USO COMBINATO DEI SISTEMI PORTATILI PIXE-ALFA E XRD PER LA DETERMINAZIONE QUANTITATIVA, NON DISTRUTTIVA, DI PIGMENTI.

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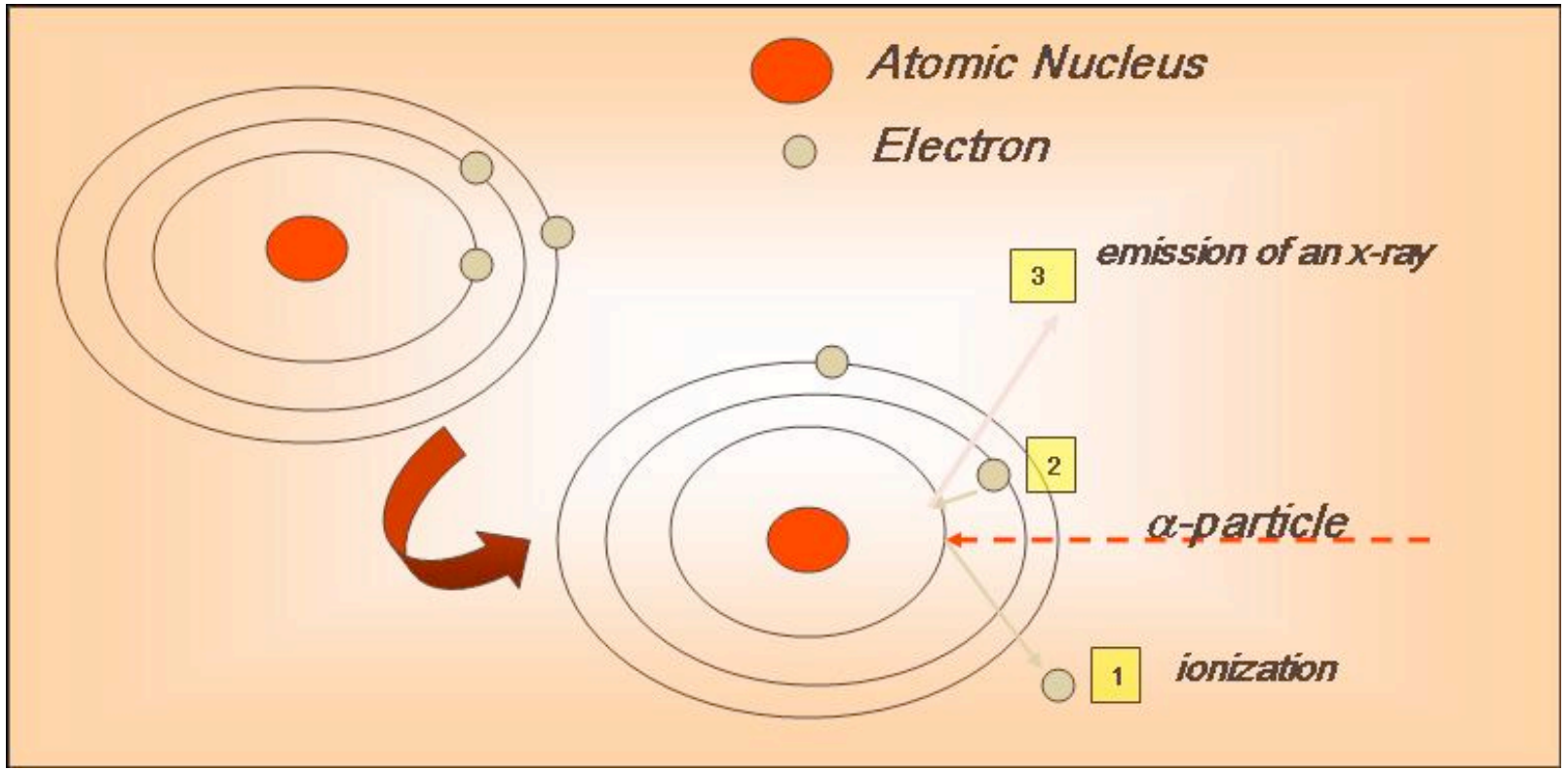
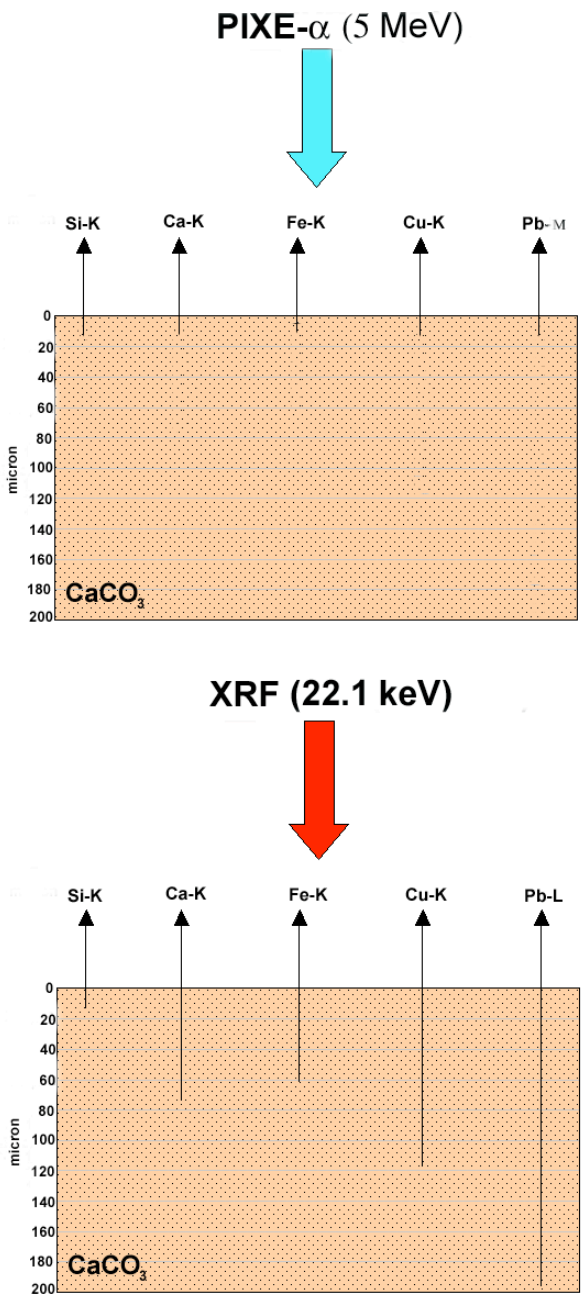
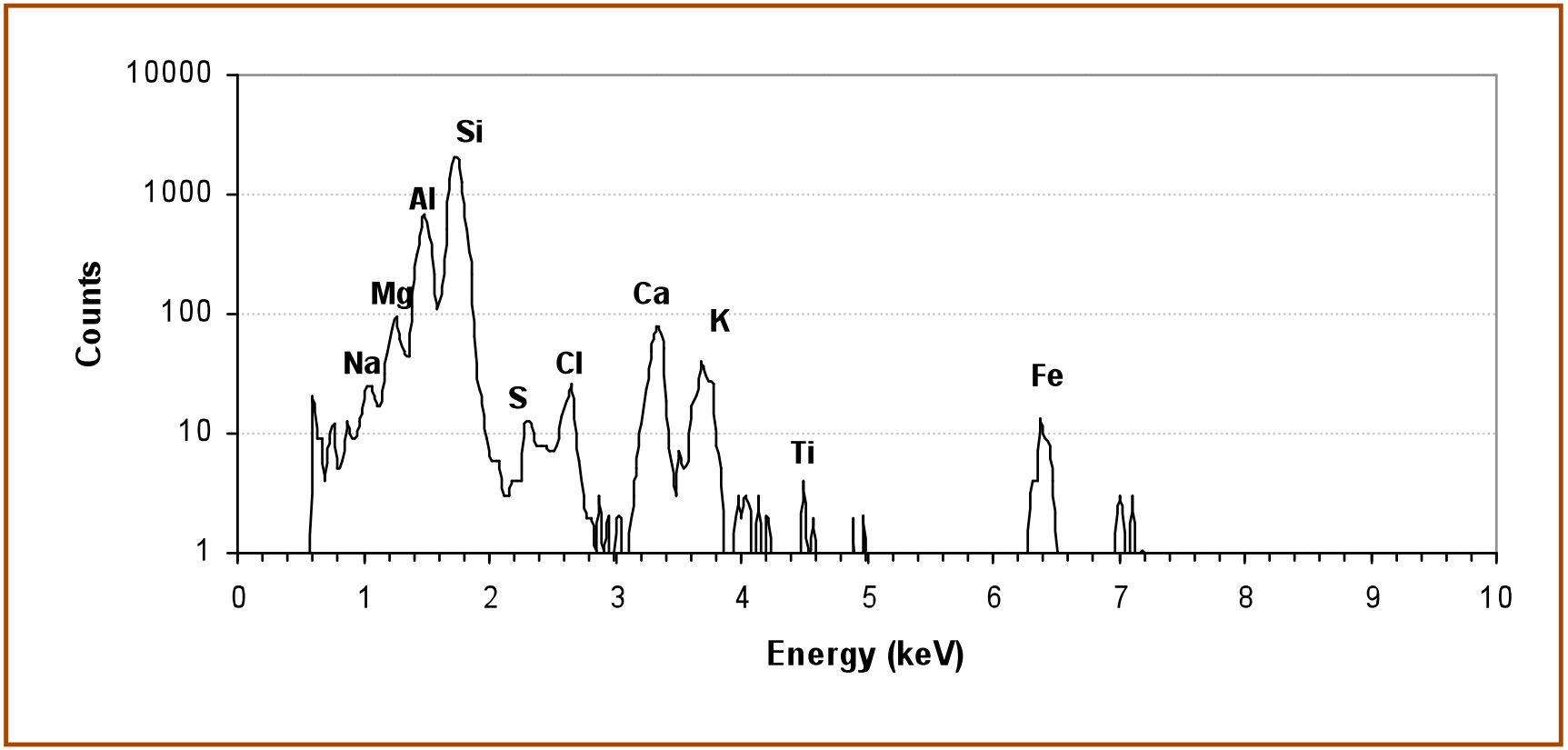
PIXE – Particle Induced X-ray Emission

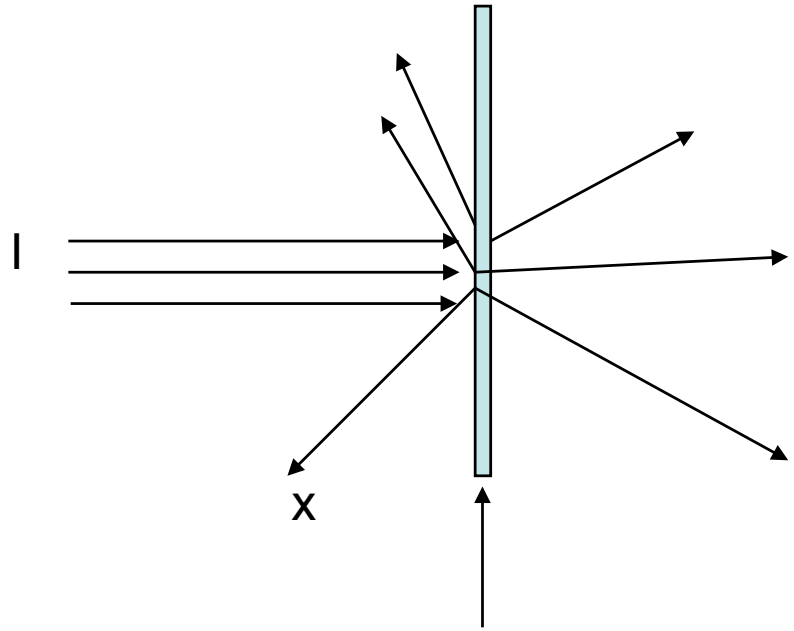



PIXE-α (5 MeV)
Si-K
Ca-K
Fe-K
Cu-K
Pb-M
0
20
40
60
80
100
120
140
160
180
200
micron
CaCO3
XRF (22.1 keV)
Si-K
Ca-K
Fe-K
Cu-K
Pb-L
0
20
40
60
80
100
120
140
160
180
200
micron
CaCO3


10000
1000
100
10
1
Counts
Si
Al
Mg
Na
S
Cl
Ca
K
Ti
Fe
0
1
2
3
4
5
6
7
8
9
10
Energy (keV)

PIXE – ANALISI QUANTITATIVA

TARGHETTE SOTTILI



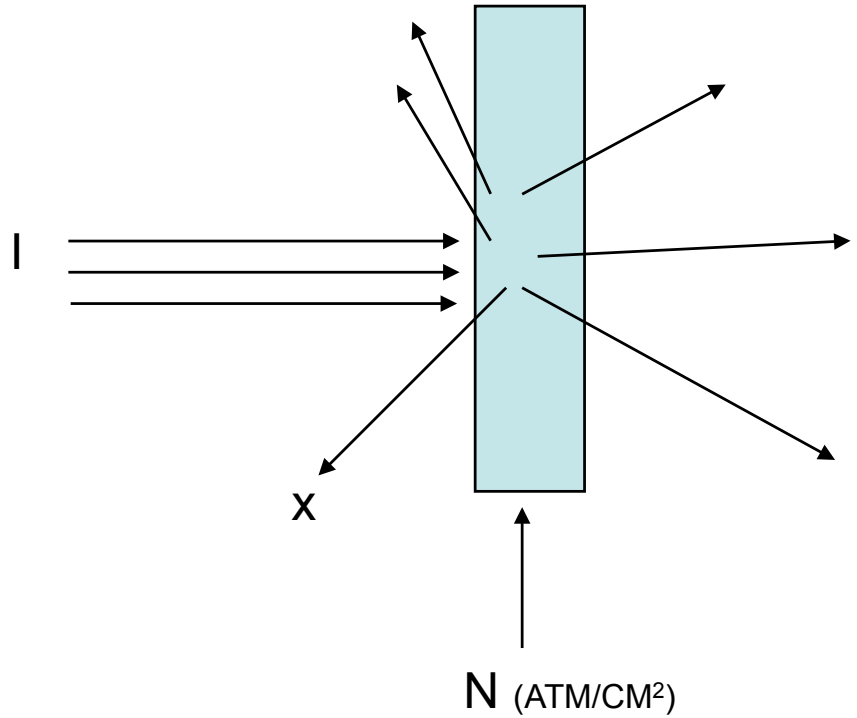
N (ATM/CM^2)

$\sigma = X/(NI) \rightarrow N = X/(I\sigma)$

X' rivelati = f(X, Assorb, $\Delta\Omega$)

PIXE – ANALISI QUANTITATIVA

TARGHETTE SPESSE



$\sigma = X/(NI) \rightarrow N = X/(I\sigma)$

X' rivelati = f(X, Assorb, $\Delta\Omega$, Auto-Ass.+altri effetti)

Auto-assorbimento dipende dalle concentrazioni che si vogliono determinare

AUTO ASSORBIMENTO

1) Tutto quello che rivelo nello spettro è tutto quello contenuto nel campione (Elementi Visibili)

2) Quello che rivelo nello spettro è solo parte di quelllo che è contenuto nel campione (Elementi Invisibili)

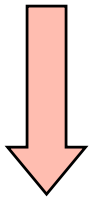
ENTRAMBI I CASI VENGONO RISOLTI PER MEZZO DI PROCEDURE DI ITERAZIONE

Nel Caso 2 è necessario che gli elementi invisibili (tipicamente Ossigeno, Carbonio o altri radicali) siano legati stechiometricamente agli elementi visibili

IL SOFTWARE GUPIX (PRODOTTO DALL'UNIVERSITA' DI GUELPH, CANADA) PERMETTE IL CALCOLO DELLE CONCENTRAZIONI

PROBLEMA PRINCIPALE:

COME STABILIRE QUALI ELEMENTI INVISIBILI, LEGATI STECHIOMETRICAMENTE AI VISIBILI, SONO PRESENTI ?



Occorre servirsi di altri metodi di analisi di composti (per es. Raman o XRD)

PROCEDURA

PIXE-α

XRD

NON DESTRUCTIVE

IN SITU

Major and minor elements determination, from Na to Zn (K-lines) and higher Z elements (L and M lines)

Determination of the possible mineral species constituting the pigment

CHARACTERIZATION OF THE CHEMICAL ELEMENTS COSTITUTING THE PIGMENT

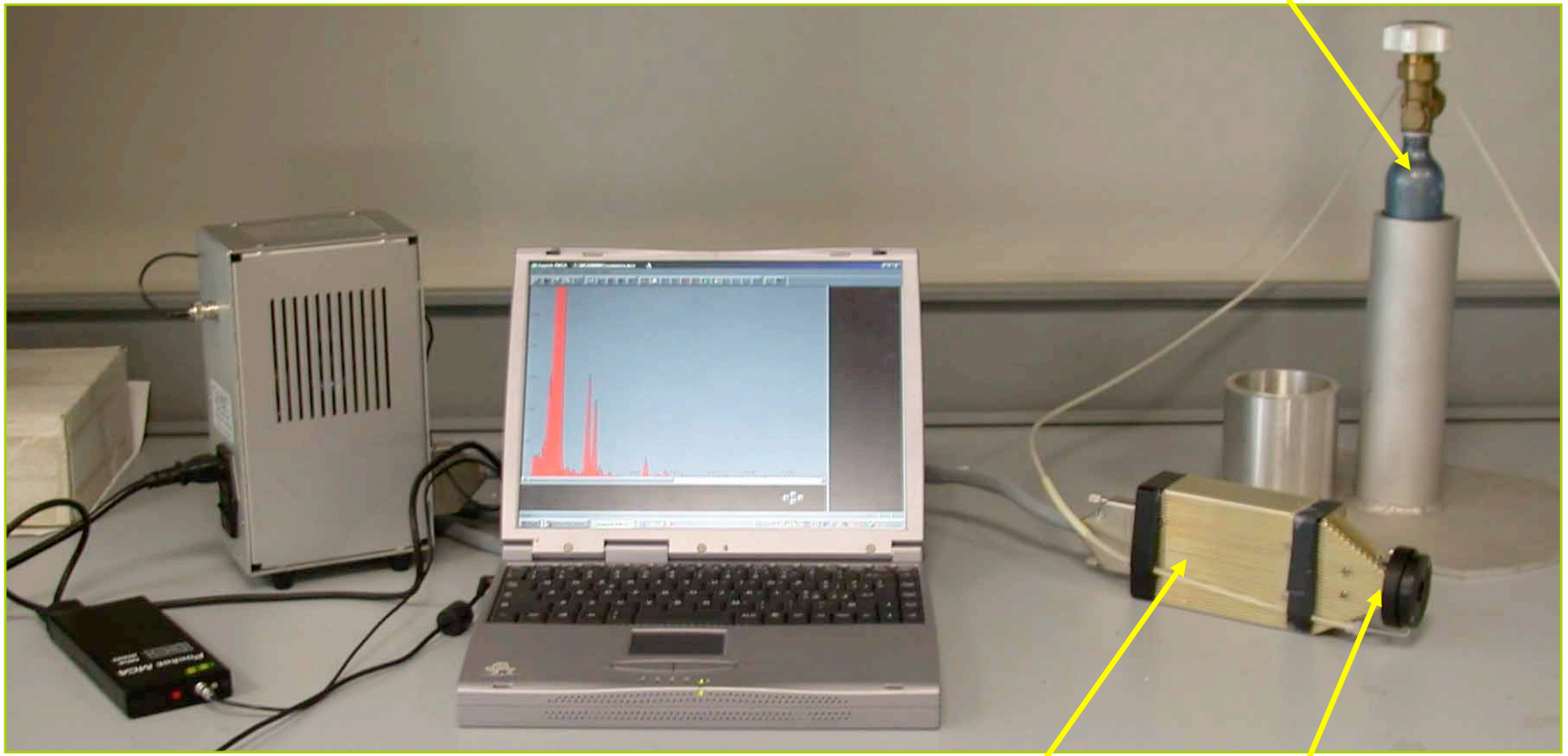
DETERMINATION OF THE PIGMENT'S NATURE

QUANTITATIVE ANALYSIS

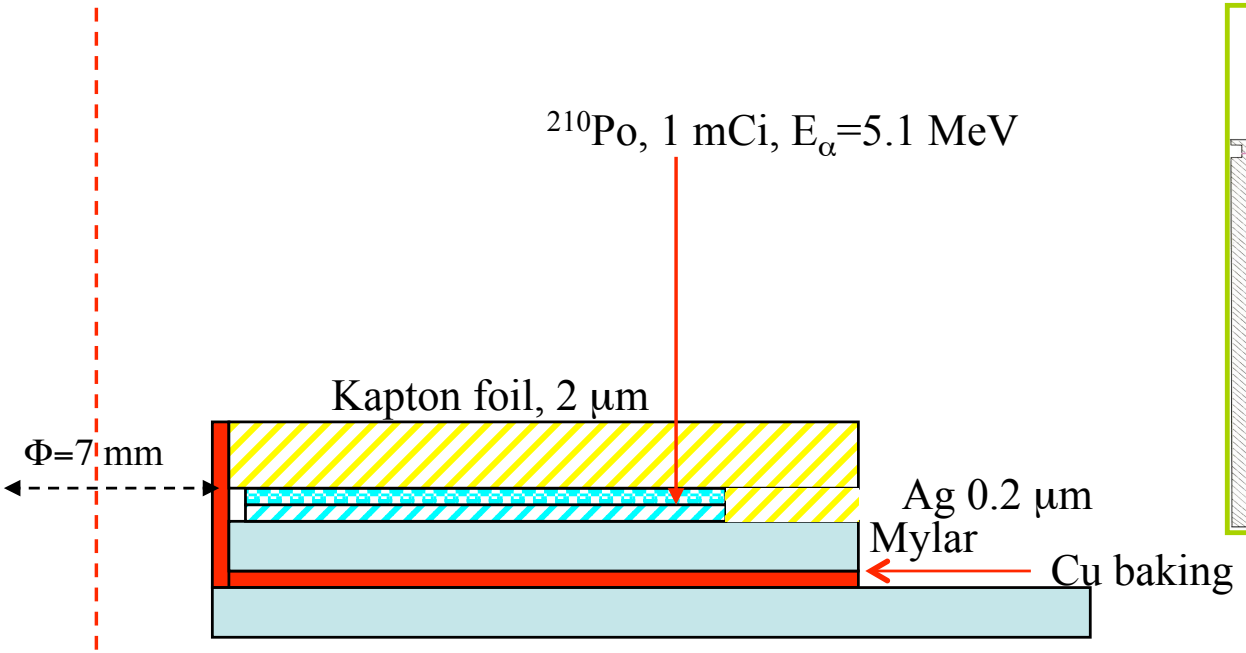
APPLICAZIONI AD AFFRESCHI DI EPOCA ROMANA

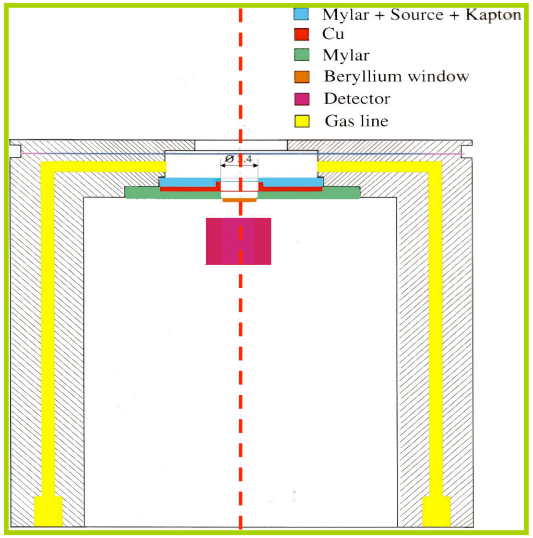
E’ INDISPENSABILE OPERARE CON STRUMENTAZIONE PORTATILE!

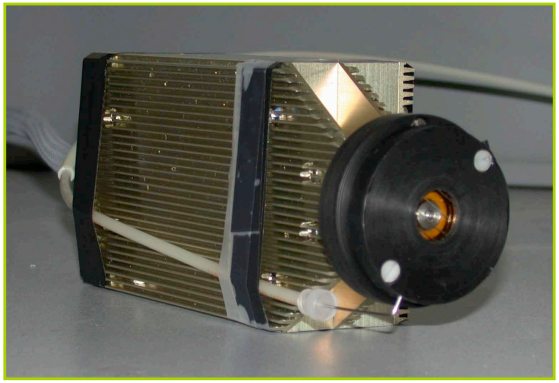
The PIXE-alpha spectrometer



THE SOURCE


^{210}Po, 1 mCi, E_α=5.1 MeV
Kapton foil, 2 μm
Φ=7 mm
Ag 0.2 μm
Mylar
Cu baking

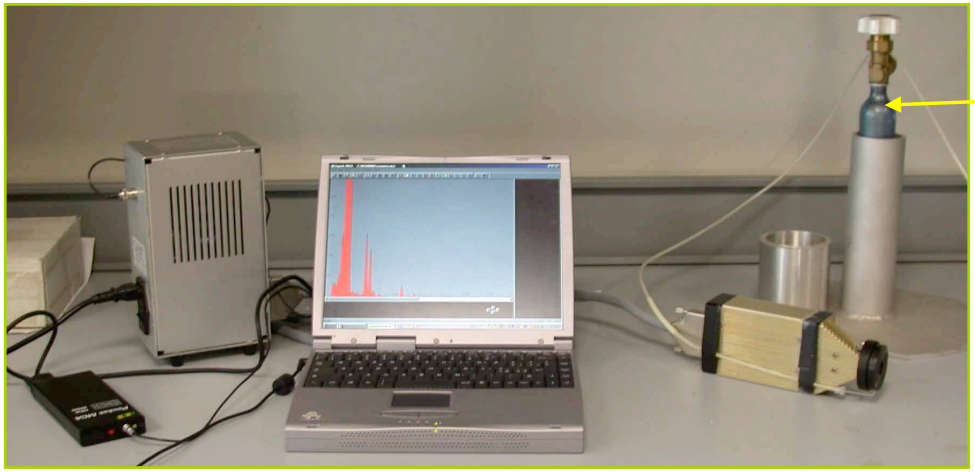

Mylar + Source + Kapton
Cu
Mylar
Beryllium window
Detector
Gas line



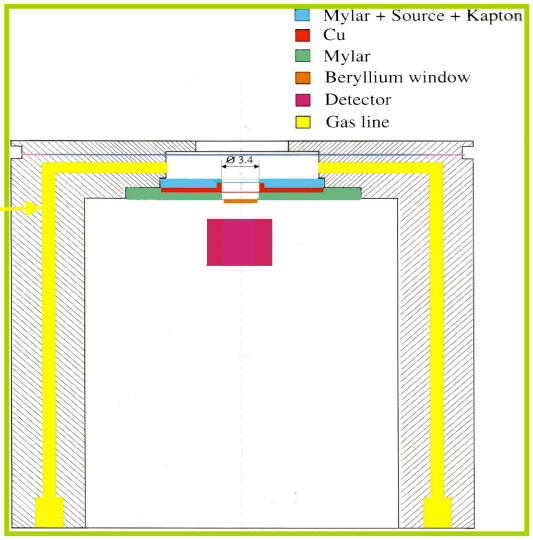
THE DETECTOR

- Peltier cooled
- Si drift
- 10 mm^2
- Resolution of 146 eV at 5.9 KeV
- 8 μm Be window
- Produced by KEVEK and assembled by EIS

The Helium Flux



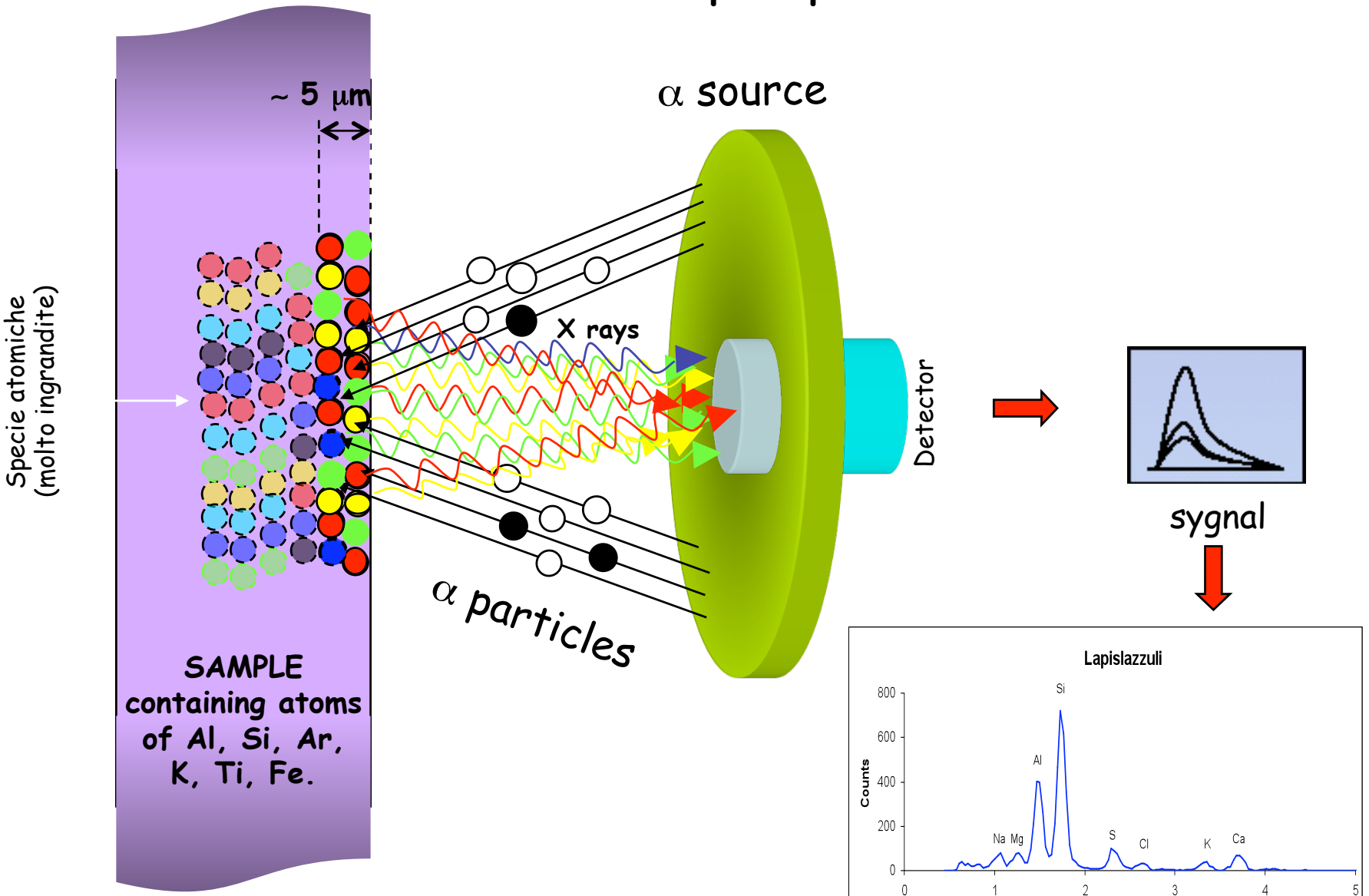
10 l/h



Inhibition of the presence of air gases, in particular of Ar ($k\alpha$=2.95 keV)

Better definition of the low atomic number elements, such as Na

PIXE - α
Basic principle

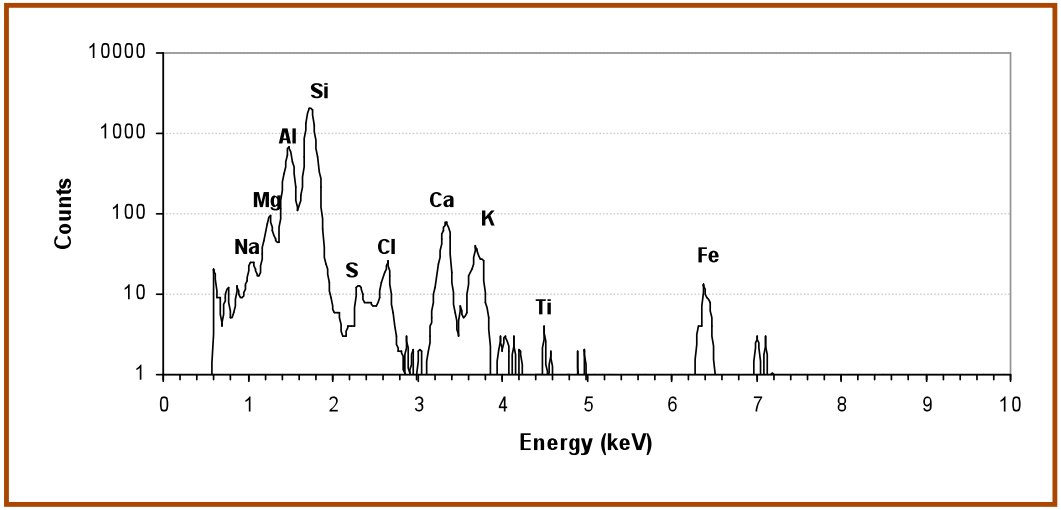


Energy spectrum of a lapislazzuli.

QUANTITATIVE ANALYSIS

Performed by GUPIX 2003 CODE .

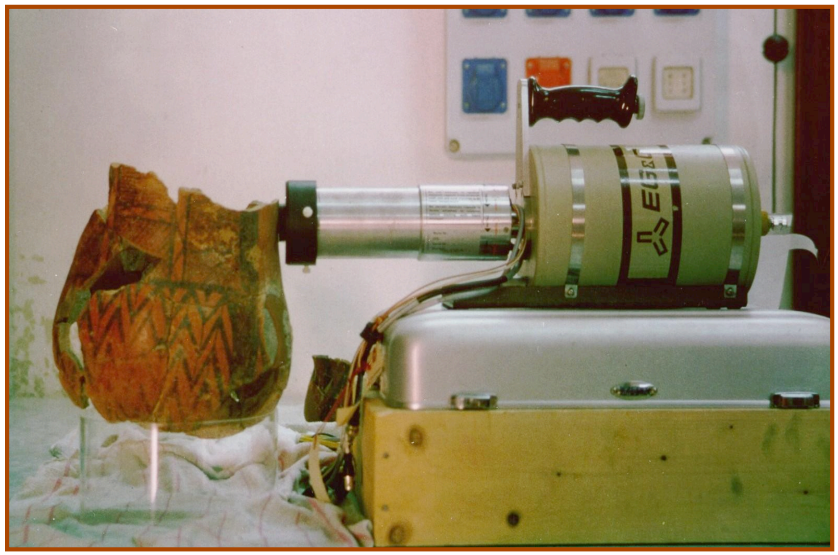
(Maxwell J., Teesdale A., Campbell J. L, 2003), in the "Matrix Calculation" Mode

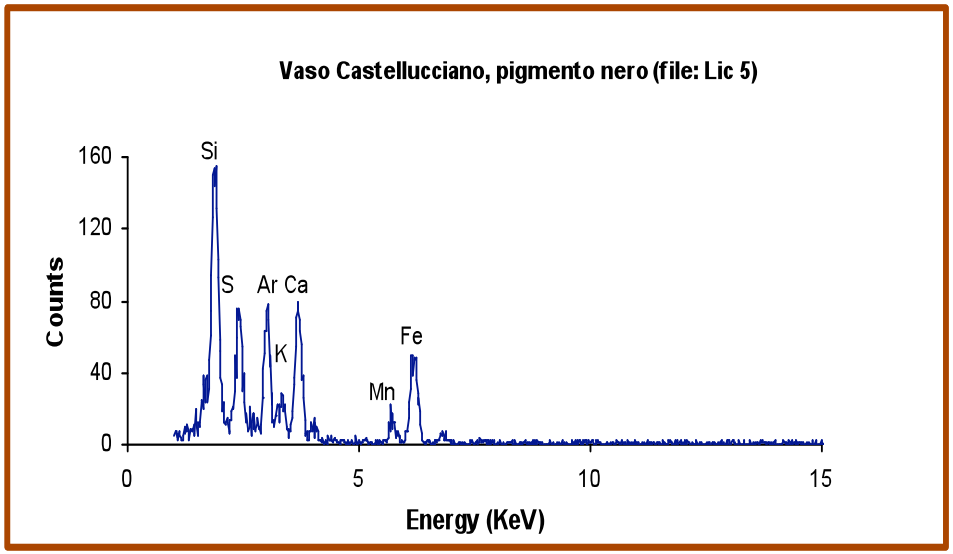


PIXE-alpha spectrum obtained from the petrological standard SCO-1

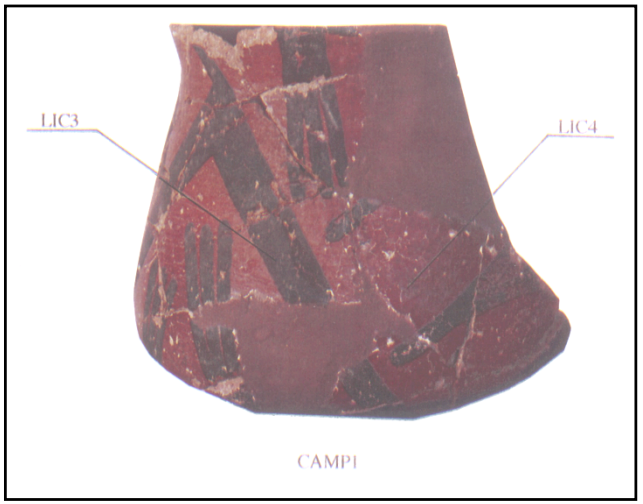
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe(III) tot
EIS	**0.8 ± 0.2**	**2.8 ± 0.4**	**16.2 ±2.2**	**64.7 ±6**	**0.3 ±0.2**	**3.5 ±0.4**	**2.8±0.5**	**0.7 ±0.1**	**5.5 ±1.6**
Ref.	**0.9**	**2.72**	**13.67**	**62.78**	**0.21**	**2.77**	**2.62**	**0.63**	**5.14**

Comparison between the results of the PIXE-alpha analysis and the certified data of the SCO-1 reference standard. Values are in %.



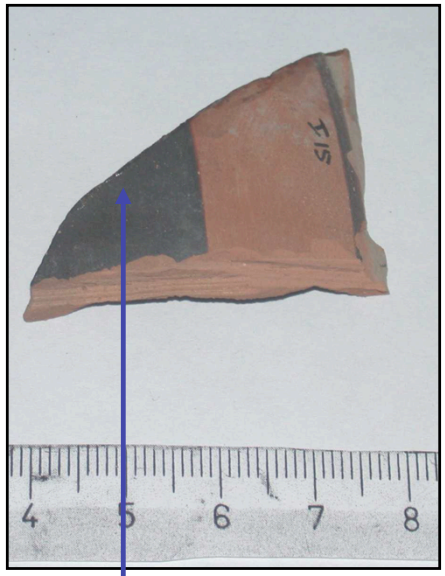


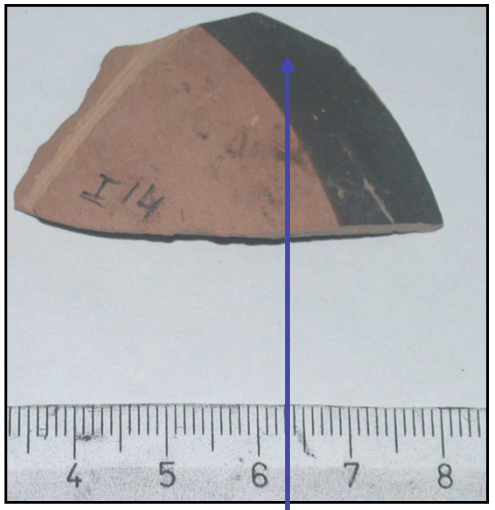
PIXE-α analysis of the red and black pigments on a Castellucciano vase, at the Archaeological Museum of Licata. The high value of the Mn/Fe (0.91) ratio in vases of Serraferlicchio style is compatible with the artificial addeed of manganese powder to the "Terra d'Ombra".

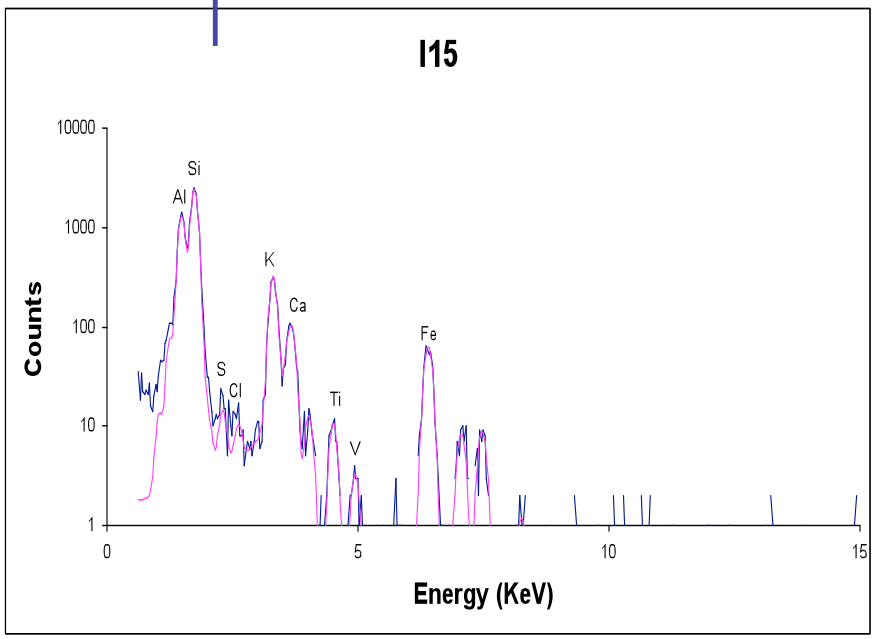


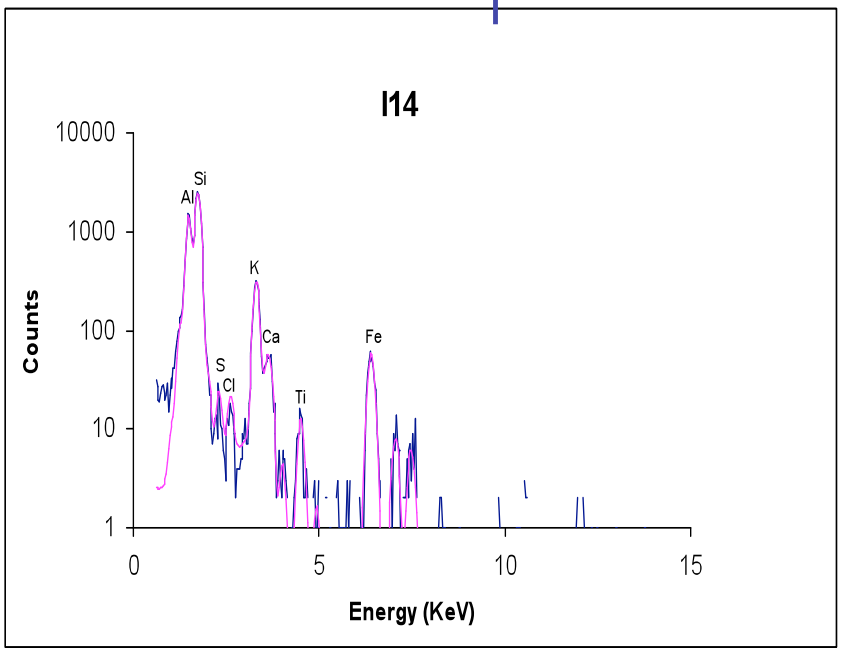
Sigla	Al	Si	K	Ti	Ca	Mn	Fe	S	Cl	Mn/Fe
Camp1 (lic3) - black	138	798	173	46	827	190	208	1115	95	0.91
" (lic4) - red	65	664	209	7	757	3	252	965	94	0.01
Camp2 (lic5) - black	182	1305	211	9	775	145	490	729	129	0.29
" (lic6) - red	335	2286	445	10	730	5	379	841	142	0.013
Camp3 (lic7) - white	234	1453	184	7	695	11	55	366	19	0.2
" (lic8) - black	218	1364	152	16	564	48	125	199	64	0.38
Camp4 (lic9) - black	220	1298	249	21	330	186	294	316	206	0.63
Camp5 (lic10)-white	502	3597	199	23	575	4	200	84	34	0.02
" (lic11) - red	353	3019	233	70	412	14	726	131	55	0.019

Black pigment analysis on Ionic pottery

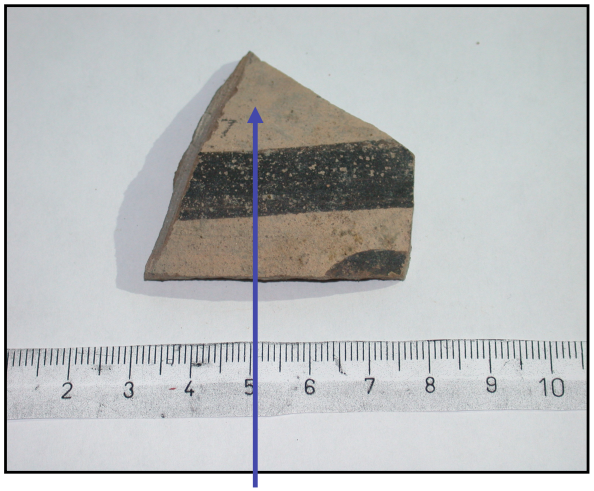


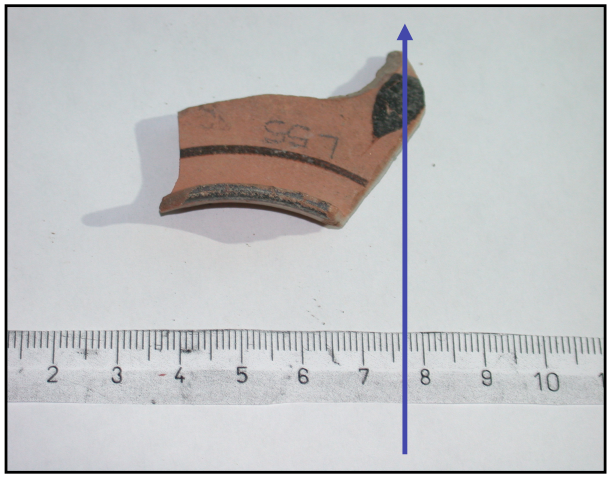


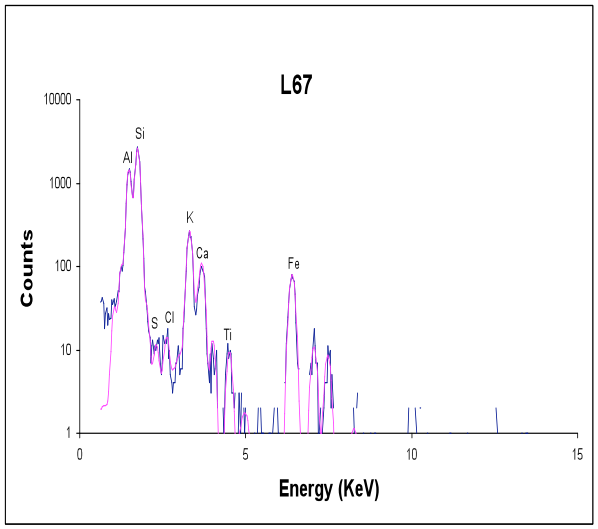


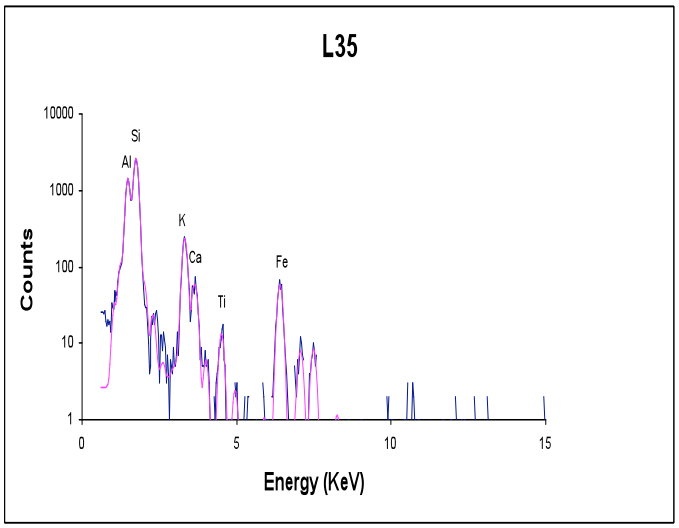


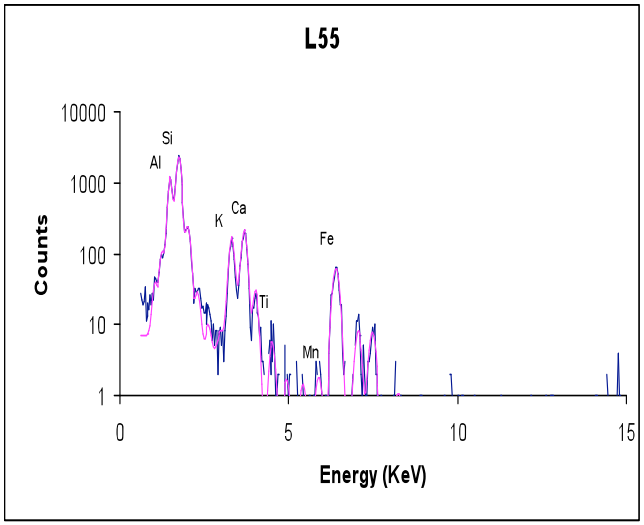
Black pigment analysis on Local pottery

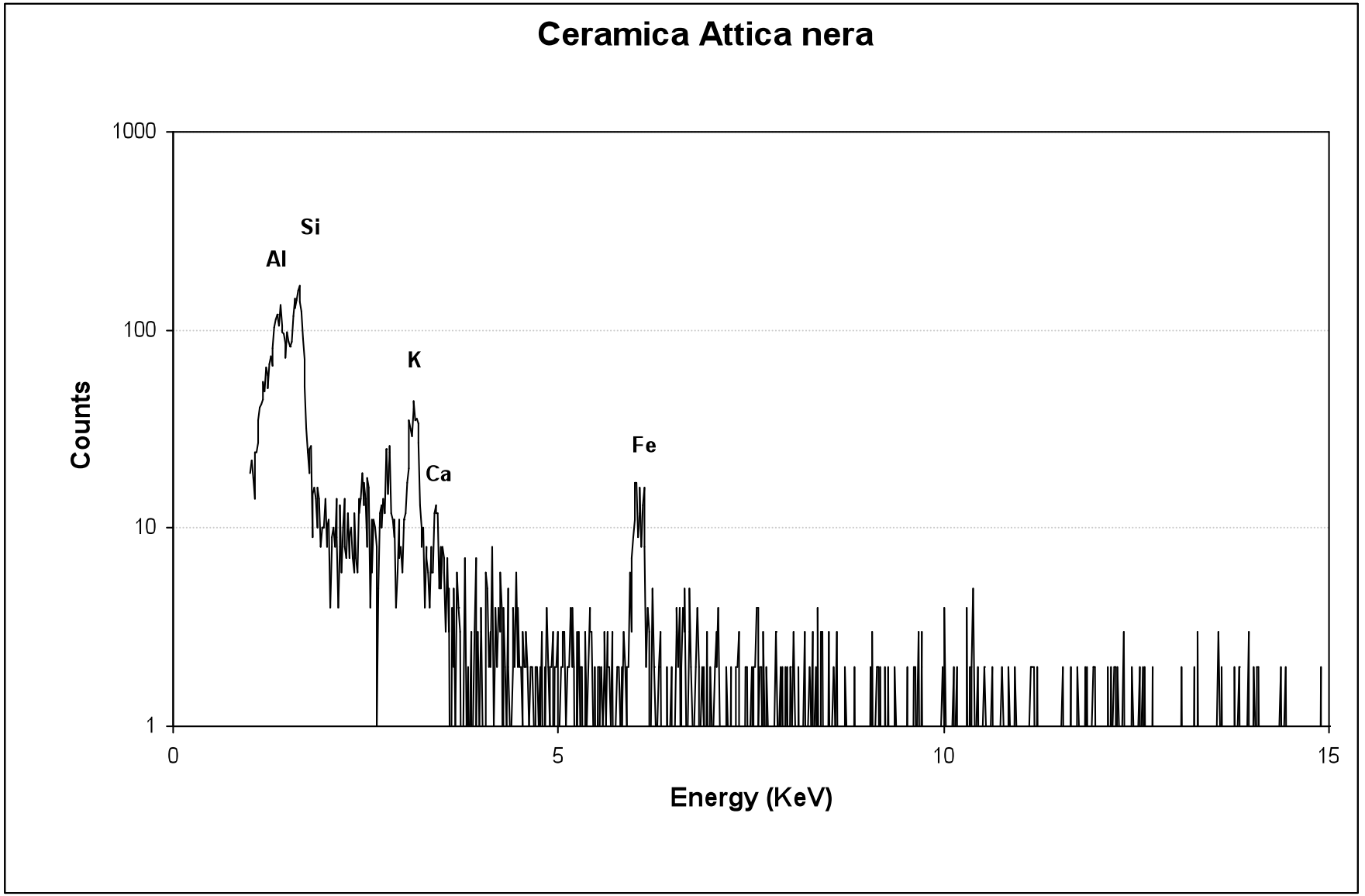











Ceramica Attica nera
1000
100
10
1
Counts
Al
Si
K
Ca
Fe
0
5
10
15
Energy (KeV)

	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_{tot}	*****a
ATT-1	1.9	31.7	46.8	4.1	0.9	13.5	SEM
ATT-2	1.8	31.0	46.7	5.5	0.3	13.1	SEM
ATT-3	2.2	29.8	43.4	6.1	0.9	15.4	SEM
ATT-4	1.9	29.2	45.6	4.7	0.6	15.3	SEM
ATT-5	1.9	30.9	45.3	6.5	-	14.8	SEM
ATT-6	1.6	32.4	45.8	3.0	0.3	15.5	SEM
ATT-7 Laros8	2(1.5)	29(2)	42(2)	3.3(0.2)	0.45(0.2)	13(1)	PIXE-alpha
L35	2.3	25	46	5.2	1.4	12.2	PIXE-alpha
L55	2.7	22	42	3.8	7.0	15.0	PIXE-alpha
L67	2.5	23	43	5.4	2.0	16.0	PIXE-alpha
I14	2.9	25	45	7.0	1.0	13.4	PIXE-alpha
I15	2.9	24	43	6	2.8	13.4	PIXE-alpha

*Maniatis et Al. 1993 - *New evidence for the nature of the attic black gloss.* **Archaeometry 35, pp.23-24**

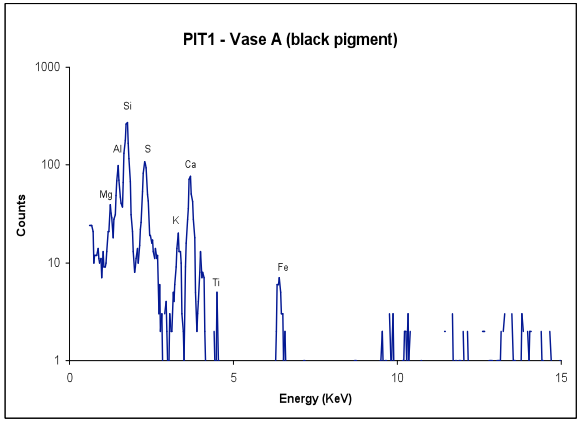
Comparison between the compositions, in %, of black "gloss" on attic pottery coming from different areas and the compositions of black pigments on "local" and "ionic" pottery coming from the Votive Deposit of S.Francesco in Catania.

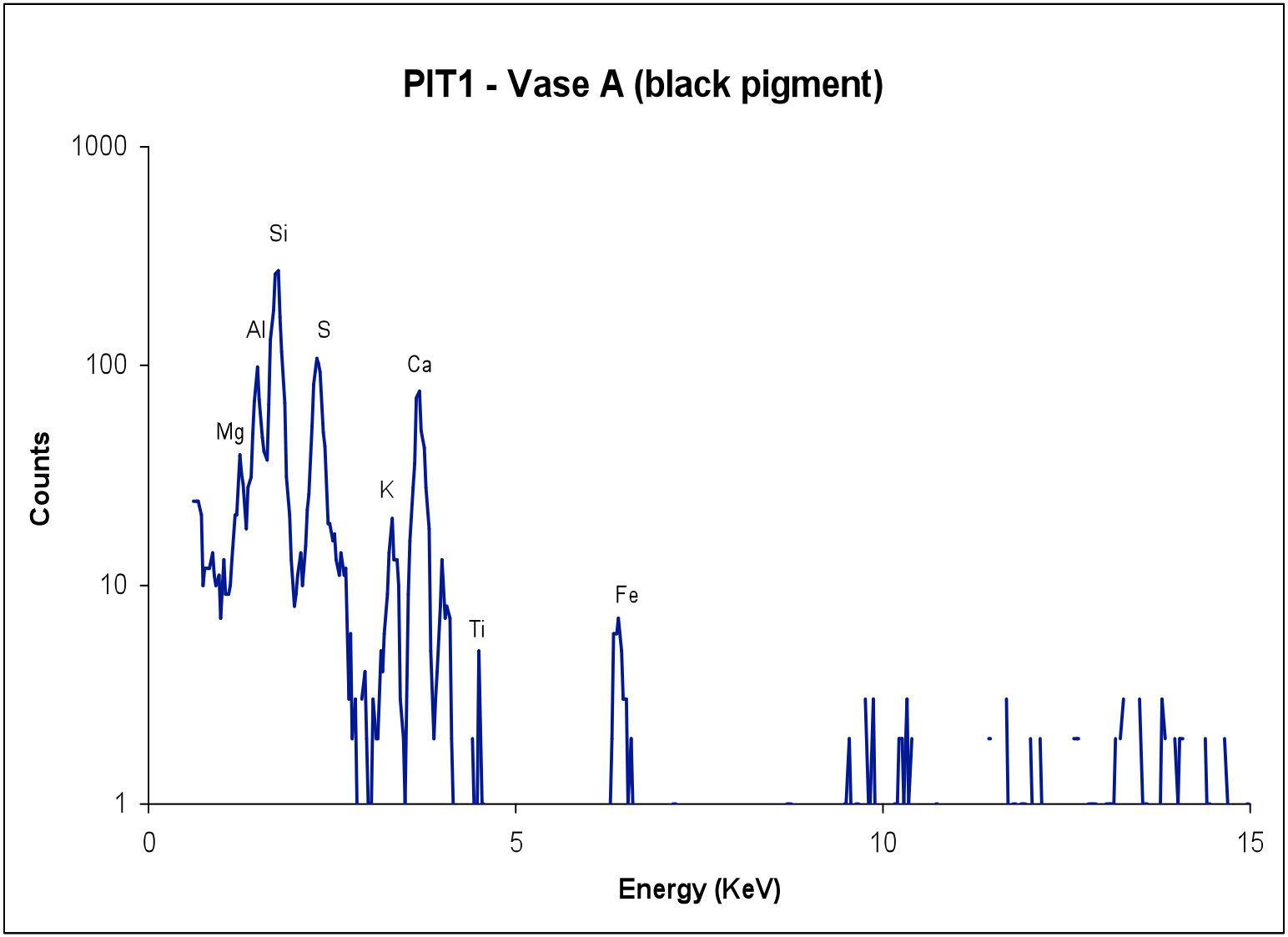
VASE A (18713)

PIT2

PIT 1

PIT 1

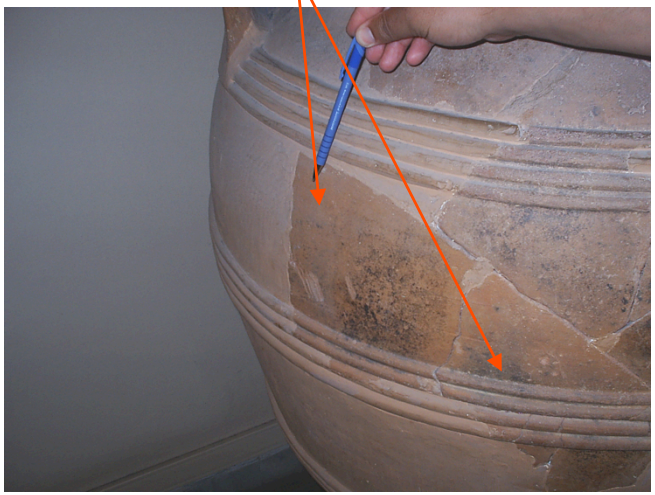



PIT1 - Vase A (black pigment)
1000
100
10
1
Counts
Si
Al
S
Mg
Ca
K
Ti
Fe
0
5
10
15
Energy (KeV)

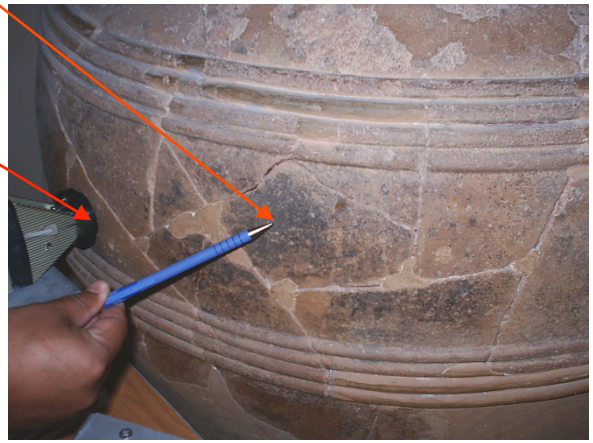
VASE B

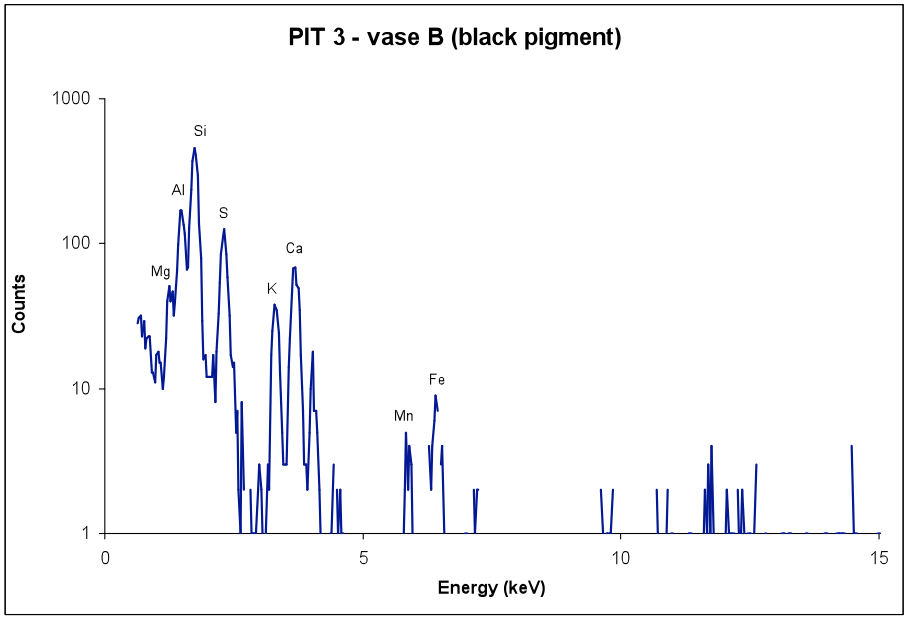
Pit 4

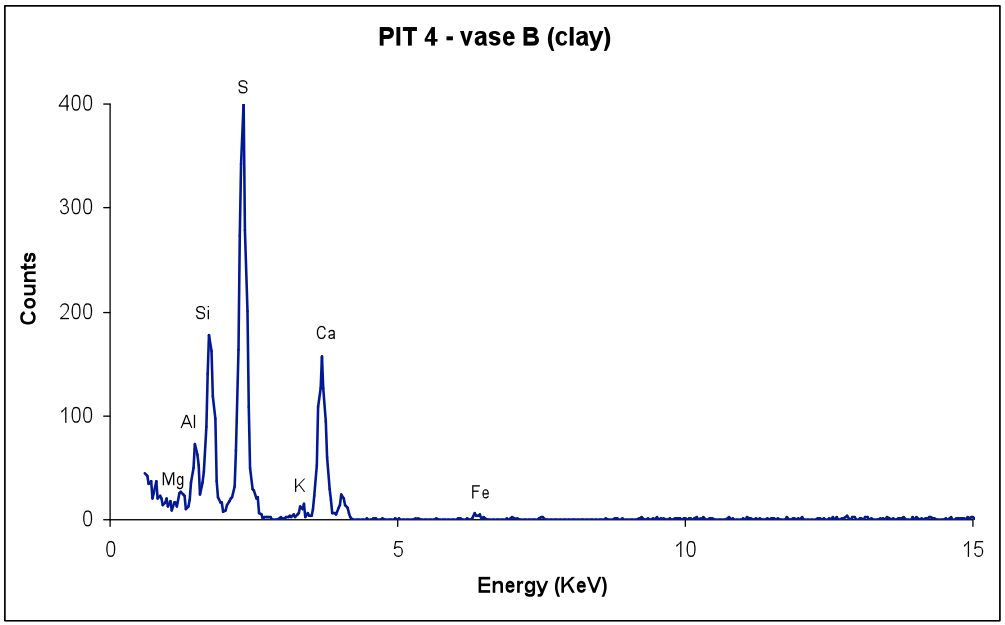
Pit 5

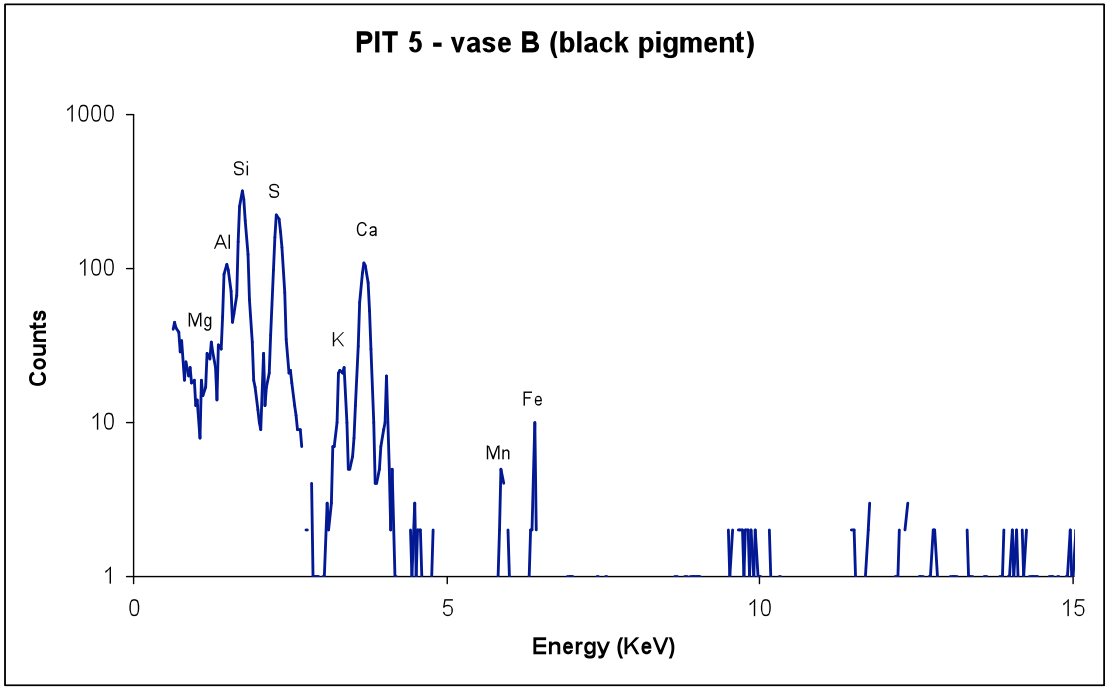


Pit 3



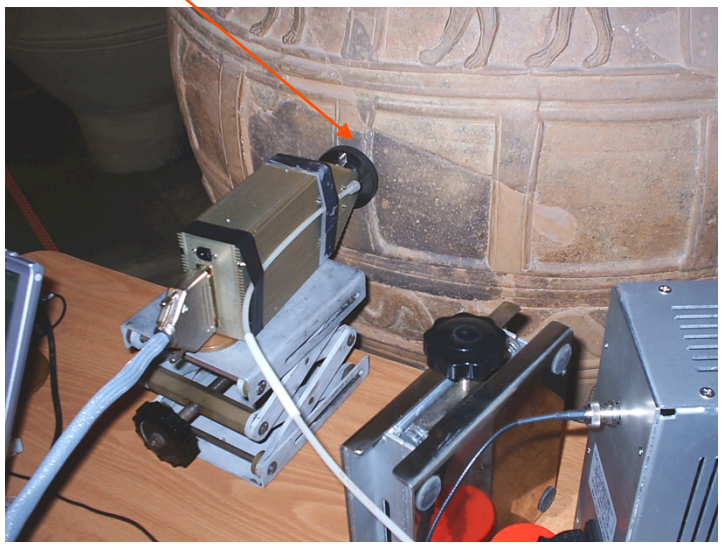

PIT 3 - vase B (black pigment)
Counts
Energy (keV)
1000
100
10
1
0
5
10
15
Si
Al
S
Mg
K
Ca
Mn
Fe

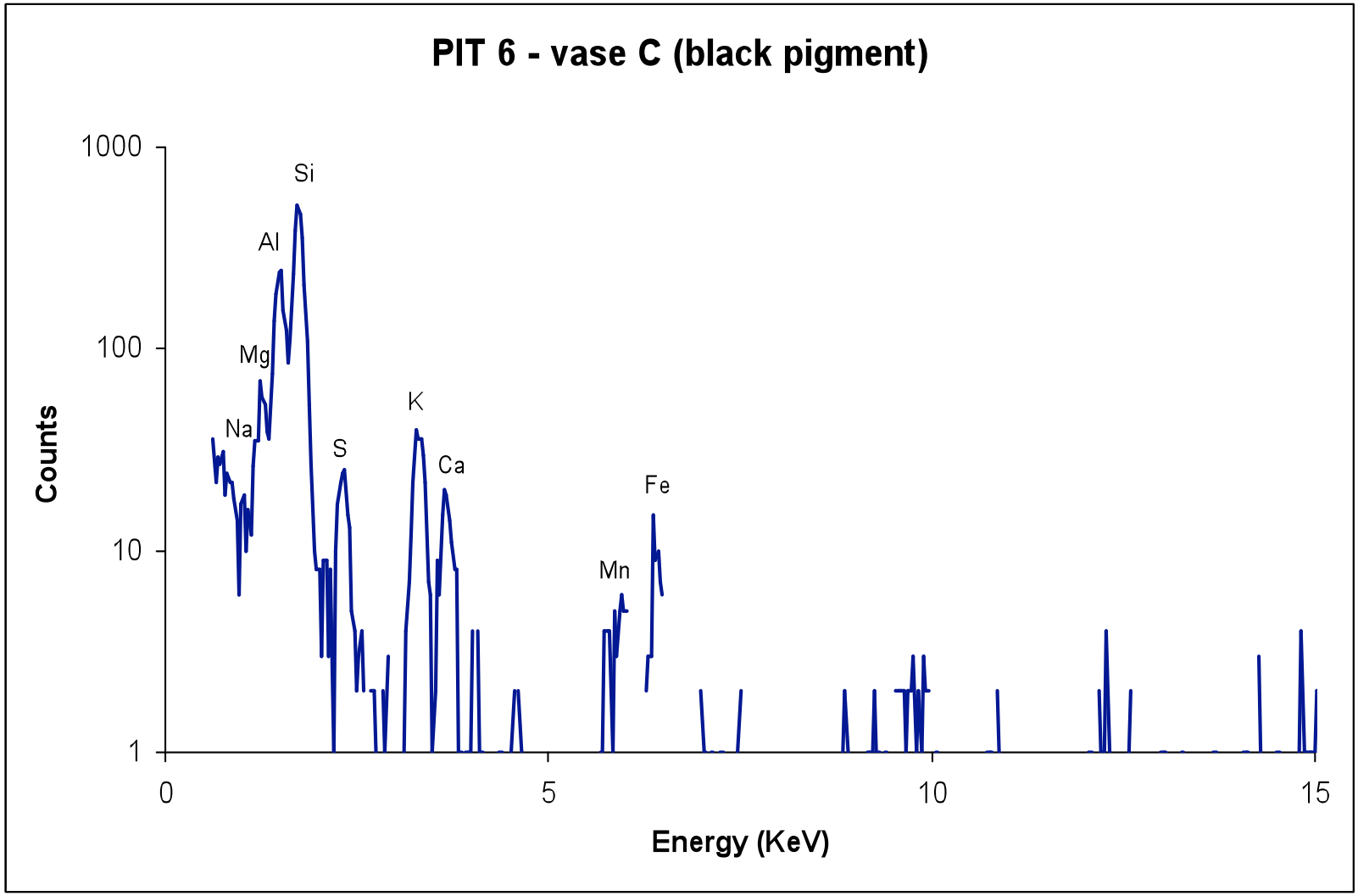

PIT 4 - vase B (clay)
Counts
Energy (KeV)
400
300
200
100
0
0
5
10
15
S
Si
Ca
Al
Mg
K
Fe


PIT 5 - vase B (black pigment)
Counts
Energy (KeV)
1000
100
10
1
0
5
10
15
Si
S
Al
Ca
Mg
K
Fe
Mn

VASE C

Pit 6




PIT 6 - vase C (black pigment)
Counts
1000
100
10
1
0
5
10
15
Energy (KeV)
Si
Al
Mg
Na
S
K
Ca
Mn
Fe

PIXE-alpha results (values in %)

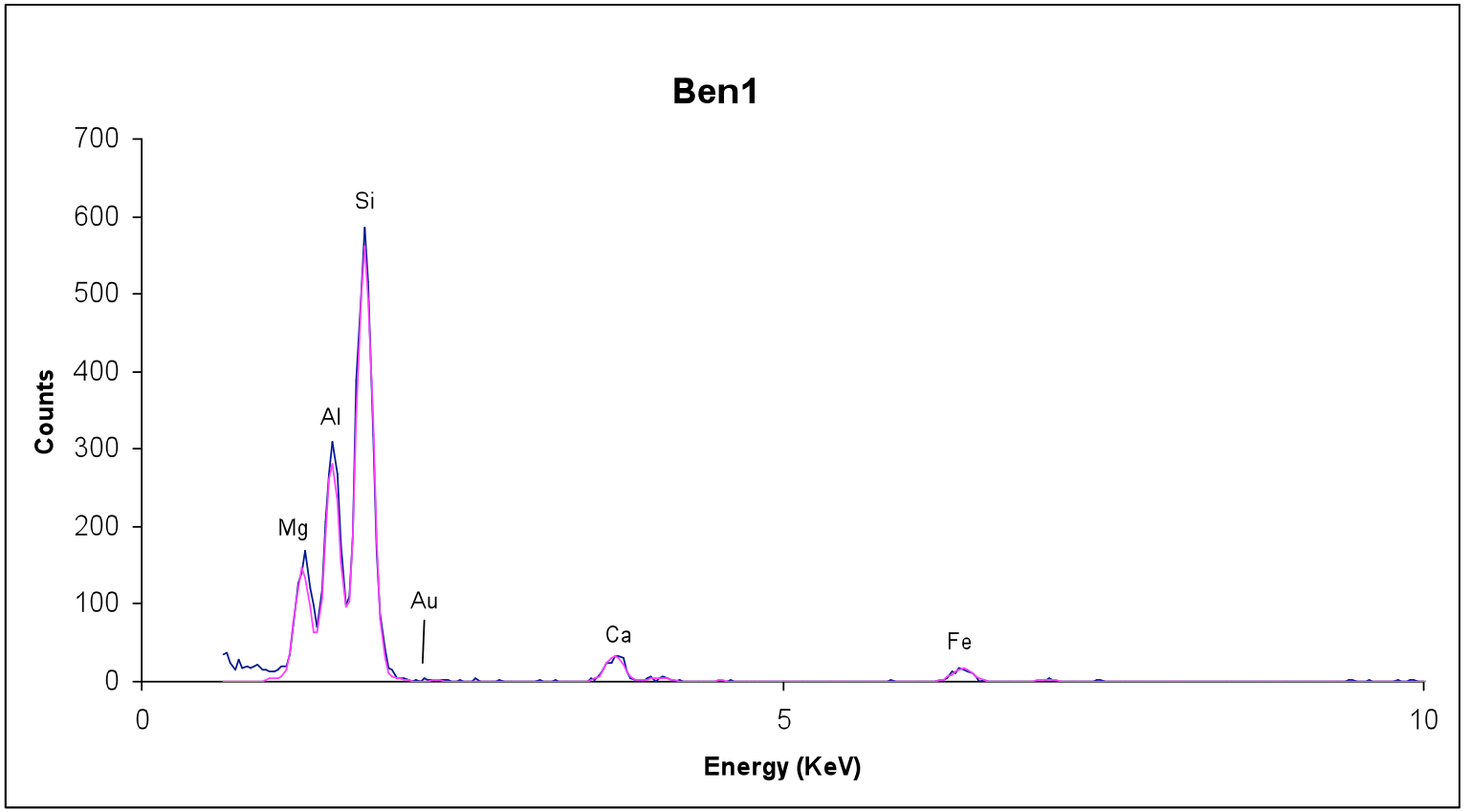
	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	ClO	K2O	CaO	TiO2	MnO	Fe2O3
PIT1	3.1 ± 1.7	6.9 ± 0.7	11.7 ± 0.8	31.2 ± 1	0	16.5 ± 0.9	0.91 ± 0.2	2.3 ± 0.3	16.4 ± 1	1.1 ± 0.55	0	9.5 ± 2
PIT2 A	n.d.	6 ± 0.9	11.4 ± 0.9	35.1 ± 1.4	n.d.	17 ± 1	n.d.	1.4 ± 0.35	14.5 ± 1	1.3 ±0.5	0	8.5 ± 2.1
PIT3	n.d.	5 ± 0.7	13.8 ± 0.7	36.3 ± 1	0.9 ± 0.36	13.3 ± 0.6	n.d.	4.8 ± 0.4	12.11 ± 0.7	n.d,.	3.2 ± 0.89	7.2 ± 1.8
PIT4 B	n.d.	2.8 ± 0.5	5.8 ± 0.5	13.5 ± 0.5	n.d.	37.9 ± 1.1	0.4 ± 0.1	0.8 ± 0.2	26.2 ± 1	0	0	6 ± 1.5
PIT5	0	4.2 ± 0.6	10.2 ± 0.7	25.8 ± 0.7	1.6 ± 0.5	25.1 ± 0.7	0.5 ± 0.1	2.4 ± 0.3	19.1 ± 0.8	0.7 ±0.3	2.7 ± 0.8	5.4 ± 1.6
PIT6 C	0	7.6 ± 0.6	21.5 ± 0.8	43 ± 0.8	1.2 ± 0.4	3 ± 0.3	0	4.6 ± 0.3	2.9 ± 0.4	n.d.	2.7 ± 0.9	11.8 ± 1.8

Inv. 1548

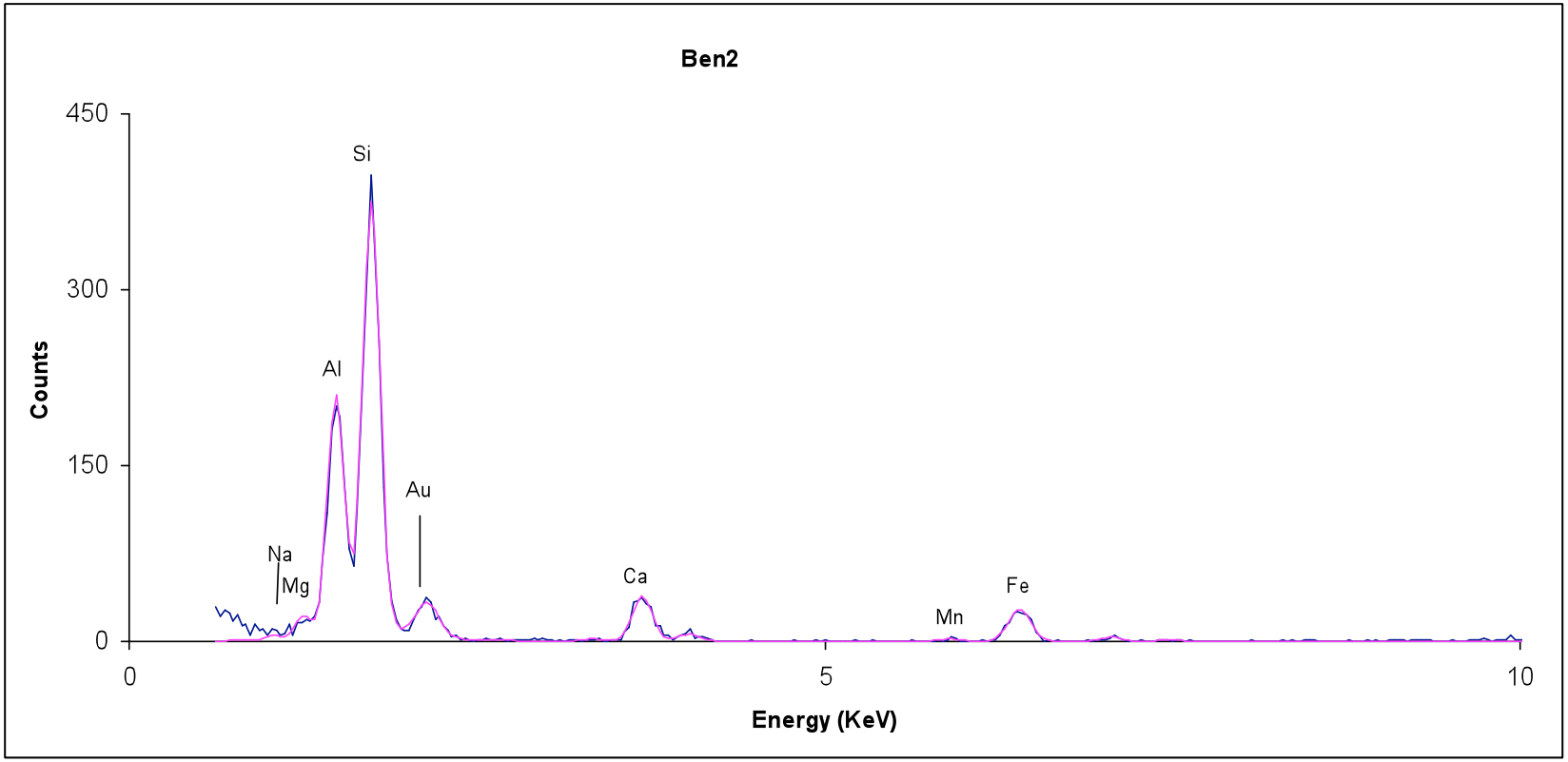
Inv. 1551

Inv. 1562

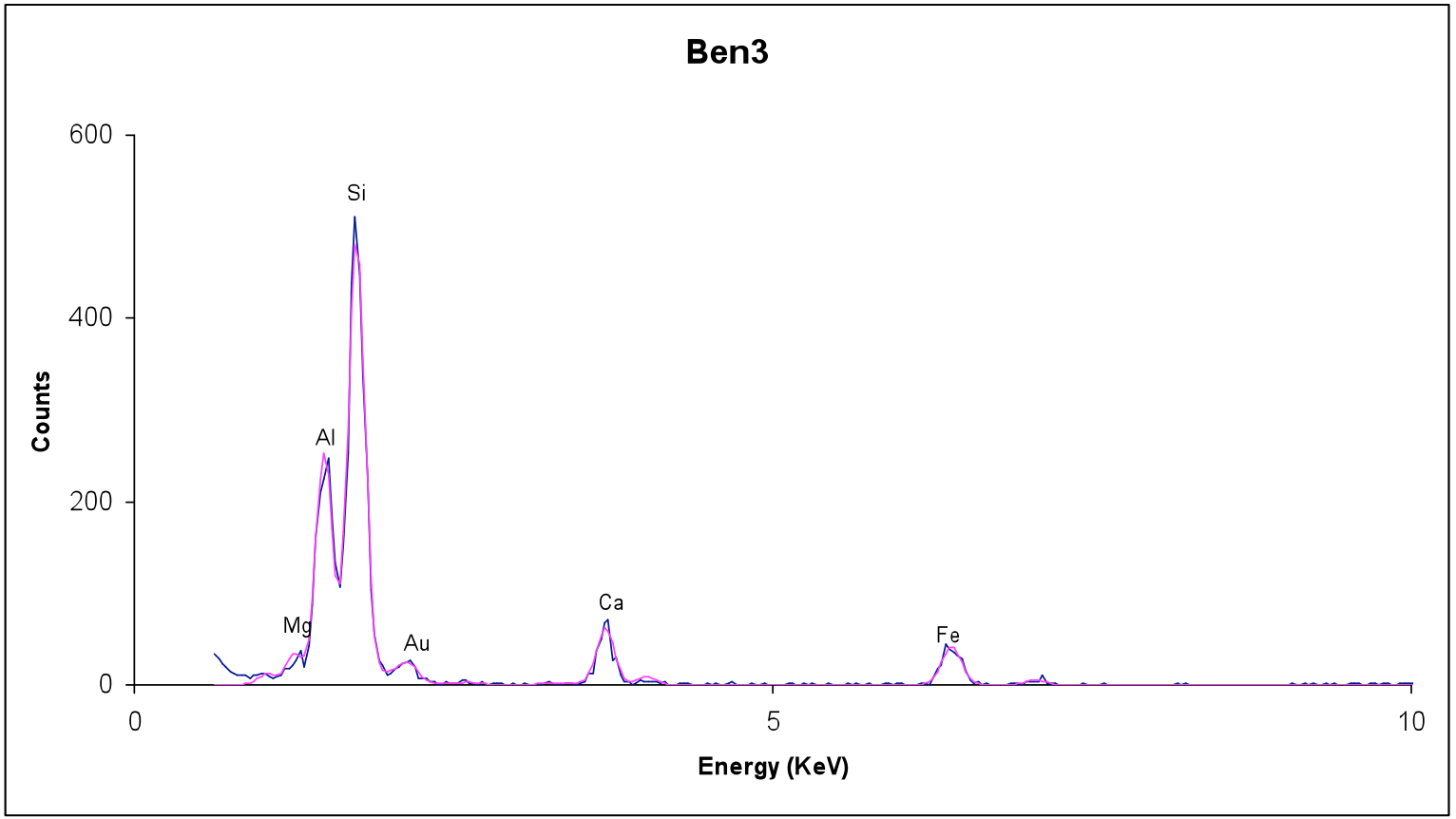
Inv. No 1551


Ben1
Counts
700
600
500
400
300
200
100
0
Si
Al
Mg
Au
Ca
Fe
0
5
10
Energy (KeV)

Inv. No 1548



Inv.No 1562



PIXE results, performed by GUPIX 2003 CODE

(Maxwell J., Teesdale A., Campbell J. L, 2003), in the "Matrix Calculation" Mode
(Values are in %)

BEN 1 - 1551

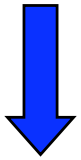
Na2O	MgO	Al2O3	SiO2	CaO	MnO	FeO	NiO	Au2O3
1.45	15.141	21.37	40.85	4.52	0.37	13.93	1.74	0

BEN 2 - 1548

Na2O	MgO	Al2O3	SiO2	CaO	MnO	FeO	NiO	Au2O3
1.85	3.18	19.61	32.85	5.93	1.58	24.65	2.22	5.88

BEN 3 - 1562

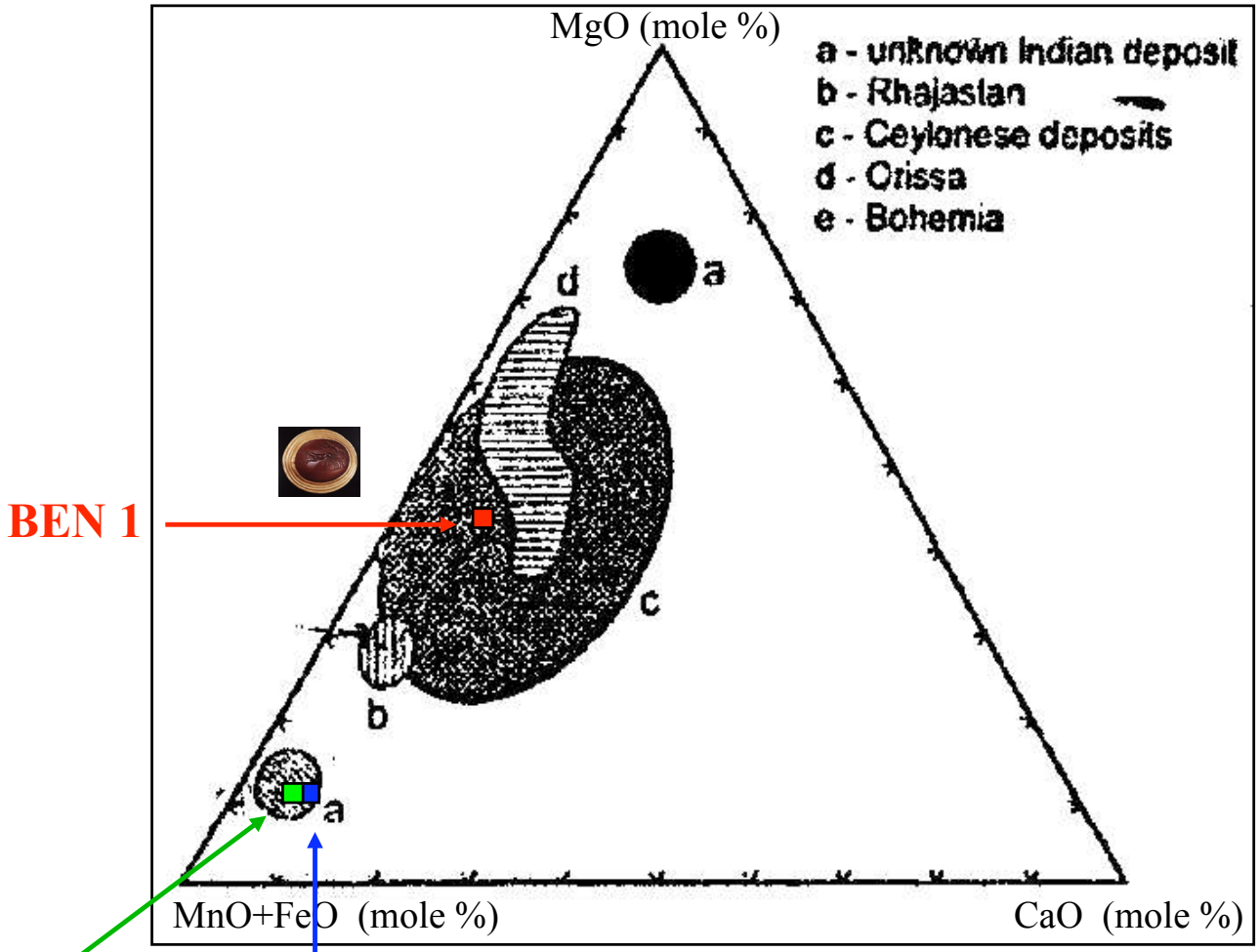
Na2O	MgO	Al2O3	SiO2	CaO	MnO	FeO	NiO	Au2O3
3.69	4	18.91	33.5	7.16	0.31	28.3	0	3.2



$Fe_3Al_2(SiO_4)_3$
Almandine-type

	Stechiometric formula of Granate	BEN 1	BEN 2	BEN 3
Al (%)	**13.3**	12	10	10
Si (%)	**20.1**	20	16	16

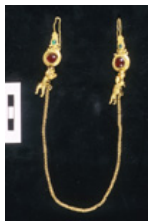
$Mg_3Al_2(SiO_4)_3$
(Pyrope-type)



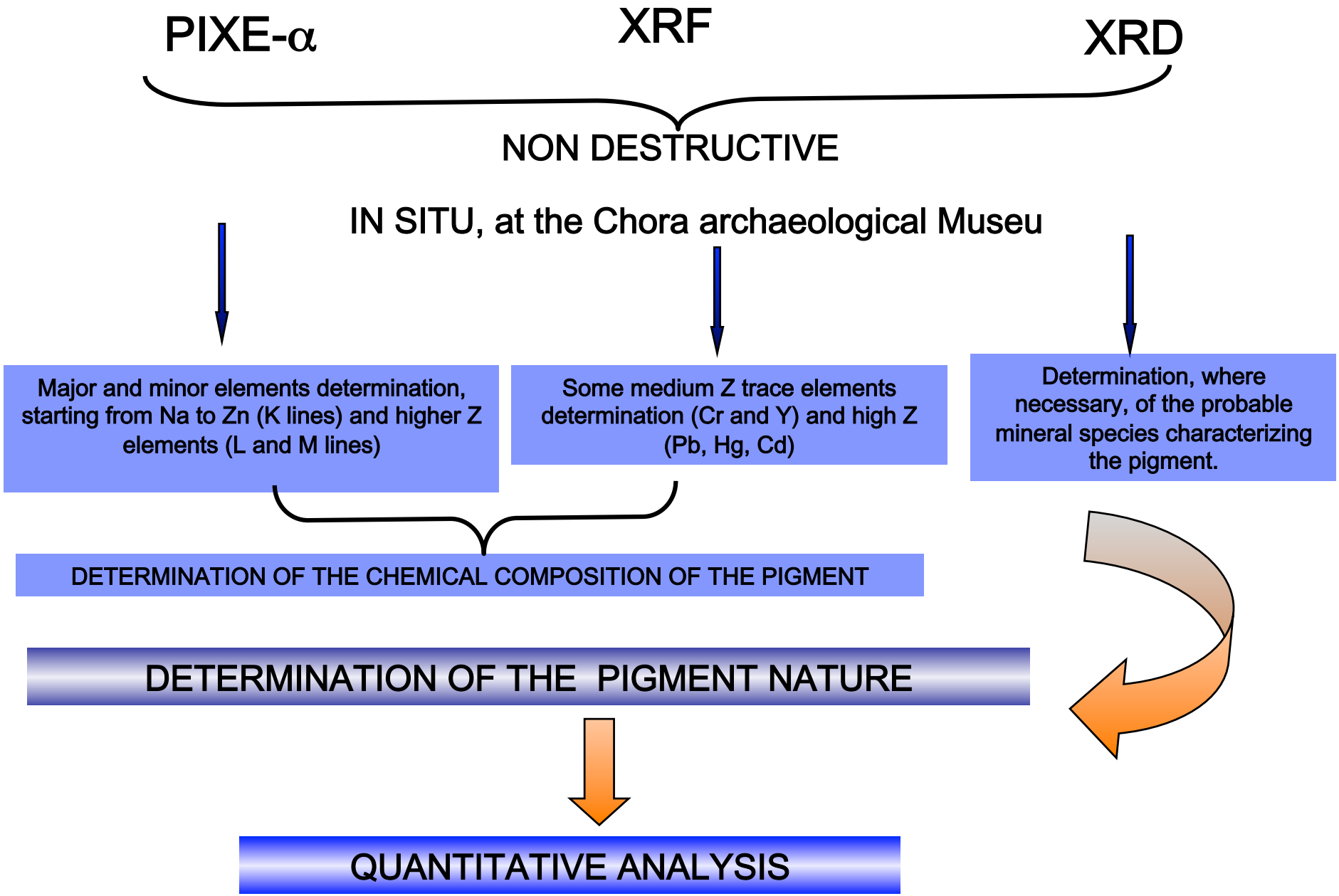
BEN 1

BEN 2

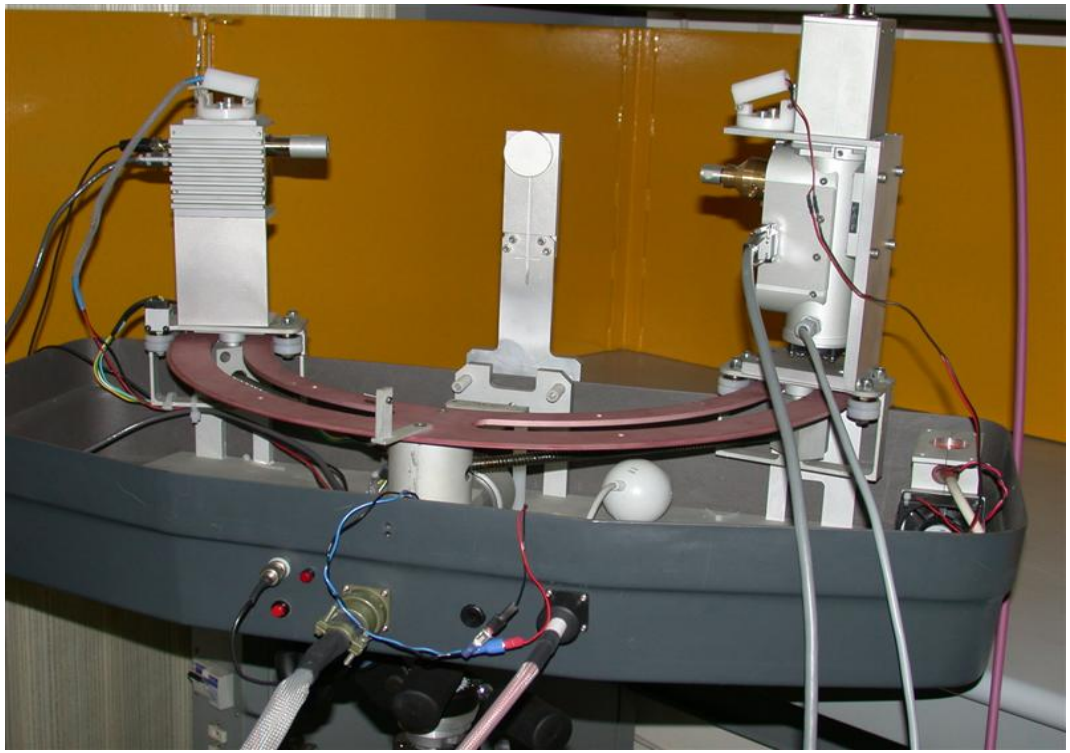
BEN 3

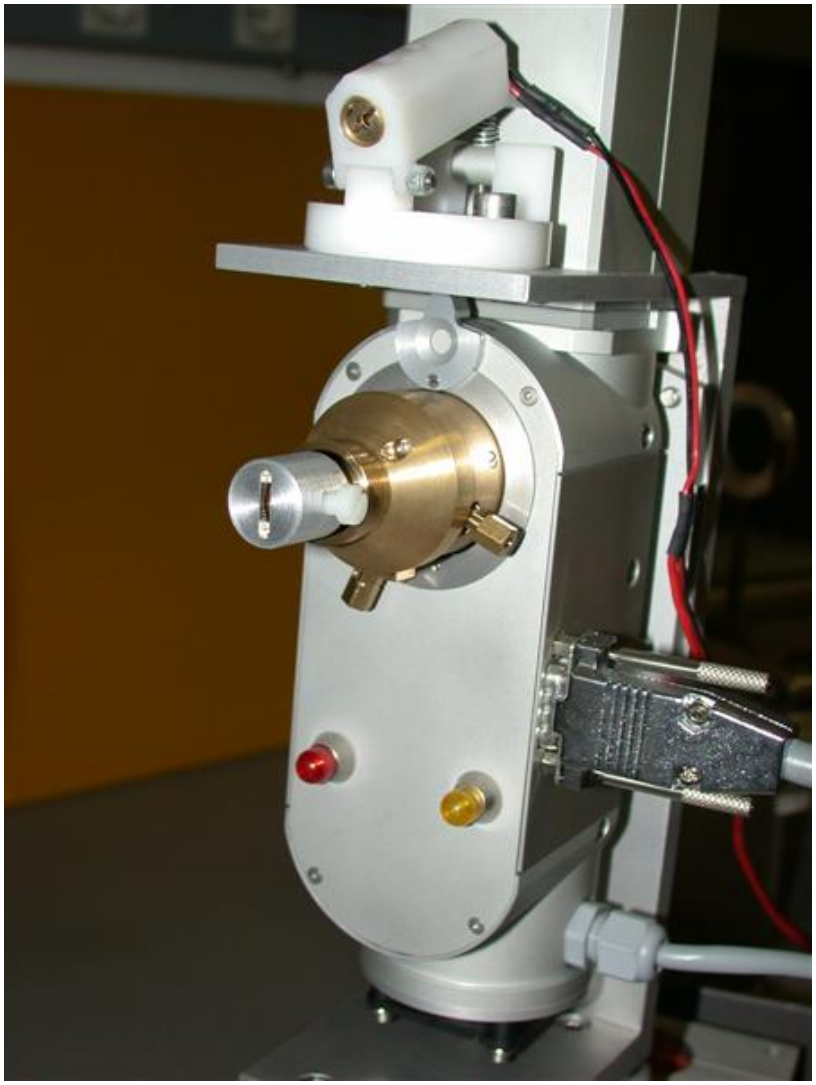


(from D. Quast, U. Schlusser, Germania 78, 2000, 1)


PIXE-α
XRF
XRD
NON DESTRUCTIVE
IN SITU, at the Chora archaeological Museu
Major and minor elements determination, starting from Na to Zn (K lines) and higher Z elements (L and M lines)
Some medium Z trace elements determination (Cr and Y) and high Z (Pb, Hg, Cd)
Determination, where necessary, of the probable mineral species characterizing the pigment.
DETERMINATION OF THE CHEMICAL COMPOSITION OF THE PIGMENT
DETERMINATION OF THE PIGMENT NATURE
QUANTITATIVE ANALYSIS

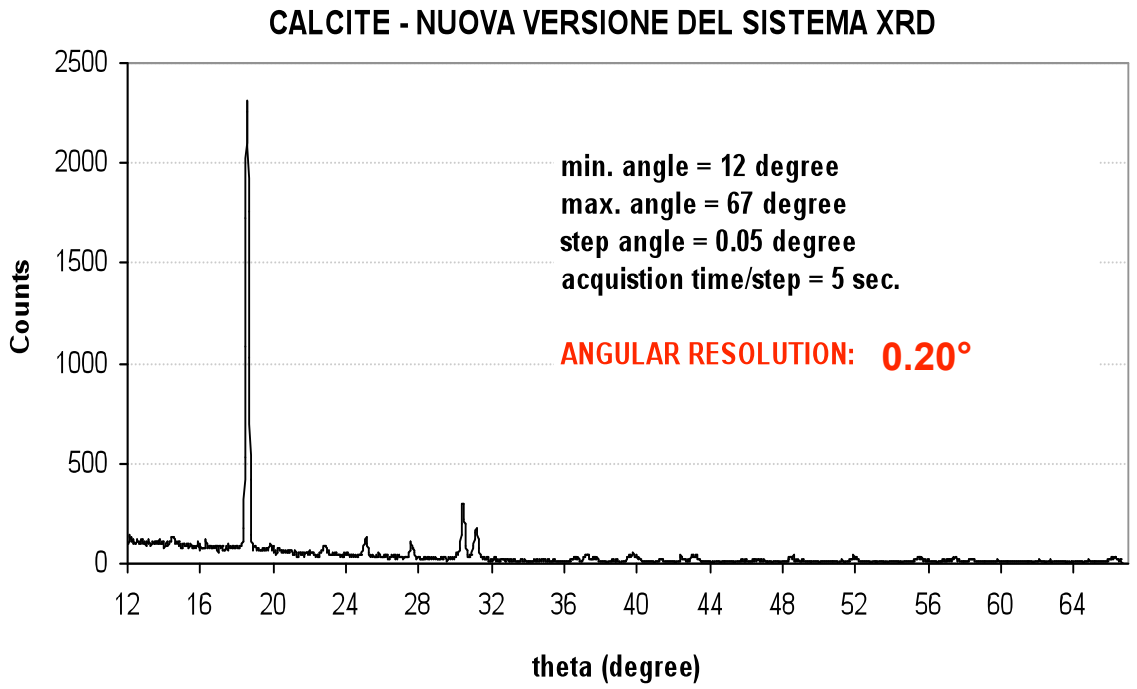
LA NUOVA VERSIONE DEL SISTEMA XRD

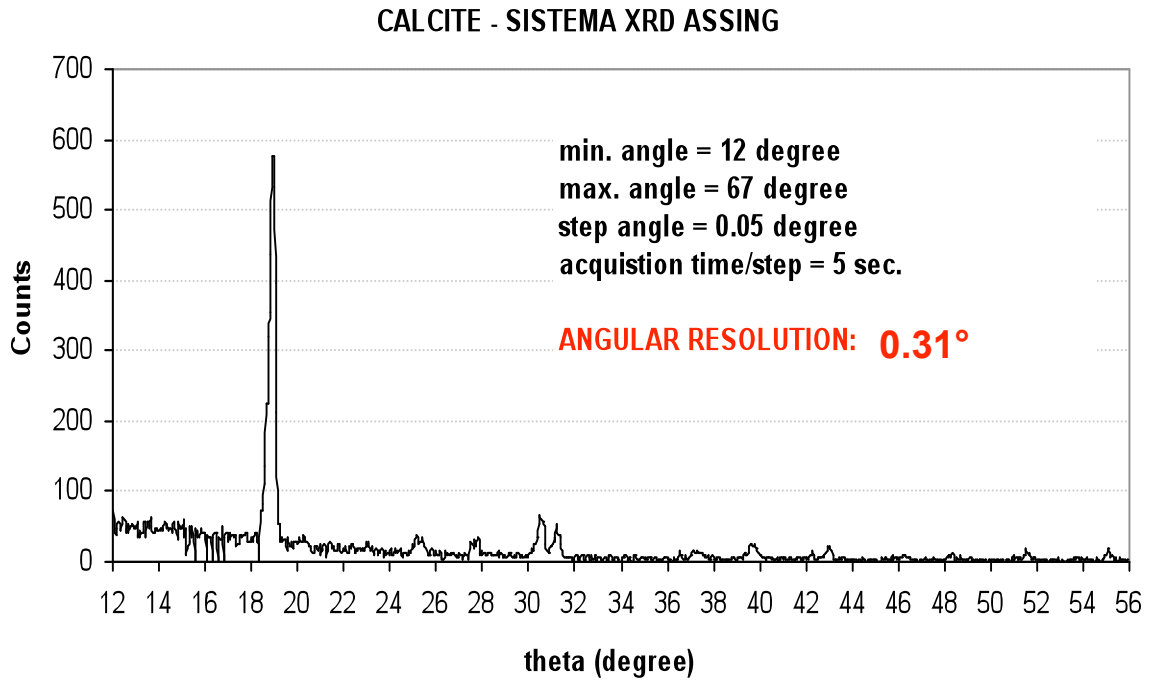




SORGENTE X: Tubo microfocus da 10 Watt con anodo di Fe accoppiato ad un'ottica policapillare parallelizzante. Lo spot del fascio è pari a 0.6 cm.

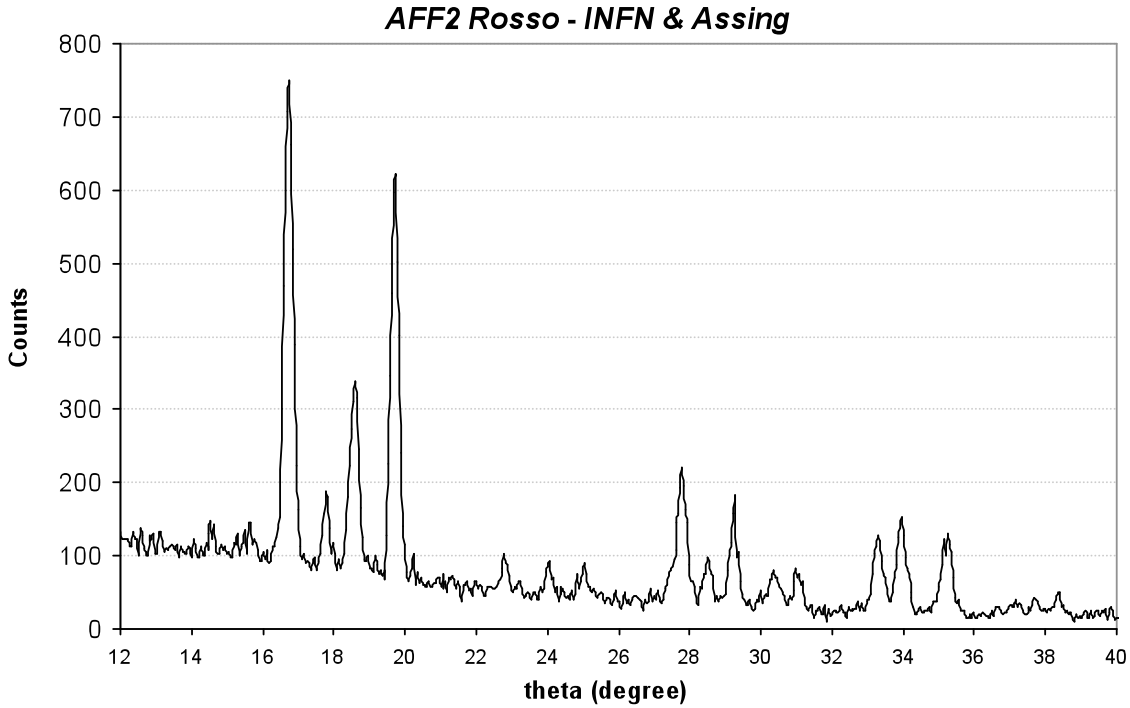
DETECTOR: rivelatore Si-PIN da 25 mm^2/500 μm e risoluzione in energia pari a 190 eV @ 5.9 keV

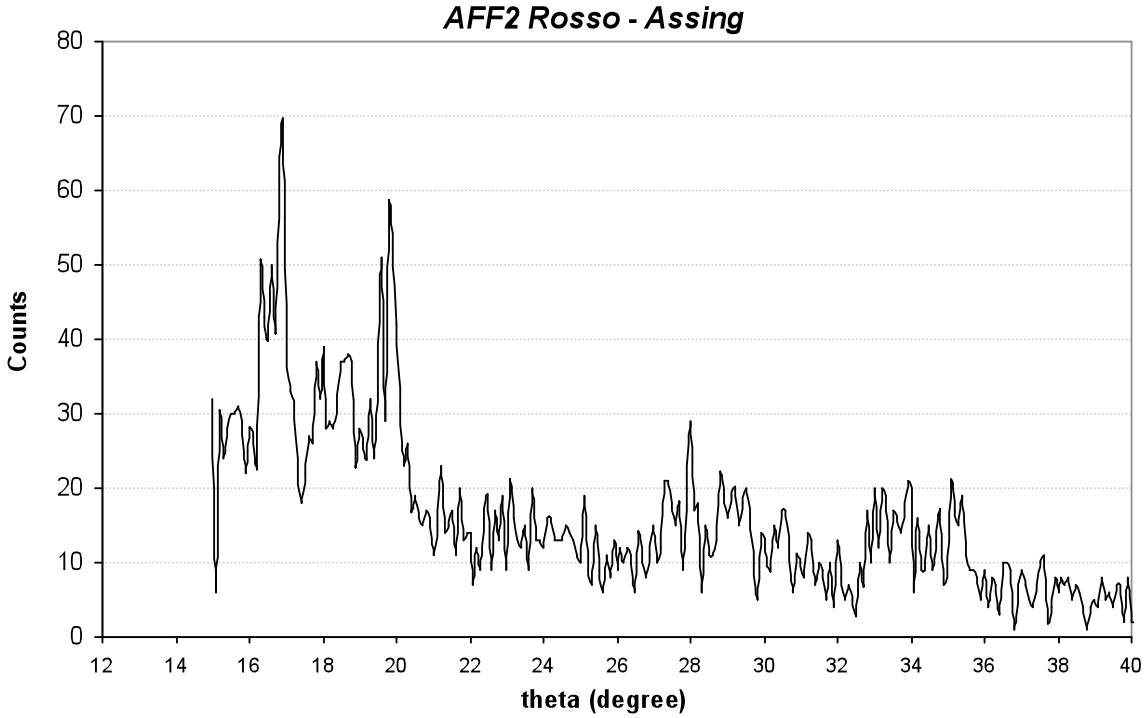


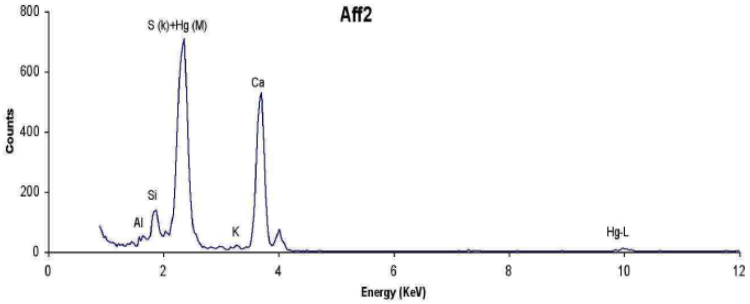


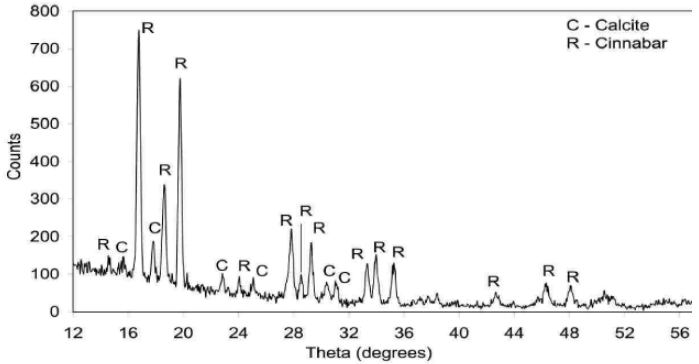
Risultati:

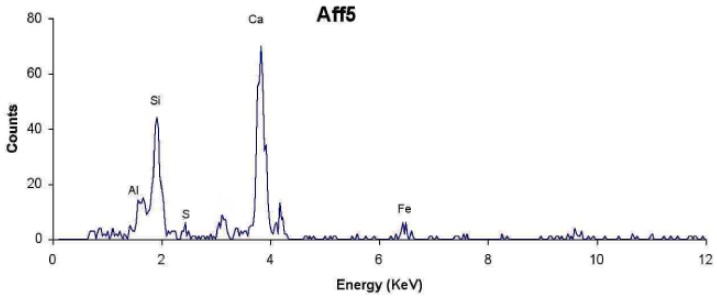
- Risoluzione angolare migliore del 40% rispetto la versione commerciale
- Intensità dei picchi di diffrazione un fattore 4-5 maggiore operando alle stesse condizioni sperimentali
- Tempi ridotti da 3 ore a circa 45 minuti.

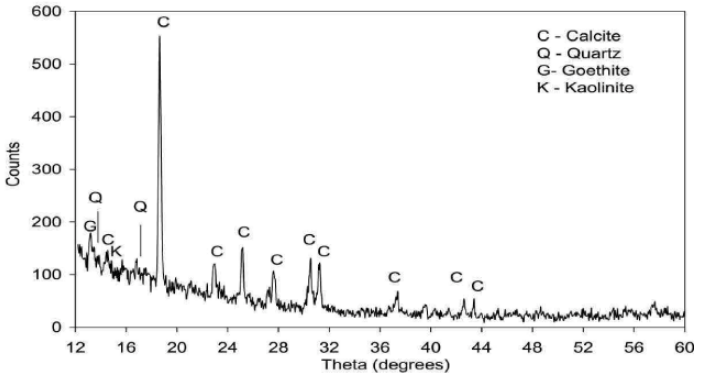

AFF2 Rosso - INFN & Assing
Counts
theta (degree)
0
100
200
300
400
500
600
700
800
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40

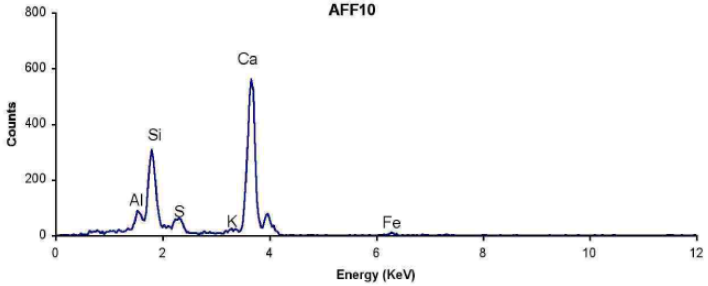

AFF2 Rosso - Assing
Counts
theta (degree)
0
10
20
30
40
50
60
70
80
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40

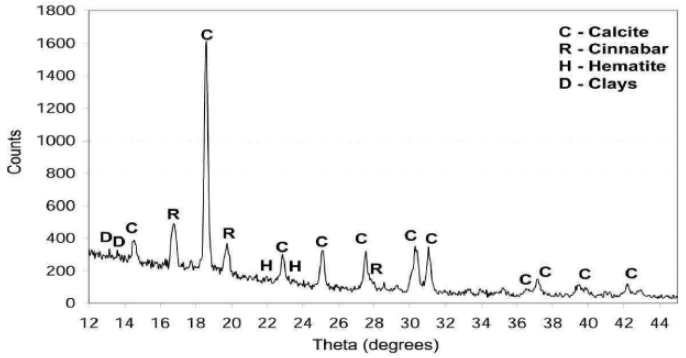

Aff2
S (k)+Hg (M)
Ca
Si
Al
K
Hg-L
Counts
Energy (KeV)

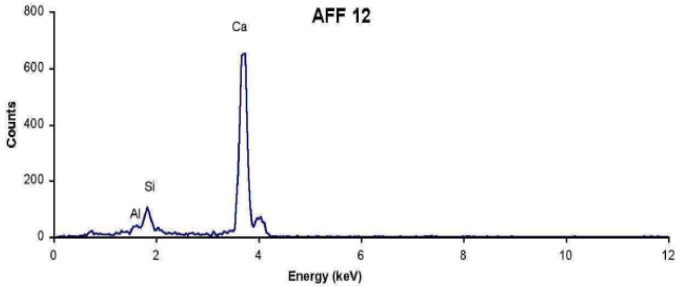

C - Calcite
R - Cinnabar
Counts
Theta (degrees)

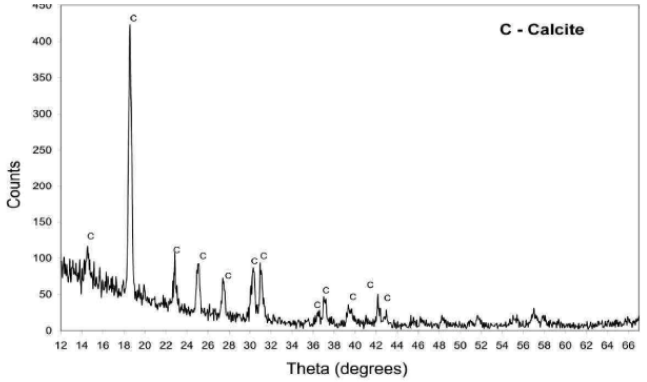

Aff5
Ca
Si
Al
S
Fe
Counts
Energy (KeV)

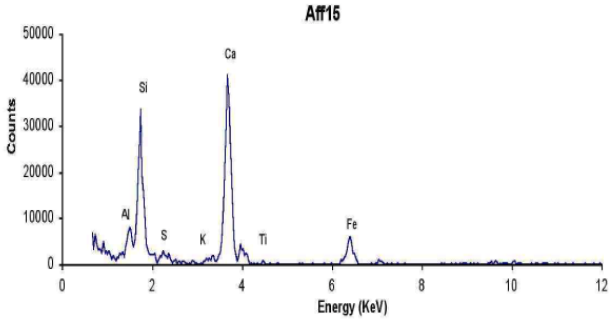

C - Calcite
Q - Quartz
G- Goethite
K - Kaolinite
Counts
Theta (degrees)

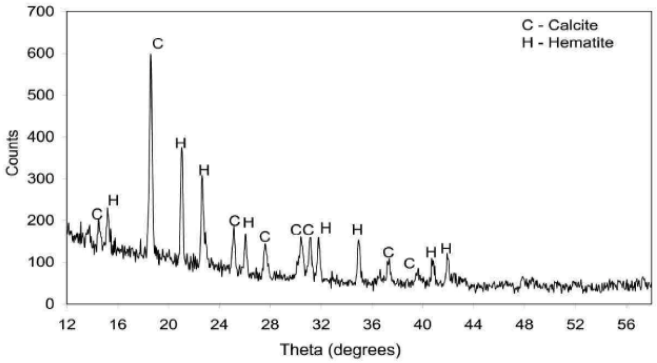

AFF10
Ca
Si
Al
S
K
Fe
Counts
Energy (KeV)

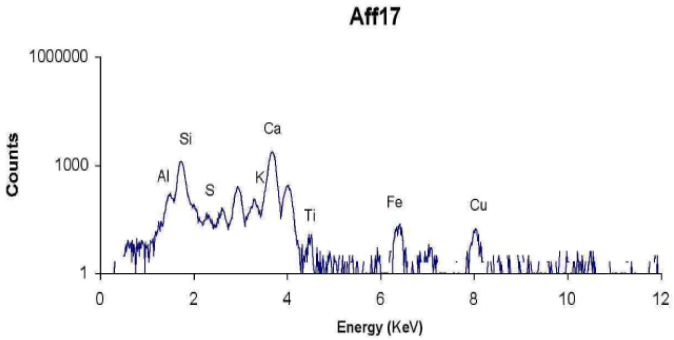

C - Calcite
R - Cinnabar
H - Hematite
D - Clays
Counts
Theta (degrees)

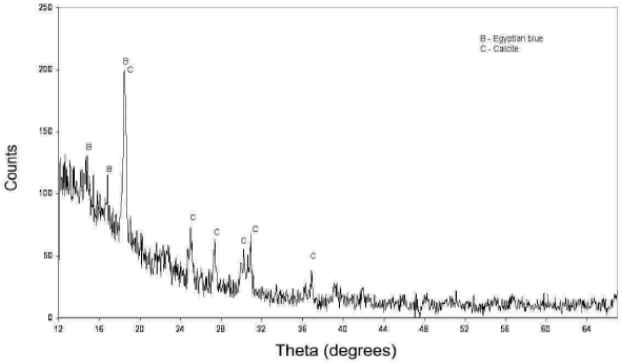

AFF 12
Counts
Energy (keV)
Ca
Si
Al


C - Calcite
Counts
Theta (degrees)


Aff15
Counts
Energy (KeV)
Si
Ca
Al
S
K
Ti
Fe


C - Calcite
H - Hematite
Counts
Theta (degrees)


Aff17
Counts
Energy (KeV)
Si
Ca
Al
S
K
Ti
Fe
Cu


B - Egyptian blue
C - Calcite
Counts
Theta (degrees)

Others* (Na, Mg, Al, P, S, Cl, K and O)

Fresco samples	Colour	$CaCO_3$ (%)	Al_2O_3 (%)	SiO_2 (%)	HgS (%)	Fe_2O_3 (%)	CuO(%)	Others* (%)	C.F.	Pigments **
Aff2	Bright red	60.2 ± 1.8	0.7 ± 0.2	2.0 ± 0.3	32.9 ± 3.3	nd	n.d	3.9	1.00	Cinnabar (32.9 %)
Aff10	Red	75.2 ± 1.8	3.5 ± 0.3	10.9 ± 0.4	2.8 ± 0.4	3.6 ± 0.8	n.d	negligible	1.00	Cinnabar (2.8 %) Red earth (Hematite 3.6%)
Aff12	White	90.4 ± 1.9	1.6 ± 0.2	3.3 ± 0.2	nd	nd	n.d	4.3	1.02	Calcite (90%)
Aff15	Brown	53.3 ± 1.6	3.5 ± 0.7	11.7 ± 0.6	nd	28.3 ± 1.0	n.d	4.2	1.01	Red ochre (Hematite 28.3%)
Aff5	Yellow	58.8 ±3.5	6.9 ± 1.2	13.2 ± 1.3	n.d.	FeO(OH) 4.2 ± 2.0	n.d.	16.84	1.04	Yellow ochre (Goethite 4.2%)
Aff17	Blue	56±1	6.8±0.4	29±0.6	nd	1.6±0.3	2.6±0.4	4.0	1.01	Egyptian blue (13 %), Calcite

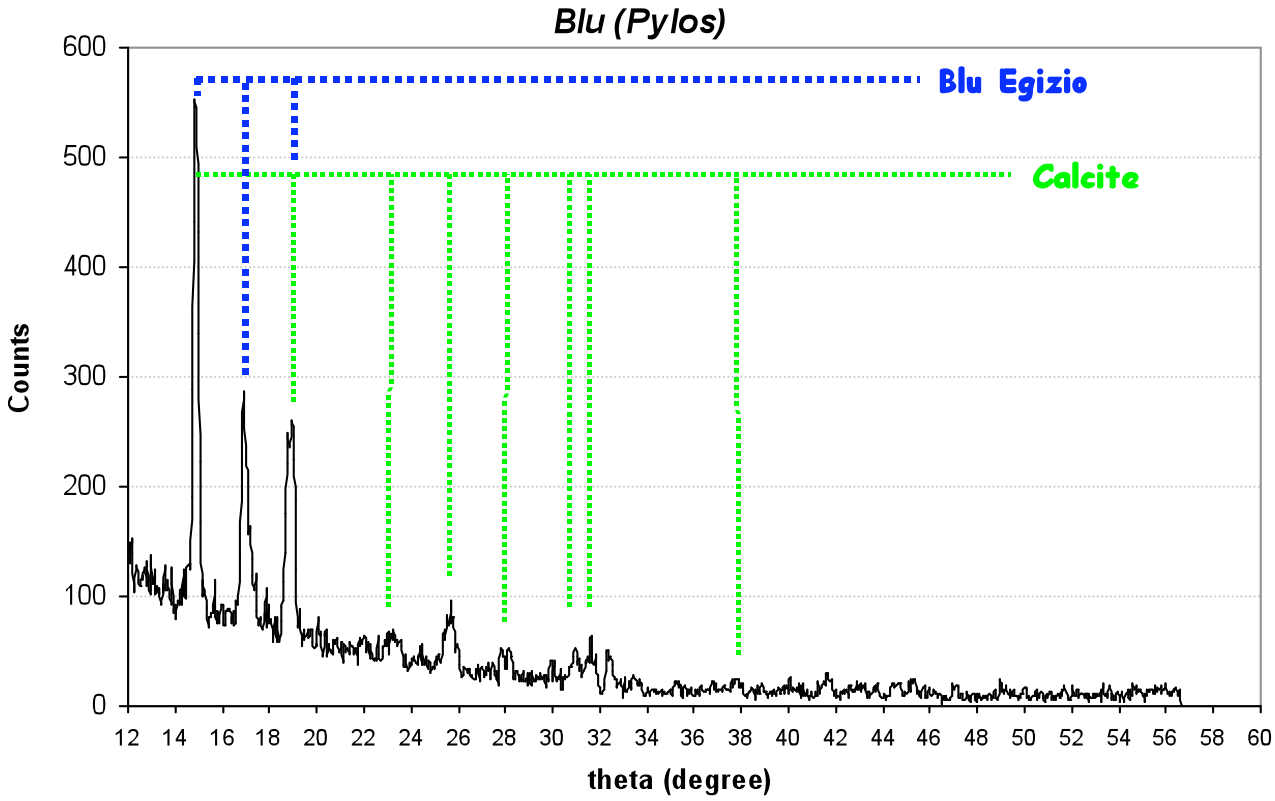
** Only the main components are reported.

Calcite and quartz are to be considered as pigments and /or as plaster components.

ESEMPIO DI APPLICAZIONE QUALITATIVE IN SITU

Caratterizzazione di un frammento delle pitture murali del Palazzo di Nestore (Pylos, Grecia)

min. angle = 12 degree
max. angle = 67 degree
step angle = 0.05 degree
acquistion time/step = 5 sec.



GRAZIE PER L’ATTENZIONE