



# ANALYTICAL X-RAY SPECTROSCOPY



Technische Universität Berlin



## *Micro-XRF: Principles, Methodology and Applications in CH Studies*

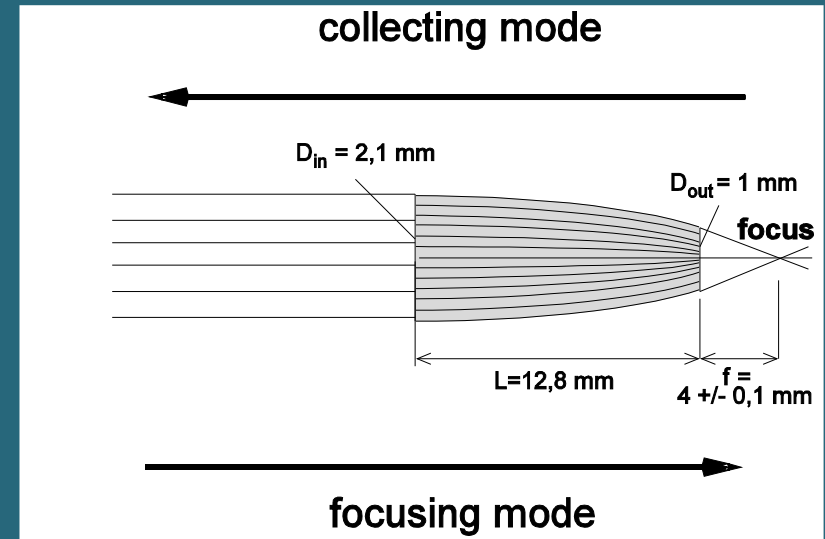
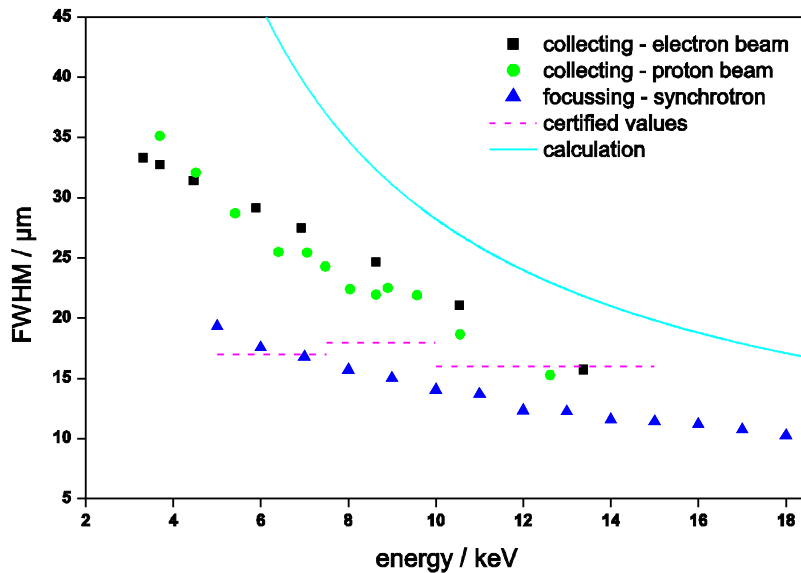
Birgit Kanngießer

# Outline

1. Basics
2. X-ray optics
3. Application Examples
4. Discussion

# Modern X-ray optics

## Energy dependency of spot size

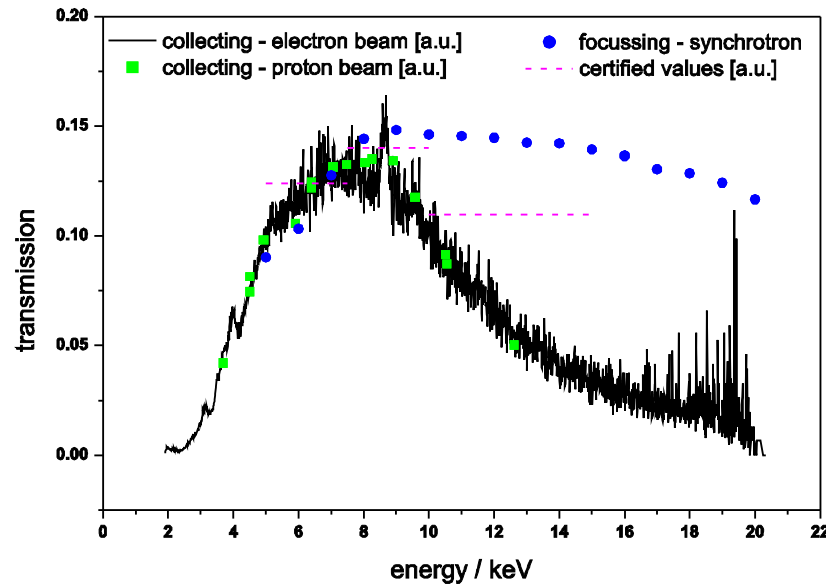


$$s(E) = d_{cap} + 2 \theta_{crit}(E) f$$

© T. Wolff et al., submitted

## Energy dependency of transmission

$$T = e^{-\mu_{air} \rho_{air} L} \frac{I_{optic}}{I_{air}}$$



© T. Wolff et al., submitted

# Micro XRF Spectrometer

Technische Universität Berlin



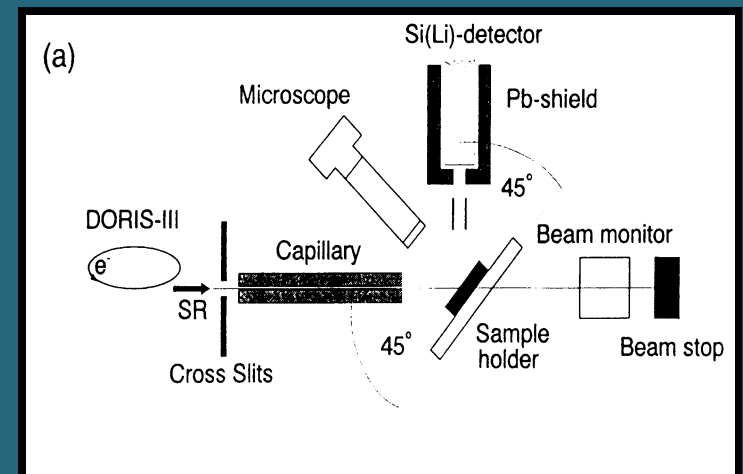
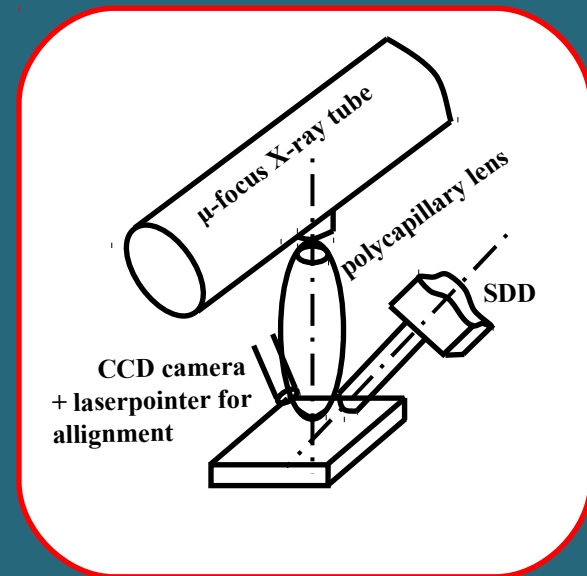
## Tabletop Spectrometers and Portable Spectrometers

- Conventional Tubes
- Microfocus Tubes
- Monocapillaries
- Polycapillaries
- Crystals, Multilayer
- Si(Li)- and HPGe-Detectors
- Drift chambers

## Synchrotron Spectrometers

- Synchrotron Radiation
- + Compound Refractive Lenses
- + Cryodetectors

Birgit Kanngießer



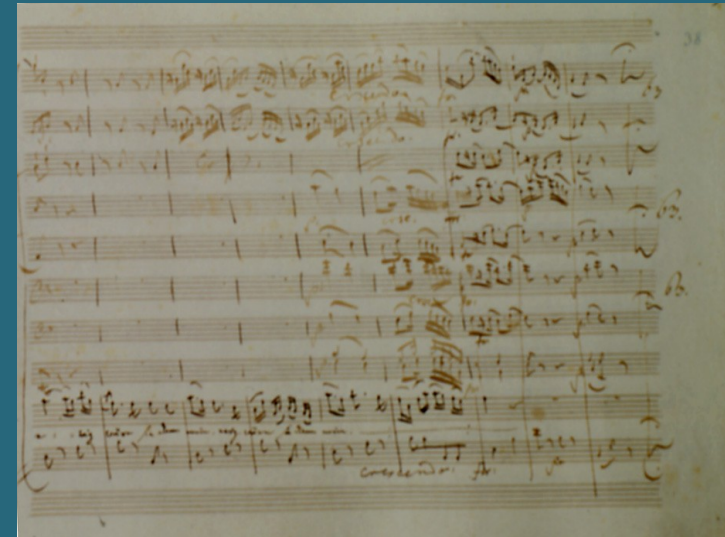
# Application Example

# Investigation of Historical Manuscripts and Compositions

Investigation of  
*historical manuscripts and compositions*  
written with iron gall ink.



Assignment of  
single sheets, corrections, amendments,  
to authors or to certain periods of genesis



by  
Nondestructive analysis of  
*minor constituents* in iron gall inks  
with Micro-XRF.

B. Kanngießer, W. Malzer, O. Hahn

Birgit Kanngießer

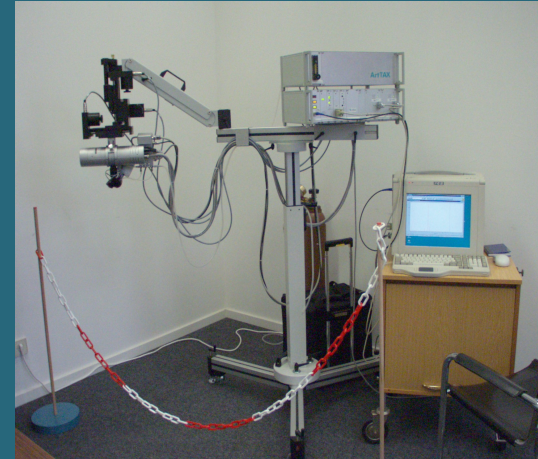
# Investigation of Historical Manuscripts and Compositions

Technische Universität Berlin



Experimental set-up:

A **portable spectrometer** is important to measure on site in the archives and museums!



Portable technique:

- drift chamber detector, capillary lens
- helium flooding for light elements
- spot size  $\sim 100 \mu\text{m}$



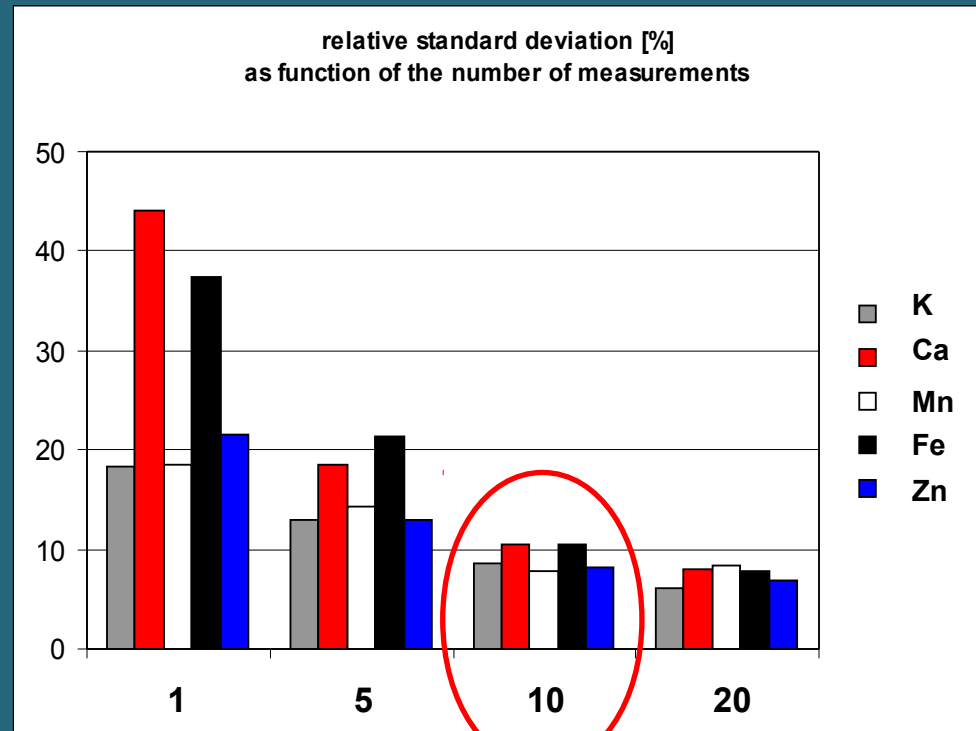
**Flexible, non-destructive investigations!**

Birgit Kanngießer

# Investigation of Historical Manuscripts and Compositions

- Considerable variance of the count rate due to the fibrous structure and inhomogeneity of the paper

∇ → An area of at least  $10 \times 100 \times 100 \mu\text{m}^2$  is measured



# Investigation of Historical Manuscripts and Compositions



f.103v:  
black browish  
iron gall ink on  
rag paper.

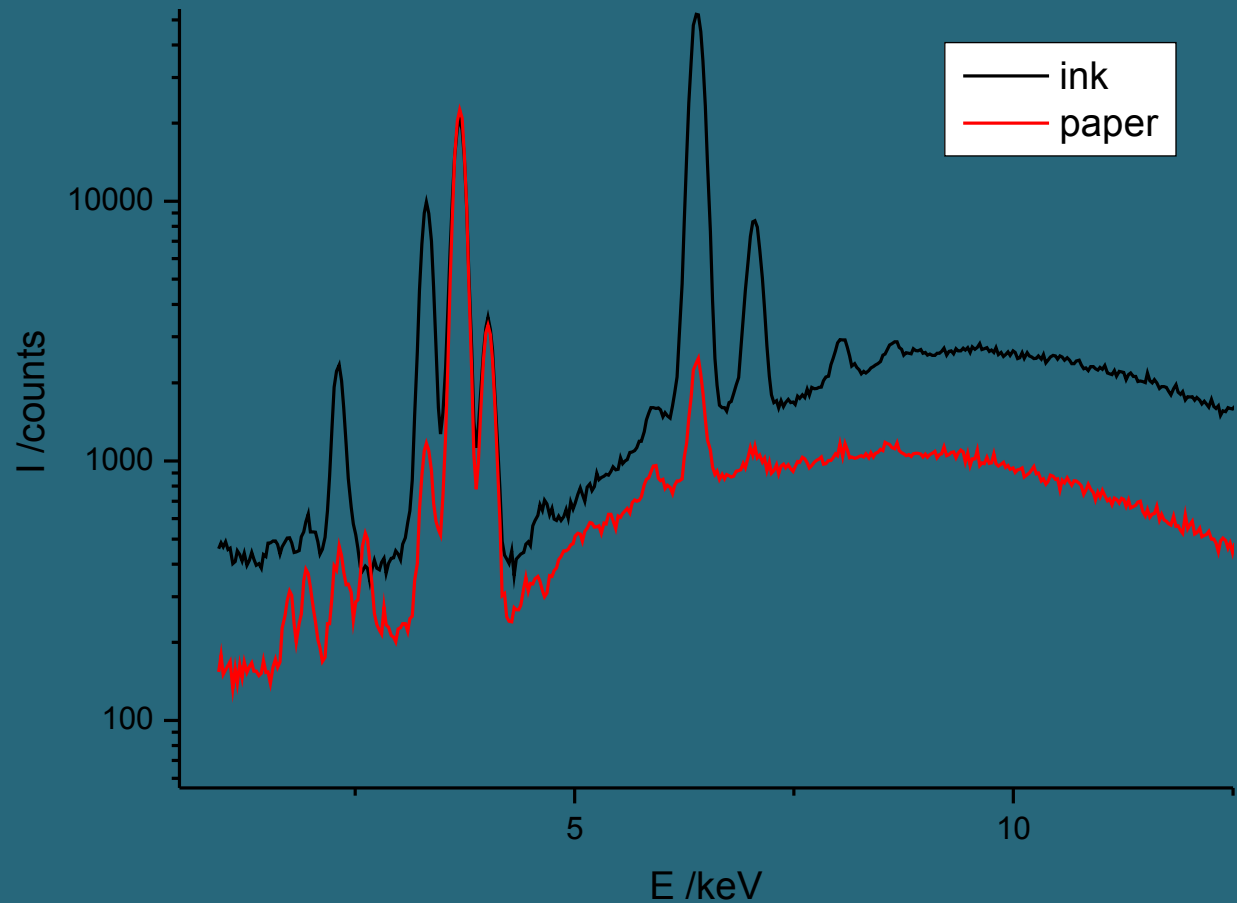
Parameter:

Spot size ca. 100  $\mu\text{m}$

30 W Mo-tube

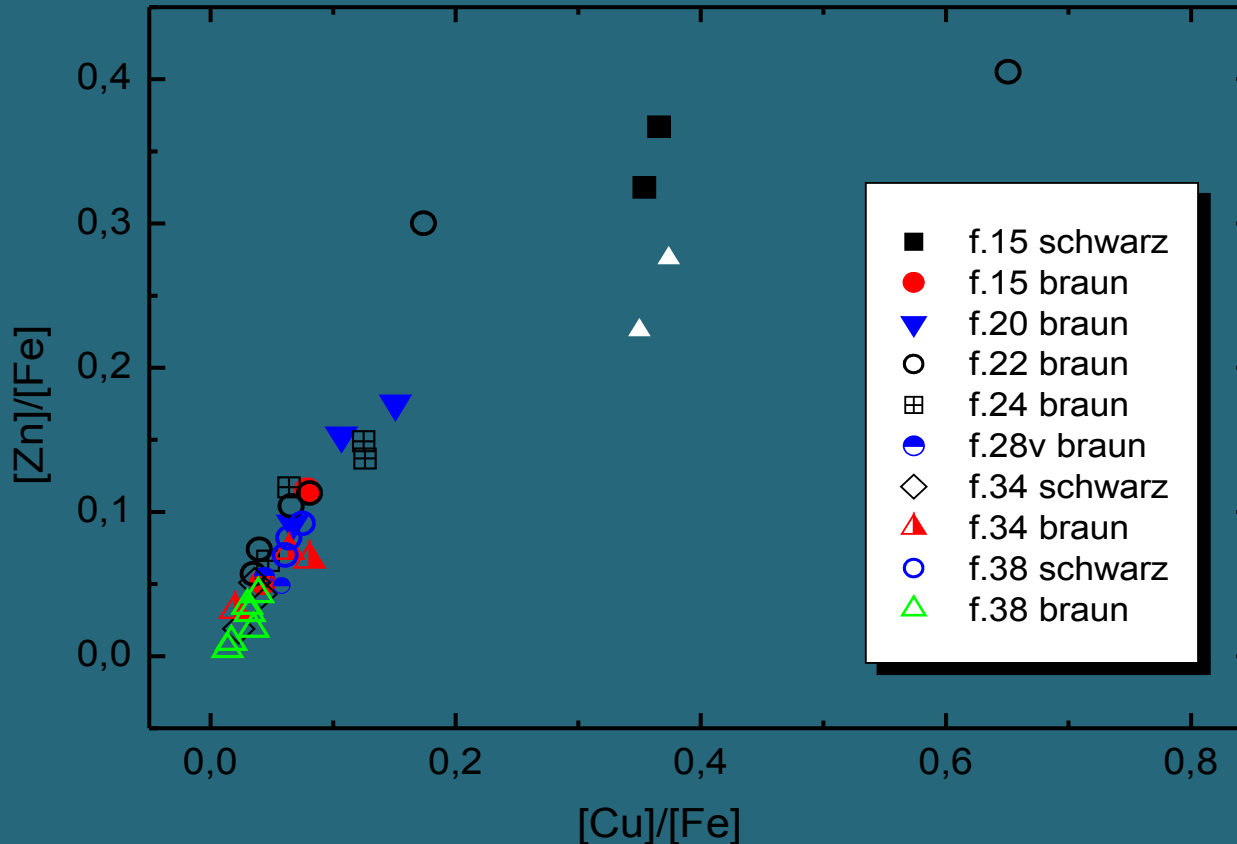
45 kV, 600  $\mu\text{A}$

Accumulation: 100 s (1t)



Investigation with Micro X-Ray Fluorescence Analysis

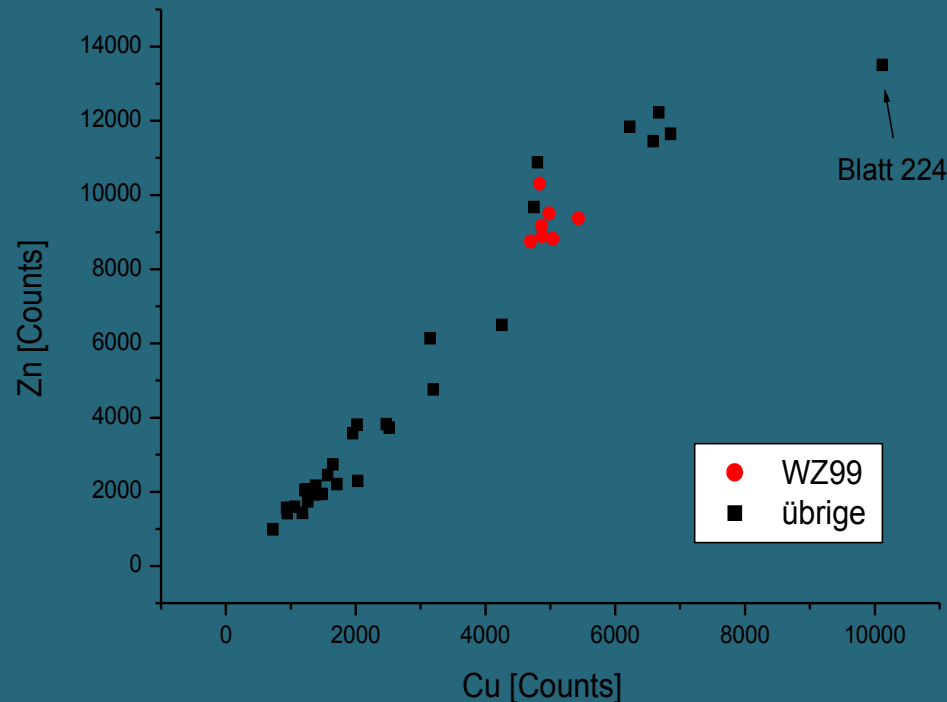
# Investigation of Historical Manuscripts and Compositions



Ratio of the Cu to Zn intensities,  
without taking the fluorescence of the paper into account.

Linear relationship?

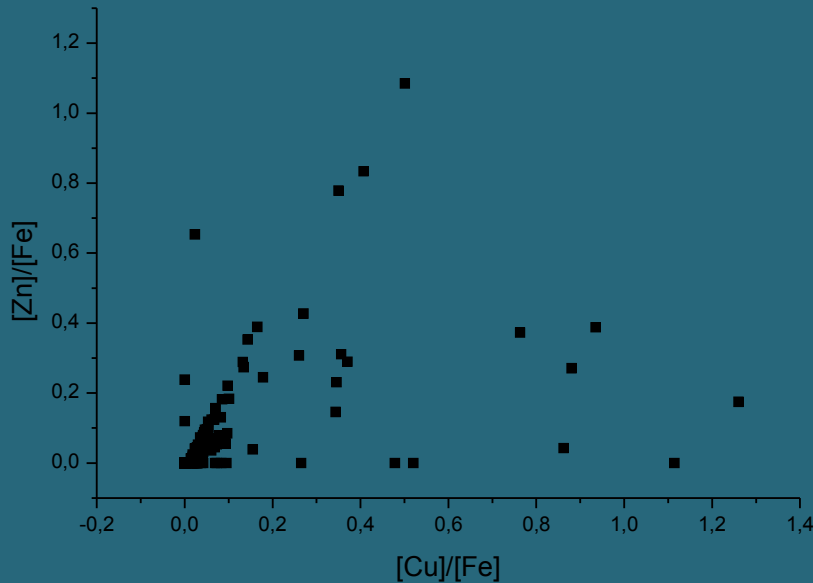
# Investigation of Historical Manuscripts and Compositions



Ratio of the Cu to Zn intensities:

The linear relationship is due to brass tools („Holländer“) for the paper manufacturing!

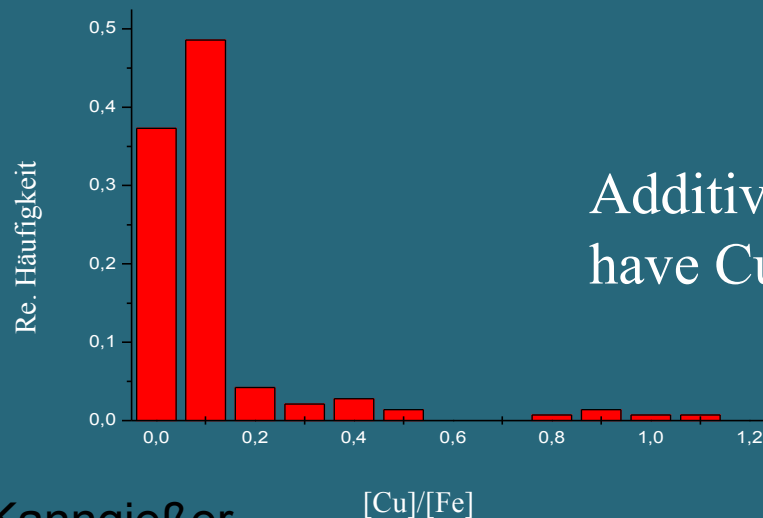
# Investigation of Historical Manuscripts and Compositions




Ratio of the Cu to Zn intensities  
The paper background is just subtracted from the ink.



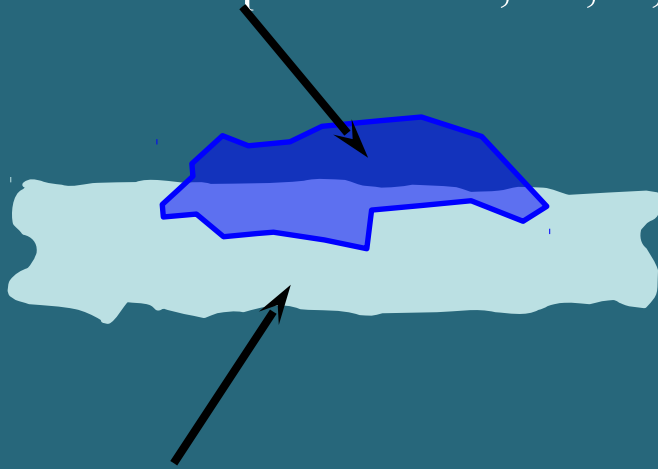
No simple additive relation for the fluorescence from the ink and the paper!



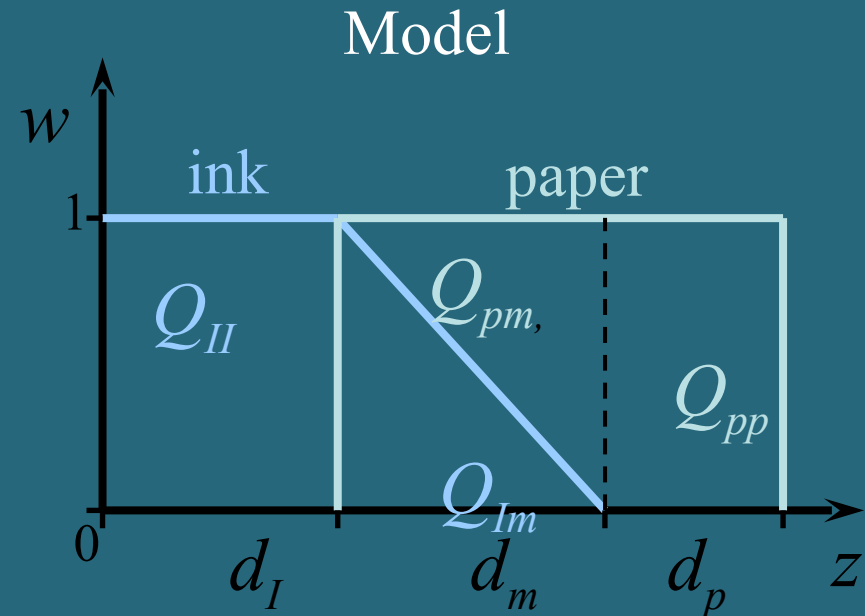
Additive assumption: ca. 35% of the samples have Cu-intensities  $\leq 0$ . 

# Investigation of Historical Manuscripts and Compositions

**Ink**  
main component: Fe  
minor components: Cu, Zn, K, ...



**Paper**  
contamination: Fe, Cu, Zn, K, ...  
Fibers of approx. 10 - 20  $\mu\text{m}$  diam.



Linear decrease of the  
ink density in the paper

$$\rho_{Im} = \rho_I (1 - \Delta z / d_m)$$

The fingerprint value  $W$

takes into account

- the paper background
- the thickness of the ink layer
- the diffusion of the ink into the paper

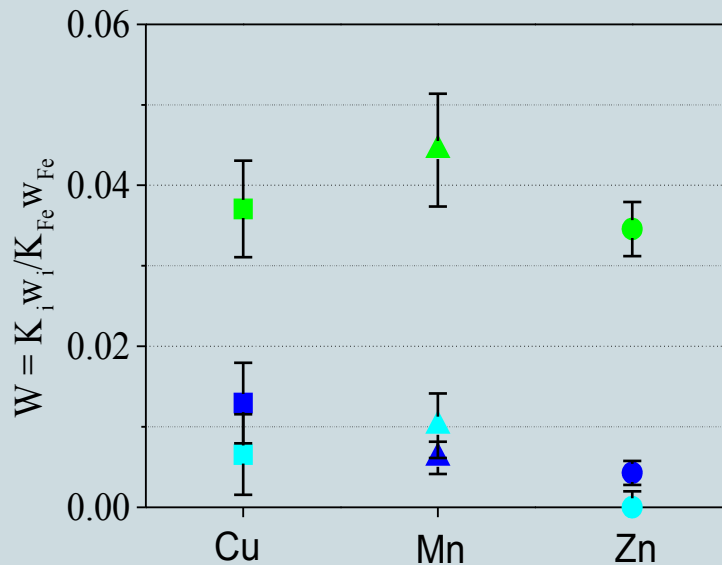
# Investigation of Historical Manuscripts and Compositions

Technische Universität Berlin



Visual inspection:  
three types of ink have been used

Investigation with  $\mu$ -XRF:



→ Two types of ink can be identified



**Folio 38 of Mozart's Zauberflöte**

Mass depositon in  $\text{mg}/\text{cm}^2$ :

light brown: 0.6 (may be diluted brown)

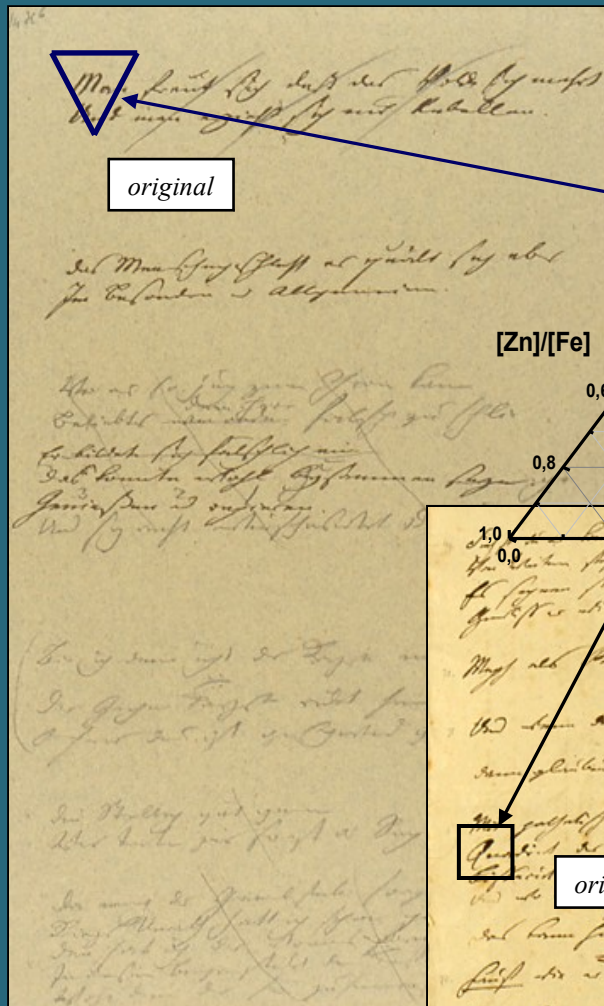
brown: 3

dark brown: 0.7

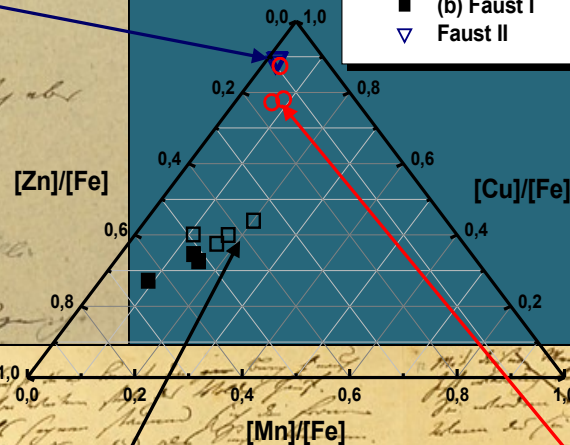
# Investigation of Historical Manuscripts and Compositions

## Investigation of manuscripts of J.W. Goethe

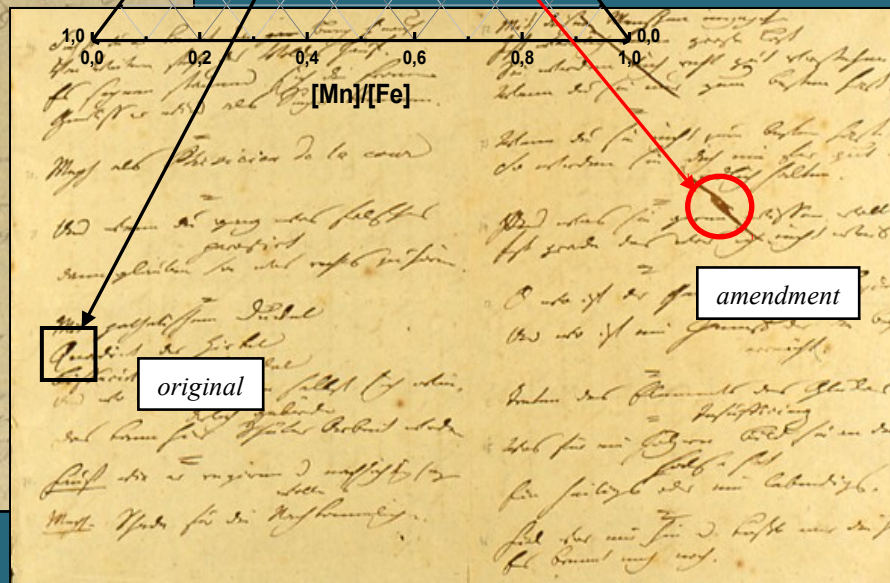
### Fragment of Faust II



original



Goethe (1749 – 1832)



amendment

original

Fragment of Faust I

Goethe- und Schiller-Archiv, Weimar

Fragment of Faust II

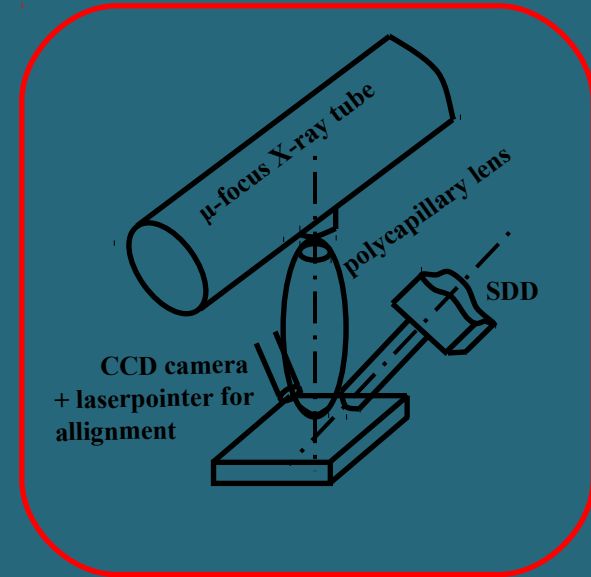
Further development : improvement of reliability and error analysis

Birgit Kanngießer

# Investigation of Historical Manuscripts and Compositions

Absolute quantification is not necessary!

A **fingerprint** which characterises the content of minor constituents **is sufficient**



To distinguish two specimen

- a **quantitative fingerprint** is necessary
- a **knowledge of the uncertainty** is desirable

## Literature:

- B. Beckhoff, B. Kanngießer, N. Langhoff, R. Wedell, H. Wolff (eds.), “Handbook of Practical X-Ray Fluorescence Analysis”, Springer-Verlag ISBN 3-540-28603-9, (2006)
- B. Kanngießer, “Quantification Procedures in Micro X-ray Fluorescence Analysis”, Spectrochimica Acta B 54 /4, 605-609, (2003).
- W. Malzer, O. Hahn, B. Kanngießer, “A fingerprint model for inhomogeneous ink paper layer systems investigated with micro x-ray fluorescence analysis“, X-Ray Spectrom. 33, 229-233 (2004).
- O. Hahn, W. Malzer, B. Kanngießer, B. Beckhoff, “Characterization of iron gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry“, X-Ray Spectrom. 33, 234-239 (2004).