

# Quantitative Röntgenfluoreszenzanalyse

*Woran wir glauben und was wir wissen.*

# Quantitative X-Ray Fluorescence Analysis

*In what we believe and what we know.*

**Burkhard Beckhoff**

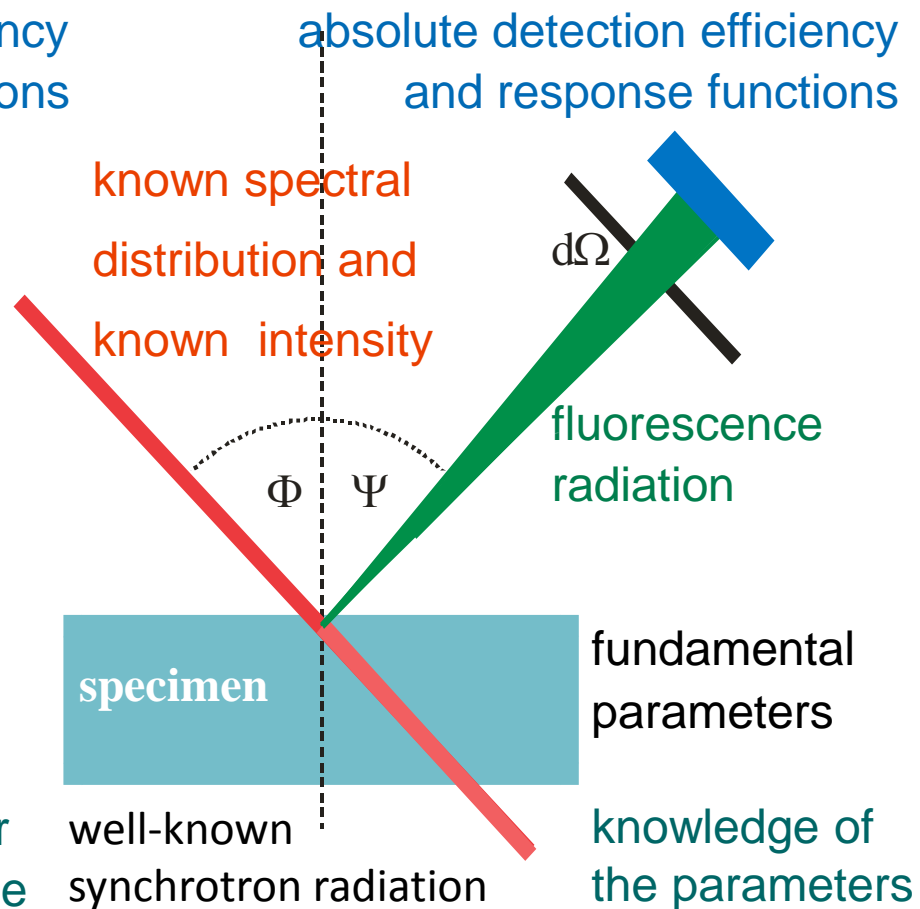
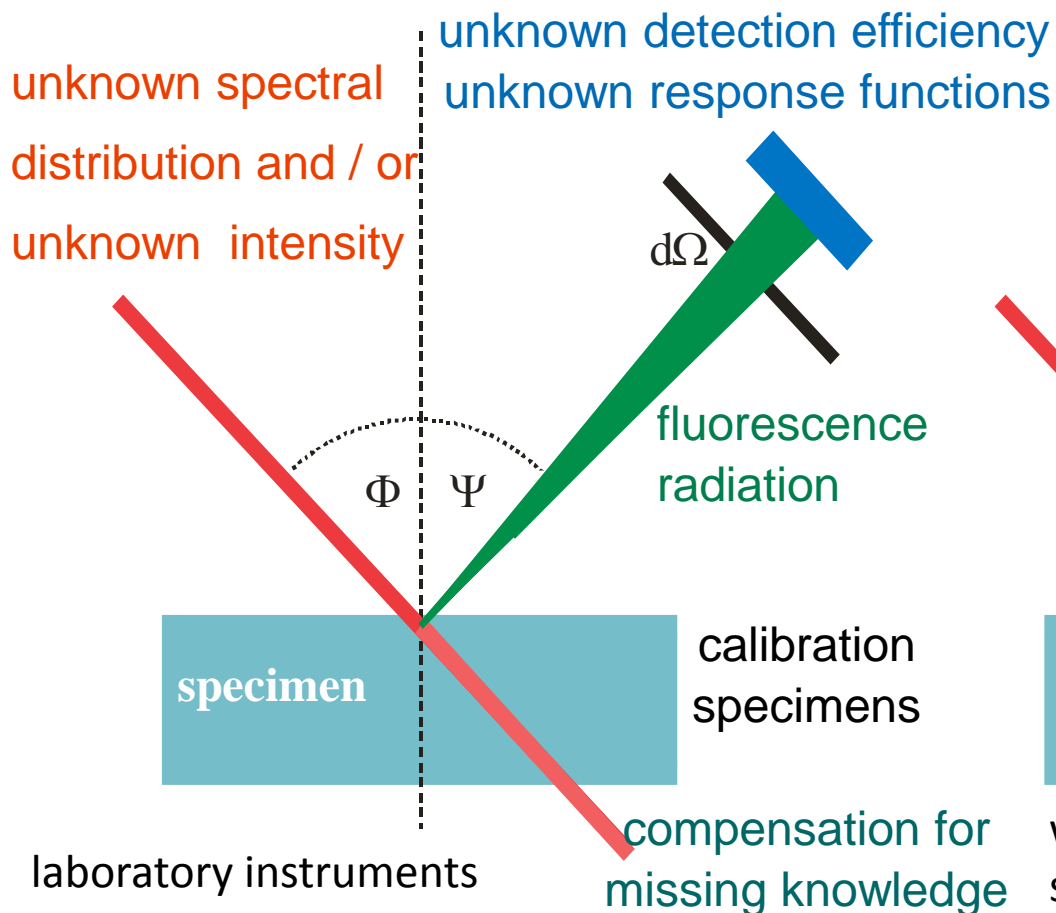
PTB Berlin, Germany

# X-ray spectrometry methodologies:

## reference-based versus reference-free approaches

reference material related technique  
based on well known calibration  
specimens or reference materials

reference-free technique  
based on calibrated instrumen-  
tation and fundamental parameters



# Synchrotron radiation based x-ray spectrometry

XRS excitation channel:

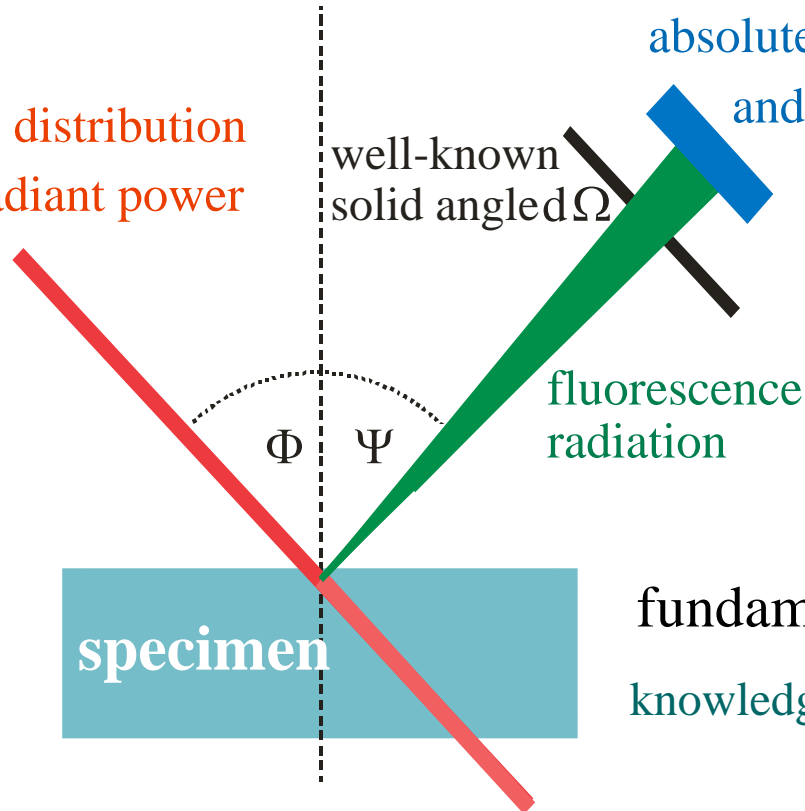
well-known spectral distribution  
and a well-known radiant power

XRS detection channel:

absolute detection efficiency  
and response functions

PTB capabilities:

- characterized beamlines
- calibrated photodiodes
- calibrated diaphragms
- calibrated Si(Li) detectors



fundamental parameters  
knowledge of the parameters

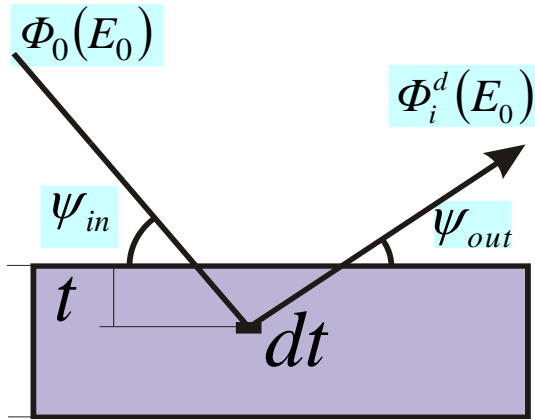
transmission  
measurements

absorption correction factors

# Quantitative XRF – primary excitation (Sherman equation)

## instrumental parameters

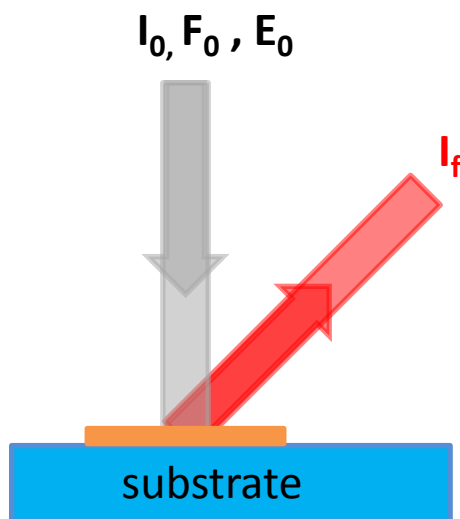
## fundamental parameters



- $\mu_s \dots$  mass absorption coefficient
- $\tau_{i,shell} \dots$  (sub)shell photo-electric absorption cross section
- $\omega_{i,shell} \dots$  fluorescence yield of (sub)shell
- $f_{i,line} \dots$  transition probability of fluorescence line
- $\rho_s \dots$  density

$$\Phi_{i,line}^d(E_0) = \Phi_0(E_0) \frac{\Omega}{4\pi} f_{i,line} \omega_{i,shell} \tau_{i,shell}(E_0) \frac{1}{\sin \psi_{in}} \times \frac{1}{\frac{\mu(E_0)}{\sin \psi_{in}} + \frac{\mu(E_i)}{\sin \psi_{out}}} \left( 1 - \exp \left[ - \left( \frac{\mu(E_0)}{\sin \psi_{in}} + \frac{\mu(E_i)}{\sin \psi_{out}} \right) \rho d \right] \right)$$

# Quantitative XRF – Sherman equation for thin layer samples



sample  
 $m_i/F$  = mass  
 deposition

$$C_i = \frac{P_i}{P_0 \tau_{i,E_0} Q \frac{\Omega_{\text{det}}}{4\pi} \frac{1}{\sin \Theta} \frac{1 - \exp(-\mu_{\text{tot},i} T)}{\mu_{\text{tot},i}}}$$

B. Beckhoff, J. Anal. At. Spectrom. **23**, 845 (2008)

$$\frac{m_i}{F_i} = \frac{-1}{\mu_{\text{tot},i}} \ln \left[ 1 - \frac{P_i}{P_0 \tau_{i,E_0} Q \frac{\Omega_{\text{det}}}{4\pi} \frac{1}{\sin \Psi_{\text{in}}} \frac{1}{\mu_{\text{tot},i}}} \right]$$

$$\text{with } \mu_{\text{tot},i} = \frac{\mu_{i,E_0}}{\sin \Psi_{\text{in}}} + \frac{\mu_{i,E_i}}{\sin \Psi_{\text{out}}}$$

R. Unterumsberger et al., Anal. Chem. **83**, 8623 (2013)

$E_0$  = photon energy of excitation radiation

$I_0$  = intensity (*photons/s*) of excitation radiation

$F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation

$I_f$  = intensity of fluorescence radiation in  $d\Omega$

$d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – Sherman equation for thin layer samples

If all relevant instrumental and atomic fundamental parameters are known, the concentration  $C_i$  of the element  $i$  in a homogeneous multielemental sample  $s$  of thickness  $T$  can be calculated without additional references using, for example, the following basic quantitation formula of X-ray fluorescence analysis:

$$C_i = \frac{P_i}{P_0 \tau_{i,E_0} Q \frac{\Omega_{\text{det}}}{4\pi} \frac{1}{\sin\Theta} \frac{1 - \exp(-\mu_{\text{tot},i} T)}{\mu_{\text{tot},i}}}$$

where  $E_0$  is the photon energy of the incident (excitation) radiation,  $P_0 = S_0/\sigma_{\text{diode},E_0}$  is the radiant power of the incident radiation to be converted into the incident radiation intensity,  $S_0$  is the signal of the calibrated photodiode measuring the incident radiation,  $\sigma_{\text{diode},E_0}$  is the spectral responsivity of the calibrated photodiode,  $\theta$  is the angle of incidence with respect to the sample surface,  $E_i$  is the photon energy of the fluorescence line  $l$  of the element  $i$ ,  $R_i$  is the detected count rate of the fluorescence line  $l$  of the element  $i$ ,  $\varepsilon_{\text{det},E_i}$  is the detection efficiency of the Si(Li) detector at the photon energy  $E_i$ ,  $P_i = R_i/\varepsilon_{\text{det},E_i}$  is the intensity of the fluorescence line  $l$  of the element  $i$ ,  $\tau_{i,E_0}$  is the photoelectric cross section of the element  $i$  at the photon energy  $E_0$ ,  $\mu_{s,E}$  is the

absorption cross section of the sample  $s$  at the photon energy  $E$ ,  $\mu_{\text{tot},i} = \mu_{s,E_0}/\sin\theta + \mu_{s,E}/\sin\psi$ , with  $\psi$  being the angle of observation with respect to the sample surface,  $\Omega_{\text{det}}$  is the effective solid angle of detection defined by both a calibrated aperture placed at a well-known distance from the sample in front of the Si(Li) detector and the footprint of the excitation radiation on the sample surface,  $\omega_{Xi}$  is the fluorescence yield of the absorption edge  $Xi$  (of the element  $i$ ),  $g_{l,Xi}$  is the transition probability of the fluorescence line  $l$  belonging to the absorption edge  $Xi$ ,  $j_{Xi}$  is the jump ratio at the absorption edge  $Xi$ , and  $Q = \omega_{Xi} g_{l,Xi} (j_{Xi} - 1) / j_{Xi}$ . In the case of flat samples excited at shallow incident angles, the modulation of the incident radiant power by the X-ray standing wave (XSW) intensity<sup>10</sup> has to be included as an additional factor. Secondary and tertiary excitation channels within a homogeneous layer or bulk sample as well as intra-layer excitation and absorption effects can be likewise included as indicated in detail in the literature.<sup>11</sup>

# Quantitative XRF – Sherman equation for thin layer samples

In general, in conventional geometry the RRS and substrate fluorescence contributions are increased and have an unfavorable impact on the deconvolution of the spectrum, due to reduced signal to background ratios. By means of the knowledge of the relevant instrumental and atomic fundamental parameters, the mass deposition  $m_i/F_i$  of the elements boron and carbon with unit area  $F_i$  can be determined using the following equation:<sup>12</sup>

$$\frac{m_i}{F_i} = \frac{-1}{\mu_{\text{tot},i}} \ln \left[ 1 - \frac{P_i}{P_0 \tau_{i,E_0} Q \frac{\Omega_{\text{det}}}{4\pi} \frac{1}{\sin \Psi_{\text{in}}} \frac{1}{\mu_{\text{tot},i}}} \right]$$

with  $\mu_{\text{tot},i} = \frac{\mu_{i,E_0}}{\sin \Psi_{\text{in}}} + \frac{\mu_{i,E_i}}{\sin \Psi_{\text{out}}}$  (1)

The components are shown in Table 1. For conventional incidence geometries,  $\Psi_{\text{in}}$  and  $\Psi_{\text{out}}$  are 45° with respect to the wafer surface.

The factor  $Q$  is composed of fundamental parameters of the respective element.  $X_i$  is the absorption edge,  $\omega_{X_i}$  is the fluorescence yield of the absorption edge  $X_i$ ,  $g_{l,X_i}$  is the transition probability of the fluorescence line  $l$  belonging to the absorption edge  $X_i$ , and  $j_{X_i}$  is the jump ratio at the absorption edge  $X_i$ :

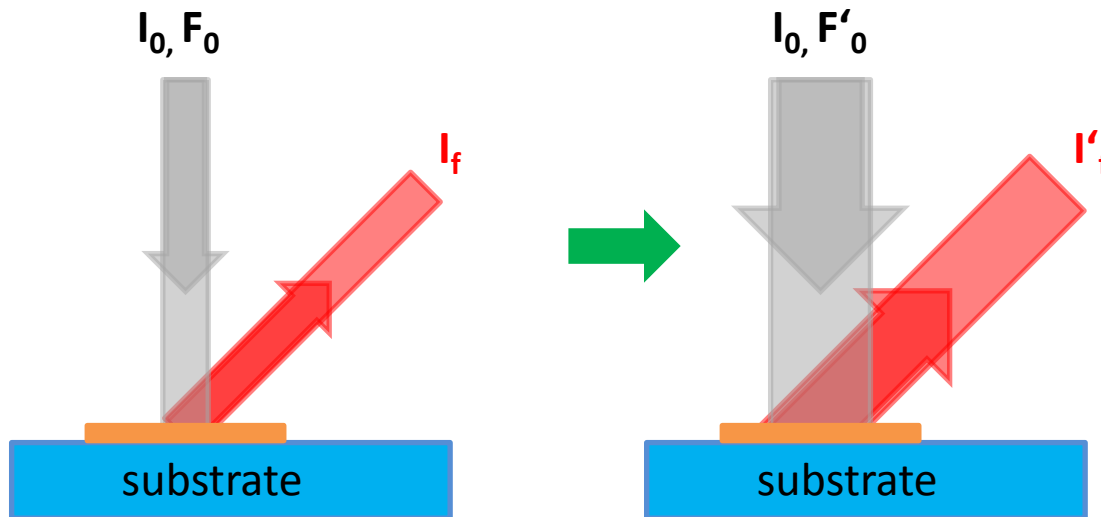
$$Q = \omega_{X_i} g_{l,X_i} \frac{j_{X_i} - 1}{j_{X_i}} \quad (2)$$

**Table 1. Overview of All Experimental and Atomic Fundamental Parameters Used in Equation 1**

$E_0$	excitation energy of the incident radiation
$E_i$	photon energy of the fluorescence line $l$ of the element $i$
$S_0$	signal of the photodiode
$\sigma_{\text{diode},E_0}$	spectral responsivity of the photodiode
$P_0 = S_0/\sigma_{\text{diode},E_0}$	radiant power of the incident radiation
$R_i$	count rate of the fluorescence line $l$ of the element $i$
$\varepsilon_{\text{det},E_i}$	detection efficiency of the SDD at the photon energy $E_i$
$P_i = R_i/\varepsilon_{\text{det},E_i}$	effective count rate of the fluorescence line $l$
$\tau_{i,E_0}$	photoelectric cross section of the element $i$ at the photon energy $E_0$
$\Omega_{\text{det}}$	effective solid angle of detection
$\Psi_{\text{in}}$	angle of incidence with respect to the wafer surface
$\Psi_{\text{out}}$	angle of observation
$\rho$	density
$Q$	fluorescence production cross section
$\mu_{\text{tot},i}$	absorption correction factor

R. Unterumsberger et al.,  
Anal. Chem. **83**, 8623 (2013)

# Quantitative XRF – influence of the beam profile



sample  
 $m_i/F = \text{mass deposition}$

Assumption:  $F_0 < F'_0$



Consequence:

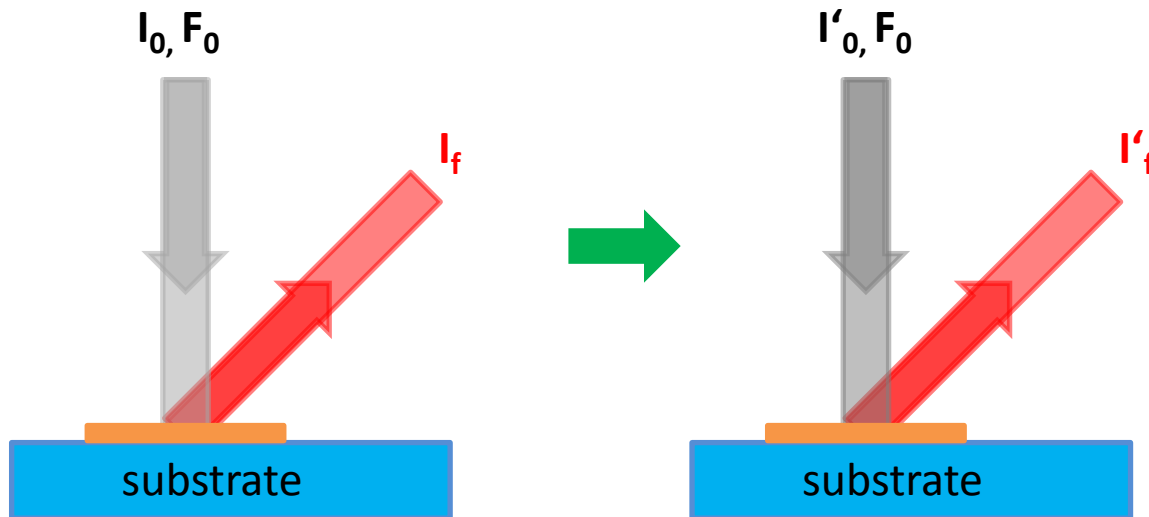
1. A:  $I_f < I'_f$
1. B:  $I_f = I'_f$
1. C:  $I_f > I'_f$
- Yes    No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection



# Quantitative XRF – influence of the beam intensity



sample  
 $m_i/F = \text{mass deposition}$

Assumption:  $I_0 < I'_0$



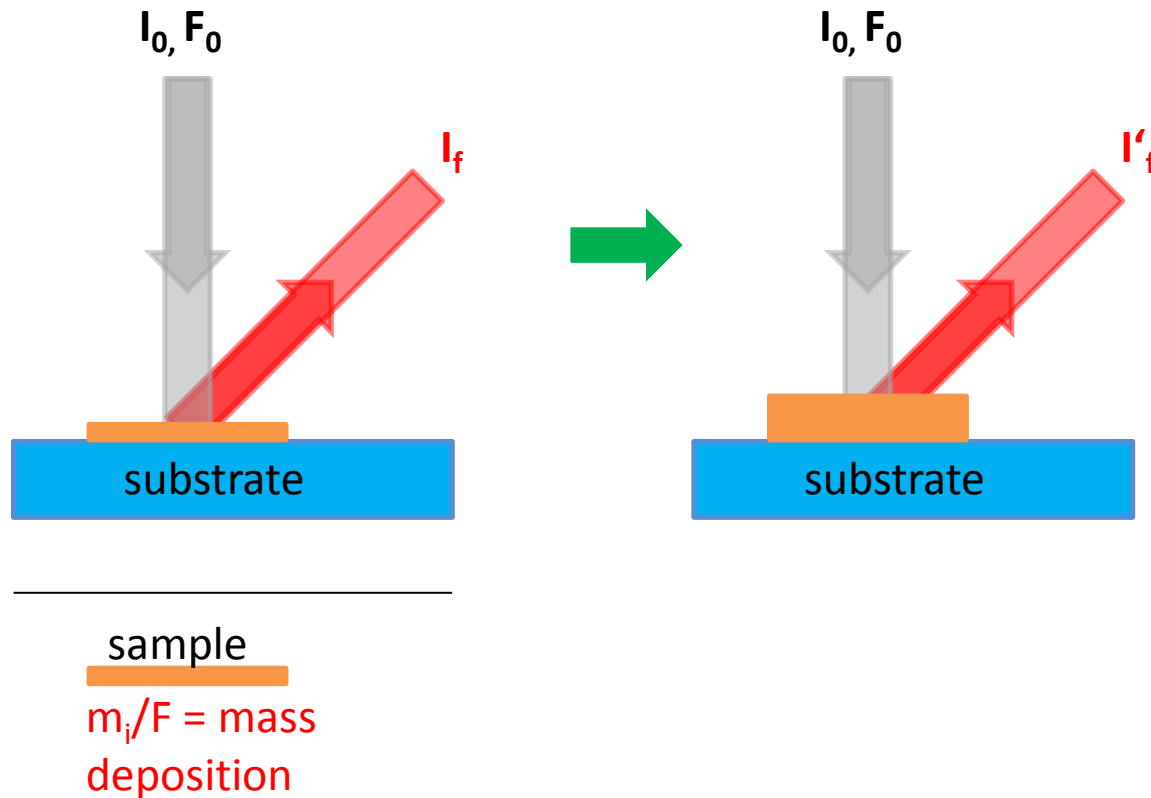
Consequence:

2. A:  $I_f < I'_f$
2. B:  $I_f = I'_f$
2. C:  $I_f > I'_f$
- Yes    No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of the sample thickness



Assumption: increase of sample thickness



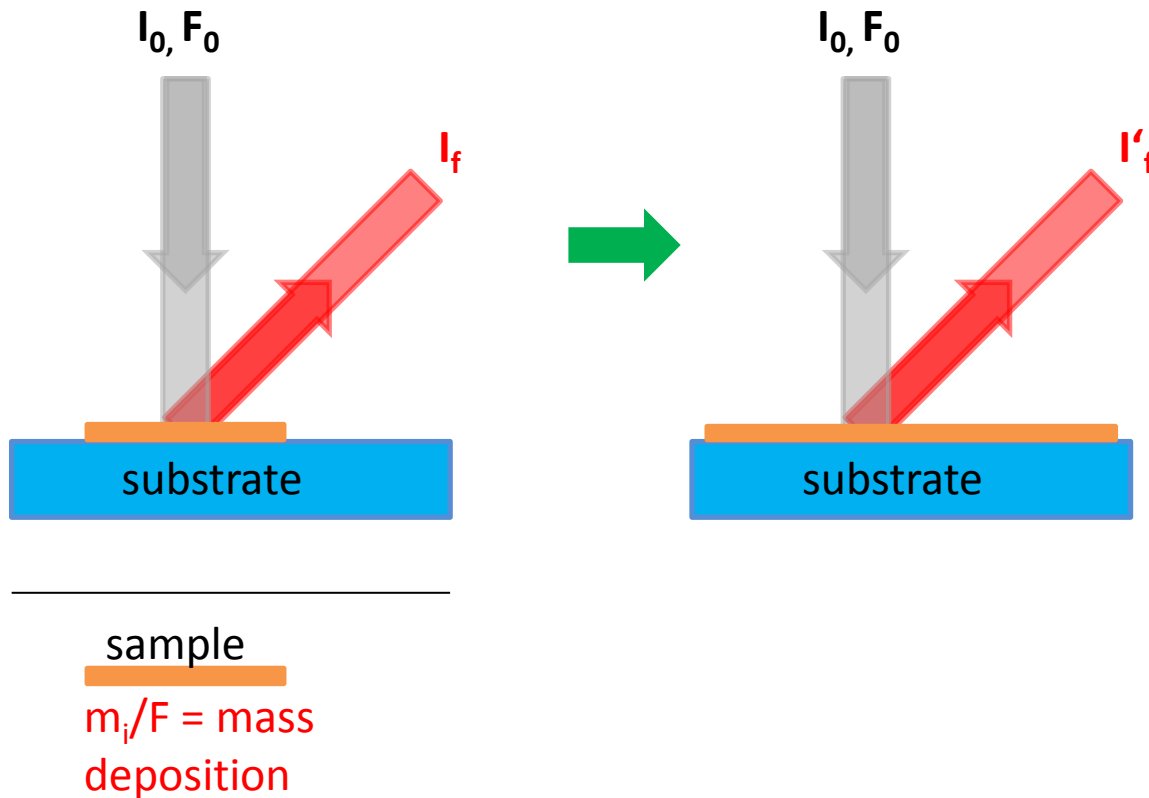
Consequence:

3. A:  $I_f < I'_f$
3. B:  $I_f = I'_f$
3. C:  $I_f > I'_f$
- Yes No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of the sample size



Assumption: increase of sample diameter



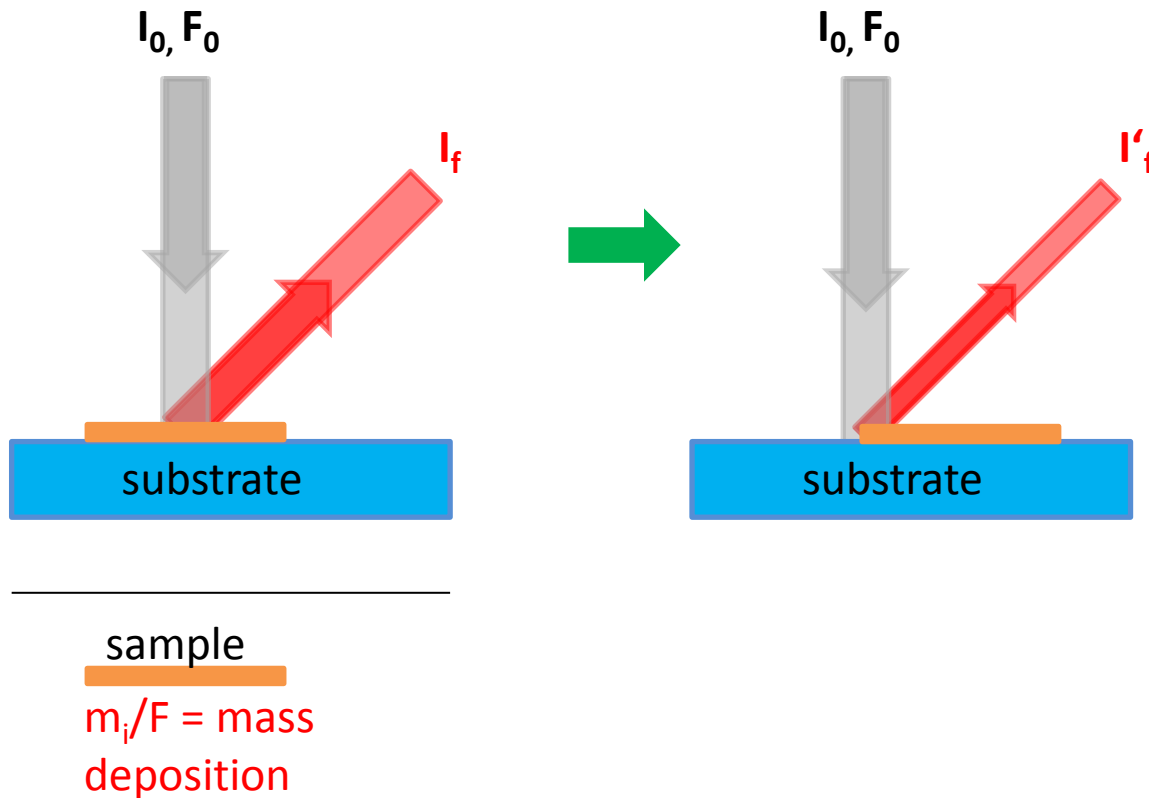
Consequence:

4. A:  $I_f < I'_f$
4. B:  $I_f = I'_f$
4. C:  $I_f > I'_f$
- Yes    No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of the sample position



Assumption: sample position influence



Consequence:

5. A:  $I_f < I'_f$
5. B:  $I_f = I'_f$
5. C:  $I_f > I'_f$
- Yes No

$E_0$  = photon energy of excitation radiation

$I_0$  = intensity (*photons/s*) of excitation radiation

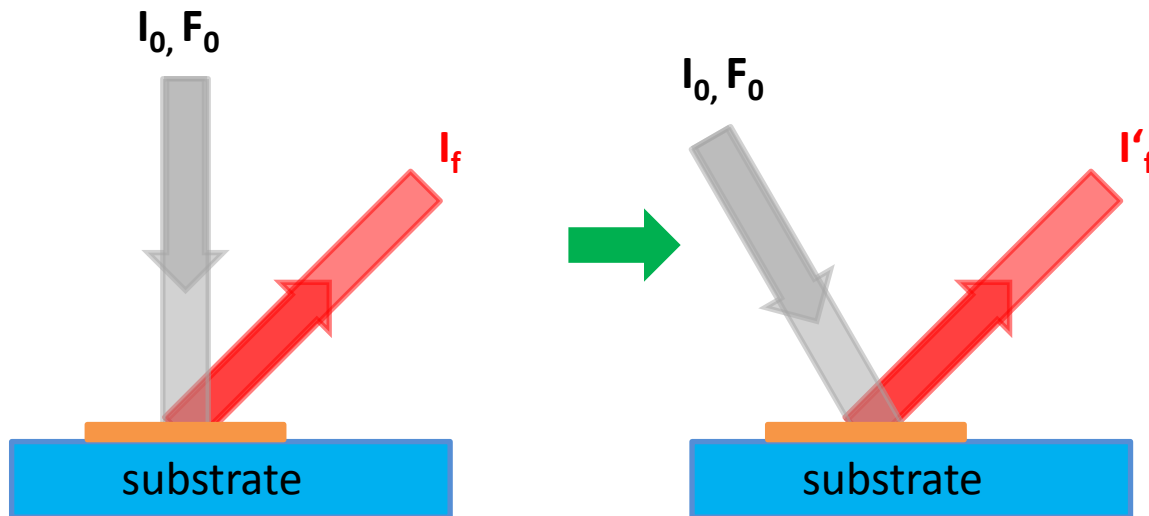
$F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation

$I_f$  = intensity of fluorescence radiation in  $d\Omega$

$d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of the incident angle



sample  
 $m_i/F = \text{mass}$   
 deposition

Assumption: **more shallow incident angle**



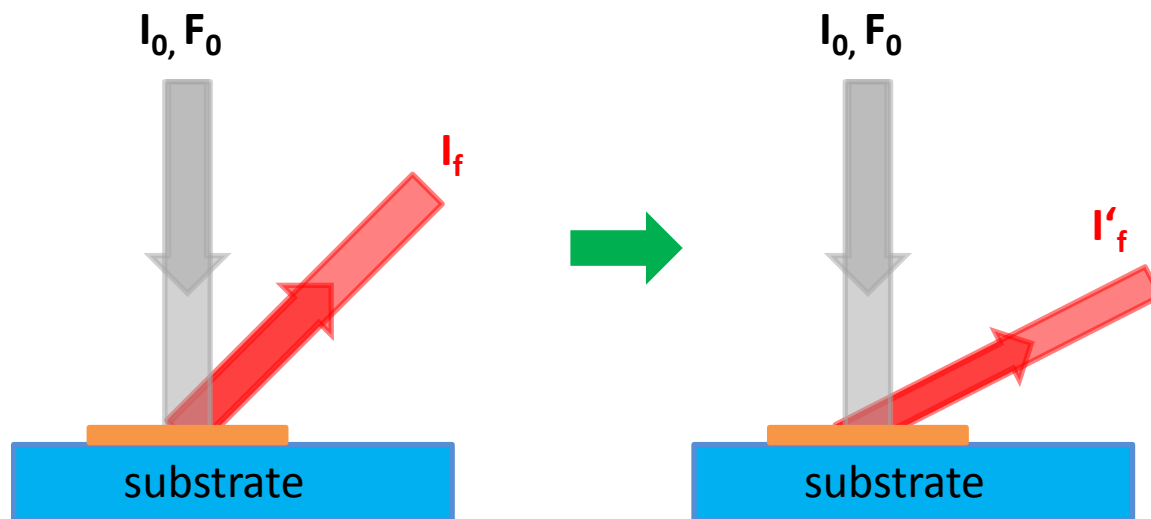
Consequence:

6. A:  $I_f < I'_f$
6. B:  $I_f = I'_f$
6. C:  $I_f > I'_f$
- Yes    No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of the angle of observation



sample  
 $m_i/F = \text{mass}$   
 deposition

Assumption: **more shallow observation angle**



Consequence:

7. A:  $I_f < I'_f$

7. B:  $I_f = I'_f$

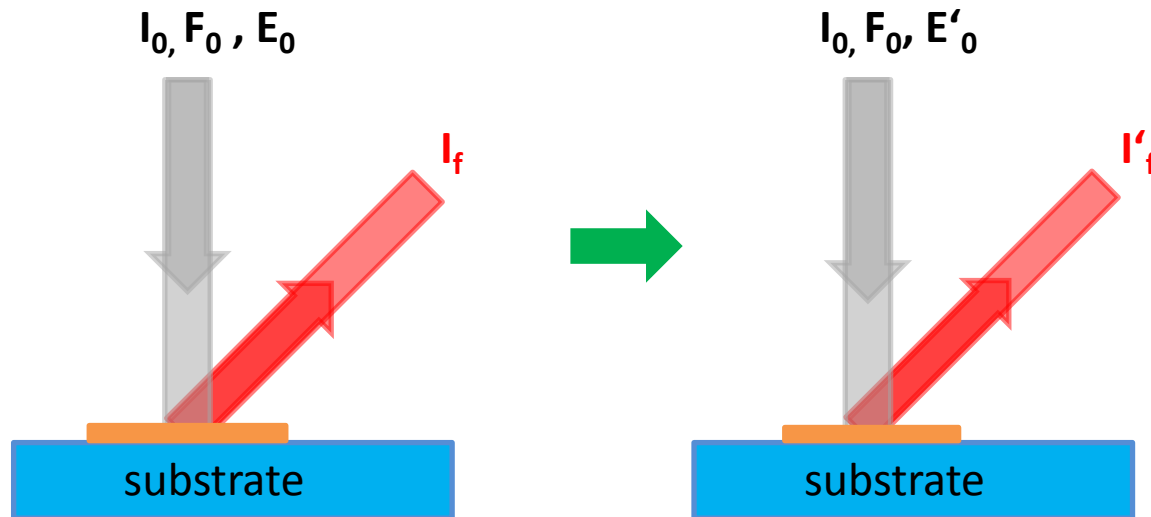
7. C:  $I_f > I'_f$

Yes No

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of exciting photon energy



Assumption:  $E_0 < E'_0$



Consequence:

8. A:  $I_f < I'_f$

8. B:  $I_f = I'_f$

8. C:  $I_f > I'_f$

Yes No

sample  
 $m_i/F =$  mass  
 deposition

Note, that  $E_0 > E_{K-abs, sample}$

$E_0$  = photon energy of excitation radiation

$I_0$  = intensity (*photons/s*) of excitation radiation

$F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

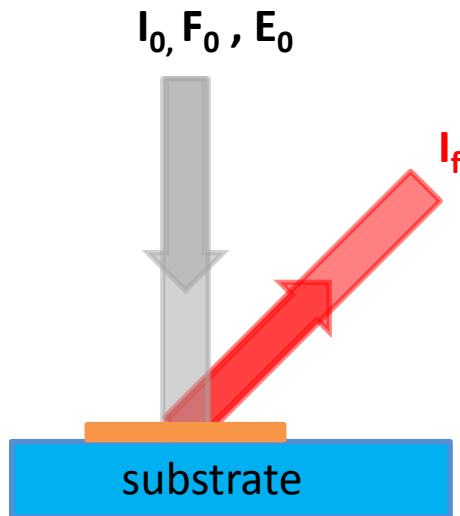
$E_f$  = photon energy of fluorescence radiation

$I_f$  = intensity of fluorescence radiation in  $d\Omega$

$d\Omega$  = solid angle (*sr*) of fluorescence detection

# Quantitative XRF – influence of experimental parameters

X-ray and IR spectrometry



sample  
 $m_i/F = \text{mass deposition}$

	Yes	No
1. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
2. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
2. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
2. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
3. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
3. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
3. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>

	Yes	No
4. A:	<input type="checkbox"/>	<input type="checkbox"/>
4. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
4. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
5. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
5. B:	<input type="checkbox"/>	<input type="checkbox"/>
5. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
6. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
6. B:	<input type="checkbox"/>	<input type="checkbox"/>
6. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>

	Yes	No
7. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
7. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
7. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
8. A:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
8. B:	<input checked="" type="checkbox"/>	<input type="checkbox"/>
8. C:	<input checked="" type="checkbox"/>	<input type="checkbox"/>

$E_0$  = photon energy of excitation radiation  
 $I_0$  = intensity (*photons/s*) of excitation radiation  
 $F_0$  = beam profile area ( $mm^2$ ) of excitation radiation

$E_f$  = photon energy of fluorescence radiation  
 $I_f$  = intensity of fluorescence radiation in  $d\Omega$   
 $d\Omega$  = solid angle (*sr*) of fluorescence detection