



**HAL**  
open science

## Actinide L-line ED-XRF and HKED Spectra Processing

E. Esbelin, V. Boyer-Deslys, A. Beres, C. Rivier

► **To cite this version:**

E. Esbelin, V. Boyer-Deslys, A. Beres, C. Rivier. Actinide L-line ED-XRF and HKED Spectra Processing. 5th ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles, Jun 2016, Montpellier, France. hal-02441895

**HAL Id: hal-02441895**

**<https://cea.hal.science/hal-02441895>**

Submitted on 26 Feb 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# ACTINIDE L-LINE ED-XRF AND HKED SPECTRA PROCESSING

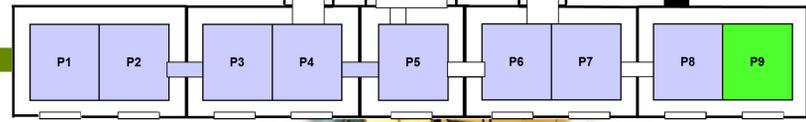
E. ESBELIN, V. BOYER-DESLYS, A. BERES, C. RIVIER

CEA, Nuclear Energy Division, RadioChemistry & Processes Department,  
Analysis and Materials Metrology Laboratory, BP 17171, 30207 Bagnols sur Cèze Cedex, France

FROM RESEARCH TO INDUSTRY



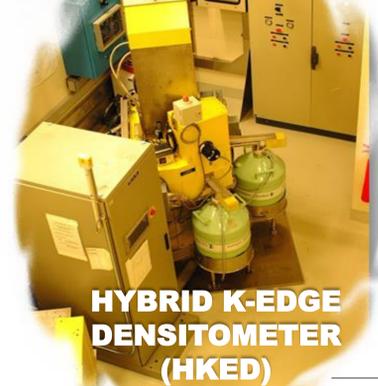
Analytical Shielded Line - CBA



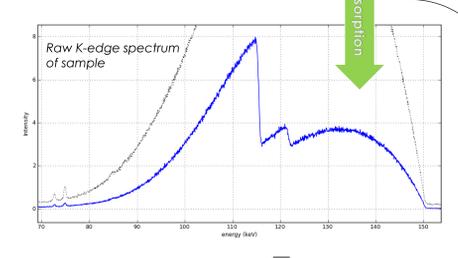
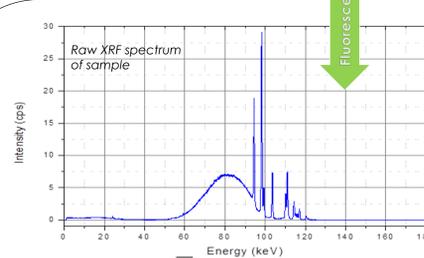
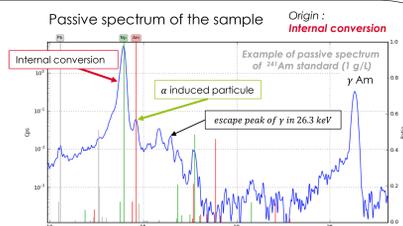
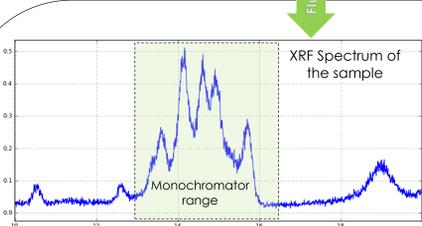
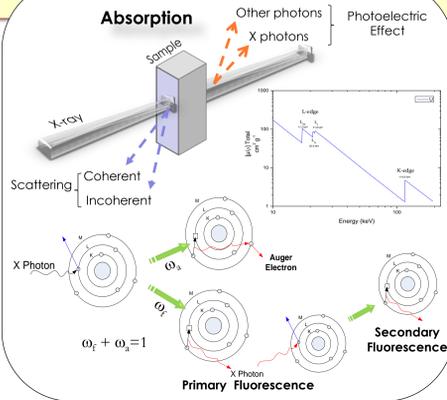
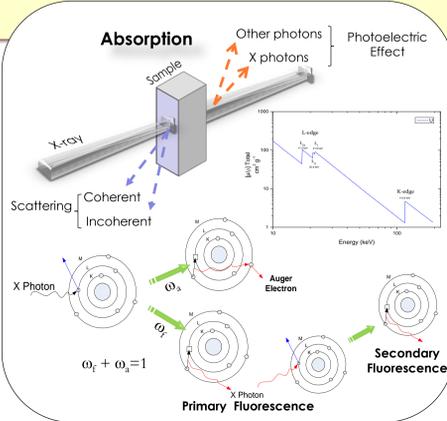
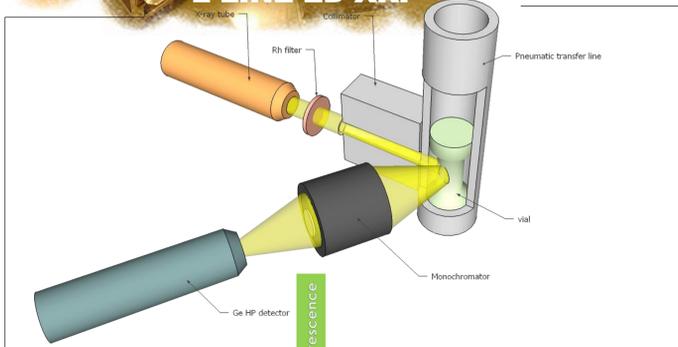
L-LINE ED-XRF

## Two NON DESTRUCTIVE ANALYSIS devices designed for high activity liquid samples

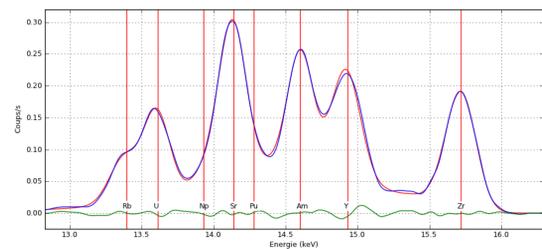
The analysis laboratory in the CEA Atalante facility at Marcoule (France) performs numerous R&D studies carried out in glove-boxes or in hot cells. The samples are measured in liquid phase, aqueous or organic.  
The concentration of the main actinides of interest (U, Np, Pu, Am and Cm) are determined by XRF in a hot cell using a device built specifically for these actinides analyses via their L-line X-ray between 13 and 15 keV.  
For sample with U and/or Pu in high concentrations, the hybrid K-edge densitometer is used. New software were developed for these devices.



HYBRID K-EDGE DENSITOMETER (HKED)



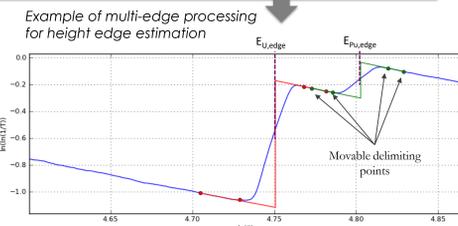
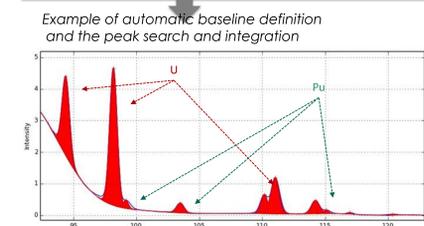
Processing (CEA software)



$$\chi^2 = \sum_{\xi=e_a}^{e_b} \frac{\{I_{mod,\xi}(C) - I_{exp,\xi}\}^2}{\sigma_{\xi}^2}$$

$I_{exp,\xi}$ : net intensity  
 $\sigma_{\xi}^2$ : variance of the measured intensity

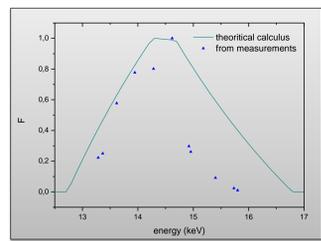
Spectra processing (CEA software)



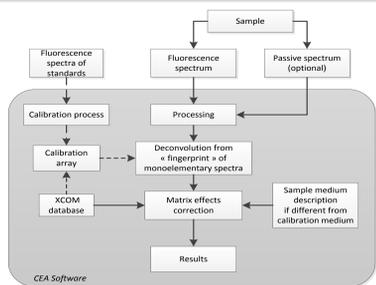
New approaches:  
- Algorithms: automatic peaks find and integrate + automatic baseline determination  
- Improvement of law for relative calibration  
- Fundamental parameters and Monte Carlo currently under study

Based on H. Othmar and M. Collins' works + possibility of manual edge determinations => very useful for wide U/Pu range

## Schematic Data Processing



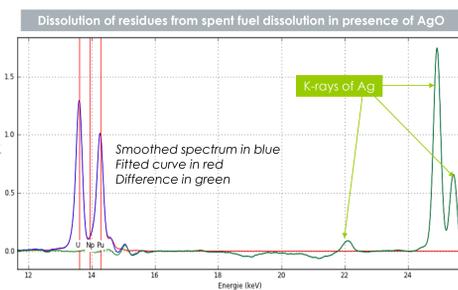
Estimation of the monochromator transfer function



Device special feature: graphite monochromator  
Available free or commercial software is unsuitable  
CEA software development with new approach for the matrix effects correction (~ Lachance-Trail)

More details in E. Esbelin, X-RAY Spectrometry 43, 198-208 (2014)

## Examples



Matrix effects (attenuation) because of high content of AgO (~90 g/L) - have to be taken into account by spectrum processing

Analytical Technique	U (mg/L)	Pu (mg/L)
L-Line XRF without correction	33.3	18.7
L-Line XRF with matrix effects correction	102.8	57.8
ID-TIMS (reference values)	109.2	59.8

## Conclusion

Analyzed elements : U, Pu, Np, Am, Sr, Zr, Br, Rb, Y/Cm, Pb

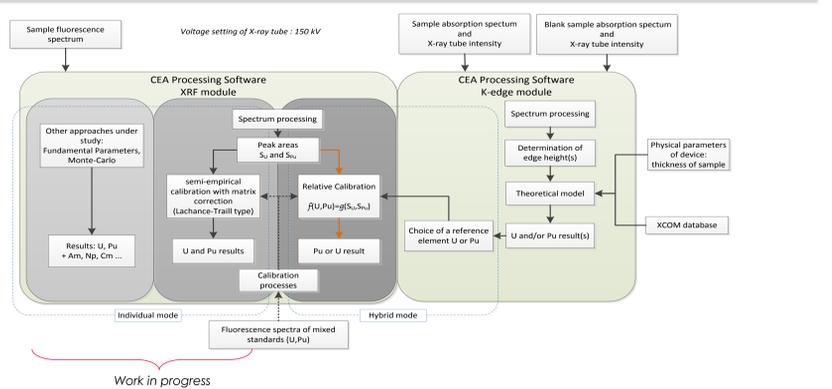
Concentration ranges:  
• 0.5 mg/L (LD) = 5 g/L (uncertainty 10%)  
• 5 g/L = 20 g/L (qualitative mode)

Counting time: 800 s/sample

Calibration : numerous standards required

Matrix effects correction:  
- Sample analysis in organic medium by simulating matrix composition and application of the correction (aqueous calibration used)  
- Continuous feedback: comparison with other analytical techniques results (large diversity of analyzed matrix)

## Schematic Data Processing



## Examples

K-EDGE	K-edge (CEA)		ID-TIMS (IAEA - OSL, Japan)		Relative deviation K-edge/ID-TIMS	
	U (g/L)	Pu (g/L)	U (g/L)	Pu (g/L)	U	Pu
	284.5	143.0	283.42	143.56	0.31%	-0.34%
	61.0	35.2	60.89	35.11	0.15%	0.37%
	143.7	82.5	142.18	81.99	1.06%	0.62%
	179.7	103.5	180.01	103.58	-0.20%	-0.09%
	212.5	104.4	212.38	104.30	0.03%	0.05%
	167.5	81.6	167.57	82.22	-0.04%	-0.71%

HKED	Standards (±2%)		Experimental		Relative deviation	
	U (g/L)	Pu (g/L)	U by K-edge (g/L)	Pu by Hybrid XRF (g/L)	U	Pu
	22.8	4.58	5	23.2	4.61	1.6%
	75.1	5.01	15	75.6	5.02	0.7%
	150.0	1.50	100	149.3	1.47	0.5%
	20.0	0.11	181.6	19.6	0.11	-1.0%
	50.4	0.23	219.1	50.3	0.22	0.2%
	302.6	0.50	605.2	298.8	0.50	0.2%
	249.1	2.45	101.7	252.6*	2.52*	1.4%

## Conclusion

Elements analyzed: focus on U and Pu for our use

Absorption (K-edge):

Concentration range:  
• >10 g/L (LQ)  
• Best accuracy >50 g/L (uncertainty <2%)  
Counting time: 800 s/sample  
No experimental calibration: theoretical model  
Matrix effects : low sensitivity

X-ray Fluorescence (ED-XRF):

Concentration range:  
• >0.1 g/L (LQ)  
Counting time: 800 s/sample  
Relative calibration (hybrid mode: coupled with K-edge)  
Absolute calibration (autonomous mode)

Work in progress about autonomous mode of ED-XRF for improvement of results accuracy.