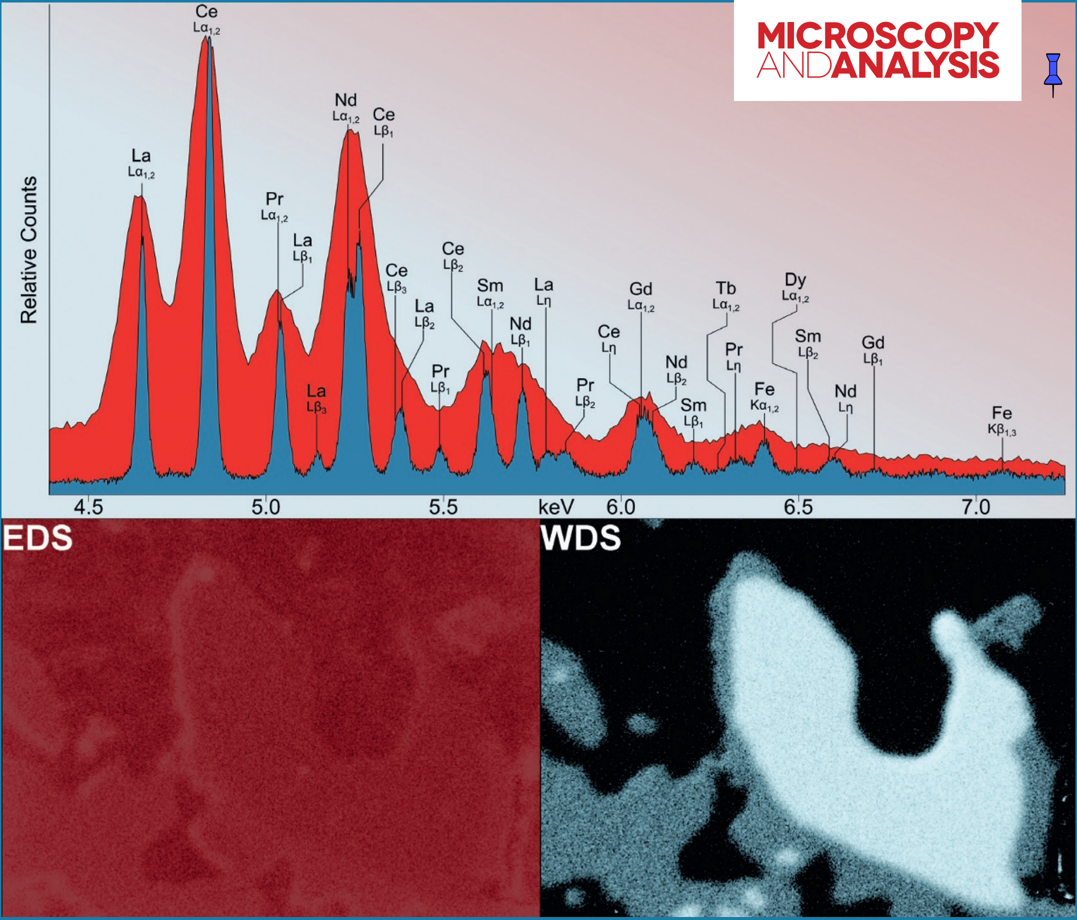
MICROSCOPY AND ANALYSIS



Wavelength-dispersive (X-ray) Spectroscopy

Essential Knowledge Briefings

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Front cover image. Top: a wavelength-dispersive spectroscopy (WDS) energy scan (blue) overlain on an energy-dispersive (EDS) spectroscopy spectrum (red), both acquired from monazite ([La,Ce,Pr,Nd,Sm,Gd]PO_4). Compared to EDS, the significantly better resolution and peak-to-background ratios of WDS clearly reveal which elements are present in a sample. Bottom: when applied to X-ray mapping, accurate elemental distributions are displayed, whereas EDS X-ray maps may be confounded by high backgrounds and characteristic X-ray interferences.

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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

X-ray microanalysis is a non-destructive technique that is widely used in electron microscopy to determine the composition and distribution of elements in a sample. Under electron bombardment, atoms emit X-rays due to changes in electron states; these X-rays are characteristic of the elements in the sample. The emitted X-rays can be analyzed using two techniques. Wavelength-dispersive X-ray spectroscopy (WDS or WDX) separates the X-rays by diffracting them with crystals, collecting one wavelength, or energy, at a time. In contrast, its sister technique, energy-dispersive X-ray spectroscopy (EDS or EDX), collects X-rays of all energies simultaneously.

The two methods are almost always used in combination, with EDS providing a qualitative overview and WDS, with its better resolution and sensitivity, subsequently refining the details, hunting for trace elements, and conducting quantitative analyses.

There is no limit to the potential applications of WDS in scientific research and industrial research and development. One of its best-known applications is in earth sciences because it is particularly adept at analyzing minerals, rocks, and soils. Much of the material collected from the Moon has been subjected to intense scrutiny using WDS. Its contribution to materials science includes more accurate and efficient determination of phase diagrams and diffusion coefficients. Another application has been in the study of the microstructure of alloys, which was greatly enhanced by WDS characterization of major, minor, and trace phases, including contamination. Also, life scientists use WDS to examine the distribution of ions in cells and tissues, such as calcium in muscle tissues, and environmental heavy metal pollutants, such as cadmium in plant tissues.

This Essential Knowledge Briefing provides an introduction to WDS as performed in electron microprobes and scanning electron microscopes (SEMs). It begins by providing a background on the physical principles of X-ray generation and spectrometry, and then outlines the development of electron microprobes over the past 60 years. It describes how WDS is performed on these instruments and details various practical issues related to their operation. Potential problems that may arise and how to solve them are reviewed. Finally, it looks at future developments in WDS that will sustain its position at the forefront of chemical analysis.

HISTORY AND BACKGROUND

The origins of WDS can be traced back to the end of the 19th century and the discovery of X-rays in 1895 by German scientist Wilhelm Roentgen, for which he received the first Nobel Prize in Physics in 1901. Roentgen was working with cathode ray tubes when he noticed that the electrical discharge caused a metal-coated screen several feet away to fluoresce. We know now that the cathode ray (or beam of electrons) had interacted with the atoms in the tube walls and caused them to emit X-rays.

Over the next 25 years, research on X-rays led to the establishment of two important concepts that were critical to the later development of WDS: first, that when excited by X-rays or electrons, atoms emit X-rays that are characteristic of that element; and second, that X-rays are reflected (diffracted) by the atomic lattices of crystals.

In 1913, Henry Moseley showed that the ordering of the wavelengths of characteristic X-rays coincided with atomic number, a relationship now called Moseley's Law. Importantly, he postulated that (electron-induced) X-ray emission could be used as an analytical technique, but its implementation had to wait another 30 years for the development of the first electron microscopes that were able to provide a controlled, focused beam of electrons.

The first electron microprobe (or electron probe microanalyzer, EPMA) was designed and built in 1950 by Raimond Castaing, a PhD student at the University of Paris. A key advance made by Castaing was the determination of absolute elemental concentrations by comparison of the intensities of the same characteristic X-ray line of a given element measured on the specimen with that on a target made of the same pure element.

Based on Castaing's prototypes, the French company CAMECA was the first to produce a commercial EPMA, the MS85, in 1958. Other electron microscope companies were quick to realize the potential of this new analytical technique and, over the next few years, there followed a range of commercial EPMAs (e.g. Figure 1) motivated by, amongst other things, the space and arms races, semiconductor development, and materials research.

These first-generation instruments were designed solely for WDS, but once SEMs came to dominate the electron microscopy market, and with the development of the solid-state EDS detector, analysts came to realize that SEMs (with their scanning beams, a wider and more flexible range of functionality, not just for spectroscopy) could also provide a sound platform for WDS.

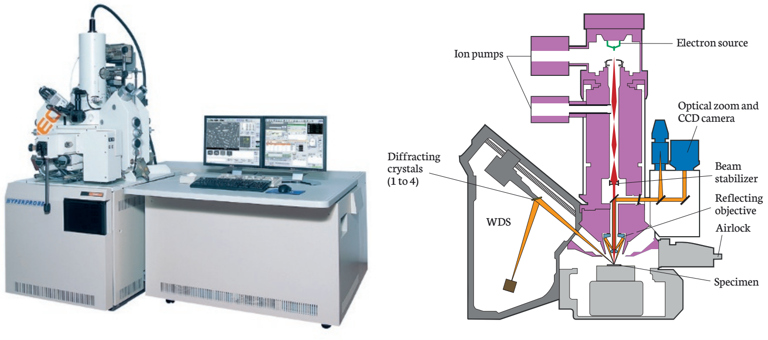


Figure 1. Latest generation electron microprobe: (left) JEOL JXA-8530F (photo courtesy of JEOL) and (right) a schematic of an Electron Probe Microanalyzer (reproduced with permission from CAMECA®)

To understand how incident electrons generate characteristic X-rays from a sample, you have to know something about the structure of atoms. In the standard Bohr model, atoms are made up of a nucleus, containing protons and neutrons, surrounded by a cloud of electrons arranged in a series of concentric shells (named K, L, M, and so on) with energy levels that increase with distance from the nucleus.

X-rays are generated in two ways. First, by inelastic scattering, where the electron passes close to the atomic nucleus and is slowed down, releasing part of its energy in the form of an X-ray photon. Since any amount of energy can be lost, the energy distribution of these X-rays is continuous so this component of the X-ray signal is called the continuum, or ***bremsstrahlung***, and forms the background in an X-ray spectrum.

Alternatively, and this is the essence of WDS, the incident electron hits an electron in one of the shells, ejecting it and creating a vacancy in that shell. The vacancy can then be filled by another electron descending from a higher energy orbit (a transition), with the excess energy being emitted in the form of an X-ray photon. Because each element has a unique set of electron energy levels, the emitted X-ray is unique to that element and so it is called a characteristic X-ray. (Hydrogen and helium are exceptions because they have only K shells and hence no higher-order shells to supply electrons.)

In WDS, characteristic X-rays are labeled using the Siegbahn notation: the element symbol followed by a letter (K, L, M, or N) for the electron shell that was ionized and filled, with two subscripts: a Greek letter and numbers identifying the donor shell and subshells that filled the vacancy. So, for example, a Mn $K\alpha_1$ X-ray line arises from a transition in a manganese atom from L subshell 3 to the K shell (Figure 2).

Vacancies may occur in any shell, giving rise to multiple characteristic X-rays for each element, especially in higher atomic number elements.

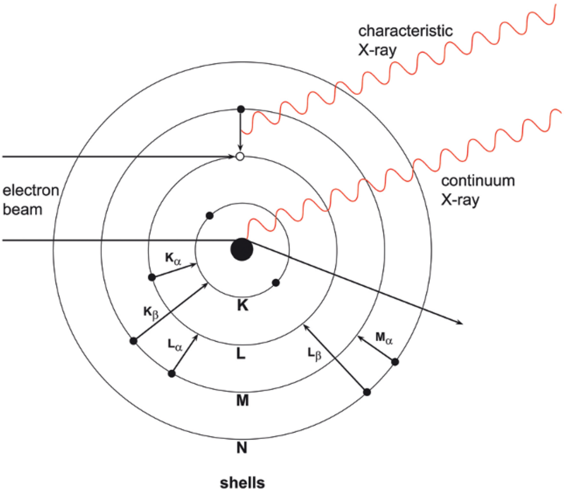


Figure 2. Model of atom showing X-ray generation and nomenclature. See text for full details. Courtesy of Dr Julian Heath

An electron needs a certain energy in order to displace electrons from the inner shells; this is called the excitation potential or critical ionization potential (E_c), and its value decreases the further the shell is from the nucleus. So an electron that is not energetic enough to displace a K-shell electron may cause a vacancy in higher L or M shells, yielding Lα or Mα X-ray emission. For example, E_c for Fe Kα is 7.11keV, whereas E_c for Fe Lα is only 0.71keV. X-ray analysts typically use Kα lines for lighter elements, Lα (and β) lines for elements with atomic numbers from about 30 to 70, and Mα lines for elements with higher atomic numbers.

It is important, at this point, to note that there are other atomic excitation/emission reactions occurring when a sample is under the electron beam. First, the incident electrons can be reflected or backscattered, and secondary electrons can be emitted. Both of these signals are used to form images of the sample.

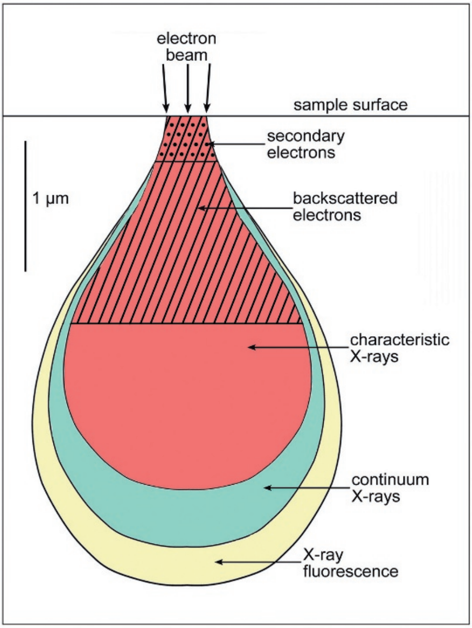


Figure 3. Interaction volume showing zones of electron and X-ray emission

Next is secondary X-ray emission, or X-ray fluorescence, caused when the emitted X-ray itself excites another atom. Third, there is cathodoluminescence, which occurs when energy is emitted in the form of light instead of X-rays.

Characteristic X-rays are emitted from a small teardrop- or pear-shaped region of the sample called the interaction volume (Figure 3). The depth of electron penetration is a function of the accelerating voltage and the average atomic number of the sample. The width of the interaction volume sets the spatial resolution of WDS, which is typically 0.5–1µm.

X-rays leave the sample surface in a hemispherical wavefront and a small cone or solid angle is intercepted by a spectrometer to form the signal in WDS.

IN PRACTICE

Three types of electron microscope are used for X-ray microanalysis: electron microprobes (EPMAs), SEMs, and transmission electron microscopes (TEMs). Microprobes are dedicated instruments that are designed specifically for microanalysis and support multiple WD spectrometers. Many analysts use SEMs to which they fit an ED and a WD spectrometer. This is done because the SEM offers more flexibility in terms of imaging modes and is more cost-effective. For the highest spatial resolution studies, a TEM is employed. WDS has been fitted to a TEM, but only rarely is that a practical microanalytical solution.

For WDS, you need an electron beam that is powerful enough to penetrate the sample and create the atomic shell vacancies that produce the X-ray emission. The electron gun contains a heated filament and draws off electrons by applying an accelerating voltage. Three types of filament are available: tungsten is standard, providing useful currents and a long lifetime; for a longer lifetime and more stability a LaB_6 can be used; but for ultimate performance, modern microprobes and SEMs now use a field-emission gun (FEG) containing a Schottky type emitter. The gun typically operates in the range 2–30kV with currents in the ones to hundreds of nanoamperes range.

Before you can undertake any WDS investigation, you must ensure that your samples are properly prepared. Materials samples must be polished to produce a flat surface with few protuberances to ensure uniform X-ray emission. For biological samples, you need to cryofix, section, and then freeze-dry the sections to ensure that there is no post-examination redistribution/movement of the ions/elements of interest. Most non-conductive samples require surface coating, typically with an ultrathin (~10nm) layer of carbon or heavy metal to prevent charging.

WDS hardware

WD spectrometers house the diffractor, the detector, and sophisticated precision-engineered mechanical linkages to control the positions of these devices and to allow the switching of diffractors. X-rays enter the spectrometer through an aperture, which may be open to the column or have a thin window to allow the spectrometer to be differentially pumped from the microscope column. The angle between the spectrometer and the sample surface is called the take-off angle and in most instruments this is set at around 40 degrees.

The spectrometer can be mounted vertically or inclined from the horizontal. In the vertical configuration, several spectrometers can be mounted around the column (typically four or five, but there can be more. A microprobe used at the Smithsonian Institute had 12 vertically mounted spectrometers).

Vertically mounted spectrometers are very sensitive to sample height, so microprobes incorporate a reflected light microscope to allow careful positioning of the sample. This is less of a problem for the inclined configuration, but then fewer can be fitted around the column.

Spectrometer diffractors

When X-rays reach the diffractor, they are selected according to Bragg's Law (Figure 4), which describes the required angle of incidence (θ) of an X-ray of wavelength λ for constructive interference to be at a maximum, so that only those X-rays can pass on to the detector and be counted.

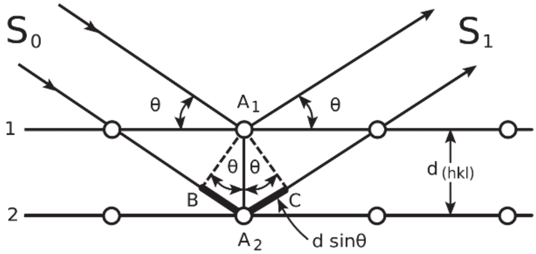


Figure 4. Braggs Law: X-rays reflected from adjacent diffractor planes will constructively interfere when their path difference 2dsin(θ) is nλ. Courtesy of ARMICRON. Wikimedia Commons (https://commons.wikimedia.org/wiki/File:Bragg_diffraction.svg)

WDS diffractors are made from a wide range of materials, but the critical parameter is the diffractor lattice spacing (*d*) because this value determines the range of wavelengths that can be collected by diffraction. Some commonly used diffractors include natural crystals, e.g. thallium acid phthalate (TAP $2d = 25.76$Å), pentaerythritol (PET $2d = 8.74$Å), and lithium fluoride (LiF $2d = 4$Å), and synthetic ones, e.g. WSi60 ($2d = 60$Å) with layers of tungsten and silicon.

Spectrometer design

When X-rays are generated by an electron beam in an SEM or microprobe, X-rays are emitted in a 3D, diverging, hemispherical wavefront. In order to accommodate diverging X-rays, Rowland circle WD spectrometers require the diffractor to be curved to ensure the same diffracting angle in all regions. This curvature imposes geometrical constraints on the positions of the diffractor relative to the sample and detector, which is solved by placing these three elements on the circumference of an imaginary circle of fixed radius called the Rowland circle. This typically has a radius of 100–160mm.

During spectrometer operation, the center of the Rowland circle is not fixed but moves within the spectrometer. The crystal moves along a linear track and is rotated to achieve the required Bragg angle (see page 24).

Once an X-ray has been diffracted, it passes on to a detector and is counted. X-rays are counted using a gas proportional counter of which there are two standard types: gas-flow counters, which contain P-10 gas (a mixture of 90% argon and 10% methane); and sealed counters, which contain xenon or a mixture of xenon and carbon dioxide. An incoming X-ray ionizes the gases, producing an electron avalanche that amplifies the signal. Electrons are collected on an axial anode wire, which yields a current pulse. Each pulse above a threshold signifies an X-ray event.

Qualitative and quantitative analysis

The power of WDS is its energy resolution and peak-to-background ratios, which are unmatched among microanalytical techniques (Figure 5). This power is revealed by qualitative or quantitative analysis. Qualitative analysis identifies X-ray lines by using peak-to-background measurements or by the inspection of WDS spectra generated by scanning the spectrometer over a range of X-ray energies, revealing which elements are present in the sample.

The power of WDS energy resolution and peak-to-background ratios can be brought to X-ray mapping. An X-ray map correlates WDS X-ray intensities with a location on the sample surface yielding a 2D map of elemental distributions. Compared to EDS X-ray maps, WDS X-ray maps are relatively free from X-ray interferences and yield accurate representations of sample compositions. In Figure 6, the EDS maps of P, Y, and Zr seem to indicate that these elements are

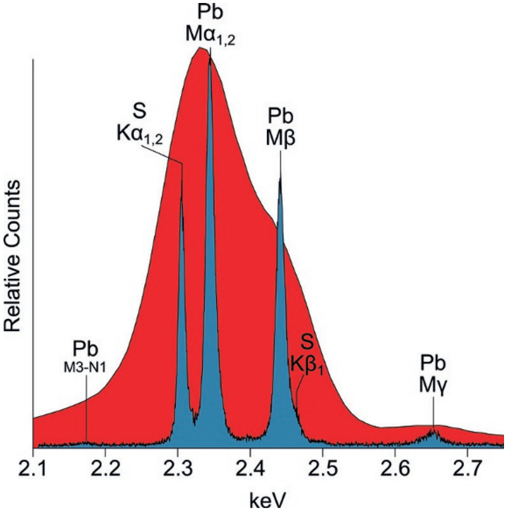


Figure 5. Comparison of WDS (blue) and EDS (red) spectra of the Pb-S-Mo X-ray interference

in the same phases. The same appears to be true for the Ti, Ba, and Ce EDS maps. However, the EDS maps are severely affected by X-ray interferences – a result of the relatively poor spectral resolution of EDS. The WDS maps reveal the true distribution of these elements.

X-ray maps can also be overlaid on an electron (secondary or backscattered) image. In this way, the distribution of elements can be correlated with specific phases or structural or morphological features of the sample such as grain boundaries, inclusions, and defects (see *Case Study 1*).

WDS quantitative analysis enables the accurate and precise quantification of elements in a sample. The quantification of trace concentrations of elements is a particular strong suit for WDS because of its strong peak-to-background ratios. The detection limits of WDS provide quantitative analyses in the 50–100ppm range (0.005–0.01wt%, elemental) with an accuracy and precision on the order of 1%.

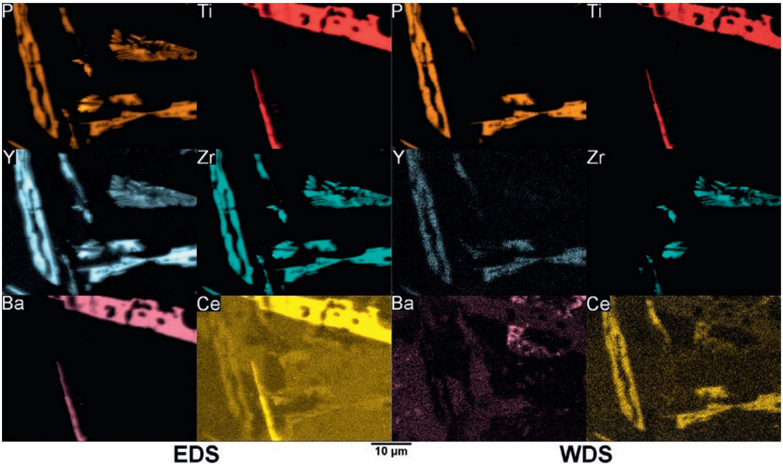


Figure 6. EDS (left) and WDS (right) X-ray counts maps of an area of lunar meteorite NWA 2727. WDS is able to resolve the P $K\alpha_{1,2}$/Y $L\beta_1$/Zr $L\alpha_{1,2}$ (2.013/1.995/2.042keV), Ti $K\alpha_{1,2}$/Ba $L\alpha_1$ (4.508/4.465keV), and Ti $K\beta_{1,3}$/Ba $L\beta_1$/Ce $L\alpha_1$ (4.931/4.827/4.839keV), which are unresolvable by EDS

For quantitative analysis, you first need to calibrate the analysis with standards, samples that have a known composition, and then compare these data to what you find in the sample under investigation. Standards are available from electron microscopy suppliers, leading laboratories, and national standards authorities.

For each element being analyzed, the typical analytical procedure is to measure the same X-ray peaks and backgrounds in the unknown and a standard under identical conditions of beam energy, probe dose, take-off angle, and spectrometer efficiency.

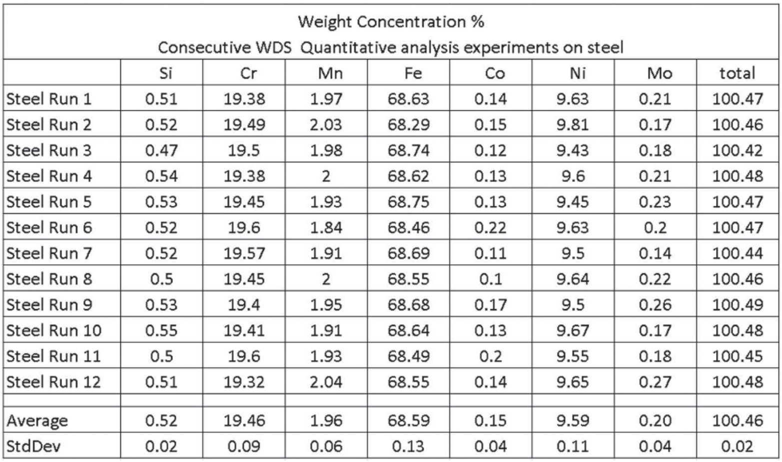
The intensity of a characteristic X-ray line is proportional to the mass concentration of the element concerned. So by comparing line intensities of your sample to that of a known standard, you can use the standard expression:

Concentration of A in sample = [Intensity of A in sample/Intensity of A in standard] × Concentration of A in standard [or $C_{Asp} = [I_{Asp}/I_{Ast}]\, C_{Ast}$]

The expression I_{Asp}/I_{Ast} is called the k ratio.

However, to calculate absolute concentrations, several physical effects must be taken into account and corrections applied to the data. These effects are known as the ZAF or PAP corrections, that is: the effect of Z (target atomic number) on the ionization (and primary fluorescence) probability, the effect of self-absorption on the final observed X-ray intensity, and the contribution of (secondary) fluorescence to the observed X-ray intensity.

Microanalysts refer to precision and accuracy when describing the reliability of their data. Precision is reproducibility and so relates to the ability to compare between samples and sample with standard – in WDS this can be less than 1%. Accuracy is the truth of the analysis and involves matrix correction and taking into account other variables such as peak interferences. The total EPMA error is a combination of both and is in the order of 1–2%. Precision is best monitored by doing multiple analyses of the same sample or phase (Figure 7). Accuracy is best monitored by the analysis of secondary standards.



Weight Concentration %
Consecutive WDS Quantitative analysis experiments on steel

	Si	Cr	Mn	Fe	Co	Ni	Mo	total
Steel Run 1	0.51	19.38	1.97	68.63	0.14	9.63	0.21	100.47
Steel Run 2	0.52	19.49	2.03	68.29	0.15	9.81	0.17	100.46
Steel Run 3	0.47	19.5	1.98	68.74	0.12	9.43	0.18	100.42
Steel Run 4	0.54	19.38	2	68.62	0.13	9.6	0.21	100.48
Steel Run 5	0.53	19.45	1.93	68.75	0.13	9.45	0.23	100.47
Steel Run 6	0.52	19.6	1.84	68.46	0.22	9.63	0.2	100.47
Steel Run 7	0.52	19.57	1.91	68.69	0.11	9.5	0.14	100.44
Steel Run 8	0.5	19.45	2	68.55	0.1	9.64	0.22	100.46
Steel Run 9	0.53	19.4	1.95	68.68	0.17	9.5	0.26	100.49
Steel Run 10	0.55	19.41	1.91	68.64	0.13	9.67	0.17	100.48
Steel Run 11	0.5	19.6	1.93	68.49	0.2	9.55	0.18	100.45
Steel Run 12	0.51	19.32	2.04	68.55	0.14	9.65	0.27	100.48
Average	0.52	19.46	1.96	68.59	0.15	9.59	0.20	100.46
StdDev	0.02	0.09	0.06	0.13	0.04	0.11	0.04	0.02

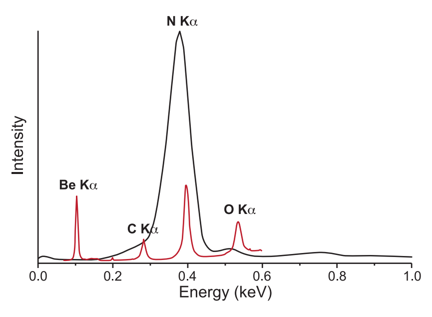
Figure 7. This example of quantitative analysis of steel shows standard deviations of 0.02–0.13 indicating excellent precision

CASE STUDY 1. Materials science: corrosion in beryllium

Research conducted by Dr Christopher Mallinson in the Department of Mechanical Engineering Sciences at the University of Surrey, UK, focuses on the study of localized corrosion of beryllium. Beryllium metal typically contains a variety of second-phase particles that form during heat treatment of the metal from elements with a poor solubility in the metal. The presence of particles at the surface of the metal has a significant influence on corrosion performance.

SEM-EDS is widely used to determine elemental distributions in a material. WDS can identify elements present at concentrations below the level that can be analyzed using EDS and can confirm the composition of a sample containing elements that have X-ray transitions of overlapping energy in EDS. In this research, the WDS system, a parallel beam WDS with a hybrid X-ray optic, provided extremely high sensitivity to light elements in order to confirm the composition and aid in the identification of second-phase particle types in beryllium metal.

The figure opposite shows an EDS spectrum (black) and an overlaid WDS spectrum (red) from a second-phase particle in beryllium. Both were acquired using a 5kV beam energy. The EDS spectrum shows an intense N Kα peak and weaker C Kα and O Kα peaks. The Be Kα peak is not sufficiently resolved above the noise to confirm the presence of beryllium in the particle. However, the WDS spectrum shows a well-defined Be Kα peak together with the C Kα, N Kα, and O Kα peaks. Carbon and oxygen are present as contamination and surface oxide film, respectively. The WDS *results show that the particle consists of beryllium and nitrogen, confirming it to be a* Be_3N_2 *second-phase particle.*



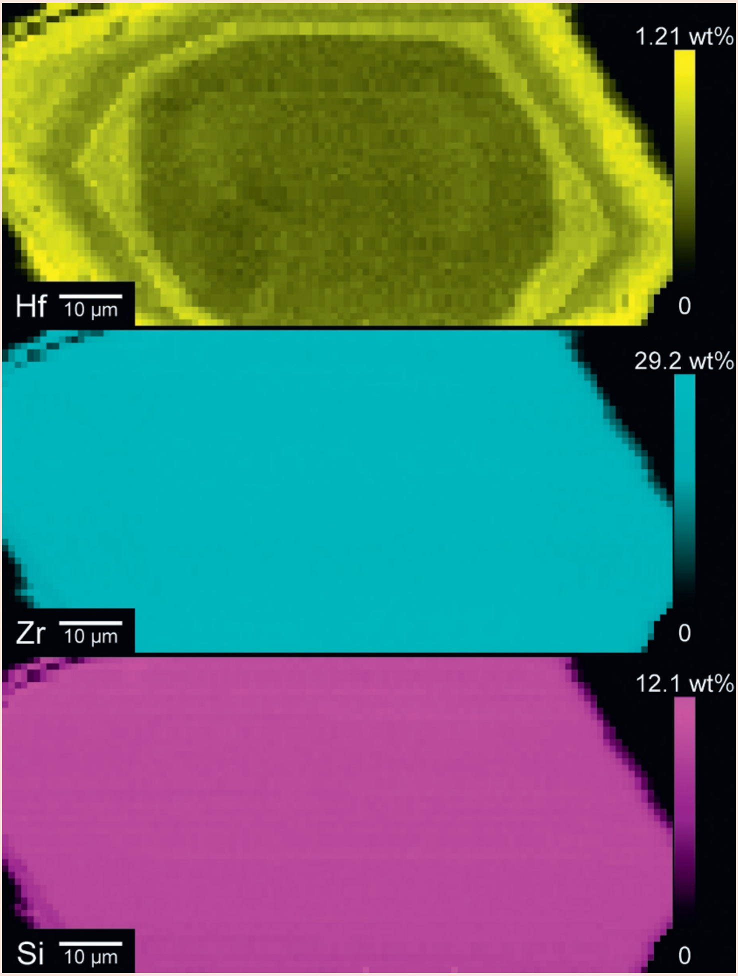
EDS (black) and WDS (red) spectra from a second-phase particle in beryllium. Acquired on a Thermo Scientific™ MagnaRay™ parallel beam WDS system, which includes a hybrid optic in order to maximize the intensity of low-energy X-rays

CASE STUDY 2. Earth sciences: mapping hafnium in zircon grains

The mineral zircon is one of the most critical geochronological tools in the earth sciences. These crystals are truly zircon-hafnium solid solutions and typically contain hafnium at tens of thousands parts per million. Zircon-hafnium ratios are used as an index of magma evolution and hafnium isotopes in zircon are an important recent tool employed to explore magma sources and processes. These isotopic ratios yield important insights into the interpretation of zircon geochronology and the magmas from which zircons crystallize.

The ability to quantitatively map trace hafnium concentrations in detail is not achievable by EDS. So Dr Rita Economos of the Southern Methodist University in Dallas, Texas, USA, uses quantitative WDS stage mapping acquired using a parallel beam WDS system with a hybrid optic on an SEM. The WDS maps are acquired by automatically slewing the SEM stage over a grid while keeping the beam at a fixed position. Each pixel of the map represents a complete WDS standards-based quantitative analysis calculated using background and $\phi(\rho z)$ *corrections. The hybrid optic, which combines grazing incidence and polycapillary optics, enables very high X-ray count rates, permitting the acquisition of WDS quantitative stage maps in practical amounts of time.*

Trace element concentrations, such as hafnium, can reveal complex zoning within mineral grains indicative of a complex crystallization history (see figure opposite).



Hafnium, zircon, and silicon quantitative elemental maps of a zircon grain picked from a granite from the Cretaceous Cadiz Valley batholith in the central Mojave Desert. The grain was mounted in epoxy resin, polished, and carbon coated. Maps are 106 × 46 pixels with a resolution of 2µm per pixel. All measurements were made using a 15kV beam accelerating voltage and a focused electron beam that was set to 206nA at the beginning of the run

PROBLEMS AND SOLUTIONS

No-one can doubt the superior resolution of WDS over EDS. This begs the question: ‘Why is EDS so much more prevalent compared to WDS?’

The answer lies in the many historical concerns regarding WDS. Fortunately, all of these have since been solved. Some solutions came by improvements in software, others by modernized hardware, and still many others by changing the fundamental design of the spectrometer geometry from the traditional Rowland circle to a parallel beam design to better match the needs of the SEM community. Here, several of these concerns are stated along with how the concerns have been addressed by modern WDS systems.

First, there is the perception that WDS is a nuanced technique, to be used only by specialists. Modern software and seamless integration of WDS with EDS in a common platform now allows for automated set-up, calibration, and on-the-fly adjustments of the WD spectrometer with minimal operator involvement.

Next, some may say that WDS is a slow technique because it can only analyze one element at a time and because complicated spectrometer motions require long drive times to move the spectrometer from one element to the next. The newer parallel beam spectrometers include high-speed hardware that allows the spectrometer to be driven from one element to the next in a fraction of a second.

WD spectrometers have historically required samples to be kept at a specific analytical coincidence point (i.e. the analytical working distance), with accuracy on the order of tens of micrometers in the electron microscope so that the spectrometers remain focused. However, the latest parallel beam spectrometers have software that automatically aligns the spectrometer by panning and tilting the spectrometer to ensure that it is positioned to maximize the count rate.

There have also been legitimate concerns that the awkward geometry of a traditional WD spectrometer would be unable to be properly mounted on all electron microscopes (particularly those with an ion gun or without a dedicated WDS port) and still maintain this accuracy of focus. Modern parallel beam spectrometers are relatively compact and can be mounted using a WDS port or an EDS port (see Figure 10, page 26).

Additionally, users wonder whether the WDS will still require high beam currents that may not be achievable in every SEM or that may damage beam-sensitive samples. The root concern here is achieving a sufficient number of X-ray counts – for all possible elements of interest – in a practical amount of time with only a single WD spectrometer.

It is true that the traditional (i.e. Rowland circle WDS) geometry is not without its limitations and restrictions. For example, in a Rowland circle WD spectrometer, when analyzing a range of wavelengths with any given crystal, the distance between source and crystal necessarily changes (Figure 8). It decreases for shorter wavelengths (higher energies). It increases for longer wavelengths (lower energies such as emitted by lighter, lower atomic number elements). This exposes a weakness of the standard spectrometer design: both the solid angle and the X-ray intensity decrease (the latter according to the inverse square law for electromagnetic radiation) with distance from the source. Therefore, the intensity of an X-ray line on a given diffractor is a function of its energy or wavelength, with higher-energy lines being more intense than lower ones.

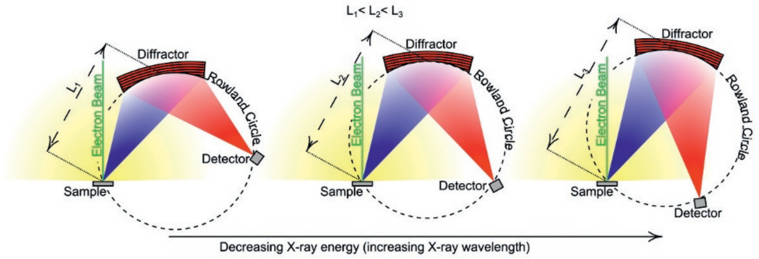


Figure 8. The Rowland Circle geometry employs a 'moving target' that creates a wide variance in actual solid angle, i.e. X-ray collection efficiency

To overcome low-intensity measurements, microprobes employ multiple (up to five) Rowland circle spectrometers that can measure one element concurrently on multiple spectrometers or can simultaneously measure multiple unique elements on individual spectrometers. One or more of these spectrometers may be optimized for low-energy analysis and others for high-energy analysis. Additionally, some spectrometers on a microprobe may be specialized by using larger diffractors or using a Rowland circle with a smaller radius to improve measured intensities. These spectrometer improvements can be accommodated because the microprobe chamber is specifically designed for Rowland circle WDS. Although this strategy is highly successful for a chamber design that is dedicated to Rowland circle WDS, it is ultimately not practical across the broad range of SEM models and chamber types. This impracticality has led to a historical hesitance to adopt WDS on a standard SEM chamber.

The Rowland circle spectrometer design has changed very little since Castaing first employed it over 60 years ago in the first microprobe. A significant recent advancement in spectrometer design was the addition of X-ray optics that collimate the X-rays as a parallel beam (Figure 9).

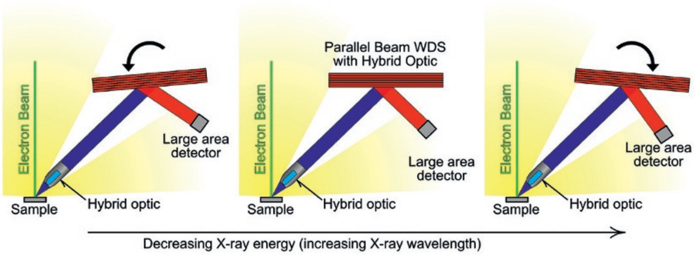


Figure 9. Illustration depicting parallel beam spectrometer geometry with hybrid optic near the sample

These new X-ray optics are of two types· polycapillary and grazing incidence. Polycapillary optics comprise a collection of several hundred thousand parallel microcapillary glass tubes only 2μm wide, each of which acts as a waveguide just like a fiber optic. A grazing incidence X-ray optic (GIXO) is a parabaloidal hollow tube with a highly polished internal surface to reflect X-rays.

The introduction of these X-ray optics has allowed a complete redesign of WD spectrometers. A parallel beam of X-rays eliminates the need for curved diffractors and the need to maintain a Rowland circle geometry, allowing the use of flat, larger-area diffractors (Figure 9). These diffractors can be mounted on a turret that can hold up to six diffractors. Therefore, you no longer need several spectrometers to cover the entire X-ray spectrum; you can use just one.

These X-ray optics have three big advantages. First, because of their parabaloidal, tapering shape, the optic can be placed close, only a couple centimeters, from the sample. This means they can collect X-rays with a much larger solid angle than Rowland circle spectrometers. For all WD spectrometers, a larger solid angle is directly proportional to the measurable X-ray intensity. The higher count rates achievable by parallel beam spectrometers can reduce the need for high beam current or minimize the time required for an acquisition. The sensitivity of parallel-beam WDS can be much greater than traditional systems, particularly for low-energy X-rays, with intensities of >8000 counts per second per nA.

Second, the parallel beam that emerges from the optics places no restrictions on the position or shape of the diffractors. So now large, flat diffractors can be used, and all diffractor positions diffract with relatively equal efficiency compared to Rowland circle spectrometers.

Third, these two types of optics can also be combined in a hybrid system with both GIXO and polycapillary optics (Figure 10). By combining a hybrid optic with multiple (typically up to six) X-ray diffractors in a single spectrometer, the latest parallel beam systems give excellent sensitivity over a larger range of the spectrum, typically 65eV–17.9keV (see Figure 11 and *Case Study 2*).

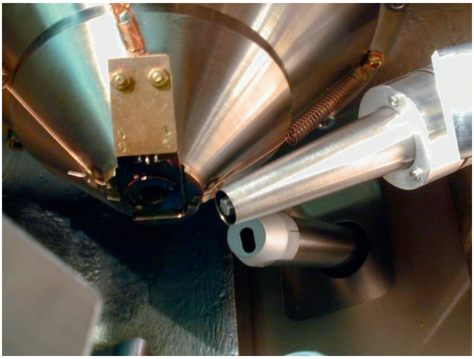


Figure 10. WDS hybrid (GIXO +polycapillary) optic inserted close to the pole piece with the WD spectrometer mounted in a standard EDS high-angle port. The EDS detector is shown nearby in the background

The result of all of these advances in software, hardware, and fundamental WD spectrometer design is a modern WDS that integrates seamlessly onto any SEM with an ease of use similar to that of EDS. Given the performance advantages of WDS over EDS

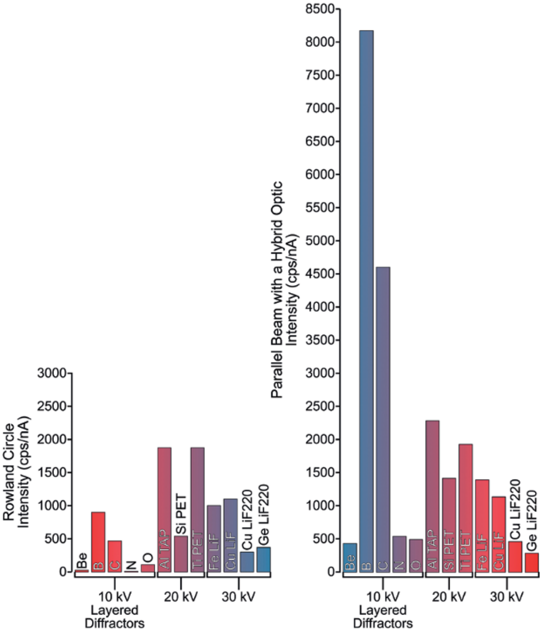


Figure 11. Comparison graphs of the best possible WDS counting intensities for (left) a Rowland circle WD spectrometer and (right) a parallel beam WD spectrometer with a hybrid optic and mounted on an SEM

and the opportunities for further improvements in WDS (see next section), it is reasonable to expect WDS installation to expand and to become more commonplace.

WHAT'S NEXT?

The electron microprobe has stood the test of time and now, over 60 years after its inception, it is still much in demand in research laboratories worldwide. With its ability to identify and quantify elements in solid samples with great sensitivity and high accuracy, there is no slowing down in demand for the latest generation of improved performance microprobes.

The improvements in WDS such as parallel beam optics for spectrometers and more sophisticated software tools that facilitate ease of use and automation of operation have made possible applications once reserved for electron microprobes to a single WD spectrometer that can be mounted on a broad range of electron microscopes.

Developers of EPMA instruments are also experimenting with using new multilayer crystals in WDS to improve the detection of lighter elements. In many cases, synthetic diffractors are better than conventional ones, giving higher count rates and helping to dampen unwanted higher-order reflections. Developers are also working to reduce the time it takes to collect WDS spectra by, for example, using multichannel analyzers. Multichannel analyzers have been adopted by the X-ray fluorescence community and could now be used in WDS microanalysis.

While a serious shortcoming of Rowland circle spectrometers is the reduced ability to analyze low-energy X-rays emitted by the light (low atomic number) elements, e.g. lithium, beryllium, oxygen, with energies in the 100eV range, grazing incidence optics used in parallel beam spectrometers enable very high X-ray collection efficiencies at very low X-ray energies. This enables the use of lower accelerating voltages (e.g. 3keV), which would enable analysis from analytical volumes with diameters on the order of a couple of hundred nanometers. WDS X-ray maps could then have a resolution that is the same as the diameter of the analytical volume.

In a radical departure from crystal spectrometry, a team at JEOL has developed a soft X-ray emission spectrometer (SXES) that uses a diffraction grating and a solid-state detector. The new SXES allows for X-rays with energies as low as 50eV to be measured, which enables the detection of X-rays as low as the Li Kα line. It has an energy resolution better than the traditional WDS and detection sensitivity that allows the measurement of boron even in the tens of parts-per-million range. The result is a solid-state spectrometer that is able to collect an entire spectrum, simultaneously, without having to move either the grating or the detector.

Some current applications of SXES include finding trace elements such as nitrogen in steels, and identifying titanium carbide and nitride inclusions in titanium-based alloys, such as the shaped memory metal nitinol. Furthermore, lithium ion battery development is an important application for WDS, and the new spectrometer design allows delineation of the Li Kα line and Li-satellite-K peak as the latter can be used to monitor the chemical state of lithium in the anode.

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