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OVERVIEW OF MICROANALYTICAL TECHNIQUES

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1. INTRODUCTION

There exist many analytical techniques and dedicated instruments on the market that allow one to obtain information about a sample related to chemical composition (e.g., qualitative set of the elements present, quantified amounts of elements, their bonding state, identification of isotopes) or to crystallography (e.g., crystal phase identification, lattice orientation, degree of crystallinity); some of them allow also to probe special characteristics like local density of states or optical properties. Each technique offers a specific combination of sensitivity and size of the sampled volume (spatial resolution), as depicted in Fig. 1. The question of selecting an appropriate technique for a given analytical task is usually answered then by comparing these limitations with the physical dimensions of the studied object and its details of interest, together with the expected level of analysed feature (e.g., amounts of elements).

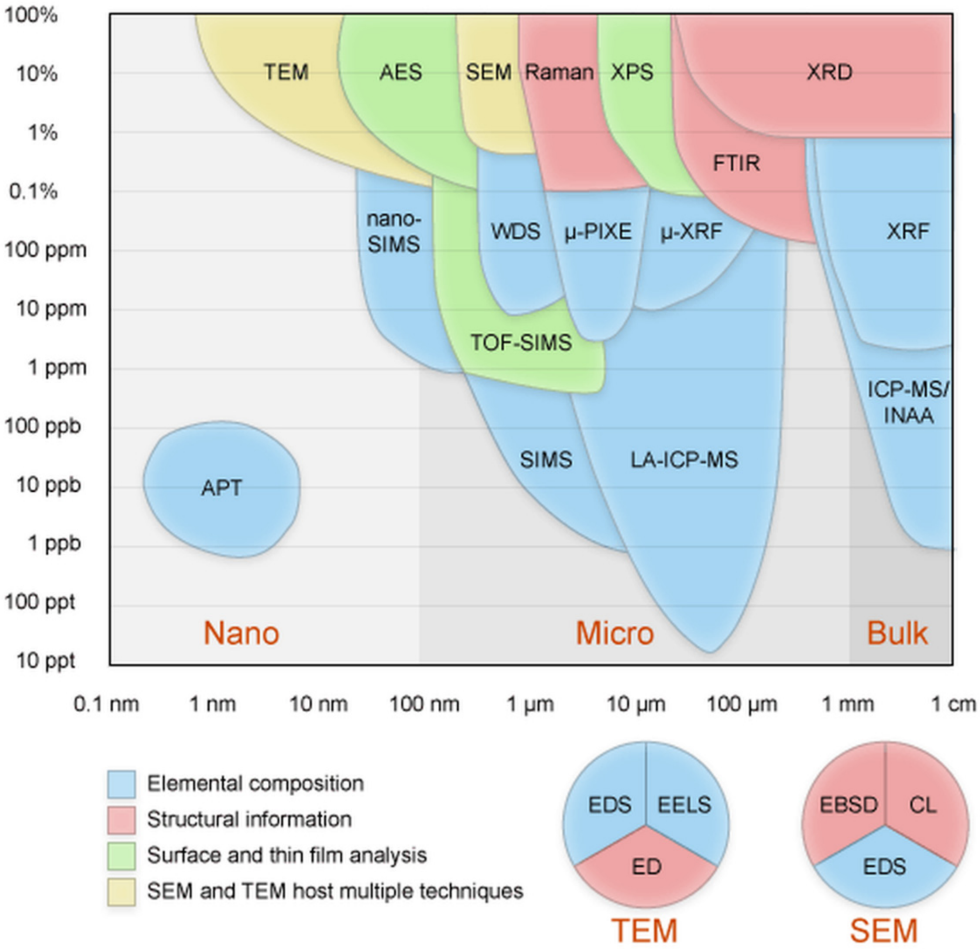

Figure 1. Spectral and spatial resolution limits of selected analytical techniques. The horizontal axis reflects each technique's spatial resolution and vertical axis sensitivity. https://github-9233.github.io/2019/04/13/MicroscopyBasics.

When we limit the discussion to the pool of techniques realised in conjunction with electron microscopes, especially if we assume the primary electrons as the triggering radiation, the list of techniques shrinks to electron probe microanalysis (EPMA) methods of energy-dispersive X-ray spectrometry (EDS) and wavelength-dispersive X-ray spectrometry (WDS), with Auger electron spectroscopy (AES) supplementing the set of elemental analyses. For thin samples in transmission electron microscope, electron energy-loss spectroscopy (EELS) and several electron diffraction-based (ED) techniques become available. Another diffraction-based technique, electron backscatter diffraction (EBSD), has become popular for routine analyses of crystal orientation in bulk as well as thin samples in SEMs. Some types of samples can be characterised in terms of their optical properties or band gap by cathodoluminescence spectroscopy (CL).

If an SEM platform is further equipped with a focussed X-ray source, the EDS detector can be chained together to provide a micro X-ray fluorescence (μ-XRF) system. Another possible expansion to the SEM platform is the addition of laser optical trains and spectrometers to form an integrated Raman spectroscopy system. A FIB-SEM can host another spectrometer for the time-of-flight secondary ion mass spectroscopy (ToF-SIMS) system capable of resolving isotopes with ppm level of sensitivity.

Other techniques mentioned in Fig. 1 either require a dedicated instrument that cannot be ported to any electron microscope platform or does not fulfill the definition of a microanalytical technique, i.e., the volume from where the information originates is larger than some hundreds of micrometres.

Analytical techniques typically implemented on electron microscope platforms generally rely on detecting a specific type of radiation produced due to electron-matter interaction (see Fig. 2).

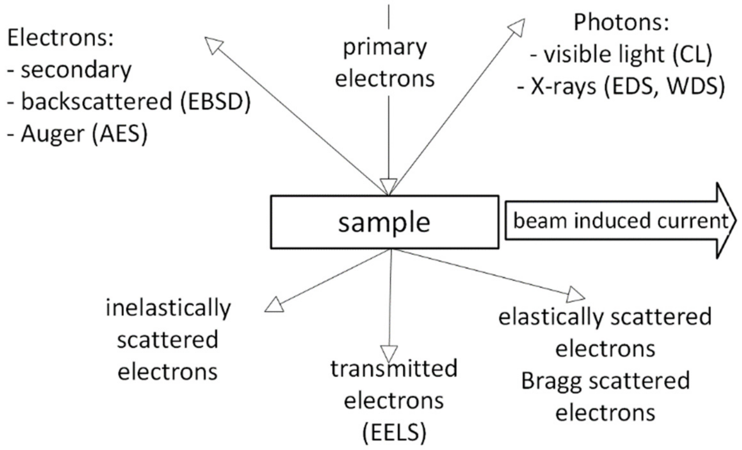

Figure 2. Electron-matter interaction and produced signals. After [1].

The techniques that require some special attachment to an electron microscope platform can be diagrammatically sorted in a similar way (Fig. 3), emphasising the role of a different kind of trigger radiation: Accelerated ions in the case of ToF-SIMS and photons (of different wavelengths) in case of Raman and µ-XRF.

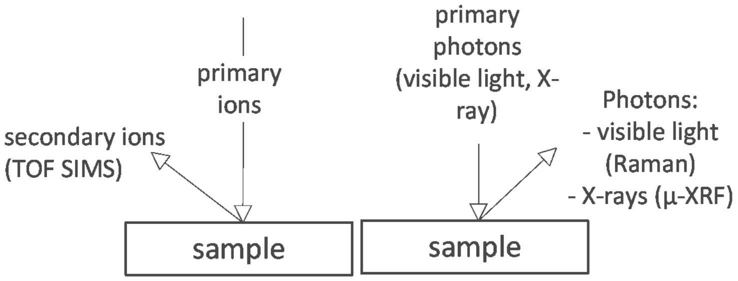

Figure 3. Ion- and photon-matter interaction giving rise to ToF-SIMS, Raman, and µ-XRF.

2. *ENERGY- AND WAVELENGTH-DISPERSIVE X-RAY SPECTROMETRY (EDS, WDS)*

Both these techniques rely on the reception and sorting of X-rays, generated during a de-excitation process that follows right after primary ionisation caused by incoming electrons (Fig. 4). They differ in the method of sorting the characteristic X-rays: either by energy (EDS) or by wavelength (WDS), which leads essentially to the same outcome – energy or wavelength spectrum containing Gaussian-shaped peaks at characteristic energies or wavelengths. These spectral peaks are typical for a given element, and their intensity can be related to the amount of the elements present.

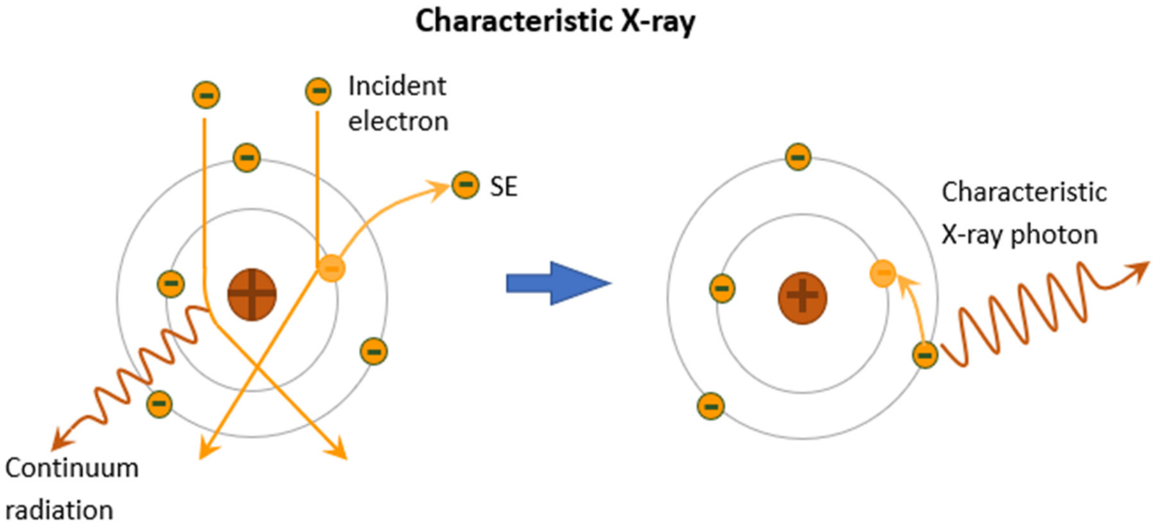

Figure 4. Generation of characteristic and continuum radiation. (Courtesy of Eva Kolíbalová).

From those two techniques, the EDS is far more routine since it is less demanding on budget to purchase and run and also on the operator skills. On the other hand, WDS is superior to EDS in terms of spectral resolution (peaks typically several units or tens of eV wide compared to more than a hundred eV in the case of EDS) and a detection threshold (sensitivity) that reaches 10^2 ppm for some elements [2].

3. AUGER ELECTRON SPECTROSCOPY (AES)

This method stems from the same ionisation process as EDS/WDS but follows another way of de-excitation of the ionised atom, which is the transfer of the excess energy onto another electron in orbit allowing it to be emitted out of the atom (Fig. 5).

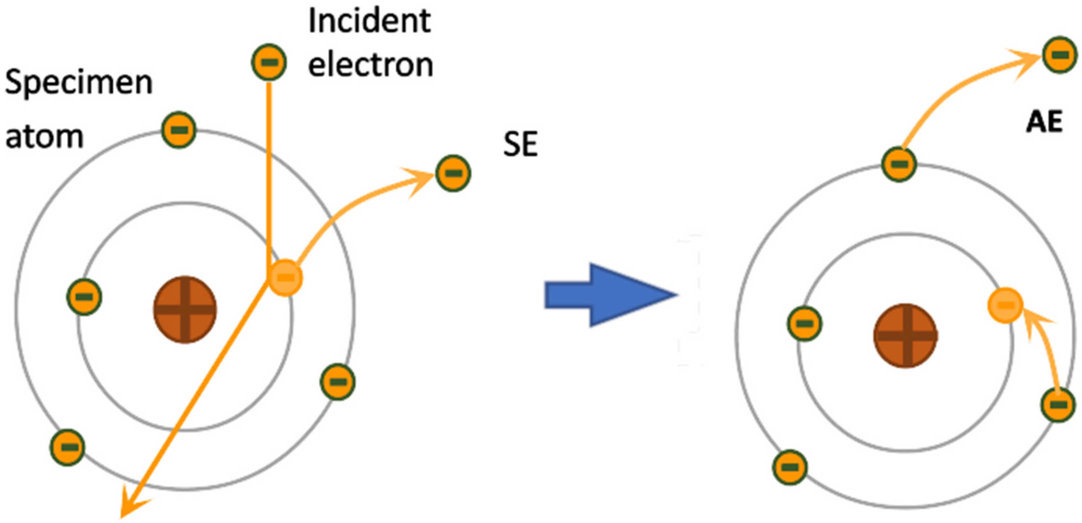

Figure 5. Auger electron emission process. (Courtesy of Eva Kolíbalová).

AES is a surface-sensitive technique that requires an ultra-high vacuum (UHV) modification of an SEM. This technique also demands extremely high sample cleanliness. The probabilities of characteristic X-ray and Auger electron emission depend on particular element – Auger emission is more probable for low-Z elements, and characteristic X-rays are more likely emitted for elements with $Z \geq 30$ [3, 4].

4. ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)

Following the same ionisation process (in a simplified approach) as for EDS/WDS and AES, we can trace the primary electrons that were the first impulse for ionising the atoms and measure the amount of energy they have lost during the interaction. This is possible in TEMs with thin samples, where a so-called energy filter can typically be mounted at the column's bottom. Since ionisation is not the only process that incurs some energy loss to the primary electrons, there is usually a whole spectrum of energy losses reaching several keV. These can be related to subtleties in electron arrangement, such as particular types of inter-atomic bonds, etc. [5].

5. CATHODOLUMINESCENCE SPECTROSCOPY (CL)

Cathodoluminescence (CL) is the emission of low-energy photons in the range from approximately 1 eV to 5 eV as a result of inelastic scattering of the high-energy beam electrons. Materials that can emit such photons are insulators or semiconductors, which have an electronic structure with a filled valence band of allowed energy states that is separated by a gap of disallowed energy states from the empty conduction band.

Detection of the photons of light can be realised either in a very simple way by a set of photosensitive semiconductor diodes with colour filters to discern the three basic spectral components, or it can be a complicated assembly of the parabolic mirror and a dispersive spectrometer with a grating, allowing for measurement of detailed wavelength spectra.

The application field of CL is mostly in geology, semiconductor development, and electrochemistry. It is usually implemented in SEMs but can also be utilised in TEMs when an appropriate sample holder is available [2].

6. ELECTRON BACKSCATTER DIFFRACTION (EBSD)

A diffraction-based technique using patterns generated upon impingement of a beam of primary electrons (PE) onto a highly tilted specimen, causing it to scatter in an interaction volume at first, giving rise to a virtual point source of electrons at a certain depth beneath the sample surface. This then increases the probability that the scattered electrons, emanating from the virtual point source, will find a suitably oriented set of lattice planes at which they diffract following the Bragg law and thus form a pair of lines on the screen of an EBSD detector (Fig. 6). The area between those pairs of lines is filled with some intensity because of energy variation among the electrons scattered in the first phase. Because of the latter, the pairs of lines in EBSD patterns are frequently called bands.

EBSD bands can be attributed to a specific set of lattice planes with given Miller indices. Assignment of those indices to a band is the indexing procedure, which can be done automatically by means of an algorithm that either uses the Hough transform to recognise the bands and then assigns the indices of planes, or pattern matching algorithm that essentially does both steps. There also exists a cross-correlation based algorithm that does not require pattern indexing, but instead concentrates on minute rotations and shifts in selected regions of the patterns to trace small lattice rotations and thus strain in the crystals.

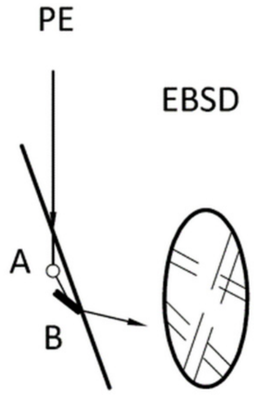

Figure 6. Schematic generation of EBSD patterns. A: scattering phase of primary electrons; B: Bragg diffraction on lattice planes.

The application field of EBSD is broad, starting with simple tasks like grain size determination and grain boundary type differentiation and ending with complex strain mappings in multiphase structures and dynamic or 3D experiments [6].

7. *MICRO X-RAY FLUORESCENCE (μ-XRF)*

The μ-XRF technique is most commonly realised in standalone dedicated instruments, but one of its modifications benefits from the wide adoption of EDS detectors on SEMs in a way that it only requires the addition of an X-ray source with some shielding and focussing optics to be able to bring X-rays as triggering radiation onto a sample. The EDS detector then collects the characteristic X-rays, and energy spectra of both electron- and X-ray-induced fluorescence can be overlaid. Elemental mapping can only be done by mechanical scanning since primary X-rays cannot be scanned.

X-rays are especially efficient in ionising, and, therefore, gaining signal from, heavier elements. The μ-XRF spectra generally contain a lower background and are better suited to analyse minor elements. The combination of μ-XRF and EDS on an SEM, therefore, brings the advantage of correlated μ-XRF and (electron beam induced) EDS to get the best spectral signal from heavier, as well as light elements. A disadvantage here is the mismatch in spatial resolution since X-rays can only be focussed on a spot of several tens of micrometres in diameter [7, 8].

8. *RAMAN SPECTROSCOPY*

Raman spectroscopy is again a technique less typical to be combined with an electron microscope, although such a combination exists. Raman spectroscopy implementation requires a laser beam to be delivered onto a sample, and the Raman scattered light to be collected by an optical system and guided to a spectrometer (interferometric or dispersive). This bulky assembly cannot fit below the objective pole piece of any SEM, so a special position for a Raman system has to be designed in the SEM chamber. The sample has to travel to a specific site for the Raman analysis. When Raman mapping is required, the sample has to be scanned mechanically. In Raman-integrated SEMs, one can correlate elemental distribution by EDS and chemical bonding information by Raman [9, 10].

9. TIME OF FLIGHT SECONDARY ION MASS SPECTROSCOPY (ToF-SIMS)

A ToF-SIMS technique can only be implemented in a FIB-SEM, because of the necessary presence of the source of primary ions to bombard the specimen. A spectrometer that can measure the mass-to-charge ratio of the sputtered ions works usually on the time of flight measurement principle since it provides a good combination of mass resolution and physical "bulkiness" of the detector. A focussed beam of ions brings the benefit of several hundreds of nanometre-wide lateral resolution. In contrast, the depth resolution can be controlled by the dwell time of the ion beam and can be as shallow as an atomic monolayer.

A unique feature of ToF-SIMS is the ability to detect very light elements, like Li or H, directly. This technique, therefore, finds increasing use in battery research [11].

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