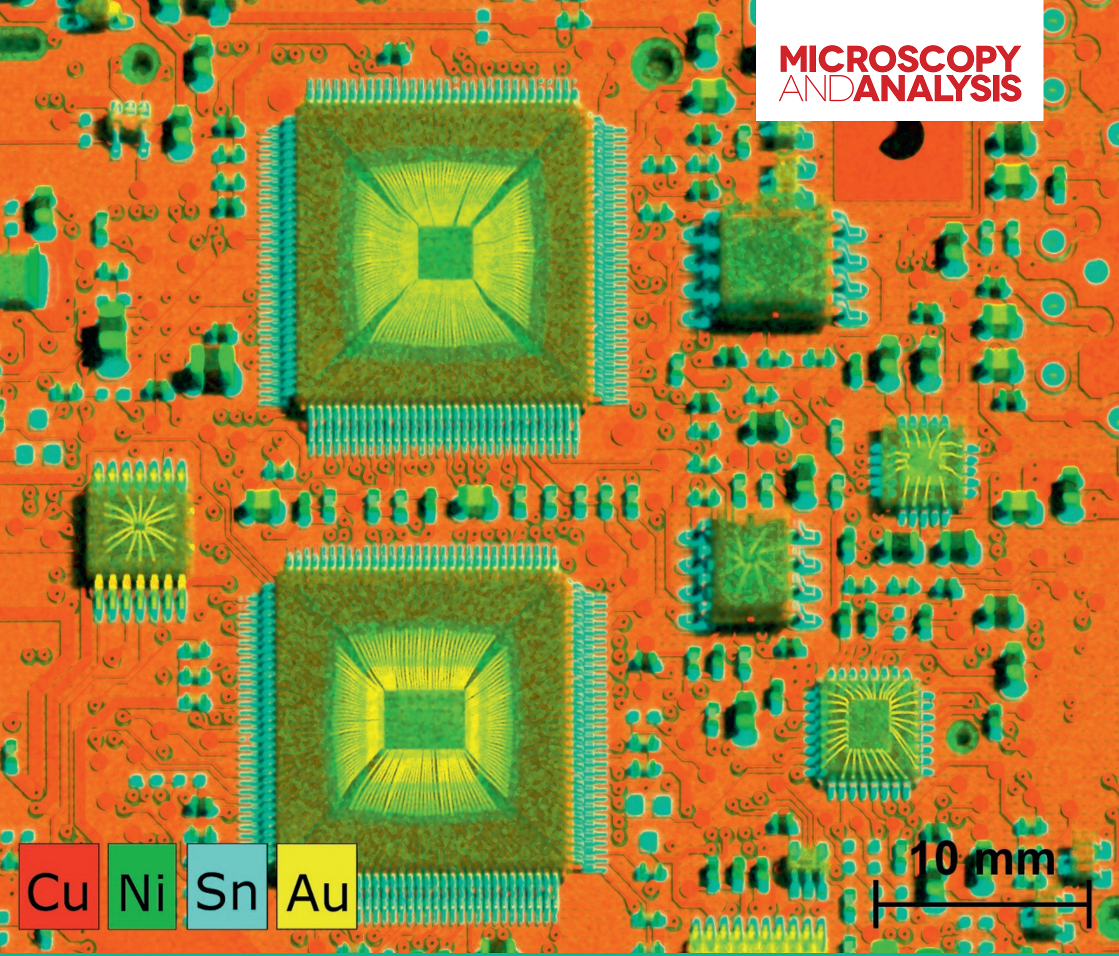
MICROSCOPY AND ANALYSIS



Micro X-ray fluorescence spectroscopy

Essential
Knowledge
Briefings

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Front cover image: high-resolution micro X-ray fluorescence map of a printed circuit board. Original size 2755 x 3010 pixels, step size 20µm. Pixel dwell time 3ms, resulting in a total measurement time of 6 hours 54 minutes. The image shows the distribution of the elements copper (Cu), nickel (Ni), tin (Sn) and gold (Au) using different colors. The gold distribution especially shows the ability of X-rays to penetrate into samples. The focused X-ray beam can pass through the plastic packaging of the integrated circuits, showing the gold wire bonding that connects chip and lead frame in high resolution. This is also a means of non-destructive quality control.

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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. Revised 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 specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION

Imagine you can determine the elemental composition of a sample without preparation: no need to polish to produce a flat, homogeneous surface, or otherwise grind, dissolve or cut sample material. Irregular-shaped specimens aren't a problem and measurement is non-destructive so the sample isn't damaged.

Micro X-ray fluorescence (micro-XRF) spectroscopy offers exactly this and more. Based on XRF spectroscopy, a powerful analytical tool used to determine the elemental composition of bulk materials as well as characterize surface composition, micro-XRF provides the same for very small samples, as well as larger samples, and with very high sensitivity.

Like conventional XRF instrumentation, samples are excited with X-rays to induce XRF emission for elemental analysis. But, thanks to the latest focusing optics, the incoming X-rays are concentrated to a small area so particles, inclusions, inhomogeneities or simply parts of a bulk sample can be analyzed to a spatial resolution of down to 15µm.

At the same time, the latest instruments can perform automated multipoint analysis, or even mapping, across larger samples, bringing quick, easy and non-destructive elemental analysis to a vast range of sample types and shapes as well as applications.

Given these benefits, researchers worldwide are turning to micro-XRF. Materials scientists were among the first to embrace the technique, analyzing, for example, elemental distribution across printed circuit boards and large metal parts. But today, geoscientists are using the method to study any type of mineral sample, forensic scientists are determining gun-shot residues, and even archaeologists are obtaining elemental analyses of ancient artefacts.

This Essential Knowledge Briefing provides a general introduction to the technique, explains how it works and provides examples of what it can do. It also outlines practical issues related to the method, describes potential problems that could arise and how to solve them, and reveals forthcoming advances.

HISTORY AND BACKGROUND

Micro-XRF spectroscopy is an elemental analysis technique first introduced around two decades ago. The method is based on the same principles as XRF spectroscopy. The combination of the multi-element sensitivity of XRF with the position information given by a focused X-ray beam provided the possibility to analyze inhomogeneous samples.

XRF relies on the emission of characteristic X-rays from a material that has been excited by bombarding it with high-energy X-rays. Fluorescence of the sample atoms takes place when electrons are displaced from atomic orbital positions, with a subsequent burst of energy that is characteristic of a specific element. This release of energy can be registered by the detector in an XRF instrument to determine the element. Details of the process are as follows.

An incoming X-ray interacts with an atom, knocking out an electron from one of its inner orbitals and leaving behind a vacancy. This vacancy in the inner orbital results in an excited, unstable configuration for the atom, so to restore equilibrium, an electron from a higher energy outer orbital falls into the vacancy. Since this is a lower energy position, excess energy is released in the form of a photon, with a characteristic energy equivalent to the energy difference between the higher and lower states.

Each element has a unique set of energy levels, so the transition of electrons from higher to lower energy levels produces X-rays with frequencies characteristic to each element. These characteristic X-rays can be used to identify the particular element from which they are emitted, and this property is used in XRF spectroscopy. The intensity of the characteristic radiation, on the other hand, is proportional to the element concentration in the sample.

Given its potential in analytical chemistry, conventional XRF has been widely adopted to determine the elemental composition of bulk materials, from metals and ceramics to polymer and biological matter. The technique has also proven instrumental to characterizing the layers of coating systems.

Solid samples, powders and particles can all be analyzed via XRF – the analytical process is non-destructive. But unfortunately, sample preparation is not. For XRF analysis, samples are typically cut, ground, fused or polished prior to analysis, either to produce a homogeneous sample surface that represents the entire sample or simply to fit the material into the sample holder. But what if the user doesn't want to damage the surface of a sample? And what if he or she wants to analyze inhomogeneities or small structures in a specimen? Then micro-XRF holds the answer.

Unlike conventional XRF, micro-XRF can be used to analyze small samples, or small, inhomogeneous features on different-shaped objects, without sample preparation. Here, the incoming X-rays are focused to a much smaller spot size on the sample surface, so that micrometer-sized features can be analyzed.

When introduced, the technique was only available at a few X-ray synchrotron beamlines. These facilities had sophisticated optics to concentrate incident X-ray beams to small spot sizes, and could generate X-rays powerful enough to induce sufficient fluorescence radiation from these small sample spots.

Analysis away from the synchrotron hasn't been so easy. X-ray tubes have been used as X-ray sources, but originally the only way to concentrate the radiation and excite small sample areas was to use apertures that could collimate and restrict the X-ray beam. However, using collimators available at the time to narrow the beam blocked some of the X-ray flux from the source to the sample. The end result was a relatively low fluorescence yield from a sample and poor analytical sensitivity.

And a lack of X-ray optics hasn't been the only problem; at the time, users were also struggling with the available photon-counting X-ray detectors. These energy-dispersive spectroscopy (EDS) detectors measure the energies of photons emitted from a material during XRF, converting these values to voltage signals of proportional size to determine the abundance of different elements.

The first XRF instruments relied on gas-filled proportional counters, produced in a range of shapes and sizes and containing a chemically inert noble gas, such as argon or xenon. Here, incident X-rays are absorbed by the gas atoms to generate ions and electrons, with the electrons then accelerated in the electrical field of the detector. The electrons gain enough energy to ionize more gas atoms, creating an electron avalanche for collection by the detector's counting wire, which is converted to a voltage output and processed for measurement.

But while the aim of any EDS detector is to convert the X-ray energy into a voltage signal as accurately as possible, these detectors had a limited energy resolution. Elements with characteristic XRF lines of similar energy within a sample could not be separated, making the analysis of unknown samples very difficult. What's more, these devices also had a limited photon count rate capability.

Luckily for micro-XRF analysis, higher sensitivity semiconductor-based EDS detectors have since been developed. The first Si(Li) detectors comprised silicon crystals 'drifted' with lithium.

Here, incident X-rays are absorbed in the crystal volume and, like gas-filled converters, are converted to a charge by the ionization of atoms. The electrons are then converted into a voltage signal by an electronic preamplifier, fed into a pulse processor and converted to a digital value for measurement. The output from the preamplifier is a voltage 'ramp' so each X-ray appears as a voltage step on this ramp.

Compared to gas-filled detectors, this detection process in the Si(Li) detector results in a much better energy resolution. And crucially, these detectors can measure X-ray photons of different energies almost simultaneously while delivering good energy resolution.

Still, these Si(Li) detectors had a key weakness: to maintain efficient operation, the devices needed to be operated at low temperatures with liquid-nitrogen cooling. So with this in mind, the next generation of detectors – PIN diodes – were electrically cooled. The higher energy resolution of both types of detectors meant the devices were widely used for the analysis of unknown samples.

The demand for ever higher photon count rates and even better energy resolution continued to fuel the development of faster, more efficient detectors, and more recently, thermoelectrically cooled silicon drift detectors (SDDs), with an excellent energy resolution and the highest photon count rate, have emerged.

A typical SDD is fabricated from high-purity silicon with a large area contact to face incoming X-rays. When a bias is applied to the detector chips, detected X-rays are converted into an electron cloud with a charge proportional to the energy of the X-ray.

Special drift field structures guide these charges to an extremely small readout anode and, as with the Si(Li) detectors, are converted to a voltage signal with an electronic preamplifier. The signals are converted to a count by a pulse processor.

Today, relatively cheap PIN-diode detectors are still commonly used in low-cost XRF spectrometers, offering a better energy resolution than proportional counters. However, SDDs have become state-of-the-art technology in the field of microanalysis, outperforming the original Si(Li) detectors in almost every aspect. Thanks to the use of fast pulse processing with low electronic noise, most of the incoming photons contribute to the available signal, giving highly efficient devices.

But while the development of SDDs has provided a welcome boost for micro-XRF analysis, the introduction of X-ray capillary optics that focus X-ray beams to small spot diameters has been equally important.

Monocapillary optics came first. Here, high-intensity X-rays are channeled through a glass capillary by total reflection inside the capillary, to generate a micron-sized beam.

Prototype micro-XRF instruments using these optics were developed in research organizations, and a few commercial instruments also emerged. However, the excitation intensity delivered by the focused X-ray was too low to deliver a reasonable elemental analysis, so instead, developers of micro-XRF turned to polycapillary optics.

Polycapillary optics capture a large solid angle of radiation from the X-ray tube, essential to maintaining X-ray flux density and producing brilliant radiation. This high-flux beam then propagates through the bundle of glass capillaries by total reflection and is concentrated to a small spot size – spot sizes in today's instruments are only 20µm – to intensely excite this area (Figure 1).

This increased intensity delivered to the sample, coupled with the small focal spot, enhances spatial resolution. This breakthrough has been critical to driving micro-XRF from the synchrotron into the laboratory, leading to the development of benchtop micro-XRF, as used in laboratories around the world.

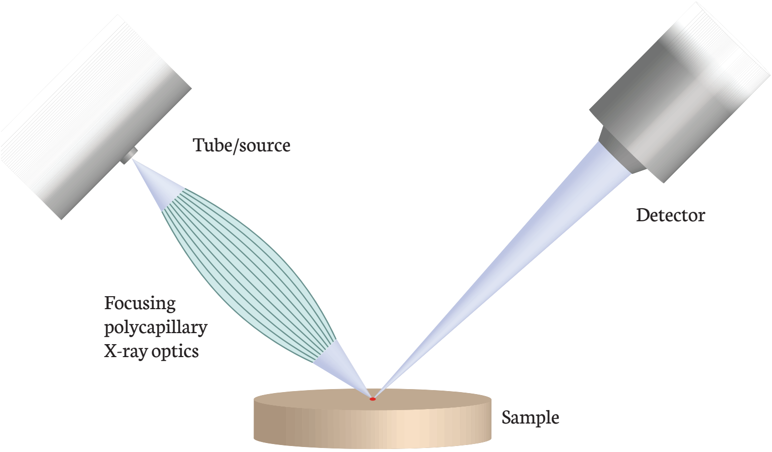

Figure 1. Polycapillary optics. A convex arrangement of capillary optics is placed between the X-ray tube and sample to shape the beam to a small spot size on the sample, generating high fluorescence intensities

Today's key instruments are used in a wide range of electronic, geological and biological applications. For example, electrical and electronic equipment can contain toxic elements such as lead, chromium and cadmium. Limits are heavily regulated, and compliance testing can be carried out with micro-XRF.

In life sciences, micro-XRF can be used to analyze elemental distribution in biological samples, detecting light elements such as sodium under vacuum. For example, the analysis of small, transparent, fast-moving planktonic crustaceans called *Daphnia*, also known as 'water fleas', is important to environmental control. Here micro-XRF provides analysis of single elements within the organisms, even detecting trace elements.

Other applications include quality control in solar cells, minerals in geological samples, composition of coating layers, corrosion products of metals, and many more.

IN PRACTICE

So how exactly does micro-XRF work? A typical high-end instrument comprises several key components: a high brilliance X-ray source, polycapillary focusing optics, the X-ray detector, a sample chamber and a motorized sample positioning stage (Figure 2). The use of these components will now be described.

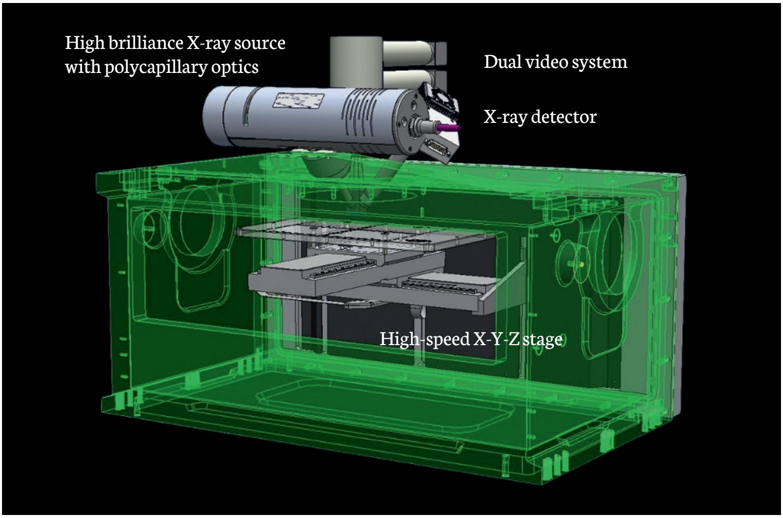

Figure 2. A look inside the M4 TORNADO

X-ray source

The main requirement for a micro-XRF source is to produce radiation with high brilliance that can intensely excite a small area on a sample. With this in mind, today's instruments typically use an air-cooled low-power X-ray tube, which emits radiation through a side window. These micro-focus tubes produce high-brilliance radiation combined with much smaller tube spot sizes at the tube target than alternative tube geometries. For example, the M4 TORNADO is equipped with a rhodium side-window X-ray tube that has a maximum tube power of 30W and a tube spot diameter of less than 50µm. For more flexible sample excitation, instruments can also be fitted with an additional X-ray tube. This second tube could have a rhodium, molybdenum or tungsten target material; the different spectral distribution from each can be selected according to spectroscopic application.

Polycapillary optics

To excite a sample, the micro-focus X-ray tube is used with polycapillary optics to shape the beam to the smallest spot size on a sample. Placed between the X-ray tube and sample, this complex bundle of glass capillaries is bent so that one side points at the X-ray source tube spot and the other side points towards the focal spot in the sample chamber.

These capillaries are used to capture a large solid angle of radiation from the X-ray tube and focus tube radiation on a very small spot. For Mo K radiation, the spot size can be less than 20µm, resulting in a spot-intensity increase of 10 000 times or more compared to a collimator spot of the same size.

Detecting X-ray fluorescence radiation

For a sample excited with high efficiency, the high flux of fluorescence radiation needs to be detected and processed. For this purpose, energy-dispersive silicon drift X-ray detectors are used in many micro-XRF instruments.

Bruker has developed an SDD known as XFlash for its micro-XRF spectrometer, which provides an energy resolution of less than 145eV, at more than 300 000 incoming counts per second.

Typically a 30mm^2 active area detector collects incoming X-rays from a large solid angle. The device does not require liquid nitrogen cooling, but instead is cooled with a vibration-free thermoelectric Peltier cooler. It also contains a monolithically integrated on-chip field effect transistor to act as a signal preamplifier.

Information depth

XRF has several key advantages: it is surface-sensitive and, depending on the sample matrix and energy of the analyzed X-ray photons, results originate from relatively large volumes of the sample. For quantitative analysis, the analyzed volume of the sample must represent the material being characterized. This means that a clear knowledge of the so-called information depth – the layer of material that contributes to the measured signal – is important.

During analysis, the incident radiation penetrates a sample and is scattered and absorbed. The absorbed X-rays excite atoms and these emit fluorescence radiation, which can also be absorbed on its way to the sample surface.

The absorption of this fluorescence determines the information depth and depends on three key factors: incident X-ray energy, sample matrix density and the line energy of the excited element (Figure 3).

Using such a chart, the information depth can be estimated for different elements (or line energies) as well as for different matrices. Taking silicon within a high-density steel matrix, characteristic radiation can only stem from the first 400nm of a sample surface. In contrast, for silicon in a lower density matrix, such as glass, fluorescence radiation absorption is less and the information depth increases to around 5µm.

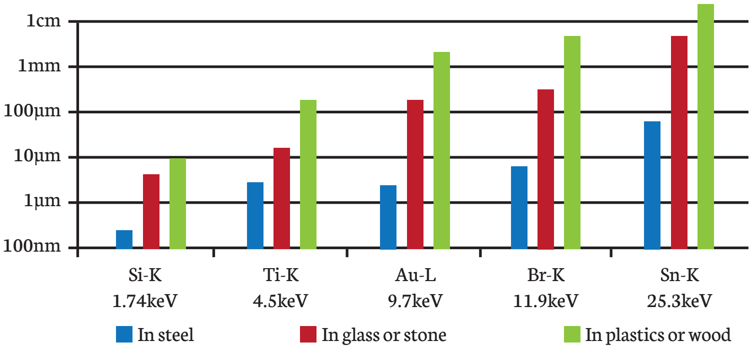

Figure 3. Information depths of selected element fluorescence lines in different matrices

Data processing

With micro-XRF analysis, the user can rapidly map elemental distributions across a wide range of materials. However, samples are typically inhomogeneous and irregularly shaped, so standard-based analysis models that rely on uniform and high sample volumes cannot be used in most cases.

Consequently, the quantitative analysis software in today's micro-XRF systems primarily uses standardless fundamental parameter models. These models can be applied to a range of different matrix types and are independent of excitation conditions.

If, for example, a user wants to analyze a single point on a sample, analysis software will locate and label element peaks, and also present element intensities and concentrations, with possible analytical errors. Spectra are calculated and compared with measured spectra, while spectral background and sum peaks are also calculated.

For sample analysis, the full spectrum is calculated using the Sherman equation starting with assumed concentrations. The composition of the sample is calculated iteratively, typically for a few iterations, until the predicted and measured spectra converge within given limits in less than a second.

For the analysis of inhomogeneous materials, distribution analysis is an important tool. A user can identify variations of specific element intensities across an entire sample. A significant advantage of micro-XRF originates from a combination with position-tagged spectrometry. Here, a complete spectrum is saved for every pixel during a high-speed scan of an area on a sample, to create a complex dataset (also called a data cube). This is often also referred to as hyperspectral imaging.

In the M4 TORNADO, this type of data handling is called a HyperMap and generates a four-dimensional dataset (Figure 4). Such a dataset contains two dimensions for spatial distribution (X and Y), a third dimension for the spectrum energy, and a fourth dimension for the intensity of each spectral channel.

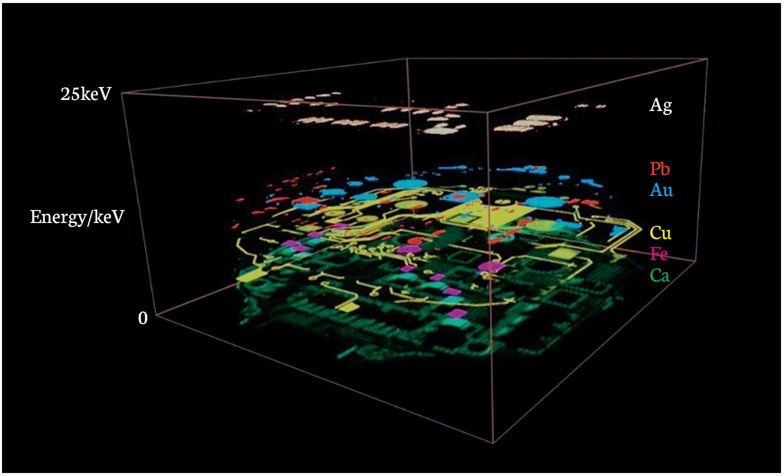

Figure 4. Visualization of the four-dimensional HyperMap dataset with spatial coordinates X-Y, photon energy (Z-axis), *eg* for selected elements, and count rate represented by the color intensity

Crucially, the dataset offers a wide variety of options for post-processing. For example, a user could look at the spectrum of every pixel or sum up the spectra of several pixels to improve counting statistics. This information can be used to generate an elemental distribution map of a sample as well as to show intensity maps of any feature (*eg* diffraction peaks) of the spectra.

Mining the data cube

Spectroscopic information can be extracted from the dataset by using different data access tools, such as definable objects, points or lines, to analyze composition spatially within a measured area. Phase analysis can also be used to determine the distribution and proportion of different chemical phases within a scanned area (Figure 5).

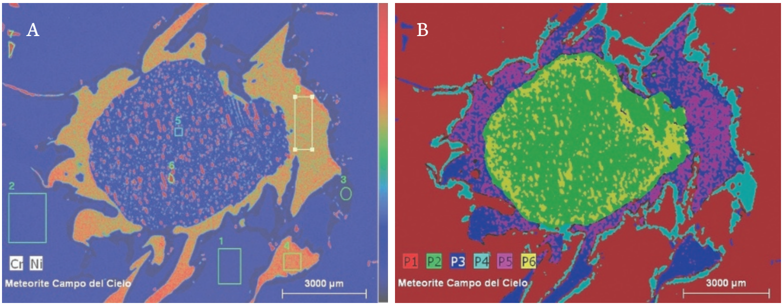

Figure 5. Phase analysis. (A) Variations in the sample composition can be studied by extracting spectra from defined areas within an element map. (B) Phase evaluation by special algorithms groups regions of similar composition using identical colors; area fraction and composition of every phase are calculated

PROBLEMS AND SOLUTIONS

While micro-XRF provides the researcher with highly sensitive and non-destructive analysis, a few issues regularly emerge. Non-representative regions of analysis, sample positioning and shadowing on a sample are a few examples, but trouble-shooting can be simple, as explained below.

Selecting a representative region on a sample is crucial for accurate analysis, and with knowledge of an element's information depth, and given the small spot size of the instrument, this should be straightforward. But samples aren't always homogeneous, and the advantage of this method lies mainly in the possibility of studying and understanding compositional variations of inhomogeneous samples.

Sometimes the user may want an elemental analysis of contaminants, inhomogeneities or, quite simply, an odd-shaped sample. Micro-XRF can analyze these samples, as well as provide information on elements up to millimeters deep inside a sample – ideal for, say, analyzing corrosion layers or coating thicknesses.

What if the user wants to analyze a powder? This doesn't pose a problem for micro-XRF analysis either. Small volumes of powders as well as small particles can be analyzed directly, depending on their size. If necessary, the particle can be fixed to a thin plastic film. To get an average elemental analysis, the sum of the signals over a larger number of particles can be calculated. Liquids can also be analyzed and are typically poured into sample cups.

With the sample prepared and the region for analysis selected, accurate positioning within the micro-XRF spectrometer is now critical. Unlike the electron beam in an electron microscope, deflecting the micro-XRF instrument's X-ray beam to different positions on a sample is almost impossible. Repeatedly moving the sample or moving the measuring head into new measurement positions is preferable and used in micro-XRF instruments. Therefore high speed and high motor precision are required to ensure quality of the measurement.

However, today's instruments include motorized stages that are typically controlled using a joystick or mouse. At the same time, user-generated programs can be applied to perform multiple measurements. Instruments also have an auto-focus function to compensate for different sample heights.

With the specimen loaded into the instrument and the representative region on a sample selected, the user should be ready to go, but some samples need special care. One tricky problem that can emerge with irregularly shaped samples is shadowing. Here, the uneven topography of a specimen can block the sample XRF signal, resulting in this problem as well as causing artifacts.

This can be counteracted by tilting the sample towards the X-ray detector. However, a second detector can also help here. Mounted in a different position to the primary detector, it can be used to identify spurious diffraction peaks often caused when analyzing crystalline material, and of course, reduce the shadowing effects of mapping rough samples.

Importantly, adding a second detector to the spectrometer also speeds up data acquisition even more, increasing the instrument's detection count rate by a factor of two.

Detection issues aside, analyzing heavier elements can also be problematic. While X-ray excitation is very efficient at analyzing mid to heavy elements, the polycapillary optics that shape the beam to a small spot size on a sample work best in the mid-energy range, reducing the intensity of incoming high-energy photons and therefore also the analytical sensitivity for heavy elements with high energy lines.

This problem can be solved by using a second X-ray tube with a tungsten target and fitted with a collimator rather than with polycapillary optics, boosting the excitation with high energy. On the downside, the use of a collimator results in reduced spatial resolution and excitation intensity during analysis. Due to the lower absolute intensity of collimators, large measurement spots are recommended in the order of 1–2mm.

In addition, several X-ray filters can also be placed between the source and sample, for example to reduce diffraction peaks or improve the peak-to-background ratio.

As with all analytical methods, micro-XRF has its issues, but these can be tackled, providing elemental analysis across myriad applications from forensic science to geology, considering that any material can be analyzed without further preparation. The following real-life case studies show how micro-XRF users are already reaping these benefits.

CASE STUDY 1. Thickness analysis of thin light element layers

Given its non-destructive operation and X-ray penetration into a sample, micro-XRF spectrometry is widely used to analyze thin layers and coatings. However, in this case study of a thin aluminium layer on a silicon substrate, the presence of light elements presents an analytical challenge.

Crucially, measurement must take place under vacuum, otherwise any air in the beam path between the sample and detector would absorb the low-energy radiation emitted by the sample. In general, a low vacuum of 20hPa (20mbar) is sufficient.

To analyze the sample, an automatic multipoint procedure acquired spectra at 70µm intervals (Figure 6). A relatively low tube power of 200µA at 50kV and 10s acquisition time proved sufficient for this layer analysis task. Analysis revealed that the majority of the layer thicknesses in this sample were around 2µm, as intended, but deviations also existed. This possibility of correlating location and layer thickness is an important tool in quality control, and can, for example, be used to identify systematic coating process problems.

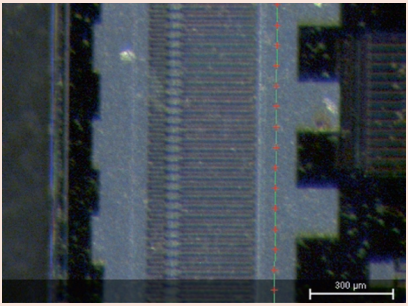

Figure 6. Multipoint analysis of an aluminium layer on a silicon substrate; the red markers connected by green lines indicate the measurement locations, 15 of 20 are visible in the image

CASE STUDY 2. Analysis of a weld seam

Micro-XRF is also suitable for the investigation of large parts, as shown by this analysis of a polished section of a weld seam joining two steel parts. Each part is fabricated from stainless steel, but with a different chromium content. The nickel-based alloy welding filler has a high chromium and some molybdenum content.

A high-resolution map of the seam – 4640 x 3160 pixels in size – took around 14 hours to record and reveals each element (Figure 7). During scanning, a step size of 15µm was used and a filter was placed between tube and polycapillary optics to suppress Bragg peaks.

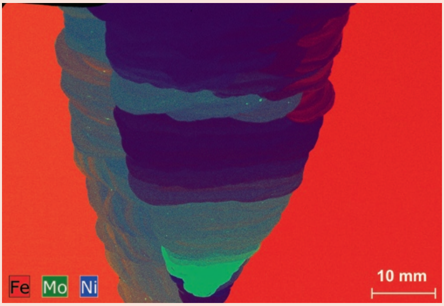

Figure 7. High-resolution micro-XRF map of weld seam

The weld seam is cloudy in appearance, due to alloying and segregation processes during welding followed by cooling and solidification of the molten metal, but several interesting details are apparent. For example, molybdenum has segregated, as can be seen in the intensely green area at the bottom of the map. Here, molybdenum concentration is more than 6.5wt%, although small local molybdenum segregates can also be seen as bright green spots within the weld.

A slight enrichment of this metal can also be seen on the left side of the seam from top to bottom and across in two places. This could stem from the steel on the left, which contains around 0.9wt% molybdenum.

The map indicates that alloying between the steel and the welding filler took place here, on the left side of the weld. However, such alloying is far less obvious on the right side of the seam.

As demonstrated during this weld-seam analysis, thin metal filter foils can be used to suppress spurious peaks in the measured spectrum by attenuating certain energies, typically in the low energy range, in the exciting (tube) spectrum. These peaks are caused by diffraction of the exciting radiation on a crystalline sample, such as steel. While these peaks can overlap with element peaks, sometimes they provide interesting information, as shown in Figure 8. Here, the five energy ranges (F1–F5) that include the highest of the Bragg peaks produced by the sample were mapped across the same sample region.

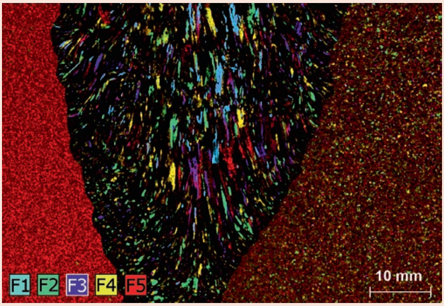

Figure 8. Map of energy ranges with highest Bragg peaks provides information on recrystallization processes

Instead of providing compositional information, this map reveals the recrystallization processes that took place during seam cooling. Dendritic crystallites emanate from the sides of the seam and grow larger towards the center, indicating that solidification in the center of the seam took place over a longer time period than at the sides.

Note that the black areas in the map do not mean that the material there is amorphous, but that the crystallites are oriented in a way that Bragg peaks are not produced within the defined energy ranges.

CASE STUDY 3. Analysis of geological samples

Micro-XRF spectrometry has proven crucial to analyzing geological and petrological samples for chemical composition, as well as element distribution, pointing to sample origin, age and genesis.

Here, a thick section of a garnet containing slate has been analyzed, with Figure 9 showing the micro-XRF overview map.

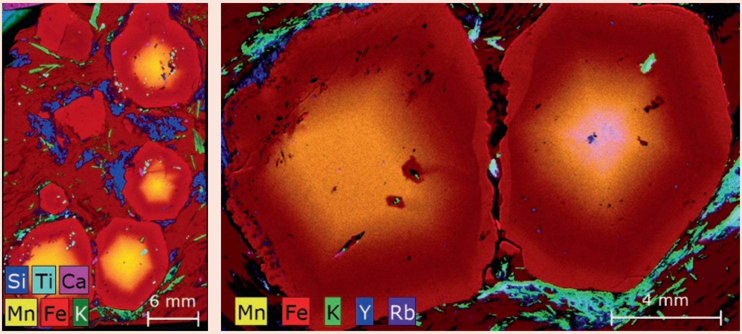

Figure 9. Micro-XRF map for a thick section of garnet containing slate; the image on the right is a detail from the bottom left with a different element selection

The map shows an obvious zonation of the larger garnet crystallites, which contain symmetrical cores that are rich in manganese (yellow) and yttrium (blue). The trace element sensitivity of the micro-XRF allows the user to determine the yttrium distribution in these samples in the low parts per million range. Results indicate that manganese and yttrium were incorporated during early stages of crystal growth.

The garnet crystallites also contain a number of inclusions of different chemistry that can be distinguished in the element distribution (colors: pink inclusions are rich in calcium, green inclusions in potassium and light blue inclusions in titanium).

Detailed analysis of a single crystallite, using a primary filter in combination with an exceptionally long pixel dwell time of 1s, provided a map with excellent count statistics while Bragg reflexes and background were suppressed to the maximum (Figure 10). Such maps can be shown as XRF intensity or quantification result distribution.

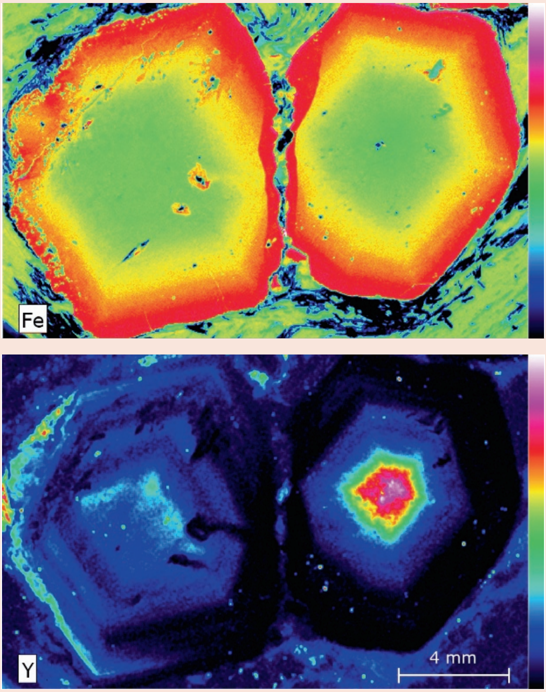

Fig. 10 Detailed analysis of single elements: quantified distributions of Fe and Y using a rainbow look-up table for display, black being concentration 0 and white the highest measured in the according map

The potential of the instrument can also be shown in such an extreme case study; the 200 000 pixel map took two days to acquire. Nevertheless, the resulting rich HyperMap data allowed further *sample composition analysis, which uncovered elements that were enriched in a single or only a few pixels of the entire map. In this case additional elements – hafnium, germanium, thorium, uranium and niobium – were identified in small mineral inclusions (Figure 11).*

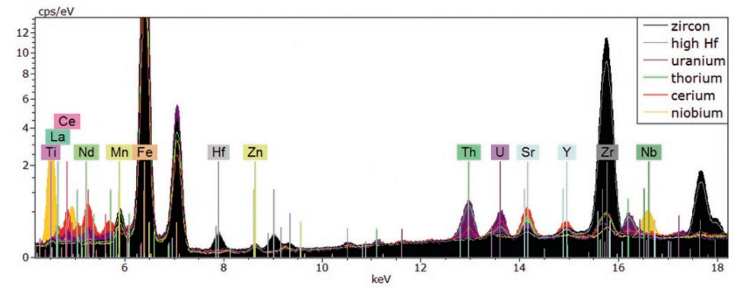

Figure 11. Spectra of different inclusions with elements hidden by the main components

WHAT'S NEXT FOR MICRO-XRF?

Looking to the future, many developments still lie ahead for micro-XRF, predominantly related to instrument speed, spatial resolution and its evaluation algorithms. Increasing incident X-ray radiation intensities or the efficiency of SDDs will lead to even faster elemental analysis and will also boost sensitivity for trace elements.

Instruments are set to get faster. For example, the use of multiple detectors can increase analysis speeds, as will the next wave of detectors with higher count rates. However, speed can also be gained by specific automatic data evaluation during routine analysis.

So far, better spatial resolution for polycapillary optics can be achieved only by sacrificing working distance between the optics and sample. For thinner monocapillary optics this distance would not change, but again the intensity will be reduced even more due to the reduced capture angle. Indeed, the smallest spot instruments are only used if speed is not relevant to the application, which is rare in today's applications.

Many researchers worldwide are also looking to improve the spatial resolution of today's instruments. For example, Takashi Nakazawa and Kouichi Tsuji from Osaka City and Chuo Universities have built a high-performance confocal micro-XRF instrument (with a second polycapillary lens in front of the detector) equipped with a vacuum chamber to reduce XRF absorption during analysis as well as to improve vertical resolution.

According to the researchers, a reduction in background intensity led to lower limits of detection compared to conventional micro-XRF. The instrument was also used to non-destructively obtain the distribution of light elements in layered materials that couldn't be detected when measured in air.

In a similar vein, while at the French National Centre for Scientific Research (CNRS), Professor Didier Tonneau, with colleagues, developed novel capillary optics to test the limits of spatial resolution of micro-XRF. Here, a polycapillary lens tightly focused the incident X-ray beam while the fluorescence signal was collected by an SDD through a range of cylindrical monocapillaries.

In this way the researchers were able to assess the impact of capillary diameter on fluorescence signal and concluded sub-1µm resolution would be possible. Interestingly, they also believed they could couple the instrument with scanning probe microscopy to simultaneously combine elemental analysis of a sample with topography.

Scanning probe microscopy and micro-XRF won't be the only example of method coupling that we will see in the future. Bruker has already merged micro-XRF with scanning electron microscopy, developing QUANTAX Micro-XRF. The instrument has a micro-spot X-ray source that can be fitted to the chamber port of most scanning electron microscopes. Samples can be analyzed with micro-XRF and EDS without position change, and users can benefit from the trace element sensitivity and the higher information depth of XRF analysis.

What's more, Professor Christoph Fahrni and colleagues from the Georgia Institute of Technology, USA, have combined synchrotron-based micro-XRF with optical immunofluorescence microscopy to study subcellular distribution of organelles in labeled cells. And Professor Gordon Brown and colleagues from Stanford University have used synchrotron-based micro-XRF with micro X-ray diffraction as well as micro and bulk X-ray absorption fine-structure spectroscopy to determine the spread of different uranium species in sediments from nuclear waste sites. Correlative micro-XRF is clearly taking off.

Fast macroscopic elemental analysis is another emerging trend, with laboratories across the world looking to analyze larger and larger samples using micro-XRF. With this in mind, Bruker has developed a large area micro-XRF spectrometer, M6 JETSTREAM. The instrument can scan areas up to 800mm by 600mm with a variable spot size down to 100µm and with speeds up to 100mm/s, and has already been used to analyze historical paintings as well as large geological specimens like drill cores and rocks.

At the same time, faster and more powerful software tools are under development for advanced data mining. So while today's micro-XRF spectrometers are crucial to the elemental analysis of myriad materials, these developments will ensure that forensic scientists, geologists, materials scientists and other researchers can continue to non-destructively analyze and explore materials at faster speeds and with ever-greater resolution.

FURTHER INFORMATION

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