

CONTRIBUTION OF X-RAY FLUORESCENCE SPECTROMETRY FOR THE ANALYSIS OF FALSIFIED PRODUCTS

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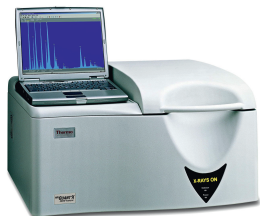
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INTRODUCTION

Falsified products are often adulterated with organic chemical substances. However, some samples may be harmful due to the presence of mineral compounds. This study demonstrates how XRF spectrometry may be benefit for the analysis of such products.

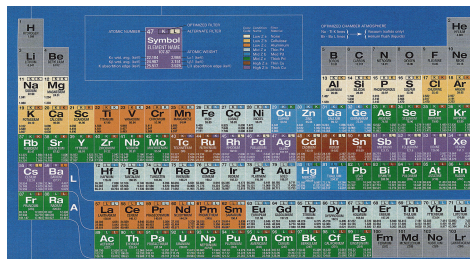
XRF spectrometer

Make and model	Thermo ARL QuantX
Source	Rhodium 50 W
Voltage range	4-50 kV (1 kV step)
Detector	Si(Li) drifted crystal
Energy range	400 eV - 40960 eV
Software	Uniquant
Chemometric method	PCA (Unscrambler X, Camo)



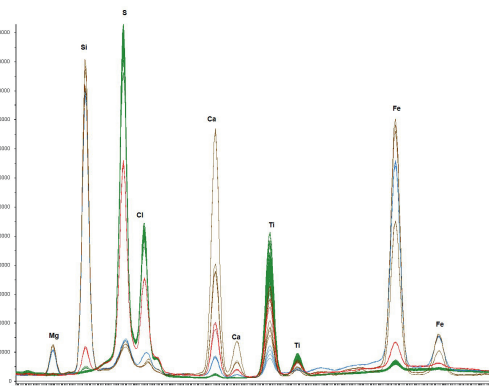
X-RAY FLUORESCENCE

X-ray fluorescence spectrometry is a method which uses the measurement of the intensity of the fluorescent light emitted by a chemical element irradiated by a continuous X-ray radiation. Energies of the electron levels are characteristic of atoms. The analysis of the fluorescent spectra of a sample after irradiation allows us to identify and to quantitate the inorganic compounds.

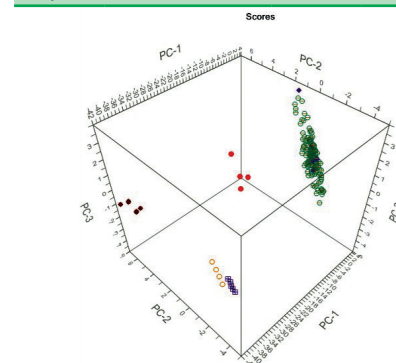


Counterfeit detection: Plavix®

XRF spectrometry detects in samples #1 to #4 unexpected elements (Si-Mg-Ca, presence of talc) and different intensities of expected elements (S-Cl-Ti-Fe) comparatively to reference profile. PCA scores plot gives a better view of the discrimination of samples. The elements S and Cl are related to the content of the active substance (clopidogrel hydrogensulfate). The elements Ti and Fe are related to the coating and the color. Sample #5 gets an inorganic profile similar to the reference profile.

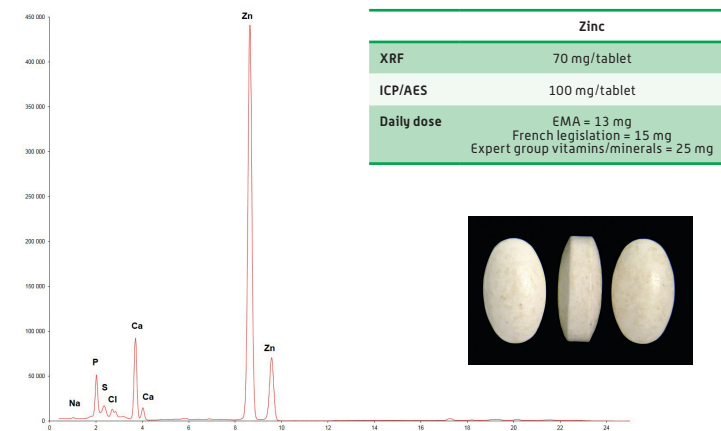


	Inorganic profile	Talc	Clopidogrel
Reference	XRF S-Cl-Ti-Fe	NIR Absence	HPLC 75 mg
Sample #1	Si-Mg-Ca-Ti-Fe	Présence	Absence
Sample #2	S-Cl-Si-Mg-Ca-Ti-Fe	Présence	29 mg
Sample #3	Si-Mg-Ca-Ti-Fe	Présence	Absence
Sample #4	Si-Mg-Ca-Ti-Fe	Présence	Absence
Sample #5	S-Cl-Ti-Fe	Absence	75 mg



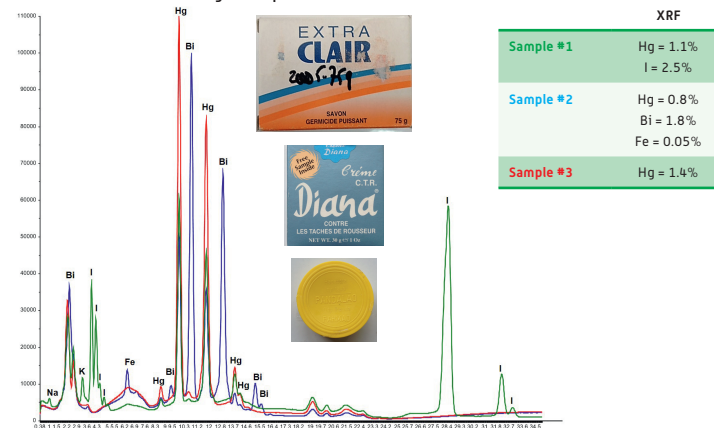
Food supplement analysis

Analysis of a tablet of unknown composition with a semi-quantitative screening. Zinc was detected with a content of 70 mg/tablet by XRF and 100 mg/tablet by ICP/MS which represents 4-8 times the recommended daily dose.



Cosmetic Product analysis

Analysis of 3 cosmetics labelled as a powerful germicide (soap) or for skin treatment (creams) but often used for skin lightening purposes. Mercury was detected with a content ranging from 0,8% to 1.4% m/m. This element is harmful for the safety of patients (kidney damage) and therefore is banned in cosmetic by European Union.



CONCLUSION

The XRF spectroscopy is a multi-elemental fast method which requires a minimal sample preparation. However the quantitation of elements may be complex with a lack of accuracy which may rise 30%.

XRF spectroscopy is very useful for comparative analysis (counterfeit detection) and for the screening for major inorganic elements (e.g. mercury in cosmetic). It is therefore a valuable tool for the analysis of falsified products.

REFERENCES

- Ortiz *et al.* Fingerprinting of sildenafil citrate and tadalafil tablets in pharmaceutical formulations via X-ray fluorescence (XRF) spectrometry, *J. Pharm. Biomed. Anal.* 58 (2012) 7-11
- Falsified lamivudine/zidovudine/nevirapine tablets : rapid identification using X-ray fluorescence technique, *WHO Drug information*, 27 (2013) 213-217