Introduction to EDS analysis

- **Reference Manual**

Innovation with Integrity

EDS

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We have checked the contents of this manual for agreement with the hardware and software described. Since deviations cannot be precluded entirely, we cannot guarantee full agreement. However, the data in this manual are reviewed regularly and any necessary corrections are included in subsequent editions. Suggestions for improvement are welcome.

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1 Introduction

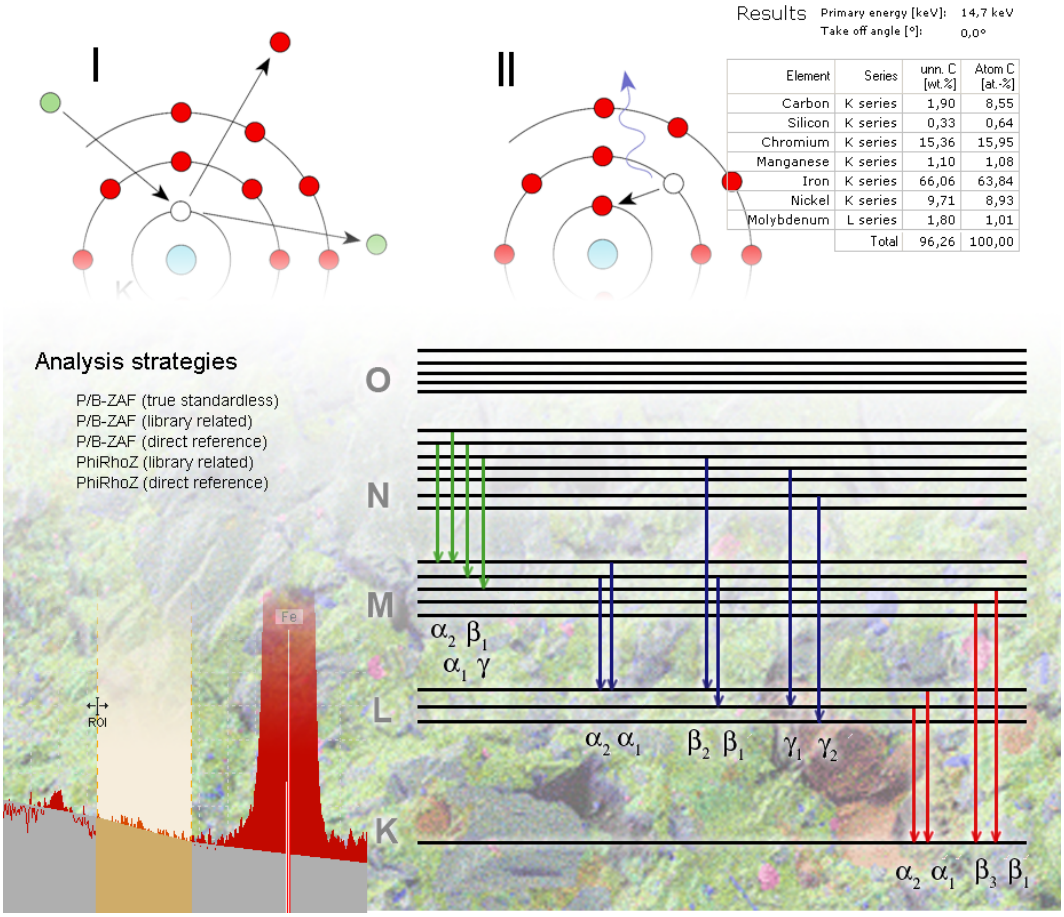
This manual offers an introduction to the basic principles of energy dispersive spectrometry (EDS). The main goal is to provide some general information on the analysis possibilities when using an EDS system and to summarize some background knowledge that will help to optimize analysis results.

The first chapter deals with different strategies for quantitative analysis, from true standardless to standard-based quantification, as well as combined analysis methods. This is followed by a description of the typical imaging functions of an X-ray microanalysis system, together with information on the acquisition of element distribution images, hyperspectral maps and line scans. A discussion on the EDS analysis limits rounds off this section.

The second chapter is dedicated to the explanation of different factors that have to be taken into consideration when performing practical X-ray microanalysis. These factors inlcude sample preparation, setup of the electron microscope, spectrometer settings and system calibration. A list of frequent analysis errors and the way to avoid them closes this part of the manual.

Finally, the appendix contains some general EDS information including topics such as the history of energy dispersive X-ray microanalysis, absoprtion and fluorescence, detector effects, etc. in form of an extended glossary.

2 Microanalysis Basics



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2.1 Overview

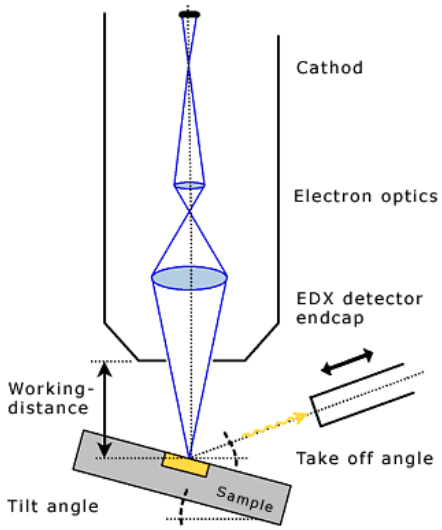


Fig. 2.1-1 Typical analysis geometry

General spectrum analysis steps

- Spectrum acquisition
- Correction of the detector effects (Escape, Shelf, Tail, Shift)
- Identification of the elements and selection of a line series for each element
- Calculation of the bremsstrahlung background radiation (e.g. bremsstrahlung)
- Deconvolution of overlapping peaks and estimation of the net intensities
- Calculation of concentrations with or without reference to standards
- Result formatting and presentation

X-ray generation. Scanning electron microscopes (SEM) or similar devices scan the specimen with a beam of high-energy electrons. By interaction of these electrons with the atoms of the specimen, secondary electrons, backscattered electrons, characteristic X-ray photons, and bremsstrahlung are generated. While the different electron detectors of the microscope (SE, BSE) deliver images of the specimen - revealing surface structure and topology - the X-ray spectrometer adds detailed information about the chemical composition for a given measurement spot or area.

Qualitative analysis. The characteristic X-rays consist of narrow emission lines, which are characteristic for the chemical elements contained in the sample. The energy of these lines is nearly independent of the chemical bonding state of the affected atoms; the electron probe microanalysis (EPMA) is element sensitive. In the resulting energy dispersive spectrum the characteristic X-rays correspond to visible peaks. Identifying these peaks yields information about the elements that are present in the sample.

Quantitative analysis. Quantitative data about the sample composition is derived from the different peak intensities by an extensive mathematical process, often referred to as ZAF or PhiRhoZ matrix correction. Bremsstrahlung X-rays, which form a continuous spectrum background, are used as additional source of information during the spectrum analysis with self-calibrating methods (P/B-ZAF, see 2.2.1).

Different approaches with and without reference to standards are commonly used and supported by the QUANTAX software. They are described in more detail in the next sections.

Automatic and interactive operation. Fully automatic spectrum analysis is used in routine analysis in industry as well as in many laboratories. The input necessary for controlling the analysis is contained in filed method settings, provided by the vendor or user.

In complicated cases the expertise of the operator may be required.

Thereby complete interactive control over critical analysis steps helps expanding the methodical limits.

Position referred methods. Combining electron beam scanning and X-ray spectrometry allows - besides classical qualitative and quantitative point analysis - analysis of randomly shaped objects, automatic multipoint analysis, recoding of concentration profiles, as well as advanced imaging methods like mapping, and element imaging. The necessary access to the electron beam deflection is normally accomplished by a secondary scan system (external scan generator).

2.2 Quantitative Analysis

2.2.1 True Standardless Analysis with P/B-ZAF

QUANTAX analysis strategies

- P/B-ZAF (true standardless)
- P/B-ZAF (standard-based)
- P/B-ZAF (direct reference)
- PhiRhoZ (standard-based)
- PhiRhoZ (direct reference)
- Film analysis

Standardless analysis. Standardless electron probe microanalysis provides quantitative composition data from evaluating a recorded X-ray spectrum by means of fundamental physical formulas and extensive atomic databases. Semi-standardless analysis, which is still being offered sometimes, substitutes part of these fundamental data and relations with spectral references provided by the manufacturer.

Modern standardless analysis is sufficiently accurate and reliable for a wide range of applications in research, education, environmental protection, production, and many other fields. The ease of use and reliability of standardless electron probe microanalysis are unique features, which, among others, account for the wide acceptance of this analysis method.

PB-ZAF. P/B-ZAF standardless analysis is a fundamental parameter (FP) based true standardless and self-calibrating spectrum analysis procedure, based on modified ZAF matrix correction formulas. Absolute concentration values are obtained without the use of explicit or implicit standards and without system factor calibration.

Using the P/B-ZAF algorithm the characteristic X-ray intensities (i.e. the net peak areas) are calculated in relation to the mean level of the simultaneously recorded bremsstrahlung background. Therefore the general system factors (electron beam current, solid angle) and a number of adverse influences cancel out each other and therefore do not influence the result of quantification. The theory of the P/B-ZAF

algorithm is discussed in the Appendix.

Internal reference. The internal reference to the bremsstrahlung is the key factor of P/B-ZAF analysis. It compensates effects resulting from absorbing surface layers and changes of effective take off angles. This successfully allows the analysis of unprocessed, rough surfaces.

Analysis conditions. The bremsstrahlung contains information on variations of detection conditions which are difficult to handle, for example excitation energies and local surface tilt. Deviations of the effective excitation energy, e.g. caused by sample charging, can be taken into account by interactively or automatically evaluating the higher energy bremsstrahlung distribution (Duane Hunt Limit). Local tilt angles can be evaluated and corrected by fitting the low energy side of the spectral background.

Automatic and interactive operation. P/B-ZAF standardless analysis can be done automatically or in interactive mode. In either case all information needed for quantification is obtained solely from the spectrum recorded by the X-ray spectrometer. No reference measurement or determination of system factors is necessary using standardless P/B-ZAF analysis.

2.2.2 Standard-based Analysis

Standard-based analysis is traditionally preferred in certain cases. In well-controlled applications standard-based electron probe microanalysis yields high precision results that cannot be achieved with any other analytical method likewise. Inevitable prerequisites are well-prepared, i.e. embedded and polished samples, high-class standard materials, very stable analytical SEMs or microprobes, and well-trained personnel.

Standards libraries. Data of standards for all elements to be analyzed by standard-based analysis is normally maintained in a so-called standards library. State-of-the-art standard-based analysis is highly automated, that means managing of numerical entries like net peak area, k-Ratios or other parameters is not required from the user any more.

Normalizing the system. With samples prepared accordingly and an appropriate standards library at hand, the only additional requirement for PhiRhoZ based quantitative analysis - in contrast to

standardless analysis - is to measure a system factor, which is mainly determined by the chosen electron beam current, the detector size and detector position. Occasionally performing a calibration measurement with a proposed calibration sample or the input of a so-called beam current factor - derived by measuring the electron beam current with a Faraday cup – is sufficient.

Accuracy. In most cases systematical errors of about 1% can be achieved even when using pure element standards or simple compounds. This presupposes tightly controlled excitation conditions, smooth polished samples, standards with matching surface conditions and - if necessary – coatings.

2.2.3 Reference-based Analysis

A special case of standard-based analysis is the direct reference measurement, - for instance -oftenly used in production control within metallurgical plants. In this case a stable composition of a certain product is verified by comparing it with certified samples of the same type.

Current References. Reference-based analysis uses the same principles as methods based on standards libraries. The only difference is that the pre-defined standards library is replaced by current reference measurements using an available standard or a reference sample. If the unknown specimen is measured right after the corresponding reference sample and using the same settings, a number of adverse influence factors will be avoided.

If the current reference is of same type as the unknown sample and all interesting elements can be related to known elements within the reference sample, no standard library has to be used. The system normalization can be omitted and quantification can yield good results even with critical specimens, like powder samples or ceramics.

2.2.4 Standard-based P/B-ZAF-Analysis

This way, the remarkable insensitivity of P/B-ZAF analysis regarding measurement conditions is maintained thus providing all advantages of standard-based or direct reference analysis strategies. QUANTAX integrates this method together with a flexible library manager and reference administration.

Using the self-calibrating P/B-ZAF standard-based analysis no system calibration measurement has to be performed.

As with any standard-based method, analysis results will be most accurate when measurement conditions, compositions and sample states of reference samples match those of the current measurement. However, with P/B-ZAF standard-based analysis these requirements are substantially reduced, achieving nearly the simplicity of standardless analysis.

2.2.5 Combined Analysis Methods

Combined analysis provides the possibility to choose the appropriate analysis method on an element-by-element basis. Therefore it may be sufficient to provide standards only for certain critical elements, while for all other - bulk or minor - components standardless analysis is adequate. This substantially simplifies the standard-based analysis. Combined analysis is also valuable in cases when standards are hard or impossible to get.

2.3 Imaging Functions

2.3.1 Standard Image Capture

Image capture. State-of-the-art microanalyzers are equipped with means for capturing the electron image additionally to the image display on the console of the electron microscope. This is useful to ease documentation and archiving. It provides means for directly setting analysis points and regions from the microanalyzer's workspace.

☞ The QUANTAX scan system is housed in the QUANTAX server PC.

External scan system. When using advanced analysis methods separate scan systems are typically used, allowing synchronization between electron beam scanning and X-ray acquisition. To ensure exact alignment of displayed image and chosen analysis position the same external scan system is also used for image capture.

The external scan system provides image resolution and scan speed setting for microanalysis, which work independently from normal image capture on the microscope. Different noise reduction and slow scan modes can be selected. Synchronizing of X-ray data and beam positions is provided in all modes.

General control features, like magnification settings and focusing, can normally still be controlled from the microscope console.

2.3.2 ColorScan

☞ QUANTAX provides ColorScan already for the primary captured image, i.e. prior to an element analysis or mapping.

ColorScan is an enhanced acquisition method which is provided additionally to standard image acquisition. While normal imaging only utilizes the electron detectors for capturing data, ColorScan also evaluates the output of the X-ray detector, allowing indicative colors to be added to the image. This way the different chemical compositions of phases, features or particles throughout the imaged area are indicated with different colors. ColorScan allows detecting inhomogeneous regions in samples and helps selecting adequate positions for analysis in order to prevent severe analysis errors.

ColorScan requires no user input whatsoever. Neither elements, X-ray window settings or assignment of colors have to be selected. In connection with the extraordinary pulse processing power of the XFlash® detector, ColorScan can produce high-definition color images in very short capture time.

2.3.3 Mapping and Element Imaging

Mapping. In X-ray microanalysis mapping means that point-by-point an X-ray spectrum is accumulated and evaluated to determine the content of certain predefined chemical elements. Each resulting element map represents the two-dimensional concentration distribution of the regarding element over the sample surface. According to the preferences of the user, element maps are displayed individually or color-coded and superimposed to form one multi-color image.

Element mapping is an adequate procedure e.g. in case of inhomogeneous specimens like metal alloys or ceramics. EDS analyzers, in contrast to WDS spectrometers, are generally able to generate maps simultaneously for a great number of different chemical elements.

Element images. An element image is a topographic survey of the specimen surface (captured by use of the electron detectors), which is colored according to the local sample composition.

Like with the tool ColorScan, element images are assembled by mixing the high-resolution electron image with individual element maps. In this case however, the user controls which element maps shall contribute to the final image and adjusts the image mixing parameters. This way high quality images, ready for publishing, can be achieved without manual post processing, marking or coloring.

2.3.4 Hyperspectral Mapping

Hyperspectral mapping (also known as Position Tagged Spectrometry - PTS) is a data acquisition method at which the acquired X-ray spectrum information is stored tagged to the pixels of the digitized sample image. In the QUANTAX system this functionality is called HyperMap. The spectrum database continually builds up during scanning of the complete sample surface or a defined mapping area. By post processing this kind of element maps, object spectra, line scans, and other can be derived from the database.

Like direct scanning position related analysis outlined above, hyperspectral mapping is useful in connection with inhomogeneous samples that require phase reconstruction, feature recognition, multipoint analysis or similar.

2.4 Object Analysis, Multipoint, and Line scan

2.4.1 Object Analysis

With object analysis differently shaped areas of the sample surface can be defined as area for analysis. In contrast to point analysis, where the electron beam remains steadily on one spot during spectrum acquisition, object analysis lets the electron beam constantly move over the whole object area while the X-ray spectrum is acquired. This helps reducing the strain on the sample surface and smoothes out local impurities like dust particles or scratches.

Scanning of enlarged objects, however, is not suitable for inhomogeneous or rough samples; quantitative analysis of spectra averaged over differently orientated or composed sample locations normally will lead to erroneous results because of non-linear spectrum mathematics.

2.4.2 Multipoint Analysis

With multipoint analysis a number of separate spots are defined on the sample surface for analysis. The spectrum of each spot is evaluated separately by means of batch processing. Different statistical options for evaluating the results are provided. Analysis results can be averaged to yield the mean composition, or sorted into different categories (phase analysis), naming only a few options.

Multipoint analysis can be combined with object analysis to multi object analysis. Full quantitative line scans and maps can be defined as special forms of multipoint analysis too.

2.4.3 Line Scan

During line scans, the electron beam scans the sample continuously along a selected straight line. Doing so, X-ray spectra are acquired and evaluated. The resulting concentration profiles for selected chemical elements are plotted in a diagram.

In contrast to element mapping or recording a full spectral data base over the sample area (hyperspectral mapping), line scanning is fast and provides an intuitive display for quantitative data. It is the standard method for examining cross sections of functional layers, welding bonds, and much more.

Prerequisite for performing line scans is a separate scan system of the microanalyzer or other adequate means for synchronizing scan and spectrum acquisition.

2.5 Analysis Limits

2.5.1 The Analysis Volume

X-ray microanalysis is surface sensitive. The information depth, i.e. the thickness of the surface layer from which most of the analytic signal originates, is defined on one hand by the ability of the high-energy electron beam to penetrate into the sample, on the other hand by the length of path the generated X-rays can travel back through the specimen. Since this path is substantially longer than depths secondary and backscattered electrons can penetrate, the information depth of microanalysis is accordingly larger than that of SEM imaging.

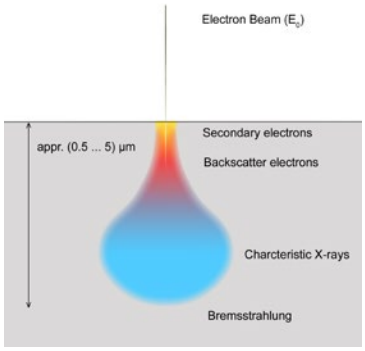


Fig. 2.5-1 Excitation and escaping volumes

Origin of the signals. The figure on the left side shows an electron beam that hits a specimen surface. The multi colored region is the volume that is penetrated by the multiply scattered primary electrons and excited to produce characteristic X-ray radiation.

The yellow and red ranges are the volumes from which electrons can escape from the surface. Backscattered electrons are detected by the BSE-detector of the electron microscope. Secondary electrons, which have less energy than backscattered electrons, originate mainly from the yellow part (secondary electrons are the most common signal source for SEM imaging).

The red and blue areas are the origin of most of the characteristic X-rays and bremsstrahlung.

Depth distribution function. The information depth spans from part of a micron to some microns depending on the high voltage of the electron gun, the mean density of the specimen matter, and the element content. Calculated depth distribution functions for a certain sample are available after quantitative spectrum analysis (refer to the QUANTAX user manual for more details).

Lateral scattering. In deeper regions the electrons are scattered in lateral direction forming a pear shaped volume in which atoms are excited to produce X-rays. This lateral size in combination with the depth distribution defines the analysis volume, which is normally in the order of magnitude of 1µm³.

2.5.2 Spatial Resolution

The three dimensional size of the analysis volume limits the spatial resolution of X-ray microanalysis to values much lower than the electron image resolution of modern electron microscopes. At a certain point the spatial resolution becomes independent of decreasing spot size. In contrary, intentionally defocusing the electron beam can be used to decrease sensitivity to small artifacts. Moderate magnification values are adequate for X-ray mapping and similar applications.

As outlined above reducing the high voltage of the electron gun enhances the spatial resolution. Excitation using low energy characteristic X-ray lines (L- and M-line series), which will travel only a short distance in the sample, can further enhance lateral resolution. But in this case detection of X-rays becomes much more critical, and analysis will be increasingly sensitive to surface contamination and specimen condition.

2.5.3 Analyzing Inhomogeneous Samples

Inhomogeneous samples require special consideration when using X-ray microanalysis. Point analysis inadvertently performed on textured material will lead to random results.

Averaging over a larger sample surface (object analysis) with inhomogeneous samples will generally not result in mean concentration values. First of all this is due to the fact that numerical two-dimensional distribution of the constituents neither matches volume contents nor mass concentrations. Secondly, non-linear relationships of spectrum analysis prevent

simple averaging of spectra from being adequate. The second reason also applies when averaging on rough sample areas, even if individual point analysis results are correct.

ColorScan, mapping and element imaging are means to detect inhomogeneous samples or to find phases and suitable spots for analysis. Automatic multipoint analysis can be an adequate method to measure mean concentrations or statistical distribution parameters.

Microtextures. Special cases are samples with microtextures in the range of the spatial resolution of X-ray microanalysis. Here the measurement conditions can only be improved by reducing the analysis volume, by using low-kV excitation or special methods like thin sectioning.

2.5.4 Sensitivity of X-ray Microanalysis

Because of the small analysis volume X-ray microanalysis is extraordinarily sensitive. Absolute sensitivity in the order of 0.1 pg and well below can be achieved in many cases. In connection with thin sections - as used for TEM analysis - even total amounts of 10^{-19} g can be detected. This corresponds to only a few thousand atoms.

2.5.5 Limit of Detection

Despite of the extraordinary low absolute detection limits of X-ray microanalysis, the limit of detection (LOD) of EDS in terms of concentration is restricted by the bremsstrahlung background, which is always present. In average and when using moderate measurement times, the detection limit for trace elements is roughly 0.1% mass concentration.

Of course this value is modulated by the matrix, being lower within biological or geological matrices, higher within heavy absorbing matrices. Optimum analysis conditions and very long spectrum acquisition times can shift the limits.

2.5.6 Accuracy and Precision

Precision and accuracy. The precision of quantitative EDS is mainly governed by counting statistics of the discretely counted X-ray quanta. Using fast X-ray detectors statistical errors well below 1% can be easily achieved even at moderate collecting times.

Accuracy is influenced by a great number of factors ranging from the property of the sample itself, the selection of elements to be analyzed, the possibility of severe X-ray line overlap, to the selection of the general quantification method. In average cases advanced standardless X-ray microanalysis has

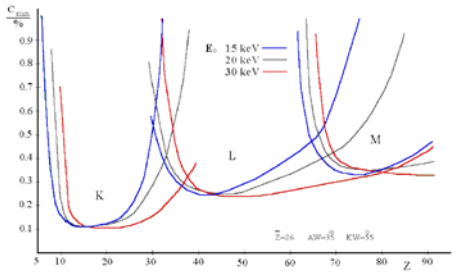


Fig. 2.5-2 Limit of detection for different X-ray line series

proven to be reliable and accurate, allowing error levels as low as 3 to 5% relatively.

Basically, the accuracy of standard-based analysis is only limited by the quality of standards and the stability of the beam at the SEM. However, error levels down to statistical limits require suitable samples, skilful selection of standards, and optimum operating conditions.

2.5.7 Special Consideration for TEM Analysis

Microanalysis with transmission electron microscopes (TEM, STEM) is special in many different ways. The most important are summarized below.

High voltage. TEMs often use extremely high-energy electron beams (100 keV and more) in order to increase image resolution and penetration of the sample. High excitation voltages give access to K-line series radiation for almost all elements of interest. On the other hand, high-energy electrons and X-rays can produce a number of side effects that are commonly not taken into consideration when using standard microanalysis procedures.

Thin sections. TEM analysis is restricted to the examination of ultra thin sections of a sample that can be transmitted by electrons. Because of this transmission of electrons, the formulas normally used for calculating X-ray generation are not valid anymore. Because of only marginal electron stray processes within the sample the distribution of bremsstrahlung becomes anisotropic and therefore hard to predict.

Whether a sample can be classified to be thin or not depends on the high voltage used and the specimen's material.

Detector position. TEMs are often not optimally adapted for X-ray microanalysis and support only horizontal detector ports. Tilting of the sample by using a goniometer stage is necessary for X-ray analysis in this case. Because of generally low beam currents, optimum detector positioning is particular important when using a TEM.

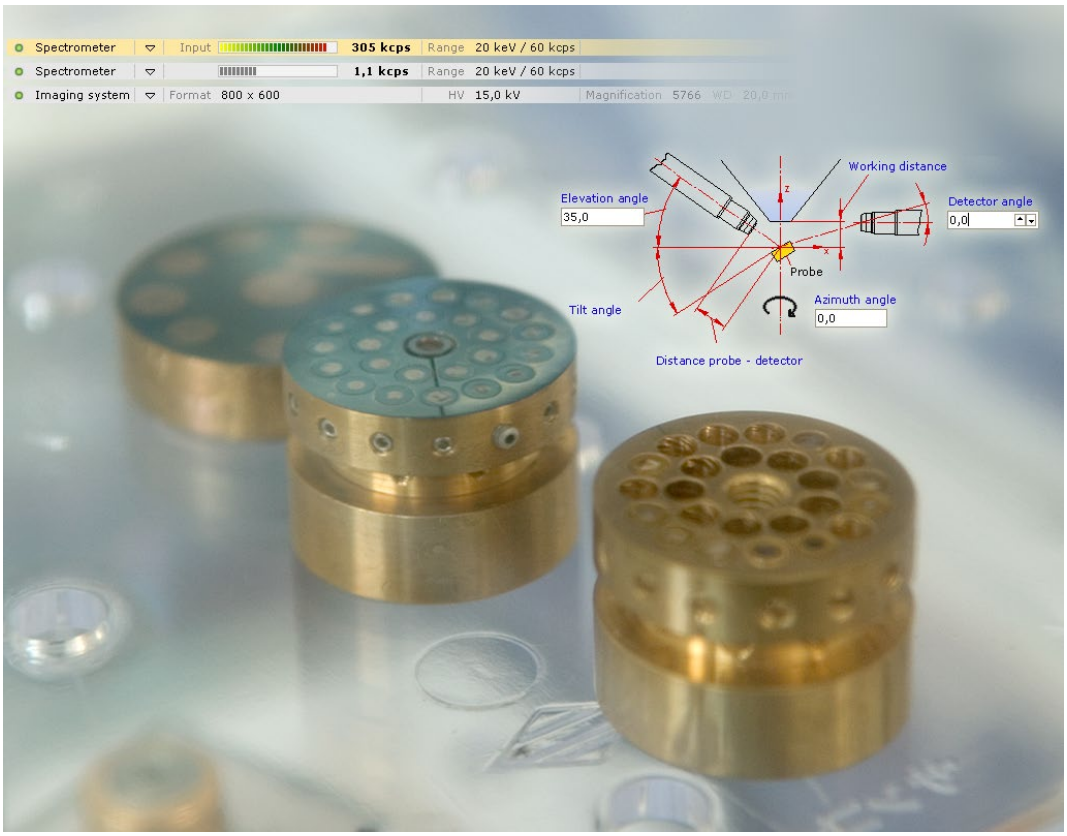
Supporting grid. TEM thin sections that are not self-supporting are placed on supporting grids. The supporting grid also serves abducting the heat generated by the electron bombardment and is therefore normally made of carbon-coated copper. X-

rays originating from the supporting grid do overlay the measured spectra. Special consideration has to be taken, when the supporting grid construction material contains elements to be analyzed in the sample.

Quantification. For standardless and standard-based quantification of specimens at TEM a number of special methods do exist. The analytical questions depend on the type of sample.

The internal features of a microanalyzer can cover only general tasks. Program options and offline quantification by specialized software may apply for e.g. biological samples. Standard-based offline quantification normally uses so-called k-ratios as interface. K-ratios are derived by comparing net peak areas of the unknown sample to standards.

3 Performing X-ray Microanalysis



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3.1 Preparing Microanalysis Samples

3.1.1 Embedding and Contacting

In average cases, samples to be analyzed with QUANTAX P/B-ZAF standardless analysis do not require other preparation than normally required for quality imaging. However, because microanalysis is surface sensitive, clean and unspoiled surfaces are prerequisites.

☞ QUANTAX interactive spectrum analysis provides means for detecting and compensating sample charging.

Samples for electron microscopy are usually embedded and contacted either using conductive resin or silver ink as conductor. For microanalysis, proper contacting is particularly important, on one hand because of the relatively high electron beam currents used, on the other hand because sample charging would depreciate quantitative results.

Isolating or poorly conducting samples need conductive coating (see section 3.1.3).

3.1.2 Grinding and Polishing

In any case grinding and moderate polishing of samples will improve precision of the quantitative analysis because of the implied cleaning, removing of oxide layers, and the well-defined local take off angel (TOA). Flawless metallographic or petrographic surfaces are not necessary if measurement spots are carefully selected to avoid scratches or other artifacts.

With standard comparison methods, normally used for high precision applications, polishing is mandatory unless the sample shows a microscopically flat surface by nature. In either case the procedure for embedding or mounting the sample must prevent inadvertent surface tilt in excess of about one degree.

Embedded samples are to be contacted using e.g. conductive resin or silver ink conduction paths. For poorly conducting or isolating samples see below.

3.1.3 Coating Samples

Isolating samples. Isolating or poorly conductive samples (glasses, minerals, ceramics, plastics) must be conductively coated whatever analysis method is used. The only alternative to coating such samples is using the variable pressure (VP) mode that is provided by certain SEMs. Variable pressure mode, however, is complicated to handle from the quantitative microanalysis point of view.

Carbon Coating. Carbon coating is a common

method and, because of the low X-ray absorption factor of carbon, the first choice for microanalysis. A variety of carbon coaters, working on the principle of vaporizing or sputtering, are commercially available.

☞ For optimum standard-based analysis, the sample and the standard are coated at the same time.

The coating must be as thin as possible while being homogeneous and contiguous. In praxis, coatings of 10 - 30 nm are proved suitable.

An alternative coating material - e.g. aluminum - can be considered in case carbon itself is to be analyzed precisely. However, coating calibration may also solve the problem.

Other coatings, like gold or platinum, may be better for high-definition imaging, but the impact on quantitative results in general will become unpredictable.

For standard-based analysis coating of specimen and standards must match tightly.

3.1.4 Sample Mounting

For average purposes and if the SEM provides an elevated detector port (detector elevation angle ≥30°), horizontal mounting of the sample is adequate. In special cases where self-absorption of X-rays within the specimen is the limiting factor, tilting the sample towards the detector, 90° take off angle (TOA) approximately, is recommended.

Tilting of sample, of course, is always necessary with horizontal detector ports that are on the same level as the specimen.

Submitting the correct geometry data to the software is mandatory for successful quantitative analysis.

The sample holder must be electrically connected to the sample stage. When a sample current meter is provided, it must be connected and in operation in order to put the stage on ground potential. Otherwise the stage is to be grounded via bypass.

3.2 Setting up the Microscope

For the purpose of X-ray microanalysis electron microscope settings differ from what is normally used for imaging purposes. Special consideration is required with the settings summarized below.

Magnification. Although the microanalyzer can capture high-resolution images, the finite X-ray

interaction volume (analysis volume) in the order of magnitude of 1 μm^3 (see also section 2.5.1) limits the spatial resolution of microanalysis, depending on high voltage (kV) and material density. Thus, useful magnification with respect to object analysis, line scan, or mapping, is limited normally to a few 1000x.

In order to perform point analysis without external scanning the magnification can be set as high as possible to reduce the area of the sample rastered by the electron beam.

Working distance. In contrast to normal imaging, the working distance (WD) cannot be freely selected when performing X-ray analysis. The correct working distance for microanalysis is a constant and depends on the design of the X-ray detector and sample chamber. The exact value is determined during system installation. Only at the specified working distance optimum detection efficiency and correct quantitative results can be achieved.

Inadequate settings of the working distance can lead to spurious peaks in the spectrum (e.g. silicon fluorescence from the supporting grid of the detector window), excess spectrum background by malfunction of the magnetic electron trap, spectrum distortion, and pulse loss. The calculated take off angle is also only correct with the approved working distance

High voltage. The high voltage should, as a rule of thumb, be twice the energy (in kV or keV) of the highest peak to be evaluated. In other words, the so-called overvoltage ratio should not be less than two for all elements of interest. Reduced voltages can be used in connection with L- and M-series analysis to increase spatial resolution. However, this is at the expense of quantitative accuracy and higher susceptibility to surface contamination.

Electron beam current. The current of the electron beam should be set according to the desired pulse density of the X-ray spectrometer (see also section 3.3.3). For high speed analysis, line scan, and mapping and with respect to sample endurance and pulse load capacity of the detector, the beam current should be as high as possible.

3.3 Microanalyzer Settings

3.3.1 Image System Settings

During installation, image area, brightness, and contrast on the screen of the microanalyzer are set to match the display on the SEM console as precisely as possible. Parameters like focusing, magnification setting, and image adjustment will be controlled via the SEM console. The result can then be observed on the SEM or microanalyzer display.

Image resolution. For the purpose of microanalysis image resolution, scan speed, and acquisition mode (line and frame averaging) can be adjusted independently of the SEM settings. Settings can be made within wide ranges according to the preferences. High image resolution settings, of course, will raise acquisition and processing times as well as memory consumption drastically when performing mapping and element imaging.

Scan mode. Noise suppression, which is often necessary for high-definition imaging, reduces the scanning speed. Mappings require even longer scan times in most cases. The measurement time can be increased, for example, through higher dwell time per pixel (for slow scan modes it can even be several seconds). In contrast to extreme slow scan, frame averaging with several fast scans succeeding one another will reduce the temporary sample strain resulting from the electron bombardment.

However long frame-averaging times require extreme stability of the scanning system in order to prevent blurring of the image. Therefore line averaging is normally the method of choice. Using this mode a defined horizontal line is scanned several times before proceeding to the next line.

3.3.2 Detector Position

Most EDS-detectors can be retracted, since the optimum position for microanalysis may interfere when performing high-resolution imaging. For X-ray spectrometry, line scan, and element mapping the detector should always be positioned to the closest position, just not touching the pole piece or the sample. In this position the solid angle is at its maximum and the lowest beam current is required for the desired X-ray signal intensity.

In some cases the X-ray detector is provided with an oblong orifice at the flange allowing shifting the detector perpendicular to its axis. This is useful to

optimize the correct working distance for EDS (see section 3.2), which is normally done only during installation.

3.3.3 X-ray Spectrometer Functions

Settings of the X-ray detector and spectroscopy signal processor influence the analysis performance. With QUANTAX most settings are either automatic or otherwise made during system installation, freeing the user from further consideration. Detailed discussion is added here only for the sake of completeness.

Maximum Throughput. The type of X-ray detector and setting of the spectroscopy signal processor determine the maximum pulse throughput of the spectrometer. The actual count rate (pulse rate) in a given situation determines how long a spectrum is to be accumulated in order to become statistically relevant. Higher throughput values correspond to reduced energy resolution and may lead to a rise of the lower energy threshold.

☞ Bruker XFlash® detectors have very high throughput capabilities and can be operated at optimum energy resolution in most cases.

The appropriate compromise between energy resolution and pulse throughput depends on the measurement task: light element analysis will require best energy resolution at low count rates, peaks in the upper energy range can be well separated at moderate settings, while element mapping will benefit from the highest throughput setting available for the given spectrometry signal processor.

Energy range. The maximum energy the spectrometer can record should be chosen to enclose all relevant parts of the spectrum, especially the full bremsstrahlung background (the upper end of the bremsstrahlung background yields information about the effective excitation voltage). If, on the opposite, the energy ranges are much larger than necessary this may affect accuracy and resolution of the energy scale.

Cooling mode. The thermoelectrically cooled XFlash® detector provides different cooling modes: maximum cooling will provide optimum energy resolution, whereas thermostat mode may be chosen if the stability of the system parameters is predominant.

3.3.4 Parameter Data Transfer

Detector parameters. Detector parameters (crystal type, window type) are fixed by the system design and installation. The correct definition within the

microanalysis software at the time of installation is crucial for quantitative analysis.

Geometry parameters. The detector elevation and azimuth angles are fixed depending on the design as well. These parameters are also defined during installation. The current tilt angle can only be automatically transferred if tilting is performed by a motorized goniometer stage. In other cases manual input to the microanalyzer before starting the spectrum acquisition is mandatory.

Microscope data. The values for high voltage, magnification, working distance and - if provided - sample tilt are often automatically transferred to the microanalyzer. In any case, the user should check correct data entry, because incorrect data will lead to erroneous quantitative results or other malfunction.

3.4 System Calibration

Different levels of system calibration are provided. The need for recalibration is determined by technical conditions, the precision requirement of the application, and - eventually - laboratory or legal regulations.

Image calibration. The image calibration recalculates the current magnification value reported from the electron microscope to obtain the scaling factors needed for the QUANTAX image capture procedures. Graphical means are provided to update the calibration from the QUANTAX system environment. Image calibration influences scale bars as well as measuring functions.

X-ray spectrometer calibration. The energy scale of the EDS detector can be calibrated from the QUANTAX system environment. To perform the calibration a test sample of known composition is to be provided for spectrum acquisition. Spectrum acquisition, analysis and maintenance of calibration data are fully automatic.

System factor calibration. For standard-based analysis using the PhiRhoZ matrix correction a system factor (or beam current factor) has to be determined. The measurement is performed using a specified calibration sample directly from the workspaces. Beam current meters (Faraday cup) can

be used instead.

3.5 Avoiding Analysis Errors

3.5.1 Checking Sample State

Cleaning. Samples for X-ray microanalysis shall always be clean and properly degreased. Organic reminders can increase the carbon signal and produce incorrect quantitative results.

Severe oxidation is to be removed by grinding, polishing or edging. However the native oxide layer on most metals is thin with respect to the information depth of X-ray microanalysis at moderate or high excitation voltages and can be tolerated with normal requirements with respect to accuracy.

For sample preparation see also section 3.1.

Spot selection. Scratches, local impurities, or dust are not problematic if the analysis spots are carefully selected to avoid these artifacts. With PB-ZAF, spectrum analysis requirements regarding surface flatness are generally rather low.

If the inhomogeneities of samples are larger than the X-ray spatial resolution (analysis volume), the selection of proper analysis points is very important. Simply averaging over different areas by object analysis, defocusing of the electron beam, or free scanning modes of the SEM will generally lead to incorrect quantitative results. Manual or automatic multipoint analysis can solve the problem (see also section 2.5.3). Analysis of sample regions with inhomogeneities in the region of (or just below) the size of the analysis volume will generally lead to reduced accuracy.

Contacting. Microanalysis samples must be properly contacted to avoid charging up. For sample coating see section 3.1.3. Also dust particles on the sample may charge up and bend the electron beam, even if the sample itself is sufficiently contacted. Any instability of the SEM image, flicker or gutter may be an indication of possible local charging up.

3.5.2 Maintaining System Calibration

Incorrect calibration of the energy axis of the X-ray spectrometer will affect auto identification of chemical elements. Especially in cases where deconvolution of overlapping X-ray lines is necessary for precise quantitative results the exact energy calibration is crucial.

With standard and reference-based quantitative

analysis (other than standard-based P/B-ZAF) the calibration of the system factor directly influences non-normalized results.

Correct image calibration of course is necessary for all image related measurements.

3.5.3 Understanding Spurious Peaks

Spurious or "false" peaks can be observed in different situations. It is crucial not to misinterpret them considering them characteristic X-rays of elements contained in the sample.

Pile-up peaks. At high count rates residual pile-up peaks at about the double energy value of strong peaks may be observed. To check for pile-up reduce the beam current by a factor of e.g. two and compare the acquired spectra. All peaks whose relative height with respect to the rest does drop by about the same factor are probably pile-up peaks.

Escape peaks. Escape peaks are completely removed by QUANTAX automatic spectrum correction.

Silicon fluorescence. Silicon fluorescence peaks (not originating from the sample) are mainly observed with incorrect detector positioning or wrong working distance. Misalignment of analysis spot and detector axis can also result from beam deflection at very low magnifications and the use of electrical beam shift features. Analyzing at moderate magnifications and using the sample stage to select the analysis spots is recommended.

With proper adjustment false silicon peaks should contribute well below 1% mass concentration to quantitative results.

Stray radiation. Backscattered electrons can reach the borders of the sample chamber and the pole piece of the electron microscope. Unresolved iron and chromium fluorescence peaks can be expected to originate from stainless steel instrument components. In certain cases stray radiation from aluminum or brass sample holder may also lead to spurious spectrum peaks.

3.5.4 Avoiding Carbon Contamination

Carbon contamination. Carbon contamination, which leads to false carbon peaks and excessive absorption of X-rays, is inadvertently produced during scanning in the SEM. Residual organic gases in the vacuum chamber, possibly originating from outgassing of the sample itself, are cracked by the electron beam. Atomic carbon and other residues are

deposited on the sample. If no special technical means of avoiding carbon contamination are at hand (cryotrap, air jet), reduce the measurement time to the indispensable limit. With homogeneous or partially homogeneous samples enlarge the measurement area e.g. by object analysis.

To check if carbon contamination is a problem at all, perform a series of subsequent measurements on the same sample location and compare the height of the carbon peaks or the quantitative analysis results.

3.5.5 Detecting Inadequate Settings

A proper setup of the analysis parameters has been discussed in the sections above. Some common errors will be summarized here:

Too short measurement time or low count rate. Too short measurement times with respect to the actual count rate leads to insufficient spectrum statistics. Especially the self-calibrating P/B-ZAF analysis requires relatively high overall counts (about 100 000) in order to become statistically stable. Check the estimated errors, which are output during quantitative spectrum analysis.

Too high count rates. Too high count rates can lead to reduced energy resolution of the detector, which may affect peak separation especially in the range of light elements. Residual pile-up peaks will also rise with high count rates.

Pay also attention to the lower energy threshold, which may automatically rise with very high count rates. Ultra high throughput settings of the spectroscopy pulse processor generally lead to threshold values that make carbon or even nitrogen peaks inaccessible.

Too low overvoltage. Low settings of the high voltage of the electron gun limit the useful X-ray range in general. Analyzing characteristic X-rays at overvoltage ratios below 2 leads to rising dependence on the actual excitation energy. Check the bremsstrahlung background in the recorded spectra (Duane Hunt limit) for the effective energy; especially with low overvoltage ratios the reading of the SEM may prove not to be sufficiently accurate.

Too high accelerating voltage. High accelerating voltages reduce the spatial resolution and increase the information depth. Especially when analyzing coatings and galvanic layers, too high accelerating voltages can cause the excitation of the bulk

material, which may lead to wrong quantitative results.

Wrong working distance. Wrong working distance will lead to reduced detector efficiency by partially shadowing the detector and furthermore to distortions of the spectrum, e.g. by altered take off angle. If necessary, check thoroughly which working distance performs best (normally the one that yields the highest count rate at otherwise equal conditions).

Wrong parameter data. Always check system settings and automatically transferred parameters. Wrong spectrum parameters will lead to erroneous quantitative results. Check spectrum parameters especially with spectra imported from unfamiliar sources.

3.5.6 Using the Right Analysis Method

Unfortunately the right X-ray spectrum analysis method that covers all different analysis situations does not exist. Besides selecting point, multipoint, or object mode and proper analysis parameters, also the spectrum evaluation strategy influences the accuracy and precision of the results.

Generally use true standardless analysis (P/B-ZAF) in cases of unknown, unprocessed, or generally rough samples. Use standard-based analysis only if reliable standard databases, measured on the same machine, are available.

Some complicated analysis tasks cannot be properly handled by automatic spectrum analysis. In ambiguous cases perform or correct element identification interactively. When performing trace element analysis select the elements that are not found by auto identification manually. With complicated samples (many contained elements) adapt the background fitting ranges according to the known peaks. Use interactive tilt angle correction and correction of excitation voltage if applicable.

Select the result normalization appropriate for the desired purpose. Especially with limited statistics (e.g. during quantitative mapping), result normalization can improve the precision drastically.

Appendix

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EDS Background Knowledge

History of Energy Dispersive X-ray Microanalysis

Fig. 3.5-1 First generation energy dispersive detector

The invention of the energy dispersive X-ray semiconductor detector (EDS) in the early sixties opened a way to perform electron probe microanalysis on virtually any existing electron microscope. The main advantages of energy dispersive detectors are their ability to simultaneously span a wide energy range of x-rays, the unique detection efficiency, and affordable costs.

In a short period of time, the existing physical models for analysis by comparison to standards, the conventional ZAF-matrix correction methods, were adapted to energy dispersive spectrometry. However, standard comparison methods did not match the ease of use of energy dispersive spectrometers that well since they are time consuming and bound to extraordinary stable and precise instrumentation.

Numerous approaches to standardless analysis by fundamental parameter calculations - often backed up by stored spectra libraries – failed to provide the desired accuracy and reliablilty. This led to the common reputation of standardless X-ray analysis as "semi-quantitative". Only the recognition of the so-called bremsstrahlung as valuable source of information rather than being only a nuisance enabled the development of true standardless quantitative EDS.

Using this information the P/B-ZAF approach substantially improved repeatability and accuracy of analysis results. Only using this method quantitative analysis of rough surfaces und irregular shaped particles became feasible.

Modern EDS microanalysis features detecting limits of less than 10^{-12}g for bulk samples to amazing 10^{-19}g in thin sections. EDS now is common in nearly every field of science, medicine and technology.

New developments in the field of EDS were mainly influenced by more and more powerful computers and growing software complexity. However, the improvement of the most critical part of the system, the semiconductor detector-crystal, soon met its physical limits and stagnated.

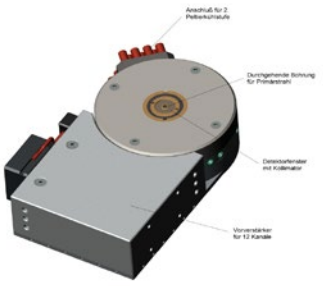

Fig. 3.5-2 Modern 12-fold SDD

This situation changed when the silicon drift detector (SDD) was invented. These chips were used for the development of the new XFlash® detector generation. These new detectors are maintenance free, do not require extensive cooling means and allow - because of their extremely fast operation- a significant reduction of measurement time. The detection speed is the key feature for element imaging, a method that produces colorful images within measurement times not much longer than ordinary image acquisition.

In 1979, during the Workshop on Energy Dispersive X-ray analysis, K.F.J. Heinrich concluded:

"If solid-state detectors of adequate energy resolution that do not require liquid-nitrogen cooling were developed, this would considerably extend the useful range of solid-state X-ray detection".

About 25 years later, the proof was at hand.

The Sources of X-rays

X-rays of two different sources are present in an electron microscope: characteristic X-rays and bremsstrahlung.

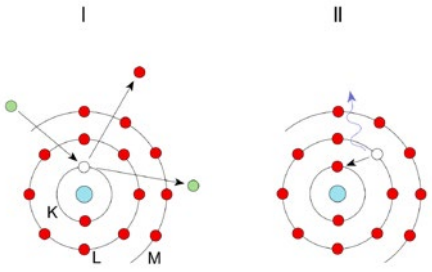

Fig. 3.5-3 Ionization and X-ray emission

Primary ionization. Specimen atoms are ionized when hit by high-energy electrons. When inner shell electrons are to be released (e.g. from the K-shell, as shown in Fig. 3.5-3) the kinetic energy of the electron must be substantially higher than the critical excitation energy E_c of the corresponding shell, which is specific for every type of atom. The ratio between the incident electron energy E_0 and the critical energy E_c is called overvoltage ratio $U_0 = E_0/E_c$. The probability of ionization referring to a certain shell (also described as ionization cross section) has its optimum at overvoltage ratios of 2 to 3.

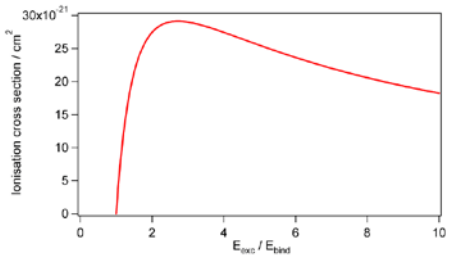

Fig. 3.5-4 Ionization cross section with varying overvoltage

The total count of ionizations caused by a defined number of incident electrons is additionally influenced by the backscatter coefficient and the electron stopping power of the specimen matter. These factors are summarized by the Z-factor of classical ZAF matrix correction.

Characteristic X-rays. Subsequently following primary ionization an electron from an outer shell fills the vacancy releasing a characteristic X-ray quantum. The quantum energy hereby equals exactly the difference of excitation energies of the two shells

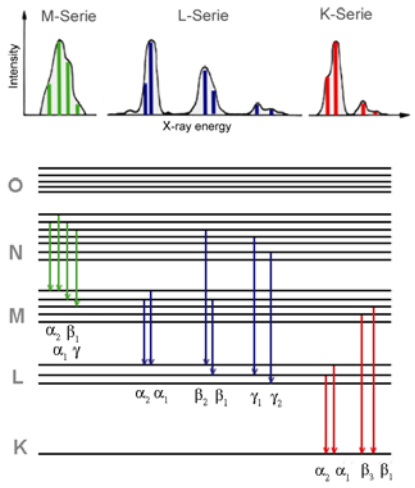

Fig. 3.5-5 Selected transitions

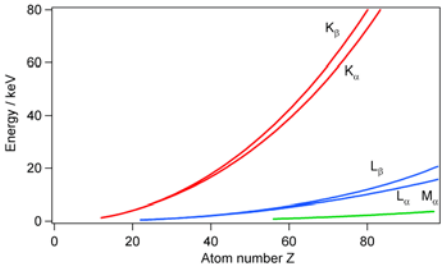

Fig. 3.5-6 X-ray line energies according to Moseley's law

involved, which are – at least for inner shells – virtually independent of the chemical state of the regarding atom.

Depending on which electron shell was holding the primary vacancy, we talk about K-, L-, or M- X-ray line series. Looking at the shell (or sub-shell) from which the electron originates that fills the vacancy, different lines can be distinguished within the groups mentioned before. The common terminology, invented by Siegbahn, reads Ka1, Ka2, Kß1, Ll, Mz ... accordingly. Meanwhile more lines and sub-lines are known than can be expressed by Siegbahn's empirical notification. All characteristic X-ray lines can be classified using the official IUPAC notification, simply stating the type of atom, the destination, and source shell name (e.g. Pb M_1N_3).

Which X-ray lines can be used for analysis mainly depends on the excitation energy available and the properties of the X-ray detector.

Moseley's law. Moseley's law (Moseley, 1913) states a simple monotonic relationship between the atomic number and the energy of a characteristic X-ray line. Nowadays exact energy values are tabulated in atomic databases and managed by software. However, Moseley's plot allows an intuitive prediction of the probability of line overlap for the different X-ray line series.

Typical intensity relations of characteristic X-ray lines, within a certain series, are called relative emission rates. Values are tabulated for all atoms.

Chemical shift. The energies of characteristic X-rays and absorption edges that are in connection with valence levels show some dependence on the chemical state of the atom. These minor shifts are barely visible to energy dispersive spectrometers and therefore mostly negligible in EDX microanalysis. The effects of chemical constitution on the fine structure of absorption edges, however, give rise to a number of advanced X-ray analysis methods (e.g. EXAFS, XANES).

Fluorescence yield. With well-defined probability when filling a vacancy in an inner shell the excess energy is released by sending forth an outer electron instead of an X-ray quantum. This is called radiationless Auger transmission and reduces the fluorescence yield, i.e. the measurable characteristic

X-rays. In the lower energy range the reduction is substantial.

Bremsstrahlung. Bremsstrahlung (literally deceleration radiation) is generated by deceleration of high-energy electrons in the electric field of an atomic nucleus. Thereby the electron looses a substantial amount of energy which is released in form of an X-ray quantum. Since any value of energy loss - from zero to the full electron energy - is possible, the bremsstrahlung quanta statistically form a continuous spectrum background.

The primary bremsstrahlung distribution is a steady function monotonically rising towards lower energies. Because of absorption and self-absorption the actually recorded bremsstrahlung background has a more complicated shape and exhibits discontinuities (edge jumps) that make fitting complicated.

Bremsstrahlung generation is the main difference between electron beam excitation and X-ray fluorescence analysis (XRF).

Absorption and Fluorescence

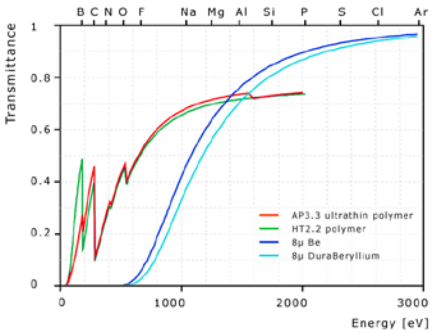

Fig. 3.5-7 Soft X-ray window transmission

Absorption law. Absorption in the low and medium X-ray energy range is basically determined by the photoelectric effect, leading to fluorescence and Auger electrons. The absorbing power of different types of matter is described by energy dependent mass absorption coefficients (MAC). These are tabulated in atomic databases. The accuracy of the MACs, which are generally submitted by a number of different sources, is one of the main quality factors of quantitative spectrum analysis software.

The absorption process follows the Lambert-Beer law quite concordantly, which states an inverse exponential relationship between transmitted X-rays on the one hand and the product of MAC and length of path on the other hand.

Detector window effects. X-rays must pass through the radiation entrance window of the detector as well as the functional and “dead” layers on the detector surface before entering the active volume of the detector. Thereby they undergo energy dependent attenuation according to the mass absorption coefficient and the effective thickness of these different layers. The absorption curves exhibit sharp edges (absorption edges) at energy values corresponding to the critical energies of the window material. Window absorption is the main reason for

non-unity quantum efficiency of X-ray detectors in the low energy range. This limits the detection of low energy X-ray lines.

Two different kinds of detector windows are commonly offered: beryllium windows for detection beginning from sodium, and light element windows, which can transmit boron (or even beryllium) K radiation.

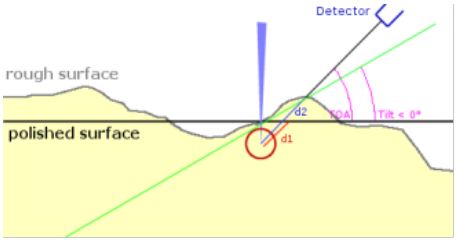

Fig. 3.5-8 X-ray absorption on rough surfaces

Self-absorption. Attenuation of the primary generated X-rays (characteristic X-rays and bremsstrahlung) also occurs within the specimen by self-absorption. Self-absorption is one of the reasons for the complicated non-linear relationship between specimen composition and detected X-ray intensities, which is a subject for matrix correction routines. The effect of self-absorption is described by the A-factor in the classical ZAF approach. Self-absorption drastically increases at lower take-off angles (TOA). Therefore take off angles below 30° should be avoided for quantitative spectrum analysis.

Rough or contaminated surfaces are the main problem for exact quantitative analysis using X-rays. The reason for this is the unknown length of the absorption path for a certain location in the sample. That means self-absorption cannot be calculated using geometrical considerations only. This problem is substantially diminished by advanced P/B-ZAF analysis (see below in this appendix).

Fluorescence enhancement. In photon induced X-ray spectrometry (XRF) X-ray fluorescence is the primary signal source. With EDS analysis secondary fluorescence, caused by primary characteristic X-rays and bremsstrahlung, is considered to be an effect of second order normally enhancing characteristic X-rays by only some percent. In some special material compositions the characteristic X-rays of one component tightly matches the absorption edge of another. In these cases fluorescence enhancement can rise to about 30%. Fluorescence enhancement is accounted for by the F-factor in classical ZAF matrix correction.

In case of inhomogeneous samples, especially when small intrusions of light elements are in a heavy matrix (e.g. the carbon content of spheroidal graphite), secondary fluorescence may need special consideration in order to avoid analysis errors.

Semiconductor Detector Effects

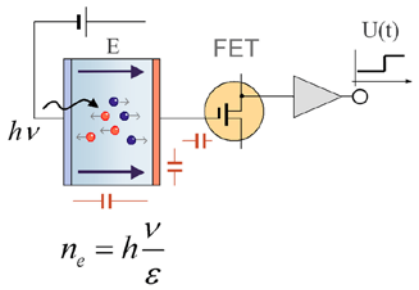

Fig. 3.5-9 Schematic drawing of Si(Li) detector

Si(Li) detectors. The classical energy dispersive X-ray detector build on of a bulk silicon semiconductor crystal which exhibits an inert volume as X-ray sensitive element. To maintain the inert volume the crystal is drifted with lithium, that is why the name Si(Li) is used. However, impurity compensation is far from ideal. The detector, as well as the first amplifier stage (field effect transistor), has to be cooled with liquid nitrogen.

An X-ray quantum, absorbed in the volume of the detector, causes a cloud of electrons and holes to be set free by successive ionizations of the detector material. Since this inert volume is virtually free from other charge carriers, the electrons and holes generated can be separated by means of an electric field. Charge carriers traveling to the electrodes located on both sides of the detector cause a displacement current that is being measured by a charge sensitive amplifier. The amplifier outputs a signal pulse, approximately proportional to the energy of the corresponding X-ray quantum.

Because of inevitable electronic noise and the statistical nature of charge generation the characteristic X-ray lines, very narrow by nature, are broadened in an energy dispersive collected X-ray spectrum. The broadening described by the full width of the peak measured at half maximum (FWHM) depends on the energy of the quantum, in a manner expressed by the Fano-factor.

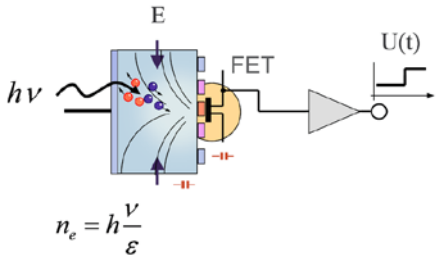

Fig. 3.5-10 Schematic drawing of SDD detector

XFlash® Detectors. The Bruker XFlash® detector is an energy dispersive X-ray detector based on the silicon drift detector (SDD) principle. A monolithically integrated on-chip FET acts as signal amplifier and allows unprecedented energy resolution.

The principle of sideward depletion of the active detector volume in connection with the integrated drift structure provides an extremely small detector capacitance. This enables use of fast signal processing techniques. The pulse throughput of XFlash® spectrometers is by more than an order of magnitude higher than what energy dispersive systems can provide.

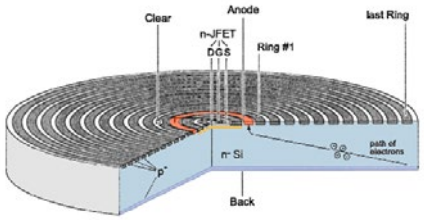

Fig. 3.5-11 SDD chip layout

The detector crystal is moderately cooled by vibration free thermo-electric coolers; any heat generated is dissipated by unforced convection with no needs for external cooling means.

A super thin radiation entrance window separates the sensitive detector area from the ambient atmosphere and guarantees good transmission of the X-rays of interest.

EDS-Detector artifacts. Due to the complex interaction processes within the detector crystal the pulse height distribution recorded in the multi channel analyzer (MCA) shows a number of artifacts. The most prominent effect - line broadening - can clearly be observed on the screen and is tackled by so-called deconvolution or peak fitting procedures during spectrum analysis.

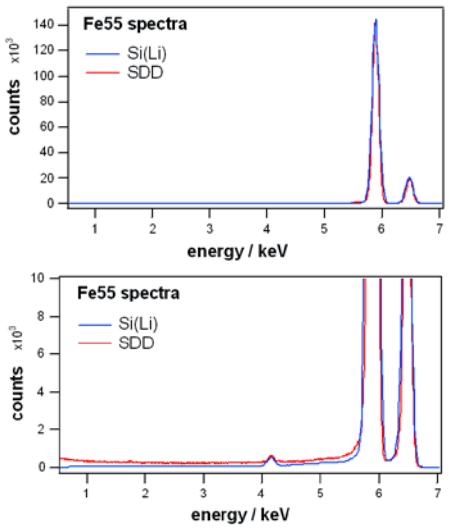

Fig. 3.5-12 Tail and shelf (uncorrected)

The main effects of second order are summarized below. Nowadays they are physically well understood and automatically compensated or taken into account by state-of-the-art spectrometers and microanalyzers.

Escape peaks. With a certain probability fluorescent X-rays escape the silicon detector material and thereby subtract themselves from the signals measured. Without Escape correction small peaks of an energy level of 1.75 keV lower than the signal peaks can be observed in the spectrum.

Shelf. Shelf is a residual background continuum, overlaid to bremsstrahlung, caused by incomplete charge collection (ICC) within the detector.

Tail. Tailing is of the same nature as shelf, and leads – if uncorrected - to slightly asymmetric peak shapes.

Shift. Some Si(Li) detectors exhibit minor peak shifts in the range of 200 ... 500 eV. These are compensated during spectra collection.

Pile-up. Pile-up peaks can be observed at higher count rates. They appear at about the double energy value of prominent peaks. The height of pile-up peaks rise with the count rate. A special hardware (pile-up rejector)

suppresses pile-up peaks as far as possible.

Conventional Quantitative Analysis Procedures

Conventional quantitative X-ray microanalysis bases on measured intensities of characteristic X-rays which are related to standard measurements, filed reference spectra, or computed values. The intensity quotients are commonly called k-Ratios. The objectives of modern matrix correction are going far beyond empirical approaches as e.g. proposed by Bence and Albee (1968). Standard algorithms like ZAF, PhiRhoZ and advanced approaches (PAP, PROZA, XPP, etc.) try to model the fairly complicated inter-elemental effects of X-ray self-absorption and fluorescence enhancement by using empirical formulas or relations derived from theory. Their aim is to reduce the number of required references and to improve accuracy.

Using modern calculation methods, internal calibration curves can already be derived from only one standard value per chemical element to be analyzed. Composites as well as pure element standards can be used as reference. Meanwhile the application of the related calculation procedure is completely automated. Still, prerequisites for precise standard-based analysis are very stable and well controlled working conditions and properly processed samples.

In contrast to that, every day use of quantitative X-ray microanalysis calls for reliability of analysis using ordinary instruments with a great variety of materials, which come as fragments, powders, dust, or environmental samples of any kind. Frequently these materials have to be analyzed in natural state.

With natural samples standard-based quantitative analysis is likely to fail just because of significant local variations across the rough or coarse sample surface. Correct matching of standards and specimens taking local structure, sample point, feature size, etc., into account is virtually impracticable.

P/B-ZAF Spectrum Analysis Background

Self-calibration. The self-calibrating P/B-ZAF method starts with peak to background intensities as primary input in contrast to absolute peak intensities as with classical approaches. This reference to relative data, i.e. ratios of peak intensities to the background, only renders the method to be completely independent from scaling factors like beam current, acquisition time and solid angle of the

detector. Moreover the considerable independency of properly chosen intensity ratios from different other influences allow accurate quantitative analysis results even under conditions of unknown absorption, which means the method is self-calibrating to the current conditions.

True standardless. The necessary reference values for determination of the fundamental peak to background ratios are provided by characterization of the bremsstrahlung, which is simultaneously detected by the EDS-detector. The bremsstrahlung normally seen as a disturbing background phenomenon just to be removed turns out to provide all necessary supplementary information that is needed for a reliable analysis. Since no other input is necessary P/B-ZAF fundamental parameter analysis is true standardless. Both, characteristic X-rays and bremsstrahlung are of the same physical nature, apart from the generation process. Therefore absorption effects, measurement errors, and detector artifacts more or less cancel out each other by calculation of the fundamental ratios, leaving only a minor secondary influence of these effects on quantitative results.

Theoretical derivation. The intensity of the primarily generated characteristic X-rays can be derived from the ionization cross-section of the respective electron shell, the fluorescence yield and relative emission rate with sufficient accuracy. However, this radiation is attenuated by absorption, possibly enhanced by fluorescence and detected at a solid angle that is hard to control. Moreover, the registered X-ray quantities are proportional to the product of electron beam current and acquisition time, which in total is expressed by the well known fundamental equation of electron probe microanalysis:

$$N_i^{char} = \frac{\Omega}{4\pi} \cdot I_0 \cdot t \cdot \omega_i \cdot \varepsilon_i \cdot q_i \cdot c_i \cdot \left(Z \cdot A \cdot F\right)_i^{char} \quad (1)$$

The so-called factors Z^{char}, A^{char} *and* F^{char} actually represent complicated terms depending on the composition of the sample. Within classic standard-based analysis heuristic procedures are used to extract the unknown concentrations from the resulting set of nonlinear equations by means of comparisons with values from the standard

database.

N_i^{char} *number of x-ray photons of the characteristic energy of a certain element i*
Ω *solid angle covered by the detector*
I_0 *electron beam current*
t *acquisition time*
ε_i *detector efficiency*
ω_i *fluorescence yield*
q_i *relative emission rate*
c_i *concentration of element i within mass fraction*
Z_i *atomic number factor*
Ai *absorption factor*
F_i *fluorescence factor*

The intensity of bremsstrahlung for a given energy range can be expressed through an equation similar to equation (1).

$$N_i^{br} = \frac{\Omega}{4\pi} \cdot I_0 \cdot t \cdot \varepsilon_i \cdot (Z \cdot A)_i^{br} \quad (2)$$

Within equation (2) the element concentrations c_i are only implicitly included in the form of the factors Z^{br} and A^{br}, representing the fact that generation of bremsstrahlung is not specific for individual elements. However other factors can be found in a similar way as within equation (1), which makes the combination of these equations a unique tool for eliminating excess parameters.

Dividing equation (1) by equation (2) results in the expressions for the so-called P/B-ratios, which are the intensity ratios of particular characteristic X-rays to bremsstrahlung for the same energy range.

$$(P/B)_i = \frac{N_i^{char}}{N_i^{br}} = \omega_i \cdot q_i \cdot c_i \cdot \frac{(Z \cdot A \cdot F)_i^{char}}{(Z \cdot A)_i^{br}} \quad (3)$$

Within this set of equations factors representing measurement conditions like solid angle, detector efficiency and electron beam current are no longer present. After determining the P/B-ratios for all elements in question from a single measured spectrum equation (3) can be solved for the required concentrations. Wendt [1], Small [2], and Statham [3] propagated this approach already a long time ago. For practical use Bruker continuously improves the fundamental procedures and adds new formalisms for dealing with light elements.

The solution of equation (3) yields absolute values for concentrations without the need for normalization. Therefore, checking the result quality is feasible by critical assessment of the sum of element concentrations, provided that all elements contained in the analyzed specimen are accessible to X-ray analysis. Otherwise a non-detectable element can be determined by difference. In contrast to standard-based analysis also in this case no reference measurement or system normalization is required.

Optimized light element and low energy line analysis (TQuant)

Due to statistical reasons, a high line density and possible deviations in the low energy background, P/B ratios acquired at energies lower than 1 keV are not suited for quantification. Nevertheless, a net count based standardless analysis for low energy lines below 1 keV combined with the P/B ZAF algorithm for elements with lines above 1 keV provides appropriate data for a standardless analysis. The net count based analysis can even be used when a sample contains only light elements or the spectrum contains only low energy lines

TQuant, an adaptive algorithm developed by Bruker, chooses the right spectrum analysis strategy for every type of sample.

Using the P/B-ZAF method, to enable standardless analysis only the primary generation rates of characteristic X-rays must be known from theory. These can be obtained with sufficient accuracy from available atomic databases. As in practical cases absorption of characteristic X-rays can be regarded as similar to absorption of bremsstrahlung ($A^{char} \approx A^{br}$). The less accurately known and more complex mass absorption coefficients of the different chemical elements are excluded from the calculation. Theoretical modeling of bremsstrahlung and fitting to the measured spectrum, provides in addition a convenient means for checking the electron energy E_0 (excitation energy) and - in case of well known detector characteristics - for calculation of a nominal local tilt angle.

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