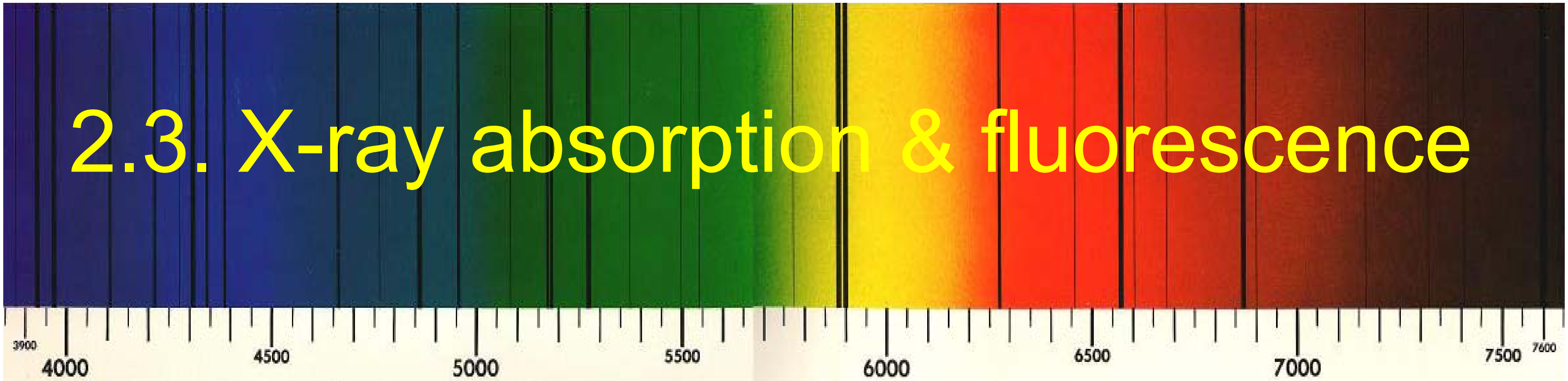
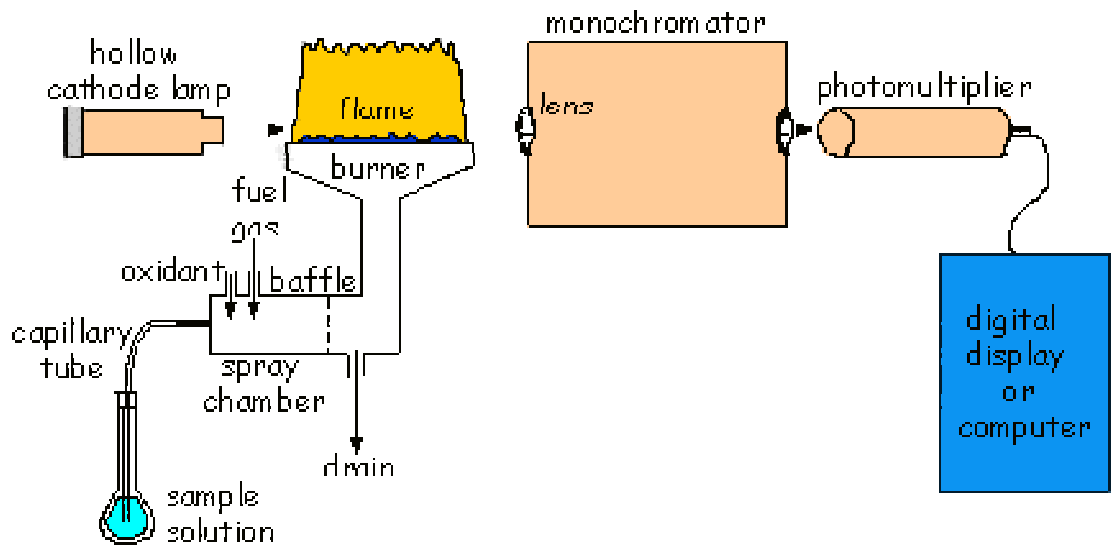
2.3. X-ray absorption & fluorescence



X-ray absorption is classical spectroscopy technique originating from absorption line analysis of solar chromo-sphere spectrum

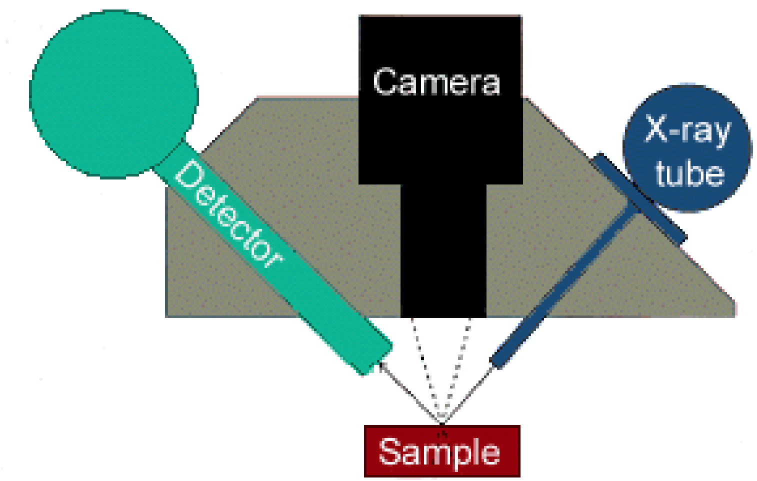
Technique has been utilized for a wide range from visible, UV and X-ray light by absorption of light or X-ray spectrum in vapor.

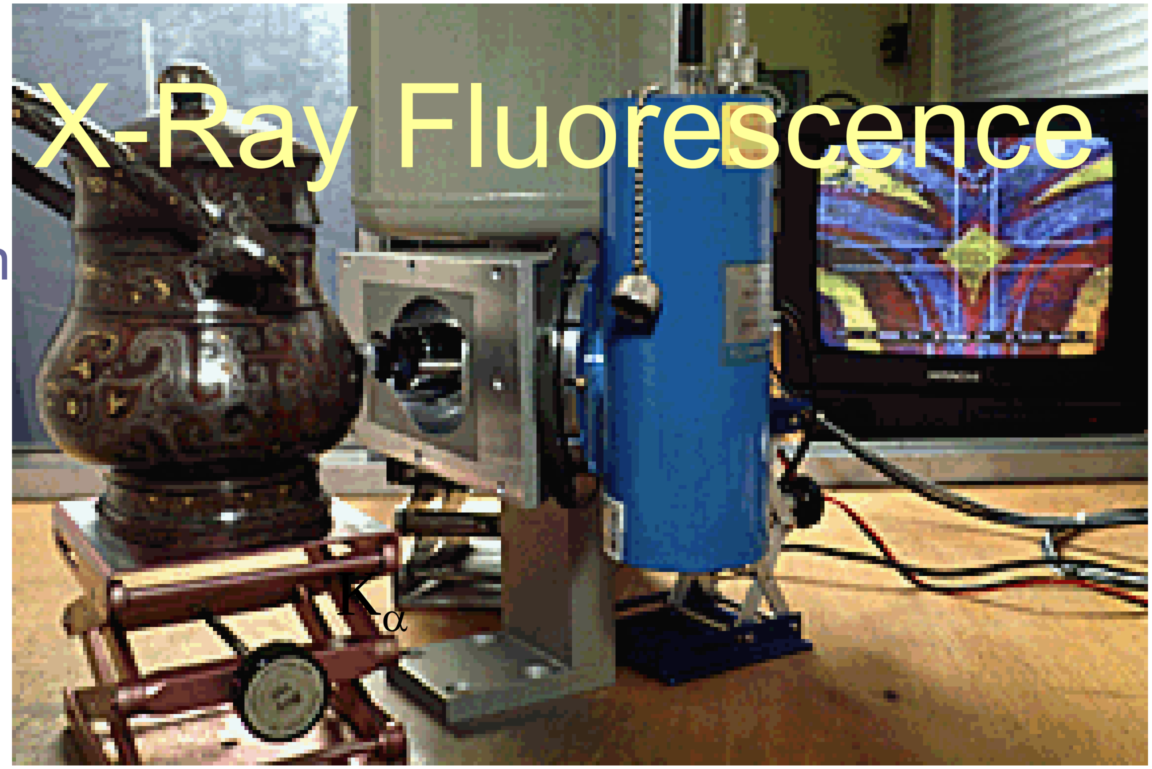
Disadvantage: probe must be chemically prepared & vaporized

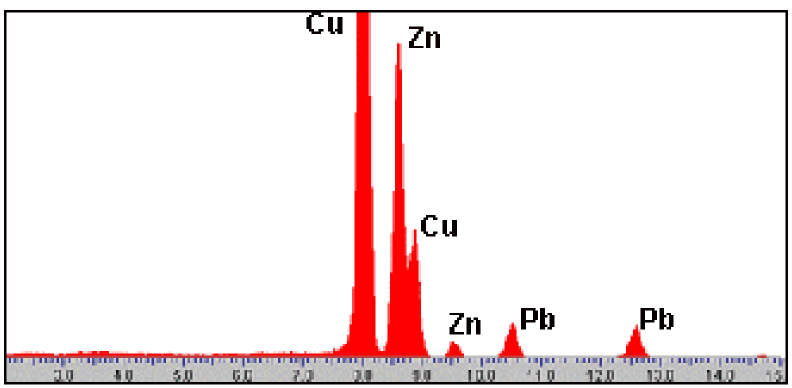


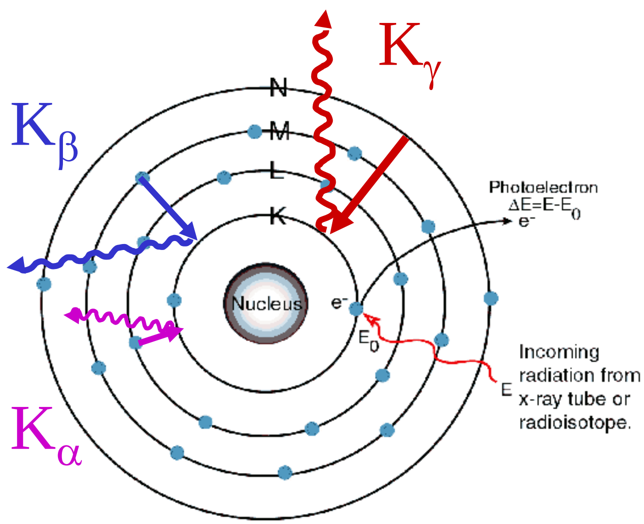
X-Ray Fluorescence

X-ray fluorescence is based on the excitation of material & subsequent X-ray emission - fluorescence -

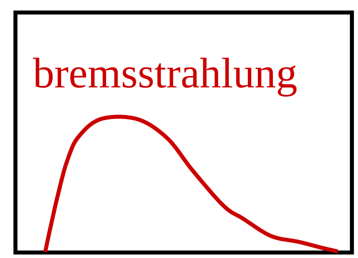








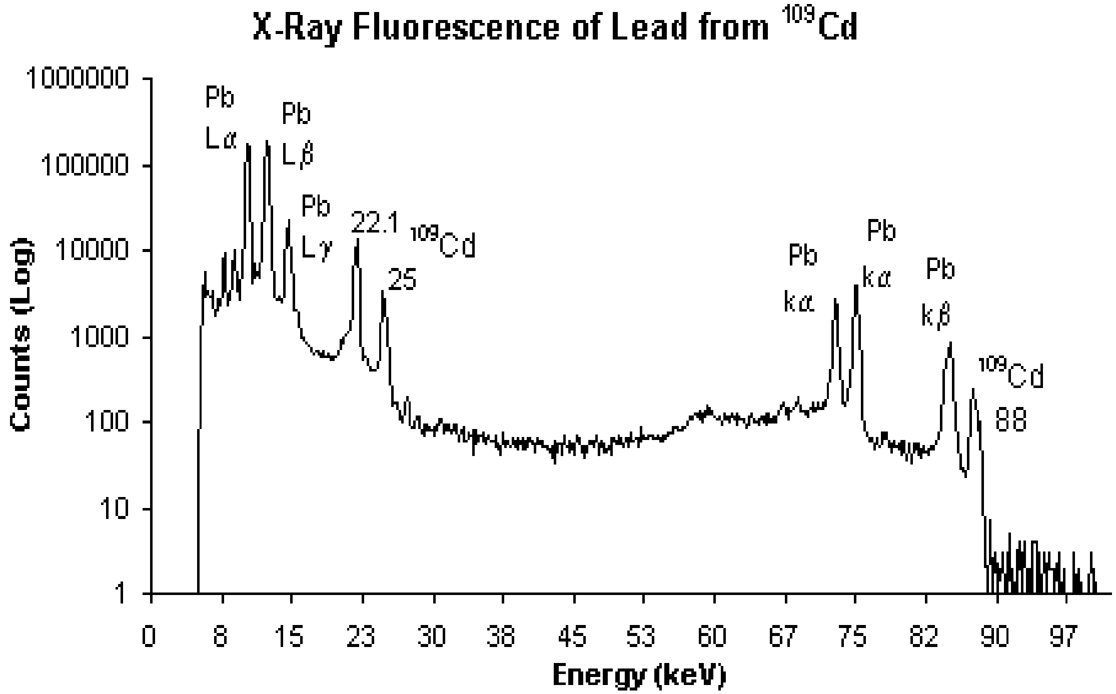
Excitation or Ionization by X-ray bombardment



Only characteristic lines for material are emitted

Analysis of X-ray energies

Advantage of X-ray fluorescence is the unique determination of element characteristic X-ray radiation, K_α , K_β , or L_α , L_β, L_γ lines



Critical component for X-ray fluorescence studies is the necessity for high energy resolution in the X-ray spectrum to separate energetically the characteristic X-ray lines of different elements.

Characteristic x-Ray Energies

The characteristic X-ray energies correspond to the energies of the K or L transitions in the atom:

$E_x = h \cdot \nu = h \cdot c/\lambda = \Delta E = E_n(i) - E_{K/L}(f)$

or it corresponds to the difference of the absorption edge energies:

$E_x = E_{K,L} - E_n$

Data for Pb; Z = 82
atomic weight = 207.210;
density = 11.3400

Absorption edges

K-edge: 88.0060 keV
L-edges: 15.8600, 15.1980, 13.0350 keV
M-edge: 3.85000 keV

Characteristic energies

$K\alpha_1, K\beta_1$: *74.9570 84.9220 keV*
$L\alpha_1, L\beta_1$: *10.54900 12.6110 keV*

Analyzing the strength of characteristic x-ray transitions gives the abundance of element in sample: good energy resolution is required

The Lithium drifted Silicon (SiLi) detector

When an X-ray strikes the detector, it will generate a photoelectron within the body of the Si. As this electron travels through the Si, it generates electron-hole pairs. The electrons and holes are attracted to opposite ends of the detector with the aid of a strong electric field. The size of the current pulse thus generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.

Applications for XRF techniques

Non-destructive applications
Analysis of small amounts <100 mg of material
Determination of chemical content and structure

- ancient coin material - metal composition
- ancient oil and varnish material
- pigment in ancient paint
- medieval scripts and miniatures

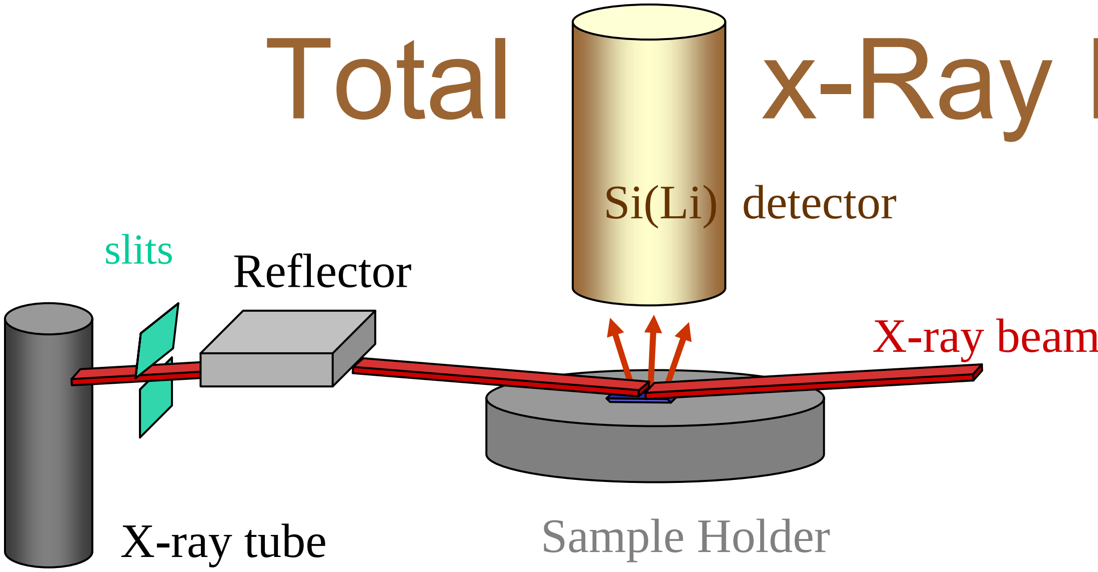
The Andrea Guarneri Violin

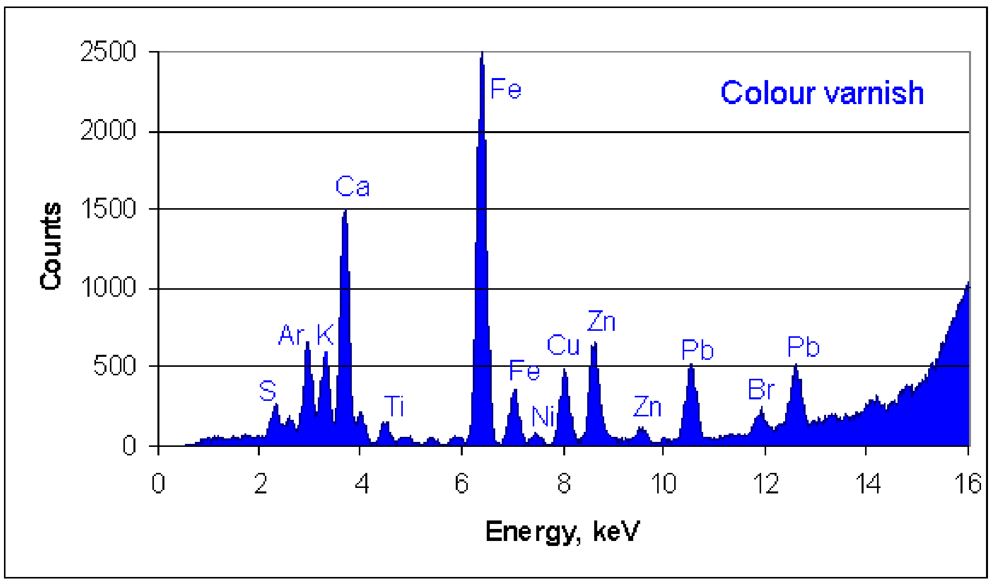
The secret of the varnish of the violins made around 1660 by Andrea Guarneri in Cremona has been solved by XRF analysis of the varnish contents - oil, resin, wax. Additional inorganic substances influence color, hardness etc. The varnishing technique of the Cremona violin builders has been lost! The detailed XRF analysis of all the contents:

- Provides the recipe for the varnish.
- Detects forgery

What kind of varnish does he use?

Total x-Ray Fluorescence

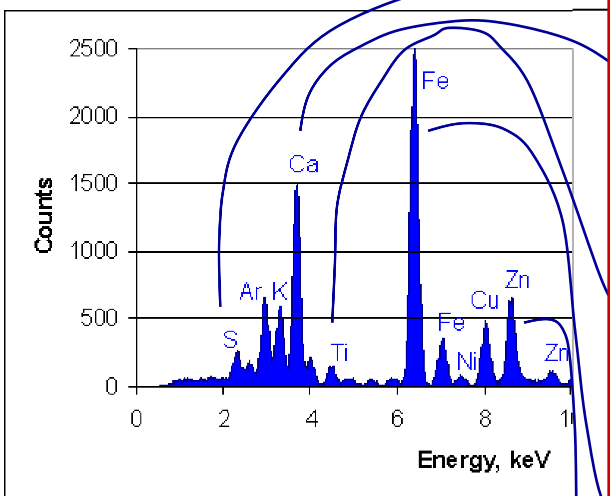




20 different elements detected:

Fe, As, Pb, pigments in varnish
Zn,Cu,Pb drying substrate in oil

Characteristic X-ray energies for varnish element K-transitionss



$$E_x = (Z-1)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right)$$

for S: $Z = 16$; $E_x = (15)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 2.29\ keV$

for Ca: $Z = 20$; $E_x = (19)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 3.68\ keV$

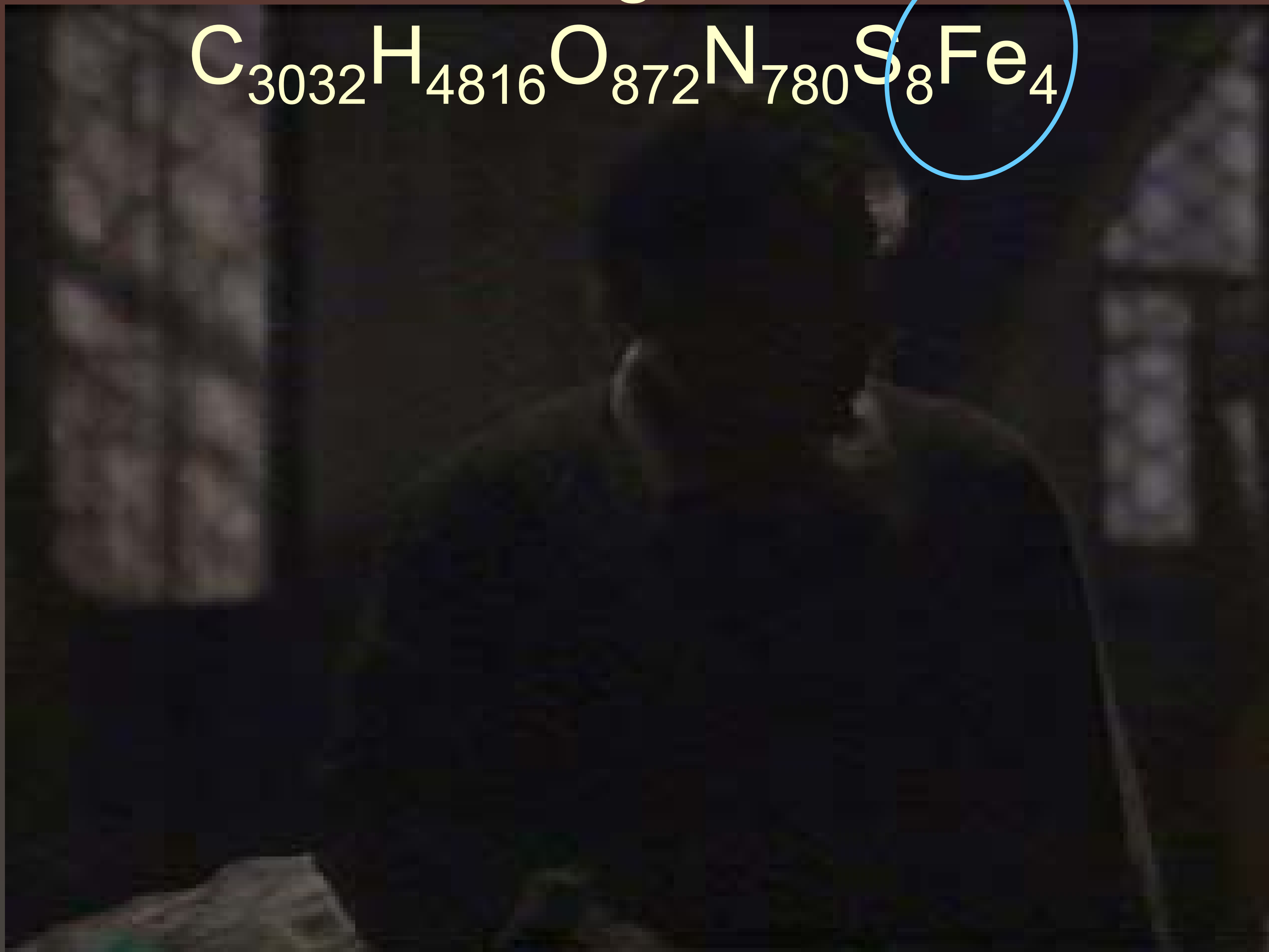
for Ti: $Z = 22$; $E_x = (21)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 4.50\ keV$

for Fe: $Z = 26$; $E_x = (25)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 6.37\ keV$

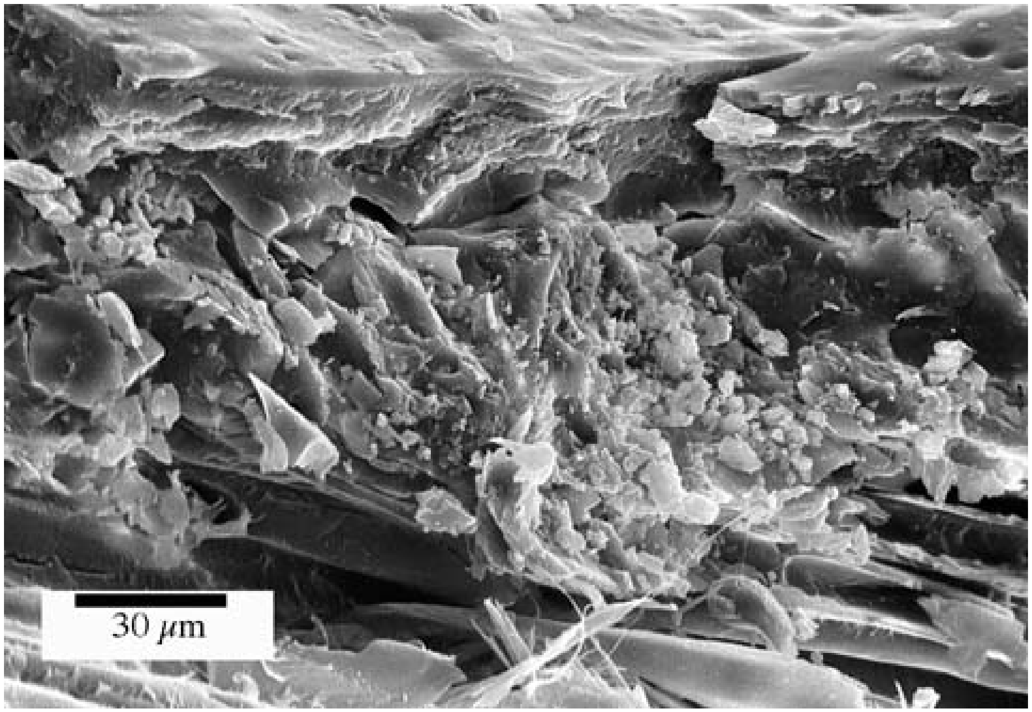
for Zn: $Z = 30$; $E_x = (29)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 8.58\ keV$

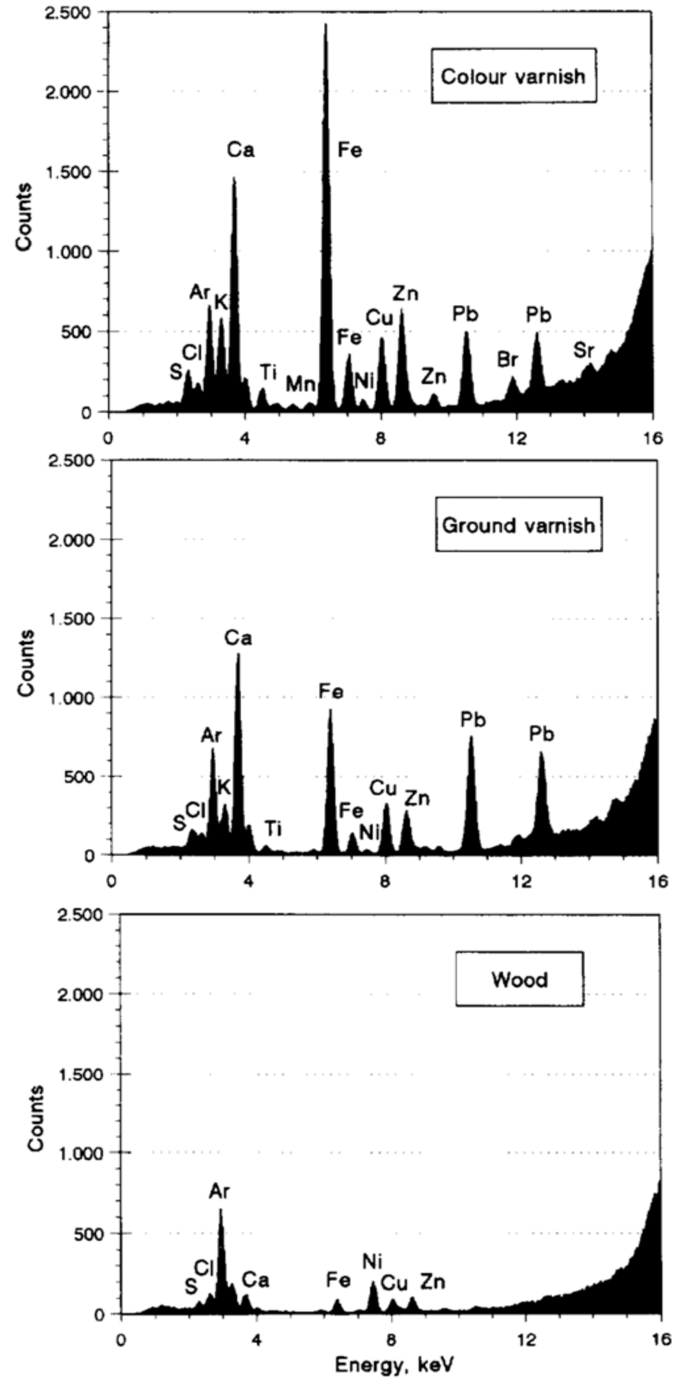
Hemoglobin:

$C_{3032}H_{4816}O_{872}N_{780}S_8Fe_4$



Varnish





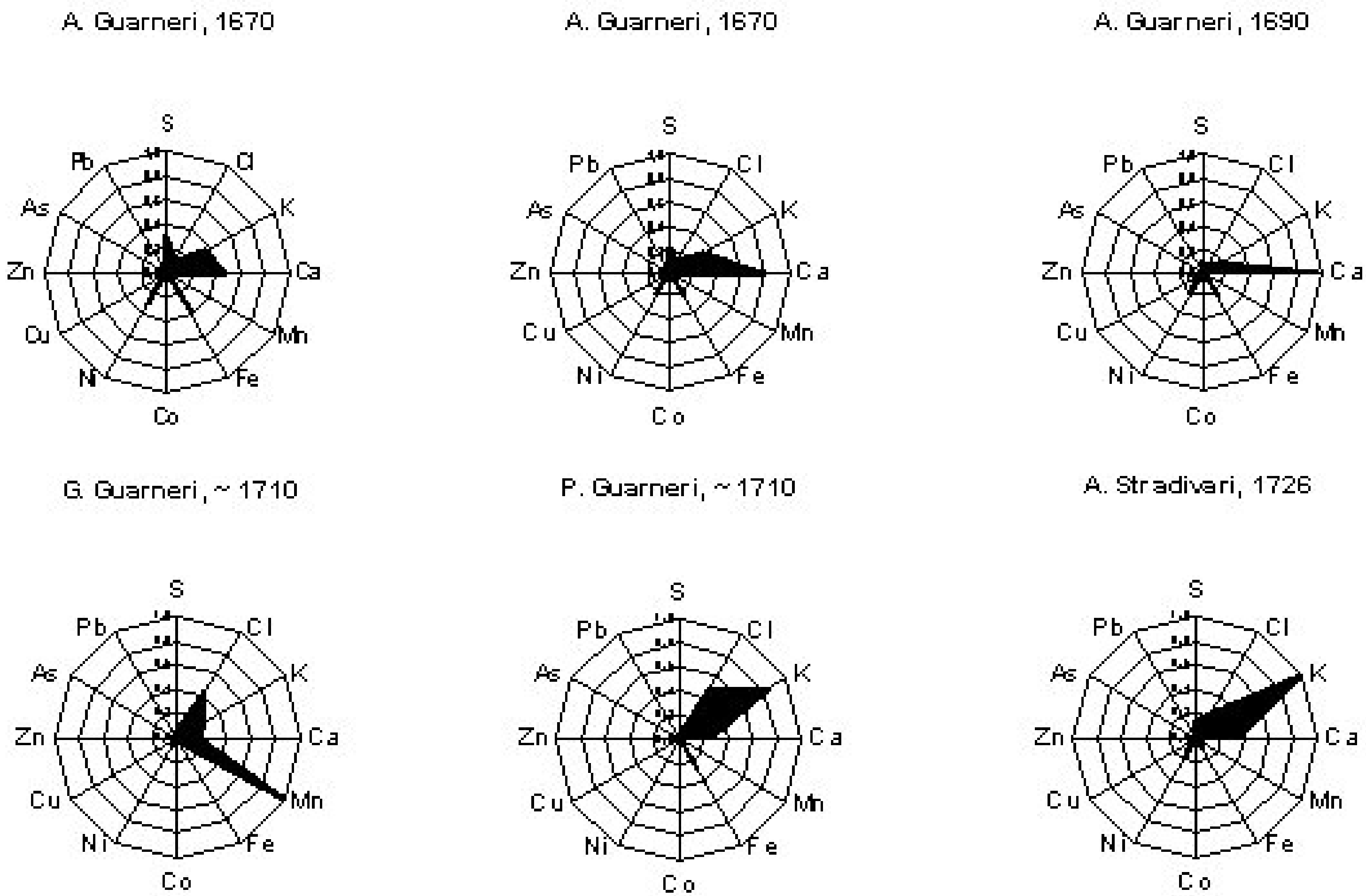
Stradivari violin

varnish, ground layer and wood

Heavy element components vary from violin to violin, indicating that different secret recipes have been used by violin makers!

A. Von Bohlen, F. Meyer; Spectrochimica Acta B 52 (1997) 1053

Comparison between Violins Recipes



Fe_2O_3 in umber or ochre; As_2S_3 golden auripigmentum, As_4S_4 red realgar; PbO yellow massicot, Pb_3O_4 red lead