



# On the Use of Ion and Cluster Beams Analysis at LAEC in Forensic Sciences: Infrastructure and Applications

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INTERNATIONAL CONFERENCE ON

## ACCELERATORS FOR RESEARCH AND SUSTAINABLE DEVELOPMENT

From good practices towards socioeconomic impact



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IAEA Headquarters, Vienna, Austria

# Overview

- LAEC IBA infrastructure for Elemental, Chemical and Molecular Analysis
- Needs for IBA Techniques in Fraud Repression Context
- Examples on the use of IBA in Fraud Repression and Forensic Studies  
*Coins, Banknotes, Drugs, Food stuff*
- Concluded Remarks



# LAEC IBA Infrastructure for Elemental Analysis

## 5-SDH Pelletron Tandem Accelerator of 1.7 MV from NEC

Protons beam:

0.2-3.4 MeV

1-200 nA

Alpha-particles beam:

0.5-5.1 MeV

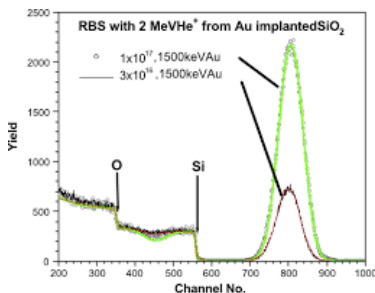
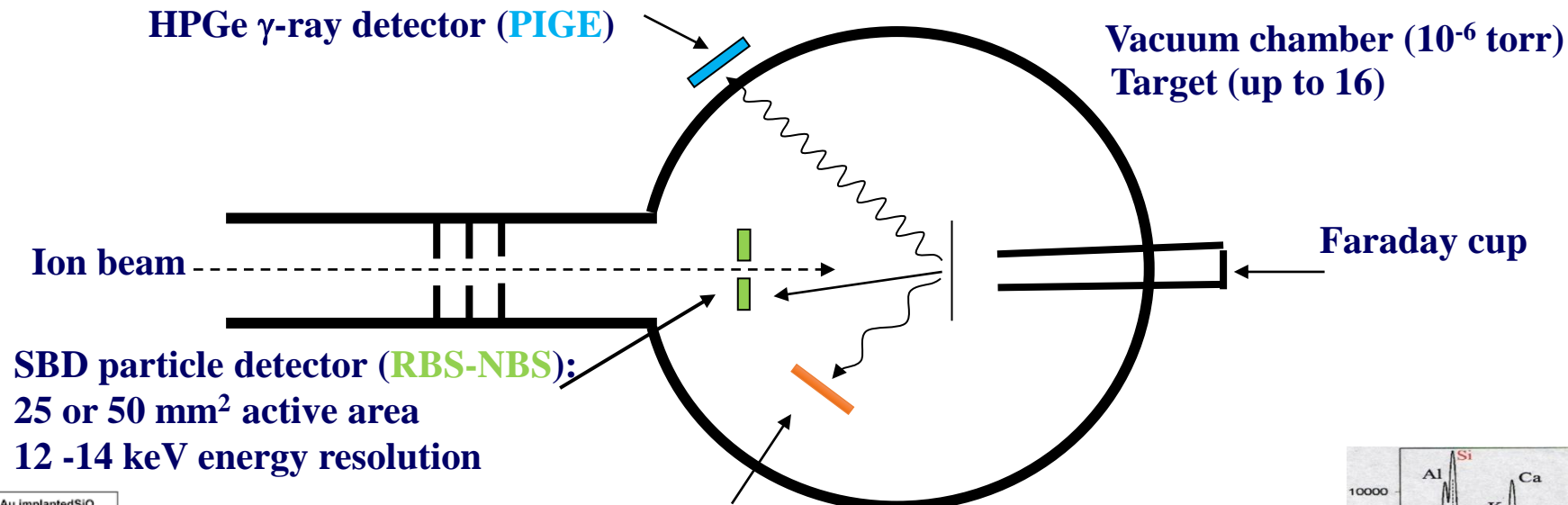
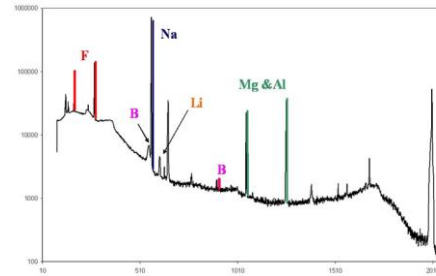
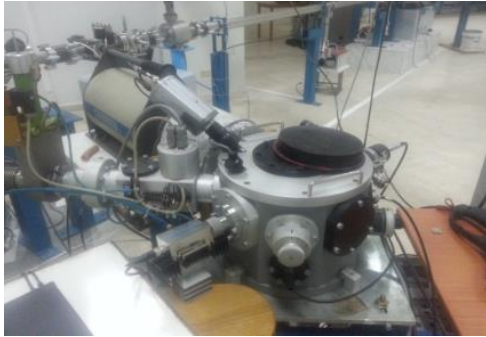
1-100 nA

PIXE – PIGE – RBS – NBS Techniques



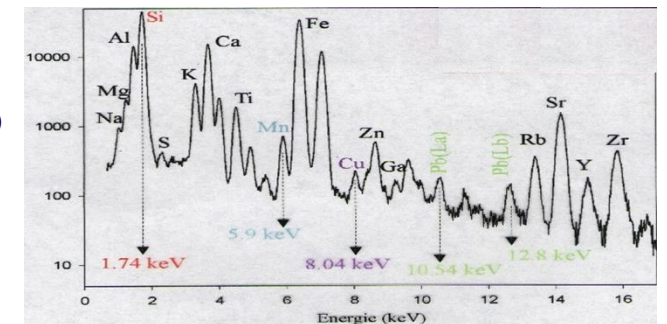


# Conventional Elemental IBA Setup



**Si (Li) x-ray detector (PIXE)**  
 30 mm<sup>2</sup> active area  
 12.7 μm Be window  
 175 eV energy resolution at 5.9 keV

**AMPTEK SDD**  
 25 mm<sup>2</sup>  
 8.5 μm  
 130 eV



# LAEC IBA Infrastructure for Chemical and Molecular Analysis

## ToF-SIMS V (Ion TOF)

Pulsed  $\text{Bi}_n^+$  Cluster analysis beam:

25-50 KeV

20 pA

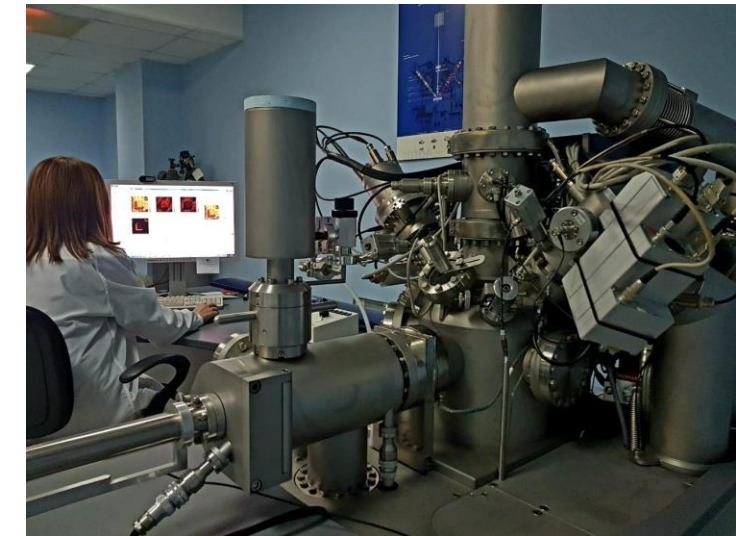
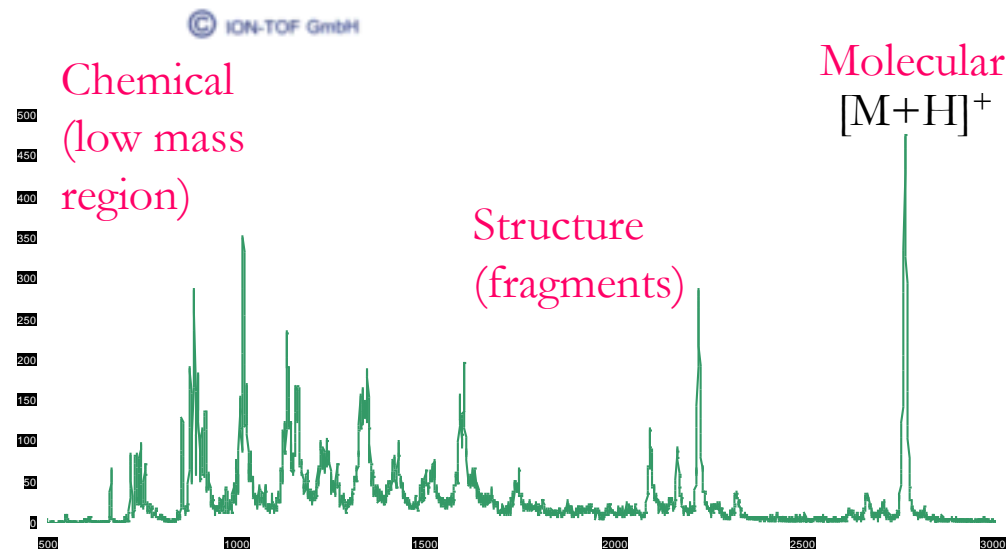
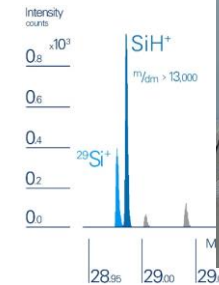
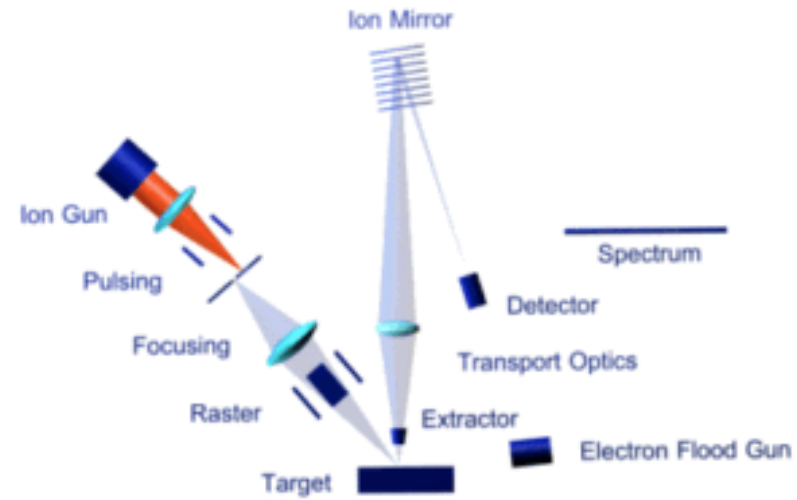
LE electron beam (flood gun):

15-25 eV

Heated/Cooled samples

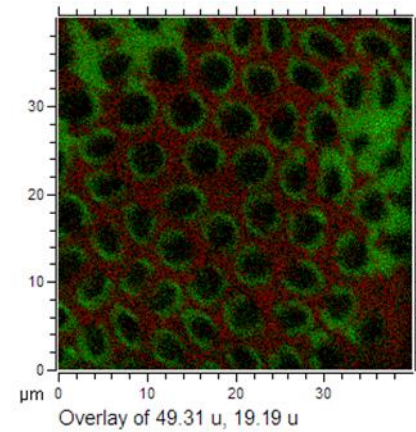
During the analysis

-190 until +600 degrees

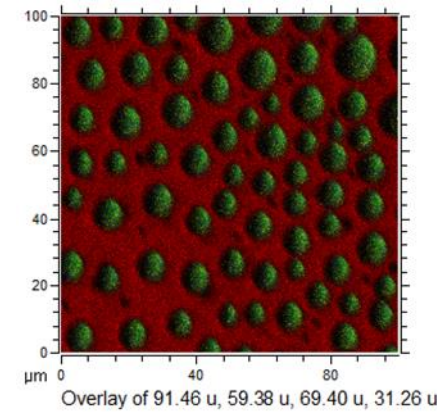


# LAEC IBA Infrastructure for Chemical and Molecular Analysis (2)

ToF/SIMS Imaging mode  
(lateral resolution 50-100 nm)



**P5FS<sub>21</sub>-b-PS<sub>31</sub>**



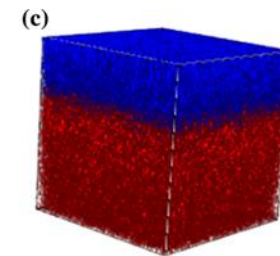
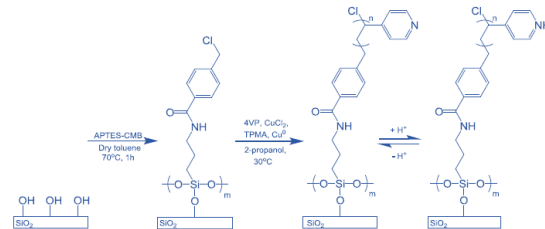
**PS<sub>45</sub>-b-PEGMA<sub>34</sub>**

**Copolymers - TOF overlay images**

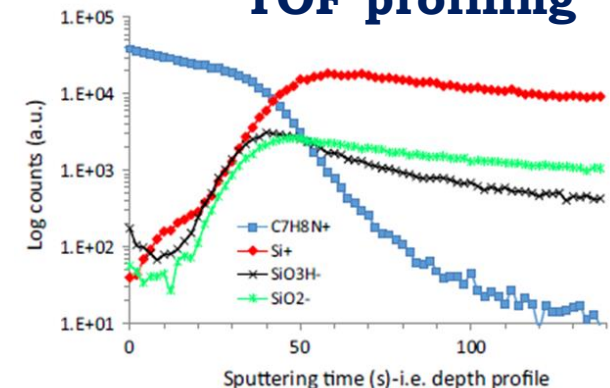
Pulsed Ar<sub>n</sub><sup>+</sup> (250 < n < 10000)

Few KeV

Soft depth profile  
(organic/thermo-fragile materials)



**TOF profiling**





# Analytical Needs and Gaps in Fraud Repression Context vs Performances of Ion Beam Analysis techniques

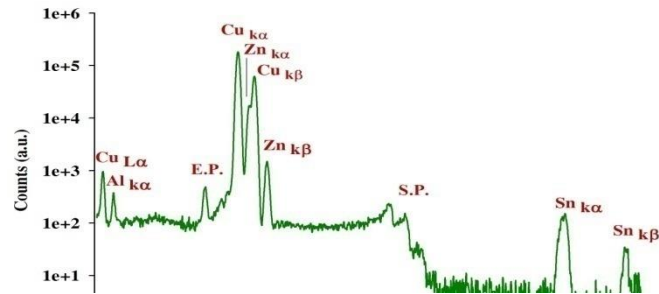
- Needs for QC of minted Coins (coating thicknesses, alloy composition,...) and printed Banknotes (Intagliot quality and thickness, Check specific security features, ink identification, ...) and to check the level of security violated by the professional counterfeiters of banknotes.
- Needs for drug testing and drug QC (% of A.I. – homogeneity of specific pills – identification of some key excipients,...)
- Needs to perform valid testing for authentication of very expensive food stuff (saffron, Vanilla,...)
- *IBA techniques are specific, sensitive, solid sample, usually as received sample analysis, elemental – chemical and molecular information can be extracted, depth profile and quantitative elemental analysis, multilayer analysis, elemental and molecular imaging and depth profile is available,...*



# Examples on the use of IBA in Fraud Repression and Forensic Sciences (1)

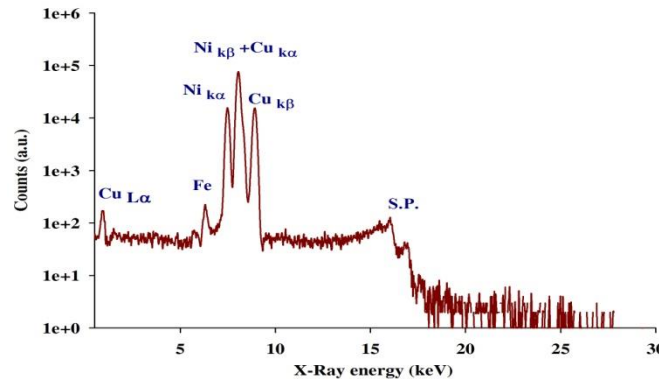
## QC of Coins : Alloy composition

### ➤ 250 L. L



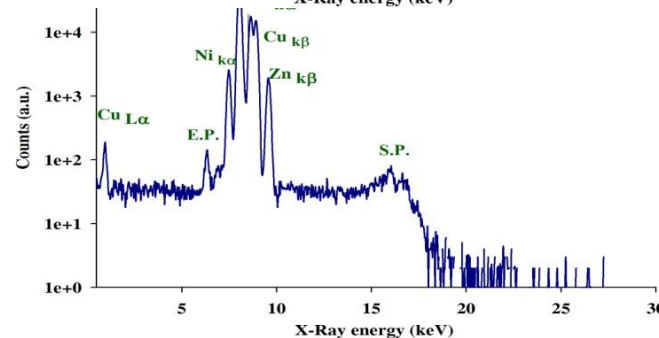
Element	Theoretical values (%)	Experimental values (%)
Al	5	$4.7 \pm 0.5$
Cu	89	$89.6 \pm 1.8$
Zn	5	$4.8 \pm 0.15$
Sn	1	$0.90 \pm 0.04$

### ➤ 100 Fils Kuwaiti



Element	Theoretical values (%)	Experimental values (%)
Ni	---	$23.8 \pm 0.8$
Cu	---	$76.1 \pm 1.3$

### ➤ 2 Euros Inner part



Element	Theoretical values (%)	Experimental values (%)
Ni	5	$5.0 \pm 0.15$
Cu	75	$75.4 \pm 1.3$
Zn	20	$19.6 \pm 0.3$

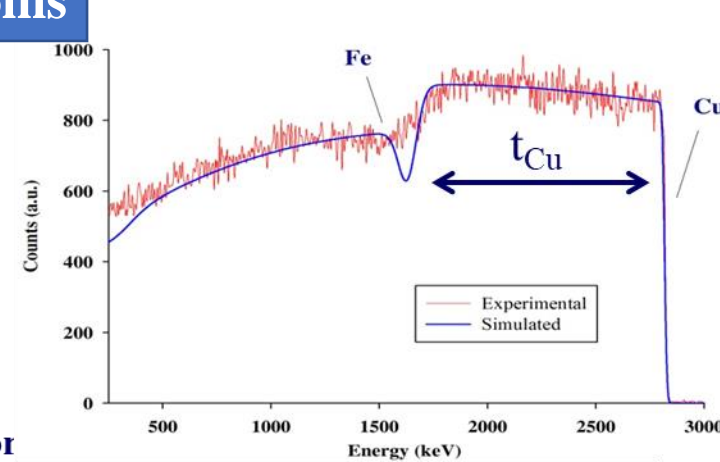
**HIGH PRECISION < 2-3%**



# Examples on the use of IBA in Fraud Repression and Forensic Sciences (2)

## QC of Coins : Thickness determination of coated coins

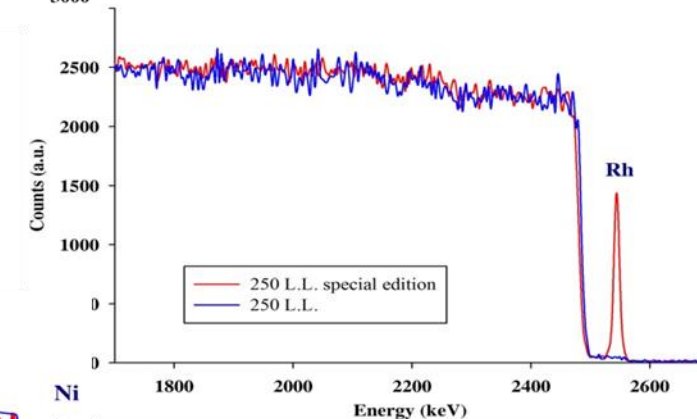
### ➤ 100 L. L



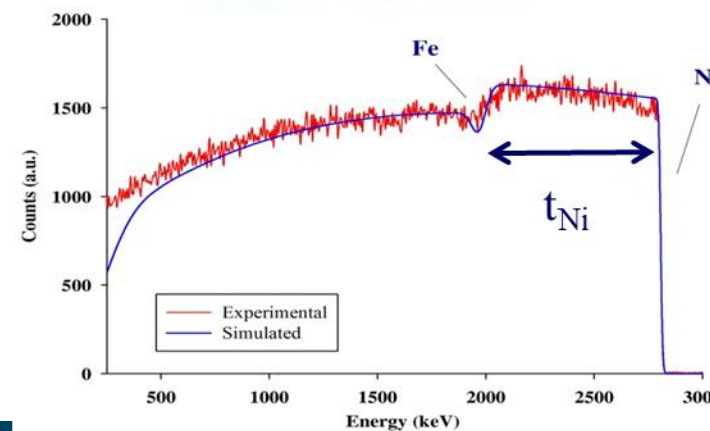
$$\text{Thickness}_{\text{Cu}} = 9.3 \pm 0.4 \mu\text{m}$$

### ➤ 250 L.L. special edition

Thin layer of Rhodium  
Thickness  $\text{Rh} = 50 \pm 1 \text{ nm}$



### ➤ 500 L.L.



$$\text{Thickness}_{\text{Ni}} = 6.6 \pm 0.2 \mu\text{m}$$

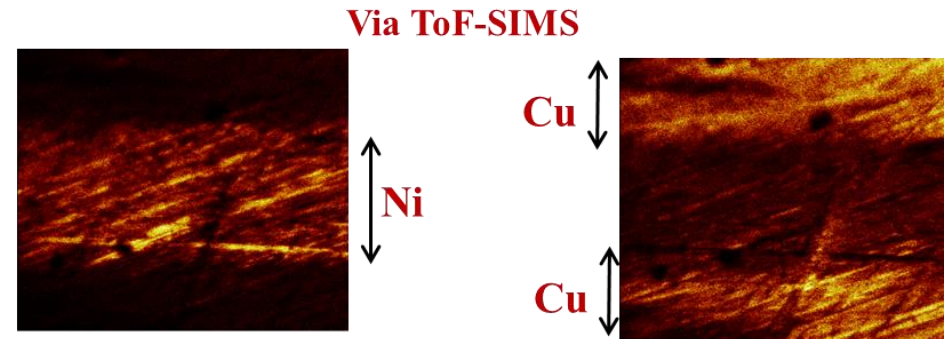
# Examples on the use of IBA in Fraud Repression and Forensic Sciences (3)

## QC of Coins : Inner layer(s) characterization

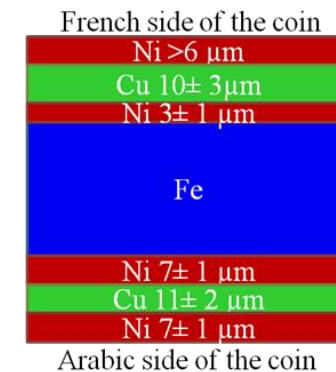
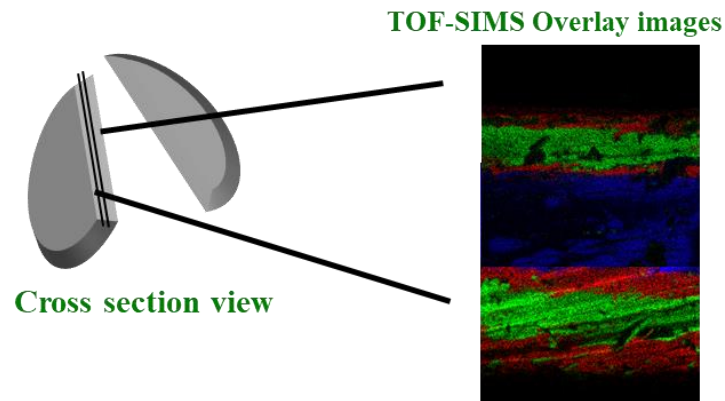
- “Inside layer” characterization (2 Euros inner part)  
Max probed depth 20-30  $\mu\text{m}$  (RBS)



Thin Layer of Ni  
( $230 \pm 10 \mu\text{m}$ )



- 500 L. L

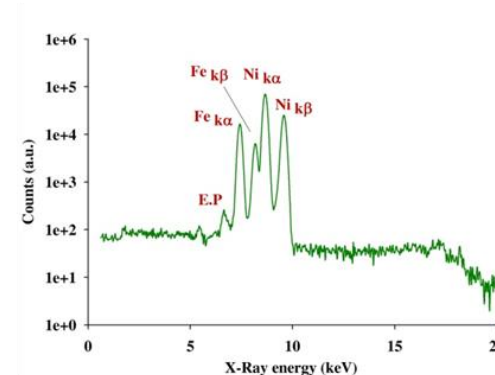


# Examples on the use of IBA in Fraud Repression and Forensic Sciences (4)

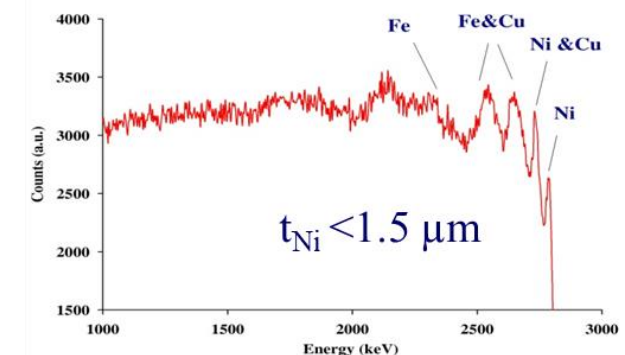
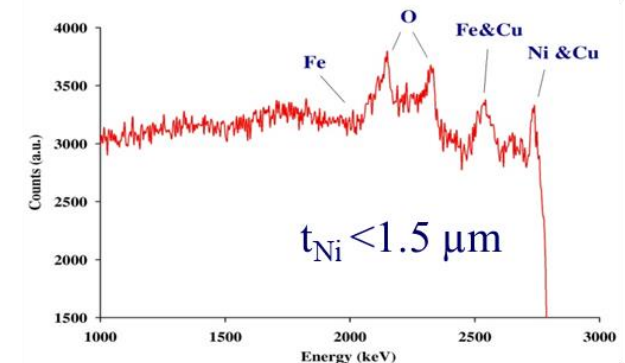
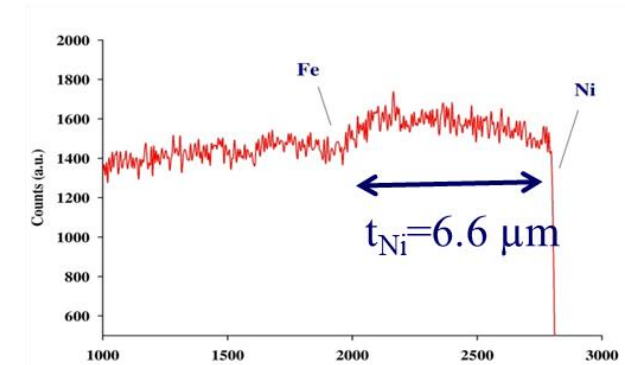
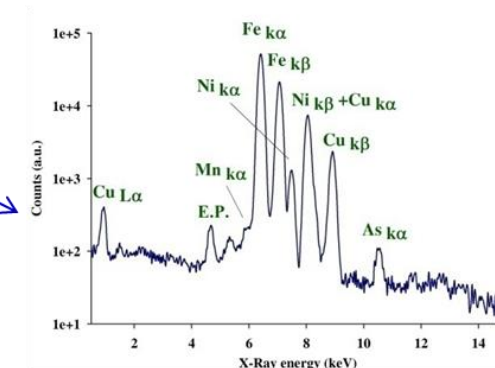
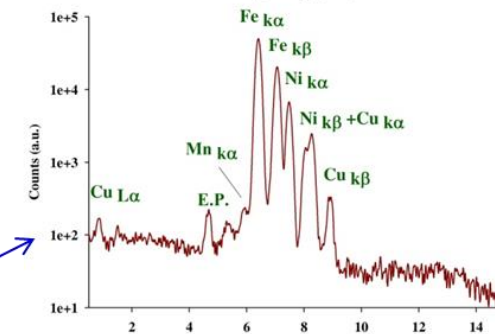
## Counterfeited Coins Analysis

Thickness<sub>Ni</sub> < thickness<sub>Ni</sub> 500 original  
**Presence of Cu**  
Irregular distribution of Ni  
Multilayer structure plated steel

➤ 500 L.L.



➤ 500 L.L.  
counterfeited





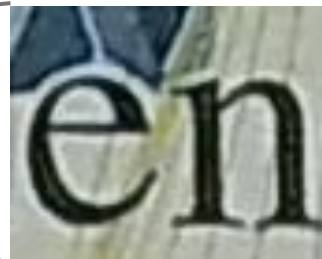


## Collaboration with the Central bank of Lebanon

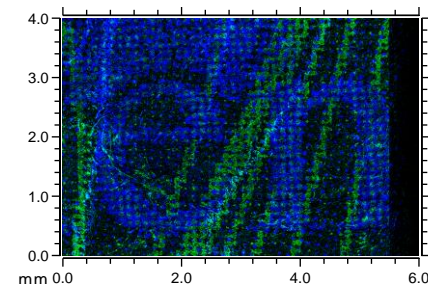
### Ink Fingerprint



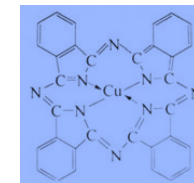
Optical image



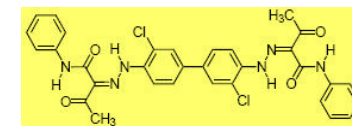
TOF-SIMS overlay image



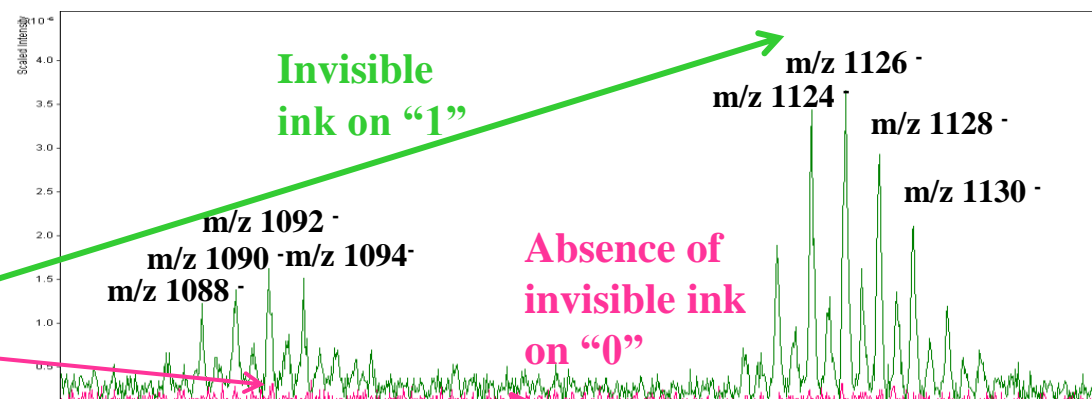
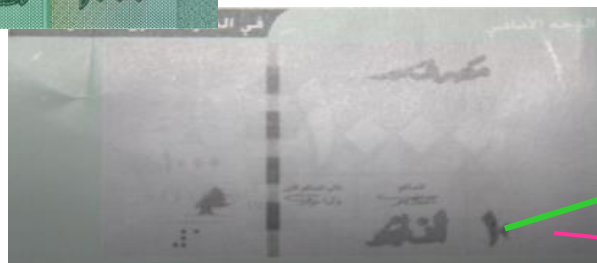
Blue pigment 15:



Yellow Pigment 12:



### I.R. Invisible Ink Fingerprint,



### Study of counterfeited banknotes

Collaboration with

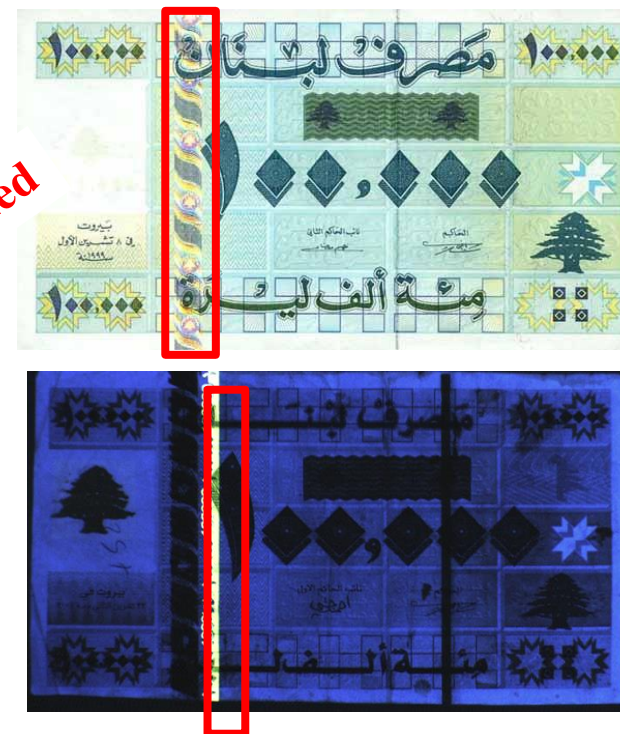


### Comparison between genuine and fake 100000 L.L.

Highest denomination (issued in 2003)



Fake 100 000 L.L



Security level 1 & 2 are breached

Counterfeit Repression Section at the central bank of Lebanon has concerns :

- 1-if the holographic stripe is under or above the printing layer?
- 2- which type of UV invisible ink was used?

### Study of counterfeited banknotes

Collaboration with



### Determination of the used materials and the level of security breached

- fake 100000 L.L. edition 2003

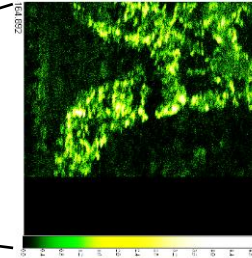
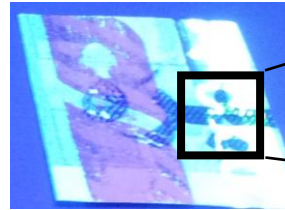
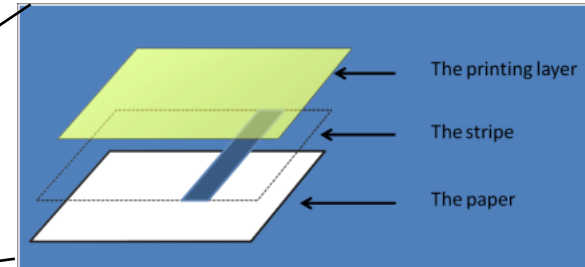
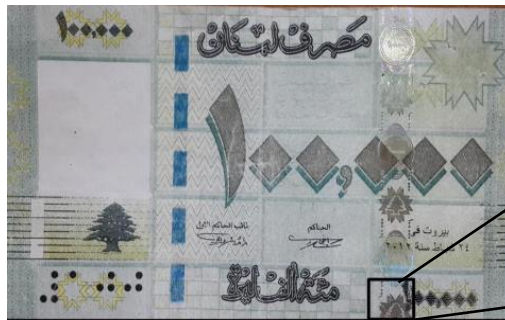
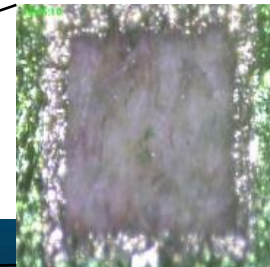


Image of one of the UV ink chemical substance after chemical characterization

- fake 100000 L.L. edition 2017



- another case: fake 10000L.L.



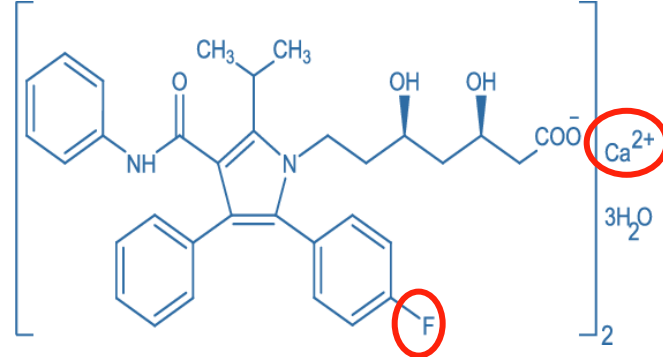
1<sup>st</sup> layer → green ink  
2<sup>nd</sup> layer → Aluminum layer  
3<sup>rd</sup> layer → printing layer



### Quality control via Quantification of the Active Ingredient(s) - Heteroatoms

#### Atorvastatin

(prevention for cardiovascular diseases)

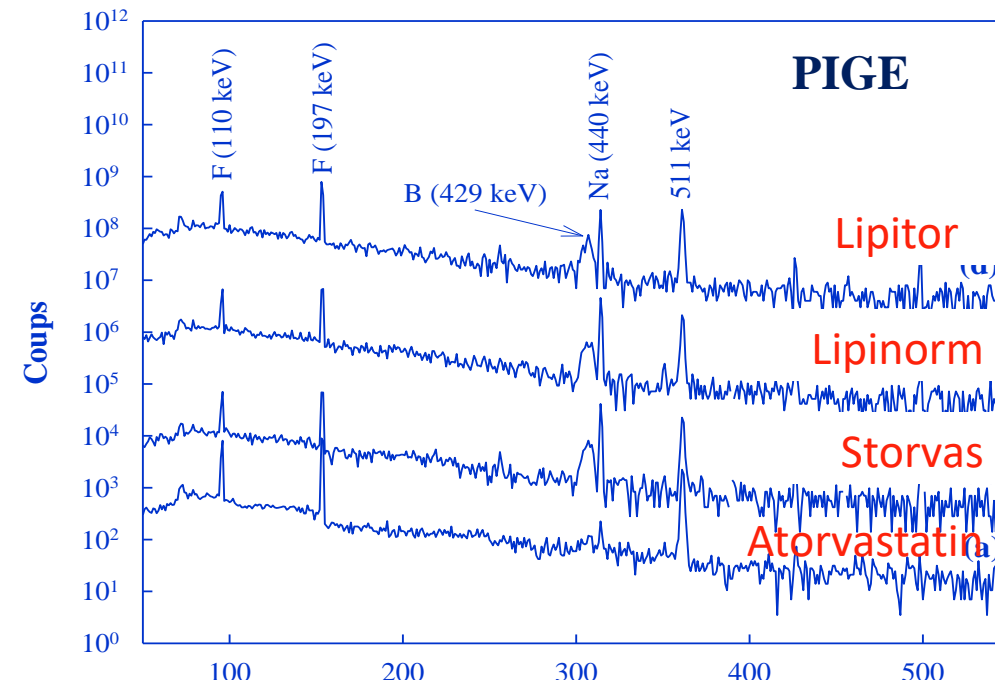


Studied Commercial Drugs:

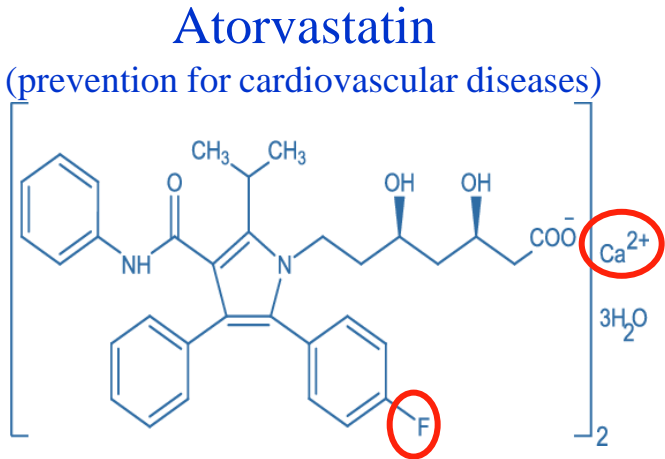
Lipinorm® 10 mg,

Lipitor® 10 mg,

Storvas® 10 mg

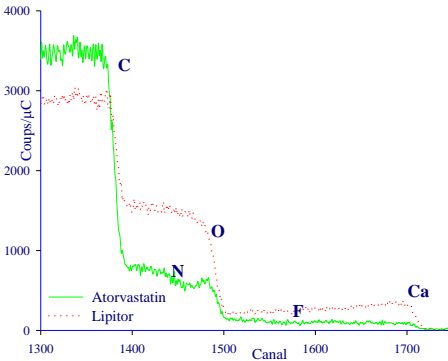


Quality control via quantification of the Active Ingredient(s)



PIGE analysis  
with matrix correction using external standards  
RBS elemental composition

$$M_{A.I} = M_{med} \times \frac{Y_{med}}{Y_{std}} \times \frac{S(E_{1/2})_{med}}{S(E_{1/2})_{std}}$$

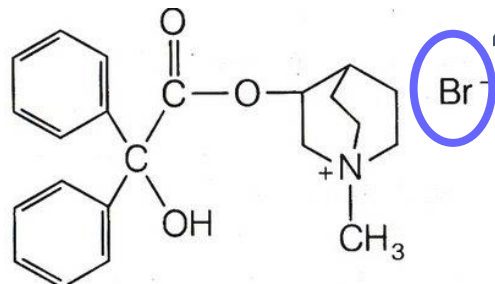


Atorvastatin (Mass in mg)		
	PIGE	UV visible
Storvas® 10 mg	11.2 ± 0.3	10.9 ± 0.4
Lipitor® 10 mg	11.0 ± 0.3	10.8 ± 0.2
Lipinorm® 10 mg	11.0 ± 0.3	11.0 ± 0.1

PIGE Results are in agreement  
with those obtained using  
conventional methods UV/Vis  
Spectroscopy

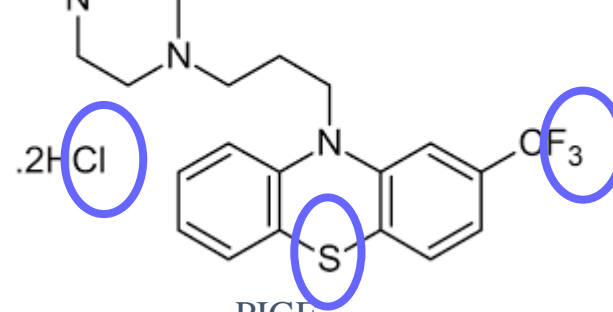
### Quality control via Quantification of the Active Ingredient(s)

Clidinium bromide (2.5 mg)



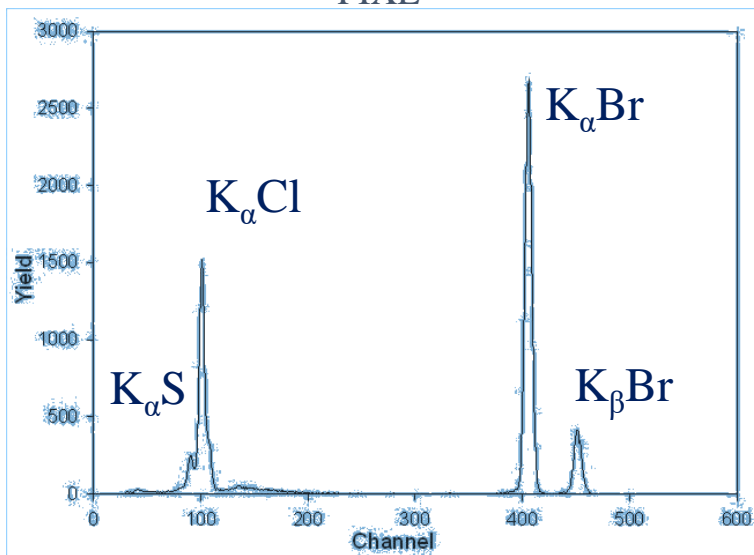
Binary drug

Trifluoperazine (1mg)

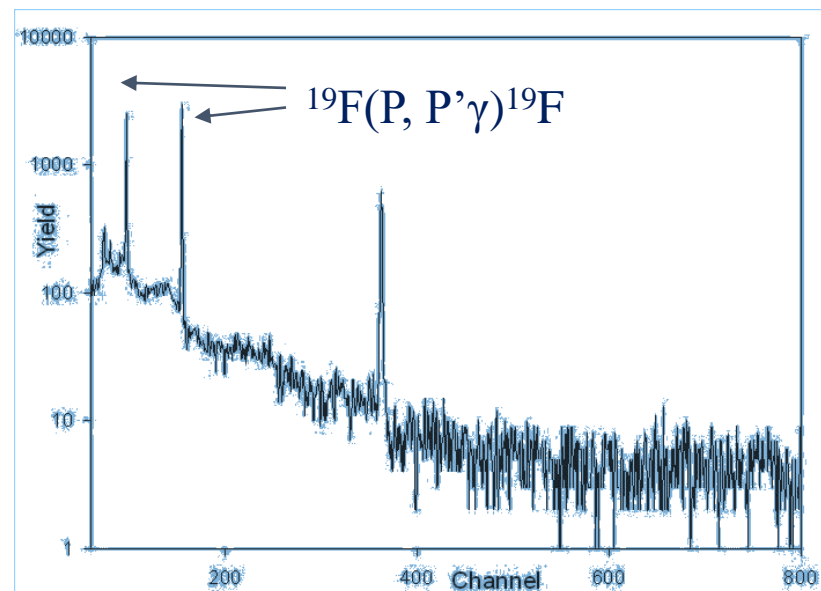


Fludinium® spectra

PIXE



PIGE



Analysed Samples:

- Standards with different % of the two A.I. and excipients.
- Fludinium commercial drug with different compositions



### Stability under irradiation:

- Samples are stable under analysis conditions (3MeV, 0.2 nA, 0.1μC, 15 min acquisition )
- Loss of Cl under ion irradiation even under condition of analysis
- Cl is not related to the A.I by covalent bond: it is thermo fragile.

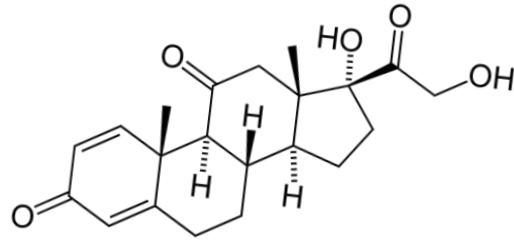
**Cl will not be considered for quantification**

**S, F: quantification of Trifluoperazine**

**Br: quantification of Clidinium Bromide**

Sample labeled composition	S via PIXE	F via PIGE	Br via PIXE
50mg A.I.1, 50mg A.I.2 3.33% S, 5.9% F, 9.25% Br	3.37%±0.16	5.7% ±0.2	9.4% ±0.2
40mg A.I.1, 40mg A.I.2, 20 mg Excipient 2.67% S, 4.7% F, 7.4% Br	2.60%±0.12	4.61% ±0.22	7.47% ±0.22
25mgA.I.1, 25mgA.I.2, 50mg Excipient 1.67% S, 2.97% F, 4.6% Br	1.62%±0.03	2.73% ±0.13	4.66% ±0.14
12.2mg A.I.1, 4.9mgA.I.2, 82.9mg Excipient 0.32% S, 0.58% F, 2.25% Br	0.31%±0.01	0.57% ±0.03	2.26% ±0.07
7.9mg A.I.1, 2.6mg A.I.2, 89.5mg Excipient 0.175% S, 0.31% F, 1.46% Br	0.18%±0.01	0.35% ±0.02	1.53% ±0.04
0.58mg A.I.1, 1.45mg A.I.2, 97.2mg Excipient 388ppm S, 691ppm F, 2692ppm Br	434ppm±43	705ppm±35	2943ppm±147

### Quality control via semi Quantification of the Active Ingredient(s): using calibration curves

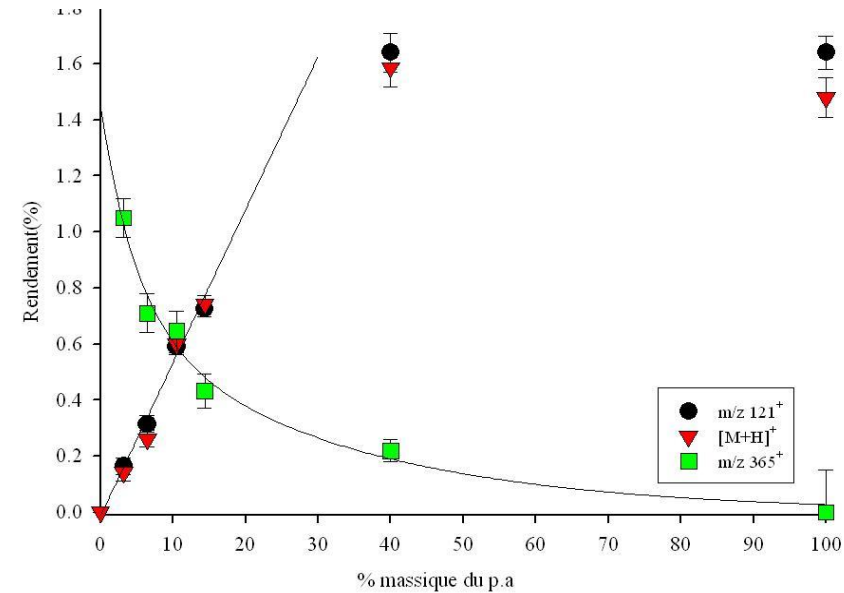
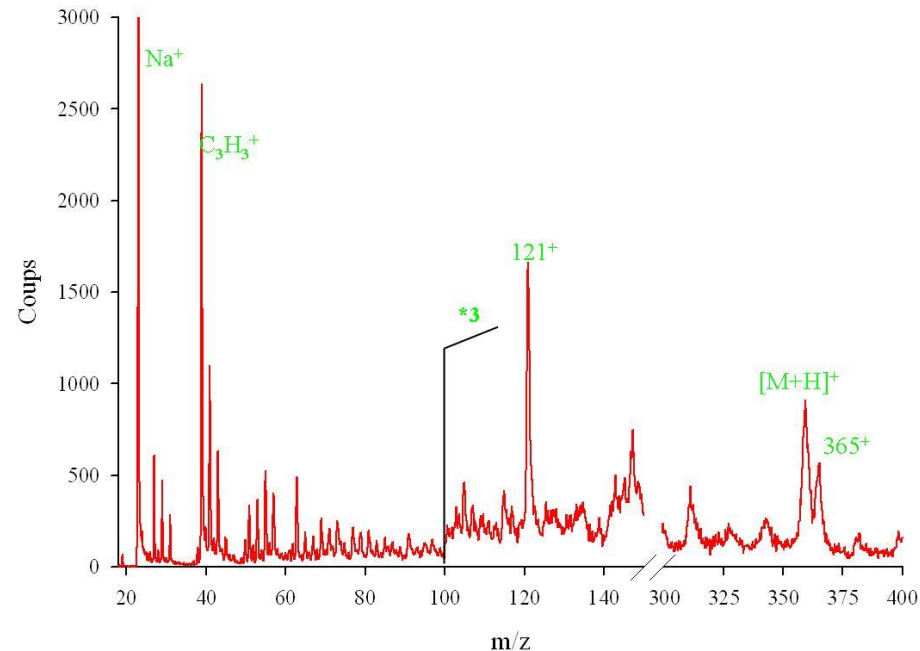


Prednisone  
(for immune system suppression)



Medicaments at 3, 6 and 14% of A.I.

Standards at 5 and 40%

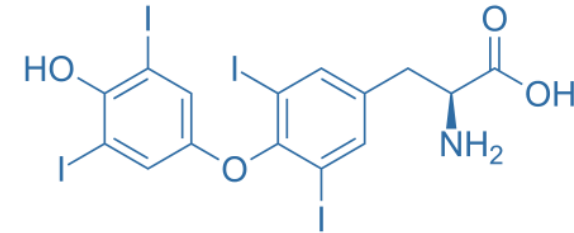


Linear Variation of the protonated molecule between 0 and 30% of A.I.

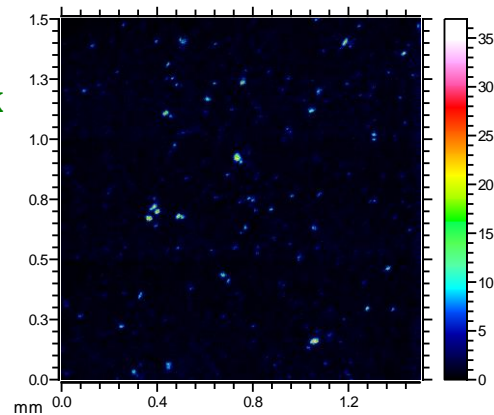
### Quality control of the Active Ingredient: Homogeneity

Levothyroxine (treat thyroid hormone deficiency)

Tablets are usually cut in half by the patients

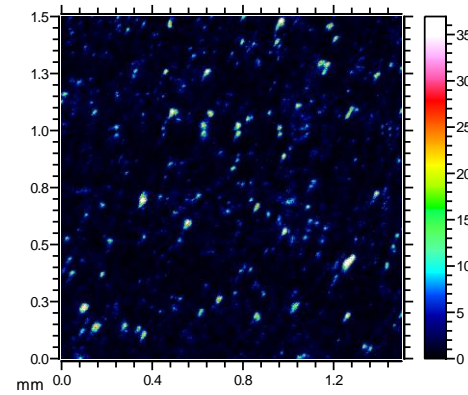


**Euthyrox  
25 µg**



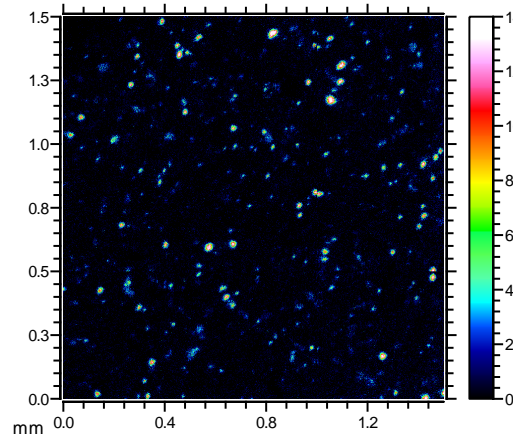
MC: 37; TC: 4.059e+005

**Euthyrox  
100 µg**



MC: 37; TC: 7.726e+005

**Euthyrox  
125 µg**



MC: 14; TC: 1.655e+005

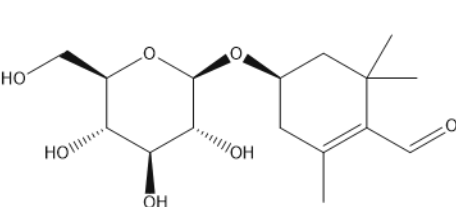


Saffron most expensive spice (10000 €/kg).

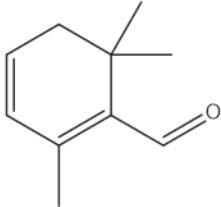
3 principle chemical families

- color→ crocetin and its derivatives
- taste→ picrocrocin
- smell→ safranal

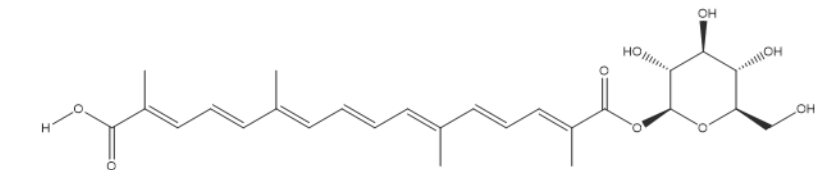
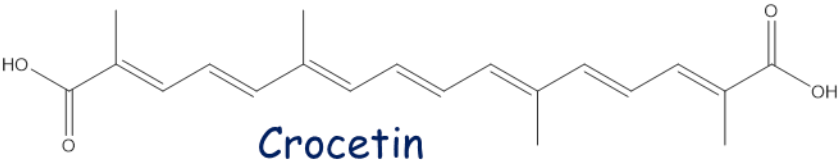
Saffron used in pharmaceutical drugs.



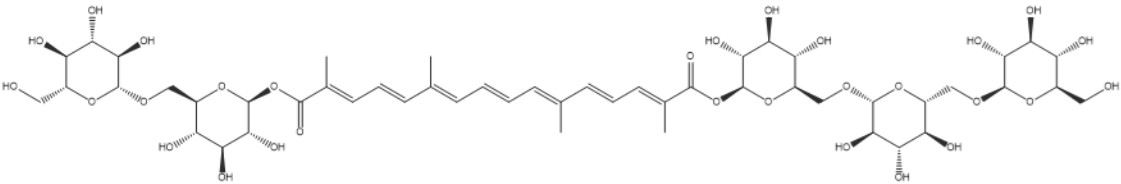
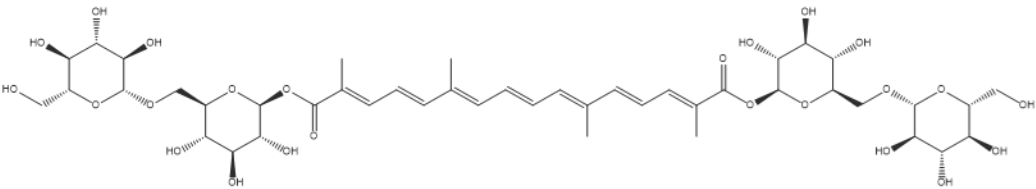
Picrocrocin



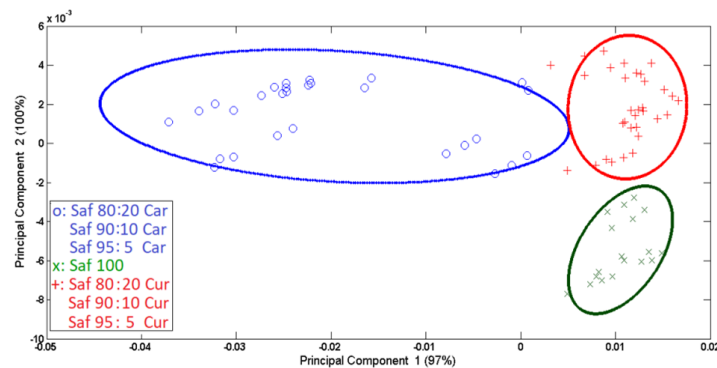
Safranal



Crocins

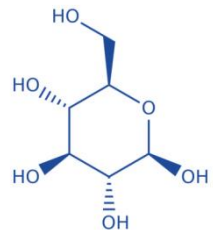


## PC1 separation → characteristic peaks of carthamin



## PC2 separation

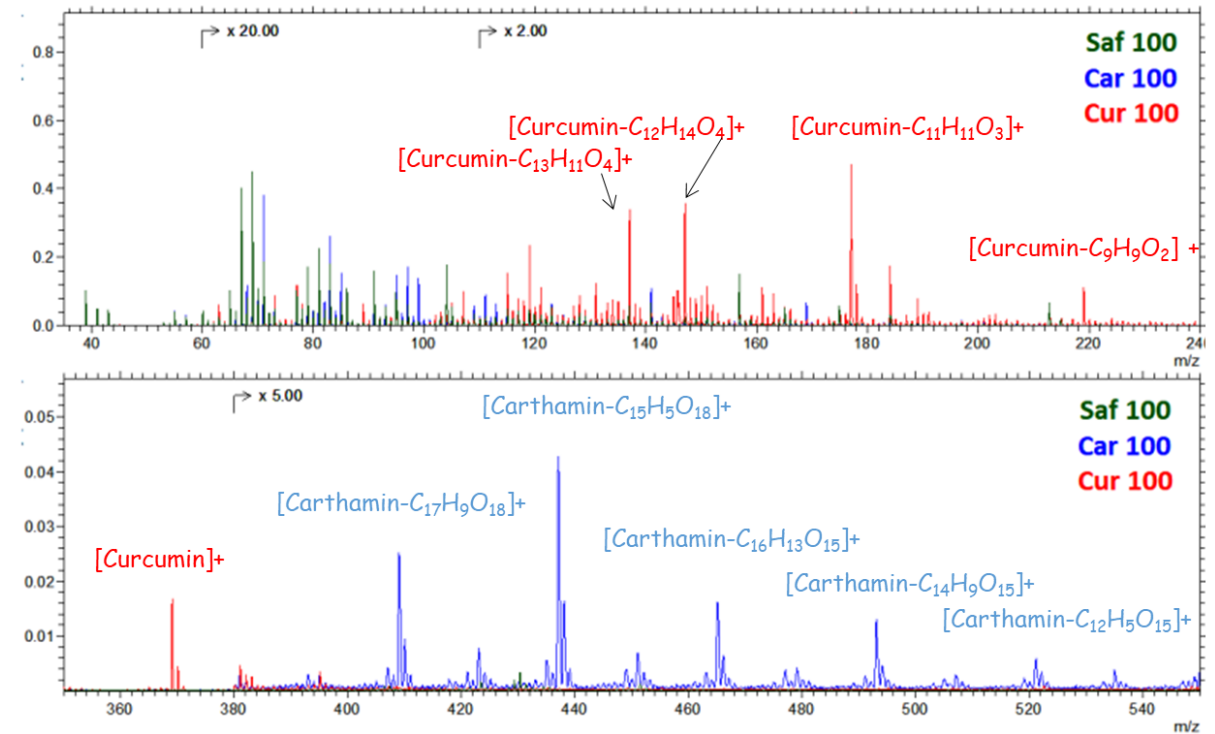
### D-Glucose



### Minerals

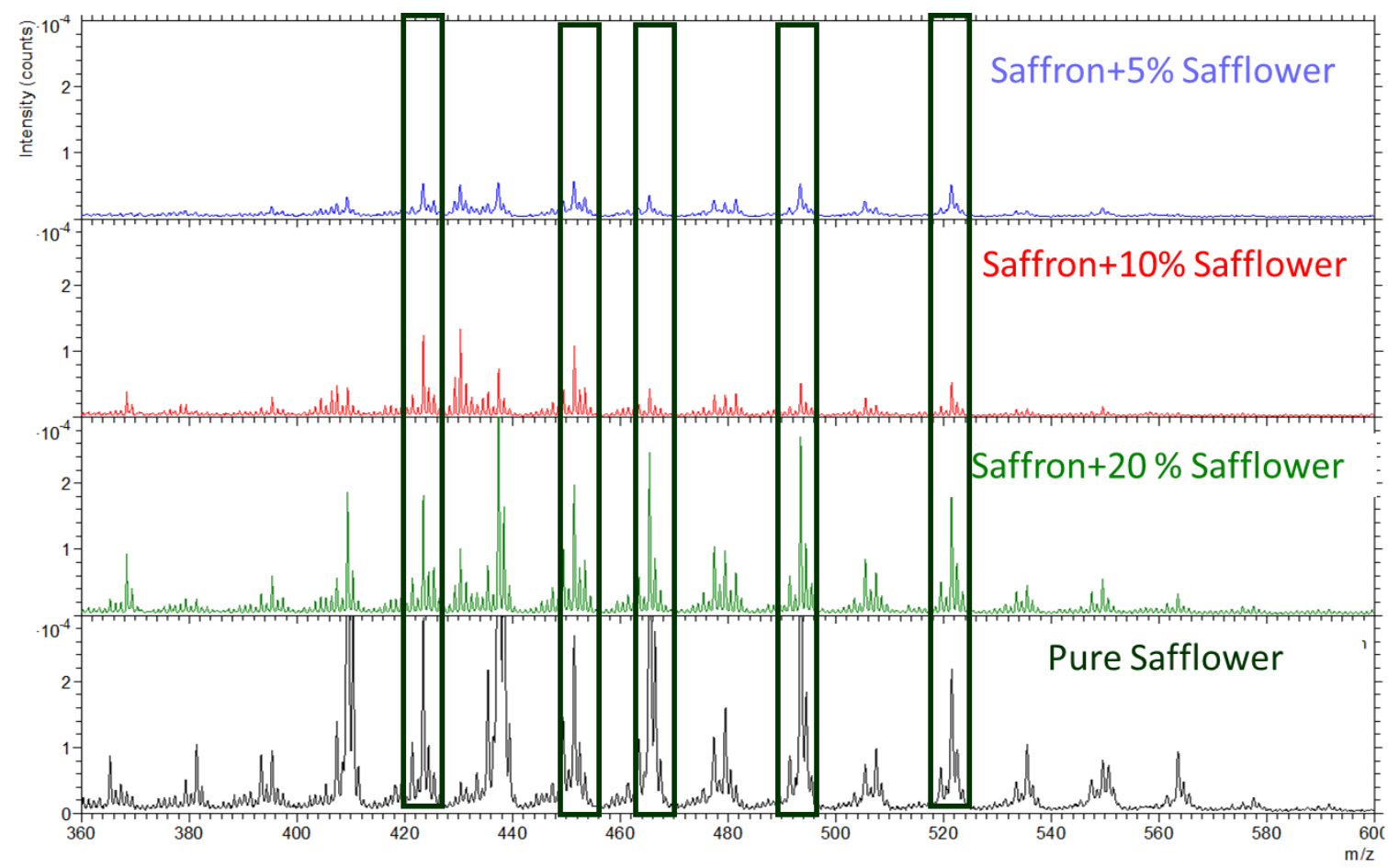
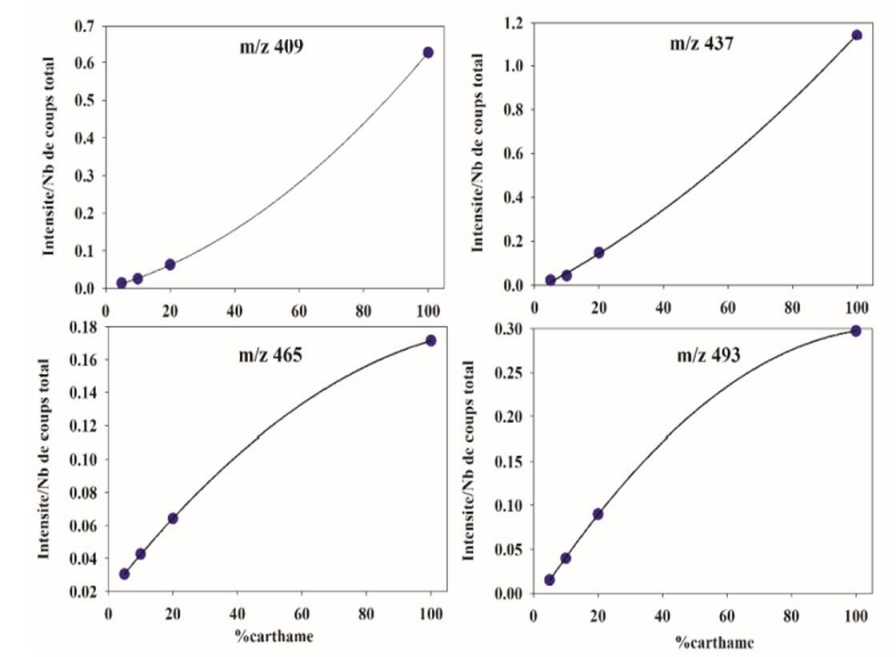
- Potassium
- Magnesium
- Phosphorus
- Sodium

## 1<sup>st</sup> time analysis and identification of Saffron, curcumin and safflower (carthamin) pure samples



Use of Principal Component Analysis (PCA) to separate between pure saffron samples and saffron adulterated with 5, 10 ad 20 % with Curcumin and Safflower respectively

## Semi-quantification of the plants adulterants' quantity



# Concluded Remarks

- Elemental and Molecular IBA analysis are very promising in various fields related to fraud repression and forensic studies. These techniques can be seriously considered, for their originality and performances, to be a part of the analytical arsenal used in the field.
- The Accelerator and ToF-SIMS laboratories at the LAEC are promoting IBA techniques in the field of fraud repression in collaboration with law enforcement agencies, specialized directorates, local industries and various research centers and show the usefulness of these techniques in the field where are in some application quasi unique to deliver the needed information
- A flagship TC project in this domain is proposed for the next TC cycle
- Different studies on counterfeited banknotes, adulteration in drugs and in expensive spices as well as in the domain of the authentication of painting are ongoing in our laboratory. The UHV condition for ToF-SIMS analysis still one of the major challenges together with the matrix effect, facing the analysis of real samples. Analysis of complex mixture !!





Thank you

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INTERNATIONAL CONFERENCE ON

# ACCELERATORS FOR RESEARCH AND SUSTAINABLE DEVELOPMENT

From good practices towards socioeconomic impact



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