

Lectures - Session IV, Wednesday, June 22**L16****LOCAL ELECTRON MICROANALYSIS IN MICROPROBE AND ELECTRON MICROSCOPES****V. Stary**

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Electron microanalysis use the electron beam to excite X-rays and deduce from their intensity the qualitative and quantitative elemental composition of material. As analytical technique, it can be incorporated in electron microscope to utilize the production of X-ray photons in observation both of thin and bulk samples in various types of electron microscopes. The quantitative method for bulk samples was firstly used by R. Castaing in France, the method was improved by K. F. J. Heinrich in USA. The special devices for application of this method are usually called "microprobe", so the method is often called "Electron probe microanalysis" even though the microprobe is the name for very thin electron beam, used for local microanalysis. After some theoretical information the basic possibilities of the method are reviewed, and some practical examples are given.

The atomic concentration in bulk sample are calculated from the intensity of emitted X-ray radiation using our knowledge of electron-matter interaction, i.e., scattering and deceleration of electron and absorption of X-ray in sample. During the way of electron through the matter, electron interacts with atomic nuclei and with electrons by elastic and inelastic way. Due to the elastic scattering the electron beam mainly increase its width. Simultaneously, the part of electrons can change the direction back to the surface. Inelastic scattering causes mainly the energy losses. The angular deviations are much lower than for elastic scattering, even though they exist. The energy losses are mainly given in materials with „free“ electrons by scattering due to the plasmon excitation, in other way by the interband and intraband excitations. Generally, the energy decrease is described by „stopping power“. It gives approximately the maximal depth of electron trajectory. In bulk sample, the thin beam creates in material the shape of approximately pear, called "interaction volume".

For electron microanalysis, we should know:

- For which elements, compounds and alloys does the electron microanalysis give the reasonable results and for which not,
- What is the minimal content (concentration, number of atoms, mass) of element we are able to measure,
- If the bulk material is homogeneous (and we define the mean concentrations) or inhomogeneous (and we define the distribution of elements in sample),
- Especially for film, we should decide, if we are interested on average element content or the dependence of concentration on depth in sample,

- If the method is destructive with disordering of material or non-destructive, etc.

There are two basic systems for detection and analysis of X-ray from sample: the first one separates the X-rays according to energy (EDS system), the second separate the X-rays according the wavelength (WDS system). Both systems are widely used in the practice.

From the peak energy in EDS spectrum or the angle of maxima in WDS spectrum we can define the types of elements in sample and the qualitative analysis can be proceed (with some limitations). For precise knowledge, we must have the quantitative limits of detection, because in the definition of non-presence of sample we should also tell what is the minimal content we are able to prove. For this reason, the critical value, the minimally detected amount and minimal measurable values of concentration should be defined for each element. For thin samples, when the number of collision of electrons with atoms in thin sample is low (e.g., one collision per electron) the energy losses are relatively low and electron energy is relatively constant, the semiquantitative analysis can be made directly from the intensities, supposed $c_i = 1$.

At quantitative analysis of bulk material we need to calculate the concentrations (i.e., mass fractions c_x) of presents elements. The physical processes what should be taken into account are as follows:

1. slowing down of electrons;
2. elastic scattering at atoms, connected with change of direction, including the possibility of backscattering;
3. ionisation of atoms with possible emission of X-rays;
4. indirectional ionisation of atoms by both characteristic and bremsstrahlung radiations and fluorescence;
5. absorption of generated X-ray radiation in the path through the sample to the detector.

For calculation of concentrations usually two methods are used, ZAF and Phi-Ro-Zet. The base of both methods will be presented.

The depth of information is given by the size of interaction volume. Causing the lateral resolution, the method allows two modifications: local microanalysis and chemical mapping. At local microanalysis, we position the electron beam on defined place of sample and we obtain the information from one "point" of sample. Because we usually see the image of surface as (secondary or backscattered) electron image, we can position the beam on places, which are



interesting for study. At chemical mapping of area, the beam moves in some net of points and matrix of concentrations of individual elements is created. There is the possibility to measure in each point of matrix all the spectrum, which is time spending or to measure only selected energy windows for some elements (or background). The next possibility is the movement of beam along the line, for example to cross the interface. In this case we shall see for example the drop of concentration of element in question at interface.

As conclusion, the X-ray microanalysis is very important method for the study of composition of materials as well as of biological objects. The reasonable results are obtained in the range of tenths of percent. Moreover, due to possibility to use very thin electron beam, very good lateral resolution can be obtained.

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Extended contribution submitted.

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RTG. FLUORESCENČNÍ SPEKTROSKOPIE

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Rentgenová fluorescenční analýza (XRF) patří k základním metodám, kterými disponují mnohé analytické laboratoře. V příspěvku bude stručně shrnuta historie rtg. fluorescenční analýzy, načrtnut princip metody a uvedeny

metody analýzy dat – bezstandartní metoda založená na tzv. kappa koeficientech (deJongh) a tvorba kalibračních křivek. Budou též zmíněna omezení uvedené metody.

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METODY POVRCHOVÉ A TENKOVRSŤOVÉ ANALÝZY PRVKOVÉHO SLOŽENÍ (XPS, AES, SIMS), DIFRAKCE FOTOELEKTRONŮ

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Metody elektronové spektroskopie XPS („X-ray Photoelectron Spectroscopy“ – rentgenová fotoelektronová spektroskopie) a AES („Auger Electron Spectroscopy“ – Augerova elektronová spektroskopie) a metoda SIMS („Secondary Ion Mass Spectroscopy“ – hmotnostní spektroskopie sekundárních iontů) patří k nejrozšířenějším metodám analýzy chemického složení materiálů. Přednáška se zabývá teoretickými a experimentálními základy výše zmíněných metod v míře nutné pro správné pochopení experimentálních dat, jejich kvalitativnímu i kvantitativnímu vyhodnocení.

Metoda XPS je založena na fotoelektrickém jevu. Energie emitovaných elektronů je charakteristická pro jednotlivé prvky a je ovlivněna rovněž chemickým stavem,

v jakém se prvky v látce nacházejí. Tato skutečnost umožňuje kvalitativní i kvantitativní vyhodnocení výsledků měření. Přesnost kvantitativních výsledků závisí na struktuře studovaného materiálu. U metody AES jsou sekundární elektrony emitovány Augerovým procesem. Podobně jako metoda XPS i AES poskytuje informace o chemickém složení a stavu studovaného vzorku. Část přednášky bude věnována metodám vyhodnocení experimentálních dat s ukázkami jejich praktických aplikací.

Metoda SIMS spočívá v měření hmotnostních spekter iontů vyražených z povrchu studovaného vzorku pomocí svazku iontů o určité energii. Odtud můžeme potom určit koncentraci jednotlivých prvků v povrchové vrstvě

materiálu. Protože dochází k odprašování povrchových vrstev během měření (DSIMS – dynamický SIMS) je možné tuto metodu s výhodou použít pro hloubkové profilování a měřit tloušťku jednotlivých vrstev ve vícevrstevných materiálech. Kvantitativní analýza je znesnadněna celou řadou efektů, které je nutné při vyhodnocování experimentálních dat zohlednit. K nejdůležitějším patří maticový efekt, preferenční odprašování, kráterový efekt, promíchávání atomů a další. K velkým nevýhodám metody patří její destruktivnost. To je možné omezit pomocí metody SSIMS (statický SIMS), která používá velmi nízké intenzity primárního svazku. Je třeba mít na paměti, že v tomto případě analyzujeme pouze svrchní vrstvu studovaného vzorku.

Poslední část přednášky bude věnována metodě difrakce fotoelektronů XPD („X-ray Photoelectron Diffraction“). Tato metoda vychází z měření úhlové závislosti emise fotoelektronů z povrchu krystalické látky. Směry emise jsou silně ovlivněny strukturou látky v nejbližší blízkosti emitujícího atomu zejména takzvaným dopředným rozptylem. Experimentálně získané obrazce se porovnávají se simulovanými obrazci. Tímto způsobem je

možné určit malé posuny atomů na rekonstruovaných a relaxovaných površích nebo pozice molekul adsorbovaných na povrchu pevných látek. Metoda vyžaduje speciální experimentální vybavení, které je dostupné jen v některých vědeckých laboratořích.

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L19

INTRODUCTION TO THE ION BEAM ANALYSIS

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The Ion Beam Analysis (IBA) is a group of analytical techniques which use a beam of accelerated MeV ions to study the composition and structure of investigated samples. The (IBA) methods are usually multi-elemental, non-destructive and relatively fast. They require only little or no sample preparation prior to the analysis. The analysis can be performed, both in the vacuum, or using the external beam (in air). Thus a variety of different samples from a single cell to historical art paintings can be analysed. The IBA methods are interdisciplinary and they find its place in many scientific disciplines as, aerosol research, solid state physics, thin layer analysis, biology, medicine, archaeology and art and in many others. However the main principles of IBA methods are now known roughly one hundred years, they start to be widely used as late as in seventies, when sophisticated semiconductor detectors and appropriate computing technology became available.

Methods

The IBA methods are based on principles of interaction of energetic MeV ions with the matter. They can be characterized and divided according to the main interaction process which is utilized by the particular method. Brief description of some common IBA methods follows.

RBS - Rutherford Backscattering Spectroscopy. It is based on nuclear elastic scattering of the incident ion and the nucleus of the target atom. The backscattered ions and their energy are detected. The RBS method can be used for quantitative determination of the amount of target atoms

(with moderate mass resolution) and also for their depth distribution. The typical depth resolution for He ions is about 10nm.

PIXE - Particle Induced X-ray Analysis. The method is based on the detection of characteristic X-rays produced by the energetic ion beam. It has a favourable detection limits (in ppm range) and provide a good quantitative results of atom concentration in measured samples with relative uncertainty below 5%. Usually elements from Na and above are detected. When the thin window or windowless detector is used, the elements down to the Boron can be detected.

PIGE - Particle Induced Gamma-ray Analysis. It is based on inelastic ion scattering or on nuclear reaction, in which gamma rays from excited target nuclei are emitted. It is well suited for the determination of the light elements, mainly for Li, F, Al, Na and B.

NRA - Nuclear Reaction Analysis. The term describes a group of analytical techniques based on nuclear reactions in which charged particles or gamma rays are producing. They are isotopically specific and are usually used only in a special cases. For instance the NRA based on the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction can be used for the fine depth profiling of the ^{18}O . The PIGE method is sometimes consider as a special case of NRA techniques.

ERDA - Elastic Recoil Detection Analysis. The ERDA method is based on the detection of forward recoiled particles. Contrary to the RBS, all nuclei (ions) which are in the sample, and also the primary particle, can be scattered (kick off) to the forward directions. Thus we have to discriminate



them. One way is to measure both velocity and the energy of each particle and calculate the particle mass. This method is called TOF-ERDA (time of flight ERDA). There are several other options to discriminate the recoils, to use electric or magnetic field analyzer, measure the ion stopping power or use thin foil to stop all highly ionizing ions (high Z ones).

RBS-Channelling refers a special use of the RBS method, when it is applied on crystalline materials. If one of the crystal axis is aligned with the ion beam direction a number of backscattered particles are significantly reduced. The position of the lattice host atoms or the number and depth distribution of defects can be studied by this method.

Ion microbeam. The beam of the accelerated ions can be focused and scan over the sample. This way, two or three dimensional information about the distribution of atoms in the sample can be obtained. A beam spot of 1 μm or smaller can be produced, using the set of slits and focusing quadrupoles. There are several tents of such systems worldwide. Above mentioned IBA methods (and lot of others) can be used in the combination with the ion microbeam. As the MeV protons are most common in such systems, an alternative name "proton microprobe" is often used.

Laboratory of IBA in Řež

We have two electrostatic accelerators at our laboratory in NPI AVCR v.v.i. at Řež. An older Van de Graaff accelerator which is able to accelerate H^+ and He^+ ions up to 3.5 MeV. It is operated from the sixties and routinely used for IBA from the eighties. At present, there are two experimental chambers at the VdG accelerator, one for RBS and ERDA analysis and the second for the simultaneous analysis by PIGE, PIGE, RBS and PESA (Proton Elastic Scattering Analysis).

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IDENTIFICATION OF IONS IN PROTEINS

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In single crystal studies of biological macromolecules identification of ligands or generally solvent molecules very often represents an uneasy task. The studied proteins undergo a lengthy process of expression, in cell modification, and/or secretion, purification and sometimes special pre-crystallization treatment. The molecules are commonly crystallized in solutions of salts and presence of unwanted metal ions in the used chemicals is not excluded.

As a result in protein crystal structures ions or other small chemical moieties are often observed bound on the molecular surface. A majority of protein crystals do not provide diffraction data to atomic or subatomic diffraction limits (1.2 Å or better). To date some 63 thousand X-ray structures deposited in the Protein Data Bank have the high

From 2005 we have also a modern 3MV TANDETRON 4130 MC accelerator. It can accelerate almost all ions (except some noble gasses) to energies from several hundreds of keV up to more than 20 MeV (for multiply charged heavier ions). There are four ion beam lines connected to the Tandetron accelerator, with several experimental target chambers for RBS, RBS-Channelling, TOF-ERDA, High energy ion implantation, ion microbeam and a universal multipurpose chamber.

The principles of selected IBA methods and examples of its application will be presented in the lecture.

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diffraction limit of data 1.2 Å or worse and about 1500 1.2 Å and better. Therefore protein crystallographers must mostly rely on other indicators of the nature of an ion than purely the height of an electron density maximum.

The sum of the utilized approaches includes anomalous scattering signal, typical coordination and bonding distances [1], statistical evaluation of typical cases, assessment of the local environment, experimental conditions such as pH, and other. Access to tunable X-ray sources with fluorescence detectors enables absorption edge checks and fluorescence analysis in some cases [2] and availability of a micrometer high energy proton beam allows element identification by microbeam Proton Induced X-ray Emission (microPIXE) [3].

Lighter ions, such as Na^+ , Mg^{2+} and Cl^- , belong to a special category as their presence in protein structures either remains unnoticed or is misinterpreted. In such cases the correct assignment of an ion type and its distinction from a water molecule rely on sufficient evidence from all available information sources.

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Lectures - Session V, Thursday, June 23

L21

ISOMERIC FORMS OF THE ORGANOMETALLIC-INORGANIC HYBRID POLYMER [Cp*₂Mo₂P₂Se₃(CuI)₃(CH₃CN)]_n

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Recently, there was an article [1] published about synthesis and characterization of a tripledecker molecule [Cp*₂Mo₂P₂Se₃], Cp* = C₅Me₅, and its use as a molecular building block in the formation of copper(I) halide polymers. Reaction of the tripledecker molecule (see Fig. 1) with copper(I) halides provides polymers of diverse dimensionalities depending on competing coordination properties of P and Se atoms.

The reaction of the tripledecker molecule with CuI in CH₃CN gave a mixture of bright-red plates and dark prisms, both with a composition Cp*₂Mo₂P₂Se₃(CuI)₃(CH₃CN)_n, in a temperature-dependent ratio. While structure of bright-red plates could be solved by classical methods as a two-dimensional polymer, the structures of the dark-red prisms was modulated. The modulation of tripledecker molecule is of harmonic nature. On the other hand, discontinuous modulation function are needed for the inorganic part where a cage from Cu and I atoms (Fig. 2) alternates between two positions. In three-dimensional description this lead to disorder, which is resolved using crenel modulation function.

The presentation demonstrates way how to solve and refine this kind of structure. The steps with program Jana2006 [2] will be explained together with necessary underlying theory to the extent needed for understanding the presented procedures. Finally, still unsolved problems connected with solution of the title structure, will be discussed.

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Figure 1. The tripledecker molecule. P yellow, Se red, Mo orange, C gray, hydrogen omitted.

Figure 2. Two positions of the Cu-I cage observed as disorder in the average structure.