a reasonable approximation of the concentrations of those elements present. However, the elements silicon (1632-1848 eV) and tungsten (1666-1884 eV) have mostly overlapping energy windows, so the gross count maps appear to be almost identical. In reality, there is no tungsten present in the sample, nicely illustrating the overlap artefacts that can be introduced with gross count mapping.

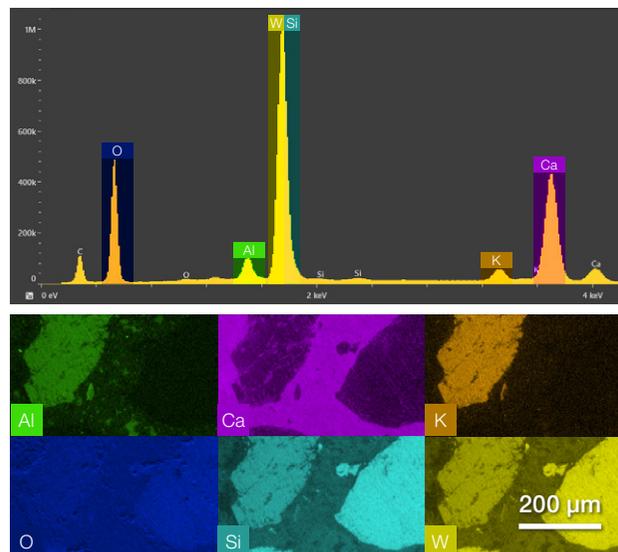


Figure 19: Gross count X-ray mapping for a mineral sample.

Quantitative X-ray Mapping

With ColorSEM Technology, all the steps of quantitative analysis are applied to each pixel in the spectral image. These include a filter fit background removal and peak deconvolution to return the net peak intensities (net counts map) and the matrix correction factors to calculate the atomic and weight percentages at each pixel. Unlike gross count X-ray maps, quantitative X-ray maps are typically free of background, geometry, and overlap artefacts. In order to achieve a sufficient number of counts to perform the quantitative operations it is often necessary to bin (or kernelize) the data. This means that the signal coming from neighboring pixels is summed. It leads to larger kernel sizes which allows to achieve a larger number of counts per spectra, albeit at the expense of a reduced resolution (Figure 20). Some modern SEM-EDS systems will automatically select a bin size based on the total number of counts present, progressively moving to a smaller bin size as more information arrives during live analysis. More advanced quantitative X-ray mapping approaches allow for multiple passes, adaptive kernel sizes and edge preservation filters.

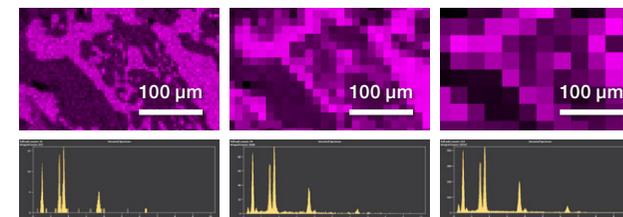


Figure 20: Fe $K\alpha$ net count X-ray maps illustrating the trade-off between spectral quality and image resolution. Total X-ray counts is 12 million, native resolution is 256 x 192.

A side by side comparison of a ColorSEM map versus a more conventional gross counts map, both acquired in 30 seconds, shows both better sharpness and more apparent signal.

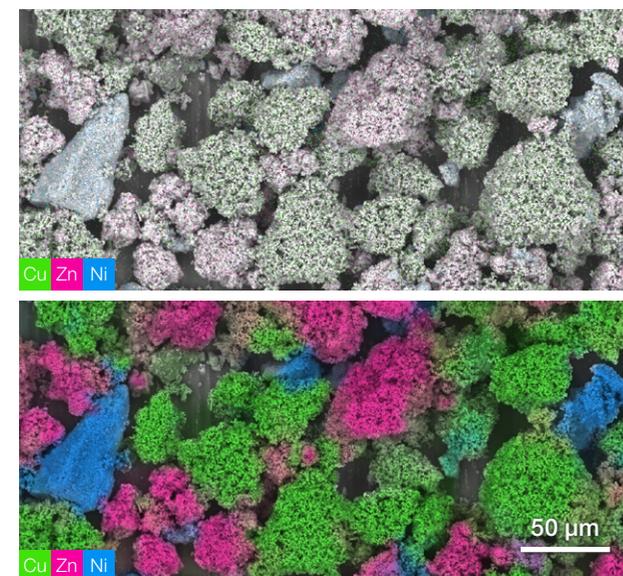


Figure 21: Traditional gross counts mapping (upper image) compared to ColorSEM mapping (bottom image)– a significant improvement in sharpness.

Live Color Imaging with ColorSEM Technology

Live color imaging with ColorSEM Technology is a new concept of analytical electron microscopy which changes the way that information about the chemical composition of a sample is collected, processed and presented to the user. Analytical information is collected fully synchronously with the electron scanning process, with precision down to a single pixel. It is then presented to the user in the form of additional color information superimposed on top of the conventional grayscale image.

ColorSEM Technology works by acquiring multidimensional data and superimposing the color maps onto the grayscale image. ColorSEM Technology increases the speed of coloring by integrating EDS data across larger areas, or segments, quantifying these integrated spectra, and assigning color to them based on the results. The segments shrink progressively as data continues to arrive before ultimately converging to a pixel-precise EDS map. A simple linear iterative clustering algorithm is used to create the segments, and it works by grouping together adjacent pixels with similar color profiles and is computed several times to get different levels of granularity. The benefits of such an approach are that meaningful quantitative maps can be achieved in a far shorter time and that edge features are better preserved. An example of the data clustering approach is shown in Figure 22 for three different acquisition times. The amount of data per segment remains approximately equal throughout the acquisition, until the point that the segments converge to a single pixel.

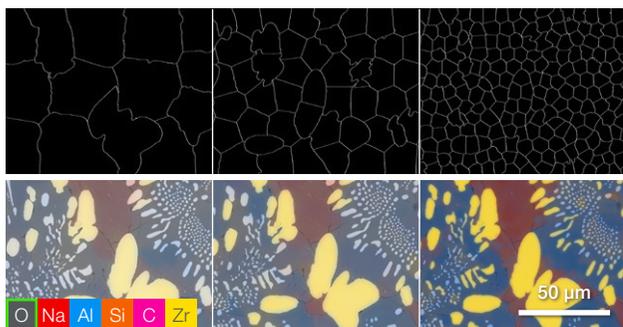


Figure 22: Live color X-ray imaging using ColorSEM Technology. Image shows a glass contaminant acquired at 10, 30 and 70 seconds; acc voltage 10 kV; beam current 0.76 nA; and dwell time 1 μ s.

X-ray Color Schemes

Assigning visible colors to the X-ray spectra during EDS mapping is a non-trivial process, as elements having similar colors should be avoided. Most commonly, three or six elements are assigned to an RGB or RGBYCM color scheme and then overlaid to display an approximate chemical composition.

ColorSEM Technology employs a powerful set of algorithms that determine, assign and blend colors in aesthetically pleasing ways that also significantly improves the legibility of the color-coded chemical composition. ColorSEM Technology uses the science of colors, selecting a pallet of compatible colors and assigning them to regions of the electron image based on quantitative EDS data. By working in the hue-saturation-luminance domain and by respecting the color dynamics in that space, ColorSEM Technology offers the user an automated color selection algorithm that can be run repeatedly with different initial conditions to arrive at color scheme most appropriate to the sample. Conditions such as color preference, fixing of selected colors, removal of elements from the analysis and other options form the boundary conditions for the color selection algorithm.

For example, for a sample containing copper, zinc and nickel (Figure 23), the colors assigned to those three elements will never be with similar hue, as this would form similarly colored regions that would be difficult to distinguish and interpret but also not easy to use for navigation, analysis or presentation. Instead, colors that complement each other well, such as pink, yellow and green, would be used to create a more visible contrast between the different compositions.

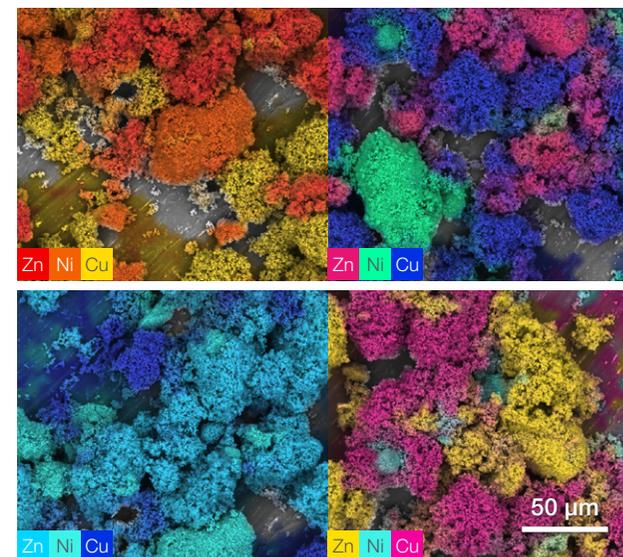


Figure 23: Color palette. Cu,Zn,Ni rich material. The 2 images on the left show the importance of a proper color palette. Both have 2 combinations of colors that make the interpretation difficult. On the right, however, the color palette presents colors that help to distinguish the different compositions and ease the navigation.

Shadow Removal

A frequent problem during the SEM-EDS analysis of non-flat samples is the issue of shadows arising from areas of the sample surface which do not have direct line of sight to the detector. Stray X-rays from these regions can still enter the detector and will appear on the X-ray map (Figure 24, left). ColorSEM Technology incorporates an active shadow detection system to remove such false X-rays from the shadow region.

An absolute threshold of count rate from the shadowed region is difficult to determine, since it is dependent on a multitude of factors, including beam current, accelerating voltage, shaping time, detector type, and position. For that reason, the ColorSEM Technology shadow detection mechanism uses a relative threshold, defined as a fraction of the average yield from the given field of view. A relative yield (and its associated error) is computed for each segment, and the segment is declared to be in shadow if the yield is above the relative threshold (Figure 24, right).

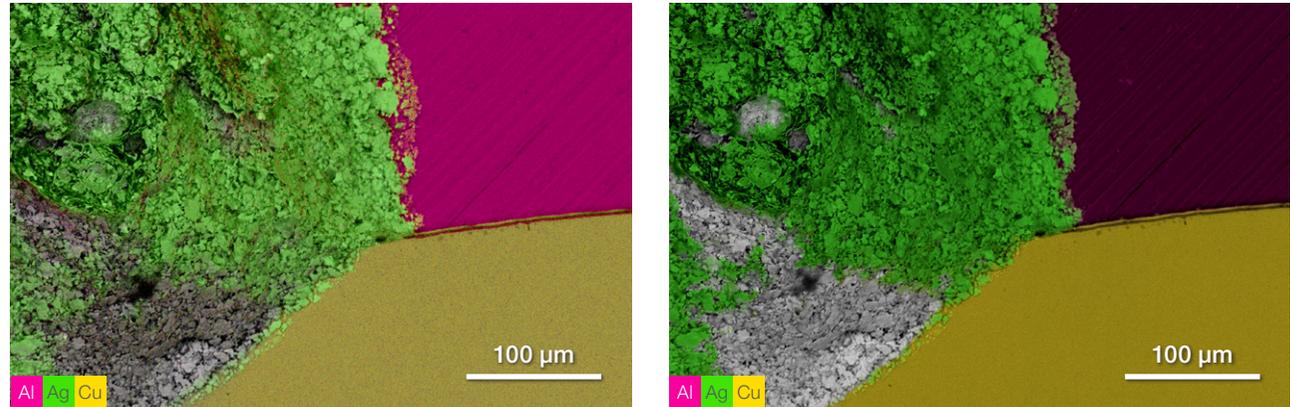


Figure 24: Shadow detection using ColorSEM Technology. The image shows a copper TEM grid glued to the aluminium stub with silver paste. Surface roughness of the dried silver paste causes shadowing of the EDS detector.

ColorSEM Technology Application Examples

Introduction

Two examples were chosen to demonstrate how ColorSEM Technology can be used to solve analytical challenges across different application areas. These examples show that the features of ColorSEM Technology excel at providing accurate results even with challenging samples.

Key features include:

- Intuitive user experience closely aligning imaging and EDS acquisition
- High-speed quantitative mapping for rapid large area analysis
- Very short pixel dwell times for the improved analysis of beam-sensitive materials
- Highly accurate quantitative analysis
- Shadow removal for the enhanced examination of topographical samples
- Ultrahigh spatial resolution X-ray imaging for nanoparticle analysis

Example 1: Analysis of Glass Contaminants

Accelerating Voltage	5 and 20 keV
Probe Current	2.1 and 4.5 nA
Pixel dwell time	200 and 1000 ns
Magnification	150 x and 500 x
Image resolution	1536 x 1094
Acquisition time	50 and 120s

Modern production methods for glass panels use a so-called float technology that yields perfectly flat glass for a variety of applications, such as LCD and plasma screens, and for building and automotive industries. Float technology enables the large-scale production of very smooth sheets with a thickness determined at the time of manufacture. During the float process, molten glass is continuously poured from a furnace into a chamber containing a bed of molten tin, on which the melt floats due to its lower density. It is critical to this process that sources of contamination are kept to an absolute minimum in order to reduce the formation of defects in the glass.

Alumina-Zirconia-Silica (AZS) refractories are often used as furnaces pavements and are one such source of defects leading to the presence of aluminum- and zirconium-based contaminants. In this example, ColorSEM Technology is used to determine the composition of the contaminants.

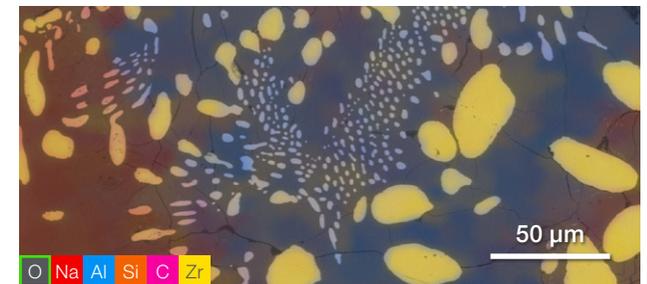
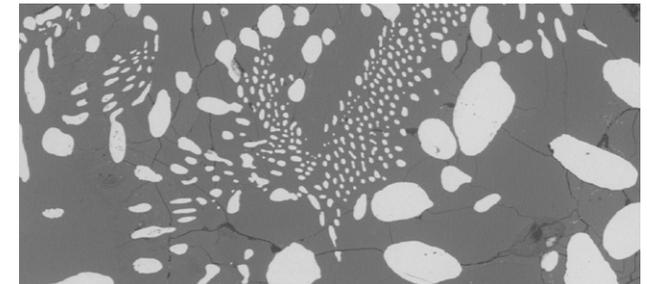


Figure 25: Top: BSE image of contaminants within a float glass. Bottom: Corresponding ColorSEM Technology live color image, showing the chemical composition of the contaminants. Acquired at 5 keV

Figure 25 shows a grayscale BSE image of the glass cross section (top), revealing the presence of inclusions of different sizes. The ColorSEM Technology image (bottom) shows overlay the EDS signal for the elements O, Na, Al, Si, C, Cu and Zr. Each element is a full quantitative map, with background removal, peak deconvolution, and matrix corrections applied per pixel.

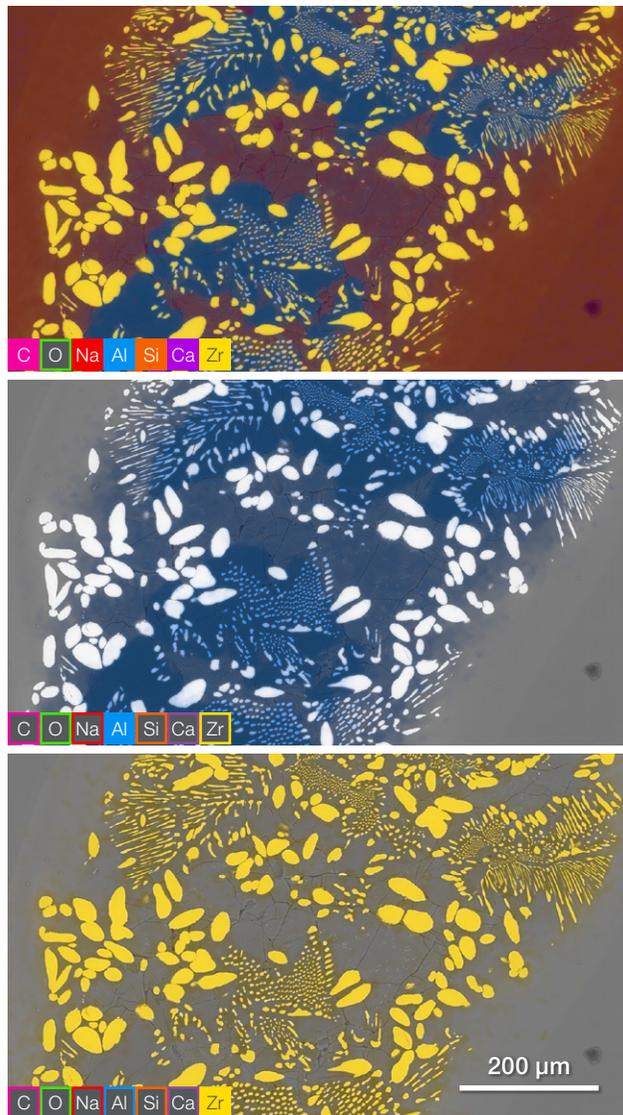


Figure 26: ColorSEM Technology image (top), Al (blue) distribution (middle) and Zr (yellow) distribution (bottom). Acquired at 20 keV.

It is possible to superimpose any combination of elements with ColorSEM Technology, either live or after the acquisition. This provides a clear understanding of the distribution of each element, and how they are related to the features in the electron image. Figure 26 is at a large field of view and confirms the presence of Zr-based precipitates included within an area with a consistent quantity of Al localized around them.

The quantitative X-ray images revealed a gradient in the colors around the inclusions, indicative of a diffusion within the glass. X-ray linescans were used to further understand the nature of the contaminants (Figure 27). These analyses confirmed that the primary elements were Zr and O, at a concentration broadly consistent with zirconia (ZrO_2). The presence of Na, Al and Si within this region was due to an infusion of molten glass elements and contaminants during the glass production process. Different quantifications have been extracted from the X-ray linescan, which also revealed that the concentration of Al increased along the linescan from 7% to 32%.

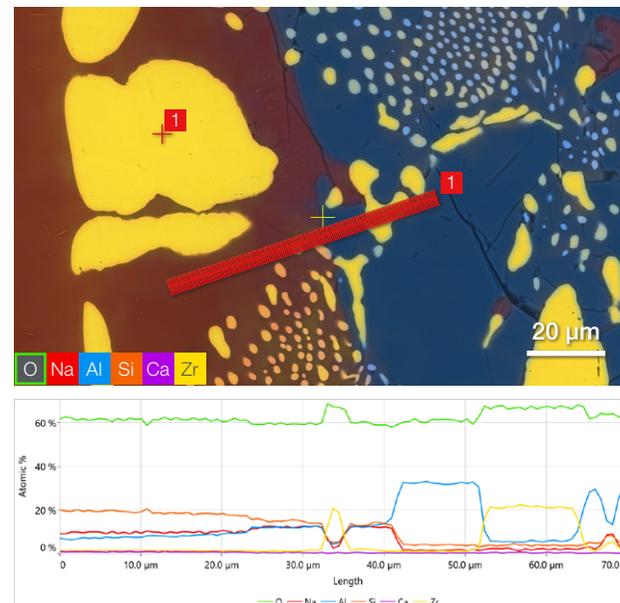


Figure 27: Top: ColorSEM Technology image combining live color imaging, Point & ID and mode and linescan in a single plot. Bottom: corresponding linescan (100 points) revealing the variation in elemental concentration across the sample.

This shows that ColorSEM provides a detailed analysis of the elements distribution and variation along the area of interest, with excellent results also in low vacuum.

Example 2: Large Area Analysis of a Garnet-rich Gneiss

Accelerating Voltage	15kV
Probe Current	4.1 nA
Pixel dwell time	800 ns
Magnification	200x (per frame)
Image resolution	1536 x 1094
Total number of frames	13 x 13 = 169
Acquisition time	90 minutes

The second example shows the analysis of an Orthoamphibole-Cordierite garnet-rich gneiss from British Columbia, Canada. This sample has undergone extensive retrograde metamorphism in the form of impressive symplectitic reaction textures and significant replacement of Orthoamphibole Var. Gedrite ($\text{Mg}_5\text{Al}_2(\text{Si}_6\text{Al}_2\text{O}_{22})(\text{OH})_2$) by biotite $\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$. For petrologists, tying the compositional information to texture is key to understanding the formation processes. In order to interpret the petrogenetic history of the sample, it is necessary to trace the compositional evolution of the sample, particularly for the peak and post-peak tectonic journey recorded in the garnet compositional zoning and reaction textures across the sample. ColorSEM Technology makes this task straightforward since compositional mapping happens automatically, freeing the operator to focus on data interpretation.

In geosciences applications, the context of the data is often as important as the data set itself. For example, compositional heterogeneity often varies over distances greater than the normal field of view of a typical SEM. Because ColorSEM Technology enables fully quantitative X-ray elemental maps to be acquired over short timescales, this enables analysis over multiple fields of view in practical timescales. Figure 28 shows a large area quantitative X-ray map using the Navigation Montage feature, a feature that collects multiple images over a wide area automatically, to create a single image from 13 x 13 frames and a total field of view of approximately 8mm. Quantitative X-ray maps were acquired at approximately 30s per frame, giving a complete acquisition time of around 90 minutes. This is at least an order of magnitude faster than would be achievable using traditional techniques.

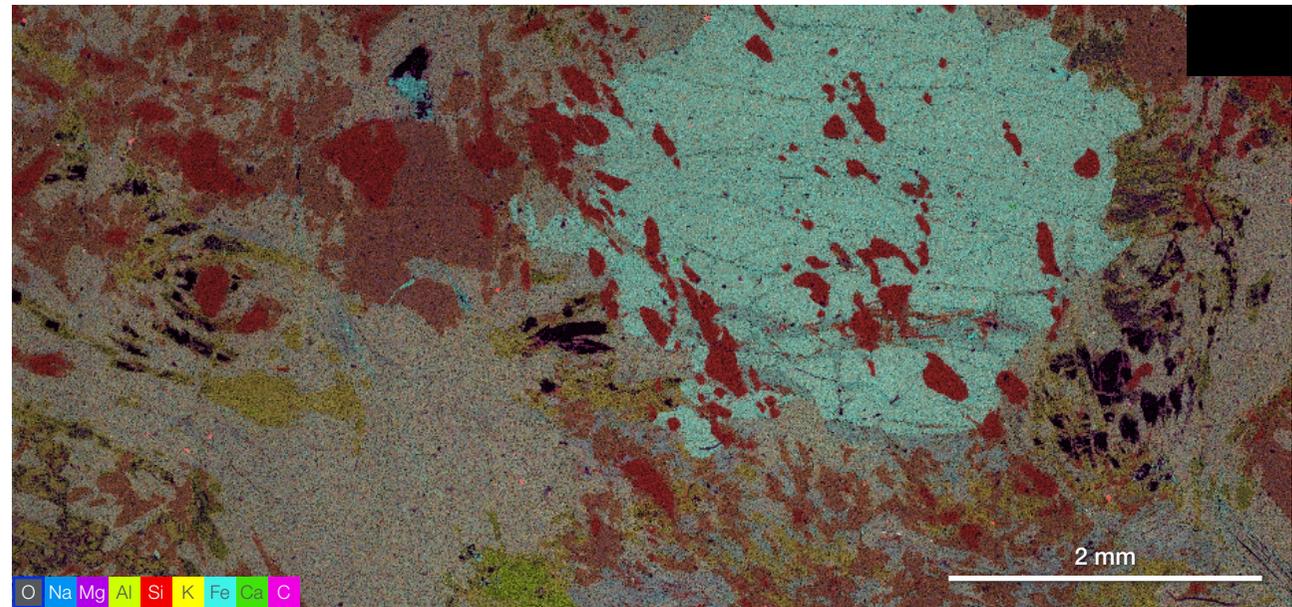


Figure 28: ColorSEM Technology navigation montage. Acquisition parameters: 13x13 images acquired. (5s per frame, 6 frames integrated per image). Total acquisition time= ≈90 mins. The electron image is overlaid in the upper right corner to illustrate the size of the individual frames.

The montage tool is useful for identifying key textural and chemical relationships, providing more complete information of the chemical variability within the grains over a large thin section. The instantaneous nature of ColorSEM Technology data permits the user to identify areas of interest for further analysis. For example, the garnets in this sample (Large, light blue grains) have reaction textures on the perimeter of grains, and as well as along fractures.

ColorSEM Technology reveals the compositional fingerprint of these textures and provides additional guidance for obtaining quantitative data via point analysis and linescans to understand the compositional gradients preserved by the metamorphic reaction. The black and white area highlighted in the top right corner of the image, which illustrates the size of a single frame, is shown in Figure 29 left. This shows that ColorSEM provides accurate visualizations of chemical variation, even in natural samples with complicated microstructures. These data help the geologist in this example to properly choose locations for more precise WDS measurements and, for this location, develop datasets for thermobarometric estimates based on precise textural interpretations for local equilibrium.

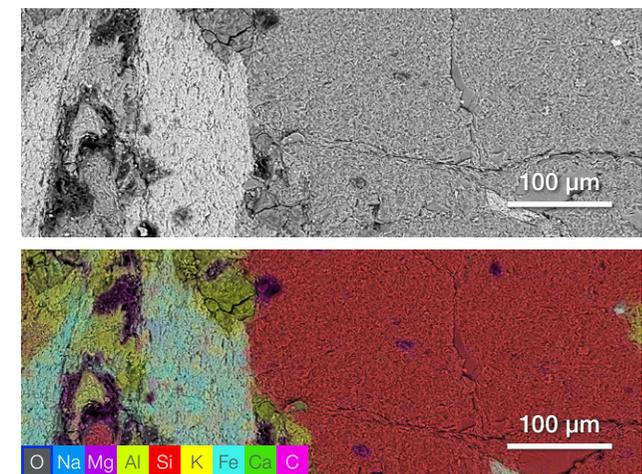
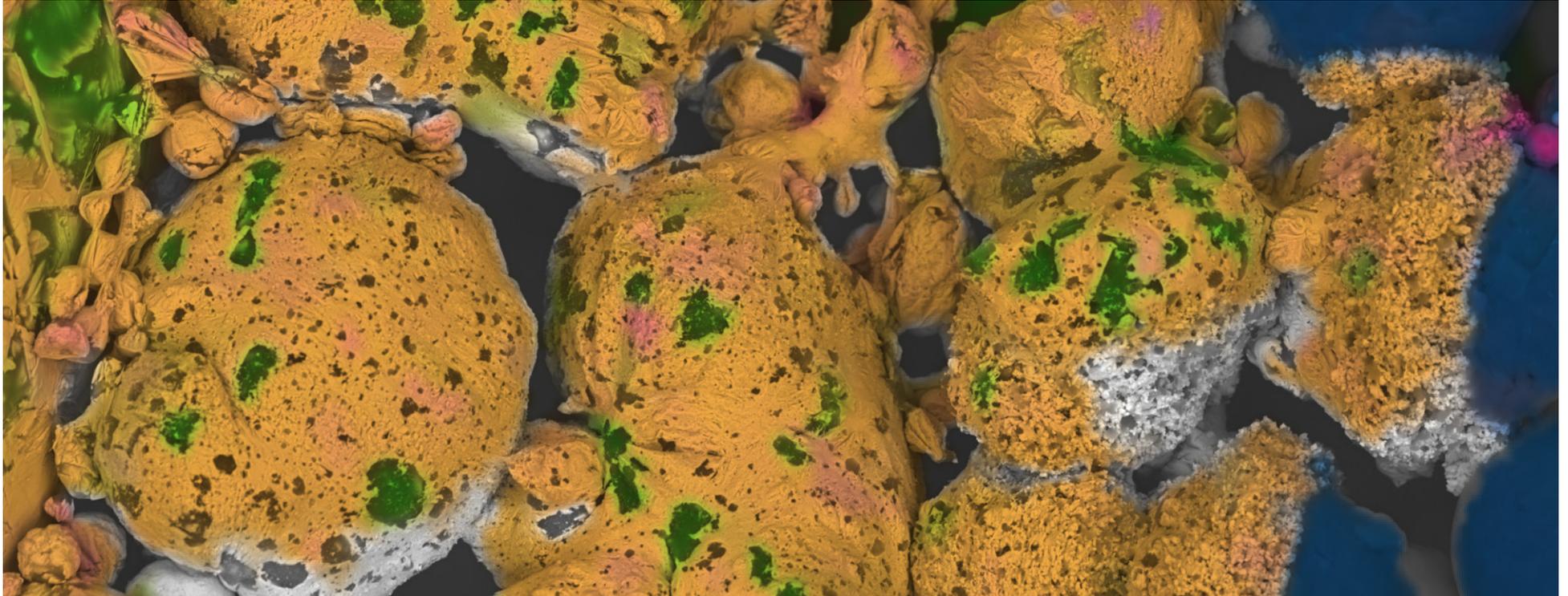


Figure 29: Single frame from the large area navigation montage presented in Figure 28 (top: backscattered electron image, bottom: colorSEM image).



AlSi₁₀Mg (aluminum precursor for 3D laser printing), bronze and gold particles. The mix has been heated up to 900 C causing the gold to migrate onto the AlSi₁₀Mg particles.

References

1. E. Gatti, P. Rehak, Semiconductor Drift Chamber – An Application of a Novel Charge Transport Scheme, Nucl. Instr. and Meth. A 225, 1984, pp. 608-614.
2. Goldstein, J., Newbury, D.E., Joy, D.C., Lyman, C.E., Echlin, P., Lifshin, E., Sawyer, L., Michael, J.R. - Scanning Electron Microscopy and X-Ray Microanalysis, Springer US, 3rd edition, 2003.

Find out more at thermofisher.com/ColorSEM