

# Trends in X-ray Microanalysis: Enabling Rapid Discovery One Pixel at a Time

## Key Words

COMPASS, EDS, Elemental analysis, Multivariate statistical analysis (MSA), Phase-based analysis, WDS, X-ray microanalysis, X-ray spectra

X-ray microanalysis has the potential to extend beyond high resolution element mapping of the obvious and not-so-obvious. The real power of X-ray microanalysis is the speed and accuracy with which it can enable true discovery – uncovering the unexpected chemical phase(s) that element-based image analysis alone cannot detect given the limitations of distilling massive amounts of spectral data into meaningful chemical composition. Such limitations prevail despite larger, higher resolution detectors and faster data capture, which provide even more data, again, without a means of extracting meaningful chemical composition. A solution, which was developed by researchers at Sandia National Laboratory, Albuquerque, New Mexico, couples elemental analysis with multivariate statistical analysis to enable true discovery. When all the data is effectively leveraged – spectral, spatial, elemental, numeric – one can draw more confident conclusions than with elemental mapping alone. This paper will explore more conclusive inferences that can be made from samples ranging from simple to complex by conducting spectrum-focused analysis on a pixel-by-pixel basis. This can lead to rapid discovery of elemental phases that are not revealed by elemental mapping alone. The Thermo Scientific X-ray Microanalysis version of multivariate statistical analysis is known as COMPASS, and is available for the NORAN System 7 microanalysis system and its EDS and WDS detectors.

## The Analyst's Challenge: Arriving at a Conclusive Answer

Most experienced researchers and analysts know what to expect when examining electron images. Hence, point-and-shoot X-ray microanalysis data capture has been sufficient at verifying that expected elements actually exist. However, given the scale and complexity of today's materials and applications, simply verifying "reasonable expectations" may limit discovery – that is, discovering the existence and location of unexpected elements and compounds.

**"If you do not expect the unexpected,  
you will not find it;  
for it is hard to be sought out, and difficult."**

*Heraclitus (c.535 BC - 475 BC)*

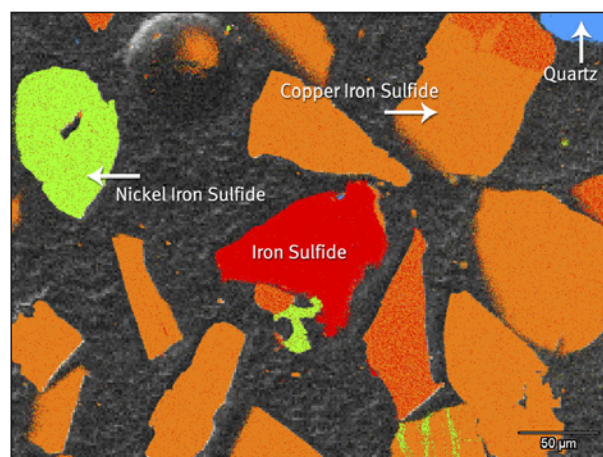


Figure 1: COMPASS automatically identifies the phases from Spectral Imaging data (256 × 192 px, 200 seconds, 150 c/p, 4000 μs/pixel)

What is the value of finding an unexpected element? In quality control and analysis applications, the value lies in the opportunity cost of allowing a manufacturing process to continue producing parts that may eventually fail in some way. For researchers, the opportunity cost is the time lost pursuing a discovery that may not yield the anticipated results.

## Applying the Conventional EDS Paradigm to Overcome Contemporary Challenges

While spectral mapping has long been associated with time-consuming image capture and analysis, today's high speed, high resolution data capture – at more than 100,000 counts per second – not only speeds the data capture process, but also provides higher resolution elemental maps resulting from sophisticated spectral imaging software. Now analysts can verify what they expect and also identify discrete, unexpected elements.

However, elements rarely exist in discrete elemental states. They exist in phases – phases whose majority content often masks the presence of an important minority element despite advances in spectral imaging

and mapping technology, such as deconvolution of spectral curves. Elements typically form compounds of atoms that commonly include oxides, sulfates, chlorides or alloys. Analysts can detect the base elements of such discrete elemental phases using conventional EDS. However, they are challenged with identifying the precise phase with an actionable degree of certainty. Equally challenging is ensuring that the final image, which begins as an electron image followed by point-and-shoot capture or element mapping, highlights the region of interest where the unexpected element is located – a nearly impossible task with point and shoot or basic element mapping alone.

## COMPASS finds elemental information other methods cannot

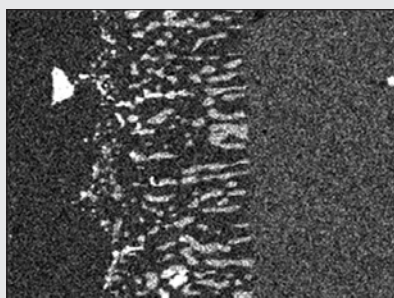


Figure 2: Gross counts elemental map of Mo-L X-rays. Increased brightness indicates more characteristic 1 X-ray intensity.

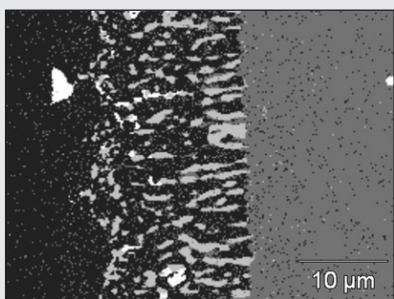


Figure 3: Phase map of five phases found in the sample. The white phase is the Nb-enriched phase.

For example, a production turbine blade was sectioned and polished for EDS analyses in the scanning electron microscope. The electron image showed sub-micron particles in a band parallel but distant to the surface of the blade. The challenge was to fully characterize the particles in the sample at low SEM beam energies. A spectral imaging data set was collected at 5 kV, 256 × 198 pixels. The nominal composition of the alloy was Ni-20Cr-12Al-4Mo.

Elemental maps of the known elements were displayed. The bands on the right and left of the particles had varying amounts of the primary elements (Ni, Cr, Al) with the region between the particles having a third composition. The particles in the central band were found to have a high concentration of Mo (Figure 2). The results appear quite conclusive; however, advance processing techniques including deconvolution and multivariate statistical analysis indicated the presence of another particle phase.

Using COMPASS software, an analysis was performed on the same data and provided map-spectrum pairs for each of the chemically unique phases in the sample. However, instead of the expected four phases as found by the elemental map method (three bands of Ni-Cr-Al and Mo-enriched particles), another particle phase was presented (Figure 3). Close examination of the phase spectrum of these new particles finds that these particles also had an enrichment of Mo-L and also a higher enrichment of

Nb-L (Figure 4). This Nb contribution was easy to miss in the original data set because of the heavy overlap of the Nb-L lines with the Mo-L lines, the very low composition of the Nb in the alloy, and the very few number of pixels contained within the Nb-enriched phase.

When the results from the COMPASS analysis found that there is an enrichment of Nb in the particles, that element was added to the elemental map list and quantitative map results were produced (Figure 5). The deconvolution routines were able to separate the contributions of the Nb-L and the Mo-L X-rays in the overlapped peak and provide elemental maps that showed the true spatial distribution of the elements. The Nb-L quantitative map reinforced the COMPASS phase map results that not all of the particles are exclusively Mo but some of the particles are enriched with Nb. Careful measurement of these particles indicates that they are between 0.3 and 0.5 μm in width.

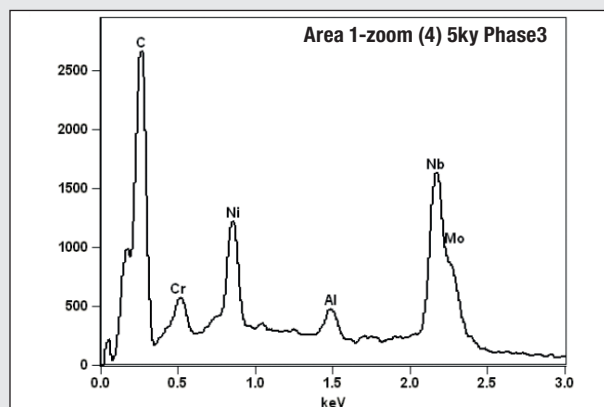


Figure 4: COMPASS phase spectrum of the Nb-enriched phase found in the sample. Note that the Nb-L and Mo-L families of X-ray lines have a very large overlap of a number of peaks, but COMPASS was able to differentiate their contributions in the two sets of particles.

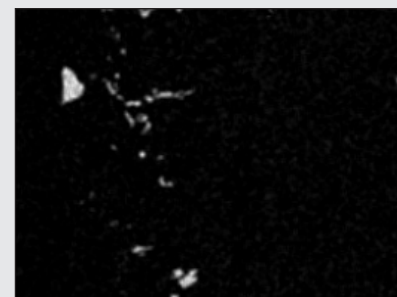


Figure 5: Nb-L weight percent quantitative map of the sample. The quantitative routines are able to extract the Nb-L contribution from the Mo-L contribution and provide the true distribution of the elements in particles.

“We examine parts – usually a visual defect such as a crack, spot or residue and must identify what it is. Our analysis is conducted on parts ranging in size from small circuit boards to very large mechanical parts. The Noran System 7 gives us direction as to where to go. Just because I don’t see something doesn’t mean it’s not there. Sometimes impurities, though small, may impact the part. I find the enhanced image allows me to see spots that appear to be the same, but are actually different. The point and shoot feature saves a lot of time in that I can shoot a specific spot, and I don’t need to go to a high resolution on each capture. Overall, the system is faster... I can get better images at a lower kV.”

*Principal Chemist at energy controls and storage company*

To date the solution has been to acquire more data from a wider area of interest and to refine the spectral images to reduce overlap – a solution, which has helped pinpoint the potential for additional elements, yet fails to provide conclusive evidence; i.e., actionable data. Thermo scientists refer to this phenomenon as the “verge of discovery.” Until the introduction of COMPASS into EDS, the only option was to gather additional data from a wider sample size or range and look for similarities – more image capture and more mapping and analysis – more work for the time-constrained equipment.

With COMPASS our scientists have discovered that conclusive evidence exists within the initial data when spectra are examined on a pixel-by-pixel basis – phenomena the scientists refer to as “discovery” – finding an element that the analyst did not know was present or the result of uncovering a completely unexpected element. Discovery brings the researcher closer to a breakthrough and the analyst closer to a solution.

COMPASS facilitates discovery. When COMPASS is employed in spectrum-focused analysis, the researcher’s and analyst’s time is optimized, and the data analysis process is streamlined. The key distinction is that instead of characterizing an entire area of interest based on a few point and shoot locations, COMPASS enables more definitive characterization because it is based on all of the spectra from every pixel in the imaged area as opposed to only a few hand chosen spectra in point and shoot. More data... yes; more time... not really; more accurate results... absolutely.

## Pixel-Focused Analysis: The New Paradigm in EDS

For the past 30 years, elemental maps and filter-based correction of peak overlaps in quantitative maps have represented a good start in identifying “hidden” or discrete elements. However, such elements remain just that – discrete elements. Rapid discovery is about making the connection between discrete elements to infer deeper conclusions about elemental mixtures (ratios) with greater reliability and confidence and to do so quickly and repeatably.

Traditional EDS analysis: Obtain the X-ray spectra and then immediately transform those spectra into atomic identity in order to quantify detected atomic elements – poses inherent drawbacks, which can introduce errors. Ultimately, discovery is constrained at the expense of additional time and resources. Given that the data quantified from the original, global spectrum forms the basis for *all* further analysis or interpretation of the sample. Working with the base X-ray spectra at each pixel throughout the analysis provides several major advances and overcomes the drawbacks inherent in traditional EDS.

“We use the NORAN System 7 for defect analysis. Often I find that the defects primarily originate in the raw materials. The system helps me identify the composition and where it came from. I have two detectors going at 40,000 counts per second, which reduce shadows and quickly provide high resolution and a lot of data. Now I can prove beyond the shadow of doubt. Mapping indicates hot spots, which are right on top of the defects, and the system helps me make a very rapid determination of the origin of the defects. What used to take me all night, I can do in about 15 seconds. We’re manufacturing, so time is money.”

*Laboratory Analyst at leading coatings and adhesive manufacturer*

## Rapid Discovery: Gaining More Accurate Answers Faster with Less Acquired Data

By working with mapped spectra and avoiding peak identification and quantification until the very end – or by avoiding it all together – analysts can arrive at more accurate answers faster with less acquired data and eliminate user or “black-box” algorithm bias.

“All entities move and nothing remains still.”

*Heraclitus (c.535 BC - 475 BC)*

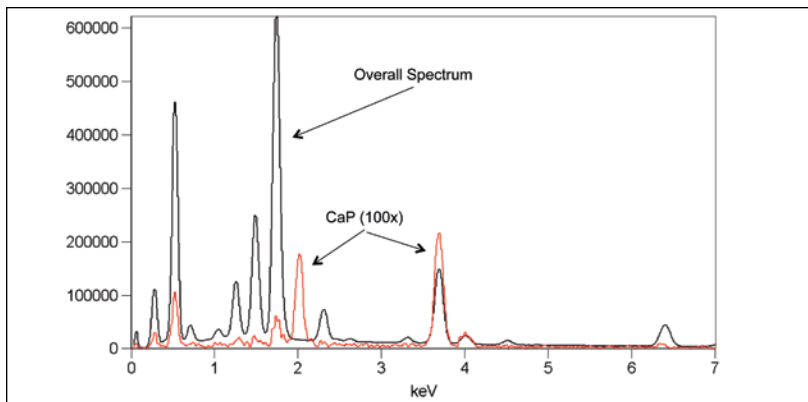


Figure 6: Spectral display showing the overlap of the cumulative spectrum from all pixels in a spectral imaging data set (black) and the spectrum from very small particles of a Ca-P enriched phase (red). Note that the amplitude of the P peak at ~2 keV cannot be detected with conventional peak identification routines.

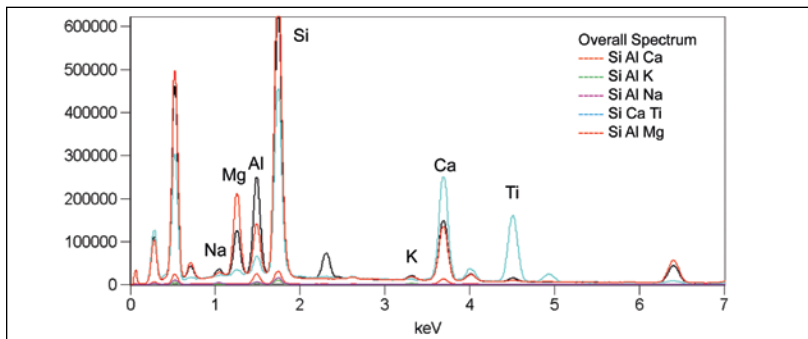


Figure 7: Spectral display of the overlap of the cumulative spectrum and a number of Si-Al-X compounds found in the sample. Trying to distinguish the elemental overlap in the spectra and specific location in a map can be a difficult task even for experts unless statistical techniques are used.

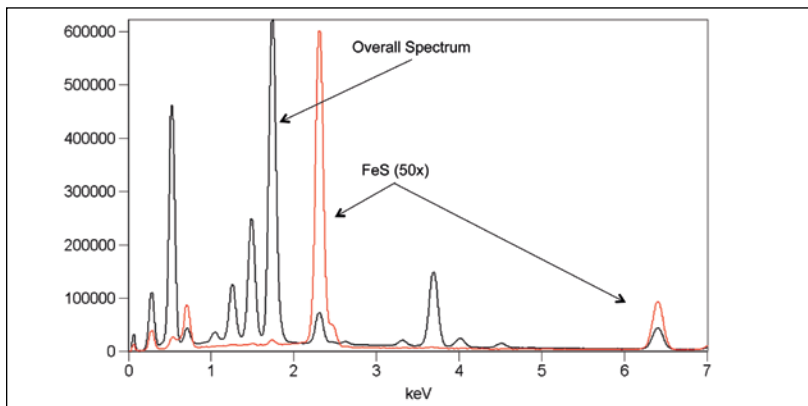


Figure 8: Spectral display showing the overlap of the cumulative spectrum from all pixels in a spectral imaging data set (black) and the spectrum from small particles of a Fe-S phase (red). By extracting the spectrum of the Fe-S particles, a correct determination of the composition can be made.

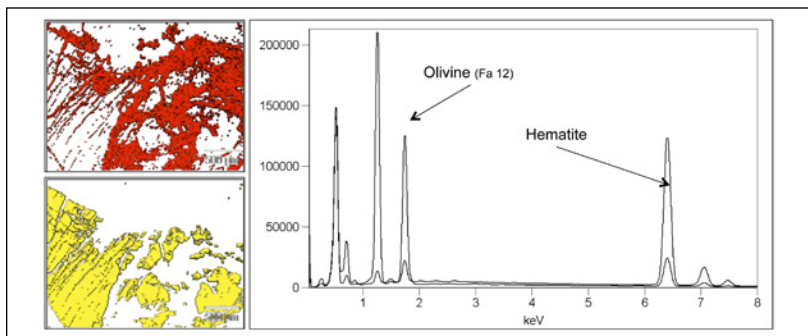


Figure 9: Compound maps and spectra for Olivine and Hematite found in the analysis area. The compounds were identified by matching each spectral shape to the best match in a database of compound shapes, not by traditional spectral peak identification methods. COMPASS performs spatial separation before peak identification and aids in spectral deconvolution of peaks.

Any modern analyzer will run an advanced deconvolution scheme to properly separate, identify and quantify overlapping peaks. Manual intervention is typically also allowed. In traditional EDS data processing, any errors in this deconvolution or identification or quantification process will be carried forward through all further analysis and interpretation. In modern EDS data processing, COMPASS accelerates interpretation with less data and time.

**Three examples show how mapped spectra can improve accuracy and speed discovery.**

**1. Ensure the early detection of minority elements with greater accuracy.** When the deconvolution, identification or quantification process fails to detect a minority element located in a specific region of the sample the analyst unknowingly eliminates any analysis of that element from the outset. (See Figure 6.) However, when investigating individual pixel spectra, these minority elements are easily found and reported to the analyst for interpretation.

Additionally, many materials are composed of multiple phases that incorporate the same base composition but are each uniquely defined by a specific minority element. These spectra are nearly identical and typically involve significant peak overlap. Separating the phases via spectral analysis is far more effective than attempting to quantify the whole spectrum and using that as a basis for phase identification. COMPASS can find these subtle differences and report them to the analyst. (See Figure 7.)

**2. Speed and simplify analysis of complex geological samples.** Advanced deconvolution may prove unnecessary or may be better performed on a simpler set of spectra. Figure 8 shows an FeS phase embedded within a complex geological sample. Separating the spatially unique FeS phase first and then quantifying the associated spectra involves a vastly simpler – and therefore more accurate – analysis.

**3. Eliminate non-value added analysis and hasten phase identification.** In Figure 9, the analyst avoids peak identification altogether and instead matches the sample against a pre-defined spectral library to quickly identify hematite intermixed within olivine based on spectral identification.

“When comparing this software package to similar software packages, we like the additional control on EDS range (kV), spatial mapping options (dwell time, refresh rate, drift correction, etc), post processing tools, and the choices in point-and-click (size, contrast, time, etc.)”

*Senior Research Scientist at leading coatings producer*



### Pixel-by-Pixel Spectral Data: The Discovery Engine

Until the advent of COMPASS, conventional element mapping was the only efficient method for characterizing a sample with EDS. Thus, point-and-shoot data capture coupled with elemental mapping became the analyst's preferred method for elemental characterization.

Although point-and-shoot sample measurement takes approximately five minutes, analysis time is still significant in mapping, deconvoluting the spectral curves and arriving at an answer that may not be an accurate representation of all elements present in the sample.

On the contrary, beginning the analysis with image capture but rastering the area of interest to capture spectra at each pixel within the area of interest can drastically reduce time spent analyzing the data, eliminate the need to conduct further measurements and provide more conclusive results. Rastering the whole field-of-view may take only as long as a traditional multi-spectrum analysis; however, COMPASS automates the identification of phases to quickly and accurately characterize the sample in far less time than conventional EDS spectral analyses.

For example, the following sample indicates sulfide compounds embedded in epoxy. The electron image contrast is insufficient to identify the phases.

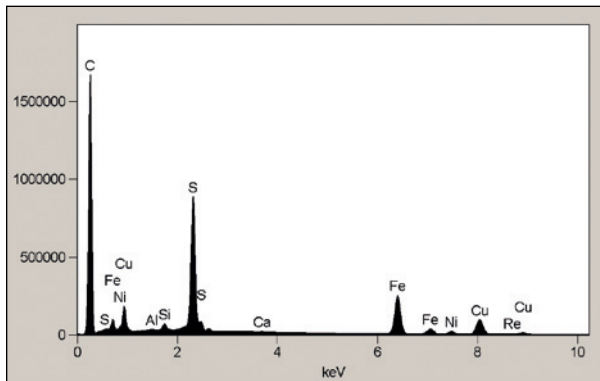
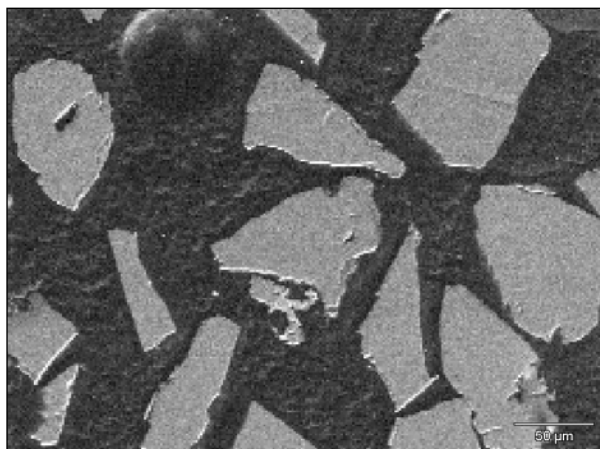


Figure 10: The spectrum indicates significant Fe, Cu, S in C epoxy binder

Applying COMPASS and referencing a Match Library for sulfides, the software automatically identifies the phases from the spectral image without additional input and arrives at the same answer even when sparse data is collected.

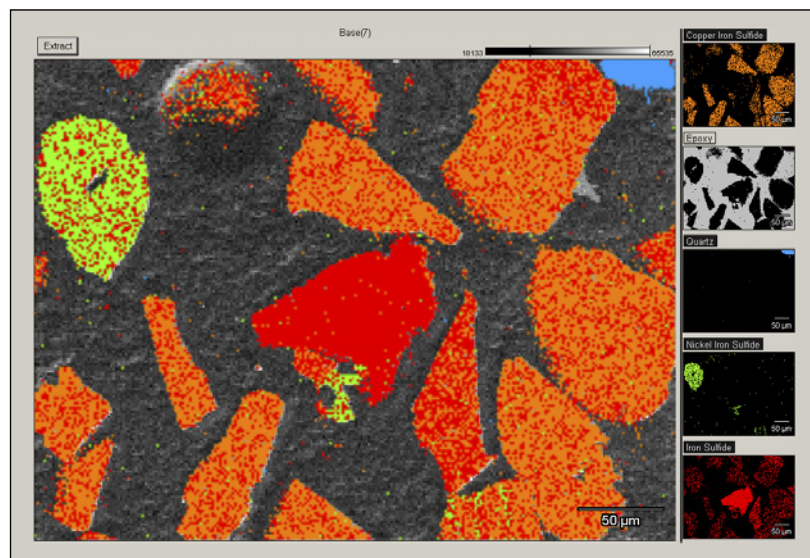


Figure 11: 256 × 192 pixel acquisition, 15 counts/pixel

In the next example, defect analysis of a turbine, beginning with pixel by pixel spectral data at the onset of analysis enabled the analyst to automatically distinguish subtle detail of the phases outside of the majority region. The following electron image indicates two unique phases exist within the material.

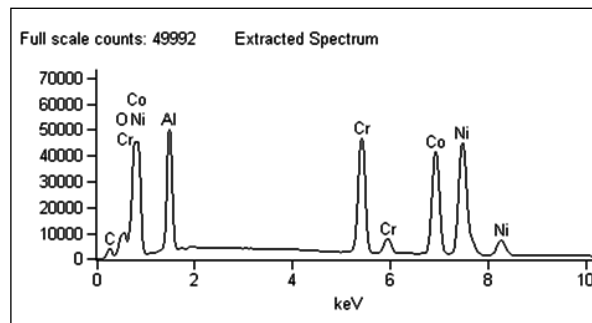
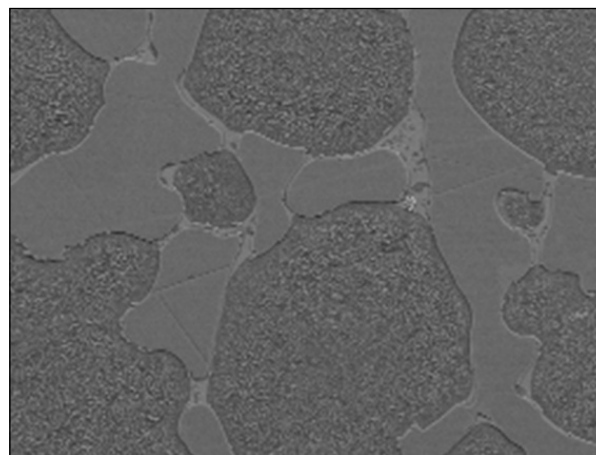


Figure 12: The spectrum indicates significant Ni, Co, Cr, Al

Although quant maps of the analyzed region identify the two phases qualitatively as NiAl-enriched and CoCr-enriched phases, COMPASS enabled the analyst to automatically identify the same phases, but also finds an additional Y-enriched phase, thereby locating and quantifying a chemical not obvious to the analyst.

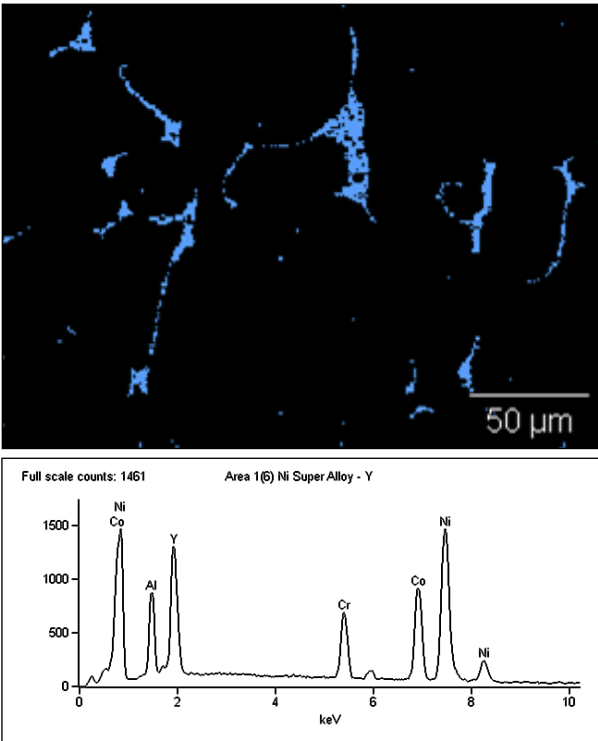


Figure 13: Going a step beyond Quant maps, COMPASS automatically identifies an unexpected phase in the sample.

In the final example, analysts examine a sample of the Huckitta meteorite to understand all of the phases in the sample.

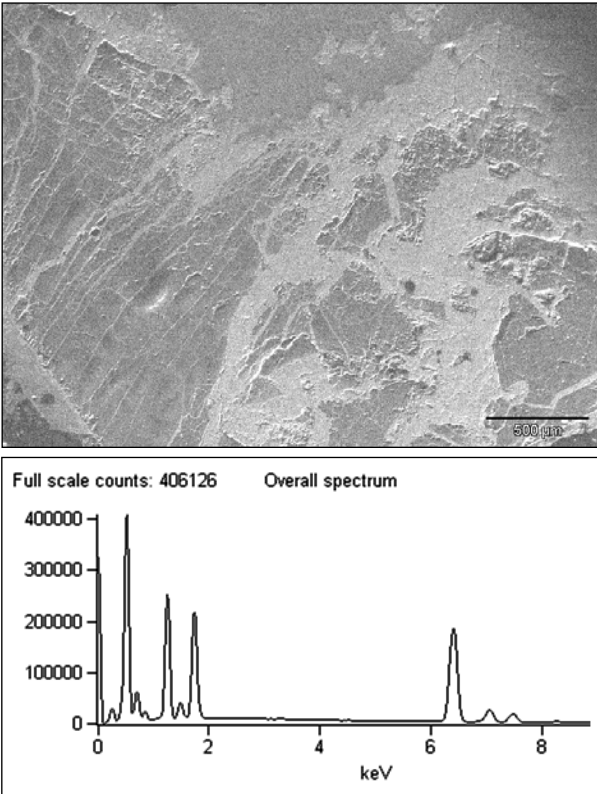


Figure 14: SEM image at 45× magnification and associated spectrum (5.7 microns/pixel)

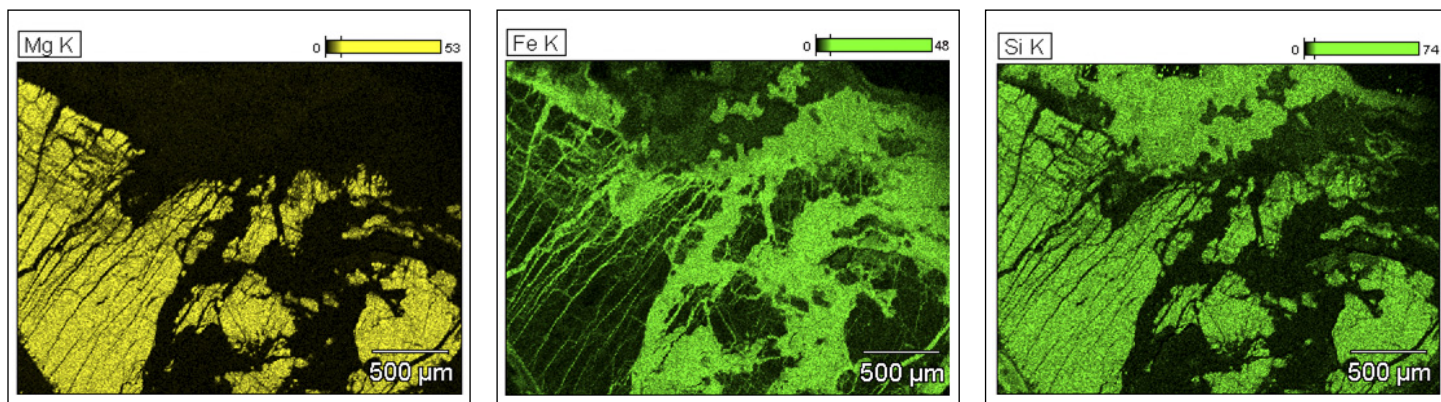


Figure 15: Quant maps indicate three primary elements – Mg, Fe and Si

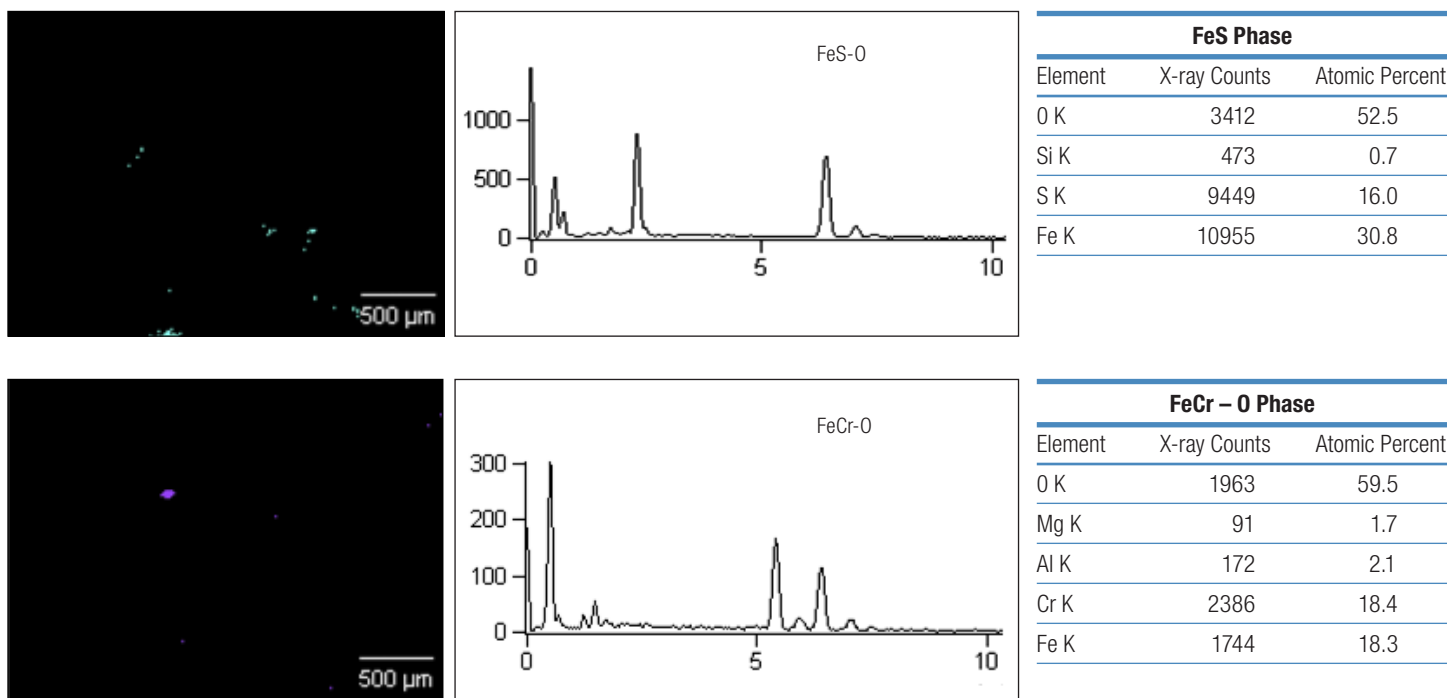


Figure 16: COMPASS also automates the identification of phases that are unexpected and would otherwise go undetected.

Although the quant element maps indicate three primary elements, COMPASS automatically identifies the distinct phases within the map including Hematite, Olivine,  $\text{SiAlFeNi-O}$ , and  $\text{SiFeNi-O}$ ; all of which the experienced analyst would expect to see. However, in addition to the previously mentioned distinct phases, COMPASS identifies two additional phases defined by previously unknown trace phases –  $\text{FeS-O}$  and  $\text{FeCr-O}$  – and also identified the unique phase which they compose. (Figure 16.)

With COMPASS the analyst can automatically map the location and quantity of the majority elements – same as conventional EDS. COMPASS also identifies the majority phases, but also finds unknown trace phases that quant mapping could not detect.



## Conclusion

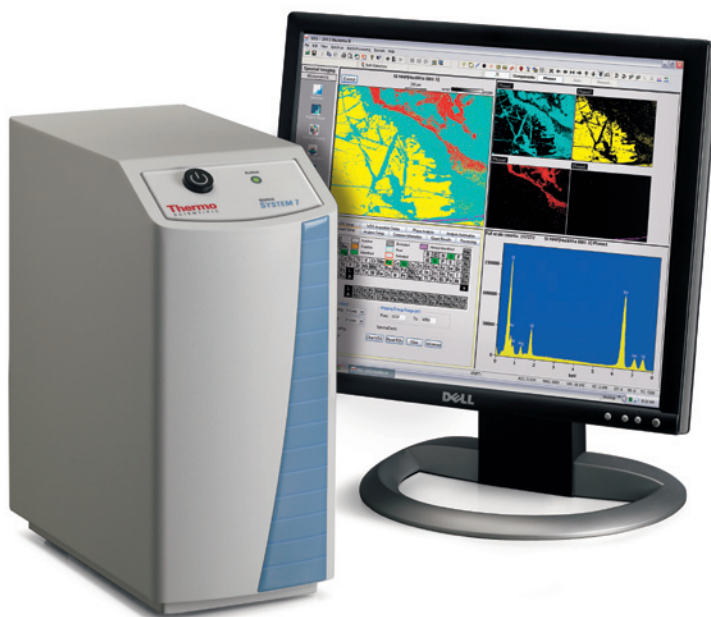
Discovery by today's standards means consistently coming to the right conclusion faster and more accurately. Accelerating discovery can bring greater efficiencies to quality control analysis and expedite research and development. The conventional EDS workflow limits discovery and does not result in an accurate representation of all elements present in the sample. Conventionally, the EDS workflow begins with a single measurement of an area of interest rastered to generate X-ray spectra. The modern EDS workflow begins with the collection of a spectrum at each pixel in the image and is created in about the same amount of time. The application of COMPASS hastens and automates discovery by generating spectral phases from which it automatically maps and types discrete elemental phases. From these spectral phases, researchers and analysts can infer with great confidence. The benefit to the analyst is twofold – first it enables the rapid discovery of unexpected elemental phases, and second, it does so more efficiently and repeatably from a single measurement of the area of interest.

"I use COMPASS for diffusion analysis because it provides a much better visual than point and shoot. It helps me find anomalies that point and shoot may miss.

I also use COMPASS for R&D because the quick turnaround time allows research to progress more rapidly. Once researchers realized the quick turnaround time, they submitted more samples that they otherwise couldn't afford to submit. This resulted in them gaining critical knowledge that they would have missed.

The system has more than doubled productivity and makes my job easier."

*Research Analyst, Aerospace Industry*



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