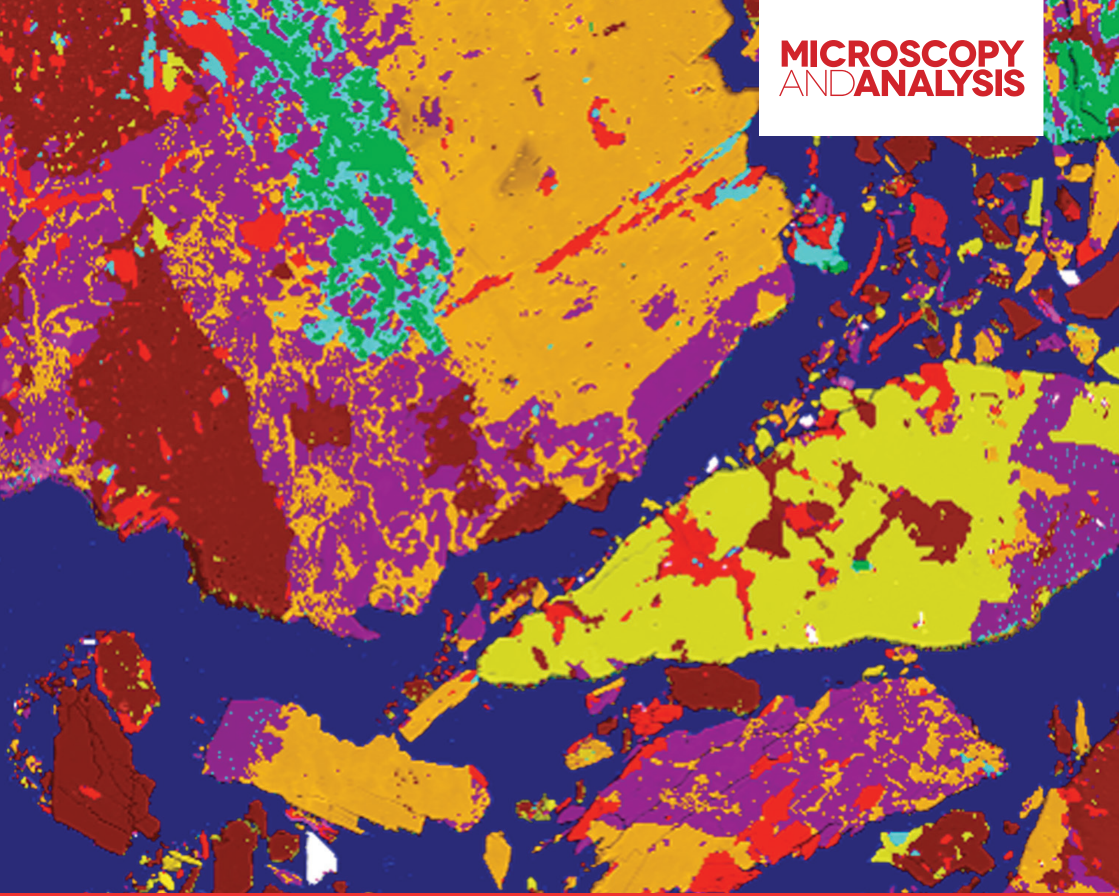
MICROSCOPY AND ANALYSIS



Energy Dispersive Spectroscopy

Essential Knowledge Briefings

EDAX
Smart Insight
AMETEK
MATERIALS ANALYSIS DIVISION

Front cover image courtesy Tara Nylese of EDAX. The aggregate material in the phase map image shown here contains various silicates and aluminosilicates with additional element substitutions. The displayed colors represent nine compound phases combined on the backscatter electron image. The full field width is 525µm.

Microscopy EKB Series Editor: Dr Julian Heath
Spectroscopy and Separations EKB Series Editor: Nick Taylor

CONTENTS

About Essential Knowledge Briefings

Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Reviewed and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each speciality. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION

As its name suggests, X-ray microanalysis involves using X-rays to study very small scales, down to the micro or even nano and atomic levels. Although there are many different microanalytical techniques, each with its own advantages and disadvantages, none is better than X-ray microanalysis for the routine chemical analysis of small volumes.

In general terms, X-ray microanalysis relies on the ability to detect X-rays generated when a specimen is bombarded with high-energy electrons in an electron microscope, with the method used to detect the X-rays defining the exact form of the technique. The X-rays can be detected using a crystal spectrometer fitted with a diffracting crystal to choose the wavelength of interest, or they can be detected with an energy-dispersive spectrometer, which can separate X-rays with different energy levels. The former is called wavelength-dispersive spectroscopy (WDS) and the latter, and the subject of this briefing, is called energy-dispersive spectroscopy (EDS).

Over the past decades, EDS has become firmly established in the scientific community. As a testament to this technique's popularity, virtually all universities and research centres now have their own EDS systems for microanalysis. With the cost of EDS systems falling all the time, more and more undergraduate students are now being exposed to this technique.

As a ripple effect, industrial applications are also on the increase, as young professionals bring this knowledge to their workplace. A further boost comes from the fact that significant technological improvements have produced more user-friendly systems, allowing even inexperienced analysts to start using EDS with ease. As a result, EDS has become a useful analytical tool in many areas, from materials science and nanotechnology, to biology and microelectronics.

After a brief look at the contributions of some of the great names associated with the development of EDS, this briefing explains the fundamentals of the technique and details the necessary X-ray instrumentation. The discussion takes a decidedly more practical tone in the following section, reviewing potential manipulations to the system for maximizing output and methods for analysing the results, among other issues. After a few tips to deal with common problems, the briefing concludes with prospective developments to come.

HISTORY AND BACKGROUND

Energy-dispersive X-ray spectroscopy (EDS) is a powerful – yet easy to use – technique that is ideal for revealing what elements – and by inference chemical compounds – are present in a particular specimen. Basically, EDS consists of detecting the characteristic X-rays produced by each element after bombarding a sample with high energy electrons in an electron microscope. Using a process known as X-ray mapping, information about the elemental composition of a sample can then be overlaid on top of the magnified image of the sample.

What makes EDS particularly useful is that the amount of X-rays emitted by each element present in a sample bears a direct relationship with the concentration of that element (mass or atomic fraction). This is why it is possible to convert the X-ray measurements into a final X-ray spectrum and assess the concentrations of the various chemicals present in a sample.

Several disciplines regularly utilize EDS, including a broad range of physical and chemical sciences, electronics and even forensic investigations. Undoubtedly, however, the discipline that has benefited most from EDS is materials science. Here, it can be used to identify and evaluate materials, including detecting contaminants or determining unknown elements, as well as for quality control screening, verification and certification. In practice, EDS's range of applications encompasses alloy design, analyzing pigments in historical documents, conducting environmental studies of pollution particulates, investigating insurance claims and monitoring asbestos levels in construction.

After the discovery of X-rays in 1895, researchers soon realised that the X-rays rays emitted by excited atoms are intimately connected with their atomic structure. As the atomic structure of each element is different, it follows that, when stimulated, each element emits a specific pattern of X-rays.

By the early 1920s, the patterns associated with most elements had been recorded. This knowledge, combined with the development of the electron microscope during the 1930s and 1940s, gave rise to the first attempts to excite specific specimens in order to measure the resulting X-rays.

However, it wasn't until 1949 that Raymond Castaing, working as a research engineer at the Office National d'Etudes et de Recherches Aeronautiques (ONERA) in France, developed the first static beam electron microscope. This involved fitting a new objective lens (to allow the passage of X-rays), a diffraction crystal and a Geiger counter (as the detector) to a commercially available electron microscope. His PhD thesis, entitled 'Application des Sondes Electroniques à une Methode d'Analyse Ponctuelle Chimique et Crystallographique', published in 1951, sets out the principles for X-ray microanalysis, still valid today.

In 1968, R. Fitzgerald, K. Keil and K. Heinrich at the University of California, San Diego, USA, developed the first lithium-drifted silicon, Si(Li), detector to measure X-ray photons of different energies virtually simultaneously. The presence of impurities and imperfections in the silicon crystal were 'compensated' by a process known as lithium drifting, in which lithium atoms are allowed to diffuse into the crystal.

During the 1970s, Si(Li) detectors became extremely popular, as researchers started to appreciate the versatility of microanalysis. When using these detectors, this technique, initially referred to as non-dispersive analysis, eventually became known as energy-dispersive X-ray spectroscopy or spectrometry.

Nowadays, Si(Li) detectors are all but gone from manufacturer's product lists, replaced by faster and more efficient alternatives. Developed in the 1970s, one of the first of these alternatives was high purity germanium (HpGe) detectors, boasting higher efficiency and resolution. Comparing the new HpGe detectors with the older Si(Li) detectors, J. Patton and A. Brill at the Vanderbilt University Medical Center in the USA confirmed these claims. The researchers showed that, due to the greater efficiency of germanium, the overall spatial resolution could be further improved by adding a collimator to narrow the beam of emitted X-rays.

Like a trend that comes back into fashion, the latest detectors rely once again on silicon. Invented by E. Gatti and P. Rehak at Brookhaven National Laboratory in New York, USA, in 1983, silicon drift detectors (SDD) use the same physics as Si(Li) detectors, but significant design changes improve their sensitivity. Fortuitously, Gatti and Rehak developed a system that can operate much closer to room temperature with just moderate cooling. These improvements make complex applications, such as detecting small inclusions in ultrapure materials or defining the complex chemical composition of aggregate particles, a possibility.

A further important development occurred in 1995, when John Friel and his team at Princeton Gamma-Tech in the USA, now part of Thermo Fisher Scientific, developed a method known as position-tagged spectrometry (PTS). The great advantage of this method is that it allows an entire spectrum to be stored at every pixel in the scanned image.

Nowadays, an EDS system typically consists of several key units (Figure 2). These include: a semiconductor detector housed with a field-effect transistor (FET) preamplifier, often in a cryostat

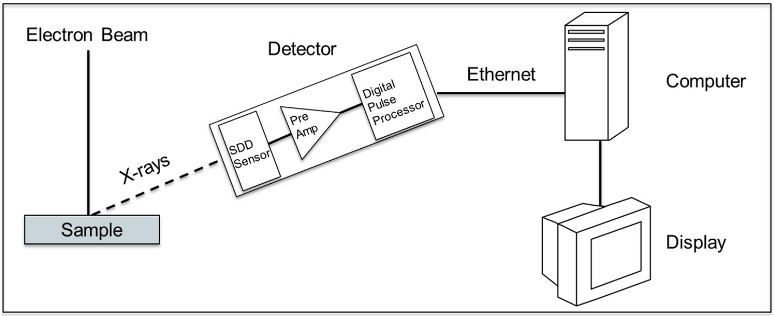


Figure 1: Components of a modern digital energy dispersive spectroscopy system.

cooled with liquid nitrogen; and a main amplifier that provides further amplification and a fast pulse inspection function to reduce pile-up events (see In Practice). All of this can be fully controlled with a computer-assisted system, such as a multichannel analyzer (MCA) or a computer-assisted X-ray analyzer (CXA), allowing for unattended and automated operation.

When the electron beam hits the sample, there is a high probability that an X-ray will be generated. The resulting X-ray escapes the sample and hits the detector which creates a charge pulse in the detector. This short-lived current is then converted into a voltage pulse with an amplitude reflecting the energy of the detected X-ray.

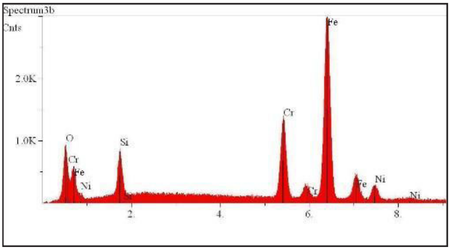


Figure 2: An energy-dispersive X-ray spectrum showing the main elemental peaks superimposed on the background.

Finally, this voltage pulse is converted to a digital signal and one more count is added to the corresponding energy channel. Once the measurement is completed, the accumulated counts produce a typical X-ray spectrum with the major peaks superimposed on the background (Figure 2).

High-energy electrons can interact with atoms in a sample in many different ways, including stimulating the emission of X-rays. In this case, when an electron (from the beam) strikes an atom, it ejects an electron originally positioned in an inner shell (K shell). To return the atom to its lowest energy state, this 'vacancy' is immediately filled by an electron moving from a higher-energy shell in the atom. In doing so, this high-energy electron must release some of its energy in the form of X-rays. As a consequence, the energy released (expressed in eV) is exactly equal to the energy difference between the two levels (Figure 3).

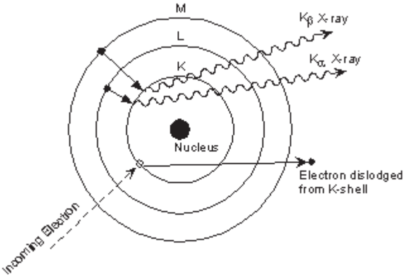


Figure 3: Excitation and emission in an atom.

To complicate the situation further, several electrons at several energy levels can potentially occupy the 'vacancy', with each releasing different amounts of energy. As a result, even a pure sample will emit X-rays at different energies. For example, if an L-shell electron drops, it emits Kα X-rays, whereas an M-shell electron emits Kβ

X-rays, with Kβ radiation possessing more energy than Kα radiation (the energy difference between M and K is higher than between L and K). However, because the most probable transition is the L to K movement, Kα radiation will always be more intense than Kβ radiation.

All elements except hydrogen and helium produce characteristic X-rays. In addition, practical restrictions concerning a minimum energy level usually exclude the measurement of lithium (0.052 keV), but all other elements, beginning with the beryllium K-shell (0.108keV), can be assessed simultaneously. Electron beams in the range of 100 eV to 20 keV are readily measured with a Si(Li) or SDD detector, and this range can be extended to 100 keV with an HpGe detector. It is this 'energy dispersive' approach that provides the great practical value of EDS, as it enables access to virtually the entire periodic table (except H, He and Li).

In addition to scanning electron microscopes, EDS systems can also be coupled to transmission electron microscopes (TEM) forming what is commonly known as an analytical electron microscope (AEM). The principle is essentially the same, but limitations concerning how the electron beam penetrates the sample results in more refined measurements in TEM-EDS, whereas SEM-EDS can struggle to identify and measure trace elements. Extra thin samples in TEM (around 10–20 nm) cause minimal spreading of the electron beam as it crosses the sample, but the larger samples analyzed by SEM systems cause more backscattered electrons to reach the detector, affecting the accuracy of the results.

IN PRACTICE

To produce the best possible X-ray spectra for subsequent analysis, it's essential to be aware of what manipulations are possible within the system. The main point to consider is the balance between the count rate (counts per second, expressed as kHz) and resolution. Extending the period for measuring each X-ray (representing low count rate), can significantly boost spectral resolution. In contrast, significantly increasing the number of counts per second will have the opposite effect. For ultimate ultimate spectral resolution, the count rate is usually kept below 2 kHz for Si(Li) detectors or below 60 kHz for SDDs. For some applications, when peaks are well defined and separated, it may be possible to increase the count rate (with the subsequent reduction in resolution) to 20 kHz for Si(Li) and 270 kHz for SDD.

Irrespective of the count rate, the period during which the detector is analysing a particular X-ray is referred to as 'live time'. In contrast, when the detector is busy processing one X-ray and cannot process the next, this is called 'dead time' and is usually expressed as a percentage of the experiment's overall time. The 'peaking time' or 'shaping time' of the electronics affect the amount of 'dead time' and spectral resolution.

From a practical point of view, it's advisable to keep 'dead time' below 30% in Si(Li)-EDS systems and below 10% in SDD-EDS systems, in order to avoid pile-up peaks and increased background noise. Pile-up peaks occur when two photons arrive at the detector at virtually the same time and are not measured as separate events but incorrectly added to the energy histogram as one single count, thus altering the results. Most current systems include an automatic correction function that makes allowances for 'dead time' and pile-up, to ensure that the analysis runs according to the user's specifications.

Another practical issue is sample preparation. Low energy X-rays in particular, such as the Kα radiation emitted by carbon, nitrogen and oxygen atoms, are strongly affected by the geometry of the sample. On a rough or fractured surface, the direction of the emitted X-rays can deviate, often quite substantially, from the ideal linear absorption path that can be achieved with a flat sample. These 'geometric effects' can inject a high dose of variability in the results, which explains why highly polished samples are preferentially used. In addition, to minimize the impact of sample morphology, software must be optimized for the specific analytical conditions.

In most cases, sample preparation is simple, and essentially the same as for reflected light microscopy. The only restriction is that samples must be compatible with vacuum conditions, as is clearly the case for minerals, polymers, metals and ceramics. Embedding and sectioning may be required for more fragile samples.

With non-conducting samples, a surface coat needs to be applied, such as a 10nm vacuum-evaporated carbon layer, to provide a way for the incident beam to cross the sample and to reduce charging effects. Crucially, this coat must have minimal impact on the electron beam and not generate unwanted X-rays.

When it comes to data analysis, two options are available: qualitative and quantitative methods. The most basic approach is qualitative analysis, which involves simply identifying what elements are present in the sample by matching each peak to an element list.

In modern analyzers, these steps can be fully automated. In some cases, the software can even compare the peaks with tabulated energy values and check for inconsistencies.

However, Dale Newbury's team at the National Institute of Standards and Technology (NIST) in Gaithersburg, USA, has recently questioned such practices. The authors argue that automation is extremely vulnerable to misidentifying even major peaks, especially for trace elements. With this in mind, the team described a possible strategy for manual qualitative analysis.

Their method involves first identifying the high-intensity peaks, including all the members of families such as the K family or the L family. For example, if a K family is identified, then a lower energy L and M family of the same element must also be located. Only after the spectrum has been examined for major constituents and all possible peaks located and marked, can the remaining low-intensity peaks be assigned to minor and trace constituents following the same strategy. A major risk of not completing the first step is that unmarked peaks may be incorrectly assigned to minor and trace constituents, rather than to low-energy family members of major constituents.

To establish not only what elements are present in a sample, but also their concentrations, the analyst must proceed to quantitative analysis. This is a common procedure in the geological and materials sciences, where researchers use information on how many atoms of each element are present to help identify their parent molecules. Knowing how many atoms of oxygen are in a sample can also be used to estimate oxidation levels.

To understand the results, it's vital to know the minimum detectability limit, which is the minimum concentration of a particular element that can be detected by the system. Transition metals such as chromium, iron, copper and nickel tend to have high count rates. As a consequence, they form well-defined isolated peaks against a low background, allowing the system to detect extremely low concentrations.

In contrast, the low energy X-rays produced by carbon, nitrogen and oxygen atoms generate much lower count rates, making it difficult to detect these atoms at low concentrations. Despite these differences, the power of the technique means that EDS can usually detect an element present in a sample at concentrations of between 1000 ppm and 5000 ppm. Although in certain circumstances it is possible to obtain a higher level of detection, this achievement is limited to a handful of laboratories in the world.

Before proceeding with the analysis, however, almost invariably the background will need to be ‘cleaned-up’. In the late 1980s, J. Small at NIST described a method to predict the ‘real’ background intensity based on the X-ray energy and specimen composition. More recently, in 2003, a team from Lehigh University in Pennsylvania, USA, led by J. Goldstein, developed a more elegant mathematical algorithm that acts as a frequency filter. Their method relies on a ‘top-hat’ filter to separate the high-energy peaks from the low-energy background.

Once the background noise has been ‘toned down’, the remaining peaks are referred to as net peaks and are ready to have their intensities evaluated. If there are no overlaps, this is a straightforward task, involving simply defining and integrating a region of interest for each peak.

This task becomes more complicated, however, if some of the peaks overlap, because these overlapped peaks must first be separated.

This is known as deconvolution and can be achieved with any of several statistical methods for estimating the relative contribution to each peak. Most commercial software systems use a method known as multiple linear least squares (MLLS), where reference peaks – peaks for each element produced in isolation – are combined to fit inside the unknown peak.

An increasing trend in quantitative analysis involves the use of 'standardless' methods, as opposed to the more traditional approach of measuring elemental standards to determine the concentration of each respective element in the sample. This new approach dispenses with standards in practical terms, instead relying on empirical calculations taking into account all the characteristics of each EDS system. Alternatively, some researchers prefer using a series of measurements performed on a remote EDS system and then adapted for each experimental condition.

This new 'standardless' approach has several advantages. It massively simplifies the operation, as there is no need to know exact parameters for each experiment. Once the X-ray spectra are complete, the analyst needs only to specify the beam energy and the elements to be analyzed, and the automated computer-assisted system provides the rest. However, Newbury's team assessed this approach and found significant errors, which the authors attributed to the uncertainties associated with the method. Nevertheless, this approach has become the norm with most commercially available EDS systems.

Finally, an increasingly popular method for analysing the results is x-ray mapping. This can be seen as the ultimate combination of x-ray spectroscopy and computer-assisted imaging. Although x-ray mapping was originally considered a purely qualitative technique, recent software developments have brought out the quantitative abilities associated with this approach. Qualitative analogue maps (also called dot maps) only had the option of dot on (element present) or dot off (element not present), but more modern quantitative digital versions can provide a continuous display associating brightness with concentration.

Initially, separate maps were created for each element (examples can be seen in images f–i in both case studies), and interpretation was done by manually combining all these maps. Current software tools, however, can produce EDS phase maps, able to evaluate all the elements present in the material, as well as their potential associations. The result is a full qualitative and quantitative analysis in a single phase map image (examples can be seen in image e in each case study).

In reality, x-ray mapping is not a new approach and since the early days of EDS researchers have used x-ray maps. For example, in 1977, J. Pawley and G. Fisher at the University of Wisconsin-Madison, USA, outlined a system for obtaining a simultaneous three-color elemental map using an SEM and an energy dispersive x-ray analyser.

PROBLEMS AND SOLUTIONS

EDS systems are simple to run and are capable of long-term operations with a high degree of reproducibility. Occasional problems do occur, even in a well calibrated system, and it's the user's responsibility to be aware of and to recognize such conditions. However, one of the biggest difficulties that research labs face is a general lack of dedicated analysts. Anybody can put a sample into the microscope, but it's essential to have somebody that really understands the output to analyze the results.

One of the most common errors made by EDS novices is peak misidentification. For trace elements, this problem is exacerbated by the diminishing number and size of detected peaks. In an attempt to minimize this problem, software manufacturers have incorporated several default conditions in their systems, which can be selected at the simple push of a button. However, this approach has attracted some criticism, with researchers arguing that analysts already rely too much on automated systems. The suggested solution is always to confirm any peak identifications manually, using the automated version only as a starting point for an analysis.

Turning to the equipment, several factors can affect the operating environment of an EDS system. For example, it's impossible to prevent electrons scattered by the specimen from reaching the detector, where they are measured as if they were X-ray photons. This is, in fact, one of the causes of background noise. Simple suggestions for avoiding this problem (and improving accuracy) include adding collimators, magnets or electron traps to the EDS system. Without these relatively inexpensive items, the effects of scattering can substantially hamper the performance of the detector, producing a high level of background noise.

Build-up of ice on the detector, as a result of cooling by liquid nitrogen, is another factor that may affect its performance. An easy way to find out whether this is happening is to analyze a polished high-purity nickel sample. Nickel produces two peaks, one at 0.849 keV (Ni-L) and one at 7.477 keV (Ni-Kα). Interestingly, Ni-L is very susceptible to absorption if there is ice build-up, while Ni-Kα suffers negligible impact. The trick is to compare the ratio between these two peaks to diagnose whether or not ice is affecting the detector. With SDDs operating at much higher temperatures, icing is much less of a problem than in the past.

An additional problem is caused by pile-up peaks (also called sum peaks), which occur when more than one X-ray enters the detector at nearly the same time. Most currently-available software offer the possibility of identifying where these peaks may be occurring, allowing the user to decide whether they're pile-up peaks or not. Some software developers have gone further and developed a routine that calculates the expected magnitude of the pile-up peaks and then removes those counts from the spectrum. As a final touch, it adds them back to the real peak. Despite these efforts, the success rate with these approaches is questionable and pile-up peaks are frequently misidentified by automatic identification software.

Lastly, there is the issue of calibration. A miscalibrated system will shift peaks to an improper energy, increasing the risk of misidentification. Typically, the system is calibrated by using test peaks of known energy, covering the full analytical span (typically from 100 eV to 12 keV). A common material for producing these test peaks is pure copper, which provides peaks at 0.93 keV (Cu-Lα), 8.04 keV (Cu-Kα) and 8.68 keV (Cu-Kβ). If further calibrations tests are needed, low energy peaks can be assessed with C-Kα (0.285

keV) and O-Kα (0.533 keV), intermediate energy peaks with Ti-Kα (4.50 keV) and Fe-Kα (6.40 keV), and high energy peaks with Pb-Lα (10.5 keV).

Despite the need for constant monitoring, the stability of modern systems is such that calibration tests need only to be performed on a quarterly basis. If there is a need for a system shutdown, it's essential to allow a few hours to re-establish equilibrium in the electronics and check calibration before resuming use.

One potential cause of miscalibration are pinholes or imperfections in the thin aluminum layer that covers the window protecting the crystal detector, which can lead to the detector being exposed to visible light. This problem is exacerbated when analyzing specimens capable of producing visible light under electron bombardment, in a phenomenon called cathodoluminescence, with the light from both sources seriously affecting the results.

In terms of applications, EDS has stayed mostly in the realm of materials science and nanotechnology. So far biological applications have been considered a niche application, mostly due to the difficulties of sample preparation. In contrast to the simple preparation for other materials, which involves little more than polishing the sample, the preparation of biological samples is far from standard, requiring cryotechniques to stabilize element positions and carbon coating to minimize charging.

Despite these difficulties, however, some research laboratories have gone to extreme lengths to adapt their specimens for EDS. This includes, for example, Sabine Agatha's team at the University of Salzburg, Austria, which used EDS to study the composition of small ciliates commonly found in marine plankton. The plankton samples were originally placed in a microscopic stub covered with conductive polycarbonate plus very fine graphite. After drying for a week, they were then coated with carbonate and finally analyzed. Results clearly identified the presence of nitrogen, demonstrating the presence of proteins in these small organisms.

CASE STUDIES

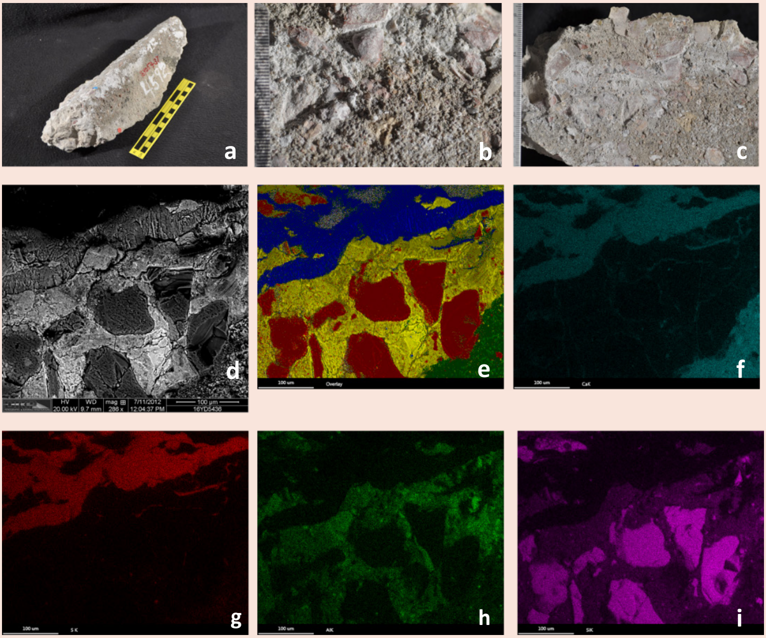
Energy-dispersive X-ray spectroscopy is one of several analytical methods used by DRP Consulting, a Colorado-based company that investigates the properties and performance of cement-based construction materials. Performing EDS in such materials can be challenging, because cement paste is hydrous and porous, resulting in low counts compared to materials such as metals and ceramics.

CASE STUDY 1

Various mechanisms can cause the structure of concrete to deteriorate over the years. One such mechanism is sulfate attack, which can severely degrade concrete over a 10–20 year period. Sulfate attack is characterised by an infiltration of sulfate ions, which, in the presence of moisture, react with the cement in the concrete. This can cause internal expansion and cracking, resulting in a significant reduction in strength.

Another mechanism is salt weathering. In this case, repeated alternation between wet and dry conditions can cause salts to crystallize, dissolve and re-crystallize in the pores of the concrete. These salts are usually sulfates such as thenardite and mirabilite, but can also be chlorides or carbonates. Salt weathering usually occurs at the concrete surface, causing progressive flaking of the outer layer, and does not result in significant alteration of cement hydration phases, unlike with sulfate attack.

When DRP Consulting received a sample of deteriorated concrete from a residential foundation, the team considered EDS to be the best way to determine which mechanism was responsible for the deterioration. The sample was characterized by a loss of the outer surface, with subsequent exposure of aggregates and formation of white deposits, probably sulfate salts. Calcium's EDS map (see image f) indicated that *sulfate attack was the most likely suspect. The absence of calcium from the central region most likely indicates leaching, which is a typical outcome of chemical sulfate attack but not of salt weathering. Knowing the sulfur distribution (see image g), it was also possible to determine the location of calcium sulfate, which showed that the attack was mostly superficial at this point.*

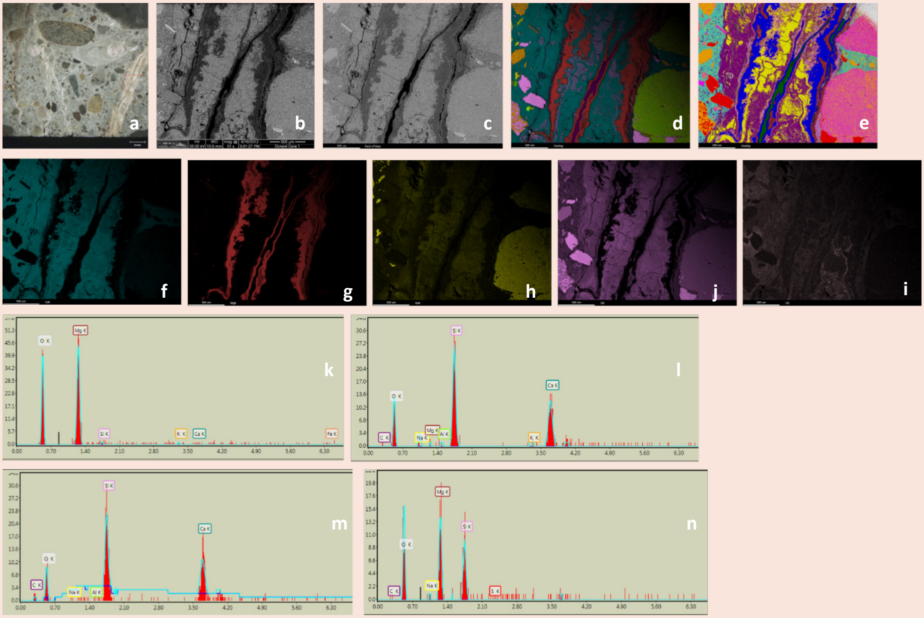


a) Photograph of received sample; this is a fragment of a multifamily residential foundation. b) Photograph showing close-up of the white deposits on the sample (scale is in millimetres). c) Photograph showing another close-up of the white deposits on the sample (scale is in millimetres). d) Scanning electron micrograph of cross-section taken through the wall; this is the area subject to EDS mapping. e) EDS phase map of area: red = silica aggregates; blue = calcium sulfate minerals; yellow = cement paste leached of calcium; green = unaltered cement paste. f) EDS elemental map for calcium. g) EDS elemental map for sulfur. h) EDS elemental map for aluminium. i) EDS elemental map for silicon.

CASE STUDY 2

DRP Consulting also resorted to EDS mapping to investigate the causes of stress observed in a sea wall affected by significant cracking, as part of an investigation to assess the best repair strategy. Light microscopy revealed cracks filled with laminated deposits of secondary reaction products, typical of a mechanism known as alkali-silica reaction (ASR). This is characterised by reactions between alkaline cement paste and silica aggregates in the concrete, producing a gel which, in the presence of water, can expand and cause cracking.

EDS analysis was again crucial for identifying the prime suspect responsible for ASR: sea water. Chlorine's EDS map (see image j) indicates where sea water infiltrated the wall. In addition, the presence of ASR by-products such as brucite and magnesium silicates, which were observed in the EDS map for magnesium (see image g) and confirmed by EDS spectrum analysis (see images l to n), further support the role of sea water. The distribution of sodium (see image h) and silicon (see image i) also show lighter areas characteristic of ASR gel.



a) Reflected light micrograph of polished surface (7.5x) showing crack with laminated secondary deposits; the red square shows the mapped area. b) Backscatter electron (BSE) micrograph (50x) of crack with laminated deposits; this is the area that was mapped. c) BSE micrograph captured by EDAX software of map area. d) Elemental map collected from region. e) EDS phase map of area: the pink, red and orange areas are aggregate particles with different compositions; the blue, violet, purple and red/brown areas are secondary reaction products; the green is carbon (epoxy). f) EDS elemental map for calcium. g) EDS elemental map for magnesium. h) EDS elemental map for sodium. i) EDS elemental map for silicon. j) EDS elemental map for chlorine. k) EDS spectrum representing composition of blue area and confirming the presence of brucite (magnesium hydroxide), which is a reaction product of sea water attack. l) EDS spectrum representing composition of yellow area, including a calcium-rich ASR gel. m) EDS spectrum representing composition of purple area, including a calcium-rich ASR gel. n) EDS spectrum representing composition of red/brown area, including magnesium silicate, which is another reaction product of sea water attack.

WHAT'S NEXT FOR EDS?

Integration is certainly the best word to describe the future of EDS. Researchers are starting to appreciate that, instead of relying on a single technique, combining various different microanalytical systems is the way forward. By using EDS to complement other techniques – from WDS, electron backscatter diffraction (EBSD) to electron energy loss spectroscopy (EELS) – scientists can take advantage of the particular strengths of EDS, in terms of speed and relative ease of sample preparation, while also benefiting from the higher resolution of WDS or the ability of EELS to determine atomic structure.

Combinations that permit researchers to overcome some of the pitfalls of EDS are likely to become particularly popular. For example, using EDS and WDS sequentially allows a more accurate characterisation of the sample in case of peak overlaps. 'Suspicious' peaks produced by EDS can be prised apart using WDS, allowing researchers to go through the sample with a fine toothcomb and really understand the chemistry of the material in fine detail.

An example of what's already possible by combining EDS and WDS comes from the University of Natural Resources and Life Sciences in Austria, where a research team led by Katja Sterflinger analyzed church window glasses showing signs of deterioration. The dual analysis identified significant differences in silica content between sodium-rich and potassium-rich glass, as well as revealing the presence of gypsum (CaSO4.2H2O), calcite (CaCO3) and other compounds in the patina covering the glass.

This is only one of many potential ways to achieve the same outcome. Other possible techniques suitable for combination with EDS include Auger electron microscopy (AEM), secondary ion mass spectrometry (SIMS) and laser microprobe mass analysis (LAMMA). This provides research teams with incredible versatility in terms of finding the combinations that are most suitable for their needs.

However, despite the benefits of attempting to improve the accuracy of EDS through integration with other techniques, the real advantage of this collaborative approach is the ability to add a new dimension to the results. A recent example, expected to become an extremely popular option in the future, is an EDS/EBSD system. This analysis can give an altogether different view of the sample, adding information about the physical arrangement of the atoms. After finding out what elements are present with EDS, further analysis with EBSD reveals how those atoms are arranged and how this arrangement changes across a small area of the sample.

In essence, this combined analysis permits a correlation between chemistry and microstructure. Some research groups are already adopting this strategy, including a group led by Jeff de Hosson at the University of Groningen in The Netherlands, which successfully analyzed the microstructure of a high-alloy coating. The combination of EDS and EBSD allowed for clear-cut identification of micron-size chromium-based crystals.

The flipside of integration is increased complexity when analysing the results. This may represent a severe limitation for small research groups in particular, as the need for a dedicated and experienced analyst becomes more evident. Software systems may be getting easier to use and more accurate, claiming to be able to 'cope' with peak overlaps and a noisy background, but a critical eye is essential for minimizing the risks of peak misidentification.

Researchers are also eager to speed up the time it takes to run each experiment. Pre-SDDs, several minutes or even hours were standard for any measurement. The introduction of more efficient detectors has considerably shortened the time required, but further developments are expected to reduce counting time to just a few seconds. Some preliminary work has already shown that counting times of just one second and a high count rate can be just as reliable for quantitative analysis as longer collection times at lower count rates.

While established research groups strive to improve efficiency and accuracy, other sectors that use EDS routinely may have different requirements. Forensic scientists, for example, are adapting the technique to meet increasing demands from police organisations for standardized and robust analytical procedures.

One example is the automated analysis of gunshot residue. Due to the size of the gunshot residue compared to the rest of the sample, such an analysis can take hours with current analytical techniques. Nadav Levin and his team from the Division of Identification and Forensic Science (DIFS) in Jerusalem, Israel, recently acquired a field-emission gun SEM (FEG-SEM) equipped with a SDD-EDS system. These are not yet common in all forensic laboratories, but promising results have demonstrated not only a significant reduction in the time it takes to analyze each sample, but also the ability to detect a higher number of particles of smaller sizes. Forensic scientists are also beginning to integrate EDS with other microanalytical techniques that are new to forensics.

Even with the development of new, more sophisticated techniques, EDS is firmly established as a standard microanalytical tool across many fields. Its suitability for integration with these new techniques will ensure that it remains at the forefront of microanalysis for the foreseeable future.

FURTHER INFORMATION

EDS section of EDAX website. (http://www.edax.com/Products/EDS/Index.aspx)

Jenkins R, 2006. X-ray techniques: overview. In: Encyclopedia of Analytical Chemistry, pp13269–13288. (http://www.spectroscopynow.com/userfiles/sepspec/file/specNOW/Enc_Anal_Chem_6801.pdf)

Schneider R, 2011. Energy-dispersive X-ray spectroscopy (EDXS). In Surface and Thin Film Analysis: A Compendium of Principles, Instrumentation, and Applications: second edition (eds G. Friedbacher and H. Bubert), Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. (http://onlinelibrary.wiley.com/doi/10.1002/9783527636921.ch18/summary)

Newbury DE, 2012. Energy dispersive spectrometry. In Characterization of Materials, pp1–26. (http://onlinelibrary.wiley.com/doi/10.1002/0471266965.com087.pub2/abstract)

Newbury DE and Ritchie NW, 2013. Is scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) quantitative? Scanning 35:141–168. (http://onlinelibrary.wiley.com/doi/10.1002/sca.21041/abstract).

MICROSCOPY AND ANALYSIS

Essential Knowledge Briefings