Workshop on EDXRS

Sources & spectral modification/optics

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Colorado Springs, Colorado

Mentioning of specific companies is NOT a recommendation!!
Principle of EDXRS

Interaction:
- Photoeffect
- elastic scattering
- inelastic scattering

X-ray source

energy dispersive X-ray detector

sample

E(keV)
Components of EDXRF

- **X-ray sources**
  - X-ray tubes: high power
  - low power
  - Rotating anode tubes
  - Radioactive sources
  - Synchrotron radiation sources

- **Spectral modification**

- **X-ray optics**

- **Detector:**
  - Filter
  - Secondary target
  - Polarizer
  - High energy cut-off
  - Monochromator
  - Focusing optics

`limited processable countrate !!`
Sidewindow tube 2 kW

- Glass Envelope
- Be Window (300 µm, 100 µm)
- Water cooling
- Electron beam
- Filament
- Copper Anode
- Target (Cr, Cu, Mo, Ag, W etc.)
- Silicone Insulation

Focal spot:
- 8 x 0.4 mm
- 12 x 0.4 mm
Spectral distribution depends on take off angle
## Low power tube

**Product**: Neptune - Water Cooled

<table>
<thead>
<tr>
<th></th>
<th>XTF6000</th>
<th>XTF5011/75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max kV</td>
<td>50.0 kV</td>
<td>60 kV</td>
</tr>
<tr>
<td>Max mA</td>
<td>5.0 mA</td>
<td>1.0 mA</td>
</tr>
<tr>
<td>Max Power</td>
<td>100 Watts</td>
<td>50 Watts</td>
</tr>
<tr>
<td><strong>Focal Spot size (nominal)</strong></td>
<td>&lt;80 microns* (W)</td>
<td>&lt;85 microns* (W)</td>
</tr>
<tr>
<td>Target types</td>
<td>W, Mo, Cu</td>
<td>W, Rh</td>
</tr>
<tr>
<td>Exit window type</td>
<td>Beryllium</td>
<td>Beryllium</td>
</tr>
<tr>
<td>Exit window thickness</td>
<td>75 µm to 254 µm</td>
<td>80 µm to 254 µm</td>
</tr>
<tr>
<td>Cone angle</td>
<td>25 degrees</td>
<td>20 degrees</td>
</tr>
</tbody>
</table>

*W denotes molybdenum target,
Mo denotes molybdenum target,
Cu denotes copper target,
Rh denotes rhodium target,
Cr denotes chromium target,
Pd denotes palladium target.*

*Focal Spot size (nominal) note:
100 microns (for W, Mo, Cu targets)
<80 microns (for W, Rh targets)
<85 microns (for W, Rh, Mo, Cr, Pd targets)
Portable tube:

Oxford: www.oxfordxtg.com

**Specifications**

<table>
<thead>
<tr>
<th></th>
<th>Reflection Target</th>
<th>Transmission Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode current</td>
<td>0.1 mA Max (3W max)</td>
<td>0.1 mA Max (3W max)</td>
</tr>
<tr>
<td>Anode (target) voltage</td>
<td>5-30 kV at .1mA</td>
<td>10-30 kV at .1mA</td>
</tr>
<tr>
<td>Power</td>
<td>Requires 15V DC input</td>
<td>Requires 15V DC input</td>
</tr>
<tr>
<td>kV control</td>
<td>0-2.5 V DC</td>
<td>0-2.5 V DC</td>
</tr>
<tr>
<td>mA control</td>
<td>0-2.5 V DC</td>
<td>0-2.5 V DC</td>
</tr>
<tr>
<td>Target</td>
<td>Rh</td>
<td>Ag</td>
</tr>
<tr>
<td>Focal spot size</td>
<td>&gt;1mm typical</td>
<td>&gt;1mm typical</td>
</tr>
<tr>
<td>Cone Angle</td>
<td>28 degrees</td>
<td>130 degrees</td>
</tr>
<tr>
<td>Cathode type</td>
<td>Cold cathode</td>
<td>Cold cathode</td>
</tr>
<tr>
<td>Dimensions</td>
<td>6.6” x 1.5”</td>
<td>6.6” x 1.5”</td>
</tr>
<tr>
<td>Weight</td>
<td>0.64 lbs (300 grams)</td>
<td>0.64 lbs (300 grams)</td>
</tr>
</tbody>
</table>
Theory of operation

When heated, a pyroelectric crystal exhibits spontaneous decrease of polarization. Hence, as the temperature increases, an electric field develops across the crystal. For a specific crystal orientation (-Z face pointing to the target), the top surface of the crystal gets positively charged and attracts electrons from the low pressure gas in the environment. As the electrons impinge on the surface of the crystal, they produce characteristic x-rays (Ta) as well as bremsstrahlung x-rays (see figure 1). When the cooling phase starts, the spontaneous polarization increases, and the electrons from the top surface of the crystal are accelerated towards the Cu target which is at ground potential. At this point of the cycle, Cu characteristic x-rays are produced as well as bremsstrahlung x-rays (see figure 2). When the crystal temperature reaches its low point, the heating phase starts again. The cycle time of the COOL-X can be varied from 2 to 5 minutes.

Features:
- Miniature size: 0.6" dia x 0.4" (15 mm dia x 10 mm)
- Low power: < 300 mW
- Runs on standard 9 V battery
- Variable end point energy: up to 35 kV
- Peak x-ray flux: 108 photons per second (equivalent to a 2 mCi source)
- Solid state: Pyroelectric crystal
- No radioactive sources
Rotating anode X-ray tubes

TUBE HOUSING DESIGNS

www.rigaku.com/protein/ruh3r.html
Radioisotope excitation

Disadvantage: cannot be turned off! - safety aspects!
# Radioisotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Fe-55</th>
<th>Cm-244</th>
<th>Cd-109</th>
<th>Am-241</th>
<th>Co-57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (keV)</td>
<td>5.9</td>
<td>14.3, 18.3</td>
<td>22, 88</td>
<td>59.5</td>
<td>122</td>
</tr>
<tr>
<td>Elements to excite (K-lines)</td>
<td>Al – V</td>
<td>Ti-Br</td>
<td>Fe-Mo</td>
<td>Ru-Er</td>
<td>Ba - U</td>
</tr>
<tr>
<td>Elements (L-lines)</td>
<td>Br-I</td>
<td>I- Pb</td>
<td>Yb-Pu</td>
<td>None</td>
<td>none</td>
</tr>
</tbody>
</table>
Synchrotron radiation
Comparison of insertion devices

- Bending magnet
- Wiggler
- Undulator
Scheme polarization plane - detector position

EDXRF with linear polarized radiation

- Linear polarization
- Isotropic emission of fluorescence radiation
- Anisotropic dipole emission characteristic
- Detector
- Atomic dipoles sample
Features of synchrotron radiation

- High brilliance
  - intensive sample excitation
  - tunability with monochromator
    - Reduction of background
    - Optimized excitation conditions
  - small source size – focusing possible

- Wide spectra range
  - Efficient excitation of
    - Light elements
    - Rare Earth elements

- Linear polarization
  - Reduction of background
Aim of all spectral modification elements:
Reduction of background due to scattering

**Physical reasons:**
elastic and inelastic scattering on sample and substrate

**Detector reasons:**
- Detector shelf
- Incomplete charge collection
- Compton backscatter from detector crystal
Filtered radiation

- **Background Reduction**

![Diagram of filtered radiation process](image)

- Source Filter
- X-Ray Source
- Detector

![Graph showing energy distribution](image)
Secondary target

→ Improved Fluorescence and lower background

Comparison of optimized direct-filtered excitation with secondary target excitation for minor elements.
Polarized radiation

Epsilon 5

www.panalytical.com
Polarization

Direct excitation (2-dimensional)  Polarised excitation (3-dimensional)
Polarization

From: handbook of X-ray spectrometry, Marcel Dekker 1993, 2002
A multilayer diffracts x-rays in a fashion analogous to a crystal. Alternating layers of high-Z and low-Z materials create a periodic structure of differing electron densities, like the atomic planes in crystals. If the phases of the waves scattered from each layer coincide, the multilayer will achieve maximum reflectivity.
Comparison of crystal with multilayer

Crystal versus Multilayer monochromator

Bandwidth of ML 100 eV in comparison to CM (2eV) @17keV

⇒ more photons for excitation
Comparison of spectral modifications

Total external reflection

\[ n \text{ (x-ray range ) } = 1 - \delta - i\beta \]
\[ \delta \sim 10^{-6} \text{ decrement } \delta \propto f_1(Z) \]
\[ \beta \sim 10^{-8} \text{ absorption part} \]

\[ \varphi_{\text{critical}} \approx \sqrt{2\delta} \propto \sqrt{\rho/E} \]
\[ \varphi_{\text{critical}} \text{ (Si, 17.5 keV)} \approx 0.1^\circ \approx 1.75 \text{ mrad} \]
\[ \text{ (Si, 500 eV)} \approx 3.7^\circ \approx 64.6 \text{ mrad} \]
Comparison of Cut-off and Multilayer monochromator

High-Energy Cut-off

E > E (<φ_{crit})

E < E (<φ_{crit})

Multilayer monochromator

E = 5.4 keV

Intensity

Cr-K_{α}

8 keV 35 keV

Intensity

Cr-K_{α}

bandwidth of ML ~100 eV

35 keV
Comparison of spectra: ML vs cut-off

Cr-tube 500 W, 100 µm focus
35 kV 14 mA 100 sec
50ng Mg, 0.5 ng Sc

ML
Cut-off

Energy(keV)

Mg Si Cl Ca K Sc Cr-Kα scatter

O Cr-tube 500 W, 100 µm focus
35 kV 14 mA 100 sec
50ng Mg, 0.5 ng Sc
Capillaries

Gain factor \( I_g \) for straight capillary:

- ratio between the effective solid angle \( \Delta \Omega_{\text{eff}} \), seen by the X-ray source (corresponding to the critical angle) and the solid angle when no reflections occur \( \Delta \Omega \) (defined by the exit end),

\[
I_g = \frac{\Delta \Omega_{\text{eff}}}{\Delta \Omega}
\]

Low-pass filter: \( \Delta \Omega_{\text{eff}} \) is proportional to \( 1/E^2 \) as \( \Theta_{\text{crit}} \) will decrease for higher energies.
Polycapillary optics

Focusing optic

Collimating optic

Half-focusing optic

X-ray source

Incoming x-rays
Focussing mirror optics

doubly curved ellipsoidal mirror,

Kirkpatrick-Baez system of 2 single curved mirrors,
Compound refractive lens (CRL) and Zone plates

CRL

\[ f = \frac{R}{2\delta} \]

Al, polymer material

\[ f = \frac{R}{2N\delta} \]

Zone plates

Zone plates are circular diffraction gratings with radially increasing line density. These lenses, known as zone plates, offer spatial resolutions which are as low as 40nm and focusing efficiencies which can exceed 50%.

For example, for a spherical hole of \( r = 300 \ \mu\text{m} \) in Al at \( E=14 \ \text{keV} \) (\( \delta = 2.8E^{-6} \)), the focal spot appears at 54 m for a parallel beam.

Array of N hole:

\( N=30 \) is reduced to an acceptable distance of 1.8 m.
Double Curved Crystals

Doubly curved crystal (DCC) optics produce a highly monochromatic, focused x-ray beam by Bragg reflection (diffraction). DCC optics capture a large solid-angle of x-rays from micron-sized as well as large point sources. These x-rays are reflect and redirected by the DCC to form a focal spot equivalent to the source size. We have refined this focusing modality by precisely and accurately bending and aligning crystals in two directions to direct only the source x-rays with a single wavelength into a focal spot. Our DCC optics can be tailored to generate a range of monochromatic beams from 1.5 to 22 keV. Very high sensitivity is created by the exceptionally high signal to background ratio (> 100,000 with a 3 watt microsource) of the focused monochromatic beam, making the DCC optic ideally suited for micro-XRF and micro-TXRF analysis.
Max-Flux® Optical System

* Gives higher flux
* Minimizes background radiation
* Lowers beam divergence
* Provides focused or collimated monochromatic beams
* Reduces of sample displacement errors
* Enables testing of irregularly shaped samples
* Available for W-L, W-M, Cu, Mo, Ti, Cr, Co and more

www.osmic.com
Parallel Beam X-ray Optics: Generation of a monochromatic 1-dimensional parallel beam

Focussing X-ray Optics: Generation of a monochromatic 1-dimensional focussed beam

Beam Compressor of a 1-dimensional compressed parallel beam

Spectral lines Cr, Co, Cu, Mo, Ag (others on request)
Mean Reflectance R > 70 %
Monochromasy Ka1 + Ka2
Divergence Df < 0.03°
(40 mm source width)

Spectral lines Cr, Co, Cu, Mo, Ag (others on request)
Mean reflectivity R > 70 %
Monochromasy Ka1 + Ka2

* Combination of a focusing and a convex bent collimating multilayer optics
* Adjustable beam width b at sample position
* Emission of a compressed parallel sub-millimeter beam
* Generation of a monochromatic (Ka1+2)
parallel spot with a width
0.25 mm < b’ < 1.0 mm

www.axo-dresden.de
Synchrotron radiation microbeam XRF

Experimental Setup @ HASYLAB beamline L

Si(Li)-detector

Mo-shielding

Beam monitor

XYZ Sample stage

15 mm

Focal size: 13-30 µm

ML → intensity gain of 80-100
only small increase of scatter peak

C.Streli DXC07 Workshop EDXRS 35
2-D-image

X3800 g
41 X 41 px
5s. / px

From Zoeger
Confocal Setup at HASYLAB

20 x 22 x 14 μm³ (lateral x depth x height) for Au Lα
3D-imaging

From Zoeger
Total Reflection X-ray Fluorescence analysis (TXRF)

- background reduction
- double excitation of sample by both the primary and the reflected beam
- small distance sample - detector (~1mm): large solid angle

Analytical features:
- small sample amounts required (ng, some µl)
- detection limits in the pg range with X-ray tube excitation
- detection limits in the fg range with Synchrotron radiation excitation
- Simple quantification (thin film approximation) by adding internal standard
- angle dependence of fluorescence signal: particle – film - implantation
Comparison of Water standard reference sample

Standard EDXRF spectrometer TN5000

ATI-TXRF spectrometer

C. Streli 2002
Angle dependence of the fluorescence signal

\[ \varphi = \varphi_{\text{crit}}/2 \]

\[ \varphi = \varphi_{\text{crit}} \]

\[ \varphi = 2\varphi_{\text{crit}} \]

Influence on detection limits:

\[ LLD = 3 \cdot \frac{\sqrt{N_B}}{N_N} \cdot m_{\text{sample}} = \frac{3 \cdot \sqrt{I_B}}{S(\text{cps/ng})} \]

- \( N_B \) reduced
- \( N_B \) enhanced by factor of 2

\( \square \text{Reduction of detection limits} \)
Depth profil and thin layer analysis

Depth profile

Ni depth profile (rectangular)
Mo-Ka excitation

Reflecting layer on surface

Ni layers on Si substrate
Mo-Ka excitation

Determination of:
- thickness
- Composition
- density

C.Streli DXC07 Workshop EDXRS
NEW X-MET3000TXS - Robust, hand-held EDXRF analyzer for the measurement of heavy metals in soil

**Oxford Instruments** has launched the new X-MET3000TXS - a fast, lightweight X-ray tube based soil analyzer, offering accurate and reliable identification of pollutant metals and fast analysis of their concentrations.

**XLi / XLp / XLt 800 Series Analyzer**

Designed for rapid identification and chemistry of metal alloy composition and grade verification for applications including quality control, scrap sorting, positive material identification and failure analysis.

- Miniaturized x-ray tube for high performance and reduced regulatory requirements
- Traditional isotopes or new Infiniton™ configuration to optimize performance for your application

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Conclusions:

• Sources range from very simple to very sophisticated ones (radioisotope sources / synchrotron radiation)

• Spectral modification: improve background and excitation

• X-ray optics: focusing of X-rays - microbeam - microXRF

• Combination of suitable sources, spectral modifications and optics:
  ▪ Portable EDXRF
  ▪ Micro XRF (down to 100 nm beamsize) at SR
  ▪ 3D-imaging at SR
  ▪ Special geometry: TXRF- ultra trace analysis

Acknowledgement: N.Zoeger, P.Wobrauschek