The XRF Principle:

The Fundamentals of Energy Dispersive X-ray Fluorescence Technology
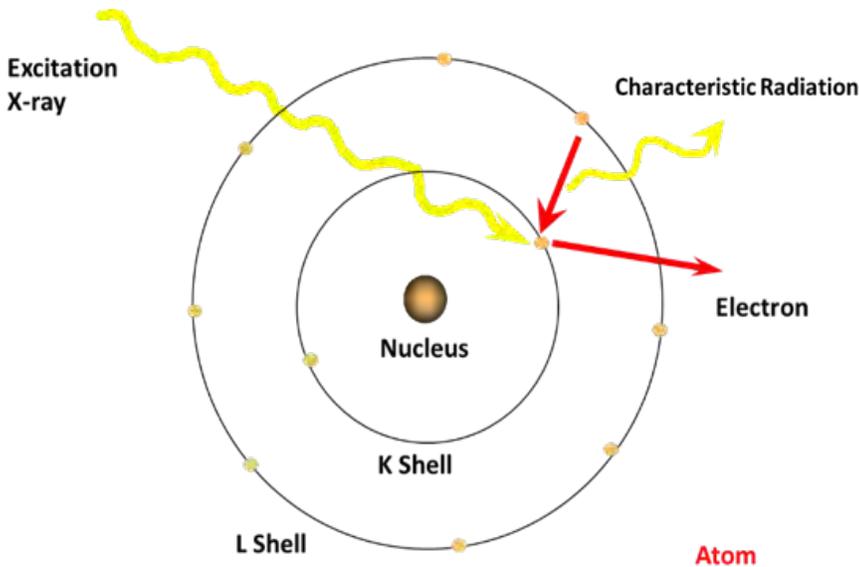
Introduction

The traditional use of X-ray fluorescence analysis (XRF) has its roots in geology. Solid samples were the first sample types analyzed by X-rays. Over the years the applications have expanded and nowadays cover the analysis of alloys, various types of powder samples to liquid samples and filter material.

Principle of XRF

The effect of X-ray fluorescence is based on the excitation of atoms in the sample. Unlike optical spectroscopy, the excitation involves interaction with the inner shell electrons rather than valence electrons as indicated in the image of the Bohr model of the atom below.

This excitation X-ray hits an inner shell electron of the atom and ejects the electron from the atom. The open position is filled by an electron from a further outer shell and fluorescence radiation is emitted. The energy of this radiation is characteristic to the specific atom and indicates what atom is present in the sample.

As many atoms may be present in the sample, X-rays with different energies will be emitted. This is depicted in the picture below. In an energy-dispersive XRF instrument the fluorescence radiation is collected by a semi-conductor detector.

The process of X-ray Fluorescence begins with an excitation (or primary) X-ray which is typically generated using an X-ray tube.
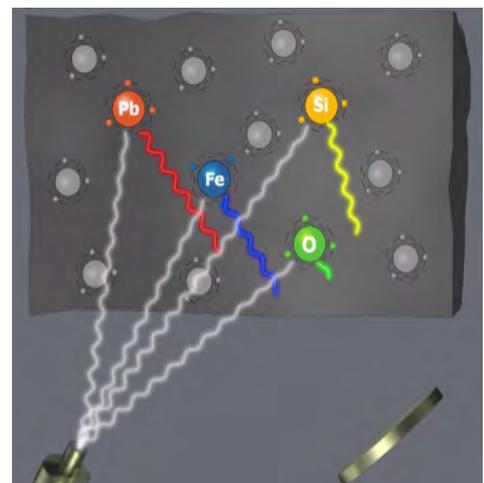
The X-rays create signals in the detector, which are dependent on the energy of the incoming radiation. The signals are collected using a multi-channel-analyzer.
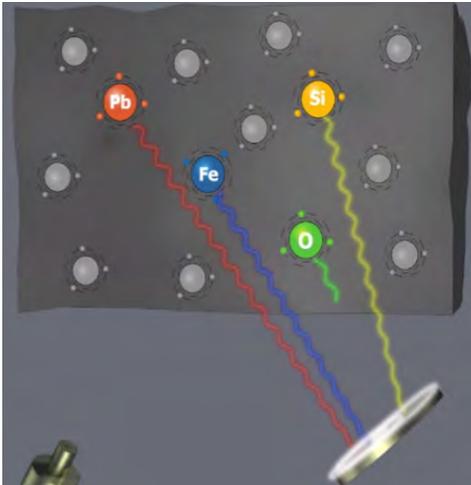
The signals are converted into a spectrum as shown below. The y-axis represents the intensity of the peaks in counts per second and the x-axis is the emission energies.
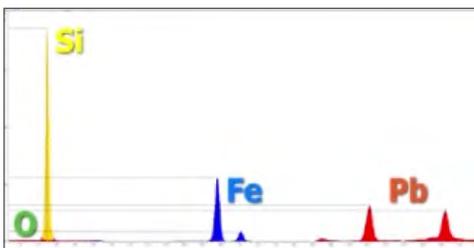

Using the energies of the peaks, the elements present in the sample can be identified.

The process handles each X-ray one by one but with high speed. Modern detectors can handle 1 million counts per second and more. Therefore the spectrum can be recorded quasi-simultaneously. Even with a short measurement time, the spectrum can give sufficient information to calculate intensities, which can be used to determine the composition of the sample.

Using a longer measurement time allows for better statistics resulting in better precision and better peak-to-background thus resulting in improved detection limits. The intensities follow a "Poisson"-statistics. The table below shows the influence of the number of counts on the statistical error of the analysis:

Number of counts N	Abs. error √N	Rel. error in %
100	10	10 %
10,000	100	1 %
1,000,000	1000	0.1 %
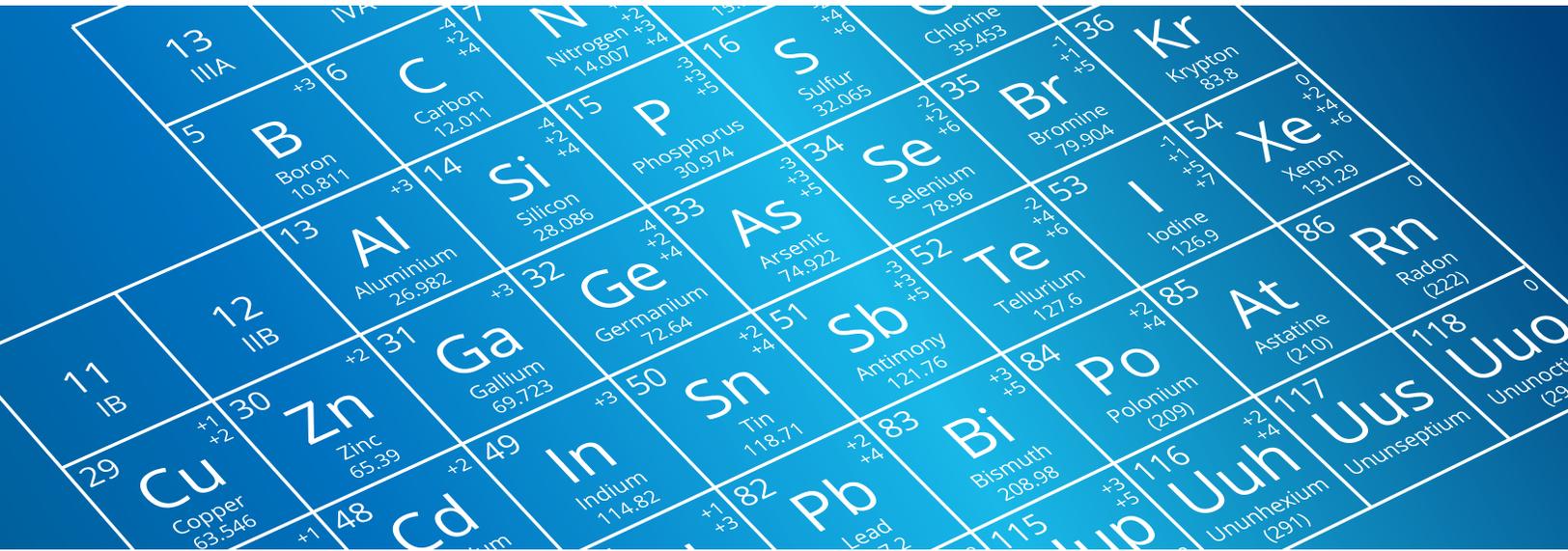
Important: Low background combined with high sensitivity is necessary to reach low detection limits!

If a highly precise analysis of an element content is required, a minimum of a few million counts should be collected. This is quite easy, if the sample contains a high concentration of an element and the detector can handle a high count-rate, but will be more difficult, if concentrations are low and the detection system is only able to handle a low count rate.

To obtain low detection limits, a combination of high sensitivity with low background is important. This becomes clear when looking at the following equation, which is used to estimate the limit of detection (LOD).

$$LOD = 3*C_0 \ \frac{\sqrt{B}}{N}$$

N: Counts of an element specific line of a standard within a Region of Interest (ROI) having a width of 1.1*FWHM (Full Width at Half Maximum)
B: Background in the same ROI as the element line
C_0: Concentration of the observed element in the reference sample

Optimization of Excitation

Many applications for XRF require only a very basic setup with tube-sample-detector.
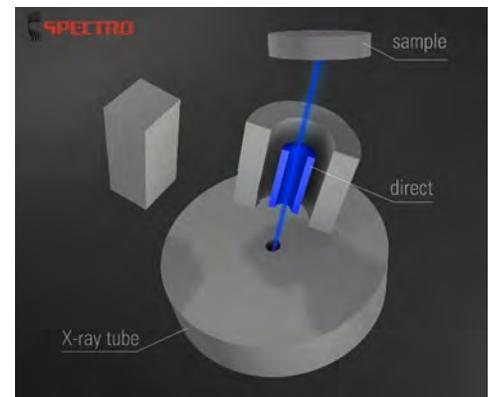

For more challenging applications, requiring high sensitivity and/or low detection limits, the optimization of excitation and detection systems becomes crucial.

High sensitivity can be achieved with a carefully selected X-ray tube. Important characteristics are the tube design (side-window, end-window, transmission window, etc.) the tube power, and its anode material.

The selection of the anode material is particularly important when high sensitivity for

a certain group of elements is required. The following schematics show the effect by using different colors to represent different excitation energies.
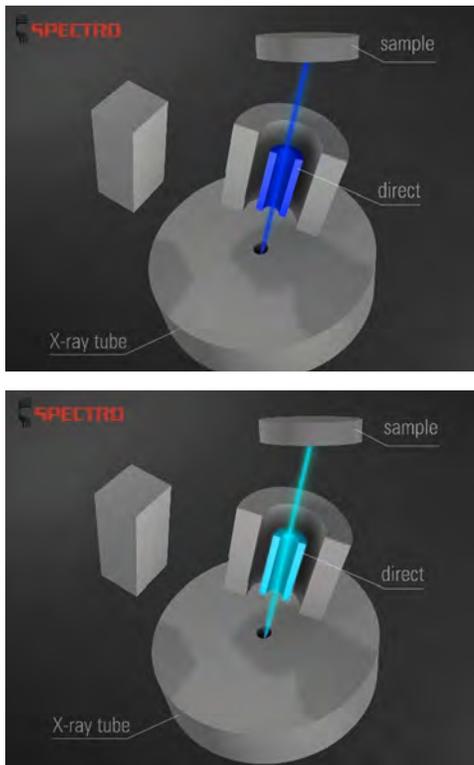

The following spectra comparison ① shows spectra from a sample excited with Pd- (displayed in blue) and Co- (displayed in turquoise) anode X-ray tubes.

For the analysis of potassium in this sample, using the Co-excitation provides higher sensitivity than using a Pd-excitation due to the absorption edge of potassium being close to the Co energy.

A good multi-element analyzer allows for different excitation conditions to achieve high sensitivity for larger groups of elements.

In order to reduce the background in the spectrum, another effect needs to be examined: A part of the excitation radiation is scattered by the sample and reaches the detector resulting in background. Using filters in the primary beam path can reduce this background but also leads to lower sensitivity. Therefore, it must be carefully selected.

Important: When applying filters in the primary beam a careful selection is required to get a good compromise between low background and good sensitivity!
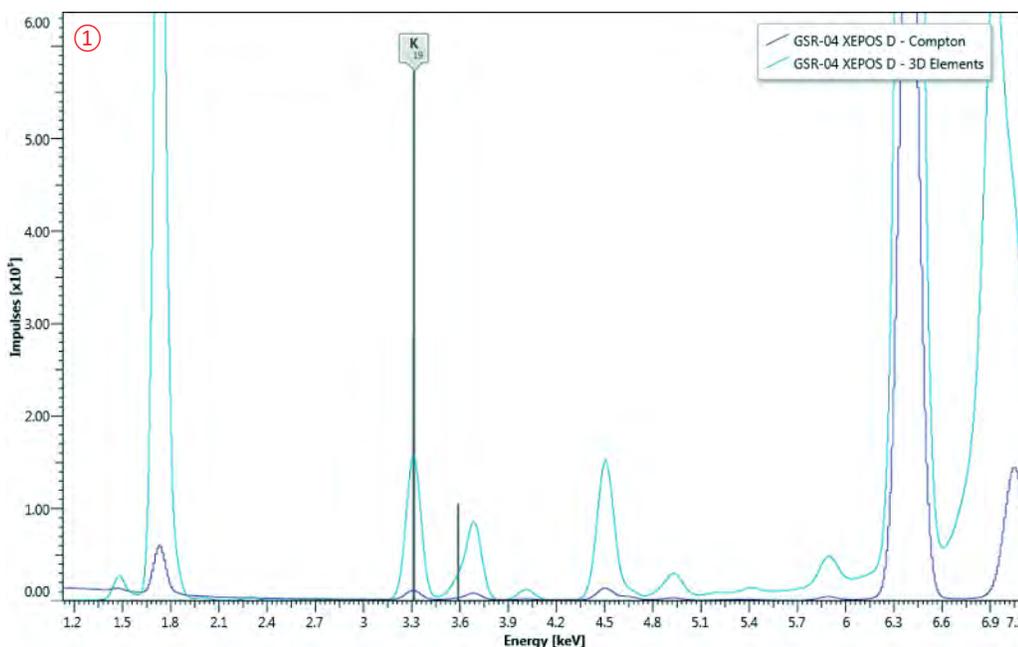
Important: The closer the energy of the excitation radiation to the absorption edge of the element of interest, the higher is the sensitivity!

simultaneous polarized/direct excitation
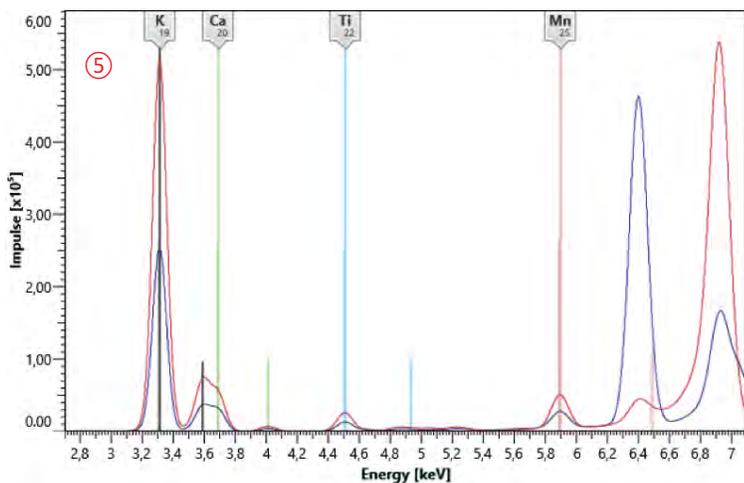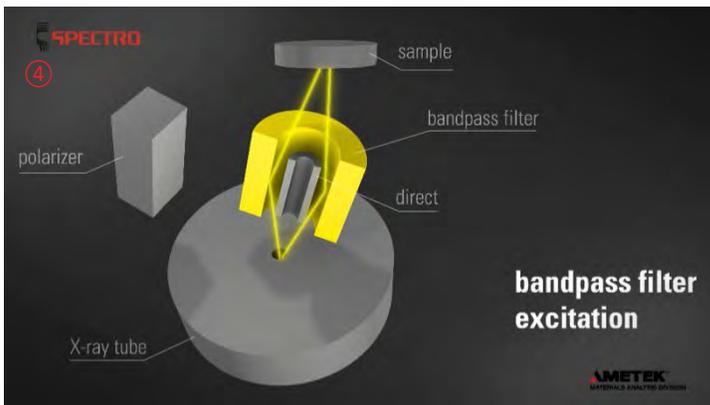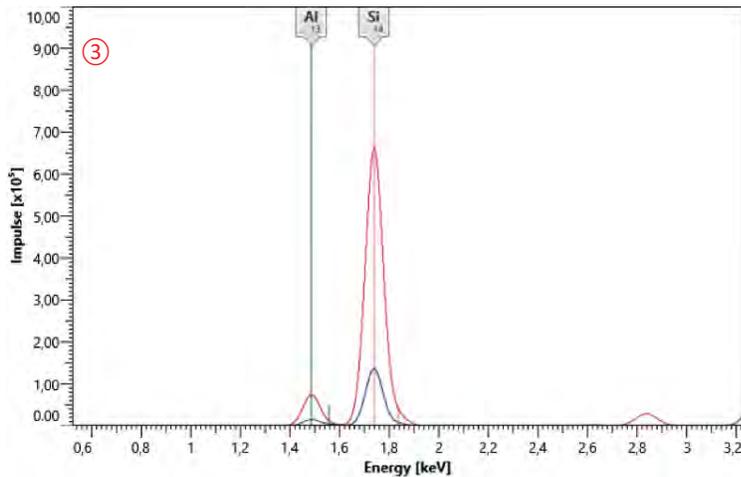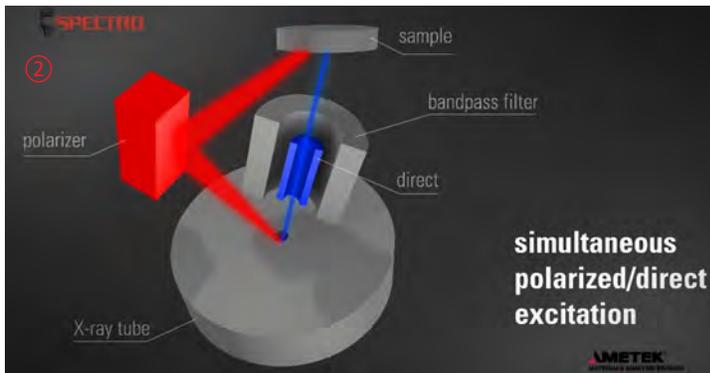
Tools such as polarizers and bandpass filters can be used to reduce this scattered background. This schematics ② shows a combined direct/polarized excitation for this purpose.

The spectrum comparison ③ shows the effect using a double curved crystal for polarization (displayed in red) to that of a direct excitation (displayed in blue).

The major benefit in this case comes from the fact, that the polarizer captures a larger solid angle of the radiation of the X-ray tube and focusses this back to the sample. With this the intensity is increased, the excitation radiation is monochromatic and polarized.

bandpass filter excitation

A bandpass-filter can be utilized to monochromatize the excitation radiation as well. The image on the left shows the schematics of this type of excitation ④.

The result is comparable to that using an interference filter in optics, such that only the radiation with a specific energy passes the bandpass filter. The excitation radiation becomes monochromatic and due to the larger solid angle compared to a direct excitation the intensity is enhanced.

The spectrum comparison ⑤ shows the effect using a bandpass filter (displayed in red) to that of a direct excitation (displayed in blue).

But besides the higher sensitivity also the background in the spectral region of important trace elements is improved. This is shown in the spectra comparison on the right ⑥.

The comparison clearly demonstrates the combined effect of lower background and higher sensitivity for the determination of trace elements like Cr and Mn.

Detection

One important aspect of the detector is its resolution. This is normally given for a fixed energy to be able to compare the performance data. The reference energy is that of Mn K_α as for testing detectors typically an Fe-55 source is used, and this emits Mn K_α radiation.

Different detectors provide different resolution. Typical detectors in ED-XRF include proportional counter detectors, Si-PIN detector and Si Drift Detections (SDDs). SDDs provide the best resolution. The advantage of a good resolution becomes evident if low concentration levels of an element with a fluorescence signal next to that of a high concentration element must be determined. Such is shown in the following spectra ⑦, comparing the effect of using a detector with good resolution (displayed in red) to that of a detector with worse resolution (displayed in blue). False positives of traces of platinum would likely be reported using the lower resolution detector.

For most applications it is important to have high count rates as discussed above. Using earlier generation detectors, compromises needed to be made either to supply excellent resolution or high count rate capabilities. A modern detection system based on SDD technology provides both excellent resolution and high count rate capabilities.
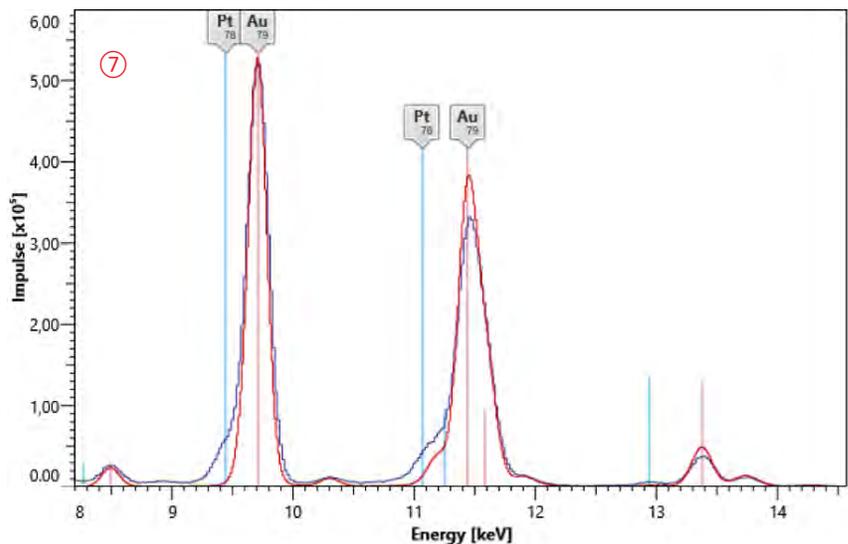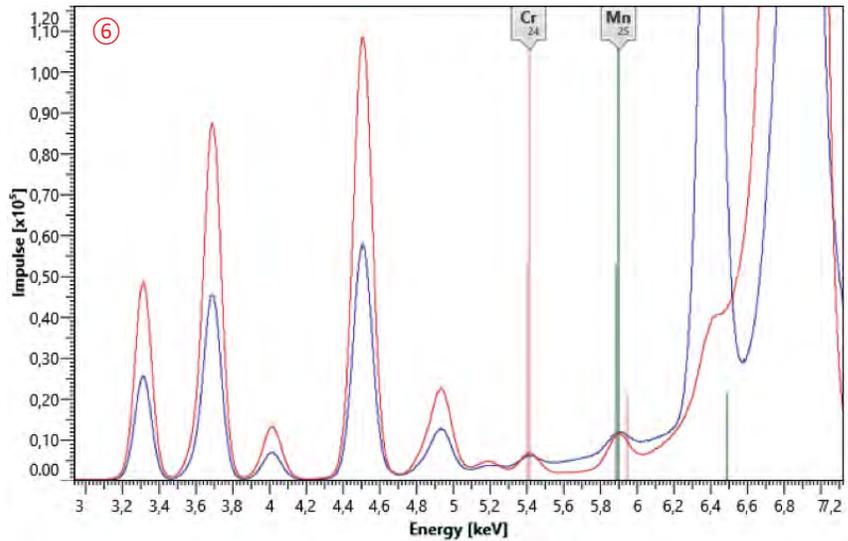
Important: When selecting a detection system in many cases it is relevant to have excellent resolution and high count rate capabilities!
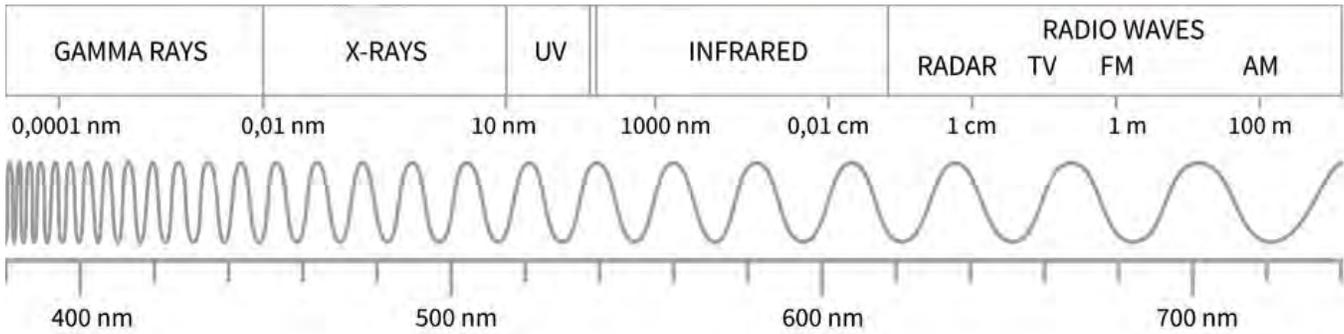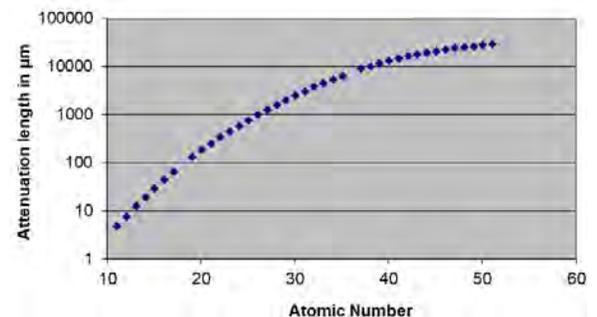
Sample preparation

Traditionally XRF is known to be non-destructive but this not always the case and the sample prep has to be selected according to the analytical goal. The selected sample prep also depends on the sample type and is certainly different for alloys, granulates, powders or liquid samples.

Typical sample prep options are:

- No sample preparation
- Filling small particles, powder, liquids, etc into XRF sample cups
- Cleaning of sample surface of a glass or alloys
- Removing of sample surfaces like oxide or coating layers
- Machining or polishing of metal alloy surfaces
- Pulverization of samples and filling the powder into XRF sample cups
- Pulverization of samples, blending the powder with binder to prepare a pressed powder pellet
- Preparation of pressed powder pellets from fine powder without binder (typically into Al-cups or steel rings are used for support)
- Preparation of fused beads, mainly from oxidic samples after blending with flux such as lithium-tetraborate or lithium-metaborate

Why is sample preparation so important? The reason behind is, depending of the energy of the X-rays, the depth from which we can collect the fluorescence radiation can be rather small. In addition, this effect is also matrix specific. Generally speaking: The heavier the sample matrix, the lower is the information depth.

To get an estimate of this effect, commonly the so called "attenuation length" is calculated. This is the thickness from which the fluorescence signal is suppressed with a factor of 1/e. The following diagram shows the attenuation length for different elements in a pure polymer matrix with the assumption of an angle of 45 degrees between sample and detector.

Depending on the analytical requirements this means that a suitable sample preparation technology must be selected. An accurate analysis of the P content cannot be done from a polymer granulate. An accurate analysis of major elements in geological samples is typically done based on fused beads. For screening applications like compliance tests larger errors may be tolerated and therefore, little or no sample prep is chosen.

Quantification

Depending on the complexity of the sample composition, matrix effects can make it challenging to determine the elemental content. Matrix effects are for example that the pri-

mary X-rays will be absorbed on their way into the sample, the same is true for the fluorescence radiation on its way out of the sample as shown in the little image ⑧. In addition, other effects like secondary excitation must be considered.

Depending on the sample matrix this will lead to different intensities and different calibration curves as shown in the big image below ⑨.

The easiest way to get accurate results is to use matrix-matching, well characterized samples for calibration. In this case typically empirical or alpha-coefficient calculation models are used.

But XRF is also well known for its ability to determine concentrations in samples without prior knowledge of the sample matrix. In fact, this is possible by using so-called Fundamental Parameter (FP) approaches. Those work best with a given sample matrix information like alloys, oxides, water, oil,…
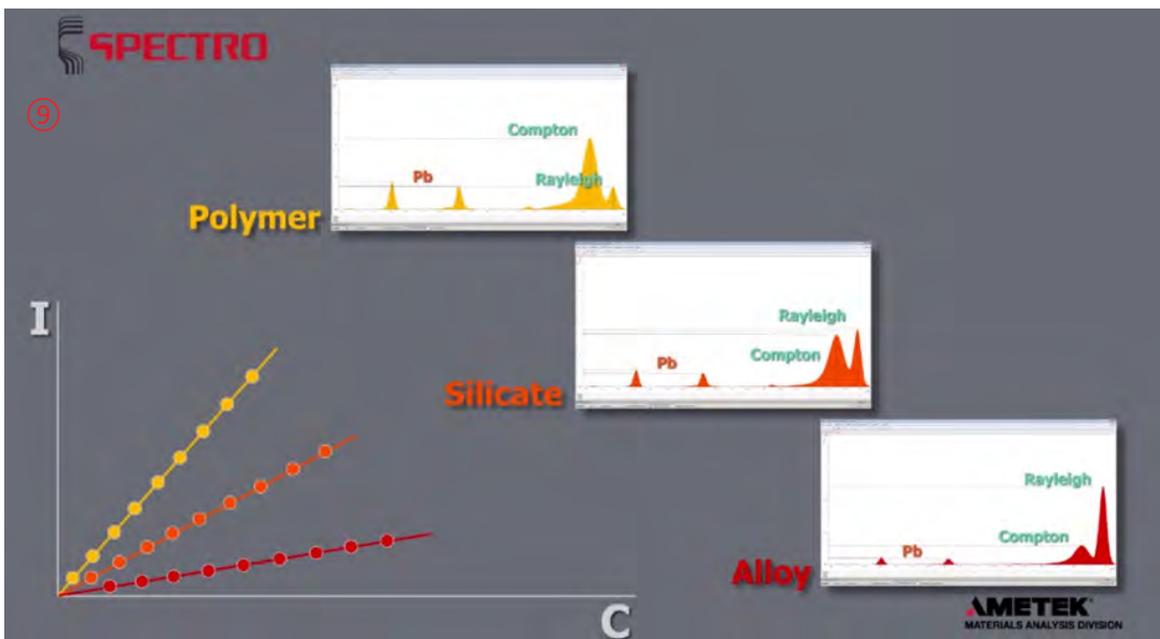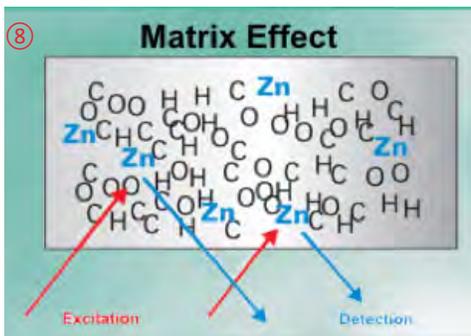
If there is no sample matrix information available a combination of fundamental parameters for the fluorescence radiation and scattering is the method of choice: At SPECTRO this procedure is called "Turboquant" (see the separate white paper and video on www.spectro.com).

Instrumentation

ED-XRF instruments are available in various configurations. There is no unique answer to the question, which instrument is the most suitable. The following image shows a variety of different ED-XRF instruments available from SPECTRO.

SPECTRO xSORT

SPECTRO MIDEX

SPECTROSCOUT

SPECTRO XEPOS

SPECTROCUBE

Application Examples

Additives in Oil/Lubricants

Application:	Check of the additive content in lubrication oil
Prep:	Pouring liquid into sample cup
Accuracy:	1-3 % rel. (typical)
LOD:	ppm
Quantification:	Fundamental Parameters, empirical
Test method:	ASTM D6481, ASTM D7751

Used oil

Application:	Check of wear metals
Sample Prep:	Homogenize the used oil, pour it into a sample cup
Accuracy:	10-20 % rel. (typical)
LOD:	ppm
Quantification:	Fundamental Parameters, empirical
Test method:	EN 15309

Wear Metals/Cooling Liquids

Application:	Check of additive elements and wear metals in oil/emulsions
Sample Prep:	Pouring liquid into sample cup
Accuracy:	10 % rel. (typical)
LOD:	ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT)
Test method:	EN 15309

Fuels

Application:	Check of sulfur content
Sample Prep:	Pouring liquid into sample cup
Accuracy:	1-3 % rel. depending on concentration)
LOD:	< 1 ppm
Quantification:	Fundamental Parameters, empirical
Test methods:	ASTM D4294, EN ISO 20847, IP 496, ISO 8754, ASTM D7220, ISO 13032

Biofuels

Application:	Check of S and trace element content
Sample Prep:	Pouring liquid into sample cup
Accuracy:	1-3 % depending on concentration)
LOD:	< 1 ppm
Quantification:	Fundamental Parameters

Waste

Application:	Screening of all elements in the range of Na to U
Sample Prep:	Pellets, powders and liquids in sample cups
Accuracy:	10-20 % rel. (typical)
LOD:	> 0.5 ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT)
Test method:	EN 15309

RoHS, WEEE, ELV, compliance screening

Application:	Analysis of Cr, Cd, Pb, Hg, PBB, Br and additional elements
Sample Prep:	direct, powder, granulates
LOD:	ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT), empirical
Test methods:	IEC 62321-3-1, ASTM F2617

Polymers

Application:	Analysis of additives like flame retardants, pigments, fillers
Sample Prep:	pressed pellets, direct, powder, granulates
LOD:	ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT), empirical

Minerals/Geology/Ceramics/Refractories

Application:	Check of main components
Sample Prep:	Fused beads
Accuracy:	0.2 % abs. for major elements (typical)
LOD:	> 100 ppm
Quantification:	Fundamental parameters or influence coefficients
Test methods:	DIN 51001
Application:	Check of trace elements
Sample Prep:	Pellets
LOD:	> 0.2 ppm
Quantification:	Fundamental parameters or influence coefficients

Cement

Application:	Check of main components
Sample Prep:	Fused beads or pressed pellets
Accuracy:	0.2 % abs. for major elements (typical)
LOD:	> 100 ppm
Quantification:	empirical or influence coefficients
Test methods:	ASTM C114, ISO 680

Metal alloys

Application:	Screening of metals
Sample Prep:	Polishing surface
Accuracy:	widely depending on element and concentration level
LOD:	> 100 ppm
Quantification:	Fundamental parameters

Metal alloy powders

Application:	Screening of metals
Sample Prep:	in sample cups
Accuracy:	widely depending on element and concentration level
LOD:	> 100 ppm
Quantification:	Fundamental parameters

Precious metals

Application:	Quantification of alloying elements
Sample Prep:	for used or polished surfaces a surface removal is recommended
Accuracy:	~ 0.1 % abs. for major elements (typical)
LOD:	> 0.01 %
Quantification:	Fundamental parameters

Ores, concentrates and tailings

Application:	Check of main components
Sample Prep:	Fused beads
Accuracy:	1-3 % rel. (typical)
Quantification:	empirical or fundamental parameters

Slag

Application:	Check of main components
Sample Prep:	Fused beads, pressed pellets or powders in cups
Quantification:	empirical or influence coefficients
Test methods:	DIN 51001

Ferro alloys

Application:	Check of main components
Sample Prep:	Pellets, Fused beads
Accuracy:	1-3 % rel. (typical)
LOD:	> 100 ppm
Quantification:	Empirical calibration
Remark:	**Ferro alloys can show severe particle size effects. Therefore, standards must represent the same grain size effects as the samples do. Commercially available reference samples are only suitable for a calibration for accurate analysis if prepared as fused bead.**

Pharmaceutical

Application:	Check of trace elements
Sample Prep:	Pellets, powder in a sample cup
LOD:	> 0.2 ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT for pharmaceuticals)

Food

Application:	Food additives and trace elements
Sample Prep:	Pellets, powders in sample cups
Accuracy:	1-5 % (typical for additive elements)
LOD:	> 0.2 ppm
Quantification:	Fundamental parameters or empirical methods

Cosmetics

Application:	Additives and trace elements
Sample Prep:	Pellets, powders in sample cups
Accuracy:	1-5 % (typical for additive elements)
LOD:	> 0.2 ppm
Quantification:	Fundamental parameters with automatic matrix correction or empirical methods

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