The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR.1744 - 8

SCHOOL ON ION BEAM ANALYSIS AND ACCELERATOR APPLICATIONS

13 - 24 March 2006

IBA applications to cultural heritage and environmental problems

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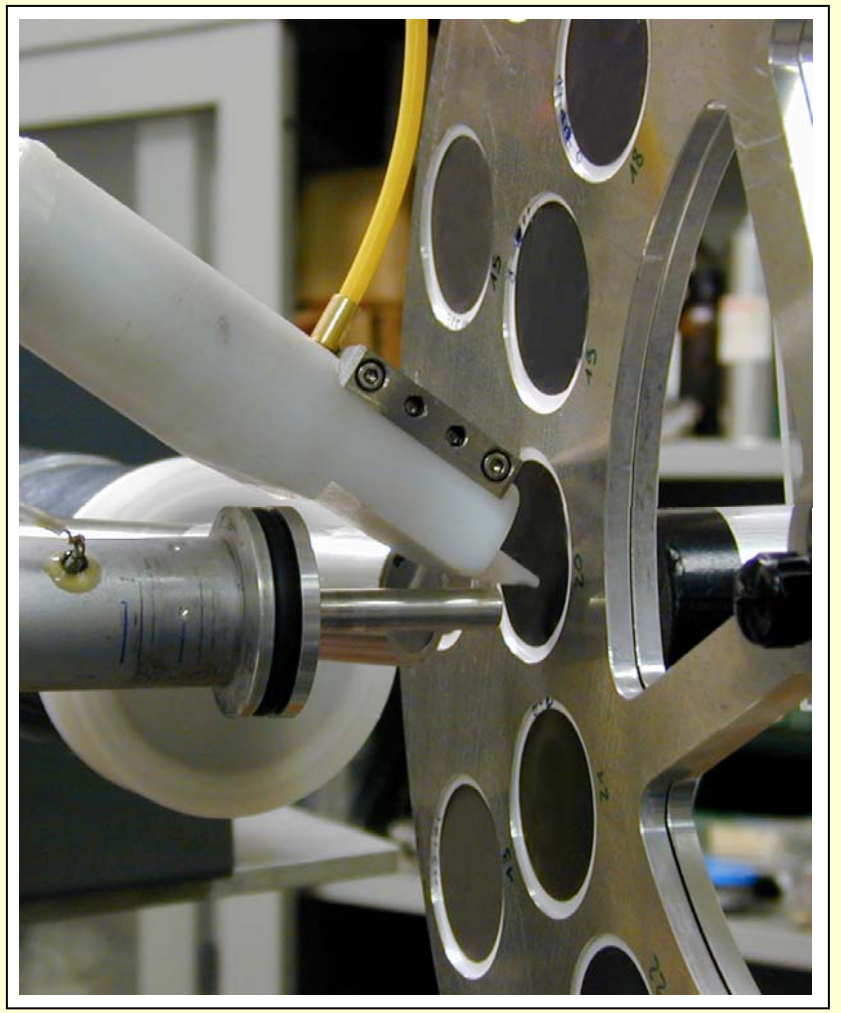
IBA applications to Cultural Heritage and environmental problems



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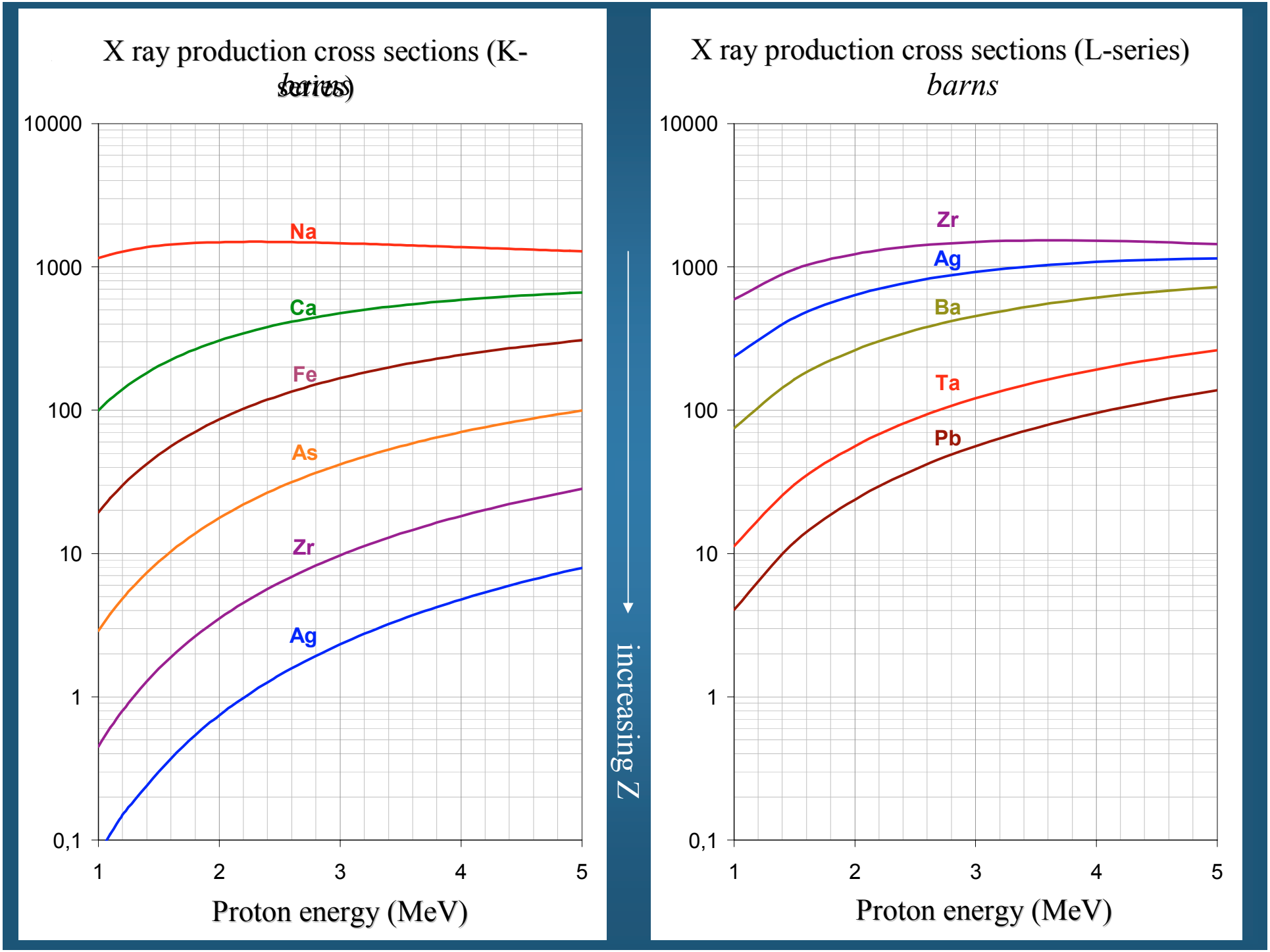
Laboratorio di tecniche nucleari per i Beni Culturali

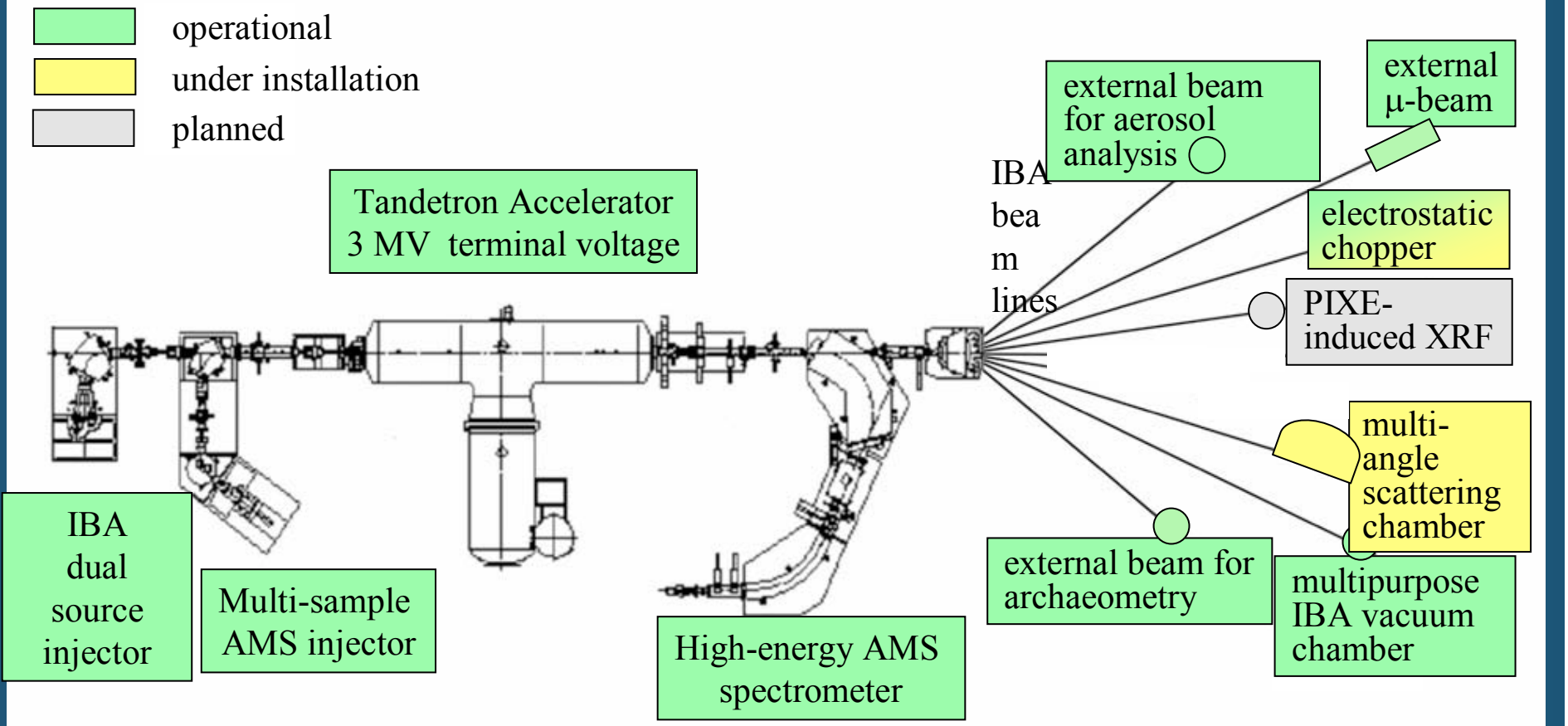
http://labec.fi.infn.it

IBA features that make them ideally suitable for C.H. and environmental studies

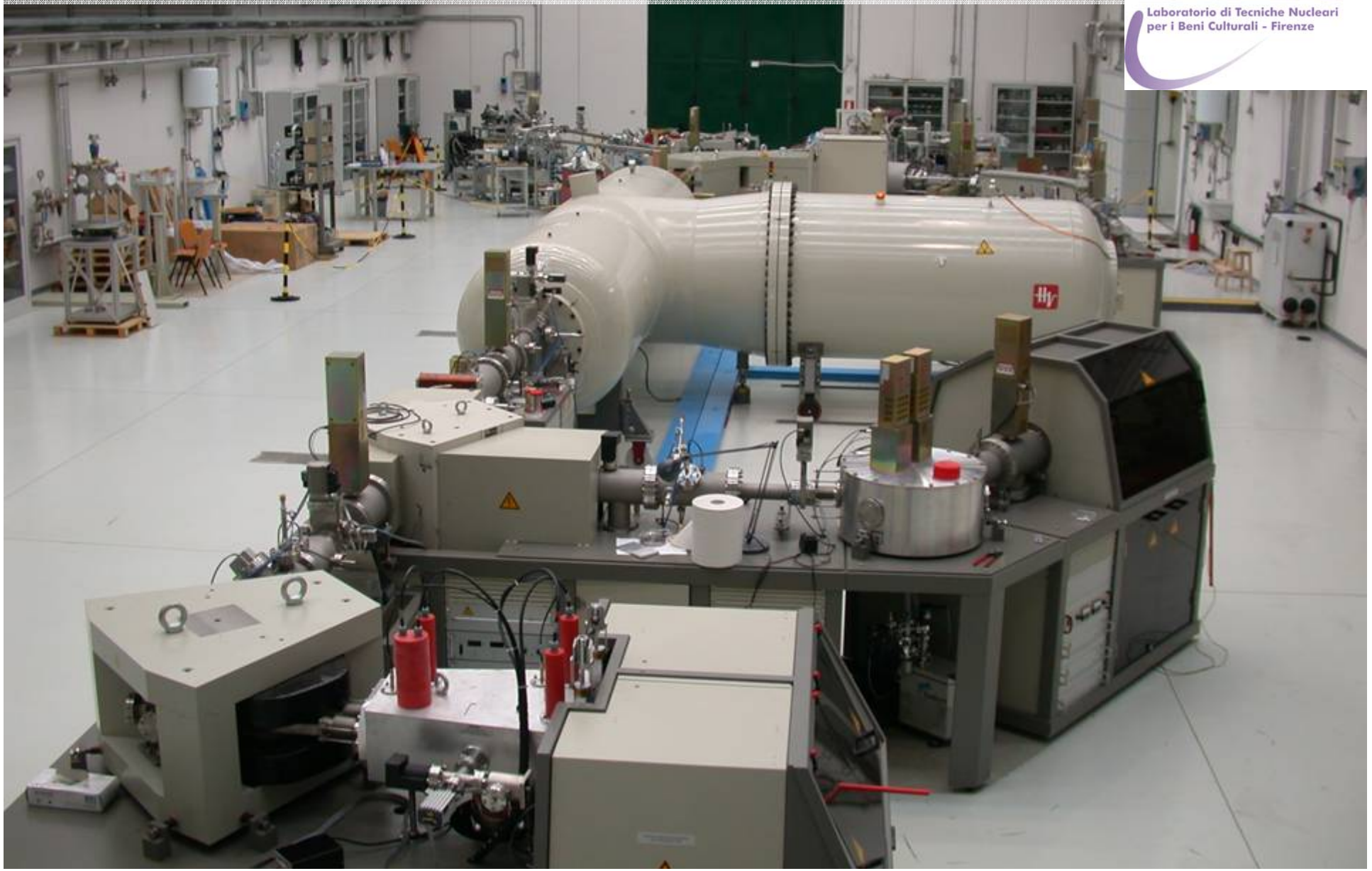
- Very large cross sections (PIXE in particular) → very low beam currents (therefore no damage), short time needed for analysis, and great absolute sensitivity (therefore analysis of very low target mass)
- Non destructivity → measurements can be repeated, also with other techniques
- External beams → no need of picking up samples, large objects, ease of handling the "targets"
- Possibility of easily varying beam energy, intensity and size, in order to find the best experimental conditions for the specific problem
- Complementary information obtained by the different IBA techniques, easily implemented in the same set-up


X ray production cross sections (K-series)
barns
10000
1000
100
10
1
0,1
Na
Ca
Fe
As
Zr
Ag
1
2
3
4
5
Proton energy (MeV)
increasing Z
X ray production cross sections (L-series)
barns
10000
1000
100
10
1
0,1
Zr
Ag
Ba
Ta
Pb
1
2
3
4
5
Proton energy (MeV)

IBA + AMS accelerator facility in Florence



Overall view of the Florence Tandetron accelerator hall



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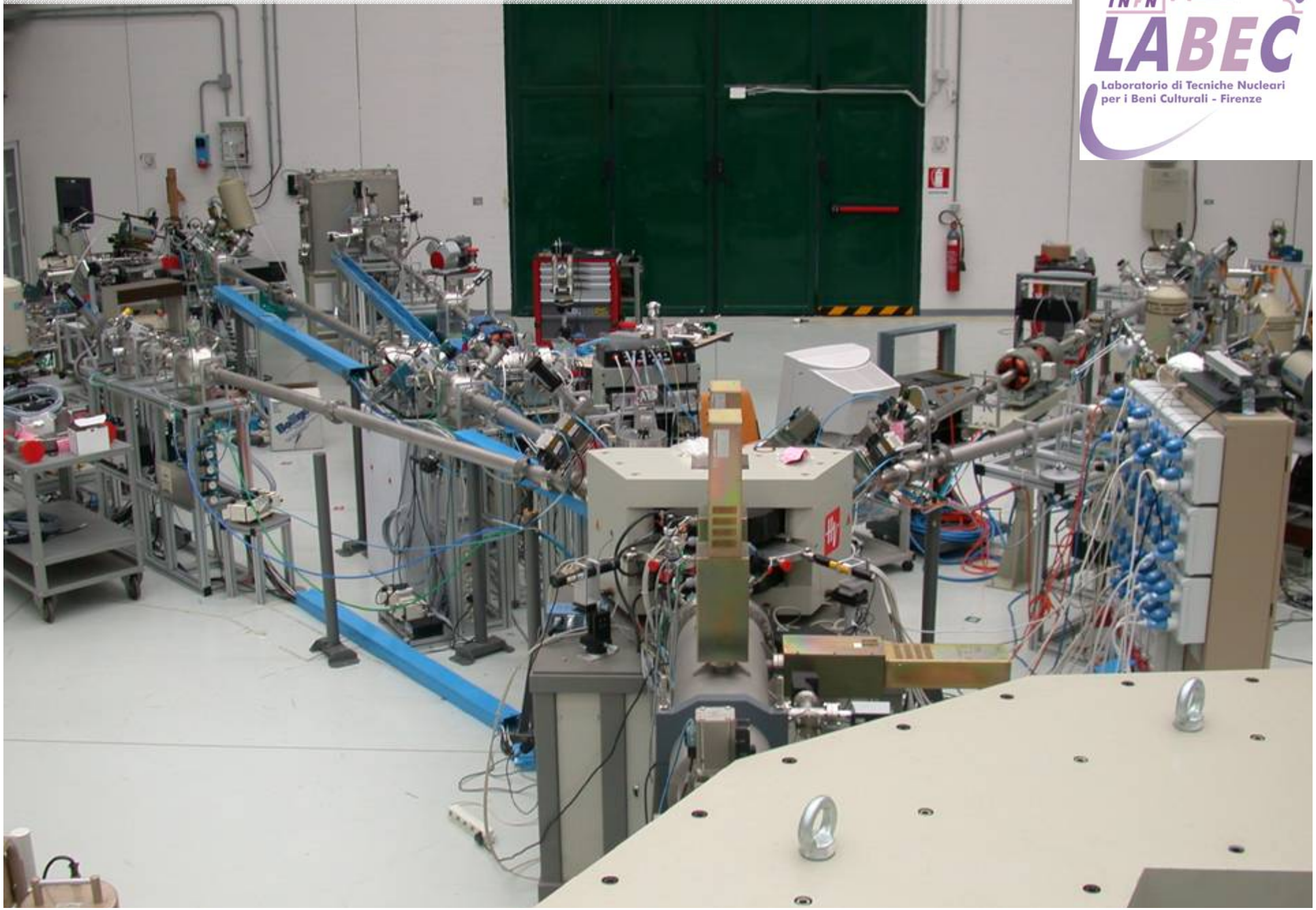
The beamlines so far installed for IBA



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X-ray detectors (PIXE)
Gamma-ray detector (PIGE)
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External-beam set-up for the analysis of paintings and other art objects

An essential facility to perform IBA especially in the field of Cultural Heritage

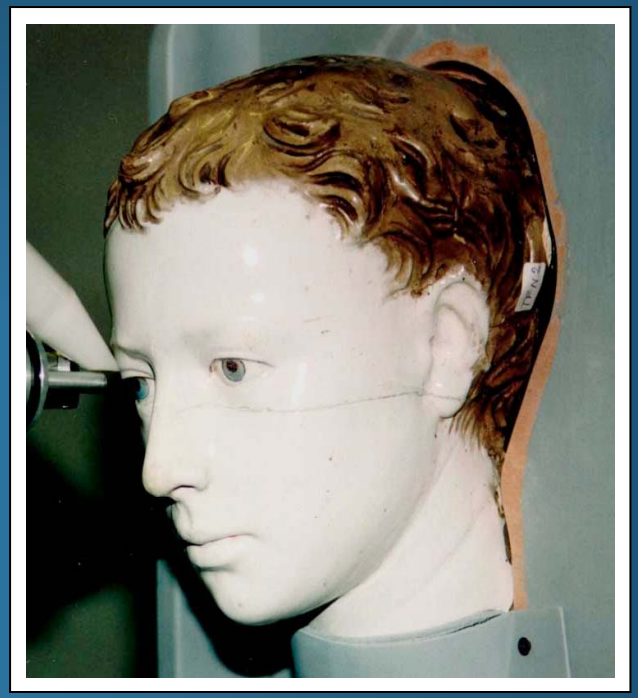
With an external beam you can investigate in a non-destructive way the complete quantitative composition of any material you may be interested in

Analysis of ancient glass,

...glazed terracottas,

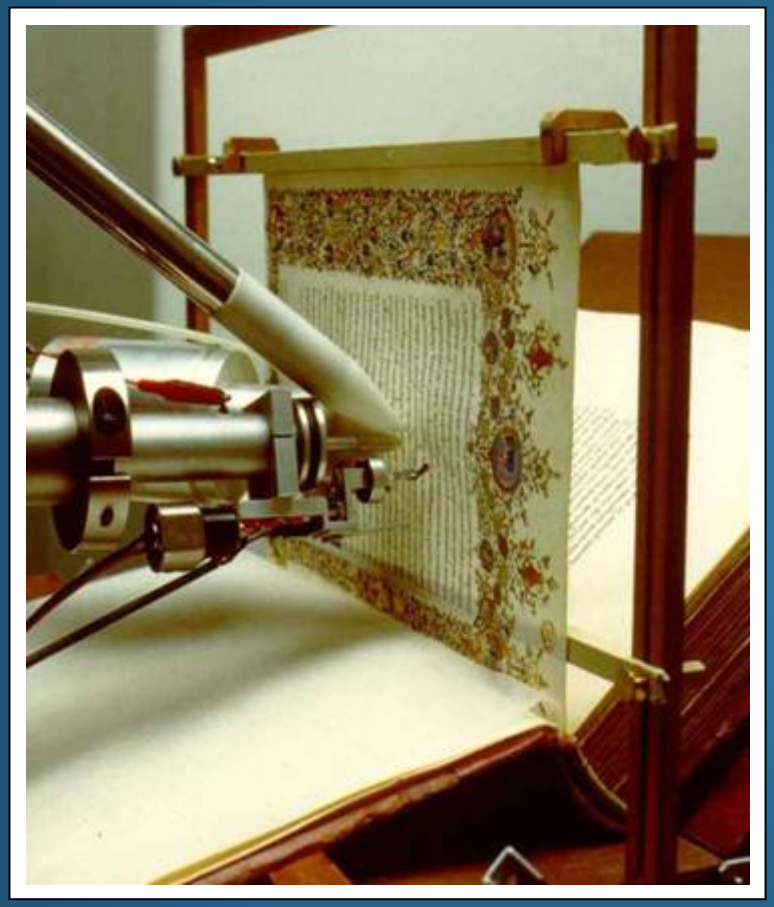
Glass mosaic tesserae found in excavations at Villa Adriana, Tivoli

External PIXE-PIGE analysis of the glass tesserae from Villa Adriana



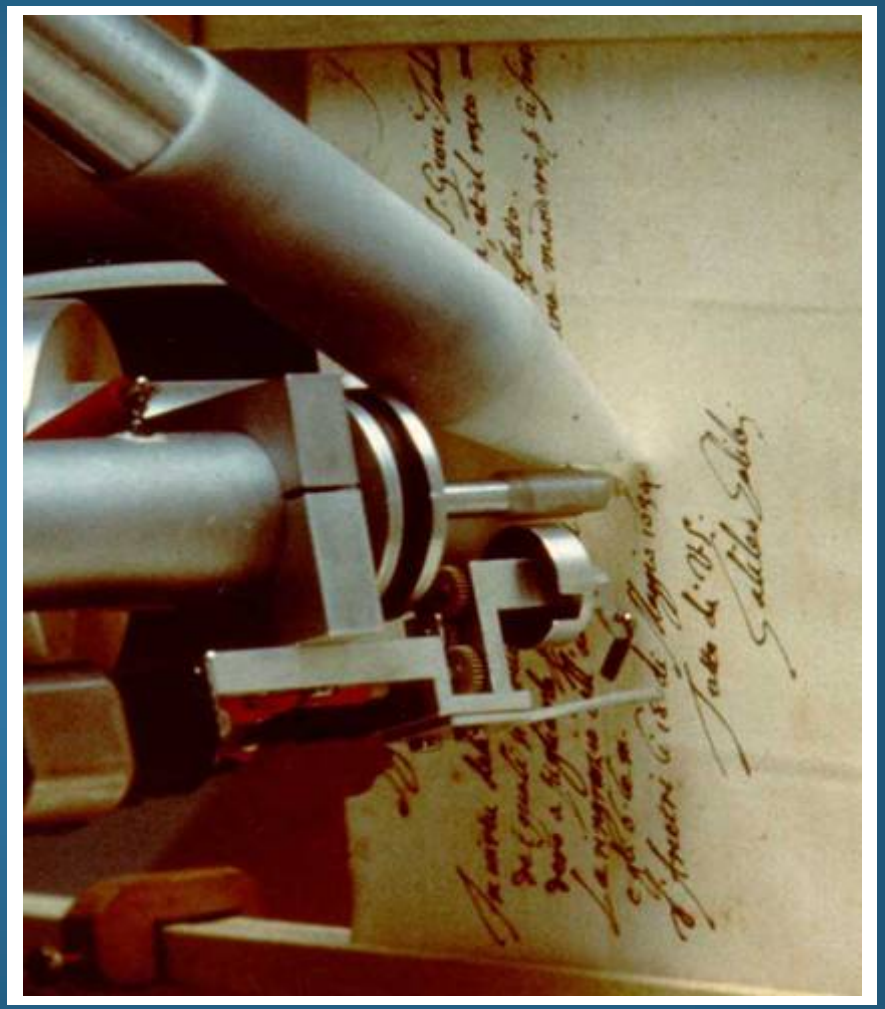
External PIXE analysis of the "Ritratto di fanciullo" by Luca Della Robbia – before restoration at the Opificio delle Pietre Dure in Florence

...ancient illuminated manuscripts,



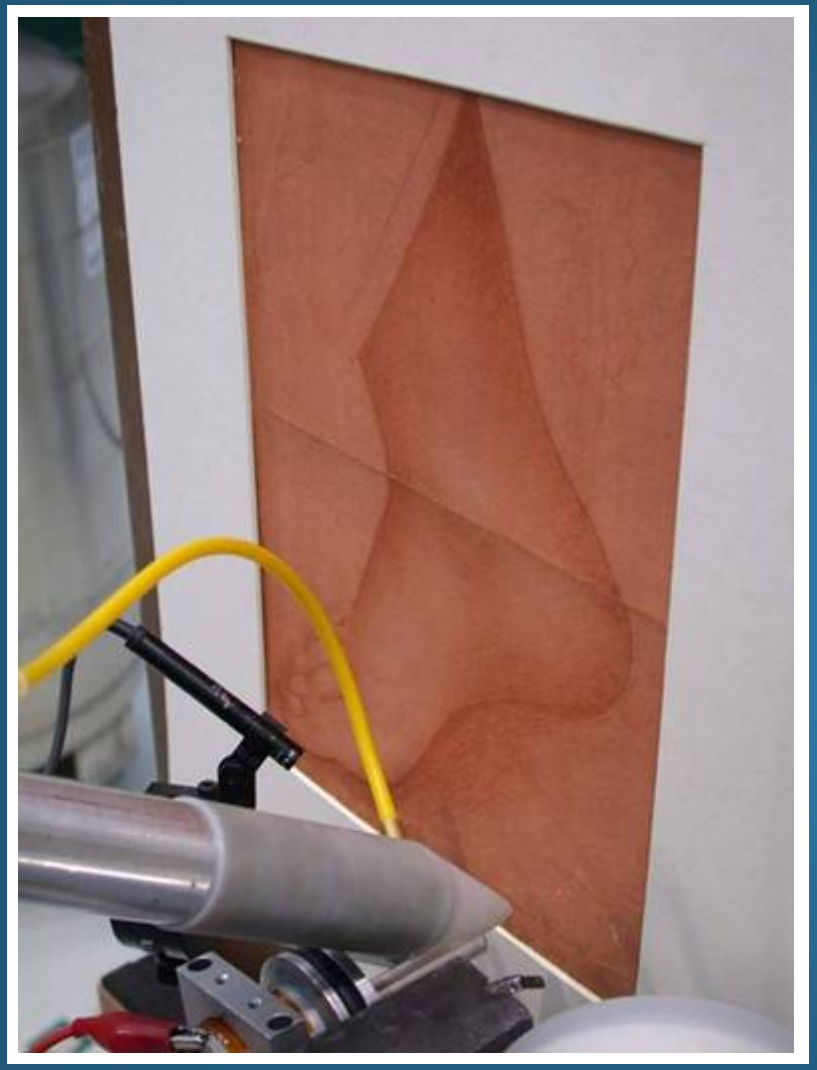
External-beam PIXE analysis of the frontispiece of Pl.16,22 (XV century, Biblioteca Laurenziana in Florence)

...historical documents,



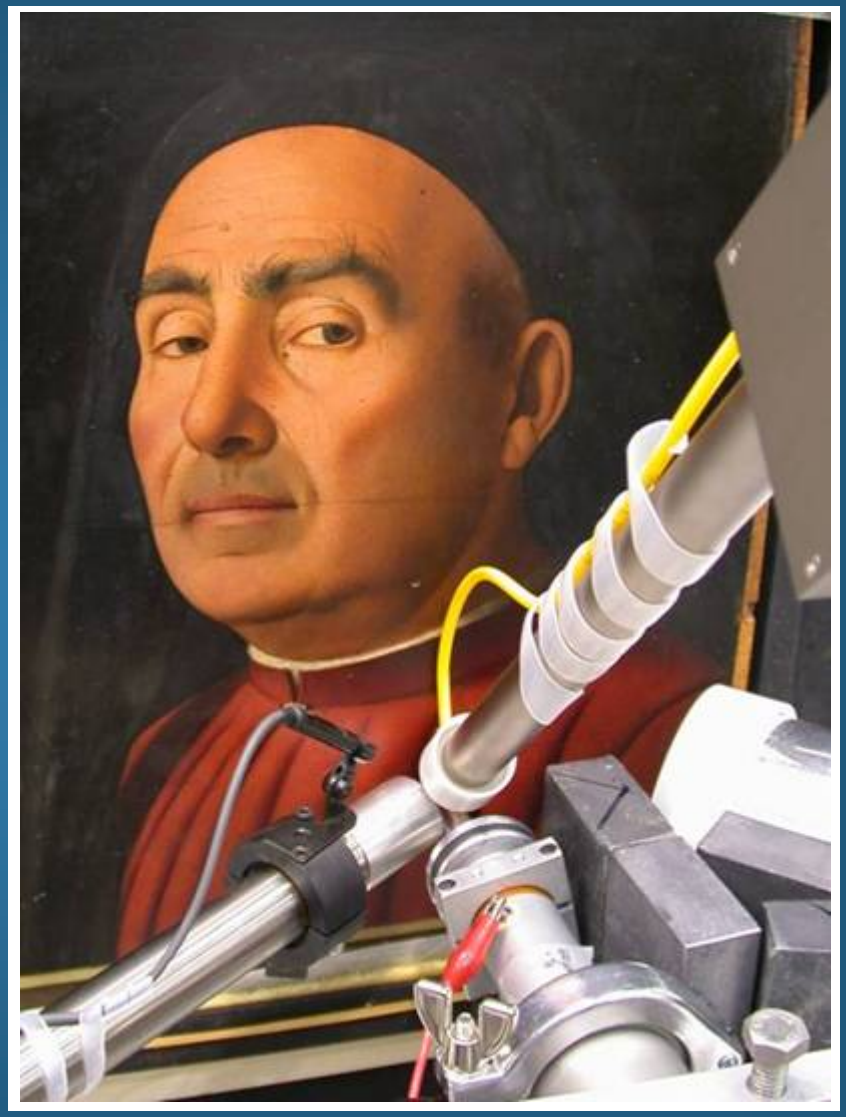
Inks in Galileo's manuscripts (Florence National Library) analysed by external PIXE

...drawings,



PIXE-PIGE analysis of a drawing on prepared paper, by Leonardo or his school

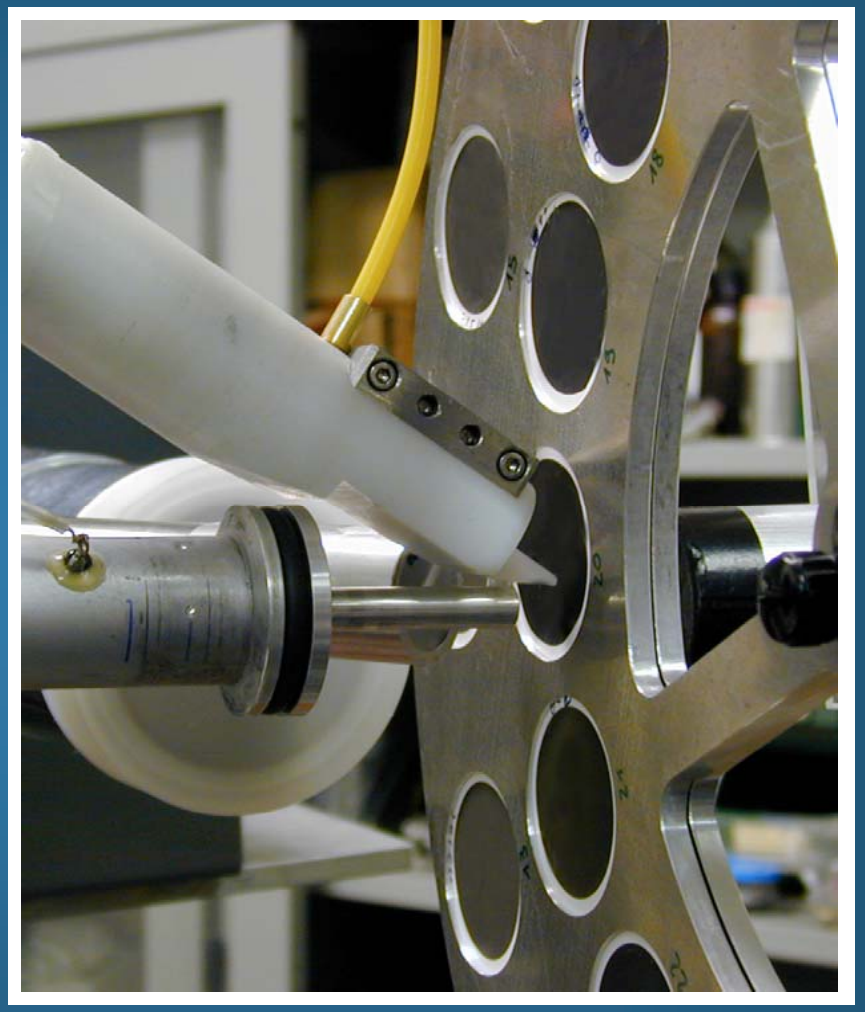
...paintings on wood or canvas,



Differential PIXE and PIGE analysis of the "Ritratto Trivulzio" by Antonello da Messina

…or analysis of aerosols collected on filters

Particulate Matter (PM) from streaker samplers (1-hour resolution)



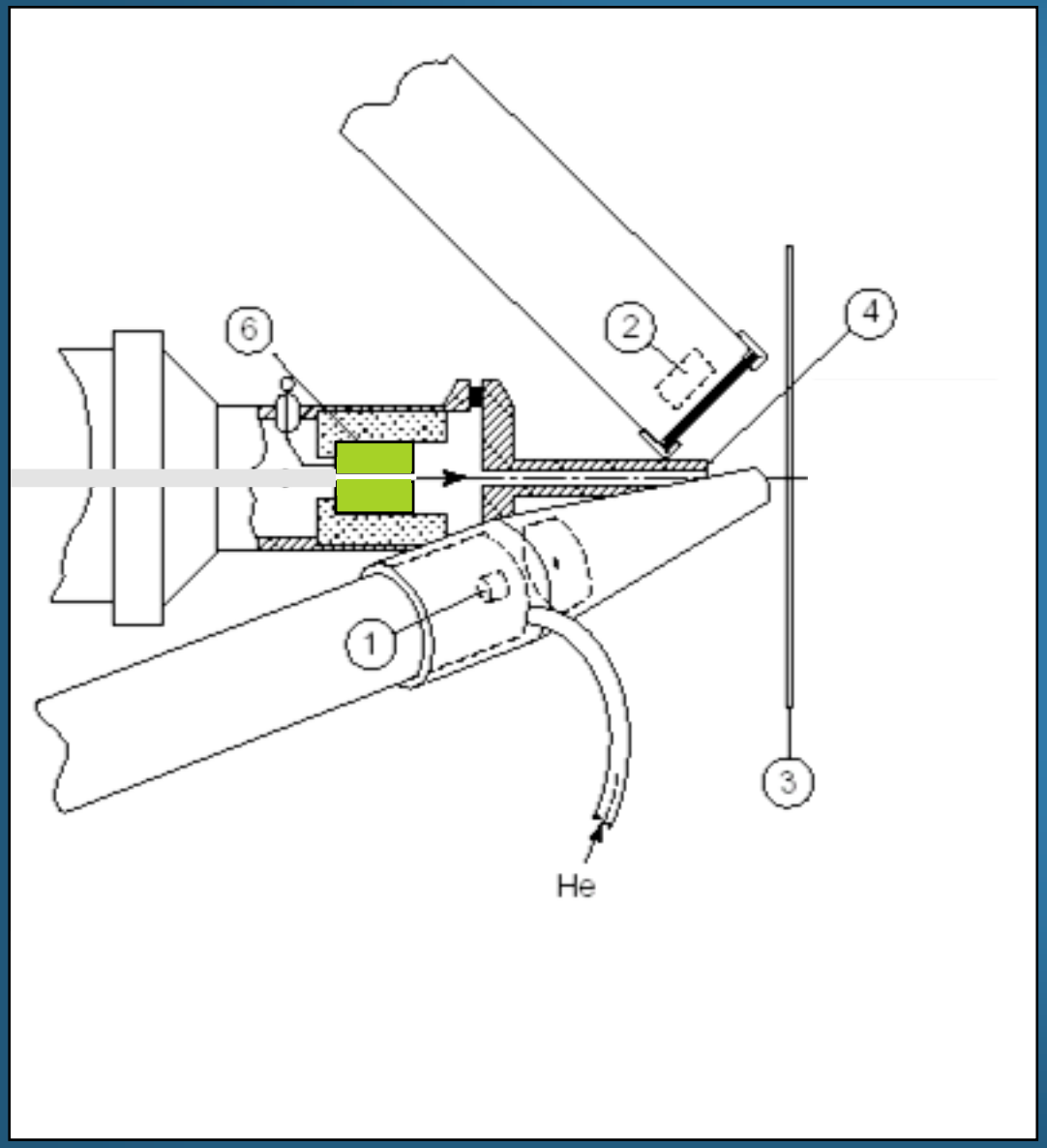
PM from daily samplers

Typical experimental conditions in applications to C.H.

- *proton beams, 1 ÷ 5 MeV*
- *5÷50 pA currents, 100÷200 s runs*
- *0.1÷1 mm beam size*
- *two X ray detectors*

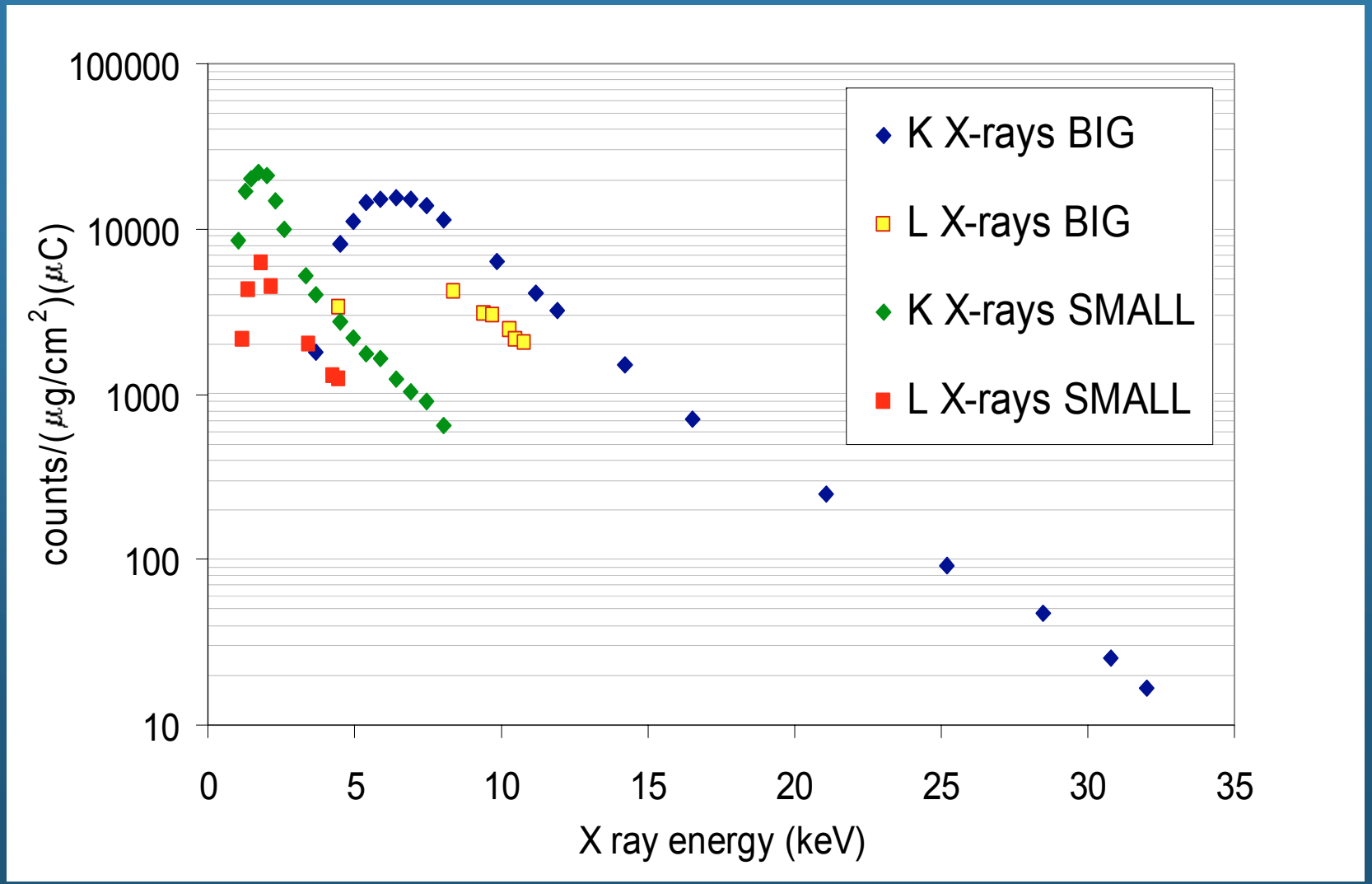
  one for lower-Z elements, covering a small solid angle; He flow for minimising absorption

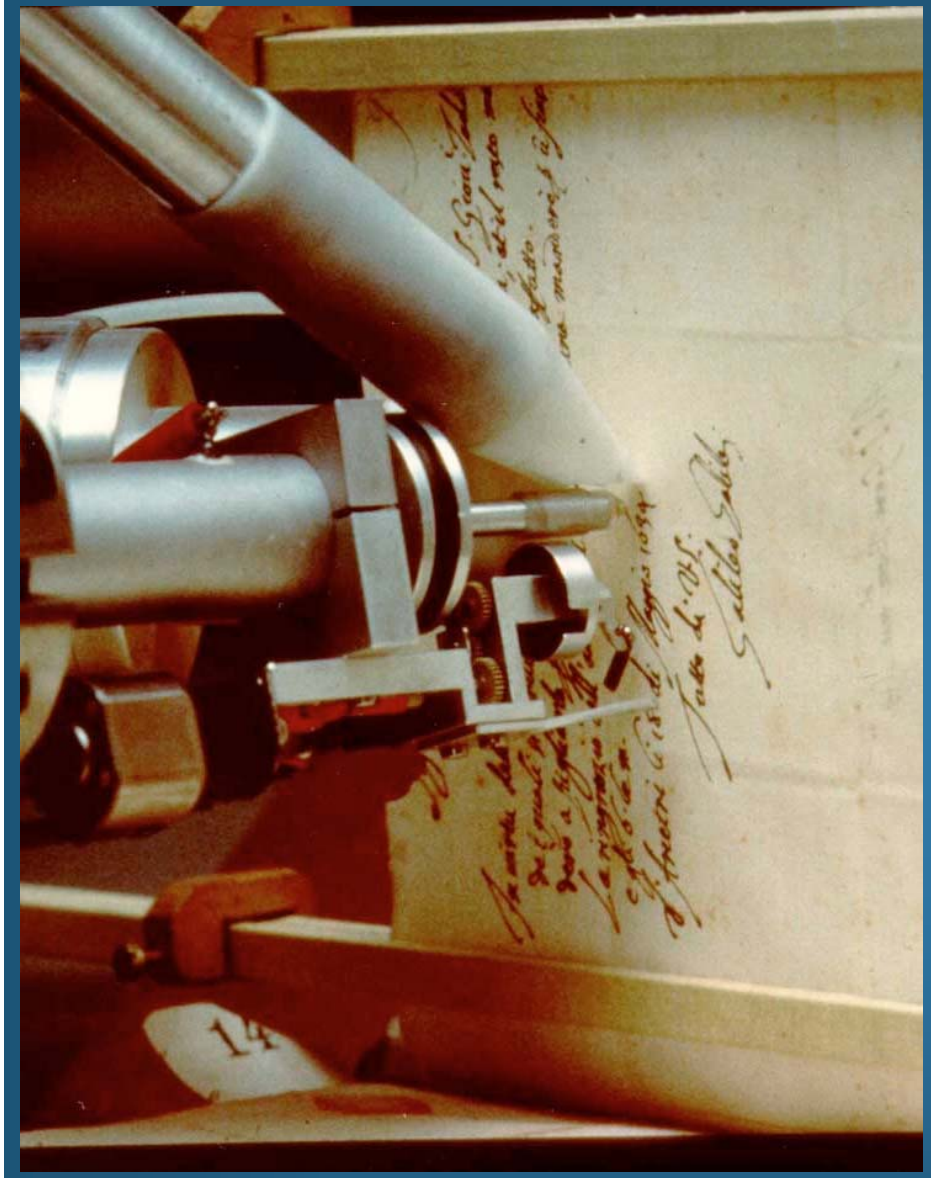
  the other for higher-Z elements, covering the largest possible solid angle and with proper absorbers to cut the high rate of low-energy X rays
- *a gamma ray detector*



Two-detector PIXE setup, collimated external beam

X ray detection efficiencies in a two-detector setup





A letter of Galileo during PIXE analysis with the external beam at the Florence accelerator

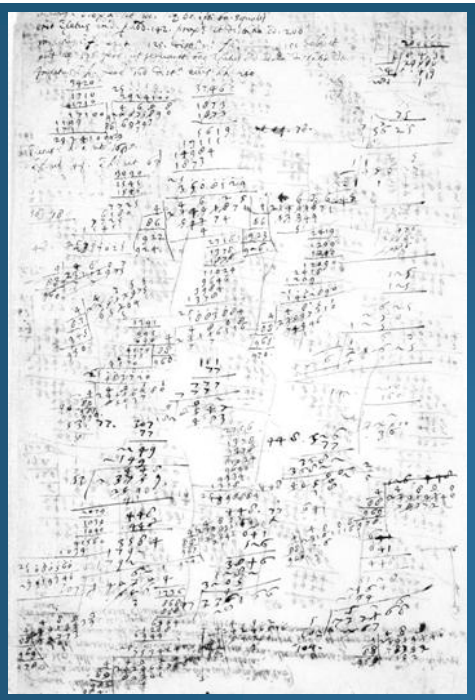
Analysis of documents of historical interest

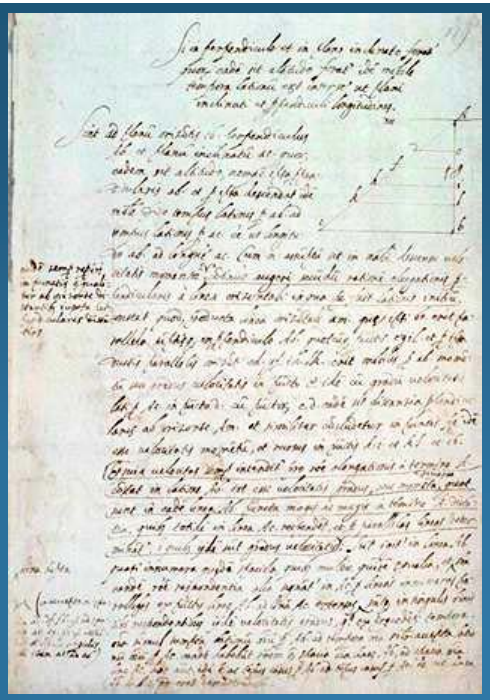
(INFN FI, Bibl.Naz. FI, MPI Berlin)

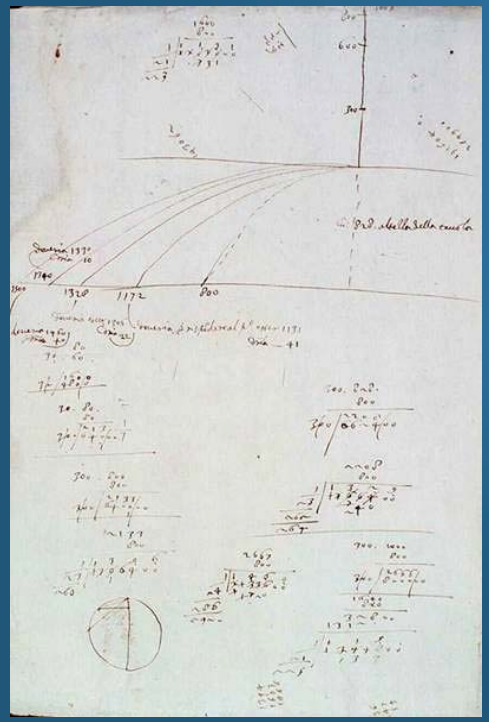
PIXE measurements to quantitatively determine ancient inks composition

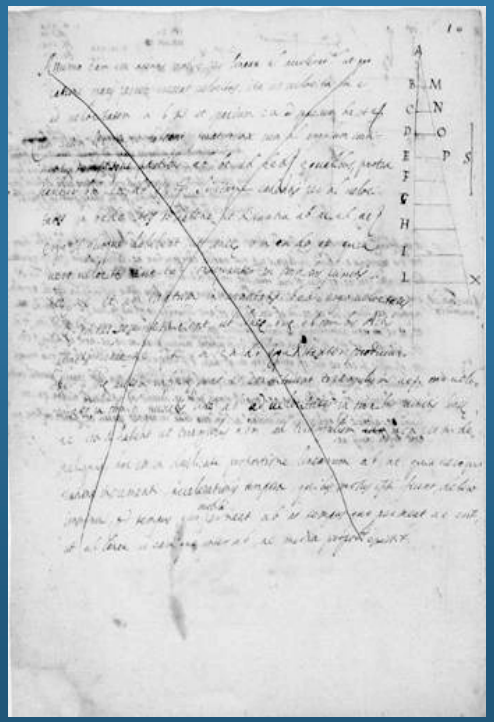
Important contribution to the chronological reconstruction of Galileo's hand-written notes about motion

Comparison of ink composition in the notes (which are not dated) with that in dated documents (letters, etc.)





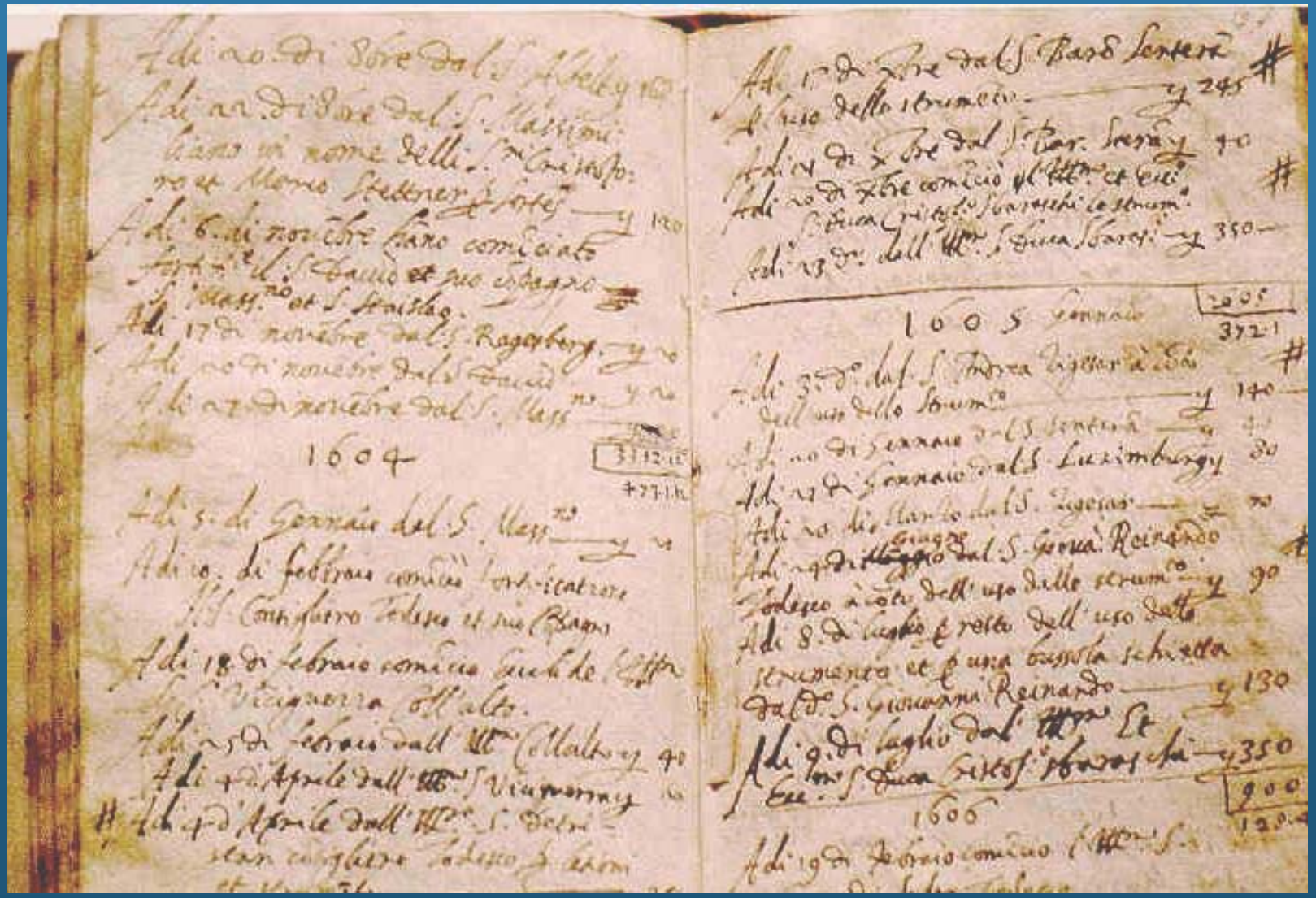




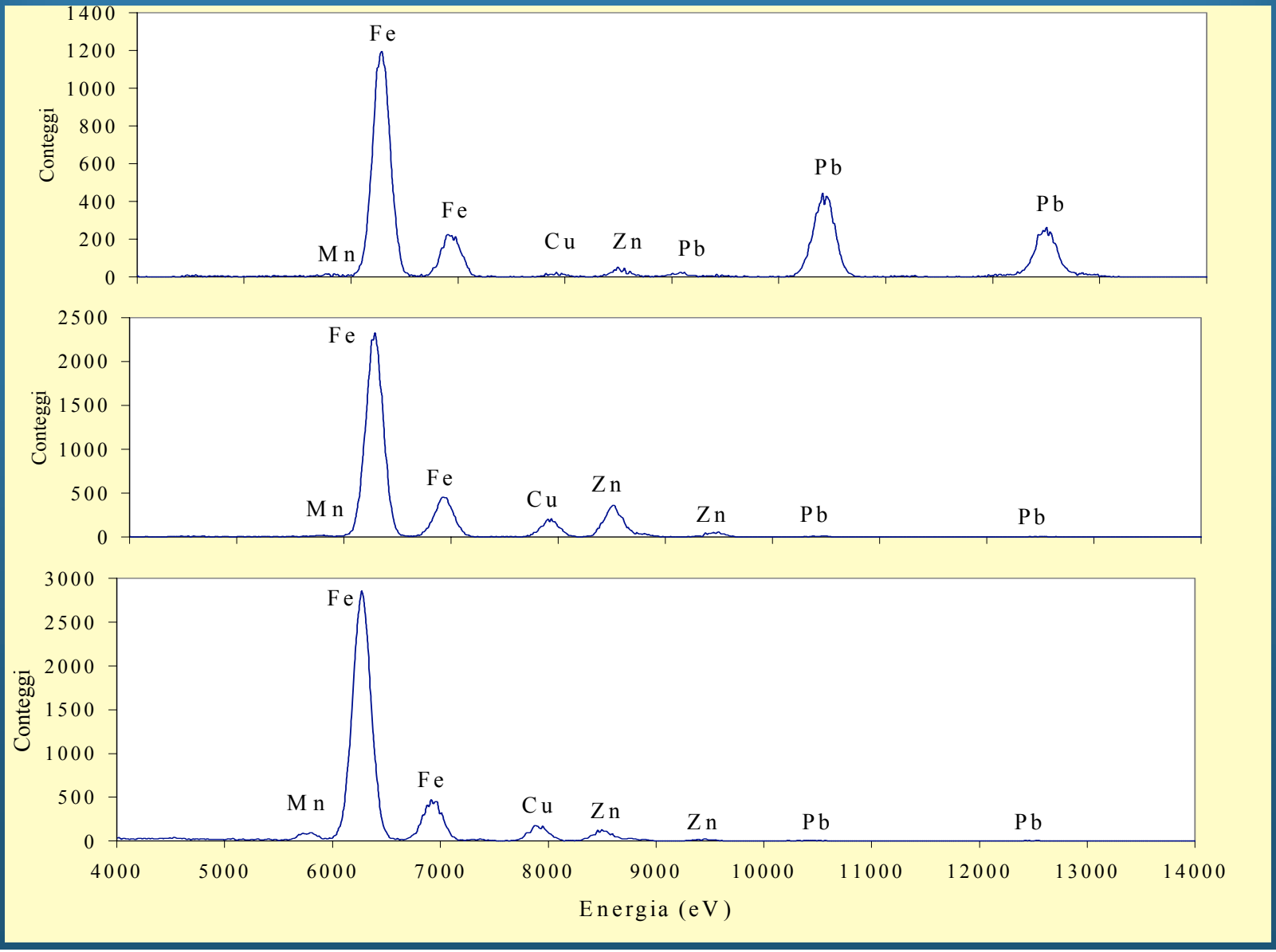
Some folios from Ms.Gal.72

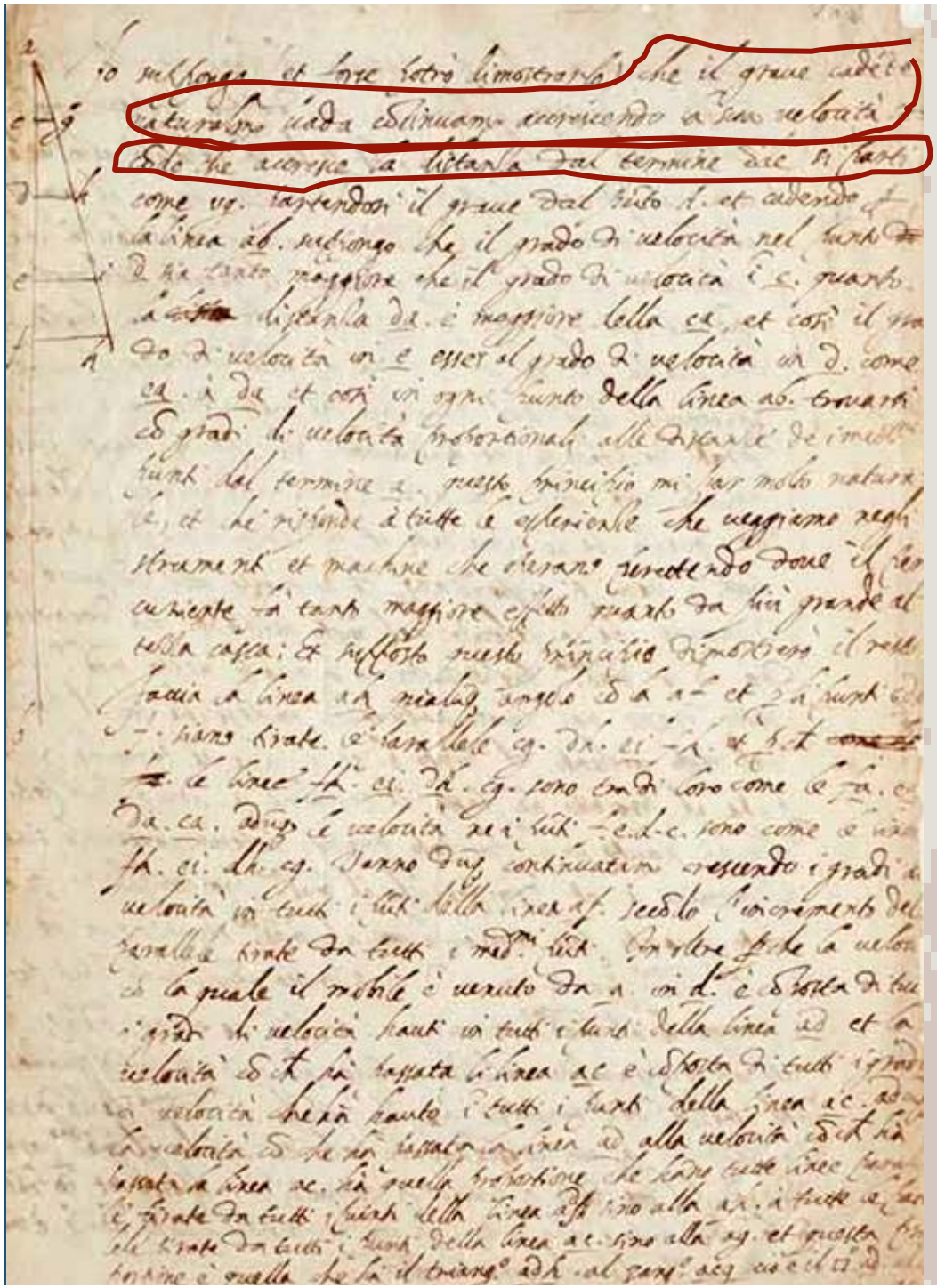
(Bibl. Naz. Firenze)

A precious "database" of dated inks: records of money transactions in Ms.Gal.26



Discriminating between different inks with PIXE





v(s), v(t), s(t)

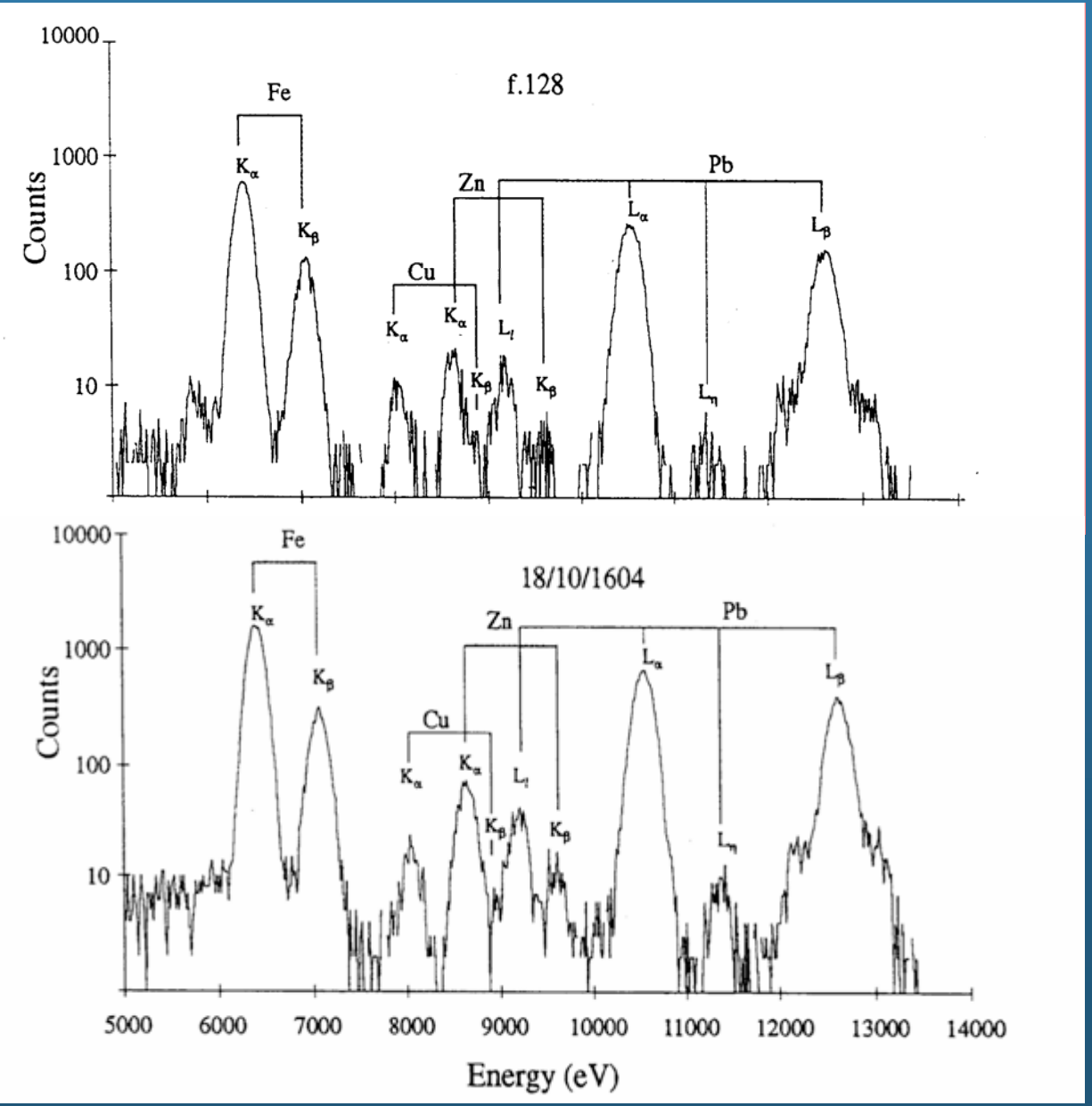
Folio 128

the "starting point"

...che il grave cadente naturalmente vada <u>continuamente</u> accrescendo la propria velocità....

...secondo che accresce la distanza dal termine onde si partì....

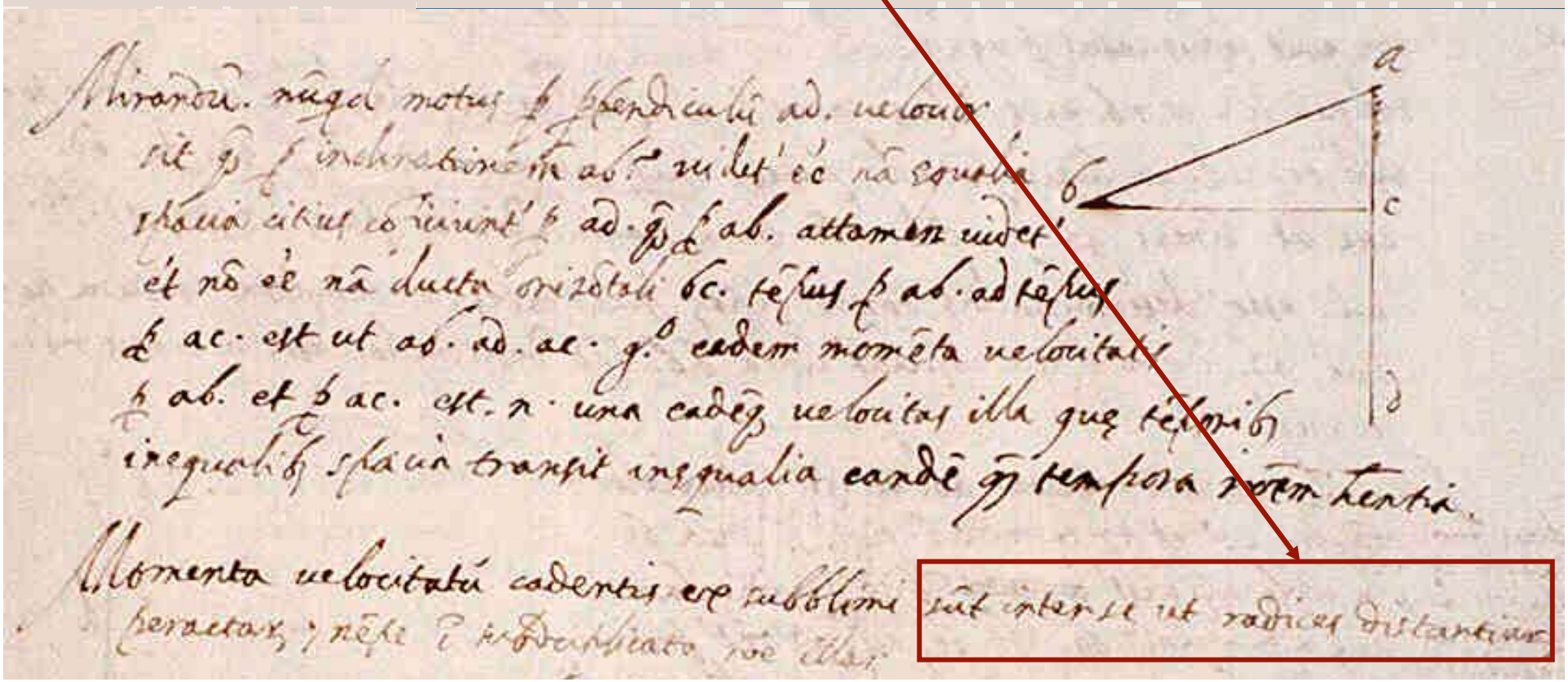
"Dating" f.128


f.128
Fe
Zn
Pb
Cu
K_α
K_β
L_α
L_β
L_γ
L_ℓ
Counts
10000
1000
100
10
18/10/1604
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Energy (eV)

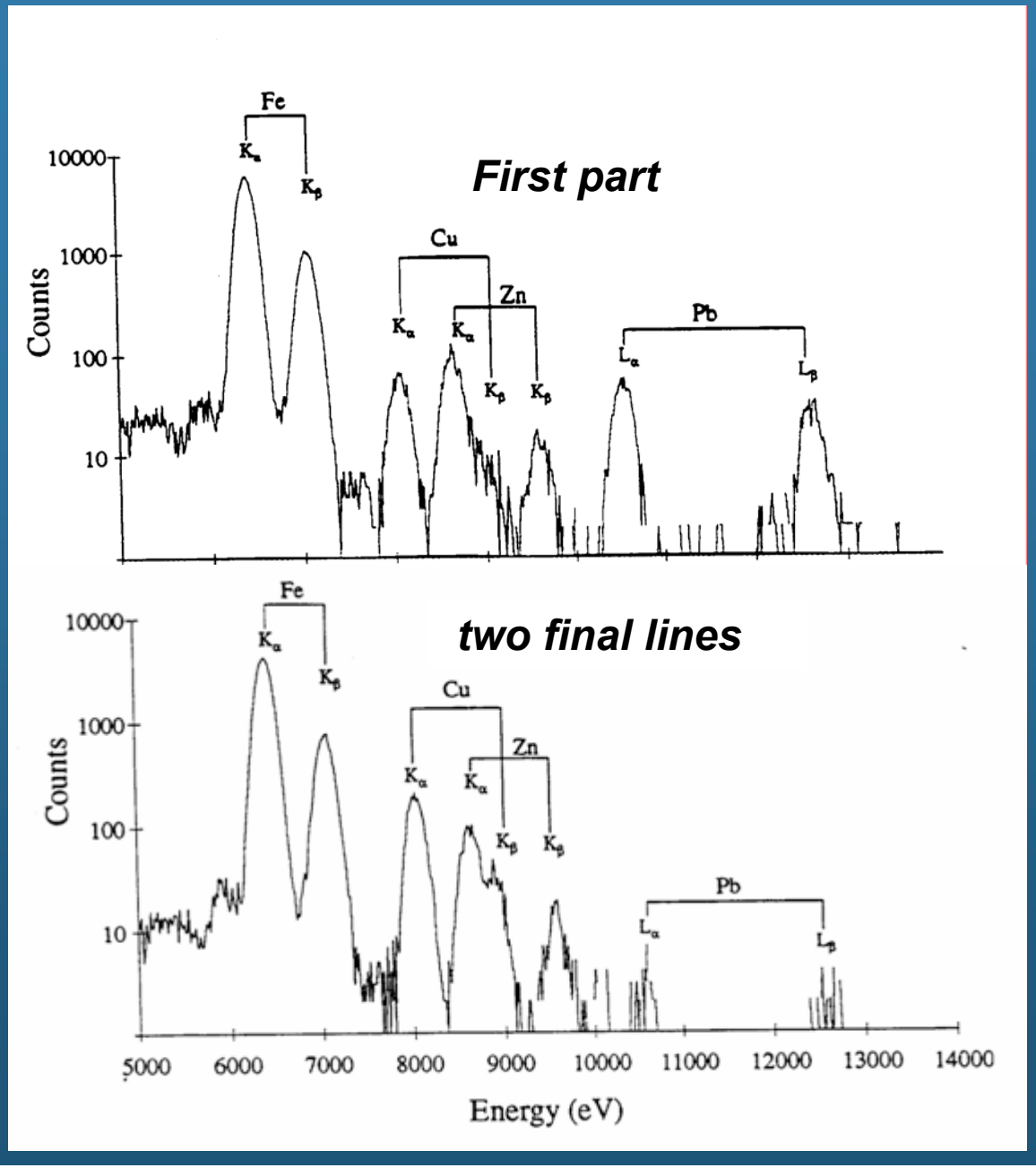
v(s), v(t), s(t)

Folio 164v – the "final result"

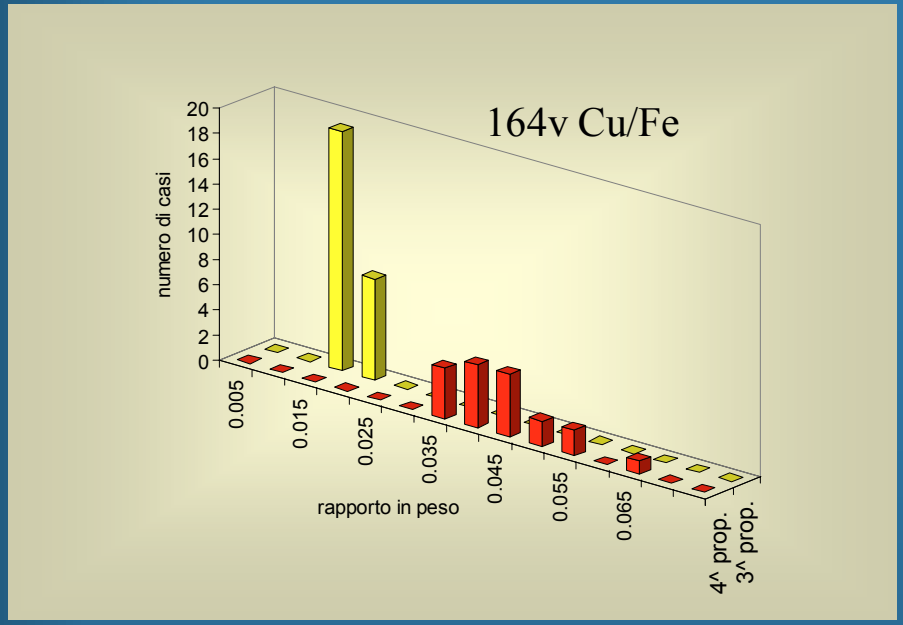
...sunt inter se ut radices distantiarum...

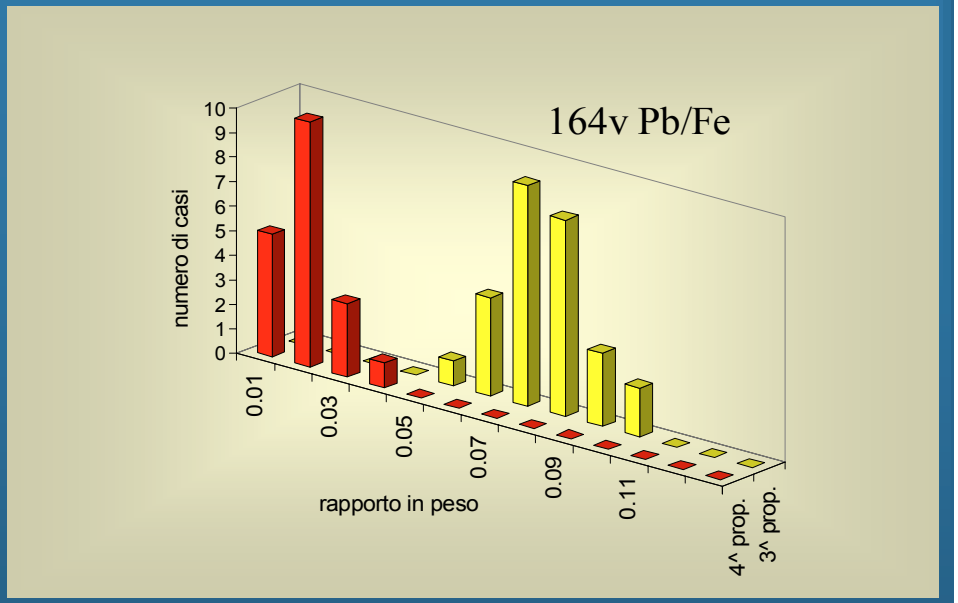


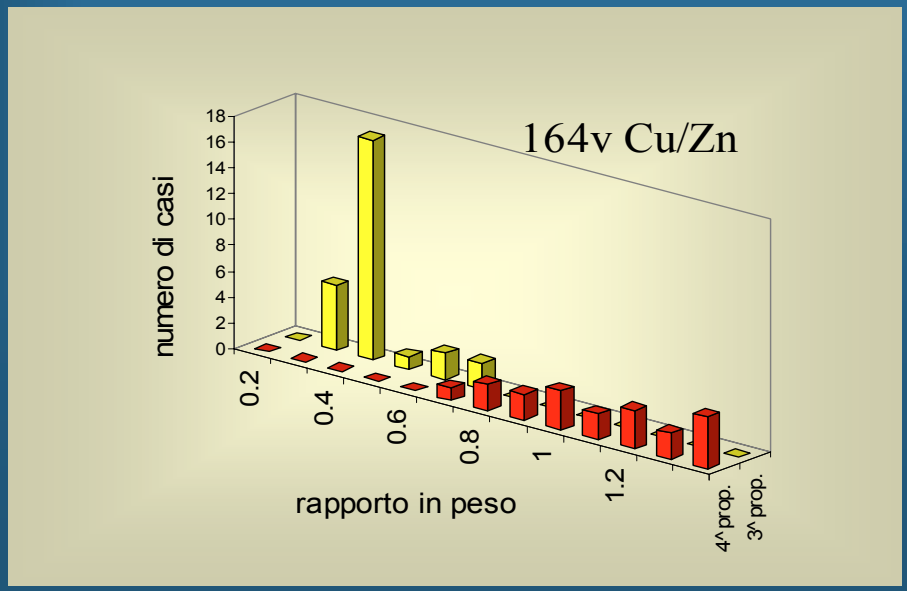
Folio 164v


First part
two final lines
Fe
Cu
Zn
Pb
Counts
10000
1000
100
10
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Energy (eV)

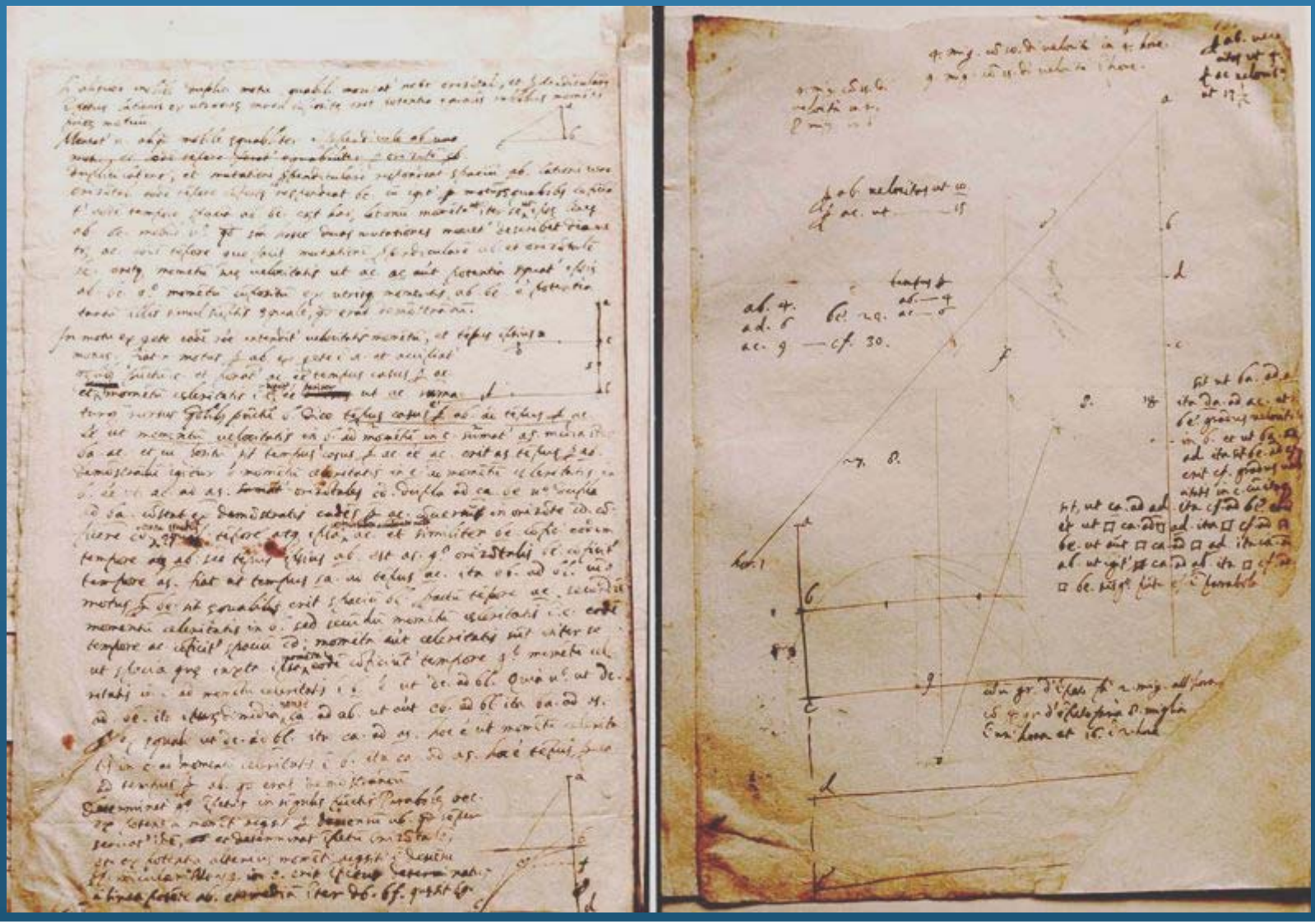
Folio 164 v – comparison between the two propositions



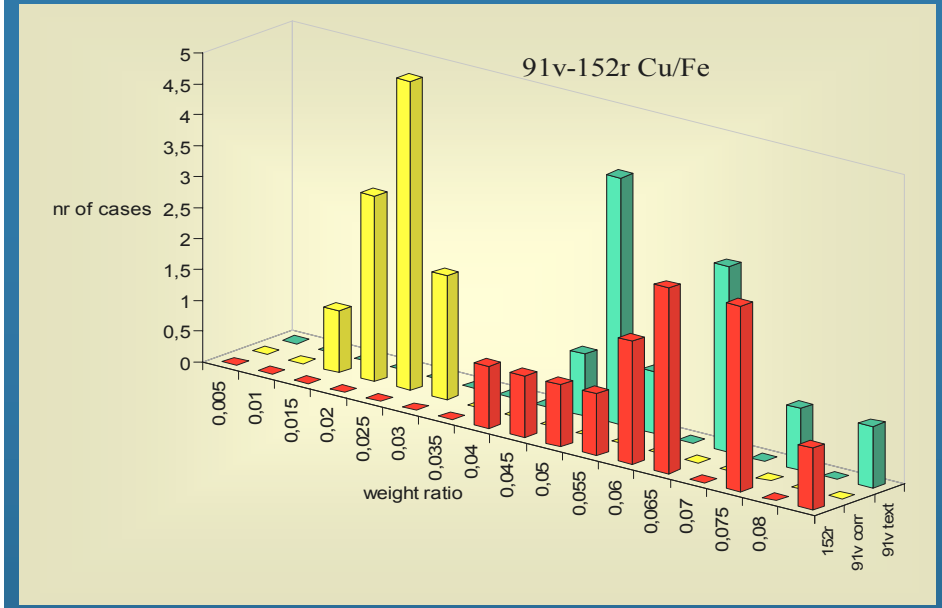


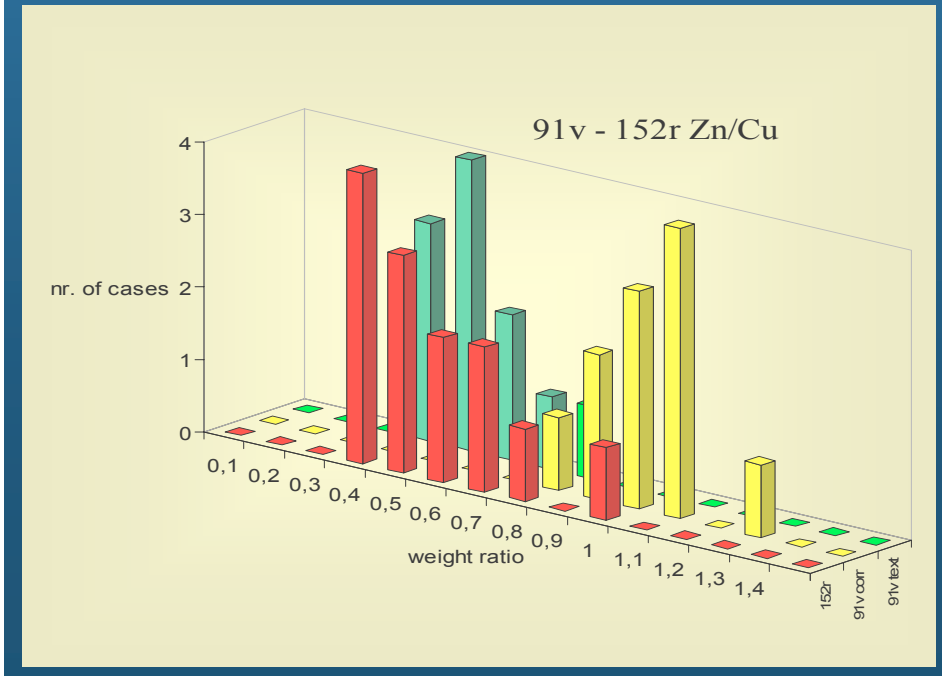


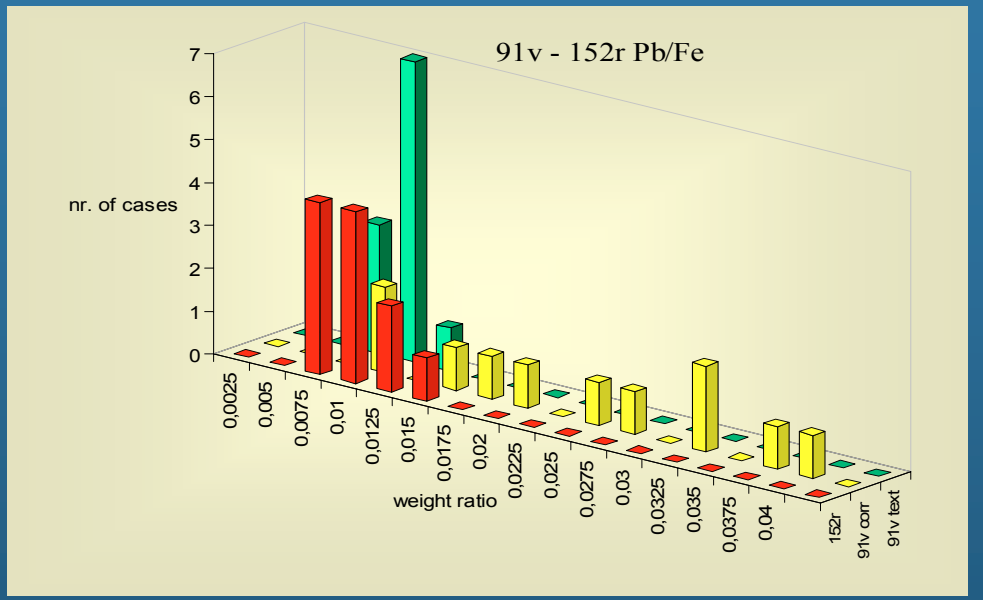
Connection between different folios (91v, 152r)

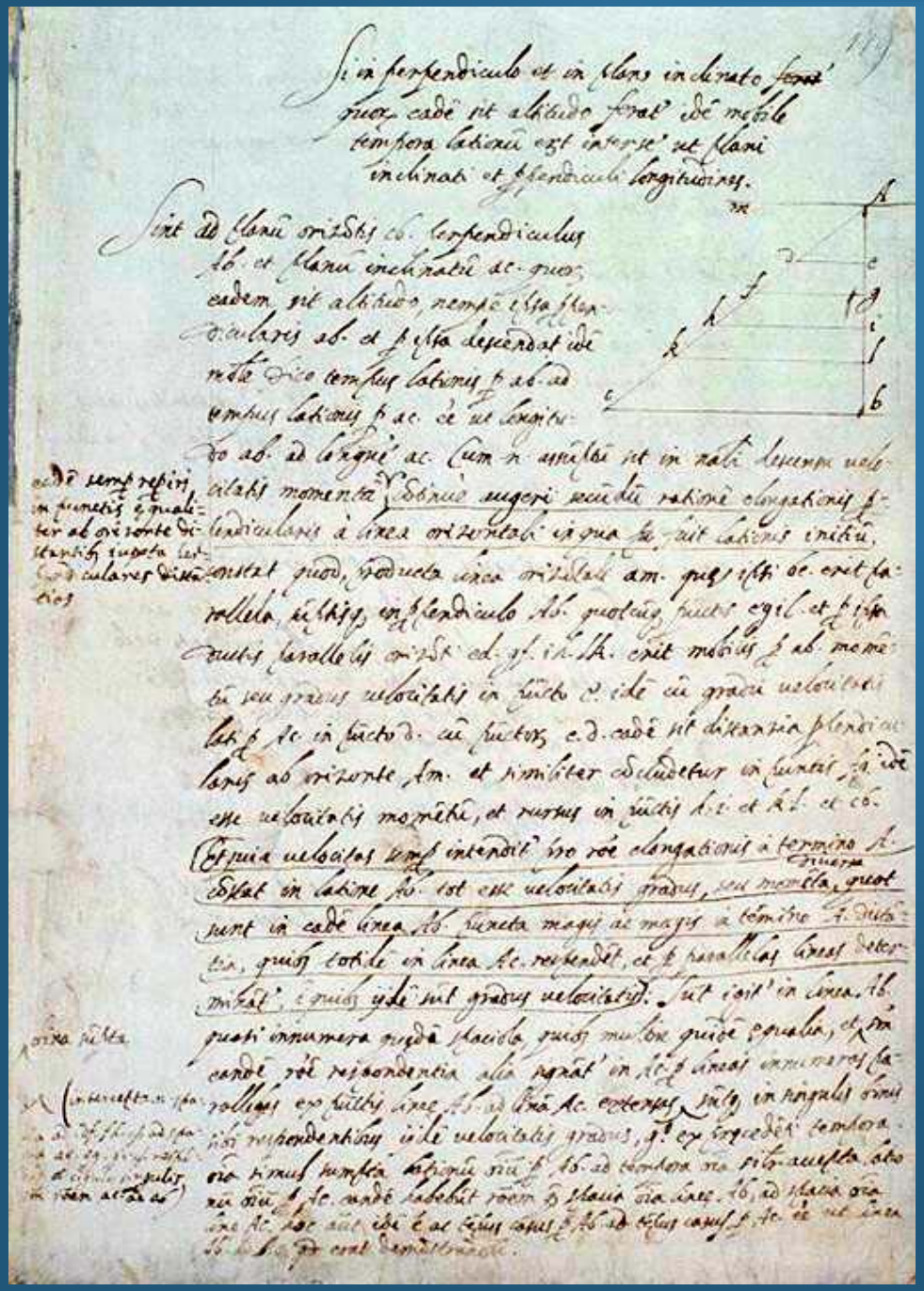


Connection between f.91v and f.152r



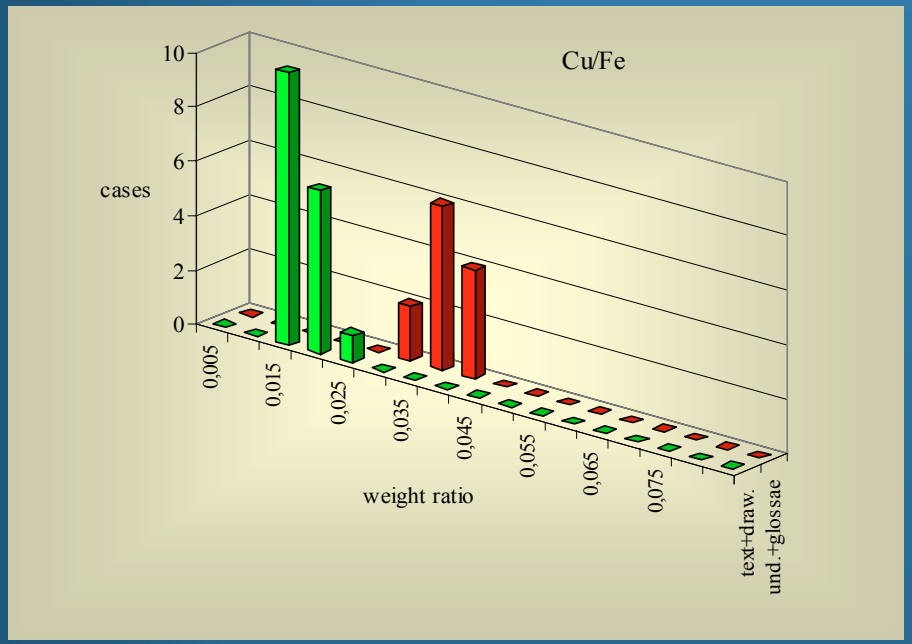


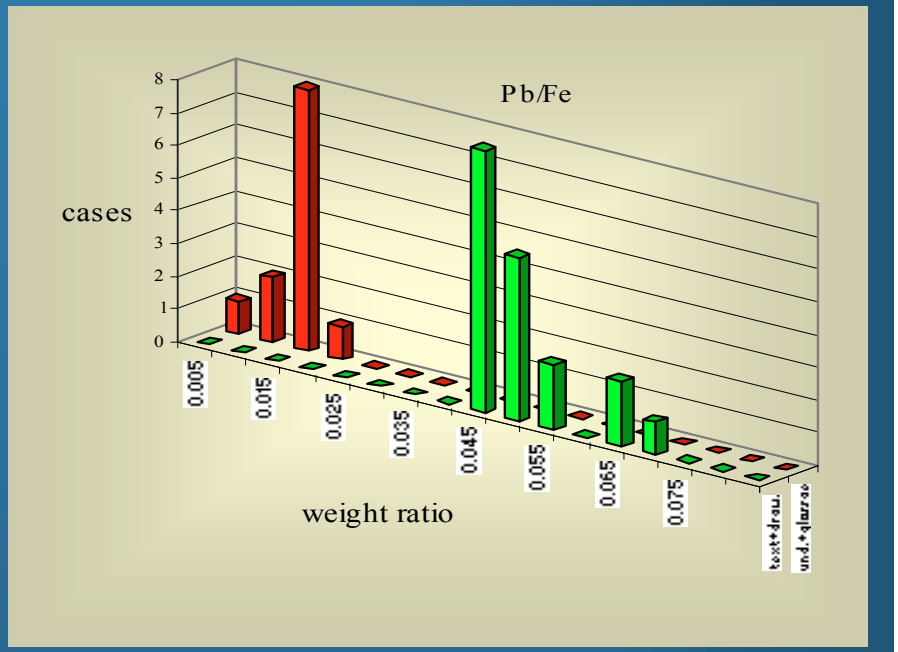


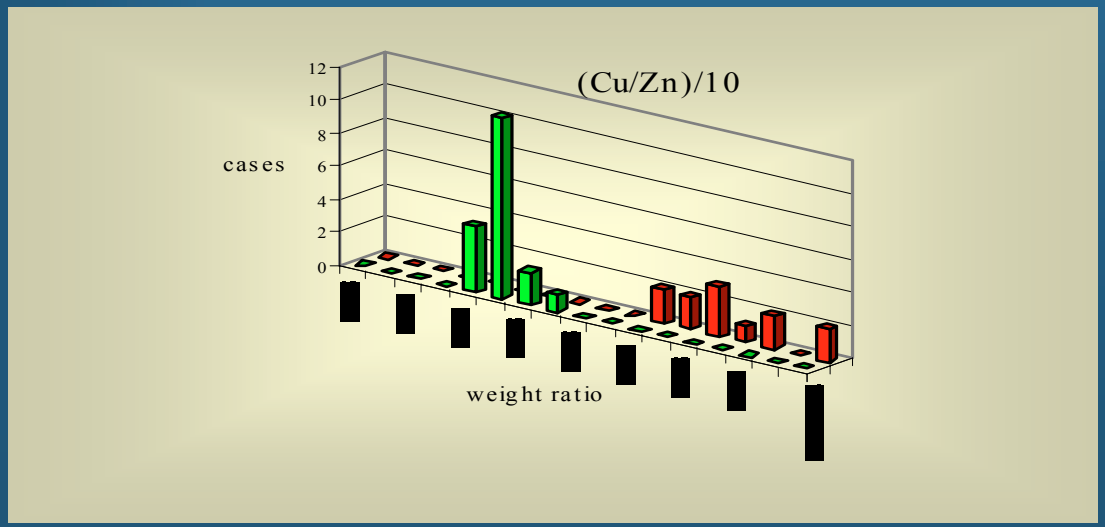


f. 179r

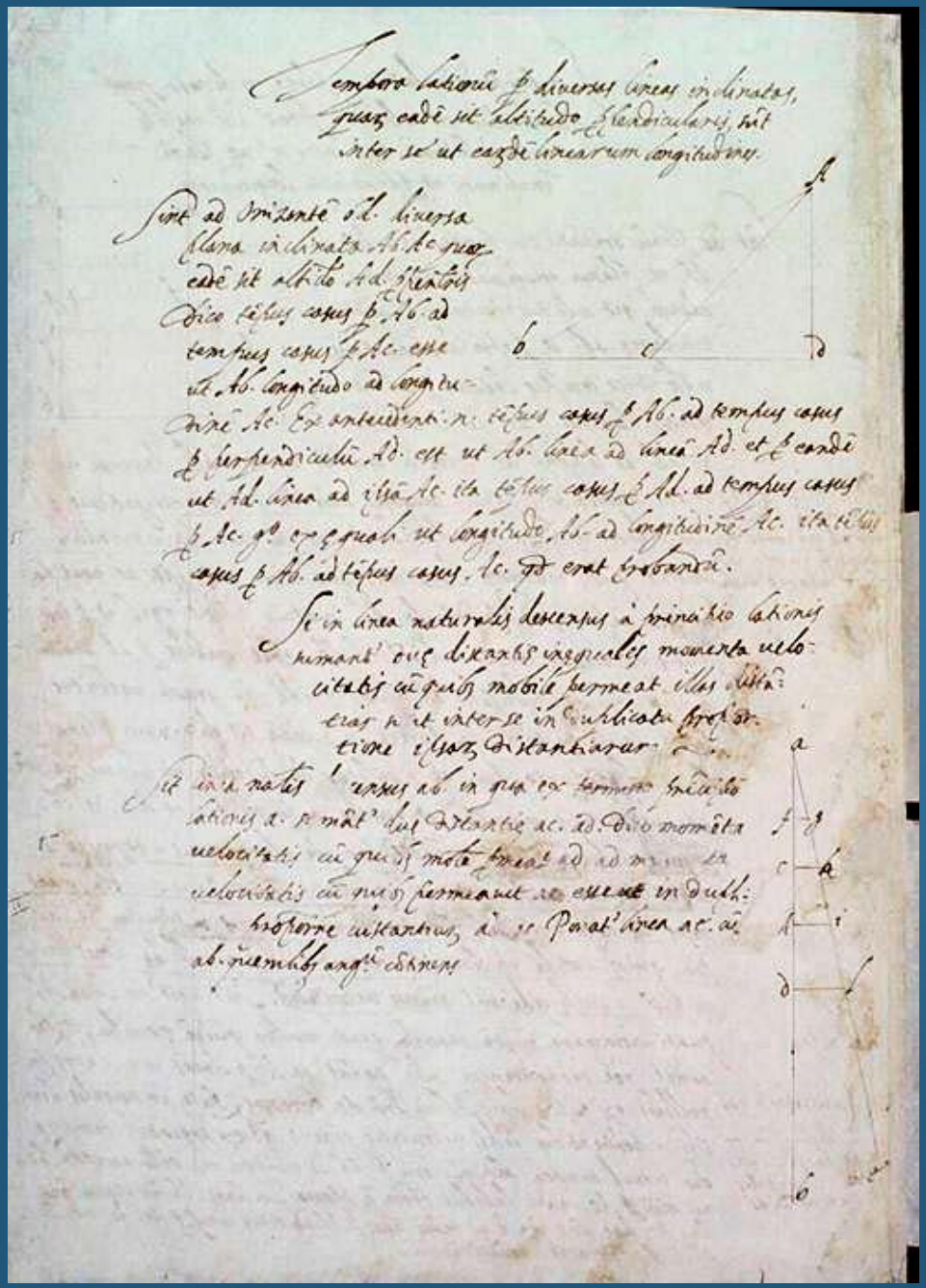
f. 179r


Cu/Fe
cases
10
8
6
4
2
0
0,005
0,015
0,025
0,035
0,045
0,055
0,065
0,075
text+draw.
und.+glossae
weight ratio

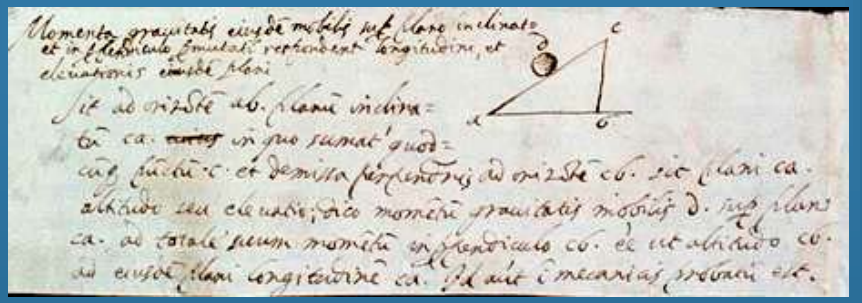

Pb/Fe
cases
8
7
6
5
4
3
2
1
0
0.005
0.015
0.025
0.035
0.045
0.055
0.065
0.075
weight ratio


(Cu/Zn)/10
cases
12
10
8
6
4
2
0
weight ratio

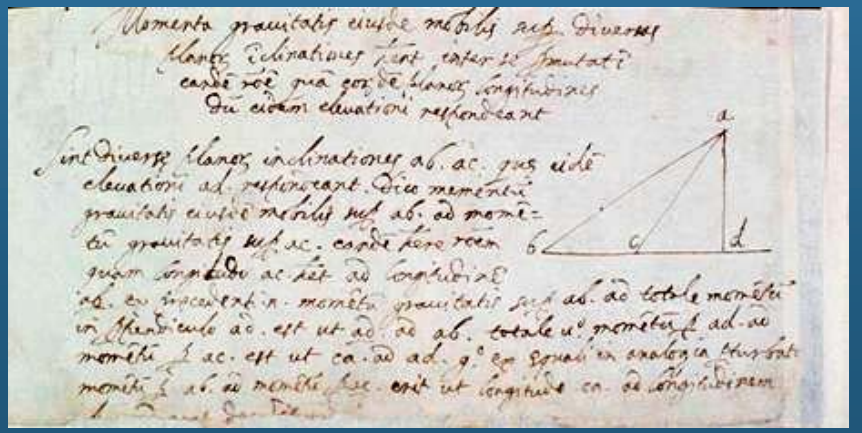
f. 179v



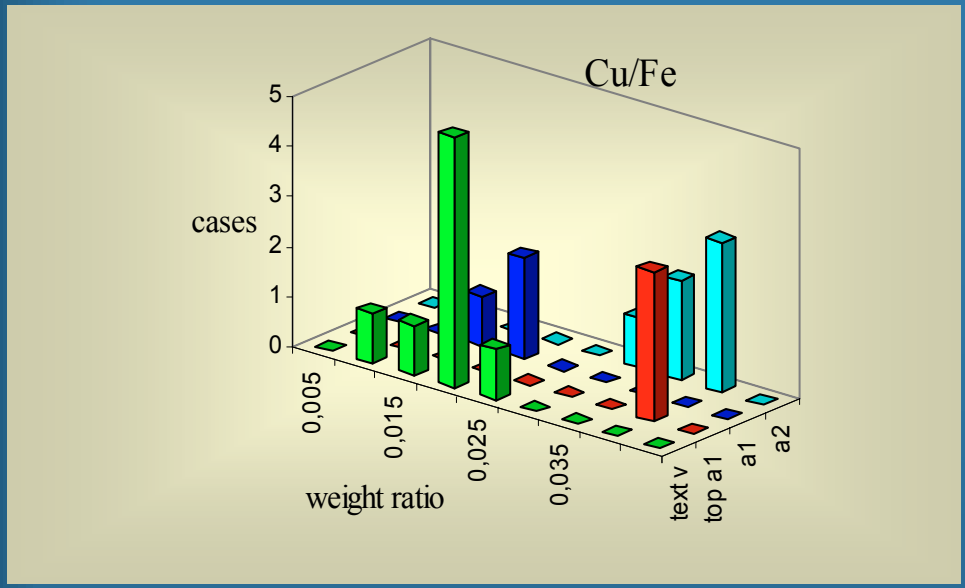
Momenta gravitatis eiusdē mobilis sup. plane inclinatū et in ē descripta figuratis respondentia longitudini, et elevationis eiusdē plani

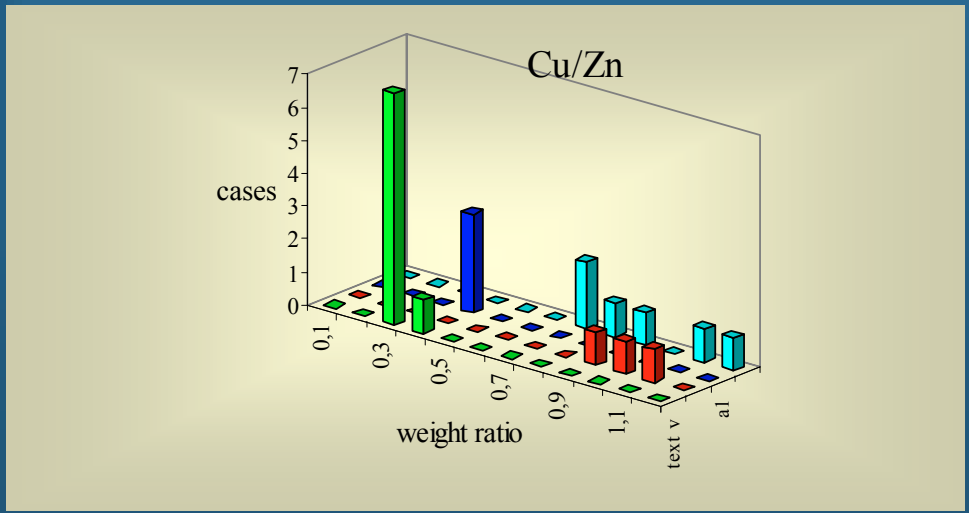


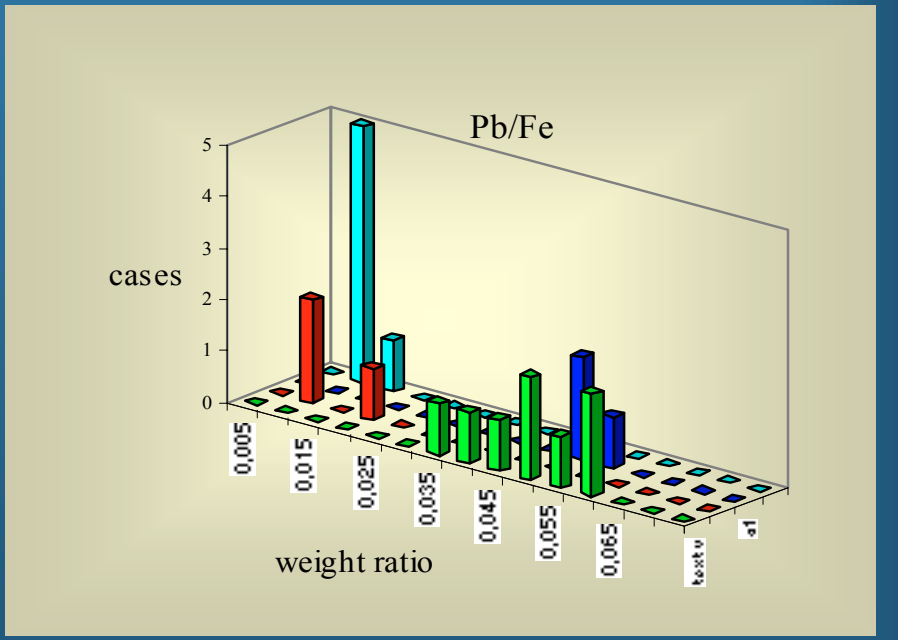
Momenta gravitatis eiusdē mobilis sup. diversas planas elevationes sēt, inter se figuratis eadē rōe qua sūt ē planis longitudines eis eisdē elevationi respondentes



f. 179v


Cu/Fe
cases
5
4
3
2
1
0
0,005
0,015
0,025
0,035
weight ratio
text v
top a1
a1
a2

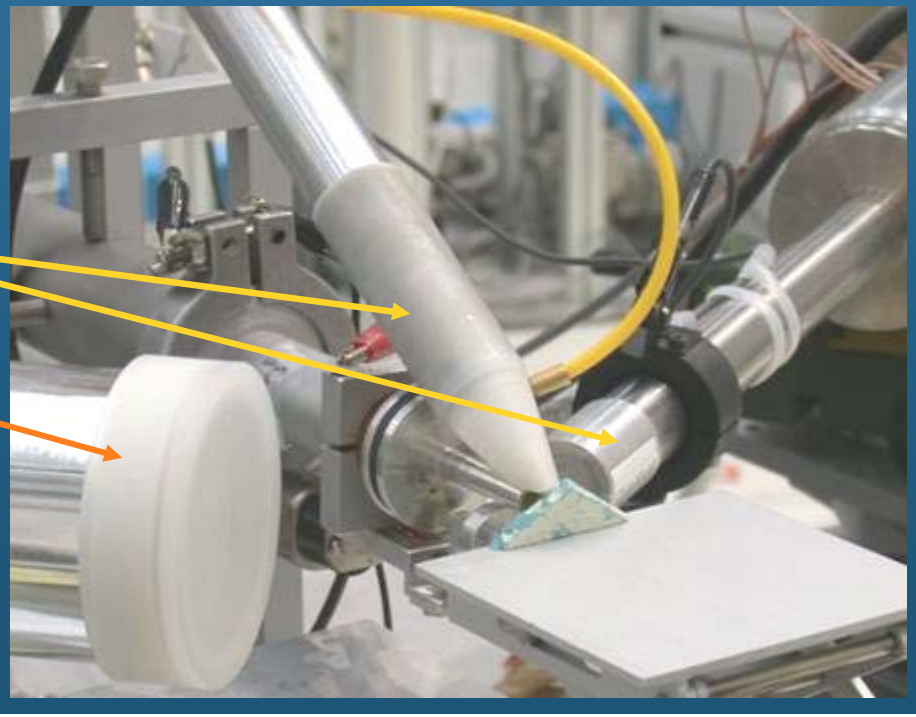

Cu/Zn
cases
7
6
5
4
3
2
1
0
0,1
0,3
0,5
0,7
0,9
1,1
weight ratio
text v
a1


Pb/Fe
cases
5
4
3
2
1
0
0,005
0,015
0,025
0,035
0,045
0,055
0,065
weight ratio
text v
a1

Simultaneous PIXE and PIGE analysis

- In most cases, great advantage in combining PIXE and PIGE:
  - by γ rays, light elements are easily detected, while their detection through X rays is impossible at all or problematic

- External beam set-up equipped with:
  - two Si(Li) dets for X rays
  - Ge(Hp) det for γ rays



Glass mosaic tesserae from wall decorations in Villa Adriana (Tivoli)

Surface inhomogeneities due to glass alterations

- **<u>Sodium</u> detection and quantification is of the greatest importance to characterise ancient glass**

In Europe, two typologies are found, depending on the component used to lower the melting temperature of silica:

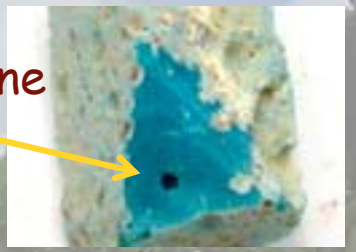
- ***natron*** **(sodium carbonate) → glass with high Na_2O and low K_2O content (as in Roman and Early Middle Age glass)**
- **Ashes from plants → glass with high K_2O content (later periods)**

PIXE and PIGE analysis of ancient glass

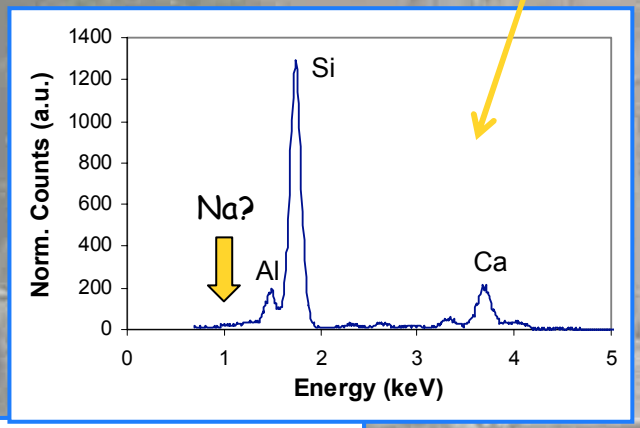
- **Surface alterations and crusts prevent from detecting sodium with PIXE**

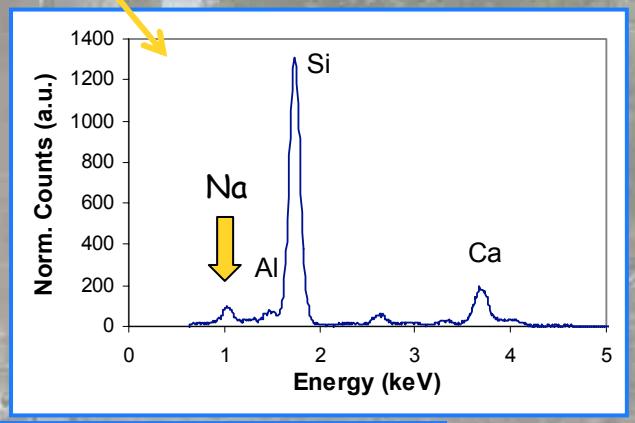
Coloured but more opaque zone (apparently with no alteration however)

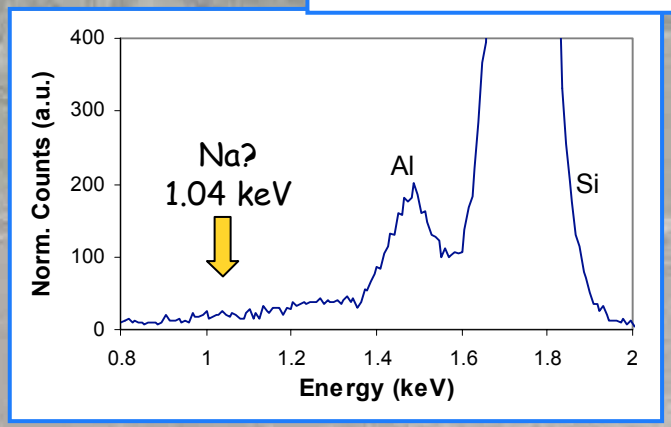
"Freshly" cut zone

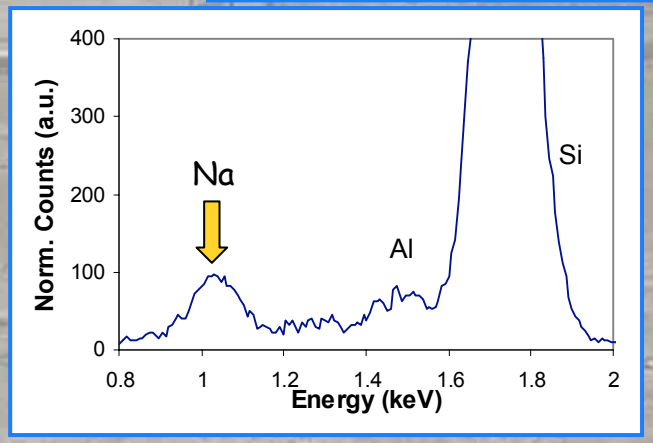


Na doesn't seem to be present...





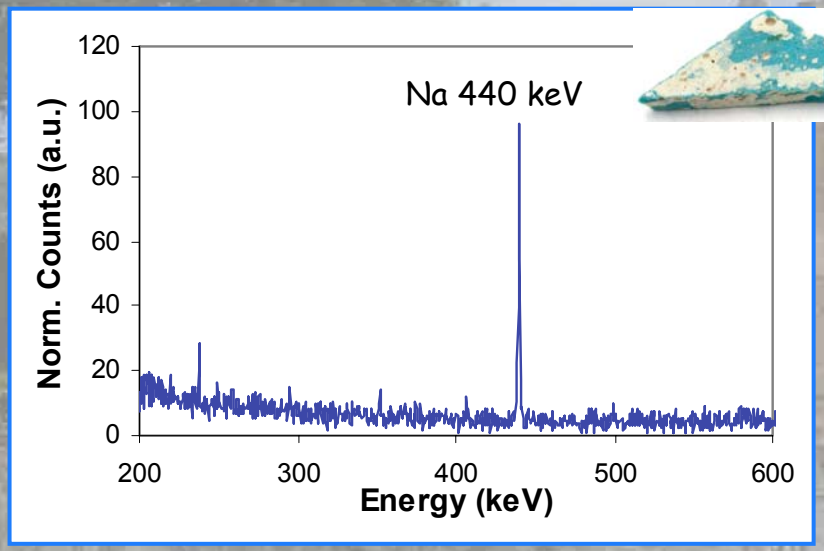




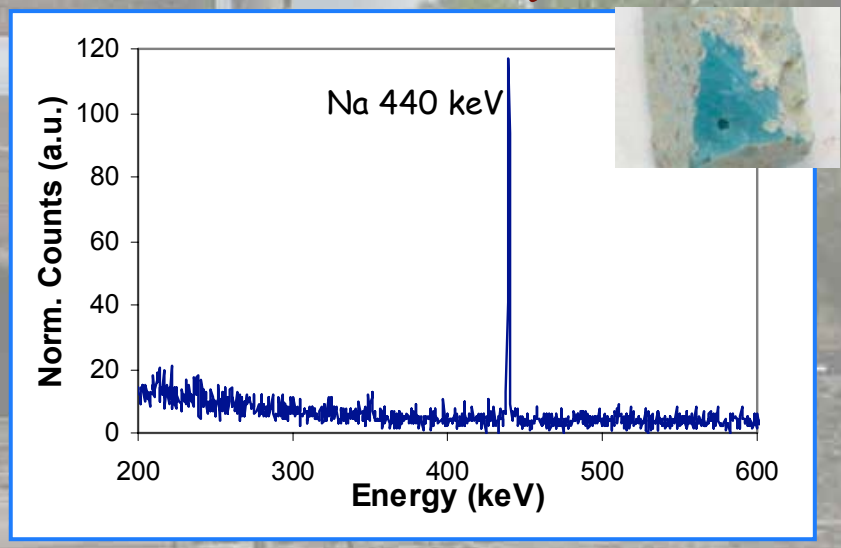
PIXE and PIGE analysis of ancient glass

Instead, using **PIGE** (Na characteristic γ-rays at 441 keV)

More opaque zone

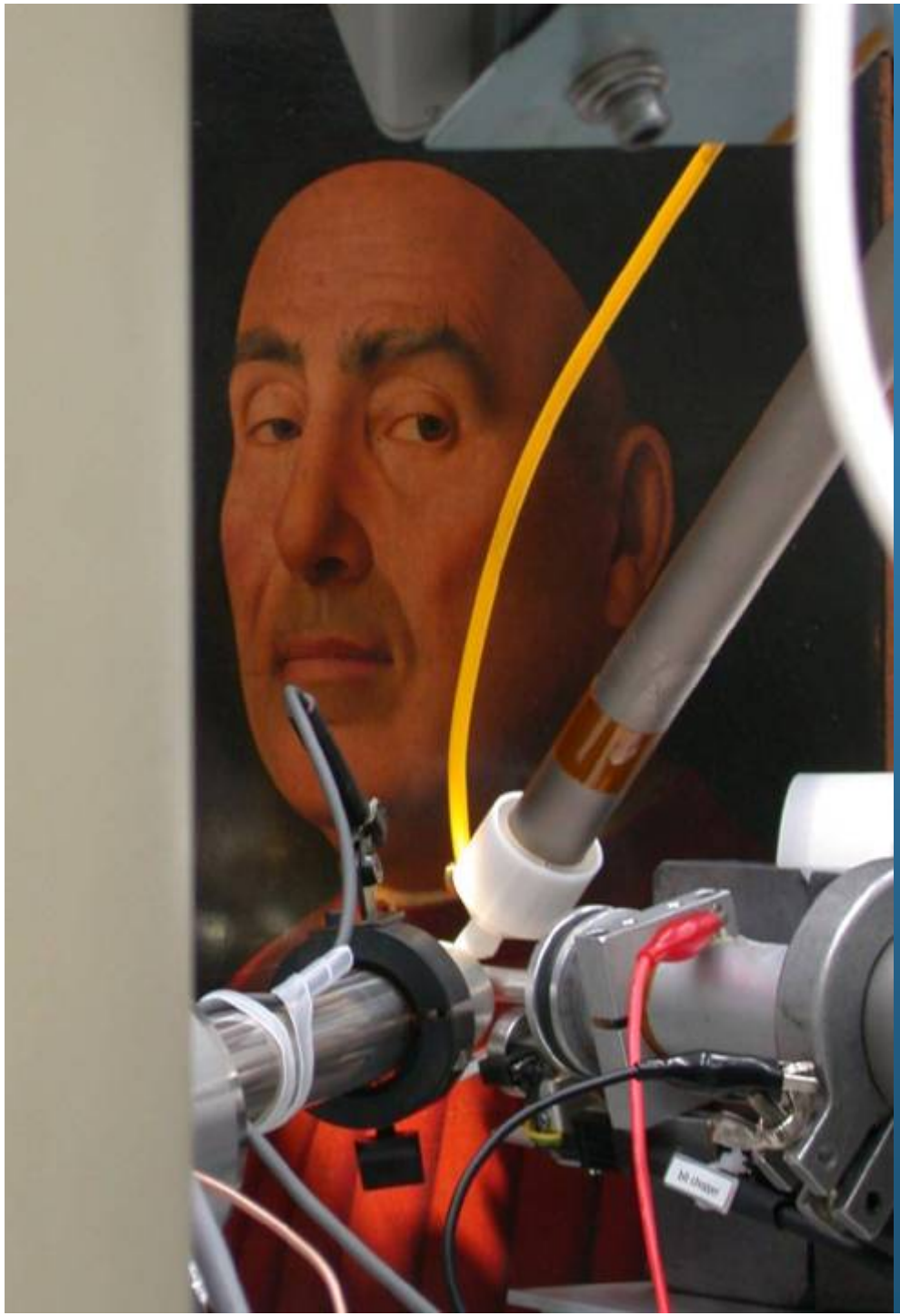


Freshly cut zone



Na can be quantified by PIGE even in the presence of surface alterations, with no need of picking up samples!

High - Na_2O were found (from 10% to 20%, depending on colour), with a composition compatible with that in typical Na-Ca Roman glass



Analysis of paintings on wood on canvas

Understanding the "secrets" of painting techniques of famous artists and/or reconstructing the history of a specific painting (possibility to be a fake, previous restorations, etc.)

PIXE – PIGE analysis of "Ritratto Trivulzio" by Antonello da Messina, at LABEC, Florence

The protective varnish layer on paintings

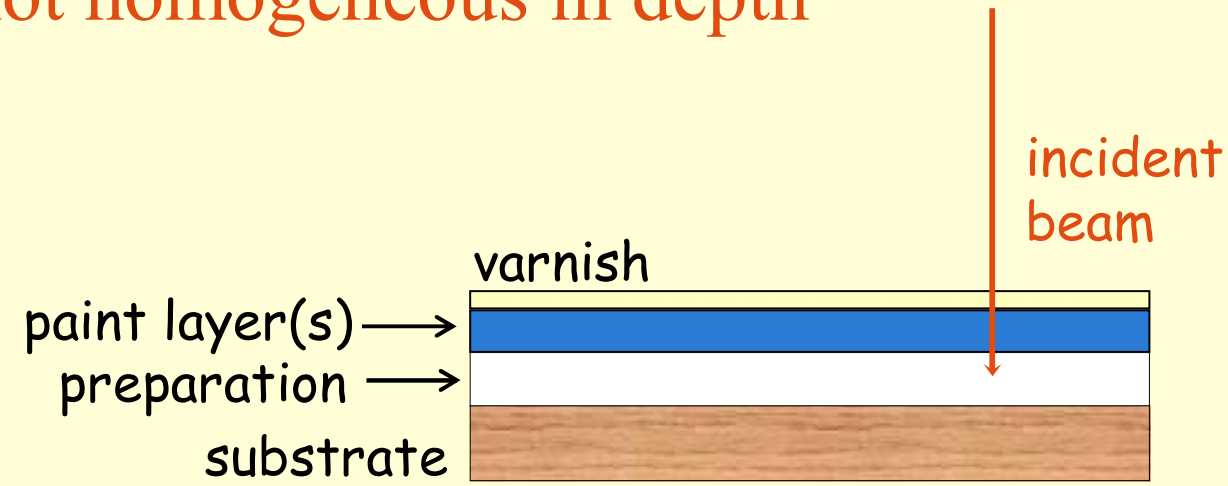
two problems

1) discriminating components in the varnish from those in paint and substrate layers

2) PIXE detection of light elements in the underlying layers (X ray absorption)

Stratigraphic analysis

If the target is not homogeneous in depth



traditional PIXE does not provide information about the stratigraphic layout of elements.

Indeed, when the beam penetrates through different layers, their contributions are added up in the spectrum with no possibility to discriminate where X rays originate from

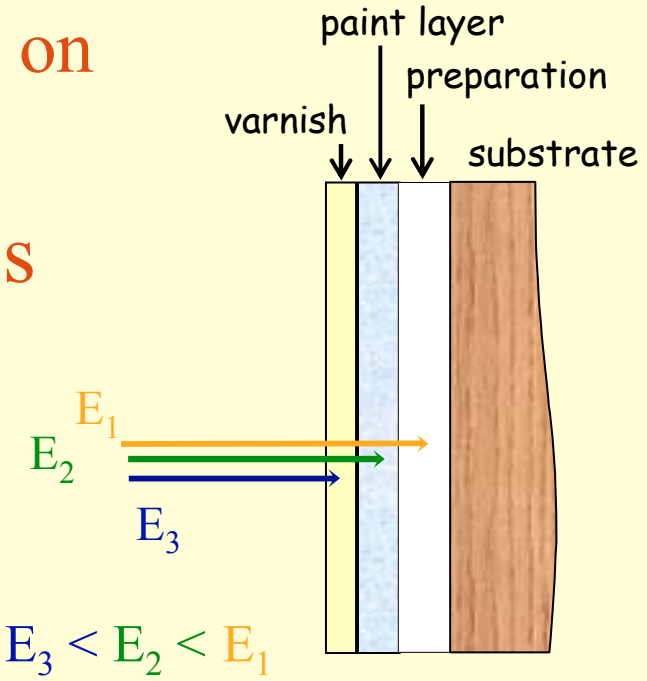
Differential PIXE

Consists in performing measurements on the same area

with beams of different energies

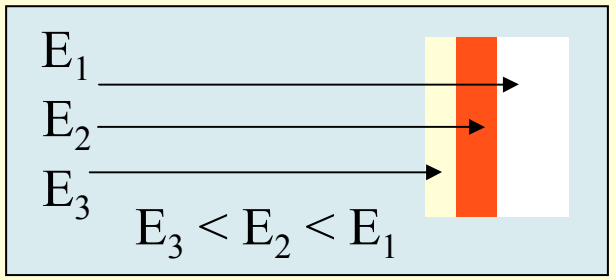
At different energies, beam ranges are different

→ probed depth also changes



By comparing X ray spectra taken at different energies, stratigraphic information can be obtained

Differential PIXE



Analysis is made complex by several factors:

The number of layers and their thickness are not known *a priori*, therefore the most suitable choice of beam energies to discriminate layers is not obvious

the same element may be present in different layers

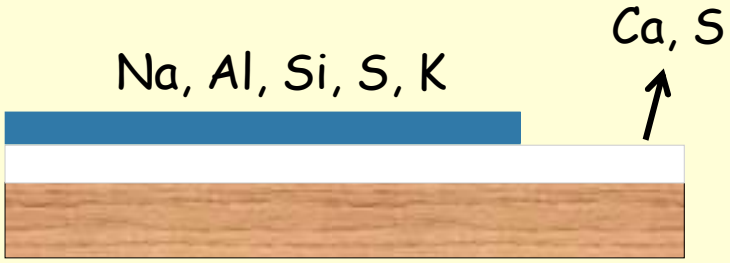
X ray production cross sections change significantly, and in different ways for the different elements, at varying beam energies ⇨ Quantitative analysis more difficult

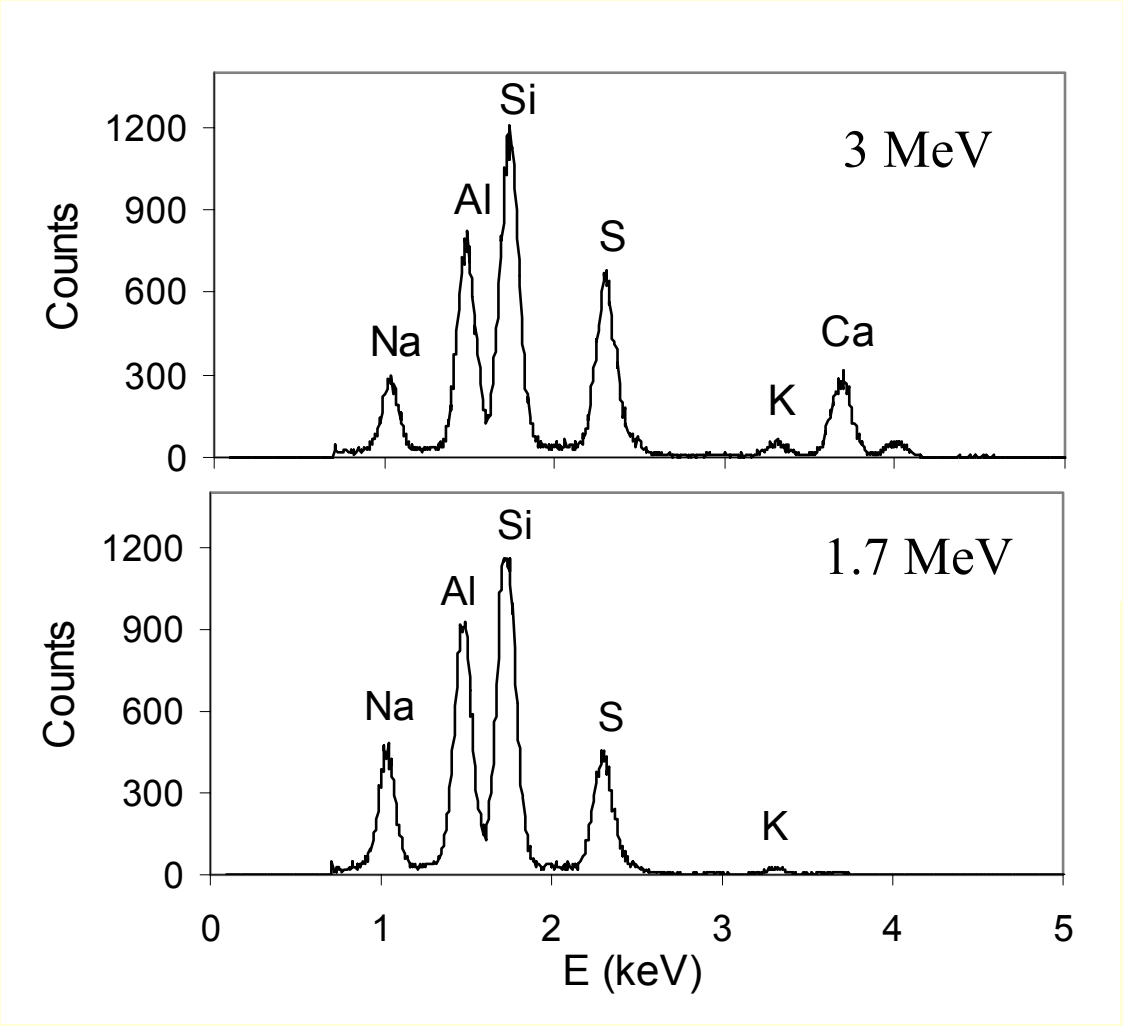
However, diff. PIXE is often a "unique" tool to learn about elemental depth distribution in paintings <u>without picking up samples</u>

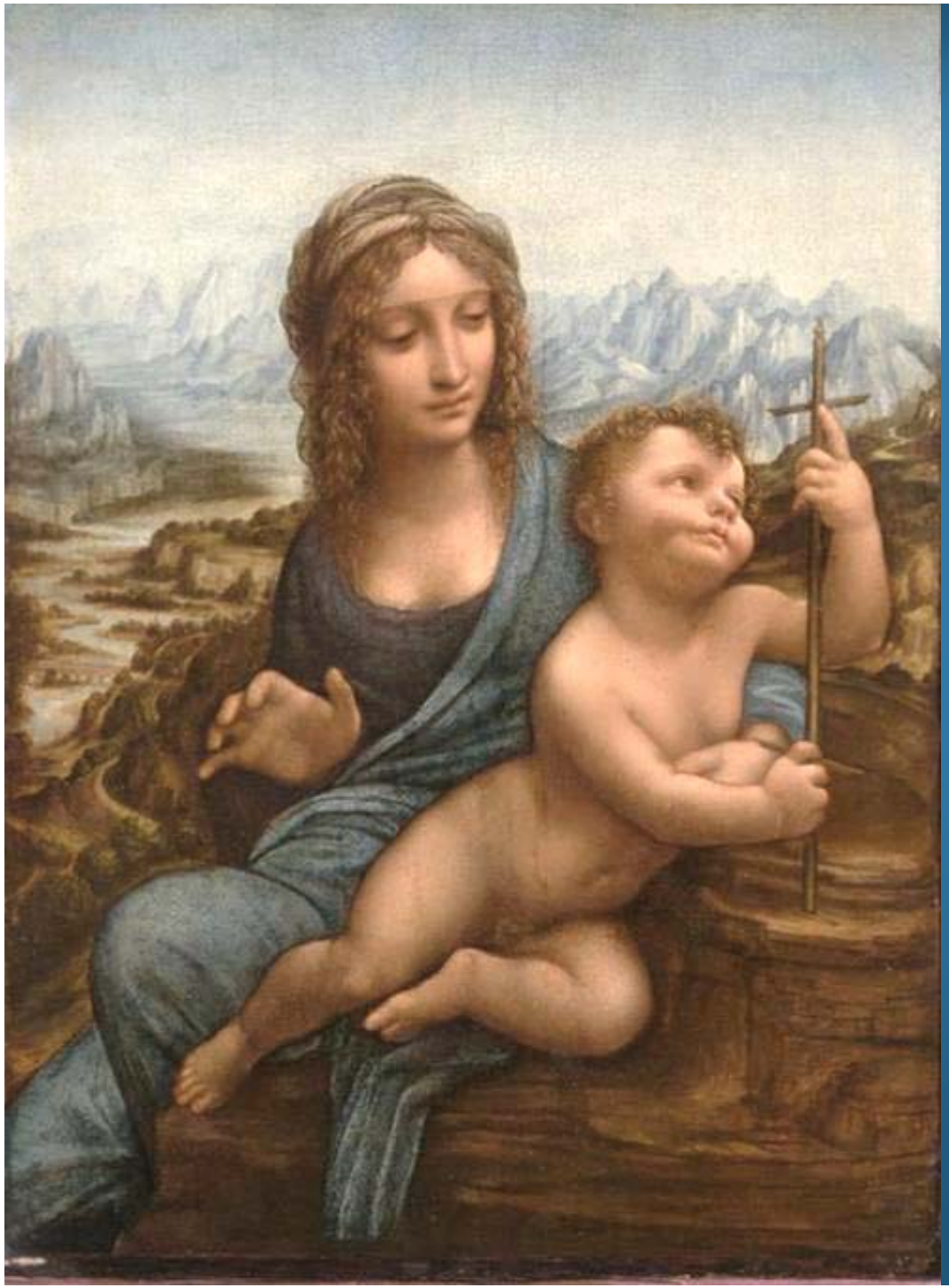
PIXE spectra at different energies

Prepared sample:

wood substrate, chalk ($CaSO_4$) preparation, lapislazuli paint







Leonardo
Madonna dei fusi
ex-Reford version

(private collection)

Oil painting on wood,
50 x 36

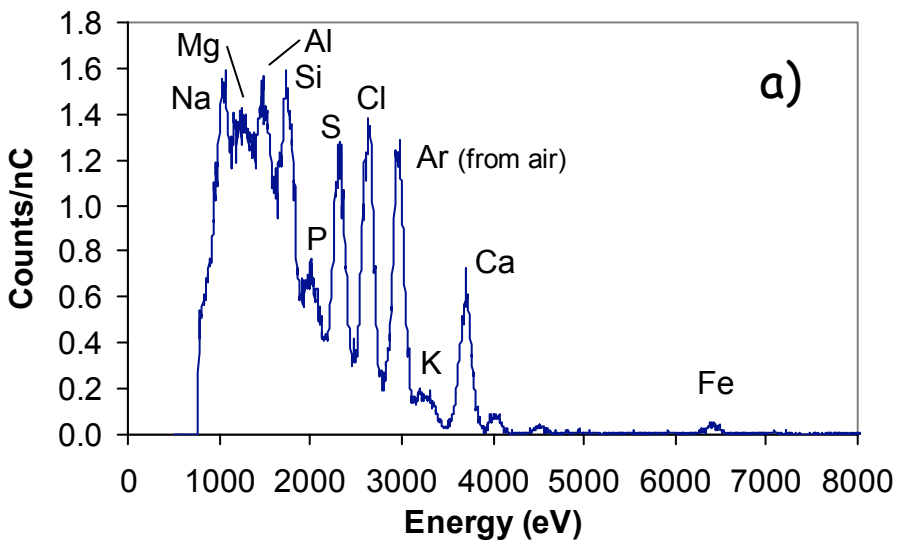
Presumably painted
in 1501

Varnish composition

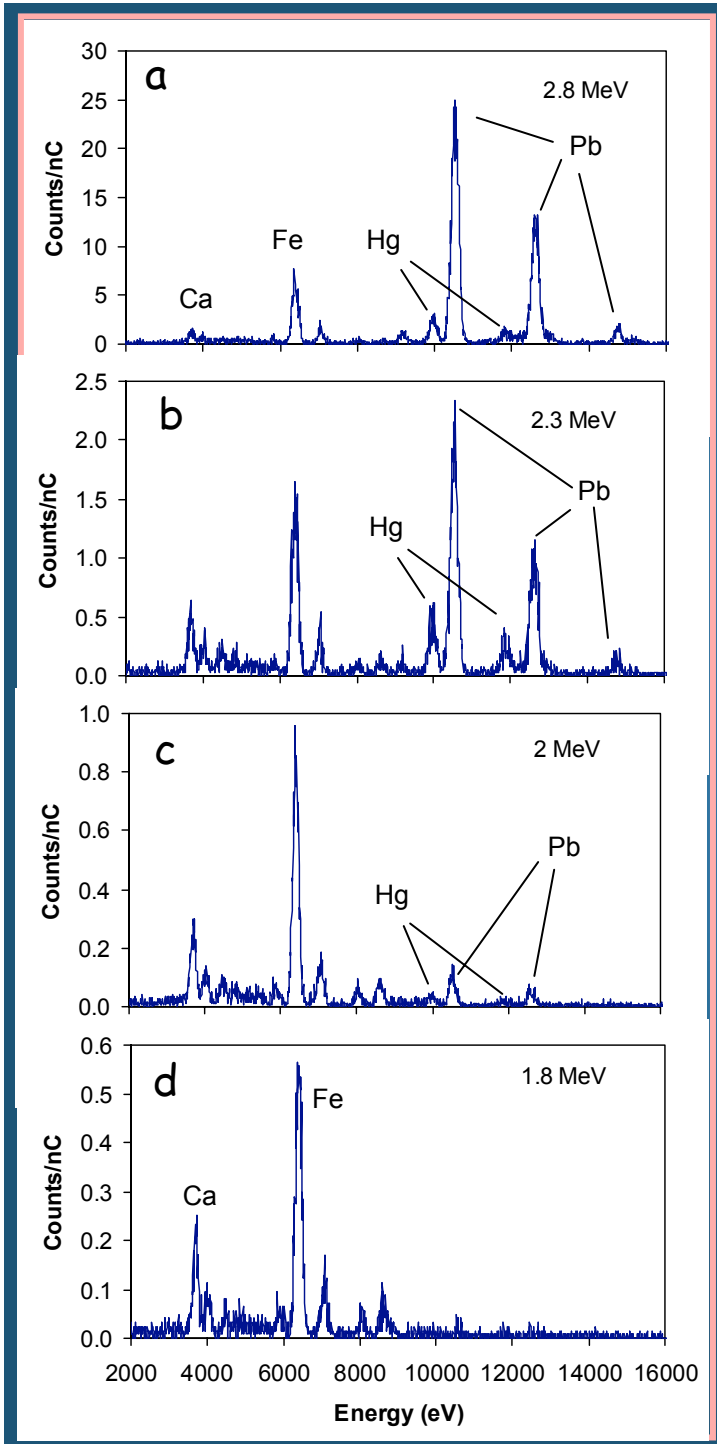
Using differential PIXE, the varnish composition was evaluated from the spectra collected at the lowest beam energy, when protons do not reach the underlying paint and preparation layers

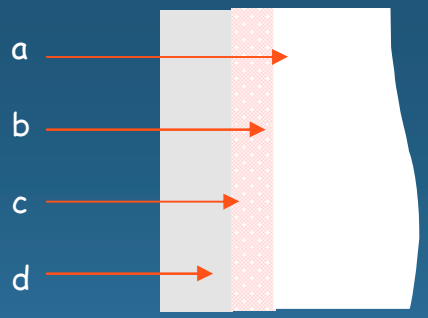
Element	Concentration
Na, Cl, Ca	~ 1‰
Fe	~ 0.5‰
Al, Si, S	0.5-1‰
Mg, P, K	0.2-0.5‰
Ti, Cu, Ba	~ 0.1‰
Zn	0.1-1‰

From the comparison of differential PIXE spectra, it was also possible to estimate the thickness of the varnish layer: from ~30 to ~ 50 micron

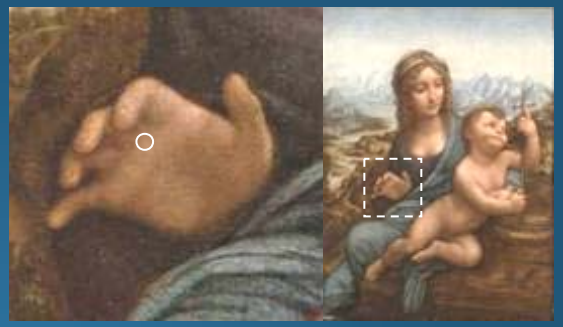


Varnish spectra for a) lower-Z elements and b) higher-Z elements





Incarnato



Fe → hematite?

Hg → use of cinnabar as red pigment

Pb → lead-white (in the paint layer? in the preparation substrate? in both?)

Ca and Fe peaks are entirely accounted for by their abundance in the varnish.

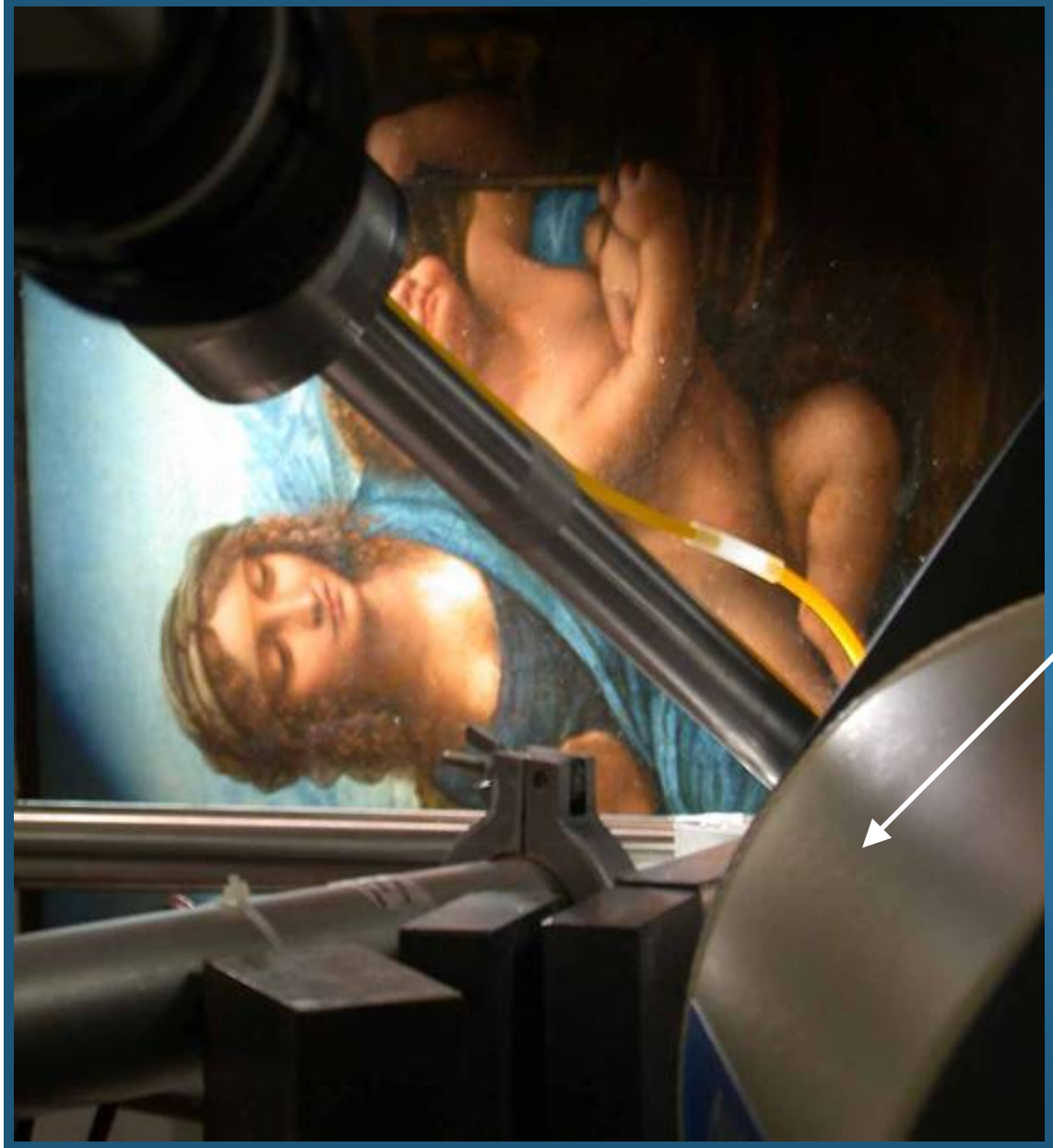
An estimate of the paint layer thickness is obtained: only 15 – 20 μm!!

The protective varnish layer on paintings

two problems

1) discriminating components in the varnish from those in paint and substrate layers

2) detecting light elements in the underlying layers (X ray absorption)

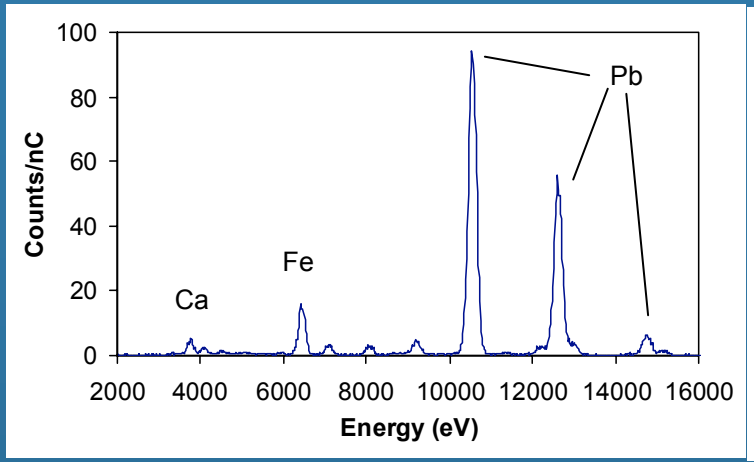


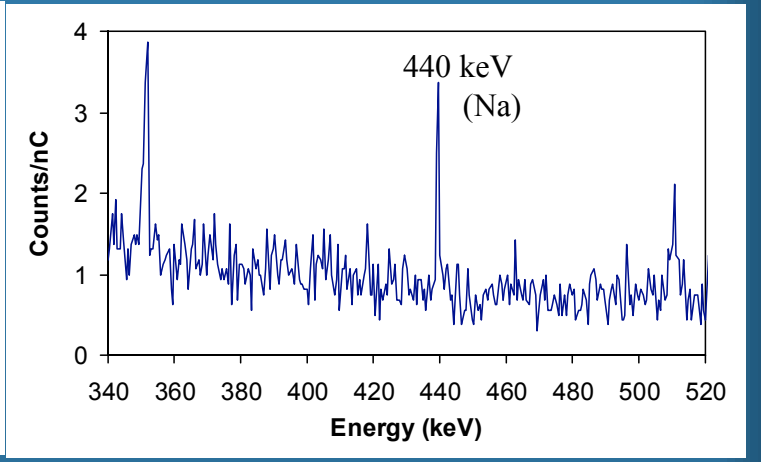
simultaneous use of PIGE to detect light elements

Identification of lapislazuli by PIGE

Mountains, pale blue, original

Pb in the PIXE spectrum mainly derives from lead white mixed in the blue paint



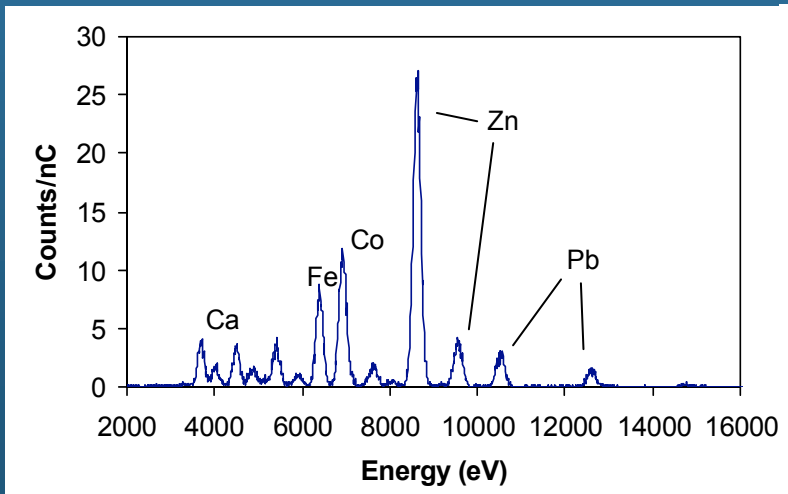


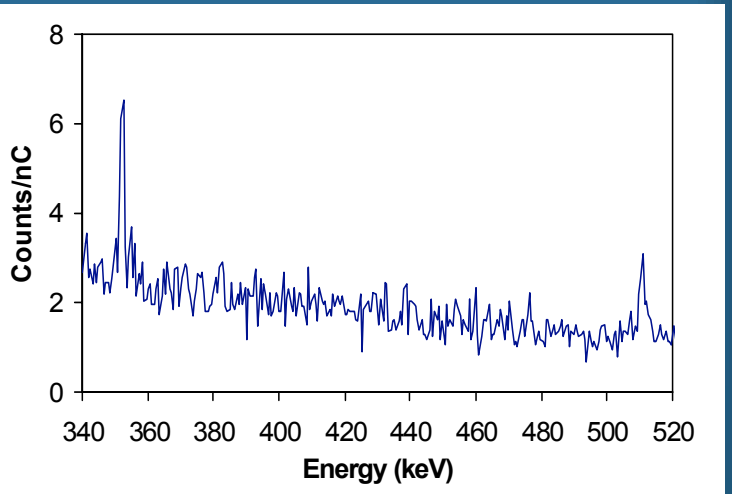
PIXE spectrum

PIGE spectrum

Gown of the Virgin, dark blue, restored

Co (cobalt blue) and Zn (zinc white) identify this as a restored detail. The small Pb peaks are due to the beam halo hitting original blue areas around (as seen by a lateral scan)

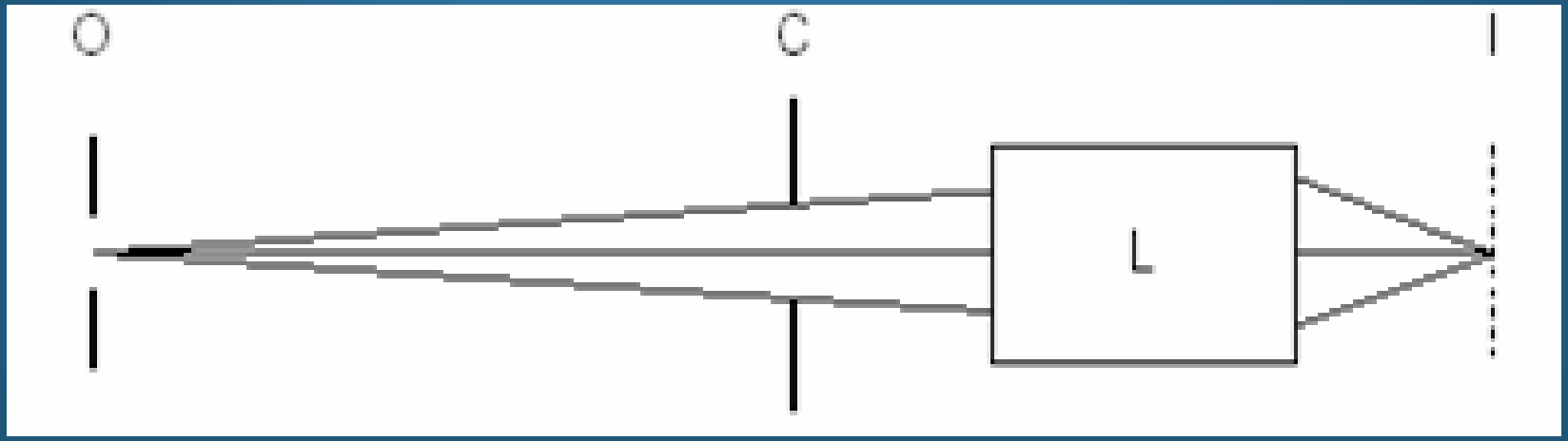




One can also produce an external microbeam

Through collimation, well defined beams of no less than 100-200 μm can be produced

Smaller-size beams are obtained with strong focusing using lenses (quadrupole multiplets)



External microbeam set-up

Si_3N_4 exit window, 100 nm thickness

Target at ~2 mm from exit window

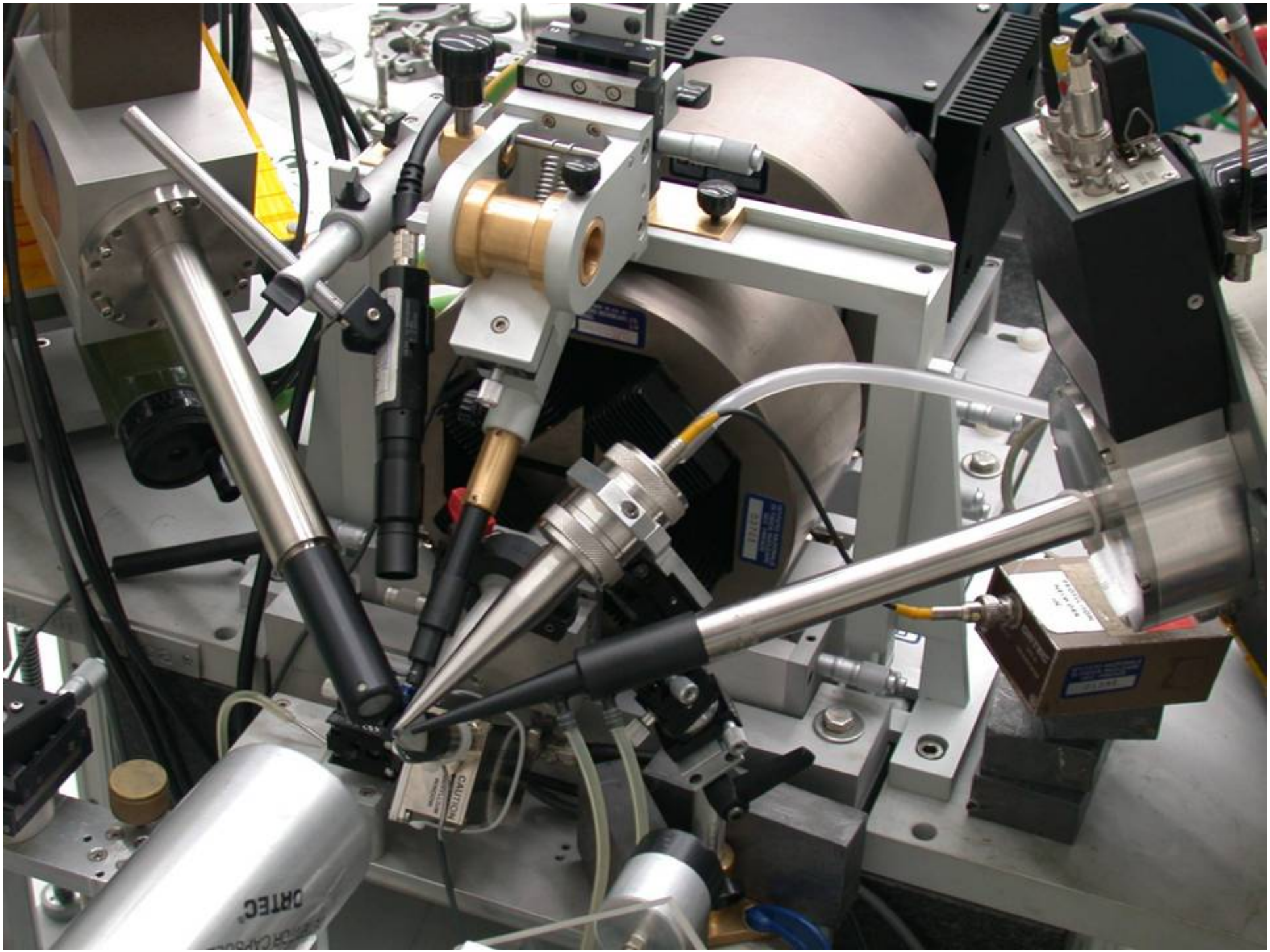
X and γ detection systems as in standard external set-up

Beam magnetic scan over the sample

Mechanical scan, i.e. sample micrometric displacement in front of the beam

LIST-MODE (E,x,y) acquisition → element maps

Minimum beam size on target: 10 μm

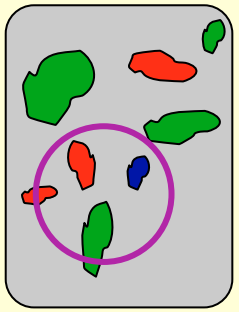

ORTEC
CAUTION

scanning-IBA for Cultural Heritage: why?

Details of small size or inhomogeneous structure (even ~100 μm) not always easily recognised by visual inspection

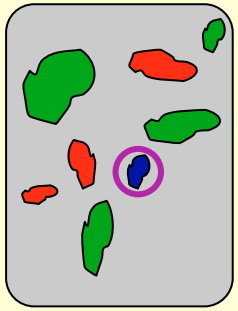
Risk of misleading information from single-spot measurements

too broad beam



risk of mixing info referring to different materials

too small beam



risk of analysing anomalous, non-representative "points"

Dramatic improvement in significance, reliability and completeness of information, using methodologies providing "compositional maps"

Scan of relatively large areas (~ some mm^2) with beams around 100-200 μm, acquiring "pixel by pixel" info

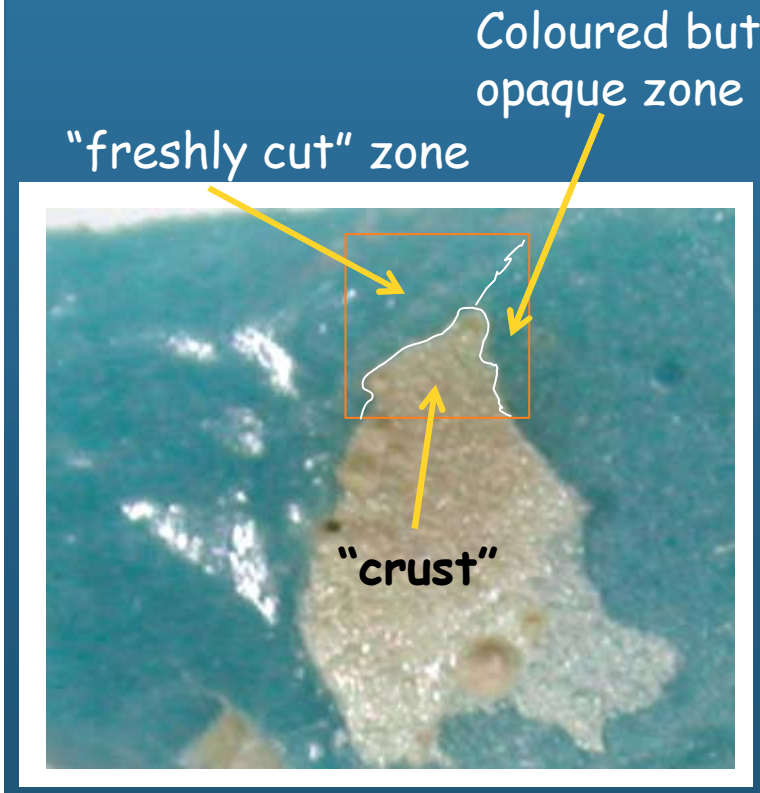
Sub milli-beam scanning IBA applications to Cultural Heritage

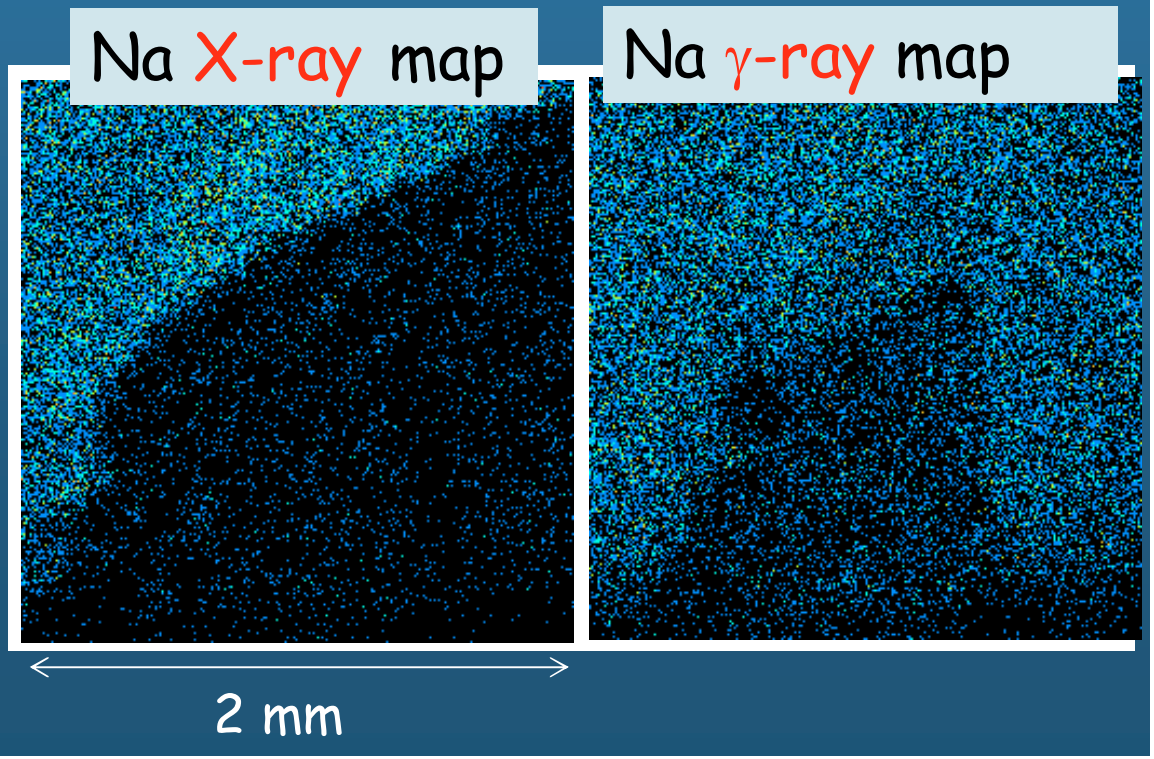
glass surface alterations

Glass tesserae from Villa Adriana (I)

Problem of detecting Na by PIXE, because of surface alterations

- Using the proton "sub milli"probe external set-up
  - ~ 80-100 micron beam size
  - Magnetic beam scan on samples

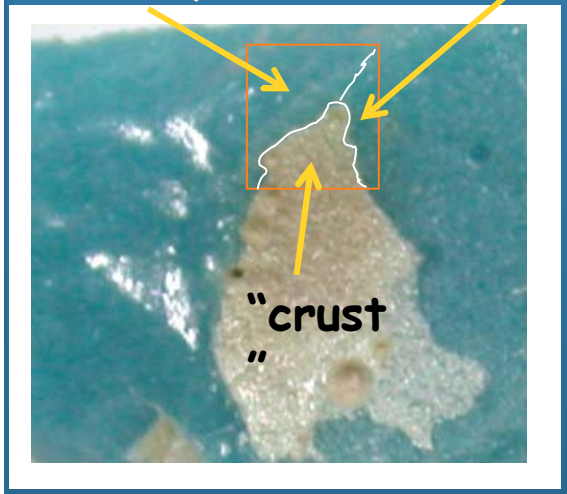




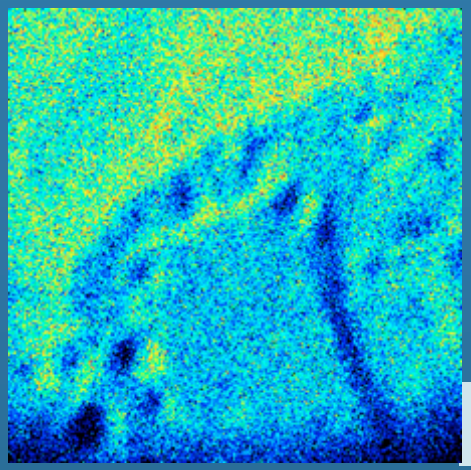
Glass tesserae from Villa Adriana (II)

Coloured but more opaque zone

"freshly cut" zone



X ray maps from other elements…

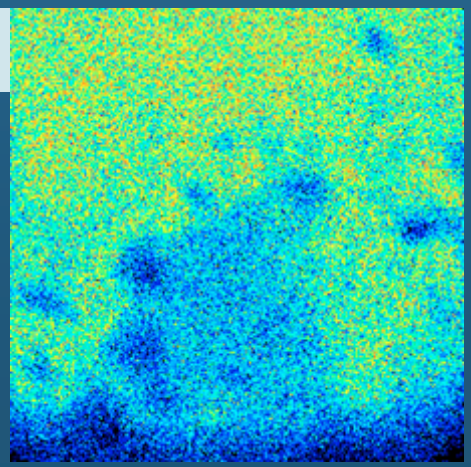


Si

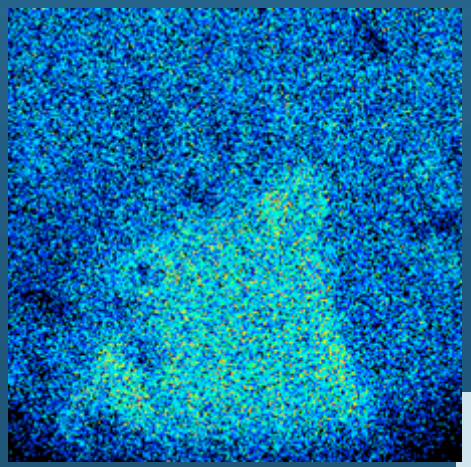
2 mm

Absorbed, though less than Na

Cu



Only absorbed in the crust (you may get an idea of its thickness…)

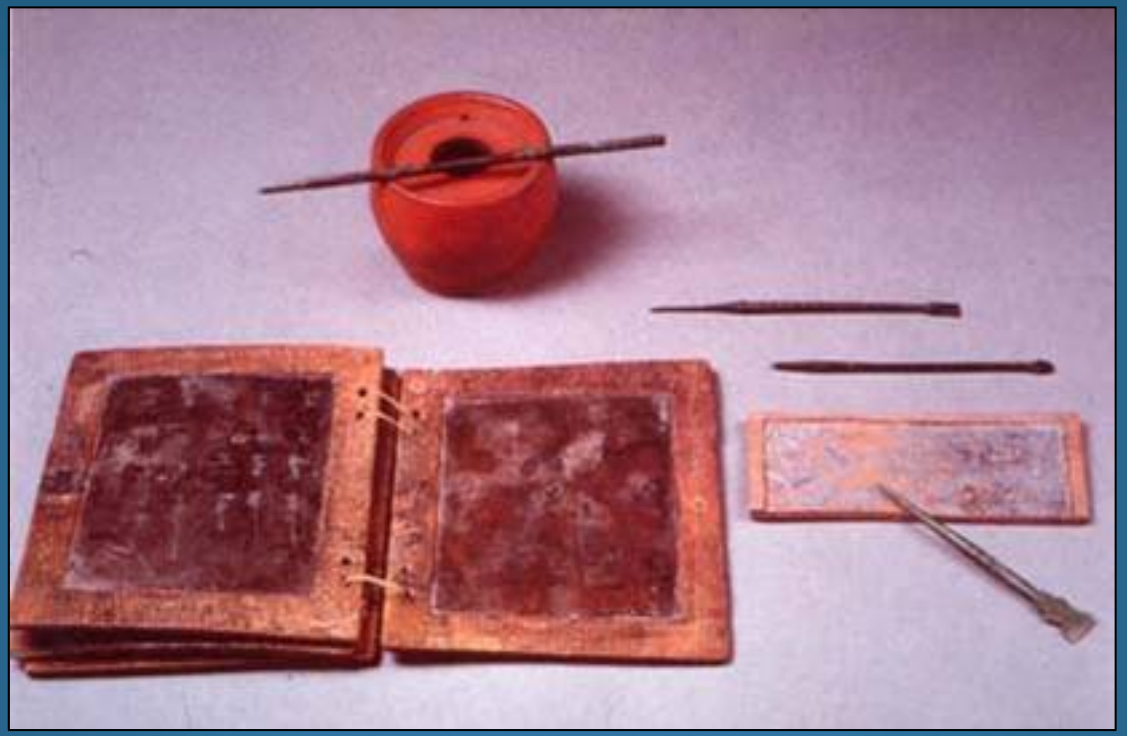


Fe

Larger contribution from the crust

Sub milli-beam scanning IBA applications to Cultural Heritage

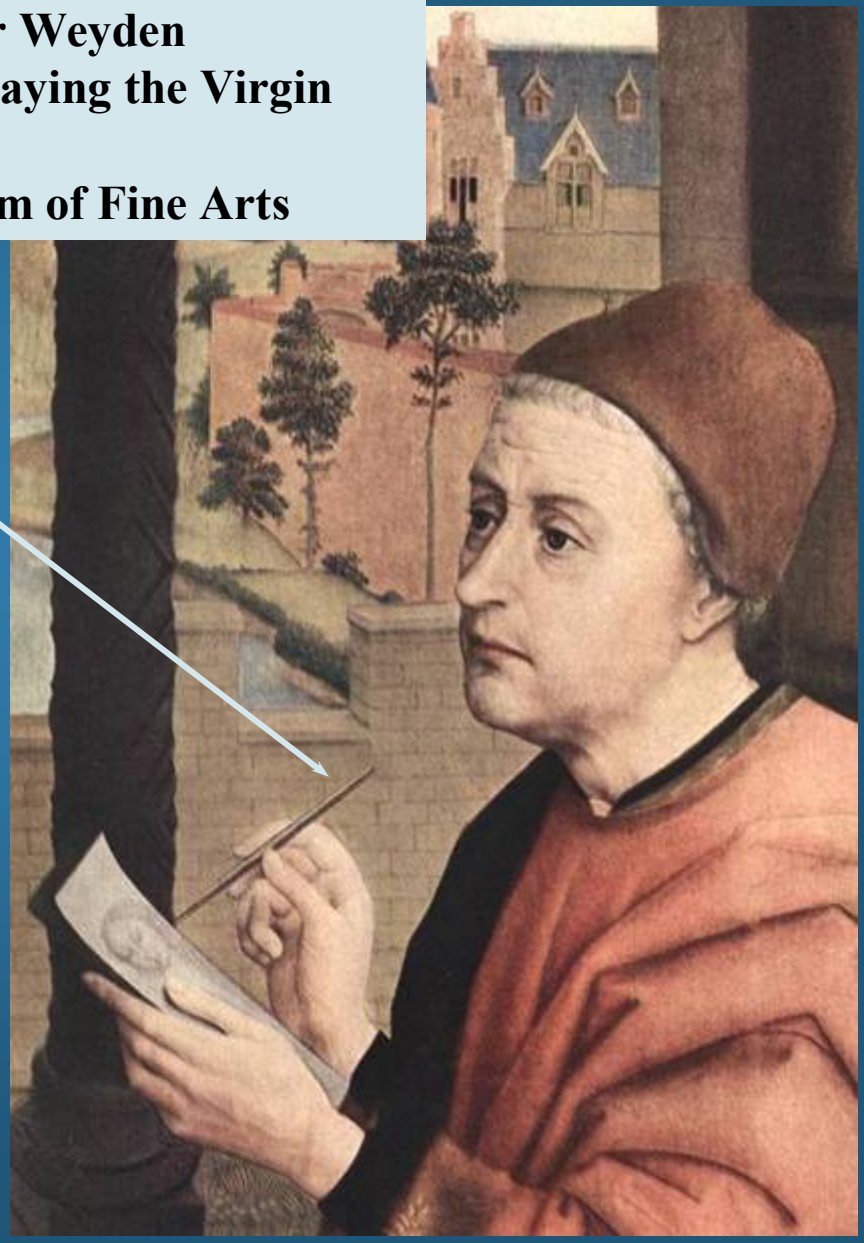
investigation of metal point drawings on coloured papers

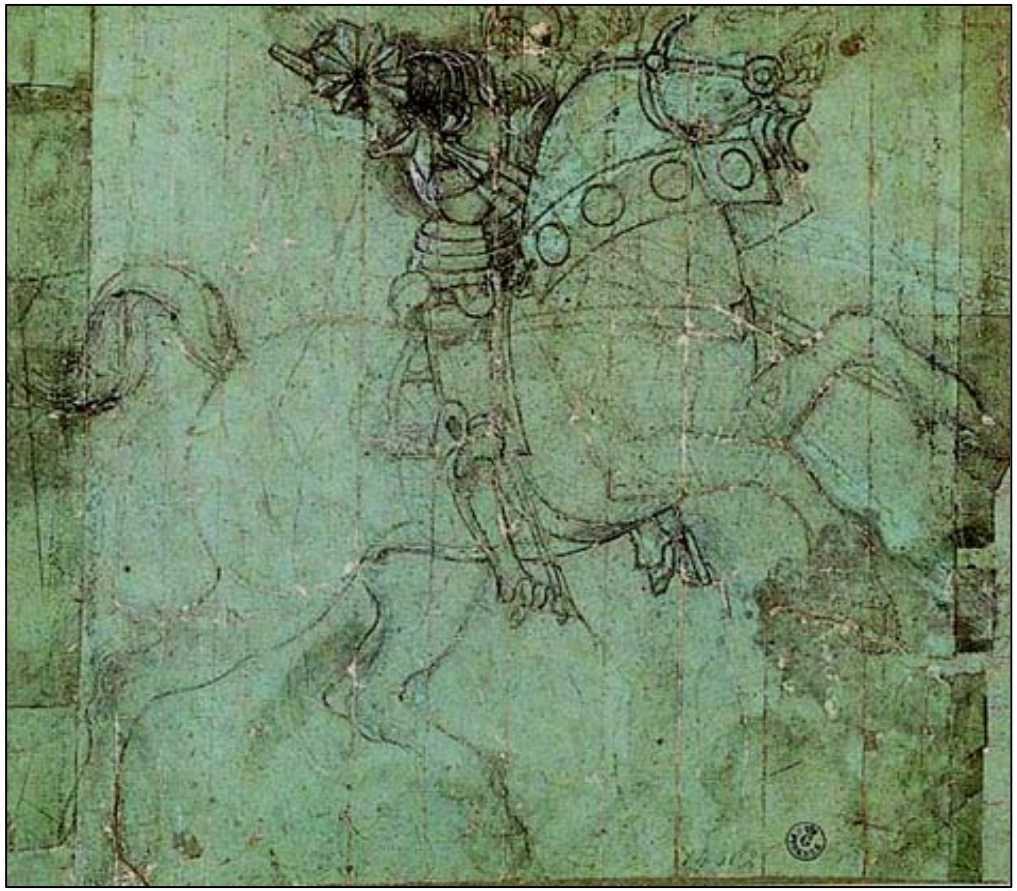


VARIOUS KINDS OF METAL STYLUS TO DRAW ON PAPER
(Köln, diocesan museum)

Silver stylus used by Hans Cranach
(Hannover, Landesmuseum)

Rogier Van der Weyden
St. Lucas portraying the Virgin
(detail)
Boston, Museum of Fine Arts





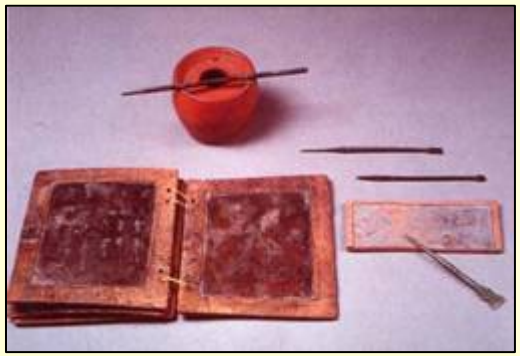
PAOLO UCCELLO – STUDY OF A KNIGHT
Uffizi, Gabinetto Disegni e Stampe
Metal point, lead white + earth-green prepared paper

PISANELLO
PROFILE OF A WOMAN
PARIS, LOUVRE
metal point on prepared white paper

LEONARDO DA VINCI
STUDY OF A DRAPERY
ROMA, ISTITUTO NAZIONALE
PER LA GRAFICA

metal point + lead white
red prepared paper

Metal-point drawings on prepared paper

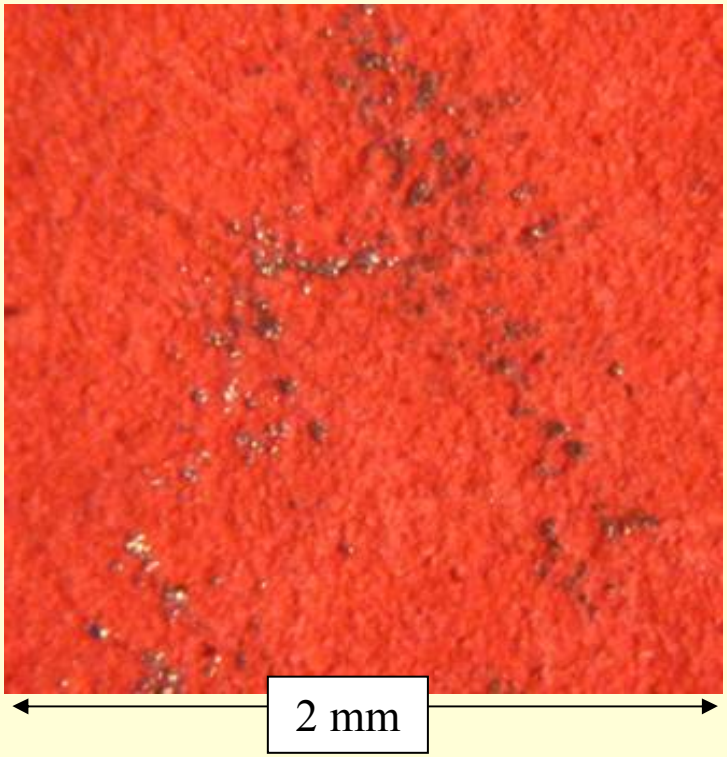


Knowledge of materials is needed for conservation purposes: one is dealing with very fragile and precious works, so far little studied, and mainly from the art-historical point of view

Problem:

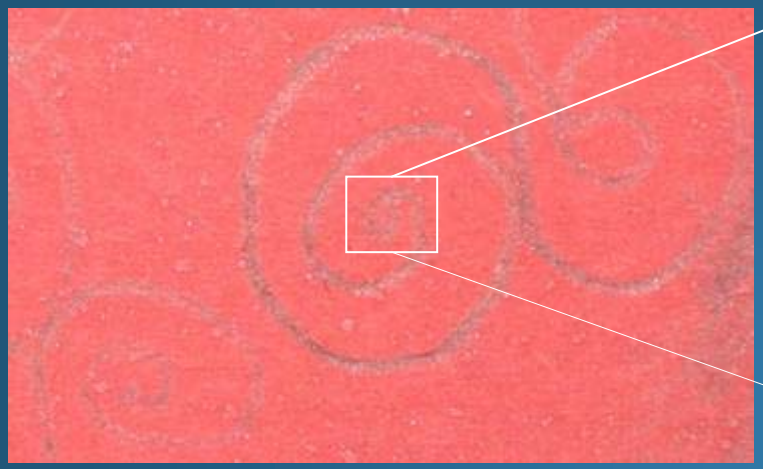
non uniform track left by the metal stylus make material identification difficult, especially when the paper is prepared using compounds of the same metal ⇩

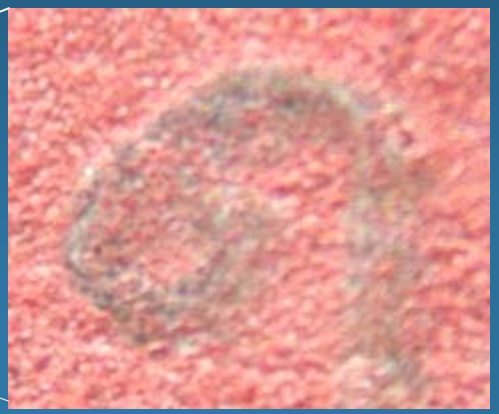
Need of a non-destructive *imaging* technique, with a space resolution of 100-200 μm at least

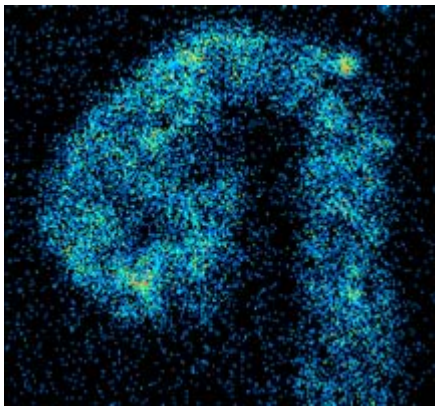


Paper prepared with cinnabar + Pb white

Cu stylus

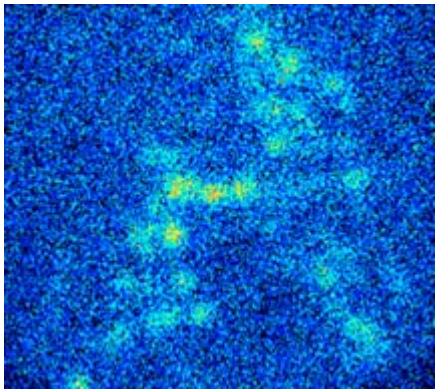






Cu map

Pb stylus



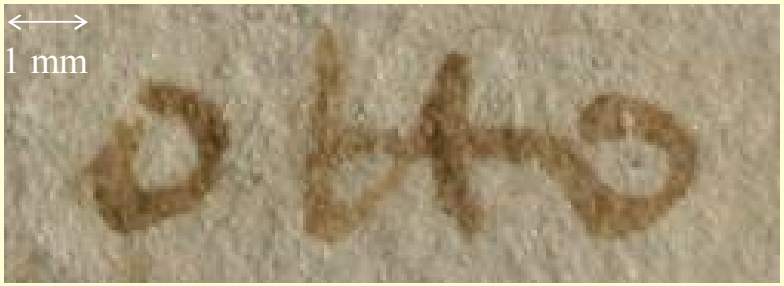
Pb map

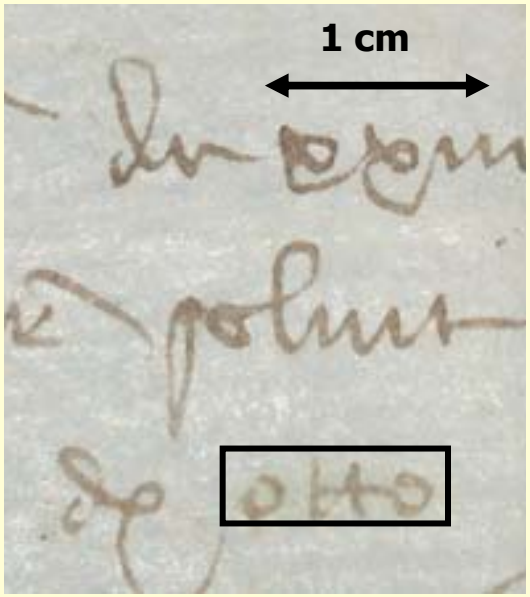
Sub milli-beam scanning IBA applications to Cultural Heritage

investigation of iron gall inks
to discriminate their different compositions

Iron gall inks

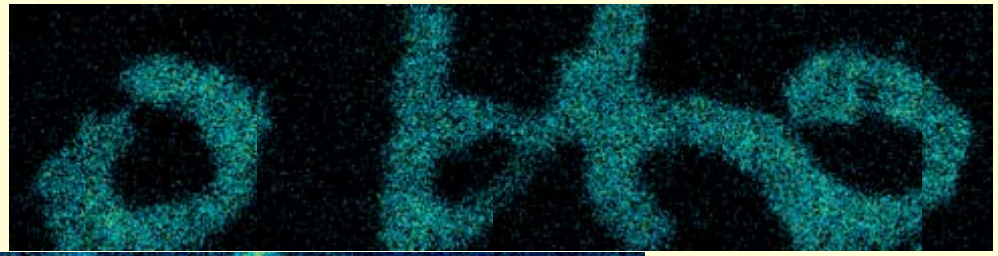
1)



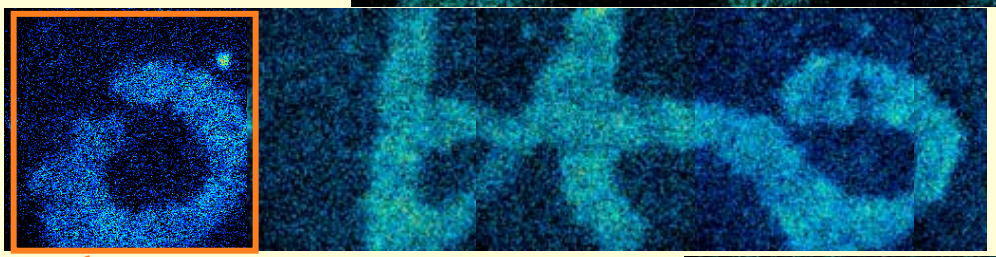


XVII century document from State Archive in Florence

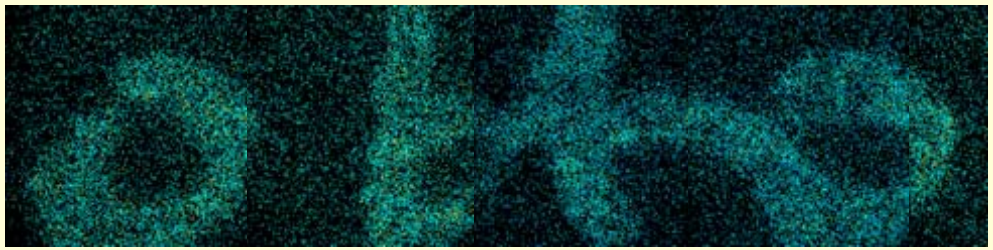
Cu X map

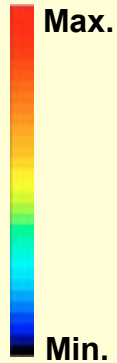


Fe X map

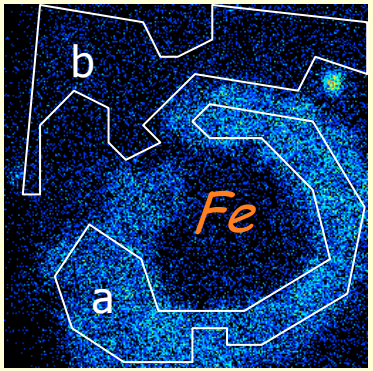


S X map

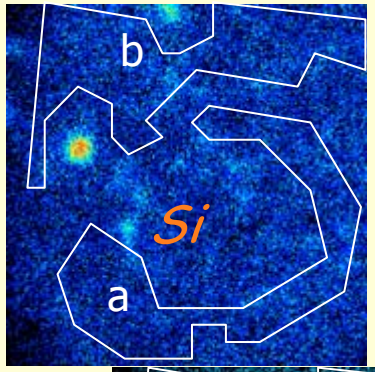


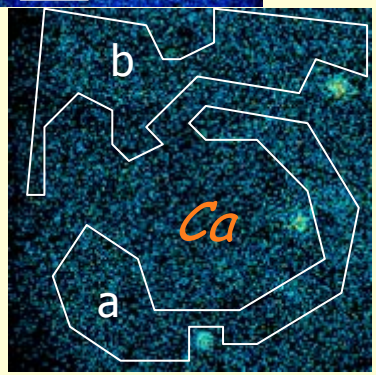


Possibility to select “good” areas, from which extracting quantitative reliable information

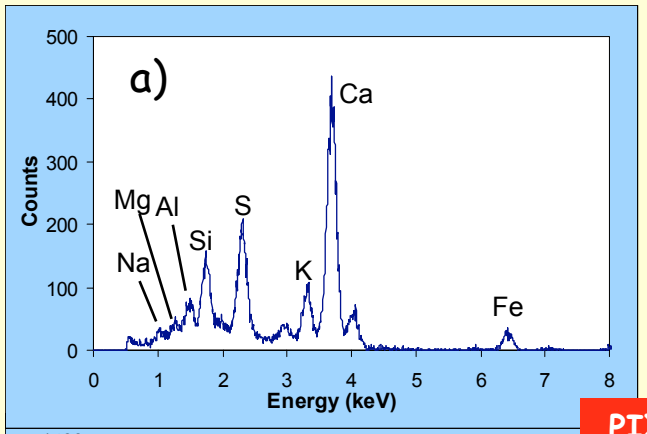


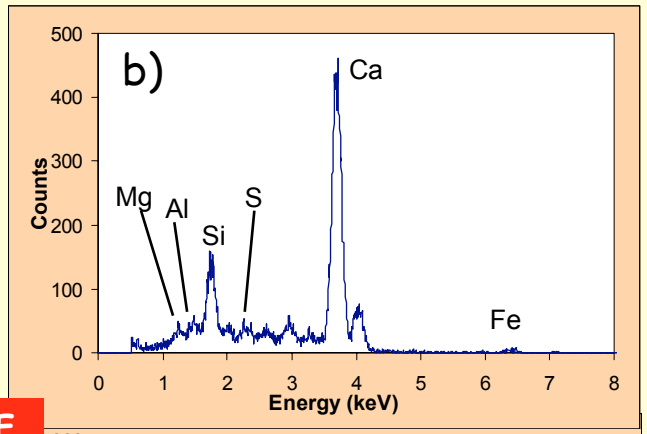
2 mm



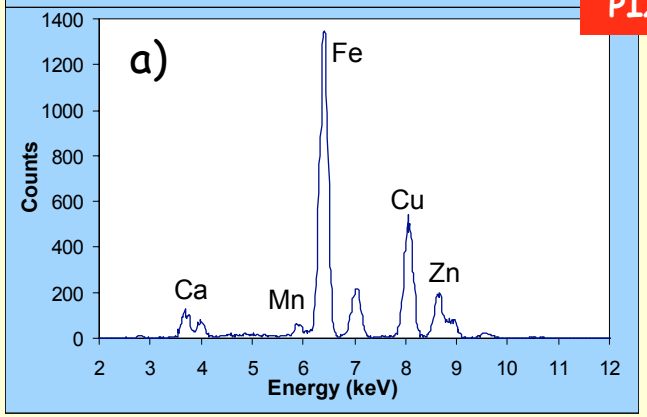


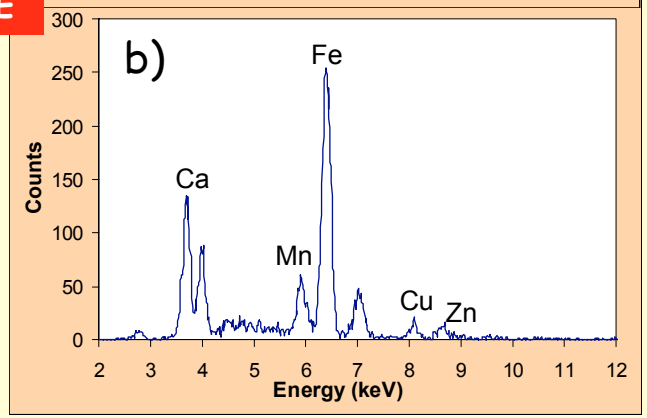
off-line spectra reconstruction



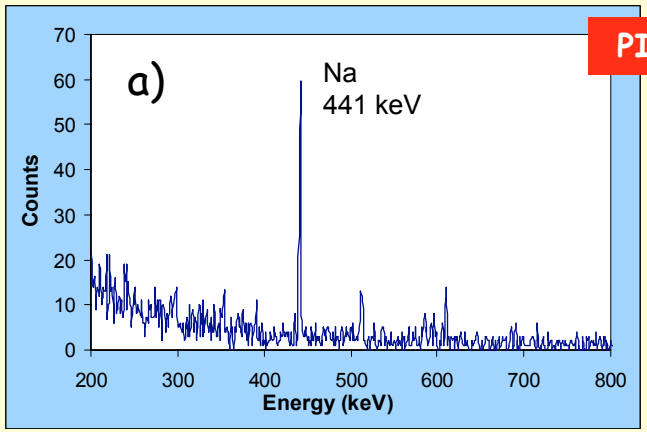


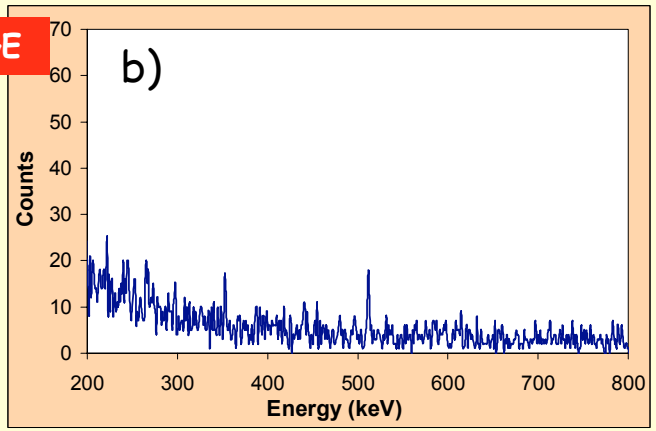
PIXE





PIGE





IBA application to air pollution monitoring

I

- *This field has historically been among the first where PIXE found useful application*
- *Still now, largely used by PIXE labs in the world*
- *The analytical problem is the scarce quantity of target material (aerosol deposited on filters), and the large PIXE cross sections help to achieve very good detection limits*

IBA application to air pollution monitoring II

- *Beam currents used are much higher than for C.H. (up to 20÷30 nA depending on the problem)*
- *Beam size is normally larger (up to some mm^2)*
- *PIGE is also standard for light elements detection*
- *Using non external set-ups, PESA (Particle Elastic Scattering Analysis) also provides very useful information*

Why studying aerosols

- to better understand the great physical processes in the atmosphere (study of climate changes etc.)
- to evaluate pollution levels and identify pollution sources in urban and industrial areas

Aerosol (also referred to as PM ≡ Particulate Matter) is continuously monitored by local authorities in the main urban areas, but in most cases only average daily concentration of PM_{10} (PM with size below 10 μm) is measured: compositional analyses and size-fractionated samplings are not routinely performed

- effects on environment and health
- origin (sources)

⇔ size and composition

⇒ It is important to measure concentration and composition of the different size fractions, and their time behaviour

Sampling

- time resolution matching specific demands
- size fractionation

➡ thin deposits (~10-300 μg/cm^2) of aerosol on filters or impactors

Composition must be obtained through techniques providing

fast runs (many samples!)
high sensitivity (conc. << mg/cm^2)
multi-elemental analysis
non destructive analysis

➡ Large quantity of data are collected (concentration of many elements/compounds in air, for a large number of samples)

Data analysis

Evaluation of air quality, correlation to other pollutants and meteorological parameters, comparison among sites, Identification of pollution sources and of their relative weight

Sampling

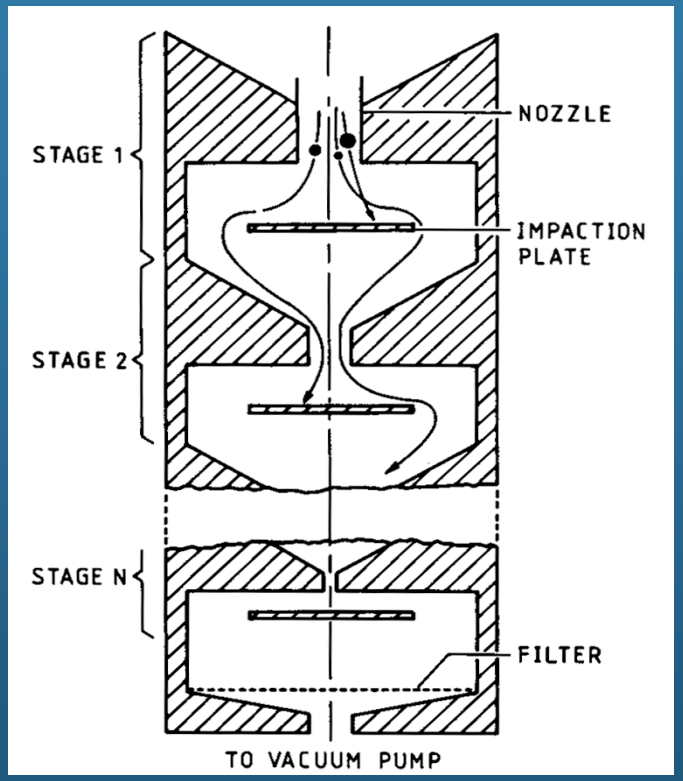
Pumping volumes of air:
Low Volume (< 0.05 m^3 /min)
High Volume (~ 1 m^3/min)

PM is collected:
by impaction (inertial samplers)
by filtration through membranes

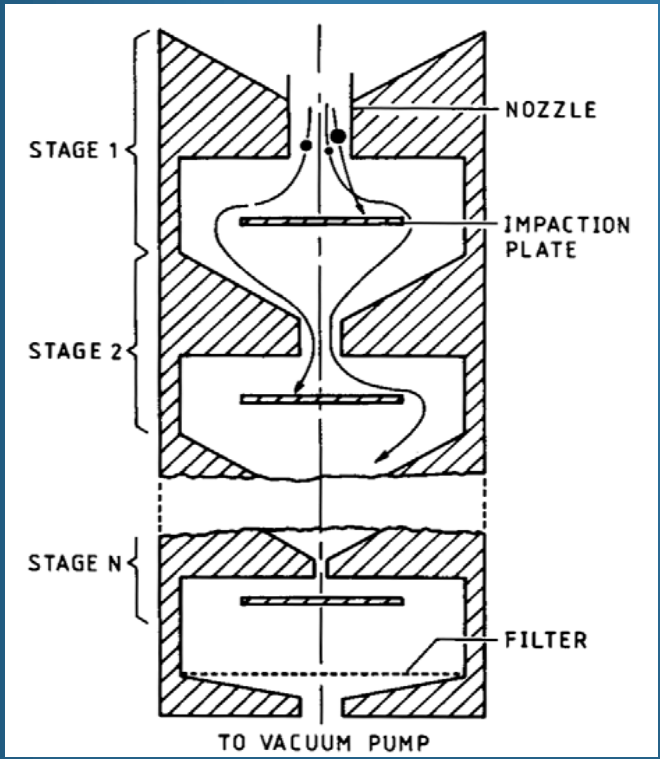
Size fractionation:
single mode (all aerosol below a certain size is collected)
multi-mode (often just bimodal to separate fine and corase fraction)

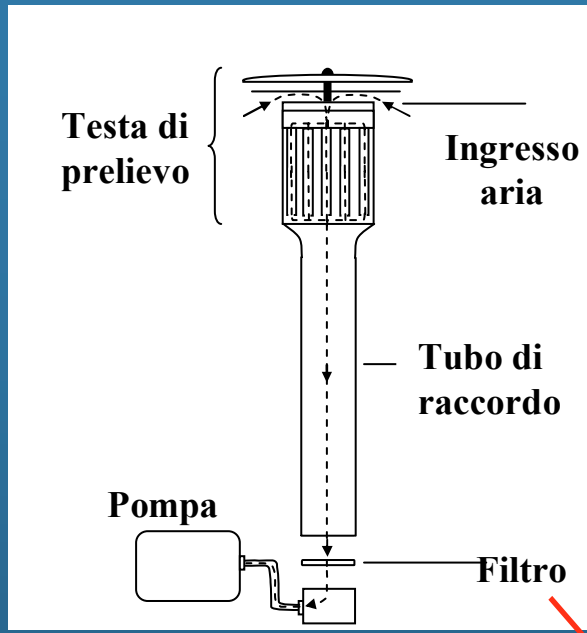
Continuous o cumulative samplers

A multi-stage inertial sampler providing size-fractionation



Samplers

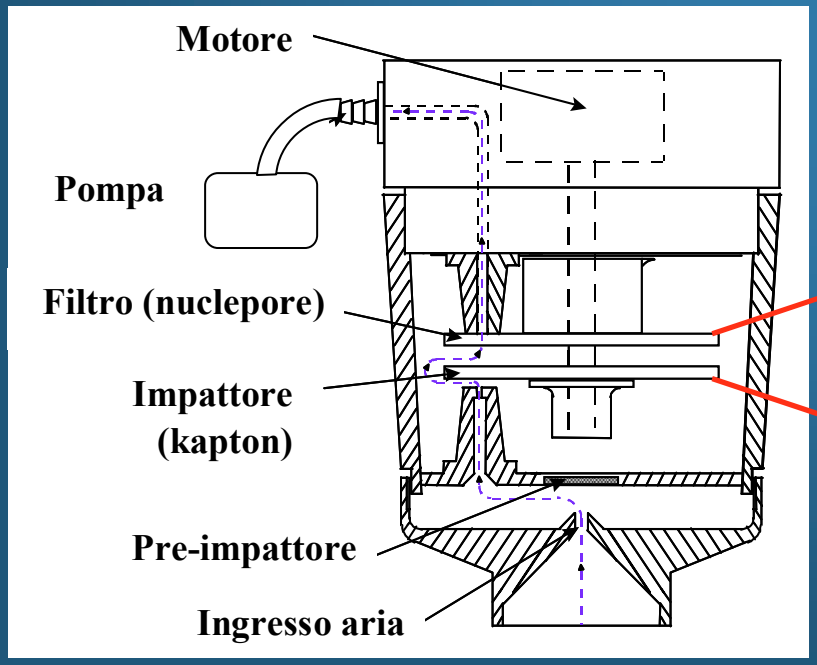




47 mm

- Sampling heads for PM_1, $PM_{2.5}$ or PM_{10}
- One-day resolution
- Mass of deposit obtained either by weighting or by β attenuation

A continuous sampler (streaker) providing bimodal size-fractionation



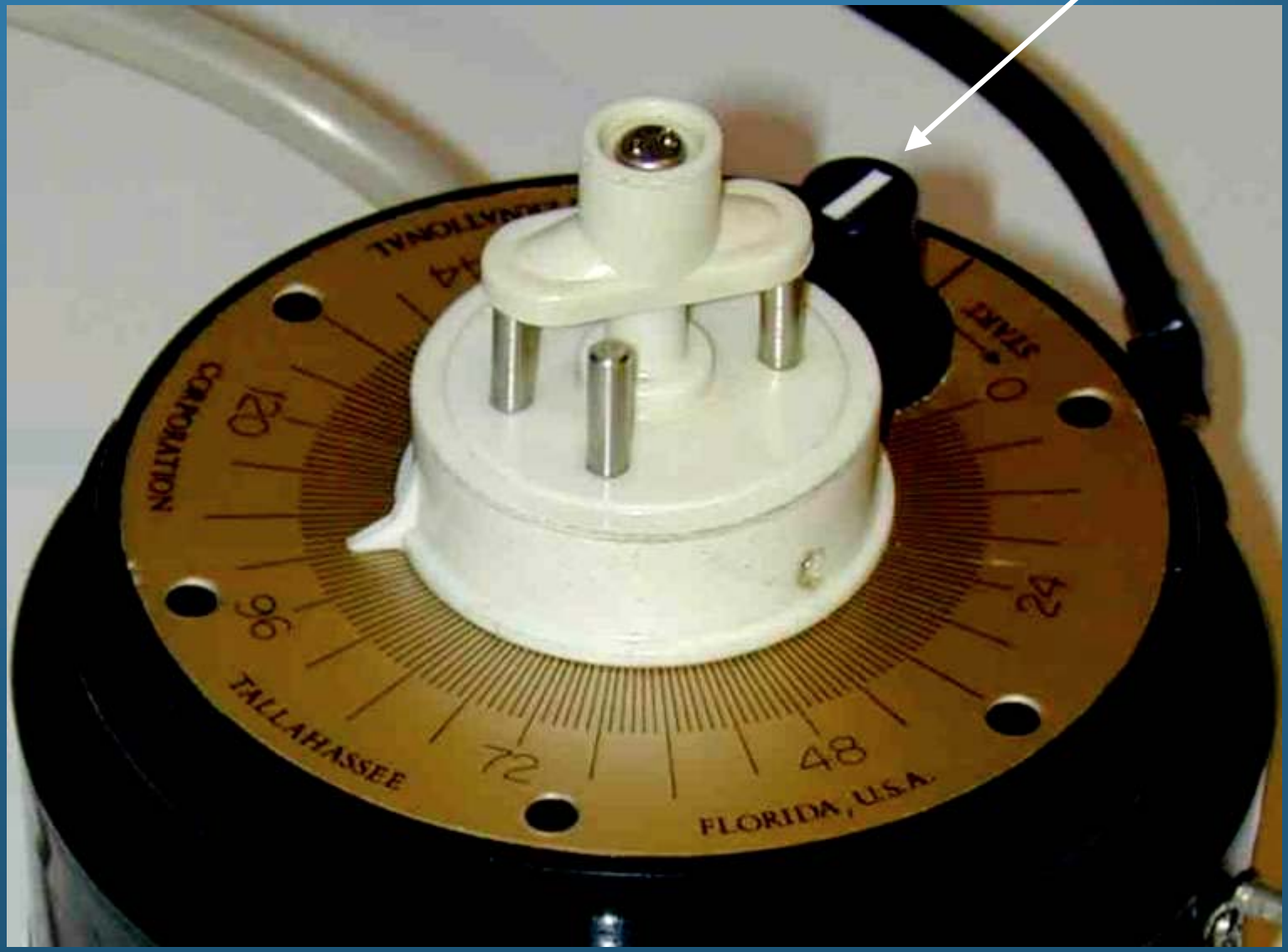
100 mm

$PM_{2.5}$

$PM_{2.5\div10}$

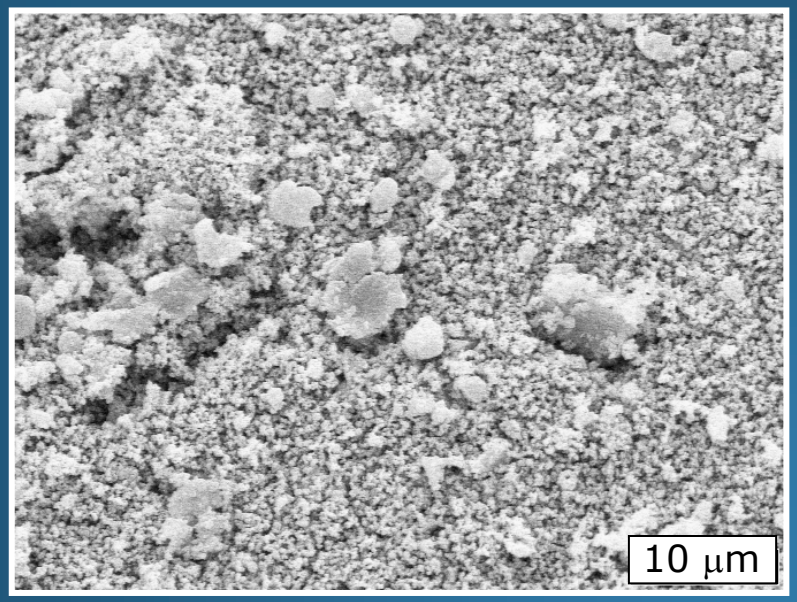
The streaker sampler

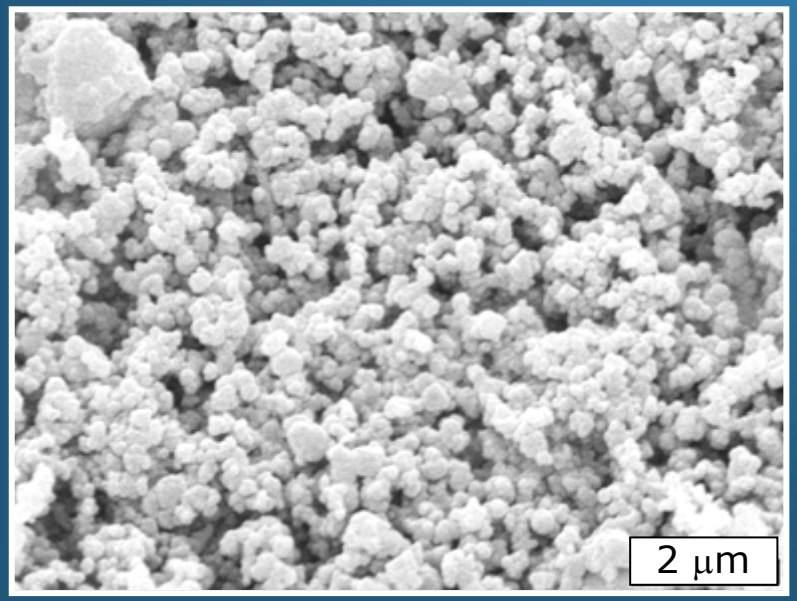
pumping orifice



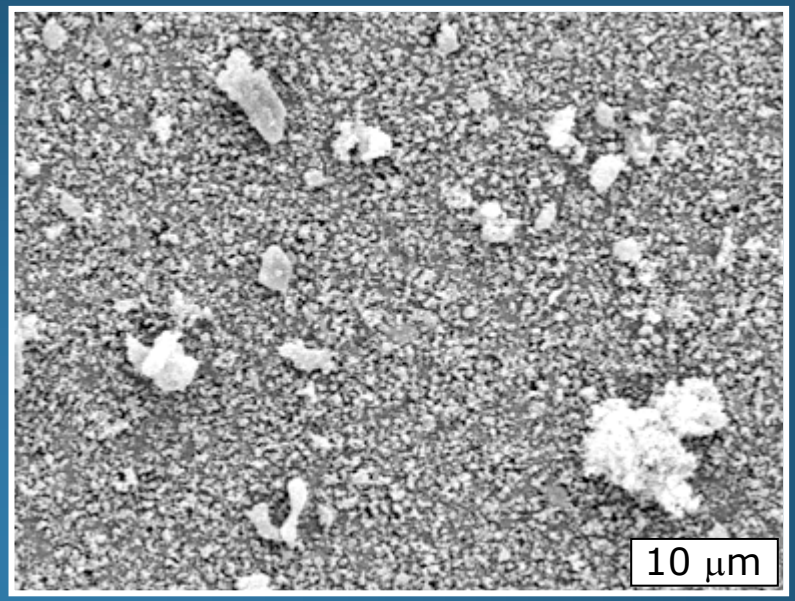
Fine-fraction ($PM_{2.5}$) filter from a streaker

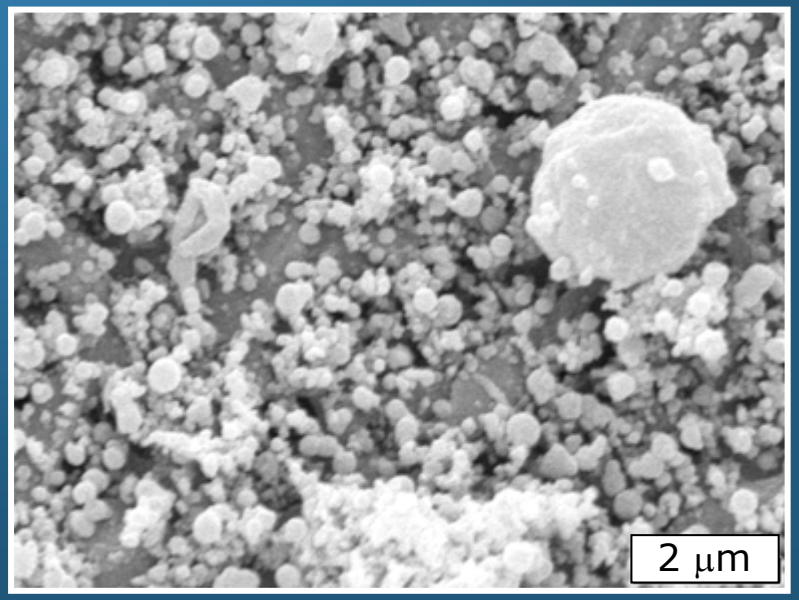
PM_{10}, ~280 μg/cm²



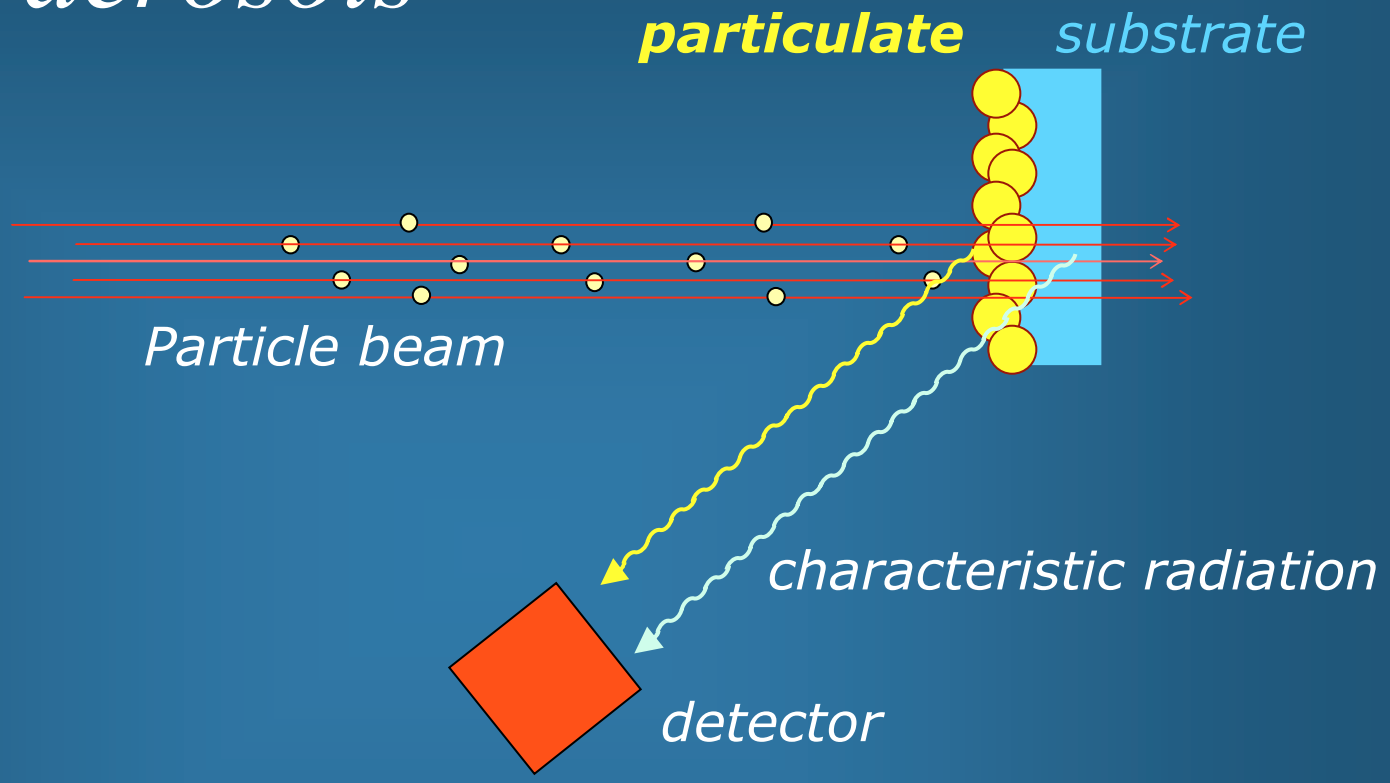


PM_{10}, ~30 μg/cm²





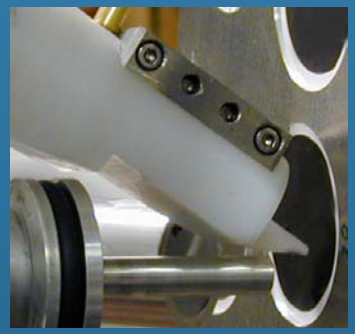
IBA on aerosols

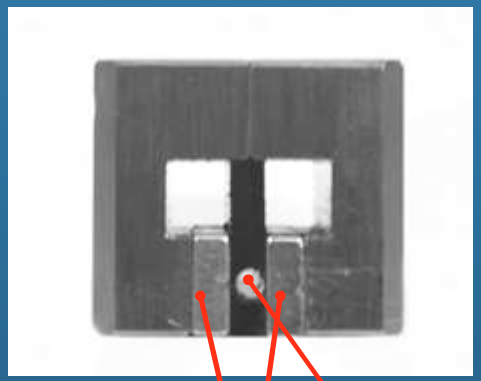


- *Particle Induced X-ray Emission (PIXE)*
- *Particle Induced Gamma-ray Emission (PIGE)*
- *Particle Elastic Scattering Analysis (PESA):*
  FS and BS (Forward and Back Scattering)

Back-scattered protons (BSP) from target

proton deflector





	WITHOUT DEFLECTOR	WITH DEFLECTOR
BSP (cts/nC)	38	0.17
PILE-UP	14%	6%
RESOLUTION (2.3 keV)	148 eV	131 eV

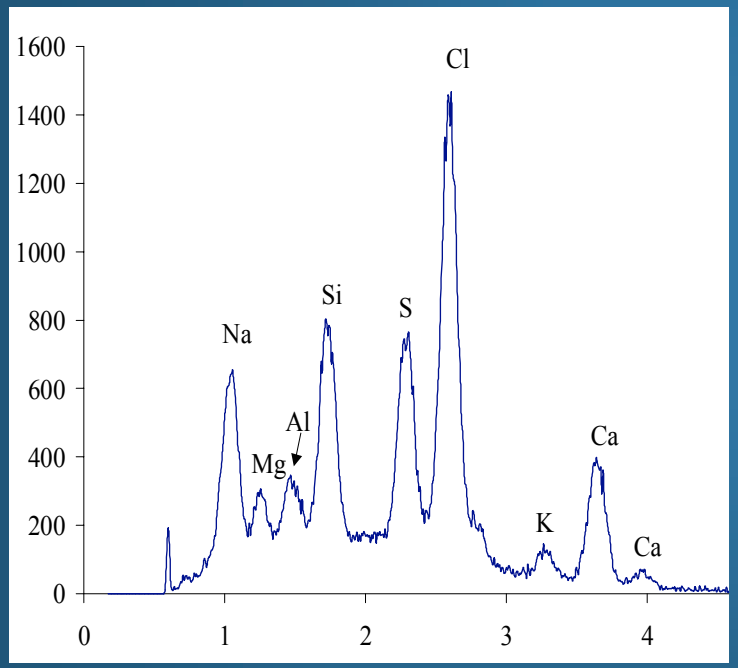
PIXE for aerosol composition

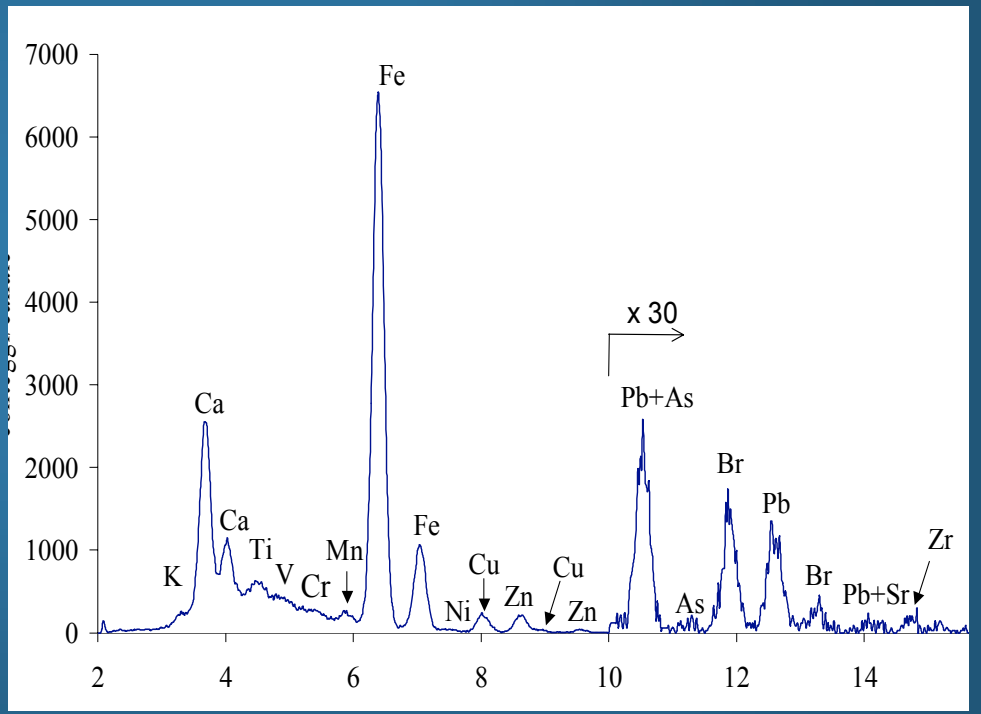
aerosol sample analysis is the main activity in about ¼ of PIXE laboratories in the world

- multi-elemental
- high absolute sensitivity (MDL 1-10 ng/m^3 in 5-10 min runs)
- no sample pre-treatments needed
- quantitative
- non destructive
- scanning on samples from streakers
- single-particle analysis is possible

X ray absorption (< 1keV) ➡ only elements with Z>10 are detected

Typical X ray spectra from aerosols

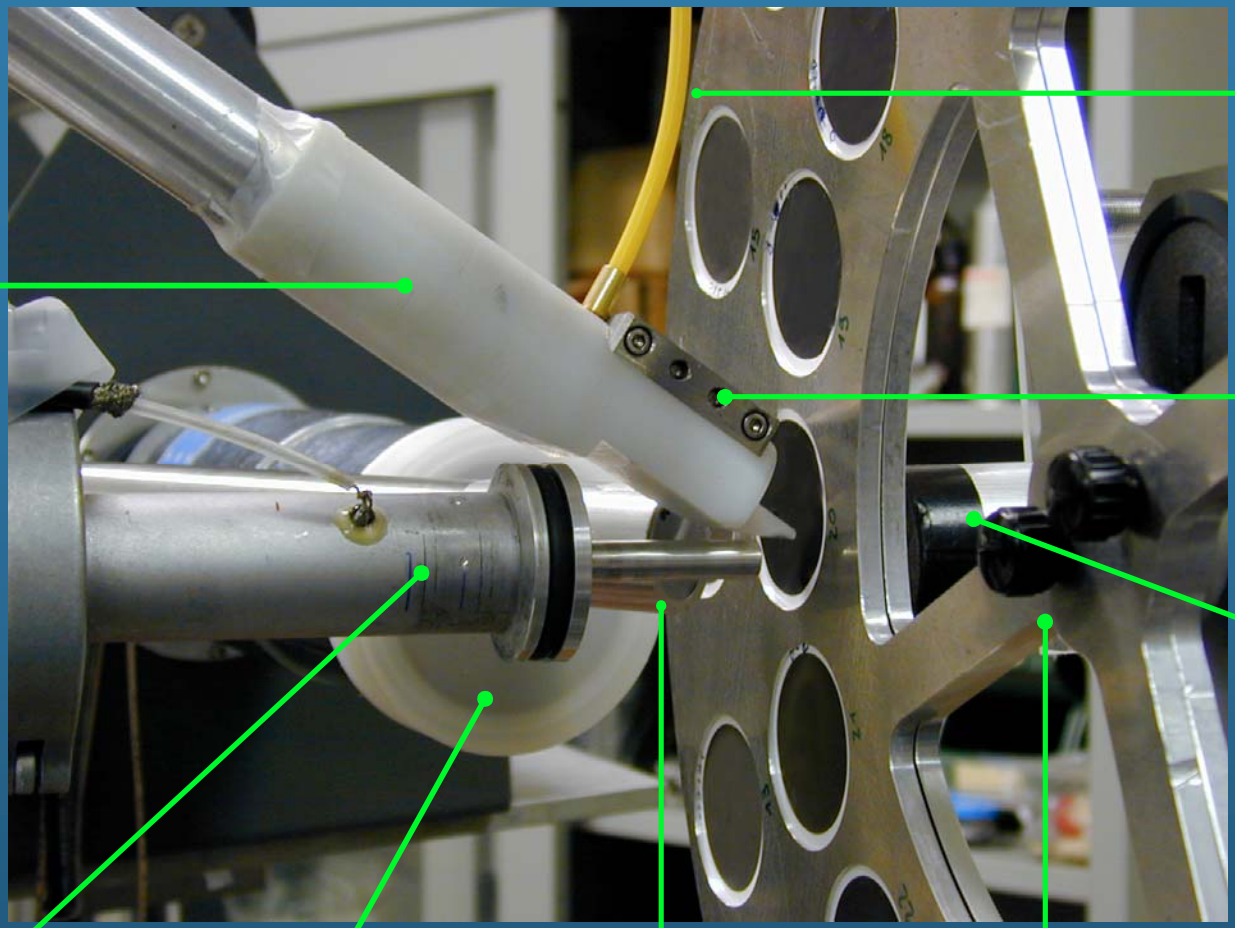




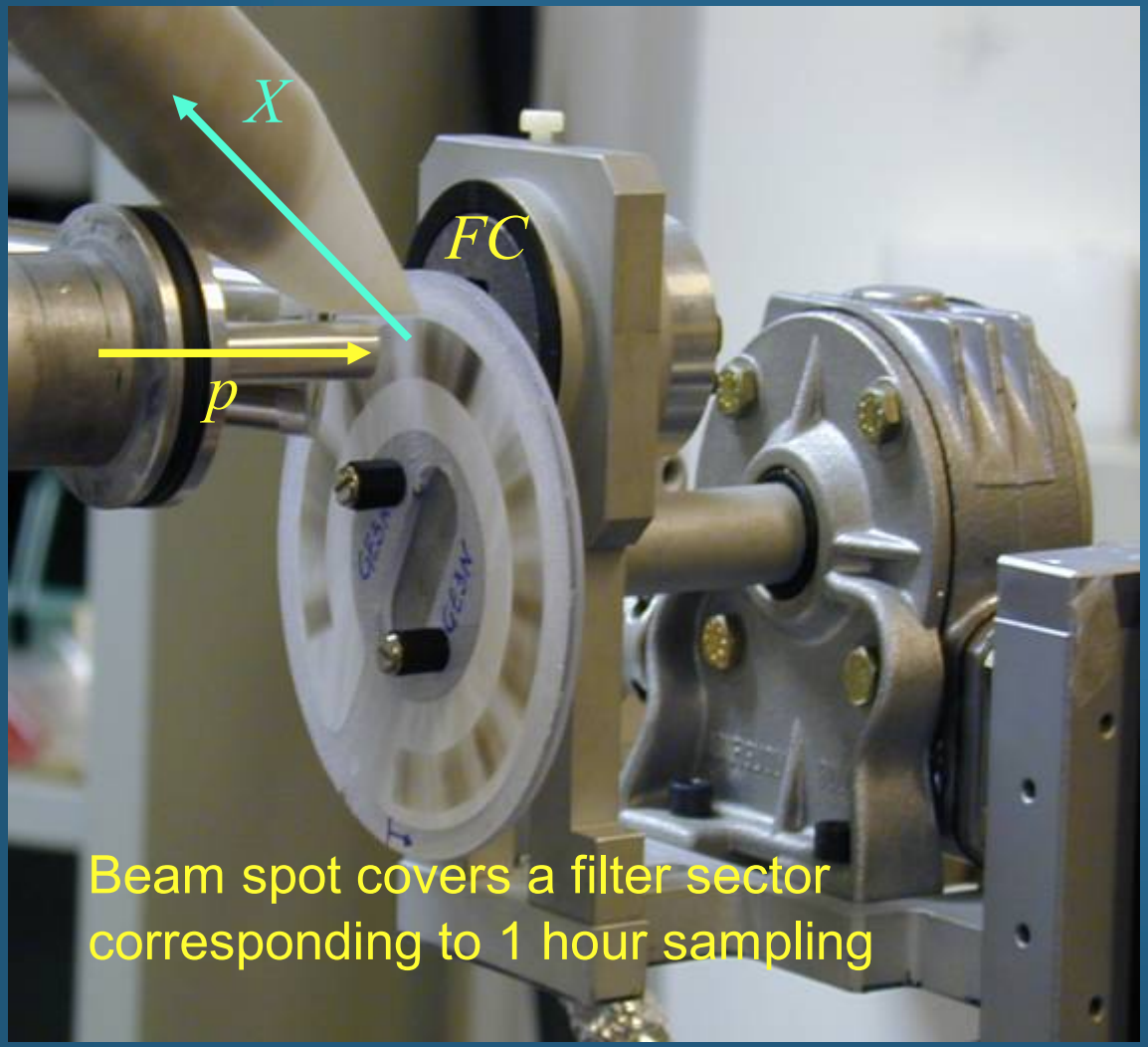
lower-Z elements

higher-Z elements

PIXE-PIGE set-up for 'one-day' samples

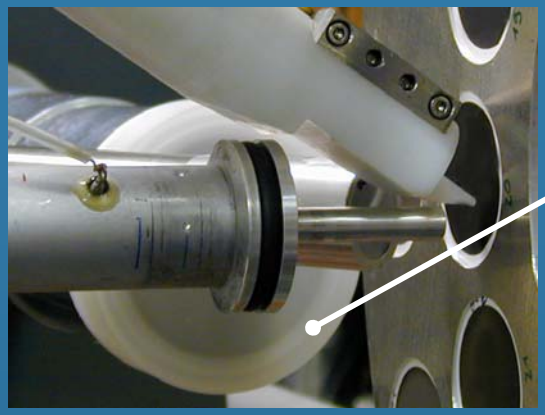


Set-up for 'one-hour' samples

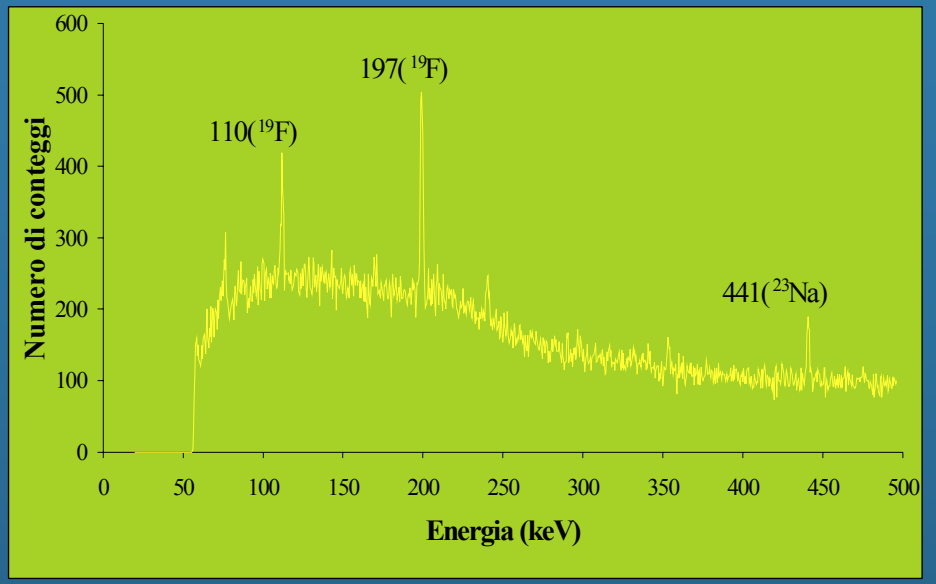


- The deposited aerosol composition is determined "point by point" by PIXE and PIGE
- One can thus deduce aerosol composition in atmosphere "hour by hour" during sampling period
- Typically, sensitivity for the detectable elements comes out to be of the order of ng/ m^3

PIGE



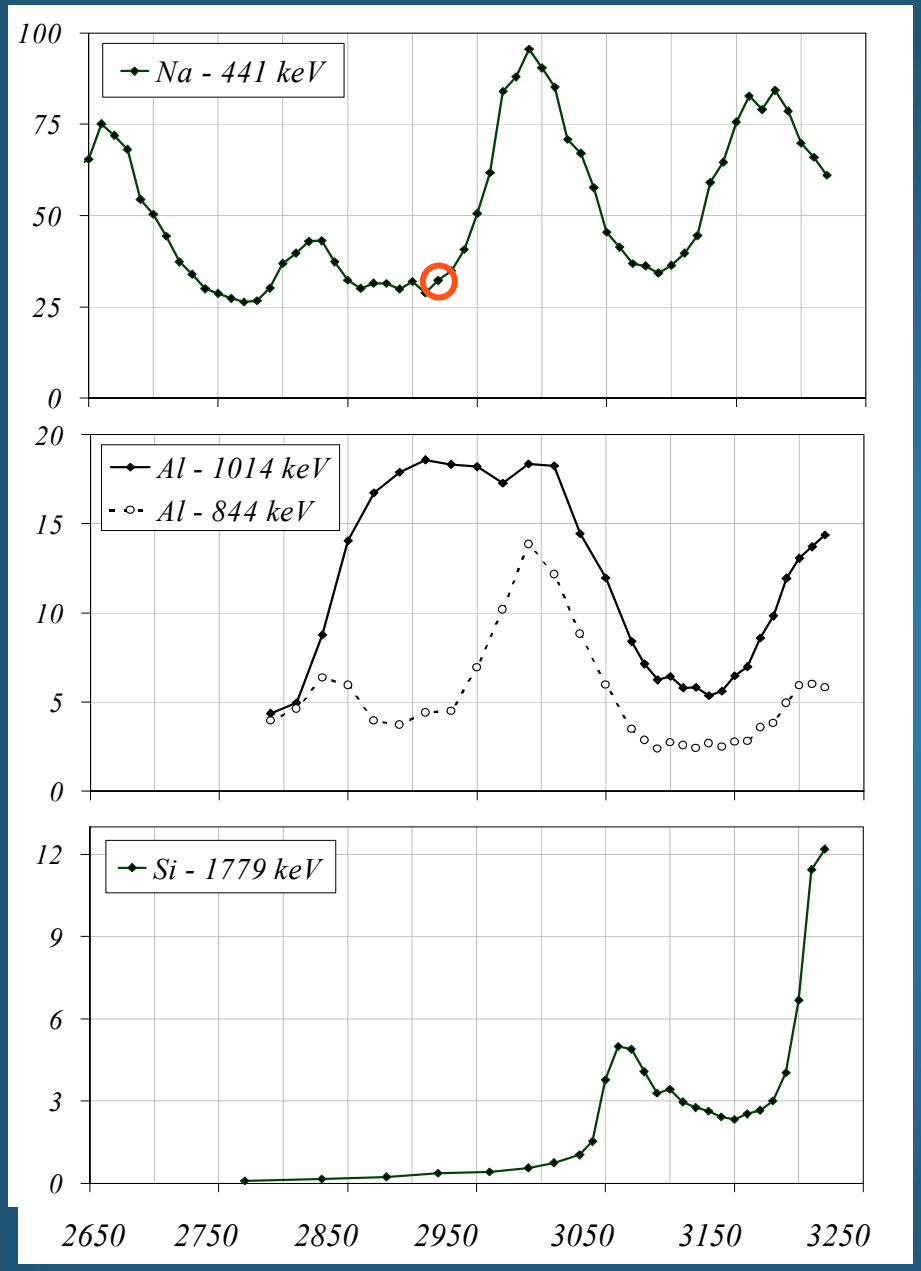
HPGe detector

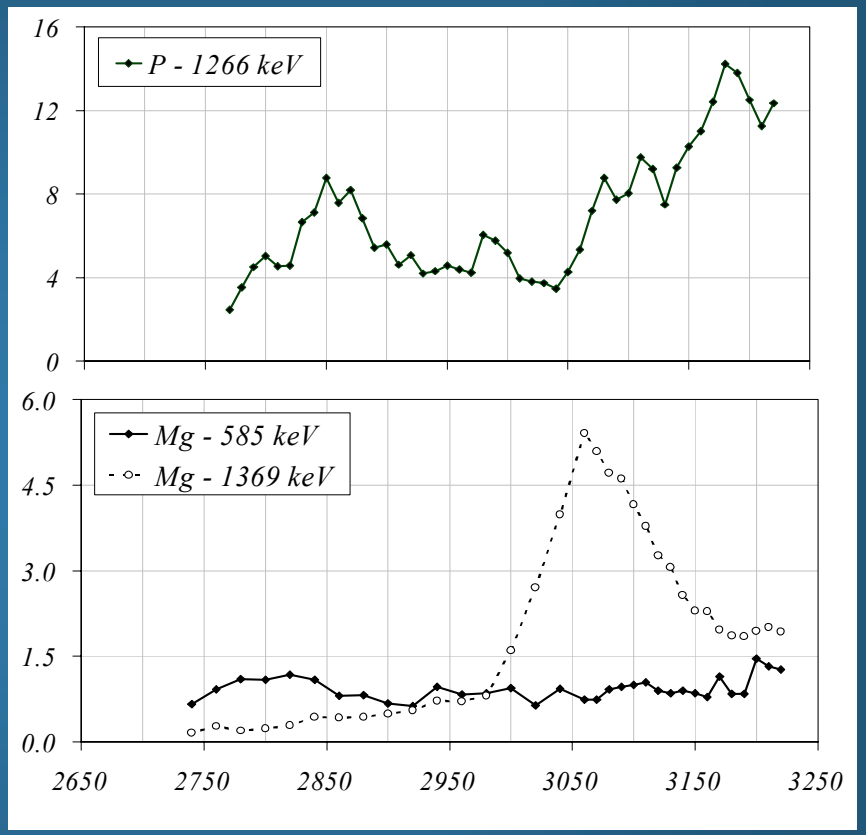


REAZIONE	*E γ (keV)*
$^{19}F\ (p, p'\gamma)\ ^{19}F$	*110, 197*
$^{23}Na\ (p, p'\gamma)\ ^{23}Na$	*441*
$^{25}Mg\ (p, p'\gamma)\ ^{25}Mg$	*585*
$^{24}Mg\ (p, p'\gamma)\ ^{24}Mg$	*1369*
$^{27}Al\ (p, p'\gamma)\ ^{27}Al$	*844, 1014*
$^{28}Si\ (p, p'\gamma)\ ^{28}Si$	*1779*
$^{31}P\ (p, p'\gamma)\ ^{31}P$	*1266*

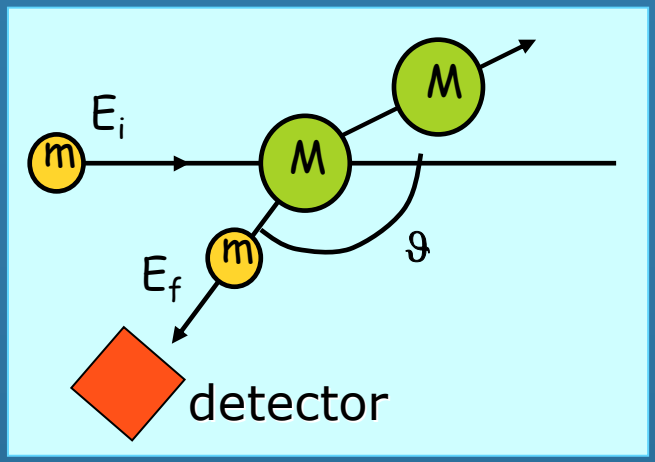
Thin target approximation

- Negligible self-absorption (γ rays)
- Generally, non-negligible croos section changes


Na - 441 keV
Al - 1014 keV
Al - 844 keV
Si - 1779 keV
100
75
50
25
0
20
15
10
5
0
12
9
6
3
0
2650
2750
2850
2950
3050
3150
3250
Proton energy (keV)


P - 1266 keV
Mg - 585 keV
Mg - 1369 keV
16
12
8
4
0
6.0
4.5
3.0
1.5
0.0
2650
2750
2850
2950
3050
3150
3250
Proton energy (keV)

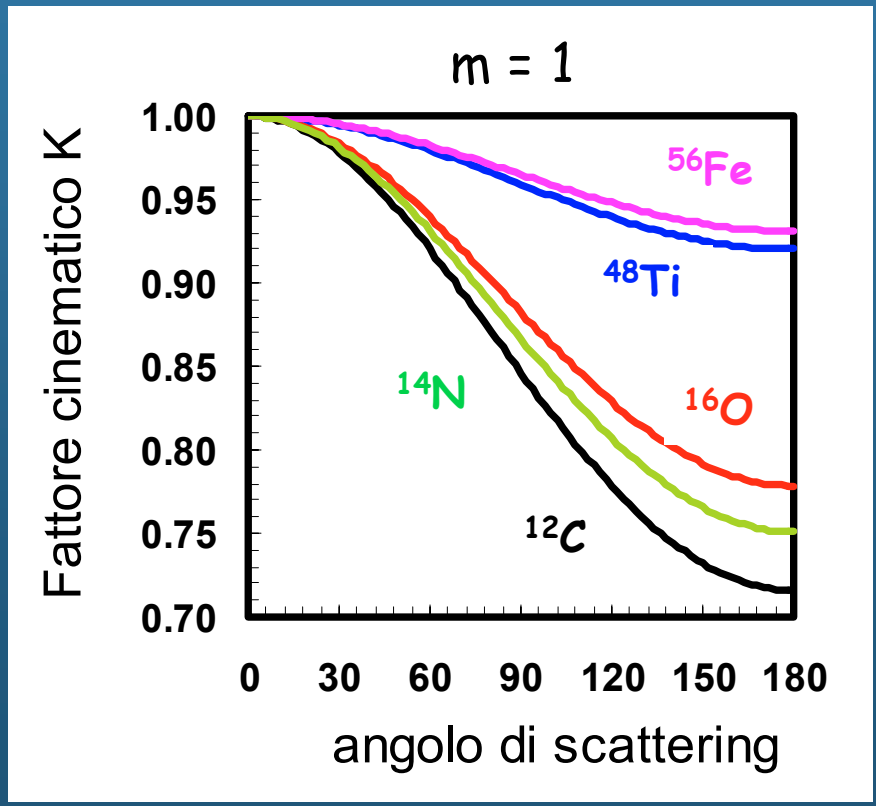
PESA (*Particle Elastic Scattering Analysis*)



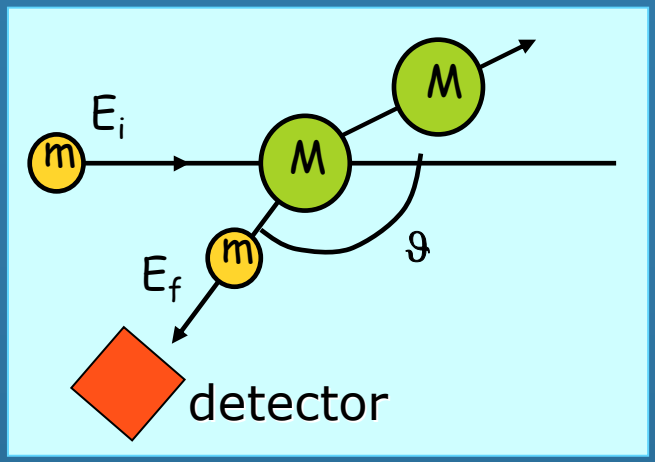
$$K(\vartheta, M/m) \equiv \frac{E_f}{E_i} = \left[\frac{\sqrt{(M/m)^2 - \sin^2\vartheta} + \cos\vartheta}{(M/m)+1}\right]^2$$

larger ΔE for smaller M (light nuclei)

Larger ΔE for larger ϑ (backscattering [BS])



PESA (*Particle Elastic Scattering Analysis*)

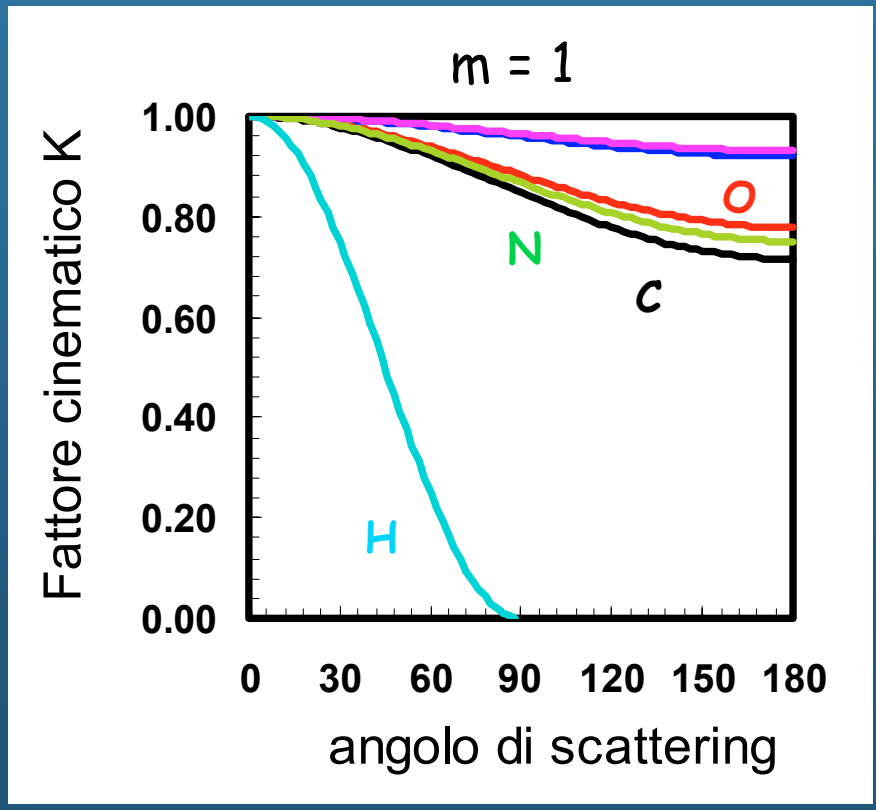


$$K(\vartheta, M/m) \equiv \frac{E_f}{E_i} = \left[\frac{\sqrt{(M/m)^2 - \sin^2\vartheta} + \cos\vartheta}{(M/m)+1}\right]^2$$

larger ΔE for smaller M (light nuclei)

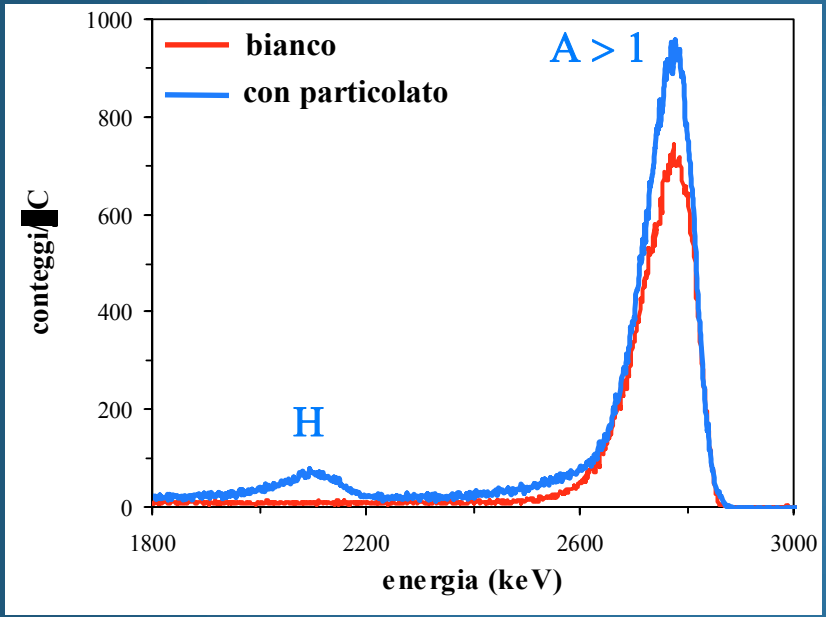
Larger ΔE for larger ϑ (backscattering [BS])

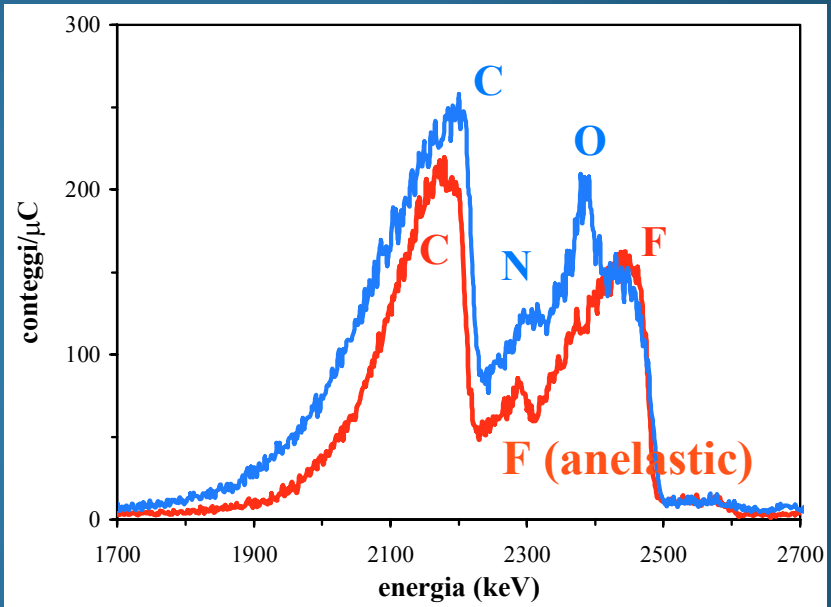
M ≤ m ⇒ only forward scattering [FS]



forward ($\vartheta = 30°$)

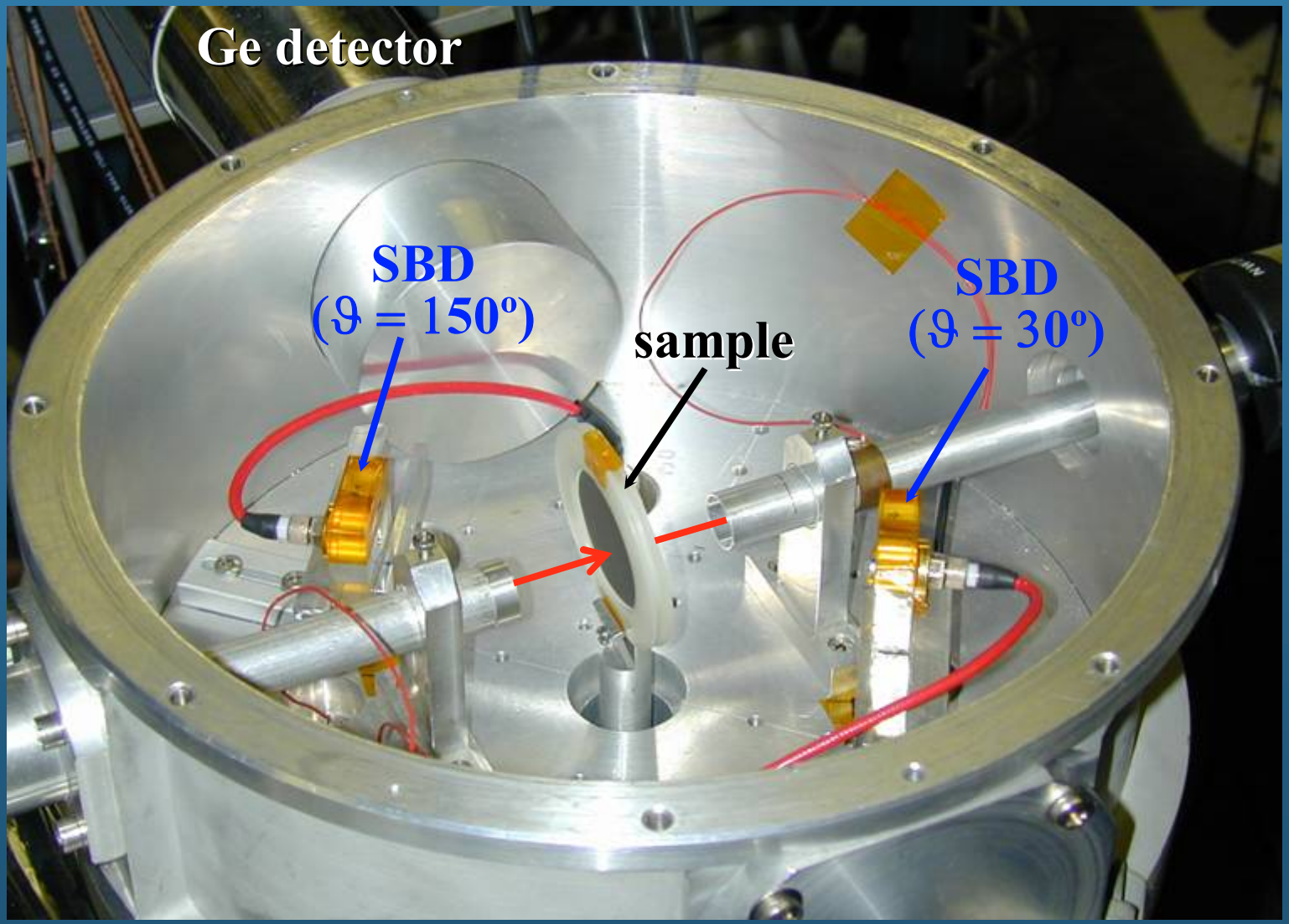
backward ($\vartheta = 150°$)





Teflon membranes

Set-up for PESA



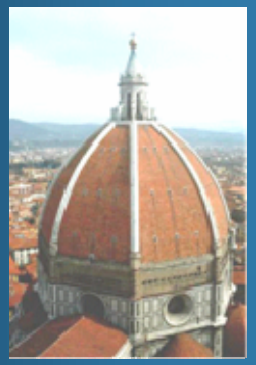
PESA on aerosol samples

- Complement to PIXE
  can detect light elements down to Hydrogen
- multielemental
- non-destructive
- no sample pre-treatments needed
- much less sensitive (sufficiently however!)
- requires set-ups in-vacuo
- difficult to find suitable filtering substrates
- more difficult quantitative analysis

Errors and MDL of elements detected by PESA

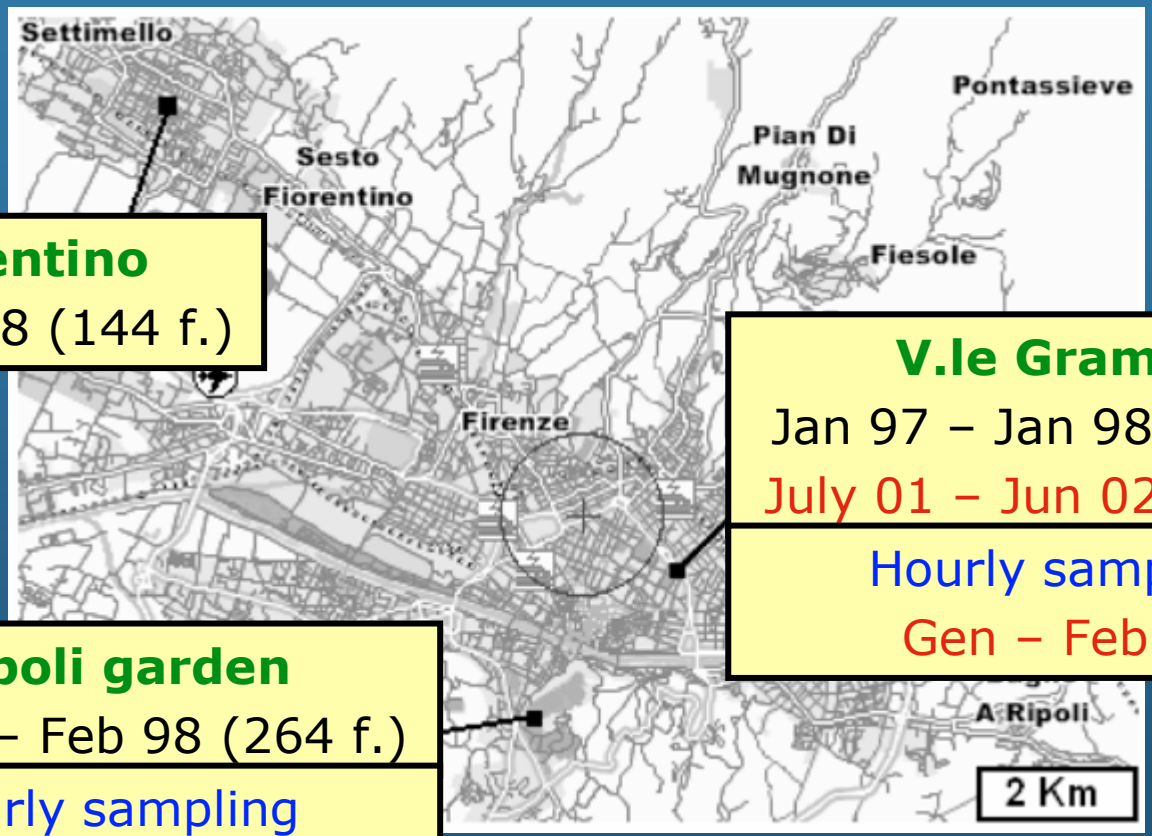
Element	Error %	MDL ($\mu g/m^3$)
Hydrogen	~ 10	0.1
Carbon	~ 10	1
Nitrogen	~ 20	0.5
Oxygen	~ 15	0.4

Some examples of results



Composition of aerosol collected in the urban area of Florence, Italy

(in collaboration with ARPAT)

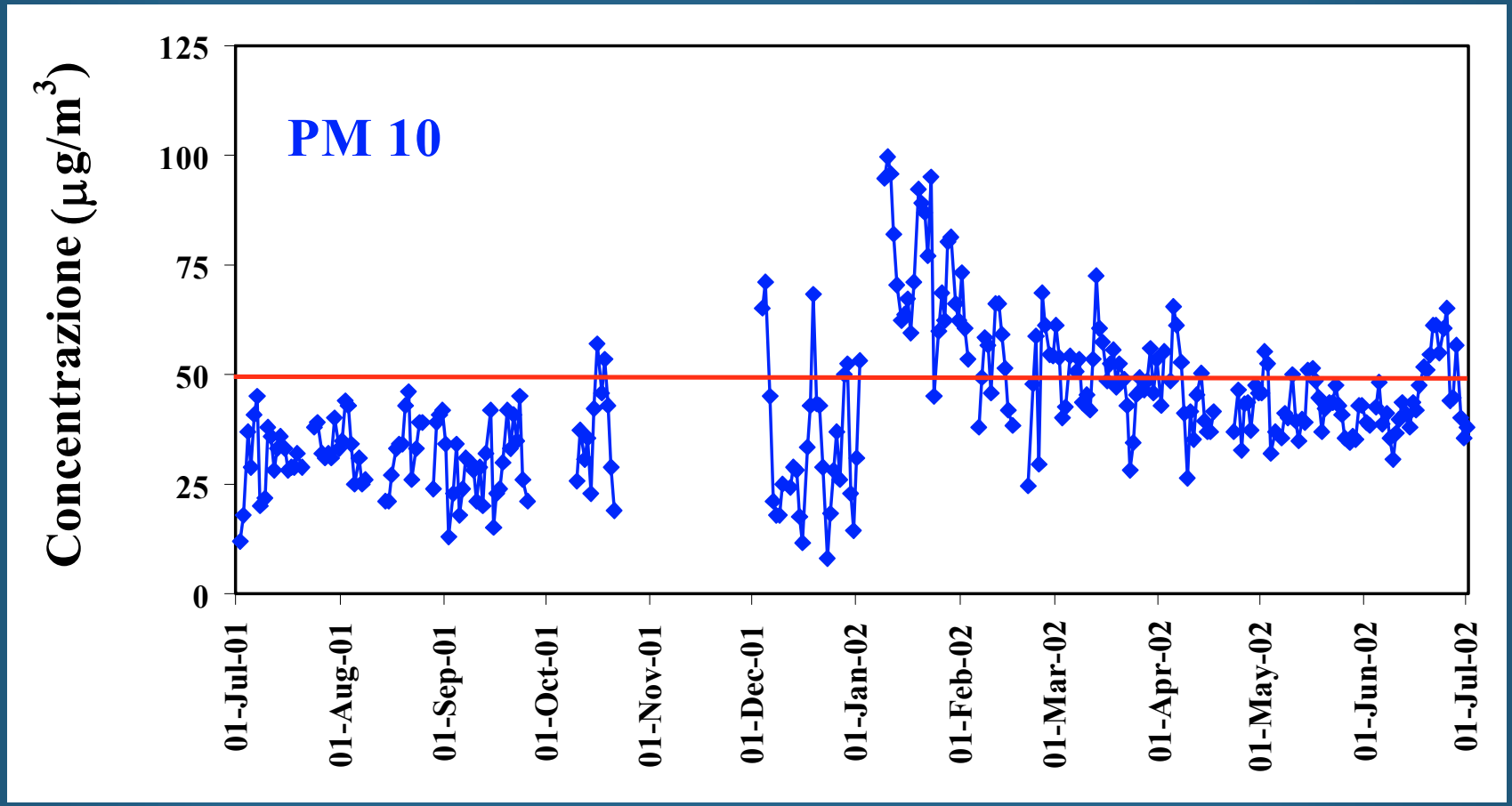


Sesto Fiorentino
Dec 97 – May 98 (144 f.)

V.le Gramsci
Jan 97 – Jan 98 (249 f.)
July 01 – Jun 02 (276 f.)
Hourly sampling
Gen – Feb 02

Boboli garden
Gen 97 – Feb 98 (264 f.)
Hourly sampling
Gen – Feb 02

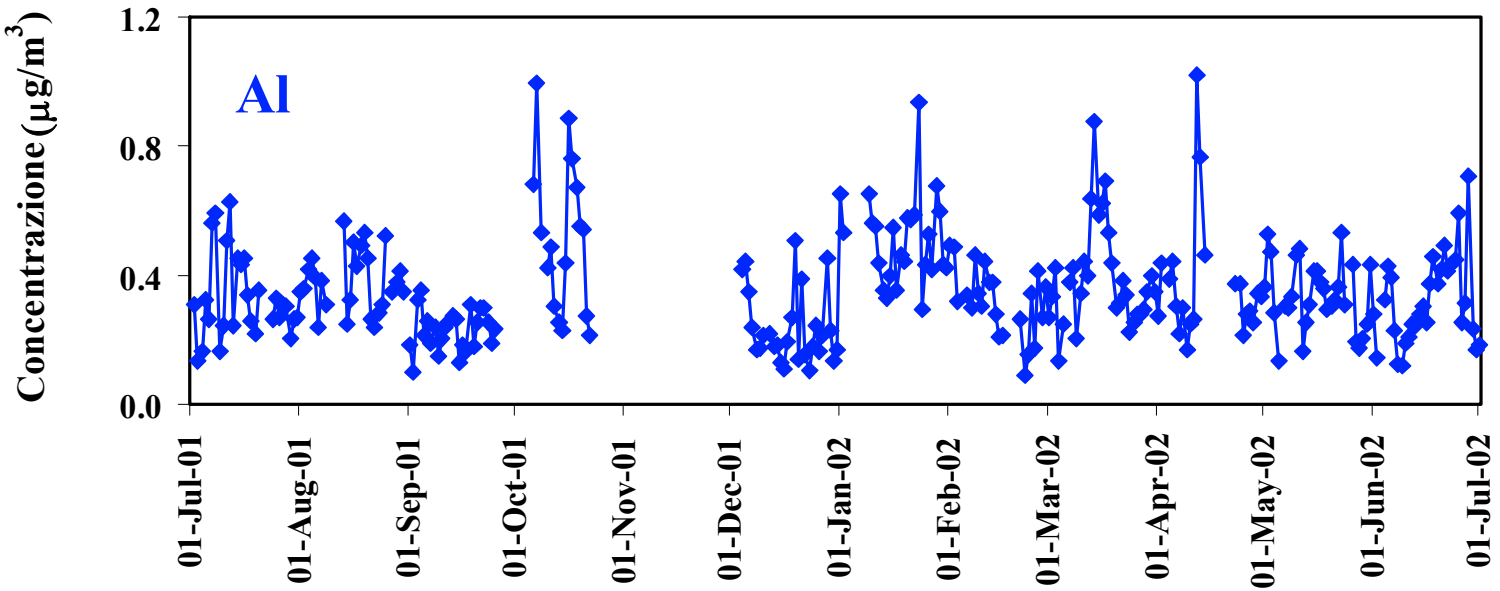
Viale Gramsci - total PM_{10} concentration (2001-02)

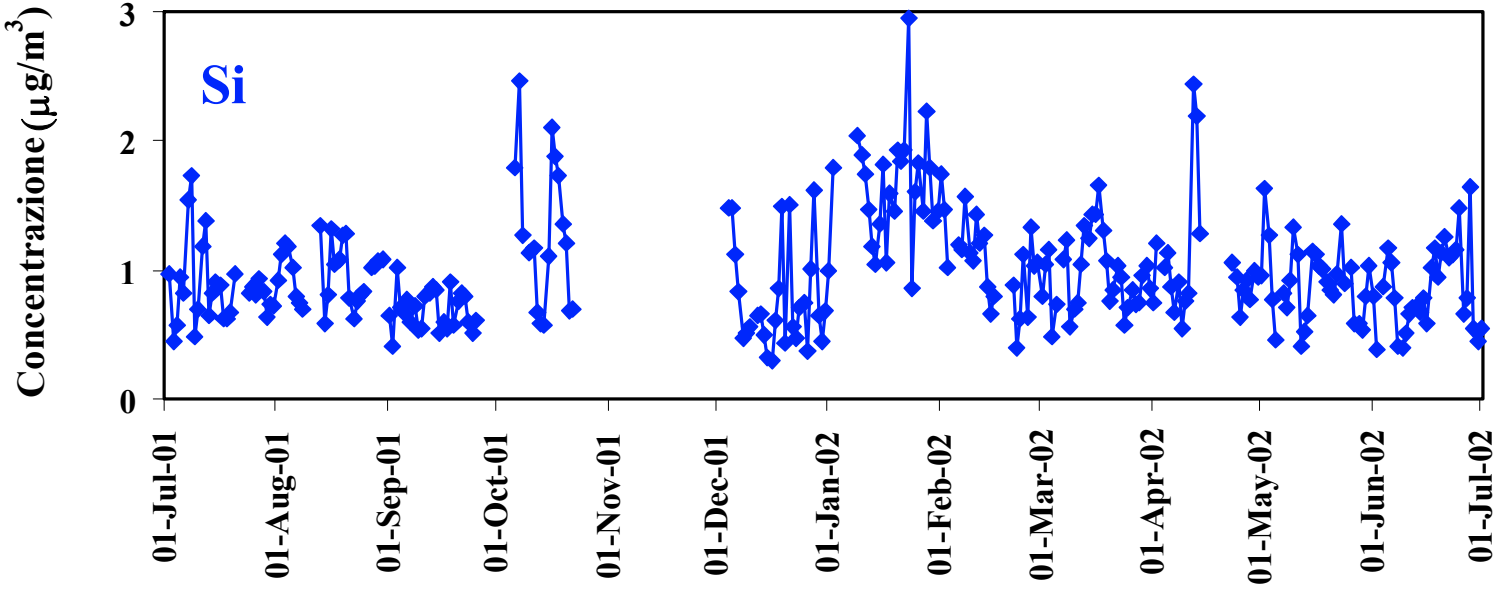


average: 43 µg/m³

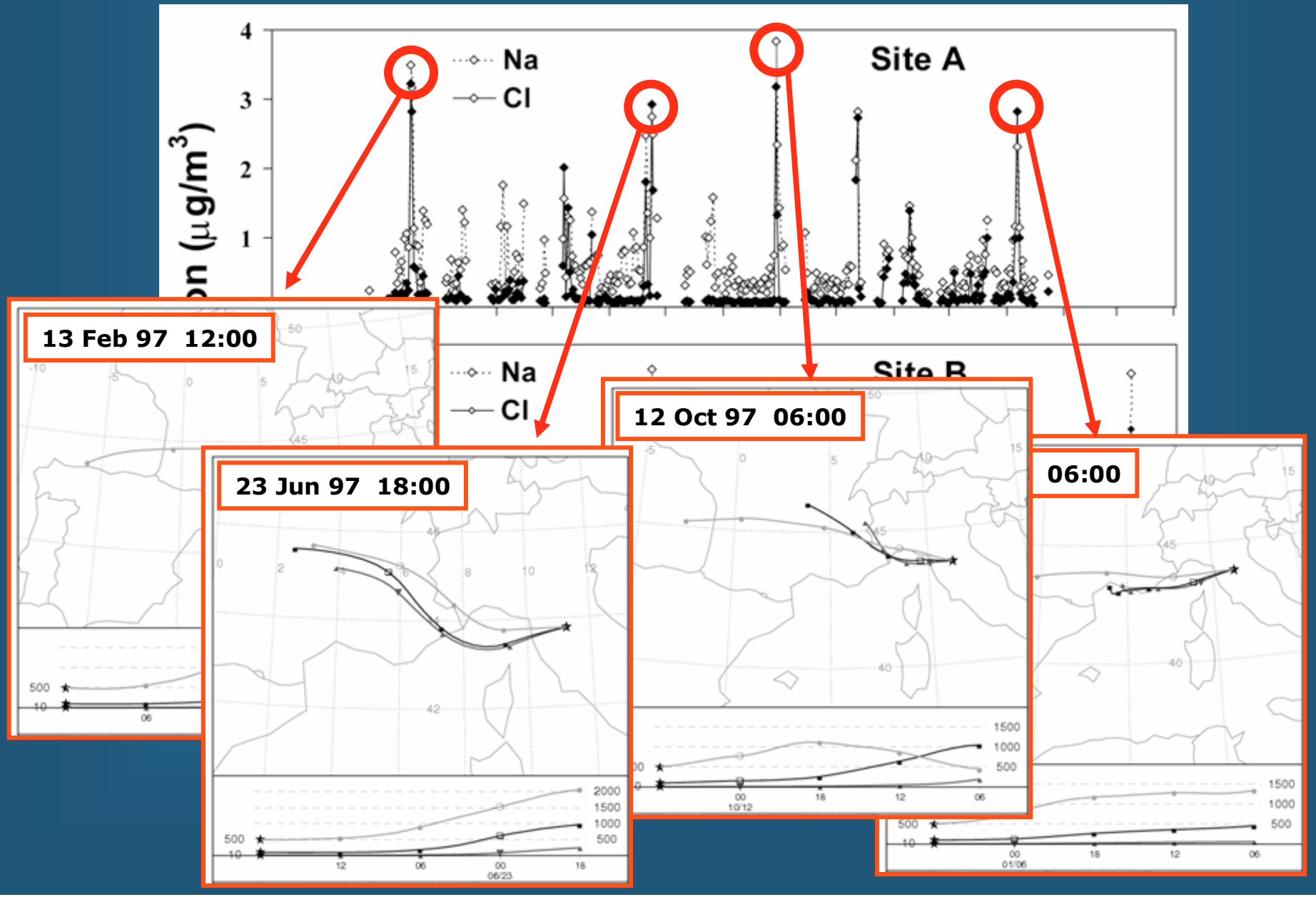
number of days exceeding 50 µg/m³ : 76

Al and Si concentration

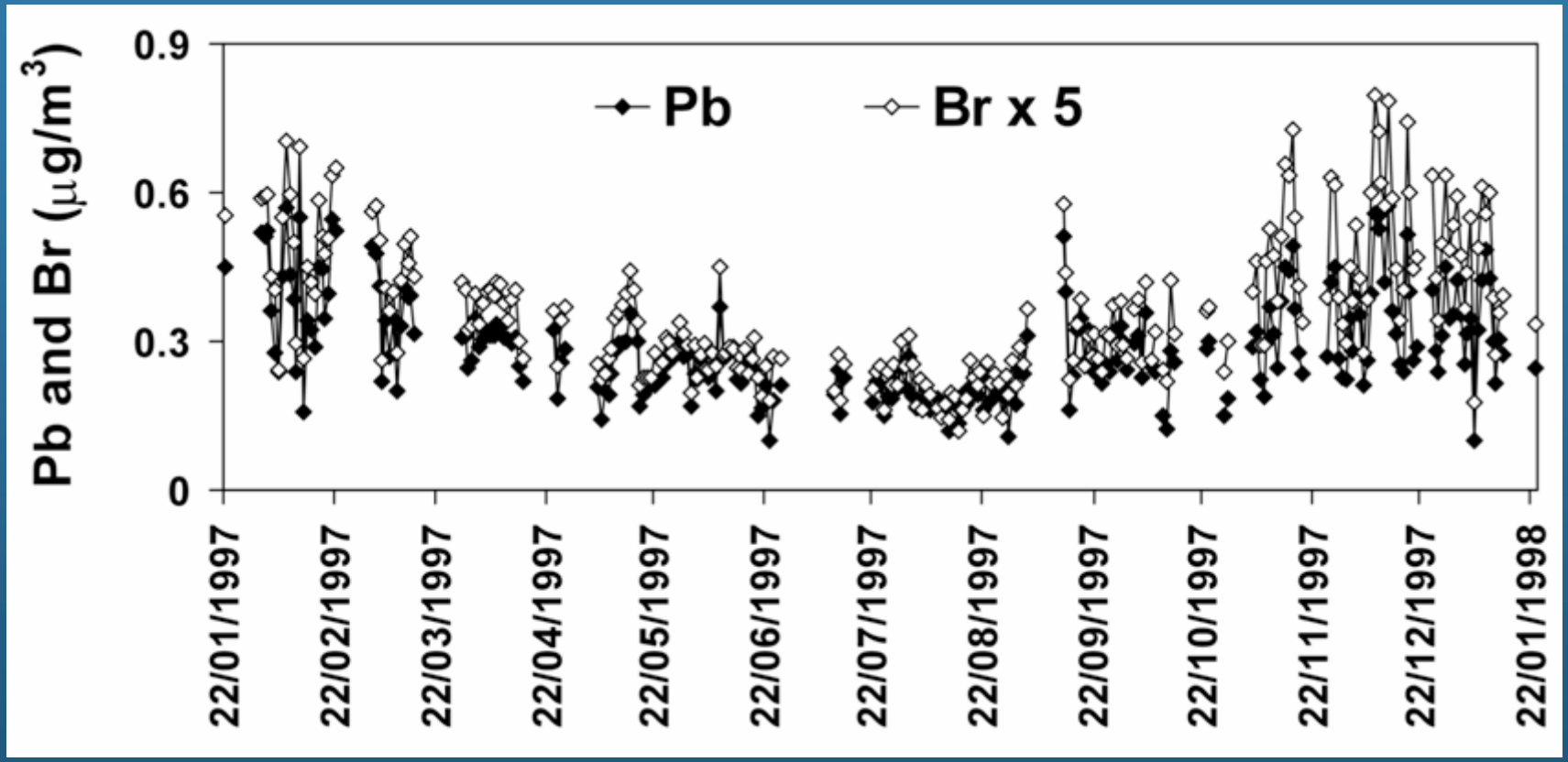




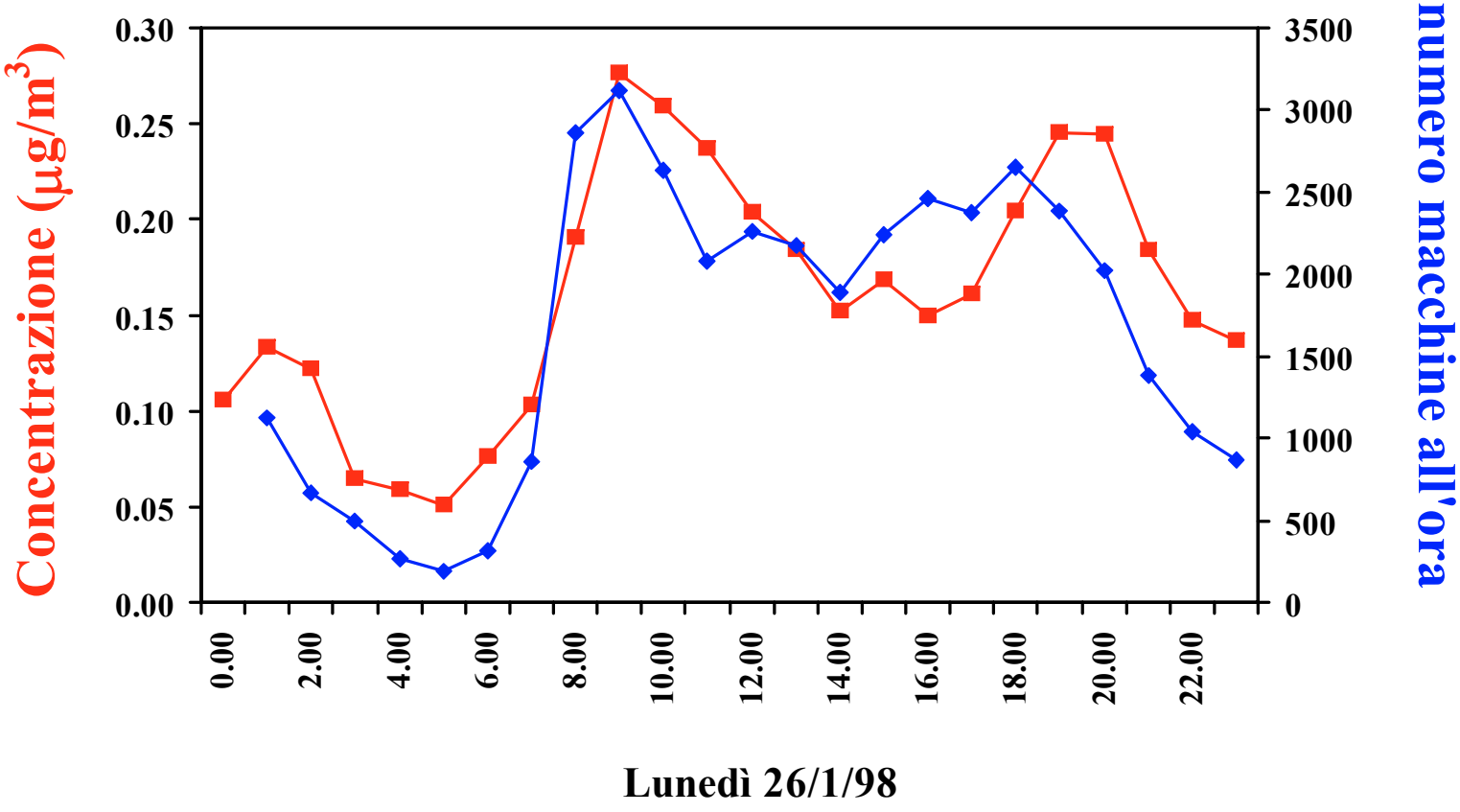
Na and Cl concentration

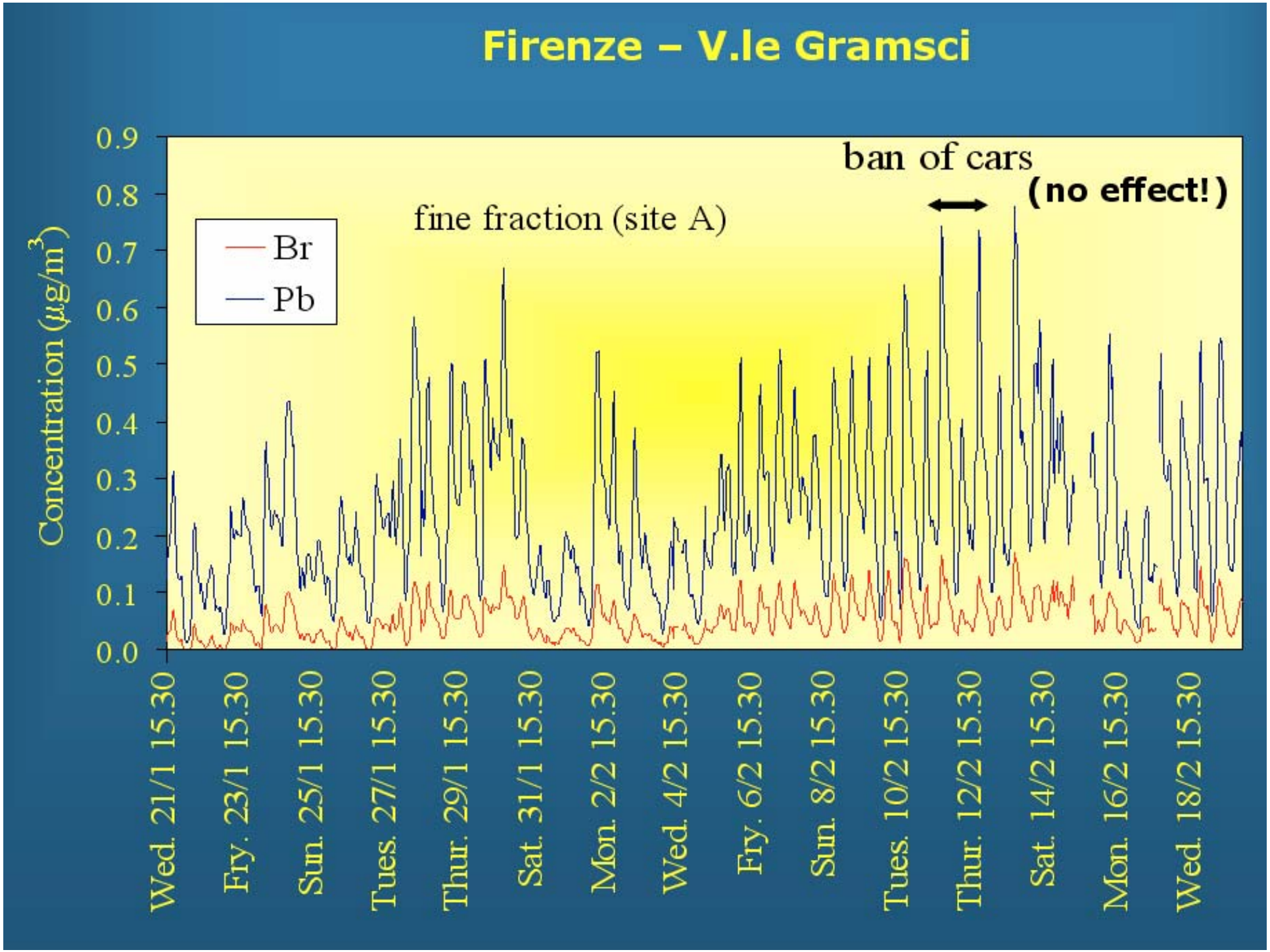


Pb and Br, before leaded gasoline ban

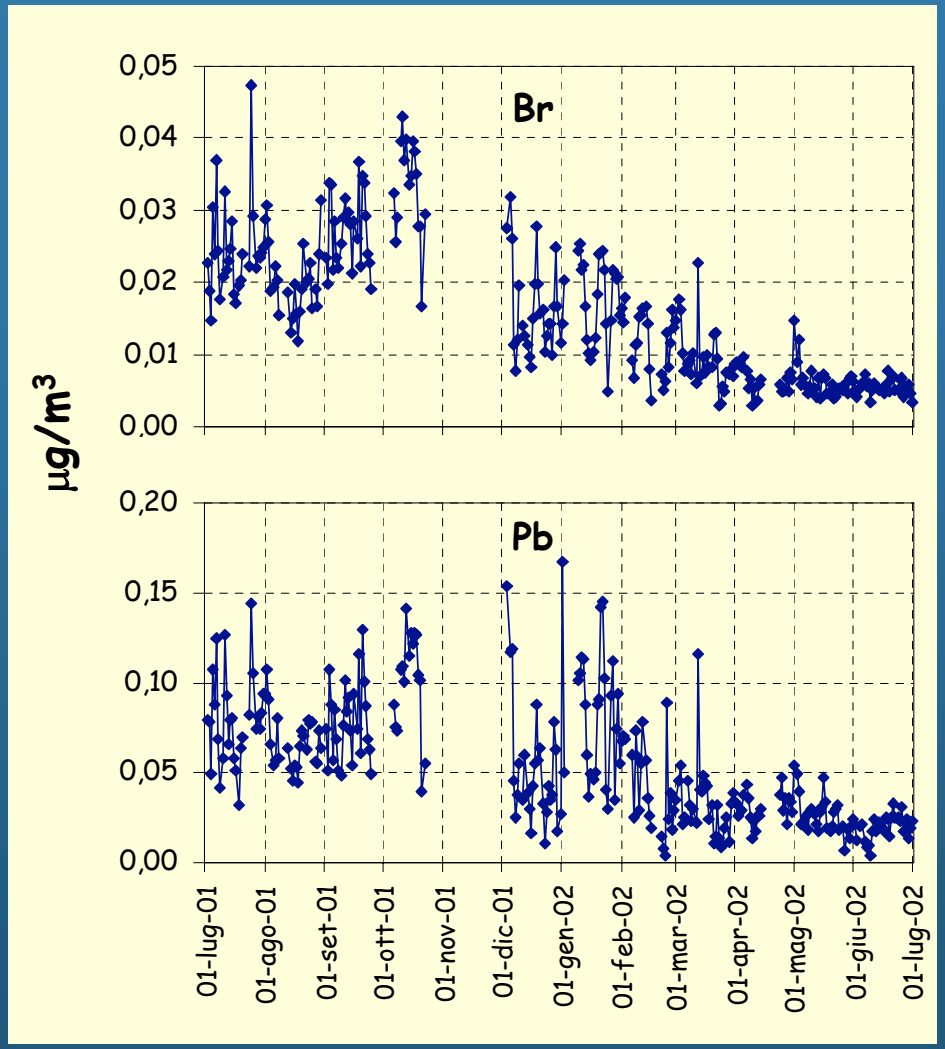


Hour by hour concentration of Pb during one day




Firenze – V.le Gramsci
ban of cars
(no effect!)
fine fraction (site A)
Br
Pb
Concentration (µg/m3)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Wed. 21/1 15.30
Fry. 23/1 15.30
Sun. 25/1 15.30
Tues. 27/1 15.30
Thur. 29/1 15.30
Sat. 31/1 15.30
Mon. 2/2 15.30
Wed. 4/2 15.30
Fry. 6/2 15.30
Sun. 8/2 15.30
Tues. 10/2 15.30
Thur. 12/2 15.30
Sat. 14/2 15.30
Mon. 16/2 15.30
Wed. 18/2 15.30

Bromine and Lead from leaded gasoline



01/01/2002:

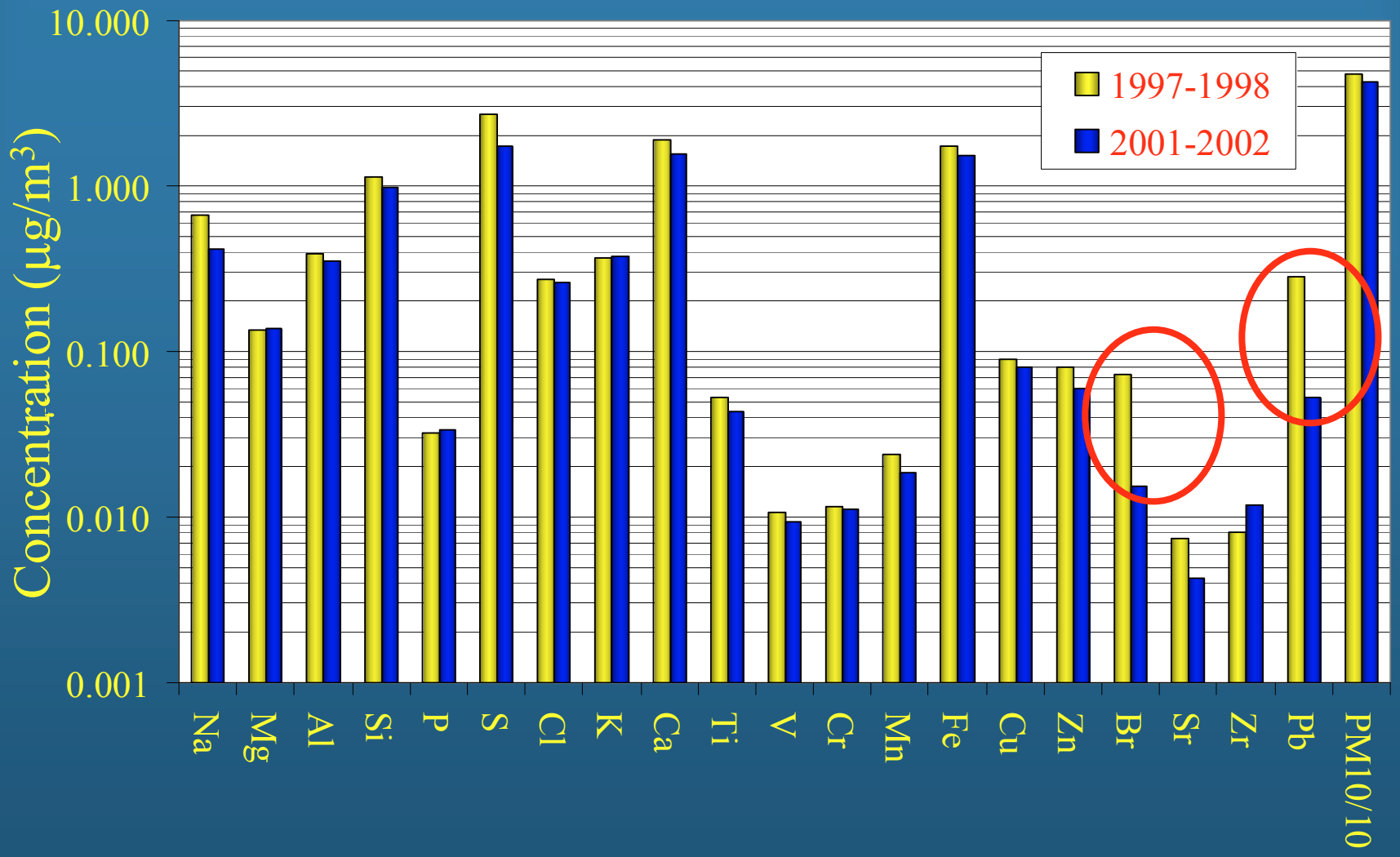
In Italy, sale of leaded gasoline is forbidden

values detected in Florence

µg/m³	April June '97	April June '02
Br	0,06	0,006
Pb	0,23	0,025

Pb limit by law ⟹ 0.5 µg/m³ yearly average

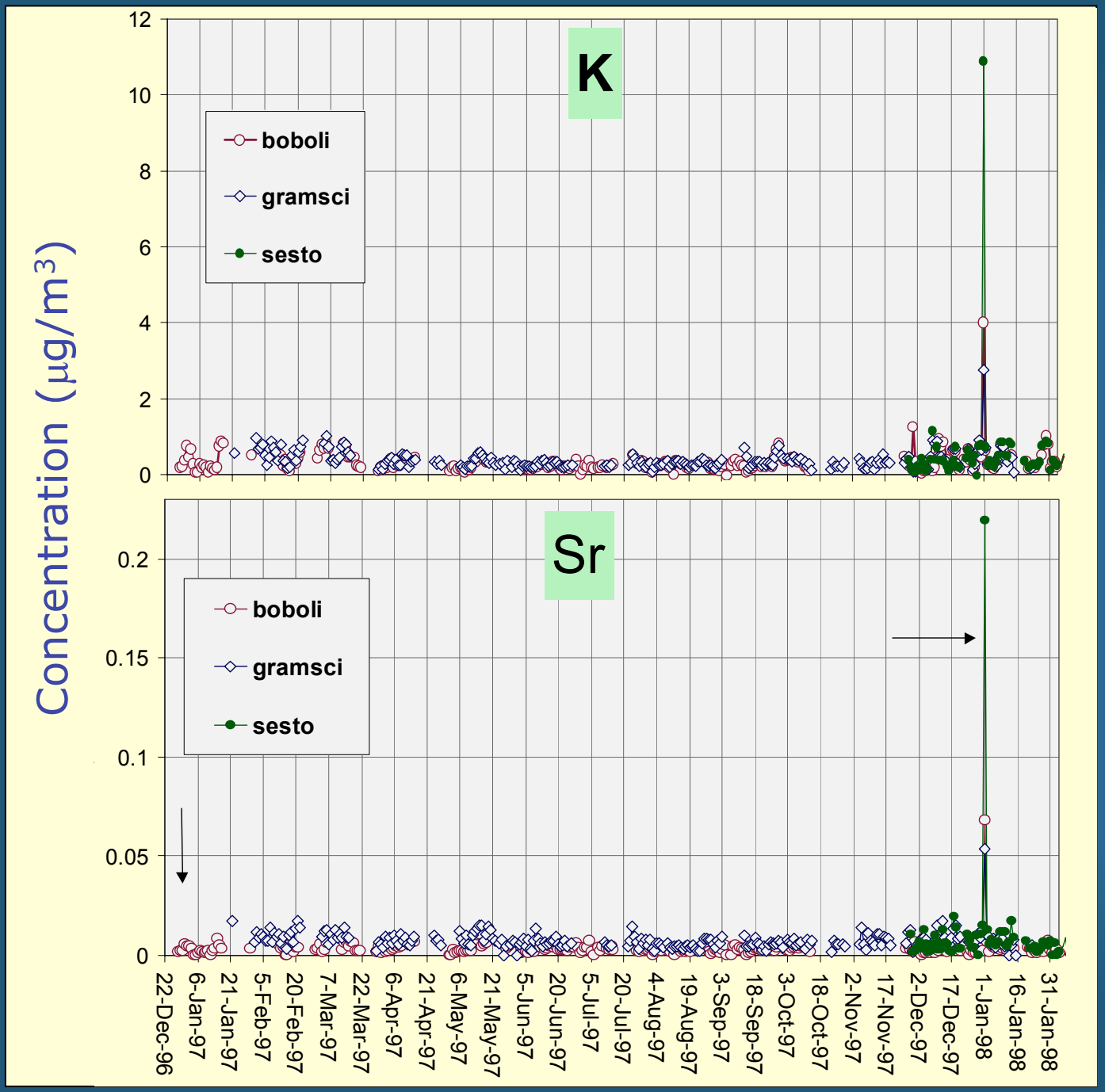
Comparison 1997-98 with 2001-02



Comparison with 1988-89

Period	*S*	*Br*	*Pb*
Sept-88	4.2	0.30	1.13
Sept-97	3.5	0.06	0.27
Jan-89	12.6	0.46	2.2
Jan-98	2.0	0.09	0.31

values in mg/m^3



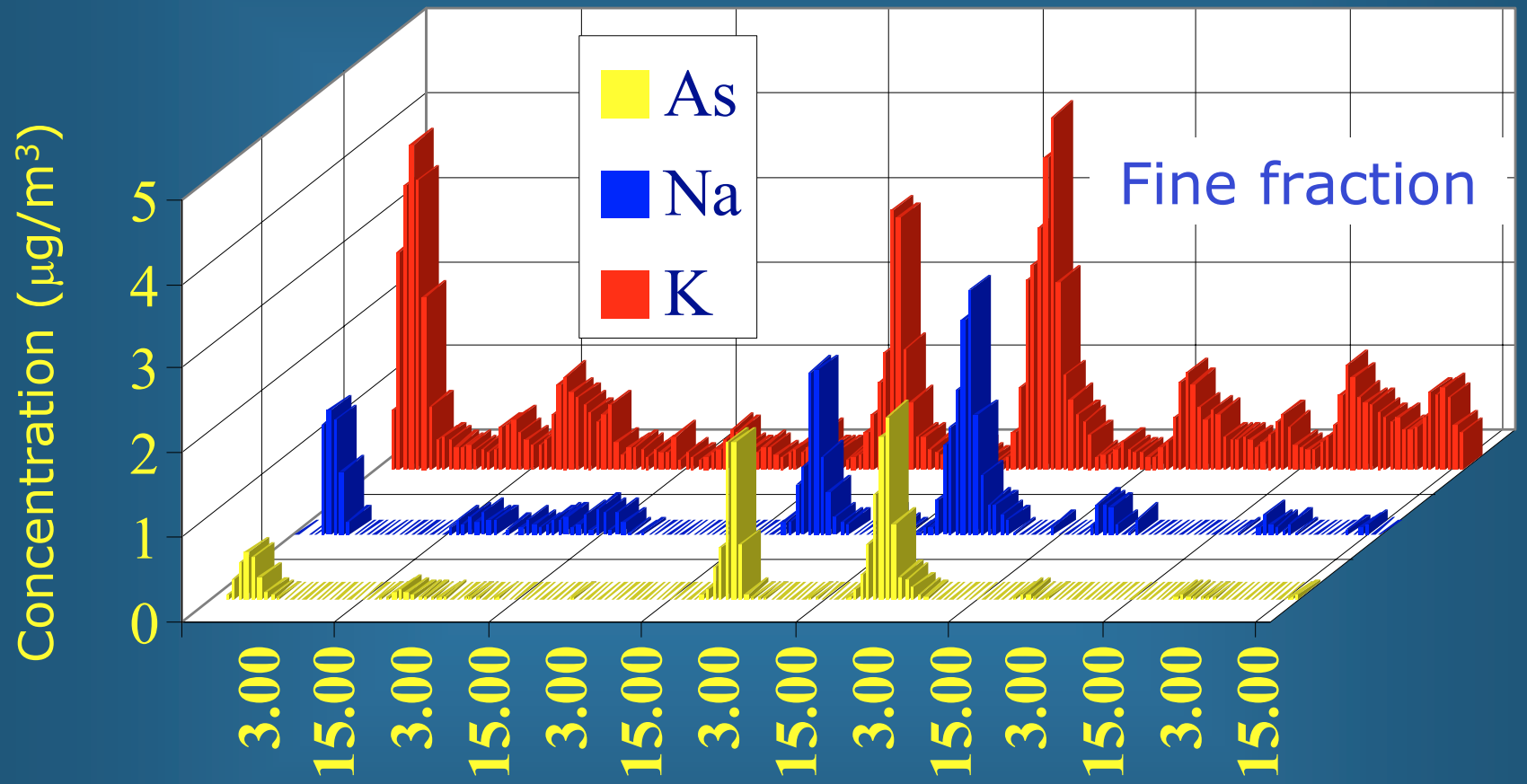
Fireworks on Dec 31

Firenze 1997-1998

Campaigns in an industrial district 20 Km west of Florence: Montelupo Fiorentino

(ceramics, glass)

Episodes of correlated Na, K, As peaks during the night (March '96)



Montelupo Fiorentino: identification of industrial releases in connection with artistic glass production

Aerosol particles maintainthe fingerprint of their source even after long-range transportation

➡

Aerosol composition and time behaviour provide information on pollution sources

Absolute Principal Component Analysis

Groups detected elements according to similarities of their time behaviour

n inter-correlated variables (concentrations)

➡

$p < n$ independent variables ('components' or 'factors')

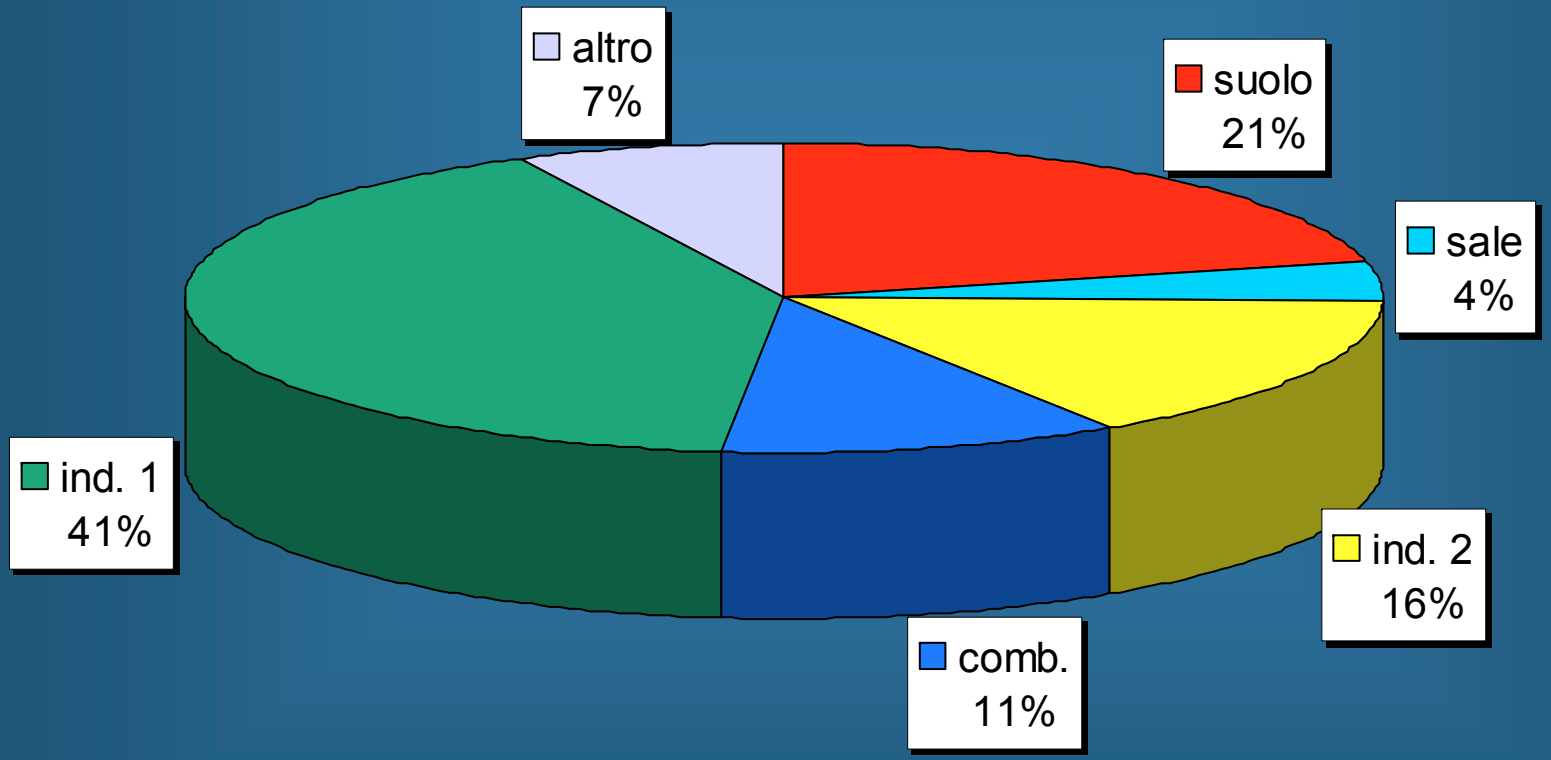
- explain a large part of the data variance
- represent the sources of partculate

Factor loadings

	suolo	*sale*	*ind. 2*	*comb.*	*ind. 1*
Na	0,16	**0,92**		0,09	
Mg	**0,86**	0,43	0,12	0,06	0,12
Al	**0,94**	0,26	0,07	0,12	0,04
Si	**0,95**	0,21	0,14	0,10	0,08
S			0,14	**0,94**	
Cl	0,29	**0,90**			
K	**0,73**	0,23	0,31	0,13	0,39
Ca	**0,90**	0,09	0,23	0,06	0,18
Ti	**0,92**	0,10	0,03	0,03	0,23
V	0,38			**0,64**	0,48
Cr	0,51		0,40	0,04	0,59
Mn	**0,87**		0,24	0,05	0,34
Fe	**0,89**	0,06	0,17	0,03	0,36
Ni	0,40		0,23	0,23	**0,77**
Cu	0,38		0,45		**0,67**
Zn	0,23		**0,75**	0,09	0,33
Br		0,55	0,22		**0,68**
Pb	0,19	0,22	**0,85**	0,04	0,14

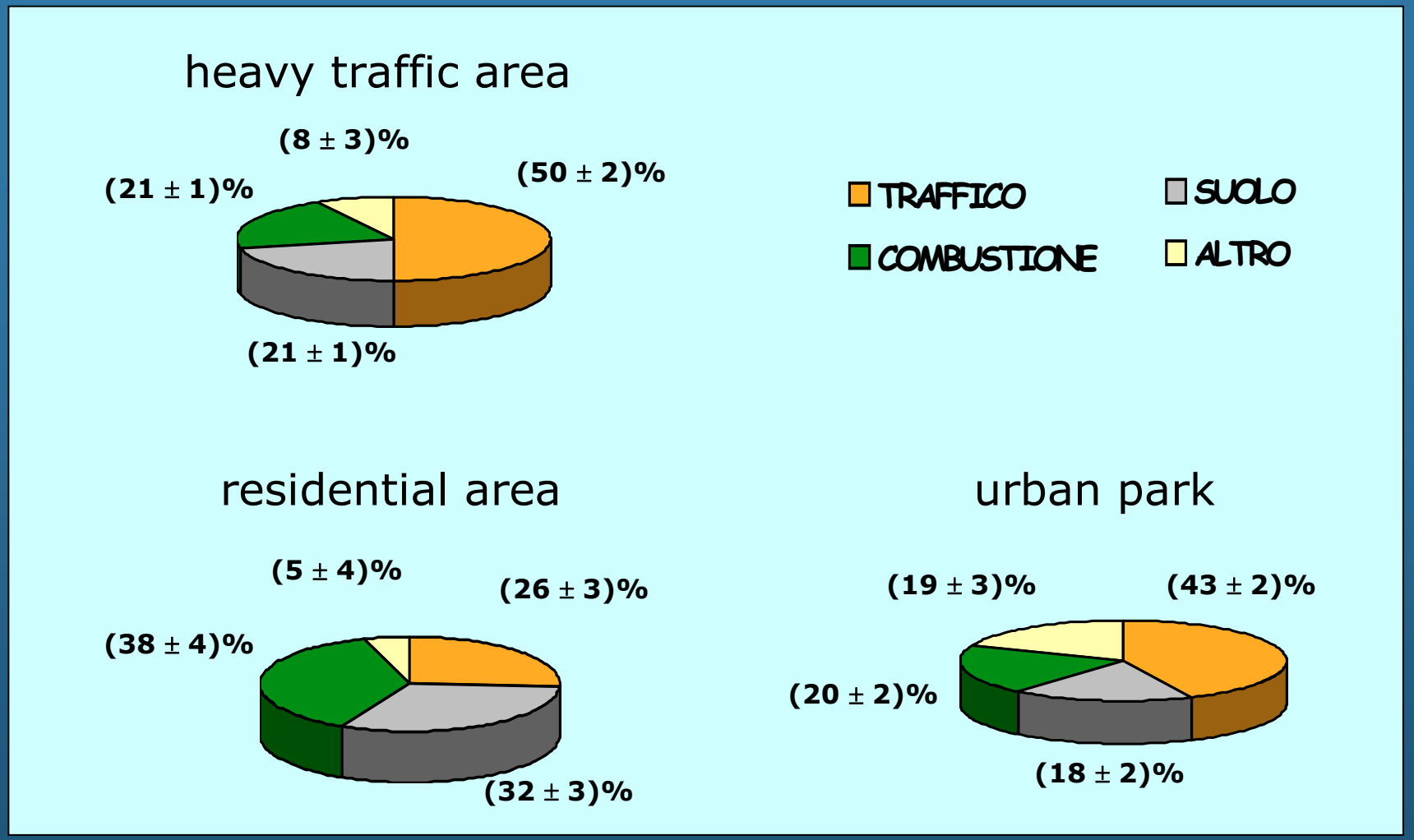
The case of Montelupo Fiorentino (industrial area)

Relative contribution of the various sources to total PM_{10} mass (annual average, 1998)



The case of Montelupo Fiorentino (industrial area)

Relative contribution of the various sources to total PM_{10} mass (1997-1998)



The case of Florence (urban area)