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A REVIEW ON ELECTRON PROBE MICRO ANALYSIS

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Abstract: **Electron probe microanalysis and microscopy is a widely used modern analytical technique primarily for quantifying chemical compositions of solid materials and for mapping or imaging elemental distributions or surface morphology of samples at micrometer or nanometer-scale. It is also known as electron micro probe analyser. The method is non-destructive and utilizes characteristic X-rays excited by an electron beam incident on a flat surface of sample. This technique uses an electromagnetic lens-focused electron beam, generated from an electron gun, to bombard a sample. When electron beam interacts with the sample, signals such as secondary electron, backscattered electron and characteristic X-rays are generated from the interaction volume. Characteristic X-rays are produced by inelastic collisions of the incident electrons with electrons in the inner shell of atoms in the sample. When an inner electron is ejected from its orbit, it leaves a vacancy which is filled by a higher-shell electron dropping into the vacancy. The higher-shell electron sheds energy in the form of an x-ray, which is characteristic of the particular element. These signals are then examined by detectors to acquire chemical and imaging information of the sample. An electron probe is capable of analysing almost all elements (from Be to U) with a spatial resolution at or below micrometer scale and a detection limit down to a few ppm.**

Keywords: **Electromagnetic lens- focused electron beam, electron gun, secondary electron, backscattered electron, bombardment of electrons, electron beam incident.**

1. INTRODUCTION

EPMA is a multi-faceted technique for determining the concentration and the distribution of elements in solid specimens, from major elements to trace constituents. The EPMA technique involves bombarding a specimen with an electron beam and then analyzing the emitted X-rays with two different types of spectrometer, a wavelength-dispersive spectrometer (WDS) and an energy-dispersive spectrometer (EDS).

EPMA can identify and analyze all the elements of the periodic table, except for hydrogen and helium, in any solid material. Because the emission of X-rays is largely restricted to the area of the material exposed to the electron beam, EPMA can produce quantitative data on highly localized spots under 1µm in diameter. It has the additional benefit of being non-destructive, meaning that quantitative measurements can be repeated as often as required.

The technique is routinely used to measure elements at trace levels of 100 parts per million (ppm). With optimized settings, modern EPMA devices can even measure elements at concentrations down to around 10ppm. In addition to spot analyses, EPMA can also map elemental distributions over small or large areas. This is done by either scanning the beam across the surface of the specimen or moving the stage that holds the specimen in relation to a fixed beam.

EPMA utilizes an electron beam focused to a very narrow point by magnetic lenses. When this beam hits an atom at the surface of a sample, it can eject electrons from the atom's inner high-energy shells (known as K, L and M shells), creating vacancies that are filled by electrons moving from the atom's outer low-energy shells. This movement of electrons from outer to inner shells releases energy, which falls into the X-ray range of the electromagnetic spectrum. The energy of the emitted X-rays corresponds to the energy difference between the shells involved in the transition. As every element has its own unique energy level spacing between shells, this process produces characteristic X-ray emissions that can be used to identify the element.

The origins of EPMA stretch back to the discovery of X-rays in 1895. Although first applied to medical fields, X-rays soon entered the fields of physics and chemistry. At Leeds University, UK, William Bragg and his son Lawrence were famed for their crystallography work using X-rays, which involved developing a critical law relating X-ray diffraction to crystal structure. In 1913, fellow physicist Henry Moseley from the University of Oxford, UK, put Bragg's diffraction law to good use, building a spectrometer to measure the X-ray spectra of elements, based on their diffraction through crystals.

Moseley's X-ray spectrometer used an X-ray tube, potassium ferrocyanide crystals and photographic plates. Moseley was able to bombard samples of available elements, measure the emitted wavelengths and then determine the frequencies of the K and L lines in the spectra (produced by electrons moving from lower energy shells down to the K and L shells). Importantly, he discovered that plotting the square root of the frequency of the lines against a suitable integer gave straight lines. The integer was revealed to be the atomic number, showing that the elements in any solid sample could be identified by measuring the X-rays emitted. Although Moseley was killed while fighting in World War I, his work had sown the seeds of an analytical revolution.

Meanwhile, developments in electron microscopy were also paving the way for EPMA. In 1932, the German company Siemens built the first electron microscope. In 1944, James Hillier and Richard Baker at RCA Laboratories, Princeton, USA, filed a patent for an 'electronic microanalyzer', which partnered an electron microscope with an energy-loss spectrometer and was able to analyze low atomic number elements. However, they never constructed a working model and post-war communication difficulties meant their development was never widely publicized.

Then, in the late 1940s, Raimond Castaing, a research engineer at the Office National d'Études et de Recherches Aéronautiques (ONERA), a French government research institution for aero nautical applications, developed the first electron microprobe while studying for his PhD. ONERA had obtained two electron microscopes in 1947, and Castaing used the microscopes to investigate the X-rays emitted from alloys bombarded by electrons. Castaing adapted one of the electron microscopes to turn it into a probe and used a Geiger counter to detect the emitted X-rays, but found that he could not discriminate between elements using this technique. However, he cleverly resolved this issue by building and fitting a spectrometer incorporating a unique quartz crystal to diffract particular wavelengths.

Castaing unveiled this novel technique at the First European Conference on Electron Microscopy in 1950. Castaing's PhD thesis, entitled Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et crystallographique (Application of electron probes to a localized chemical and crystallographic analysis method), was published in 1951. This thesis sparked worldwide interest in X-ray microanalysis, and much of the instrumentation and theory set out in it remain valid today.

In the years following Castaing's thesis, ONERA built two proto - type electron microprobes, one of which was sent to the Institute de Recherches de la Sidérurgie, a French metallurgy research institute. However, no patent was filed and industry was quick to see the commercial and analytical potential of the technique. Based on Castaing's prototypes, the French company CAMECA (Compagnie des Applications Mécaniques et Électroniques au Cinéma et à l'Atomistique), a subsidiary of the Compagnie Générale de la Télégraphie sans Fil, was the first to produce a commercial EPMA, the MS85, in 1958. CAMECA still develops EPMA instruments today – its latest model the SXFive was launched in 2011 (Figure 1)

As quantum entities, X-rays have characteristics of both particles and waves and so can be detected by either their energies or their wavelengths, which is why EPMA instruments utilize both EDS and WDS. For the EDS, EPMA instruments utilize silicon drift detectors to measure the number of X-ray photons emitted at different energies. This gives a rapid semi-quantitative analysis and is mostly restricted to providing a quick identification of the major elements present in a specimen.

In contrast to a single EDS, modern EPMA instruments typically possess up to five WDSs, each of which is fitted with different A B Figure 1. (A) The MS85 – the first model of commercial EPMA. (B) The SXFive – CAMECA's latest EPMA generation diffracting crystals that reflect specific wavelengths. The multiple WDSs provide a more precise and accurate analysis, as they have the ability to produce spectra with higher spectral resolution (5–10eV typically) than EDS (120–130eV typically).

EPMA instruments also house an optical microscope for pinpointing the area of interest and three detectors for capturing the cathodoluminescence (CL), secondary electrons (SE) and back - scattered electrons (BSE) that are also emitted from the specimen under electron bombardment. These additional signals provide information on the specimen's crystal structure, surface topography and atomic weight.

Detectors for CL, which is the visible light generated when an electron beam impacts a luminescent sample, provide valuable information not easily generated by other means, especially relating to crystal structure, highlighting trace impurities, lattice defects and crystal distortion. For example, certain CL peaks arise from the energy gap between the conduction band and the valence band in semiconductors, and so can be used to map strain and chemical composition.

For SE imaging, the electron microprobe effectively functions as a scanning electron microscope, providing topographical information based on secondary electrons directly liberated from their energy levels by the electron beam. These electrons have low energies and only those created within a few nanometers of the sample surface can escape; secondary electrons are therefore very sensitive to surface topography.

Images using BSEs show atomic number differences, based on the fact that the number of BSEs increases with the increasing mean atomic number. In the resulting BSE image, brighter areas indicate heavier mean atomic number.

The basic output of EPMA is a spectrum showing peaks that represent X-rays with specific energies (EDS) or wavelengths (WDS), with each peak corresponding to a specific element. The lateral distribution of each element is obtained, by either beam or stage scanning, after acquiring X-ray maps at peak and off-peak (background) positions. The sizes and proportions of phases identified in the analyzed material can be determined by combining several X-ray maps (Figure 2).

EPMA can also determine the concentration of the elements based on the intensities of the emitted X-rays, allowing it to conduct absolute quantitative analyses. This usually involves first collecting a spectrum with WDS and/or EDS to identify which elements are present in a specimen. Quantitative analysis is then performed using just the WDSs, by comparing the X-ray intensities measured for all the elements identified in the initial spectral analysis against standards of known composition. After matrix correction for fluorescence, absorption and atomic number effect, the concentrations of all the elements identified in the specimen are accurately determined. The results of quantitative EPMA analyses are commonly displayed as weight percentages of elements and/or oxides.[2]Electron probe microanalysis (EPMA) was performed on a Jeol JXA-8600 spectrometer.

This ability to conduct quantitative analyses is a major strength of WDS EPMA, which is recognized as the only non-destructive analytical technique able to provide absolute and accurate quantification for a specimen of interest. Using well defined standards, it is possible to achieve quantitative analysis with an accuracy better than ±1%.

2. INTRODUCTION:

Electron probe microanalysis (EPMA) is an analytical technique that has stood the test of time. Not only is EPMA able to trace its origins back to the discovery of X-rays at the end of the nineteenth century, but the first commercial instrument appeared over 50 years ago. Nevertheless, EPMA remains a widely used technique for determining the elemental composition of solid specimens, able to produce maps showing the distribution of elements over the surface of a specimen while also accurately measuring their concentrations.

EPMA involves bombarding a specimen with a focused electron beam and analyzing the emitted X-rays. It generally combines two related analytical techniques – wavelength-dispersive spectroscopy and energy-dispersive spectroscopy (which is also the subject of a separate Essential Knowledge Briefing) – in a single instrument known as a microprobe. Both techniques work by collecting characteristic X-rays and continuum released when the surface of a specimen is bombarded with electrons. As their names suggest, wavelength-dispersive spectroscopy separates emitted X-rays according to their wavelengths while energy-dispersive spectroscopy separates them according to their energies.

Wavelength-dispersive spectroscopy exhibits far better spectral resolution than energy-dispersive spectroscopy, but data collection is not as fast. When combined together in EPMA, energy-dispersive spectroscopy and wavelength-dispersive spectroscopy complement each other to produce a powerful analytical instrument. Energy-dispersive spectroscopy can conduct a quick initial analysis to identify the major elements, while wavelength dispersive spectroscopy can perform a more detailed analysis to identify trace elements and measure the concentrations accurately.

EPMA has proved particularly adept at analysing geological materials and metal alloys, able to reveal both the concentration and the distribution of elements at the sub-micrometer scale. EPMA has also found use in a wide range of other applications, studying everything from the latest advanced solar cells to archaeological material.

This Essential Knowledge Briefing provides an introduction to EPMA and its capabilities. It begins with a detailed explanation of the operation of the instrument, including an explanation of why elements emit characteristic X-rays, and outlines the major steps in the development of EPMA over more than 100 years. It also details various practical issues related to the instrument, describes potential problems that may arise and how to solve them, and provides examples of how EPMA is being used by scientists in their research. Finally, it looks at prospective future applications and how the scientists developing these innovative applications will help to ensure that EPMA continues to stand the test of time.

3. PRINCIPLE

[3] ELECTRON SPECIMEN INTERACTIONS

When an electron beam strikes a target (that is, the sample), the electrons are scattered by the target atoms. There are two types of electron scattering:

Elastic Scattering Inelastic Scattering E1 = E0, (ϕ_e>>ϕ_i)

Inelastic scattering E_1 <E_0, small ϕ_i large φ_e

Where, E_0 is the energy of the incident electron; E_1, the energy of the electron after scattering; φ_e, the elastic scattering angle; and φ_i, the inelastic scattering angle.

3.1. ELASTIC SCATTERING:

Elastic scattering affects trajectories of the beam electrons inside the specimen without significantly altering the kinetic energy of the electron (e.g., electron backscattering).

3.1.1. Electron back-scattering

When the elastic scattering angle is greater than 90°, backscattering occurs. It may also occur through multiple scattering at high angles.

3.2. INELASTIC SCATTERING

Inelastic scattering involves transfer of energy from the beam electrons to the atoms of the specimen (e.g., generation of secondary electrons, Auger electrons, characteristic X-rays and bremsstrahlung or continuum X-rays). The trajectory of the beam electron is not altered significantly.

3.2.1. Secondary electron excitation

Some sample electrons mobilized through inelastic scattering by beam electrons overcome the surface energy barrier and escape from the sample. These electrons are known as secondary electrons. It generally increases with a decrease in the beam energy.

Although sample electrons are mobilized throughout the interaction volume, their escape probability from the surface of the sample decreases sharply with depth. The escape depth of secondary electrons is only about 1/100 of that for backscattered electrons for incident beam energies in the range 10-30 keV. Hence, secondary electrons are useful in studying the surface characteristics of the sample. Samples are commonly coated with a thin film of gold that enhances the secondary electron yield.

3.1.1. [4]X-ray generation and interaction volume:

Characteristic X-rays are generated by a focused electron beam that bombards and interacts with solid materials. Mosley (1913) discovered that the wavelength of the characteristic X-ray from an element is inversely related to its atomic number Z. The range of electrons and Xrays generated by an electron beam within a sample is called interaction or excitation volume, which depends on the energy of the electron beam and average atomic number of the sample. The shape and size of the interaction volume represent the source from which analytical signals originate.

As beam electrons travel through the sample, collision processes between the beam electrons and atoms in the sample are either elastic or inelastic, depending on whether or not energy change is involved. During inelastic collisions, the beam electrons lose part of their energy. If the lost energy is high enough to overcome the critical ionization energy of an element, it will be able to remove an inner-shell electron from the atom, which leaves an inner-shell vacancy. The excited atom is not stable and a higher-shell electron will fall into the vacancy, resulting in release of a characteristic X-ray photon or an Auger electron.

3.1.2. Wavelength dispersion and focusing of characteristic X-ray

X-ray generated in the interaction volume is detected using WDS spectrometers, a key component that makes an EPMA different from other SEM although some modern SEMs may be equipped with a WDS detector. A WDS detector includes a few diffracting crystals and a gas-flow or sealed proportional counter. The X-ray source in the sample, the surface of a diffracting crystal and the gas proportional counter define an imaginary circle of constant diameter, which is called the Rowland's circle (Fig. 1). Diffracting crystals are used to disperse wavelengths of characteristic X-rays and focus a specific X-ray wavelength onto a gas-flow or sealed proportional counters for measurement. Since only a small portion of the X-ray photons from the sample reach a diffracting crystal, the intensity of the X-ray detected by WDS is generally lower than that detected by an energy dispersive spectrometer (EDS) for a given beam current.

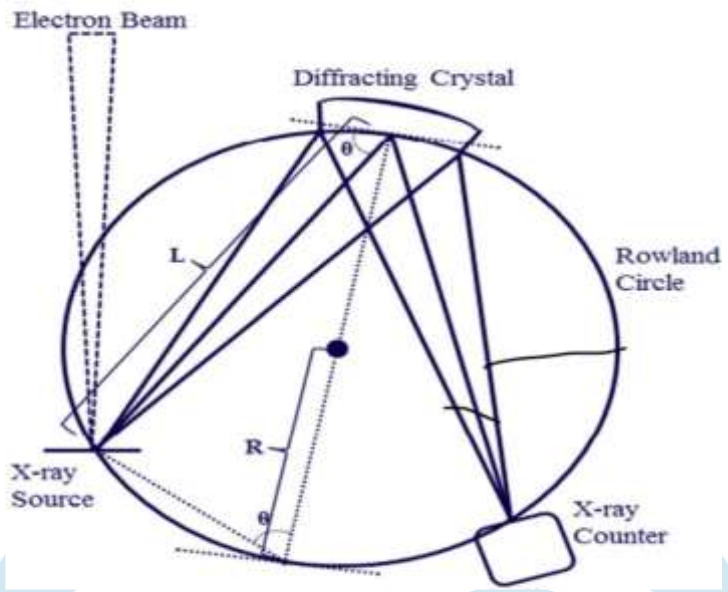


Fig. 1. An imaginary Rowland circle composed of the X-ray source in the sample, the diffracting crystal and the gas proportional counter. R — radius of the Rowland circle, L — detection position which is the distance between the X-ray source and the diffracting crystal, θ — angle of diffraction at which the diffracted characteristic X-rays are in phase and the intensity is constructively enhanced. Since L = 2Rsin θ, combining this equation with Bragg's law, nλ = 2d sinθ, yields L = nλR / d. fluorescence (F). The matrix effects must be corrected in order to obtain the actual concentration of an element

3.1.3. Standards and matrix correction:

Well characterized and accepted standards are critical for quantitative EPMA. In quantitative EPMA, the concentration of a given element in an unknown sample is obtained by comparing the intensity of a characteristic X-ray of that element with that from a standard with known chemical composition. The intensities of an X-ray line in both sample and standard must also be corrected for matrix effects, deadtime, background and instrumental drift, overlapping, etc. in order to obtain accurate results. According to the Castaing approximation, the intensity I of a characteristic X-ray is proportional to the mass concentration C of the element measured. The measured X-ray intensity of an element in EPMA is affected by the concentrations of all the other elements present in the sample. These matrix effects include mainly influence of atomic number (Z), X-ray absorption (A), and secondary.

[6]The ratio of the count rates for an element in the sample to that of pure element is called *k*-ratio. This quantity, to a first approximation, gives the concentration of the element in the sample. However, there is a necessity to correct this since the behaviour in an unknown material is expected to be different from that in a standard. The atomic number (*Z*) correction is required to account for (i) changes caused as a result of backscattering of electrons from the sample, (ii) electron energy loss due to inelastic scattering as the beam penetrates the material. Some of the X-ray photons released from the sample may be absorbed en-route to the detector or scattered out of the line to the detector. The corresponding correction factor is known as absorption (*A*) correction. The X-rays emitted by the sample on passing through it may cause secondary ionizations giving rise to further X-ray emissions. In such situation, the detected intensity is greater than the actual energy generated by the electron beam and the corresponding correction factor is known as fluorescence (*F*) correction. Models are now available for incorporating the average *ZAF* corrections.

4. INSTRUMENTATION:

[4]Following the trajectories of signals, first the primary electron beam and then the signals from the sample (SE, BSE, X-ray, etc.), the major components of EPMA include 1) electron gun, such as a tungsten filament, LaB6 or field emission gun, used to generate electrons, 2) electron column, composed of a series of electromagnetic lenses, used to manipulate the electron beam in a way similar to light optics, 3) sample chamber with a sample stage adjustable in X, Y, and Z directions, 4) detectors around the sample stage inside the chamber, 5) vacuum system for the column and chamber, 6) WDS spectrometers installed around the electron column, which are used for detecting characteristic X-rays, 7) light microscope for optical observation of the sample, and 8) a control system composed of control interfaces and panel, and computers for data acquisition and processing. The components 1 to 5 above are also common constituents of a typical SEM. A modern EPMA now includes almost all functions of a SEM, equipped with SE, BSE, EDS, and sometimes cathodoluminescence (CL) and/or electron backscattered diffraction (EBSD) detectors.

4.1. Electron gun:

There are two types of electron guns — thermionic and field emission guns. Most electron microprobes use thermionic tungsten or LaB6 filaments, but field emission gun electron microprobes are now also available and become popular. Thermionic electron emission occurs when the filament material is heated to a temperature of 2600–2700 K so that electrons have a sufficiently high thermal energy to overcome the work function energy of the filament material. A thermionic tungsten filament for an EPMA lasts usually for a few months; and high quality of vacuum within the gun area provided by an ion pump could make a tungsten filament last up to one year. A long lifetime of one or more years is usually achieved by a LaB6 or FEG gun. In an FEG, electrons are extracted from an extraordinarily sharp tungsten single crystal needle welded to a tungsten hairpin by putting an additional anode of a few kilovolts close to the tip. The main anode is used to accelerate the extracted electrons to the operating voltage. A much high, focused, monochromatic beam current may be obtained from a FEG at a low temperature of 1500 °C.

4.2. Electromagnetic lens

Electromagnetic lenses are used to focus and demagnify the electron beam emitted from the gun to an electron probe of approximately 1 to 10 nm on the specimen. An electromagnetic lens is composed of a hollow cylinder made from magnetic material and copper wire coil through which the current is running. All lenses suffer from manufacturing defects or imperfections, so an electron beam may never be brought into perfect focus by an electromagnetic lens. This phenomenon is called spherical aberration. Another type of aberration is chromatic aberration, which is caused by variations in the energy of electrons emitted by the gun.

4.3. Probe current and its regulation

The accuracy of quantitative analysis depends partly on the stability of the electron probe current. Probe current must be regularly monitored and corrected during an analytical session. One way to achieve high current stability over long analytical sessions is to use a beam stabilizer or regulating system. Several definitions related to current are used in EPMA: 1) Filament current is the current used to heat the filament for electron emission. 2) Lens current is the current passing through the coil of an electromagnetic lens. An increase in the lens current causes an increase in the strength of the electromagnetic field, which reduces the focal length. 3) Beam current is the total current emitted by the filament. 4) Probe current is the total current delivered to the specimen, which can be measured by using a Faraday cup, i.e., probe current detector (PCD). The probe current represents only a portion of the original beam current from the filament. The probe current is generally maintained at a constant value throughout an analytical session and should be reported in published papers. In the literature, probe current is often referred to as beam current. 5) Specimen current is the residual fraction of the probe current that stays within the sample. Some of the probe current bombarding the sample is backscattered out of the sample (Potts, 1987). For a constant probe current, the specimen current may vary from sample to sample depending on the mean atomic number and conductivity of the sample. Therefore, probe current on Faraday cup, not beam current or specimen current, should be reported in the experimental conditions.

4.4. Diffracting crystals

Most electron microprobes are equipped with multiple WDS spectrometers and each spectrometer with multiple diffracting crystals. Use of multiple spectrometers and multiple diffracting crystals are necessary not only for analyzing multiple elements simultaneously, but also for optimizing performance in different wavelength ranges. Common diffracting crystals include lithium fluoride (LiF), pentaerythritol (PET), thallium acid phthalate (TAP), layered diffracting elements (LDE), and pseudocrystals (PC). Theoretically, from Bragg's law, $\sin\theta$ in equation $n\lambda = 2d \sin\theta$ cannot exceed unity; it therefore defines the maximum wavelength that can be diffracted by a diffracting crystal with a given d spacing. Practically the limitations on the wavelength range that can be diffracted by a crystal are also imposed by the design of spectrometer. A lower wavelength limit is imposed by Bragg's equation as it is impossible to move the diffracting crystal too close to the specimen, which limits the θ value. Crystals like LiF with small d spacings (0.4027 nm) are good for X-ray with short wavelengths (e.g., Ti Kα to Br Kα and Sn Lα to U Lα) because their interplanar d spacings are small. Synthetic crystals, such as PET and TAP with larger d spacings, are good for longer wavelengths. For example, PET is generally good for P Kα to Mn Kα, Rb Lα to Ba Lα, and Hf M lines to U M lines; and TAP for F Kα to Si Kα, Rb Lα to Ba Lα, and La M lines to Au M lines. However, the d spacings of PET and TAP are still not large enough to accommodate the long wavelengths. The measurement of long wavelength Kα X-ray lines for light elements such as Be, B, C, N, O and F is better achieved using layered diffracting elements (e.g., LDE1 or LDE2) or pseudocrystals (e.g., PC1, PC2 or PC3). Elements H, He and Li cannot be analyzed by EPMA as their wavelengths are too long. A good diffracting crystal need to be chemically stable and insensitive to room temperature change. An electron probe laboratory is usually kept at a constant temperature close to the temperature of the chilled water to avoid problems with temperature-sensitive crystals. In addition, a diffracting crystal should have good dispersion efficiency, low X-ray absorption, and high reflection efficiency.

5. DETECTORS

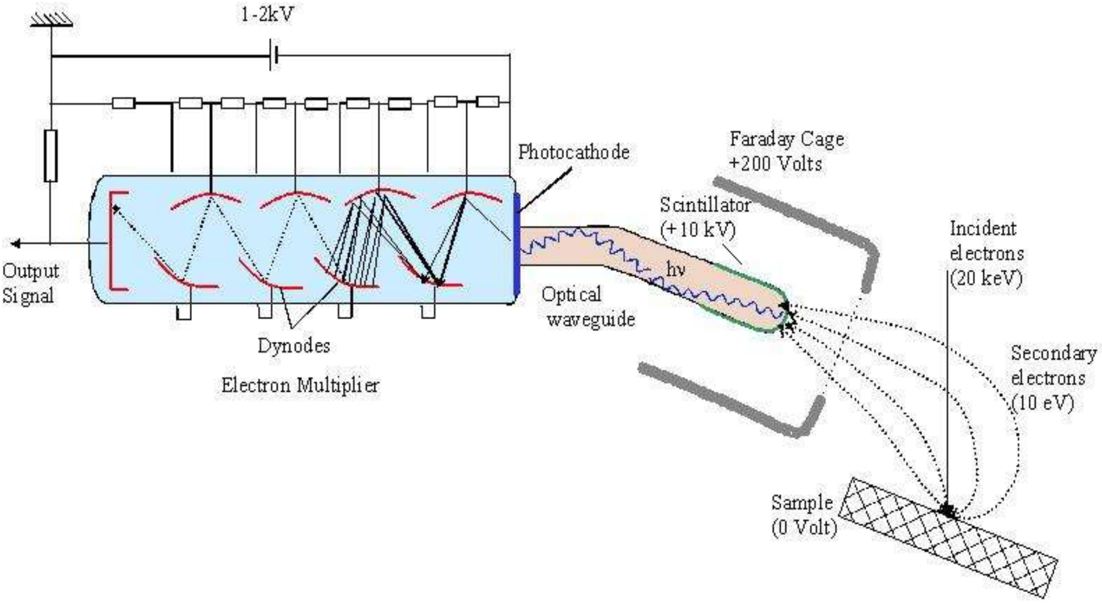
The electron microprobe can be used to obtain high resolution scanned images of the surface of a specimen by rastering the electron beam over an area of the surface. The signal is plotted on the display monitor as the beam scans thus forming a scanning image. Depending on the signal used, an image can be a scanning electron image, an elemental X-ray map or a cathodoluminescence (CL) image. Scanning electron images utilize secondary electrons (SE) or back-scattered electrons (BE). X-ray compositional maps utilize the characteristic X-rays of elements that may be obtained either through the wavelength dispersive spectrometers (WDS) or the energy dispersive spectrometer (EDS). A CL image uses the light signal generated in response to the electron beam.

5.1. [3] ELECTRON DETECTORS

Back-scattered electrons have energies between 0 keV and E0. In contrast, secondary electrons have energies in the range 0-50 eV, mostly between 3 and 5 eV. Therefore, different methods are required for the detection of the two types of electron signal.

5.1.1. Everhart-Thornley (E-T) detector for topographic contrast:

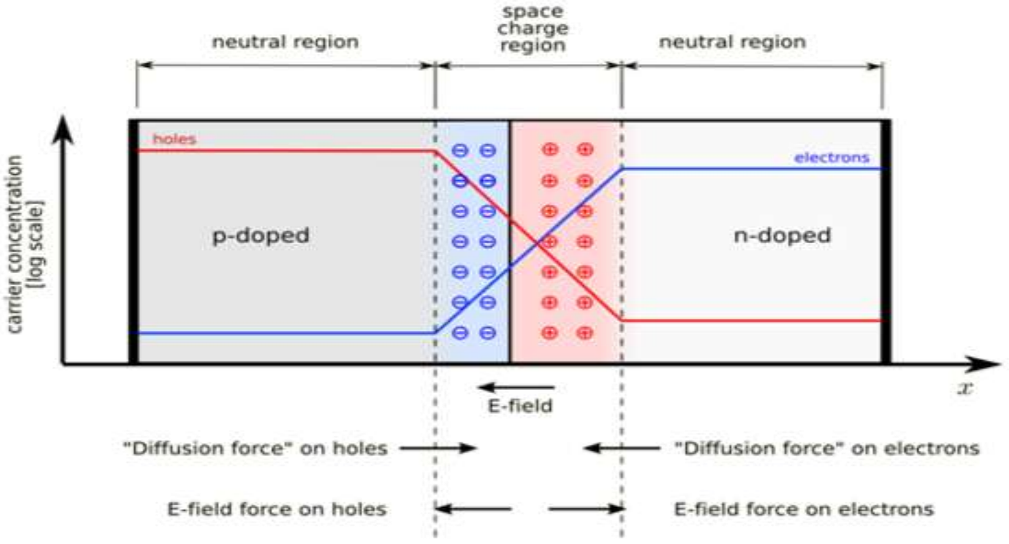
The E-T detector consists of a scintillator maintained at a large positive potential of 10 to 12 kV to attract the incoming electrons. The electrons interact with the scintillator and produce light that travels through a light guide, a solid plastic or glass rod, to a photomultiplier. Light produces electric current in the photomultiplier and the current is amplified by an amplifier. The scintillator is enclosed in a Faraday cage which can be biased to a negative or positive potential (-50 to +250 V). When the E-T detector is negatively biased, only the high energy back-scattered electrons are able to enter the detector, whereas, a positively biased E-T detector intercepts both back-scattered and secondary electrons.



The E-T detector is mounted on one side of the sample chamber receiving a highly directional view of the specimen. As a result, when imaging a fractured surface, the faces directly in the line-of-sight of the detector appear brighter than the other faces. A negatively biased detector rejects the secondary electrons and the faces not in line-of sight of the detector appear dark producing a shadowing effect. This harsh contrast is reduced when the detector is positively biased because secondary electrons produced on the faces not in line-of-sight are also pulled into the detector. The E-T detector is thus a useful tool for topographic imaging.

5.1.2. Solid-state diode detector for compositional and topographic contrast

The solid-state diode detector is a semiconductor that tracks changes in voltage in an electrical circuit as a result of electron-hole production in the detector from interactions with back-scattered electrons. It is a flat, annular wafer mounted on the polepiece of the objective lens directly above the specimen. Low energy electrons such as secondary electrons fail to produce electron-hole pairs in the diode and are not detected.



The annular detector is split two semi-circles, A and B. When signals from both parts are added (A+B mode), good compositional contrast results. The A-B mode is analogous to a stereoscopic view and produces topographic contrast.

5.2. CATHODOLUMINESCENCE DETECTOR

When semiconductors interact with energetic electrons, they produce long wavelength ultraviolet, visible and infrared radiations known as cathodoluminescence (CL). Cathodoluminescent materials have a filled valence band and empty conduction band separated by an energy gap, Egap, of forbidden energy states. When an energetic beam electron scatters inelastically, an electron from the valence band may move to the conduction band leaving a hole in the valence band. When the electron and the hole recombine, energy equal to Egap is released as a photon. This energy, Egap, can be used to identify the specimen by CL spectrometry. Presence of impurity, however, creates additional energy states in the energy gap and changes the wavelength and the intensity of the light. The light signal can thus be used to identify the impurity and obtain a CL image to study the spatial distribution of the impurity. CL can also be excited by X-rays generated in the sample. Hence, the volume of CL excitation can be larger than the primary electron interaction volume resulting in poorer image spatial resolutions compared to scanning electron images. Thin films usually produce CL images with a better resolution than bulk samples. A CL spectrometer is attached to the optical microscope port of the electron microprobe. When studying CL, the optical microscope light source is turned off so that the only light coming through the ocular is the light generated by the sample.

5.3. X-RAY DETECTORS

An electron microprobe is usually equipped with an energy dispersive spectrometer (EDS) and several wavelength dispersive spectrometers (WDS) for X-ray spectrometry. An X-ray detector is a part of the EDS or WDS.

5.3.1. Energy Dispersive Spectrometer (EDS)

An energy dispersive spectrometer (EDS) takes advantage of the phenomenon of electron-hole production by energetic X-rays in a semiconducting lithium-drifted silicon (Si(Li)) or germanium detector. Electric current produced in the detector is proportional to the incident X-ray energy. A multichannel analyzer (MCA) is used to analyze the electrical pulses and construct an X-ray spectrum for the entire energy range (0 keV to E0) in the form an energy histogram. Elements down to Be (Z=4) may be detected with a very thin window or a window-less detector. Pure Si is a semiconductor and a good material for a detector. However, Si usually contains some B as impurity that creates holes in the valence band of Si. This electron deficiency makes Si a conductor. Since B is a p-type dopant, an n-type dopant such as Li is added to Si to compensate the electron deficiency created by B. Li is applied on the surface of Si and allowed to diffuse into the crystal. This forms a micrometer-thick p-n zone at the Si-Li interface that acts as an intrinsic semiconductor. Most of the Li is removed from the surface to expose the p-n zone. A reverse bias is applied under liquid nitrogen temperature to the p-n zone, which enlarges the intrinsic zone to a thickness of a few millimeters. Li is mobile under an applied bias at room temperature. Hence, a Si (Li) detector should always be operated at liquid-nitrogen temperatures to prevent damage.

5.3.2. Wavelength Dispersive Spectrometer (WDS)

A WDS system consists of two components: an analyzing crystal and an X-ray detector known as the proportional counter. WDS takes advantage of the Bragg diffracting characteristics of an analyzing crystal to preferentially diffract the wavelength of interest toward the detector. [5] Bragg's law is defined as:

$$n\lambda = 2d \sin \theta \qquad (5.1)$$

where, λ is the wavelength of the X-ray, d is the lattice spacing of the crystal, θ is the angle of incidence and diffraction and n is the order of reflection. X-rays are reinforced after diffraction when the path lengths between two rays differ by an integral (n) of the wavelength. Combined reflections from a large number of lattice planes result in a narrow intensity distribution around a peak. For example, the measured full-width halfmaximum (FWHM) energy interval of MnKα is about 10 eV compared to the natural value of 2 eV.

In WDS, the X-ray source (point of the sample from the X-rays are emitted), the analyzing crystal and the detector are positioned on the circumference of a focusing circle known as the Rowland circle. In a Johansson type fully focusing spectrometer, the crystal is curved to a radius of curvature of 2R and then ground to R, so that its lattice planes and the focusing circle have the same curvature. The diffracted X-rays are thus fully focused into the detector. In practice, crystals are not ground because it degrades the resolution of the crystal. This compromise, known as Johann optics, does not seriously impair the spectrometer resolution. From the geometrical configuration of the instrument, λ is related to L, the distance between the sample and the analyzing crystal by the following relation: $L = n\lambda.R/d$ (4.2) (mm), where, R is the radius of the focusing circle (140 mm or 100 mm on JEOL). To detect different X-ray wavelengths, the crystal is moved in a straight line toward or away from the sample at an angle, ψ (take-off angle), the angle between the specimen-surface and the X-ray travel direction. The take-off angle is fixed by the design of the instrument. As the crystal moves, it also rotates so that the X-ray incidence angle, θ, changes. As a result, different wavelengths are diffracted. The detector moves simultaneously so that it remains in path of the diffracted X-rays. The focusing circle changes position, but its size remains the same. [7]EPMA/WDS is better than EDS

5.3.2.1. Diffracting crystal in WDS

Because of the characteristics of WDS, X-rays emitted from only a small elliptical volume of the sample reaches the detector. The shape of this X-ray focus volume depends on the shape of the analyzing crystal and is usually an extremely elongated ellipsoid. The major axis of the focusing ellipsoid is proportional to the width of the diffracting crystal and has a length of several millimeters. In electron microprobes, WD spectrometers are usually mounted vertically so that the focusing circle is vertical. In this configuration, the major axis of the focusing ellipsoid is horizontal and in the plane of the specimen-surface. A small movement of the specimen in the vertical direction may move the surface outside the focusing ellipsoid and the emitted X-rays will fail to reach the detector. Therefore, the surface is always focused with an optical microscope coaxial with the electron beam during an analytical session. The optical microscope has a shallow focus and the surface can be focused accurately. During routine maintenance, the spectrometer is slowly moved up or down while the surface is in optical focus until the X-ray counts are maximized, ensuring that the major axis of the focusing ellipsoid is on the specimen-surface. At the start of an analytical session, the surface is focused both with the optical microscope and the objective lens-controls of electron beam. This ensures that the specimen-surface is in X-rays focus when it is in optical focus. The primary X-ray production volume is much smaller than the volume of the focusing ellipsoid. Since X-ray fluorescence may occur from a much larger volume than the primary X-ray volume, a vertical spectrometer will intercept a significant amount of the fluoresced X-rays. This is a minor problem in a horizontal or inclined spectrometer. However, such configurations require low X-ray take-off angles to maximize the X-ray signal in the detector (e.g., in the horizontal configuration, the Rowland circle is also horizontal). Because of absorption and fluorescence correction issues, low take-off angles are not recommended.

5.3.2.2. X-ray detector in WDS: proportional counter

The commonly used detector in WDS is known as a proportional counter and consists of a gas filled tube with a thin tungsten wire along the tube-axis maintained at a potential of 1-3 kV. In a flow counter, gas flows through the tube. Sealed counters are also used. X-rays enter the tube through a thin window and ionize the gas atoms. The electron ejected from the gas atom may ionize other gas atoms. The tungsten wire collects the charge and creates a voltage pulse that is amplified and counted by the electronics.

Because one ionization in the gas can set off a chain of ionizations, the signal is amplified internally resulting in count rates of 0-50,000 counts per second. The gas amplification factor, a measure of the internal amplification, varies proportionally to the applied bias in the tungsten wire with a range of voltage known as the proportional counter region.

The type of gas used in the counter depends on the wavelength of the X-ray to be detected. The efficiency of detection, known as the quantum efficiency, of Xe is greater than that of Ar for short wavelength X-rays. Since the LIF and PET crystals are appropriate for short wavelength detection, these crystals are combined with sealed Xe N. counters in WD spectrometers. The thin window on a sealed Xe-counter is made of Be. Ar, diluted with 10% methane (P-10 gas), has a better quantum efficiency for long wavelength X-rays. Hence, flow-proportional counters with P-10 is combined with TAP or LDE for light element detection. The window material on a flow Ar-counter is usually an organic compound such as Formvar or cellulose nitrate. The efficiency of an Ar counter may be improved by increasing the gas pressure to 2-3 atmospheres.

6. [8] SAMPLE PREPARATION:

6.1. SAMPLING:

In many cases materials received by the laboratory are usually larger than that required for the measurement. Thus, preparation starts with the question: Which size and how many samples do I need for the measurement? The maximum size of the sample analysed depends on the design of the sample holder of the chosen instrument. For example, the microprobe at our laboratory has the following types of holders.

The maximum size of the sample is 1 or 1 Y2 inch in diameter and 20 mm in height, including mounting material or wall thickness of the holder.

A given heterogeneity of the original material results in the selection of many samples representative of a special property or treatment of the material. A properly designed sampling plan has then to be written. The number of samples can be estimated by statistical methods [1 , 2] or often it is a compromise between heterogeneity and costs. When the properties of the 121 EMAS 2012 - J(J" Regional Workshop on Electron Probe Microanalysis Today- Practical Aspects Figure 1. EPMA sample holders available at the GfE. material are unknown, the best way is to start with a small number of samples, using experience and intuition as a guide to make them as representative of the received material as possible, and to perform the corresponding measurements. In an iterative way one then has to evaluate the results and to decide on the further procedure.

6.2. SECTIONING

Many different methods [3, 4] can be used for sectioning materials, i.e. cleaving, fracturing, sawing, cutting and wire EDM. In all cases, the near-surface region of the sectioned surface is damaged more or less deeply. The depth of damage varies with material and sectioning method. Subsequent operations like grinding and polishing have to be performed in order to remove the damaged material. The focus of this article will be a short description of two commonly used methods, i.e. abrasive cutting and wire sawing. Finally, an incorrect preparation technique is reported, where a laser was used for cutting.

6.2.1. Abrasive cutting

Many types of abrasive wheels are offered by different manufacturers. The type is determined by the sort of abrasive grains, their bonding, and the porosity of the wheels. As a rule of thumb, hard bond wheels cut soft materials and soft bond wheels cut hard materials. In order to minimise the depth of damage during sectioning it is recommended to follow the instructions of the manufacturers concerning the choice of abrasive wheel, lubricant/ coolant and operating conditions.

For precision cutting and for cutting extremely hard materials, diamond-impregnated wheels are preferred. Such low speed diamond saws cut slowly, but the as-cut surface is relatively smooth and further preparation time is short. Additionally, the possibility of dry-cutting prevents contamination from the lubricant.

6.2.2. Wire saw

The device with highest precision, lowest damage and lowest contamination is the wire-saw in principle, a fine diamond-impregnated wire is the cutting tool. Although cutting rates are much lower than those of abrasive wheels the damage produced is negligible and subsequent grinding and polishing is often not necessary. It is a nearly contamination-free sizing method, since water is not used as lubricant, but it is only used to wash out the debris that would accumulate above the wire.

6.2.3. Laser induced cutting

This can be applied to a metal sheet of which an oxide scale and/or corrosion products have to be examined by EPMA. In order to avoid contamination of the surface and to have a rapid method for preparing a lot of samples, pieces of 1 m x 1.5 cm were cut from the sheet metal by a laser process (Fig. 4). Deposition of removed material during the process was prevented by a steady gas flow. 123

Since the focus of the laser beam was not well adjusted, the laser induced heat produces a damaged zone down to a depth of about 100 J..lm (see Fig. 5). The damage was not sufficiently removed in the subsequent cross-section preparation steps. As a result, the oxide scale was erroneously analysed as combined corundum (Cr,Al)20 3 (Fig. 6). Yet, the true oxide scale (Fig. 7), which consists of an outermost Cr20 3-layer with an oxidation of Al at the grain boundaries, was finally uncovered after further steps of grinding and polishing. Knowledge about the depth of damage or correspondingly, knowing how much material has to be removed, is an important issue for EPMA. Incorrect preparation techniques may alter the true microstructure and lead to erroneous conclusions. Figure 5. Laser-induced heat damage zone.

6.3. FIXING AND MOUNTING

For quantitative X-ray analysis the specimen's surface has to be flat and perpendicular to the electron beam. Alternatively, if in-situ tilting is possible, the tilt angle has to be determinable for a correct matrix correction. Mounting the specimen is essential both (i) for save handling of small and oddly shaped specimens during grinding and polishing, and (ii) for inserting the specimens in the electron microscope in an acceptable geometric way (under well-defined geometric conditions). The geometry of the mounts depends on the design of the sample holder. For simplicity's sake, this design is adapted to the one for metallographic examinations. Alternatively, an unmounted specimen can be embedded into an Al-foil under the pressure of a dye. For the analysis of a thin film a piece of coated wafer can be fixed on a face of a holder by using an adhesive tape or silver paint.

Following two main classes of mounting materials are commercially available:

6.3.1. Compression-mounting materials (or hot-mounting materials)

If the material is resistant to heat up to about 180 °C and to a pressure up to about 30 Mpa, compression-mounting is preferable due to the high vacuum compatibility. Diallyl phthalate provides relatively hard mounts and good edge retention. With the addition of a conductive filler, like copper, it is an excellent mount for electron microscopy. Sometimes, the conductivity of this type of mounting fails. This can be caused by a too big size of copper particles, or by oxidation of the copper. The use of fresh mounting powder or pounding of the powder before mounting is then recommended. Alternatively, phenolic as a resin filled with carbon can be used.

6.3.2. Cold-mounting materials

Epoxies as resins are acceptable for vacuum conditions, though curing time depending on formulation vary from 1 to about 8 hours. Be careful with other quick-curing resins, the strong emission of gases could be a problem for the microscope (contamination of apertures) and of course for the analysis. Due to the good adherence and low viscosity, epoxies are used for vacuum-impregnation of porous or brittle specimens. Vacuum-impregnation promotes the filling of voids, prevents contamination and also prevents loss of loose components. Nevertheless, epoxies produce a small amount of vapour contamination. Grinding down the material of 1 - 2 mm in height at the bottom of the mounted specimen could improve the vacuum compatibility, because sometimes the hardener is evaporated during mounting. Overnight storage in a low temperature oven or longer pre-pumping in a coating device results in the removal of the remaining volatile components. Epoxy is not very stable under electron beam exposure. Measurements have to be performed with minimum beam time on the mounting material. For vacuum-impregnation the use of conductive fillers could be a challenge, since the fillers increase the viscosity of the epoxy, preventing a poreless mounting material.

6.4. PLATING

Specimens for which it is necessary to examine the edges or the near-surface region (e.g. oxide scales or corrosion zones) are often plated before mounting, to prevent edge rounding. A relatively unproblematic and proven method is electrolytically plating with Ni. The precondition is a conductive coating like gold, which can be sputtered on the specimen's surface. Afterwards, the specimen is put into a Ni-bath solution (see Table 1) as the cathode. By connecting a Ni-sheet to the positive pole and using a stirrer for bath motion, a Ni-layer of about 60 J thickness is deposited after 6 hours at a current density of about 25 mA/cm^2.

6.5. GRINDING AND POLISHING

For grinding, Waterproofs abrasive papers, usually coated with carbide abrasive, are used. Diamond, alumina and colloidal silica are used abrasives.

7. APPLICATIONS:

1. Characterization and evaluation of standard or reference material.
2. Quantitative EPMA analysis is the most commonly used method for chemical analysis of geological materials at small scales.
3. Characterization of duplex stainless steel.
4. Analysis of chemical segregation in ferritic steel.
5. Determination of the pressure and temperature of formation of rocks.
6. Analysis of rare/complex minerals.
7. Thickness and composition of thin films and multilayers.
8. To determine a U-Th age of a mineral such as monazite without measuring isotopic ratios.
9. It is widely used for analysis of synthetic materials such as optical wafers, thin films, microcircuits, semi-conductors, and superconducting and ceramics.
10. Quantitative analysis of Iron Ore.

8. [11] STRENTHS AND LIMITATIONS:

STRENTHS:

1. Spot chemical analysis can be obtained in situ, which allows the user to detect even small compositional variations within textural context or within chemically zoned materials.
2. It can analyse even minute single phases in a material with “spot” analysis.
3. It is equipped with a range of crystal spectrometers that enable quantitative chemical analysis at high sensitivity.

LIMITATIONS:

1. EPMA unable to detect the lightest elements like H, He, L.
2. Some elements generate x-rays with overlapping peak positions.
3. Microprobe analyses are reported as oxides of elements, not as cations, therefore, cation proportions and mineral formulae must be recalculated following stoichiometric rules.
4. Probe analysis also cannot distinguish between the different valence states of Fe, so the ferric/ferrous ratio cannot be determined.

9. CONCLUSION

With its unique ability to identify and quantify elements in solid samples with great sensitivity and high accuracy, EPMA has been at the forefront of analytical technology for over 50 years and more. As the analytical demands of scientists have increased and the range of materials they want to study has grown, EPMA has managed to stay relevant. This is partly because of the inherent advantages of the technology, which were apparent from the very beginning, and partly because of the advances that have occurred over the past 50 years and more, such as high-resolution electron beams, and sophisticated software. With no sign that the ability to identify and quantify elements in solid samples will become any less useful or valuable in the future, EPMA’s position is probably secure for at least the next 50 years as well.

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