

CRM : 3 new CETAMA standards in 2016

D. Roudil, C. Rigaux, M. Crozet, C. Rivier

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FROM RESEARCH TO INDUSTRY

cea den

CETAMA







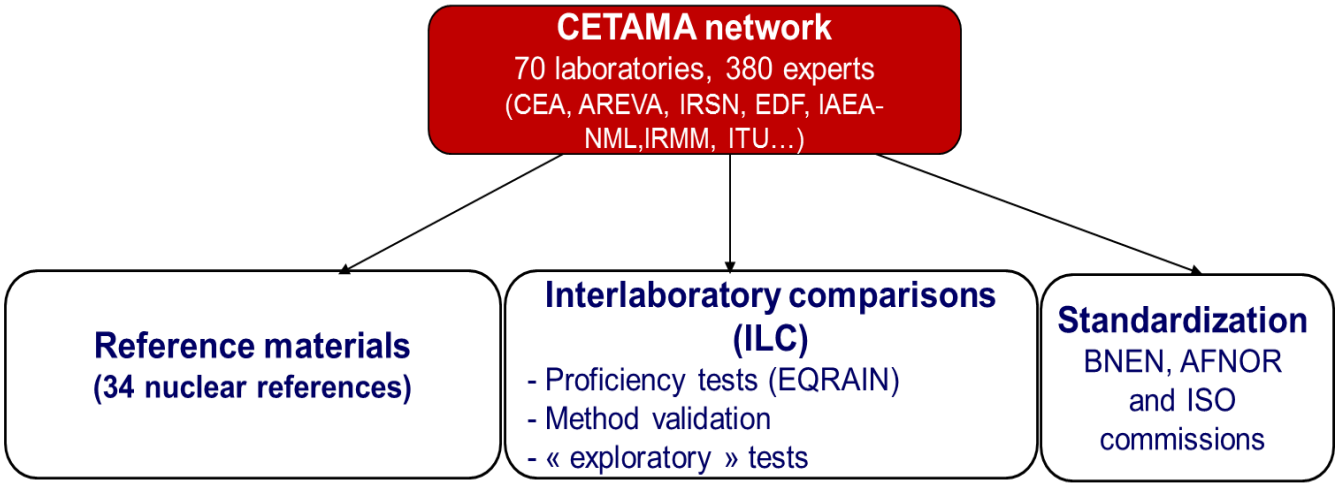
CEA Marcoule Center

CRM : 3 new CETAMA standards in 2016

CEA/DEN/DRCP/CETAMA:D. Roudil. C. Rigaux. M. Crozet.
CEA/DEN/DRCP/SERA/LAMM : C. Rivier

afaq QSE Qualité Sécurité Environnement AFNOR CERTIFICATION ISO 9001 - OHSAS 18001 ISO 14001

CETAMA MAIN OBJECTIVES IN THE NUCLEAR FIELD



CETAMA (The Commission for establishment of analytical methods) is a unit of **CEA** (the French Alternative Energies and Atomic Energy Commission) in charge of **improving the quality of analytical results** in the nuclear field

- Based on **a network** of experts and analytical labs
- **13 Working Groups** under activity

Catalog of certified reference materials for nuclear fuel cycle needs, regularly updated

34 Reference material catalog of CETAMA: recent and on going CRM

High purity standards and solutions (U, Pu and Np),

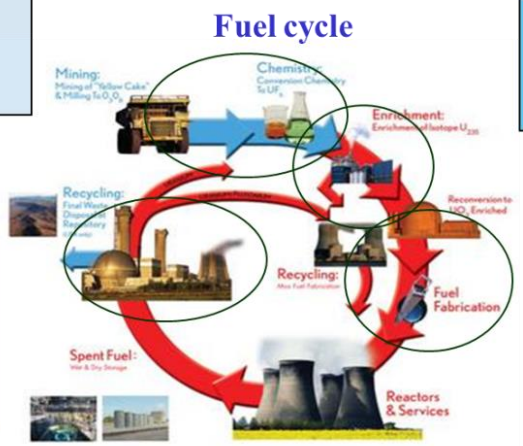
High chemical purity Pu metal MP2 renewing: MP4

PuO_2 pellets

U matrix CRMs

MIN x & Gems series (Uranate)

MP2-MP4
MIRF
^{242}Pu
^{237}Np
HDBP



MU2, OU1,OTU1
Mushrooms &
Opera series

MIRF 02
CETAMIR
Viognier
Syrha
PuO_2

Isotopic composition (U, Pu)

^{243}Am spike (IRMM collab)

Solution standards :

Chemical purification

High yield separation process

Radiolysis risk management

Solid standards:

Homogeneity (powder< pellet…)

Improvement of uncertainty assessment in the certification process

Necessity to enhance **collaborations** in the nuclear chemical metrology field

34 Reference material catalog of CETAMA: recent and on going CRM

High purity standards and solutions (U, Pu and Np),

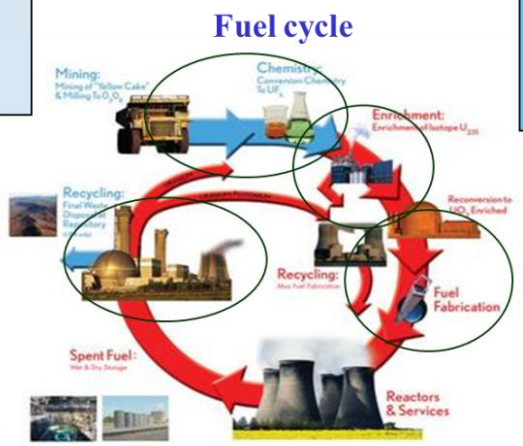
High chemical purity Pu metal MP4

matrix CRMs & impurities

- Feldspath UOC
- Nuclear 25 oxides glass
- Floralies

MIN x & Gems series (Uranate)

MP2-MP4
MIRF
^{242}Pu
^{237}Np
HDBP



MU2, OU1,OTU1
Mushrooms &
Opera series

MIRF 02
CETAMIR
Viognier
Syrha
PuO_2

Isotopic composition (U, Pu)

^{243}Am spike (IRMM collab)

RM "matrix" and impurities lead to complex developments

- A lot of matrix : mud, concrete, resin, metals
- With stable interferent, coming from the matrix itself, and radioactive ones

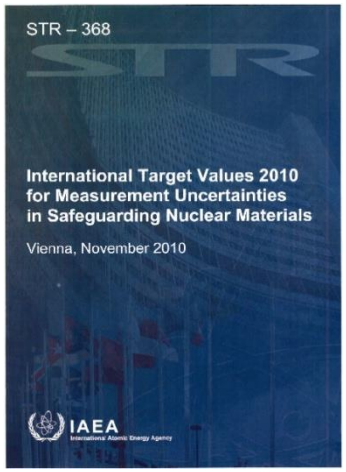
1. **Homogenized real samples** in support to method characterisation by ILC
2. Reference sample characteristics assessment : Possible use as RM

Extension to safeguards problematics

- ✓ **IAEA** specifies several **target values for measurement uncertainties** for the control of nuclear materials

  For example relative uncertainty for Pu analysis by ID-TIMS is 0.18%

- ✓ **Destructive analysis: mainly relative techniques**



Achieving these target values requires :

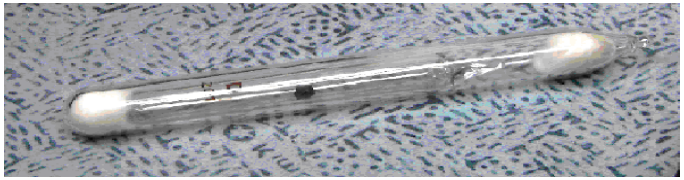
- to have a **well structured metrological scheme based on chemical and isotopic certified reference materials**
  - Characteristics of the method : trueness and precision
- **To participate in interlaboratory comparison**

Isotopic reference materials



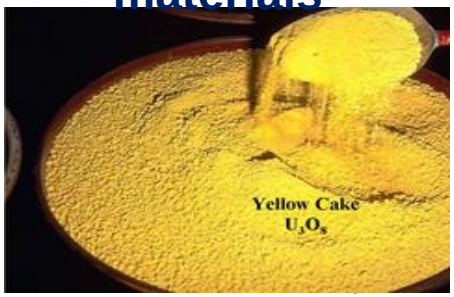
IRMM-646 reference material

High purity reference materials



CETAMA MP2 reference material

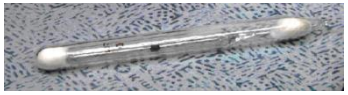
Real matrix reference materials



Use of reference materials (ISO Guide 33)

- **Material for instrument calibration**

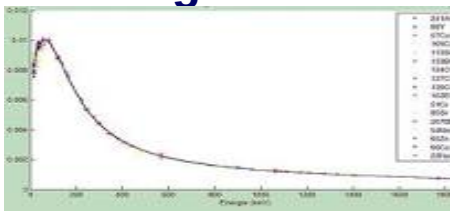
- High chemical purity RM
- Standard solutions
- Sources



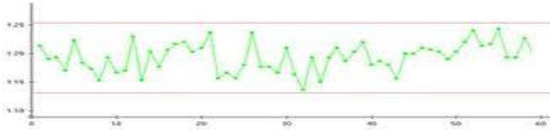


2 main uses

Calibration curve setting on



Calibration QC



- **Material for method trueness and precision assessment**

- RM « matrix »



- Isotopic spikes

2 main uses

Initial characterisation of analytical method

QC material (global measurement process)



FROM RESEARCH TO INDUSTRY
cea den

AREVA



UOC Feldspath new « matrix » CRM

Front end of fuel cycle

Safeguards and forensic

Collaboration with

IAEA/NML & NWAL expert laboratories

AREVA and CEA laboratories

More details In

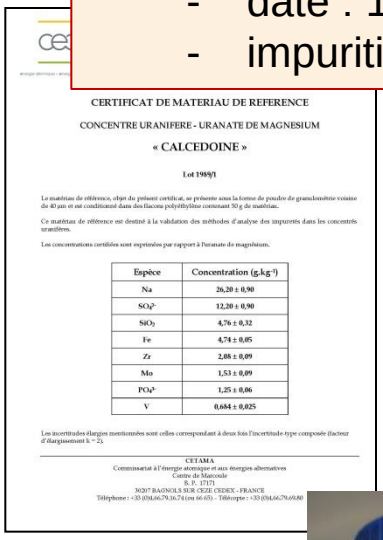
C. Rigaux et al. CETAMA TM Sept 2015
C. Rigaux et al. IAEA TM Feb 2016

UOC FELDSPATH NEW « MATRIX » CRM



UOC: FELDSPATH

- Matrix: ammonium uranate
- Certification
  - date : 1989
  - impurities: Fe, PO_4, SO_4



CERTIFICAT DE MATERIAU DE REFERENCE

CONCENTRE URANIFERE - URANATE DE MAGNESIUM

« CALCEDOINE »

Lot 1989/1

Le matériau de référence, objet du présent certificat, se présente sous la forme de poudre de granulométrie voisine de 40 µm et est conditionné dans des flacons polyéthylène contenant 50 g de matériau.

Ce matériau de référence est destiné à la validation des méthodes d'analyse des impuretés dans les concentrés uranifères.

Les concentrations certifiées sont exprimées par rapport à l'uranate de magnésium.

Espèce	Concentration ($g.kg^{-1}$)
Na	26,20 ± 0,90
SO_4^{2-}	12,20 ± 0,90
SiO_2	4,76 ± 0,32
Fe	4,74 ± 0,05
Zr	2,08 ± 0,09
Mo	1,53 ± 0,09
PO_4^{3-}	1,25 ± 0,06
V	0,684 ± 0,025

Les incertitudes élargies mentionnées sont celles correspondant à deux fois l'incertitude-type composée (facteur d'élargissement k = 2).

CETAMA
Commissariat à l'énergie atomique et aux énergies alternatives
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30207 BAGNOLS SUR CEZE CEDEX - FRANCE
Téléphone : +33 (0)4.66.79.16.74 (ou 66 65) - Télécopie : +33 (0)4.66.79.69.80

- Enlarged certification to other impurity contents :

U - Ca, Fe, Mg, Mo, V, Zr - REE pattern

ASTM C967-08 Specification for ore concentrates

Identification of the origin of the ore samples

- Uncertainty improvement



- Both **certification and PTS ILC**
- **Excess variance approach** to take into account the **spread of the results** and the **uncertainties of the laboratories**

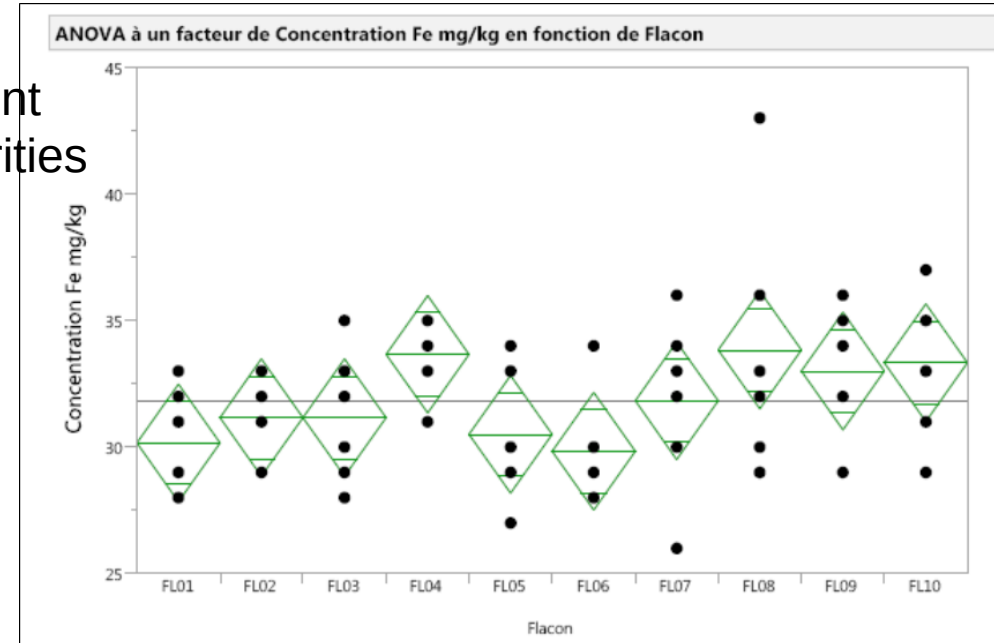


METHODOLOGY AND DATA PROCESSING

$$x_{CRM} = x_{char} + \delta x_{hom} + \delta x_{stab} \qquad u_{CRM} = \sqrt{u_{char}^2 + u_{hom}^2 + u_{stab}^2}$$

- Data processing of analysis results :
  - ❑ Potentiometry analysis of U content
  - ❑ Mainly ICP MS methods for impurities
  - ❑ Weighted mean (GUM)
  - ❑ Robust statistics
  - ❑ Weighted mean+Excess variance
- Homogeneity /stability :
  - ❑ stratified random sampling on 10 bottles
  - ❑ ANOVA statistical processing on 1 factor
  - ❑ ISO guide 35
  - ❑ Normalized deviation test (between 1989 and 2015)

element	Fe	Ca	Mg	U
U inter	13,6093	10.6019	0.17267	0.296685
U intra	8.0233	4,8233	0.0428	0.133967
U hom	0,9649	0.9814	0,1471	0.1647
U relatif (%)	**3.03**	**0.92**	**0.78**	**0.22**



Anova à un facteur

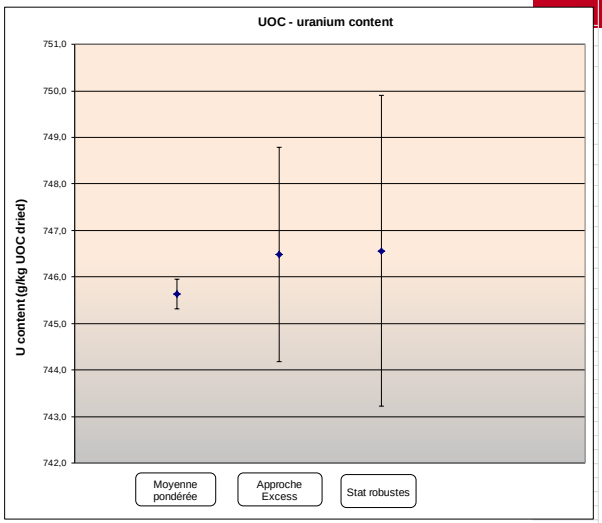
Résumé de l'ajustement

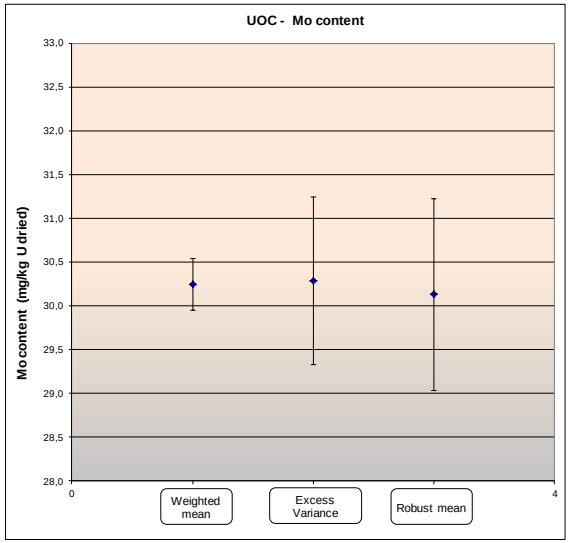
R carré	0,233903
R carré ajusté	0,096006
Racine de l'erreur quadratique moyenne	2,832549
Moyenne de la réponse	31,85
Observations (ou sommes pondérées)	60

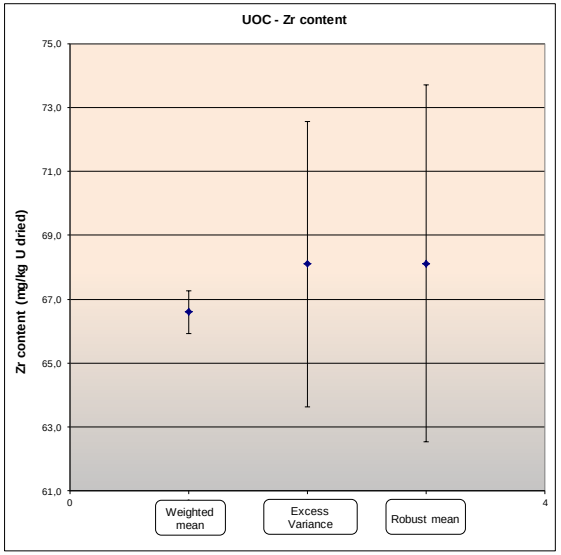
Analyse de la variance

Source	Degrés de liberté	Somme des carrés	Carré moyen	Rapport F	Prob. > F
Flacon	9	122,48333	13,6093	1,6962	0,1148
Résidus	50	401,16667	8,0233		
Total corrigé	59	523,65000			

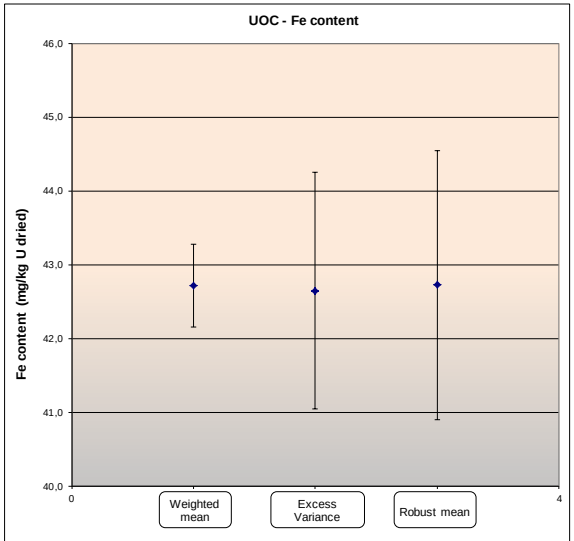
CONCENTRATION OF THE MAJOR IMPURITY CERTIFIED VALUE

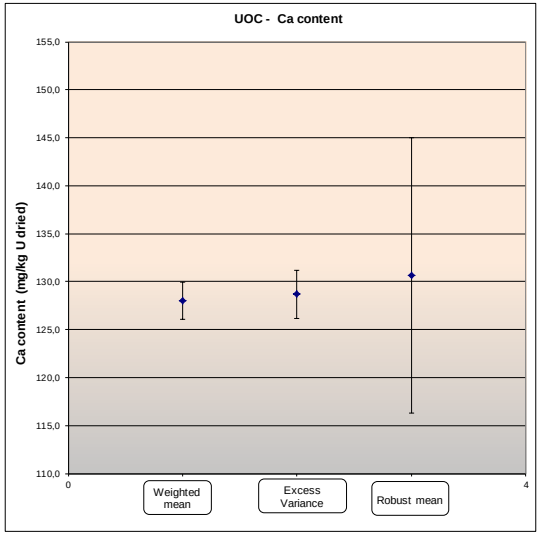


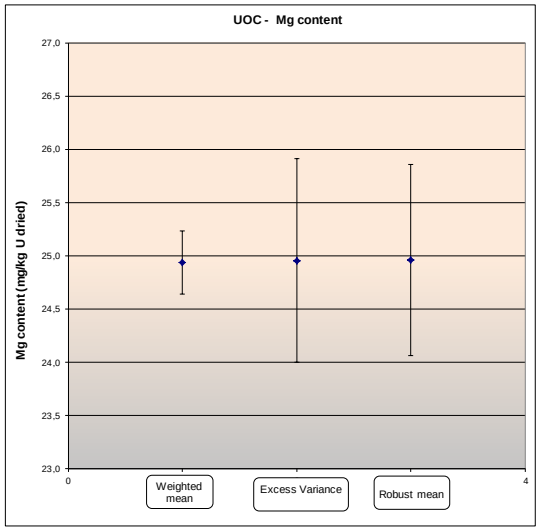




U	Mo	Zr
Fe	Ca	Mg



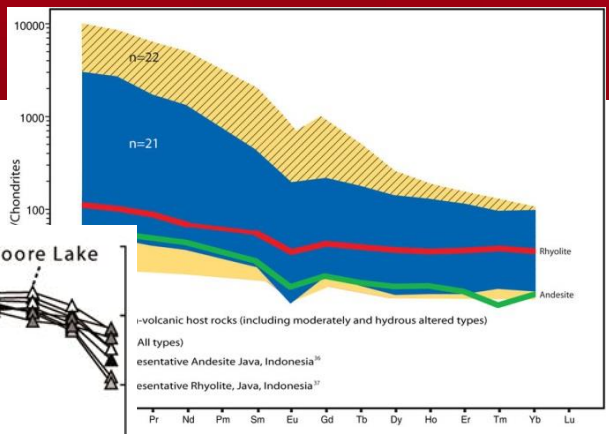


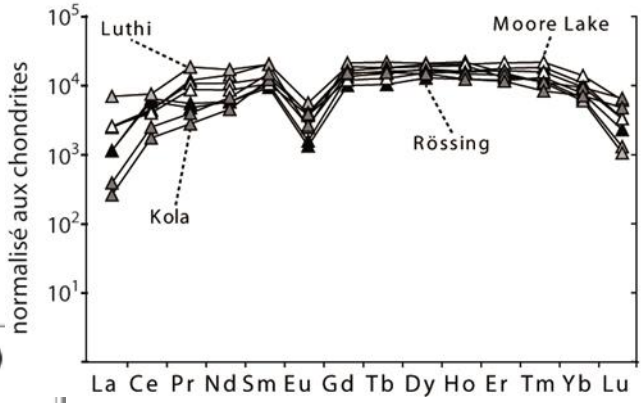


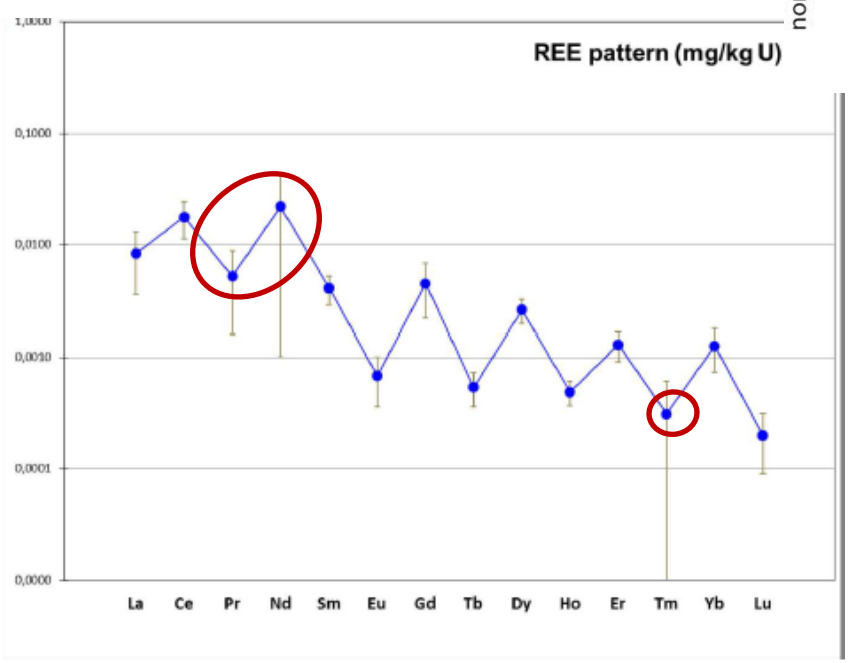
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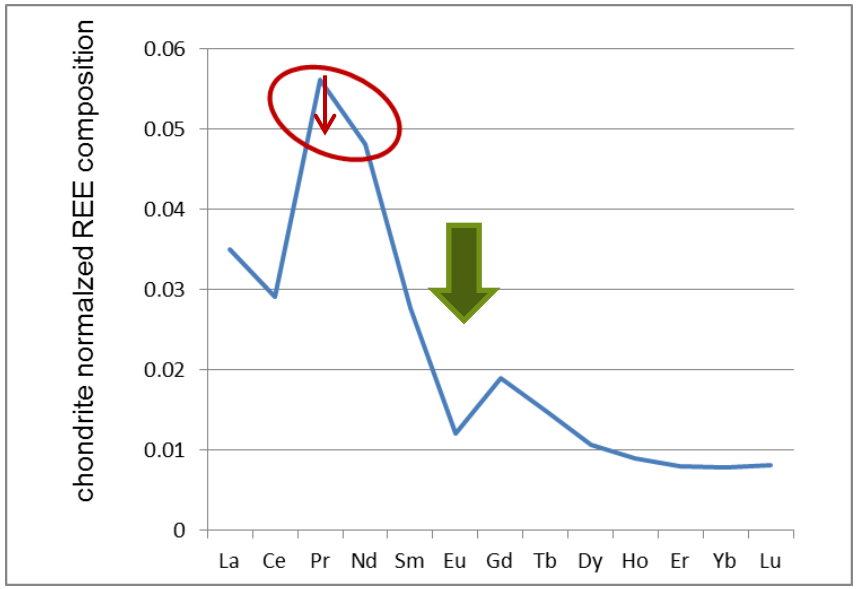
REE PATTERN STUDY

- Based on 4-6 laboratory results
- ICP MS and QMS
- Excess variance approach
- Homogeneity component : 3%









Method used: ICP-QMS
ICP-MS, ICP-SFMS, ID-HPLC-ICPMS

FELDSPATH NEW CERTIFICATE



Element	Unit	Content	Expanded uncertainties (k=2)
U	g/kg UOC dried	746,5	4,1
Fe	mg/kg U	42,7	3,1
Mo	mg/kg U	30,3	2,1
Mg	mg/kg U	25,0	1,1
Ca	mg/kg U	128,5	3,0
Zr	mg/kg U	68,2	6,1
V	mg/kg U	< 0,35	

Certified values

Eléments Terres Rares	Teneur REE (mg/kg U)	U MRC relatif à k=2 (%)
La	**0,0083**	56,6%
Ce	**0,0178**	36,5%
Sm	**0,0041**	29,3%
Eu	**0,00068**	47,1%
Gd	**0,0045**	51,1%
Tb	**0,00054**	33,3%
Dy	**0,00262**	25,2%
Ho	**0,00049**	24,5%
Er	**0,00129**	30,2%
Yb	**0,00126**	42,1%
Lu	**0,00020**	55,0%

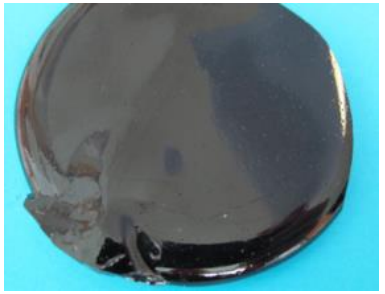
Indicative values

UOx 25 glass new matrix CRM

- Specific HLW real matrix

Collaboration

AREVA and CEA



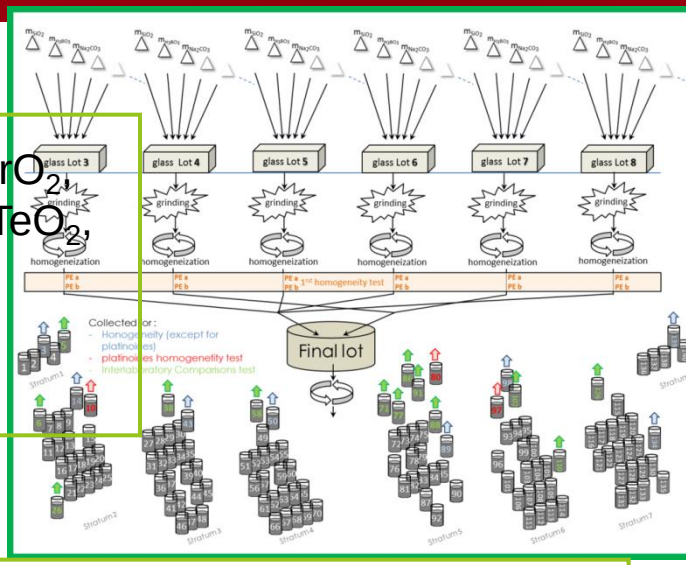
More details in

M. Crozet et al. CAC2016 (Barcelona, June)
M. Crozet et al. ASTM workshop 2016 (Vienna ,June)

NUCLEAR GLASS NEW « MATRIX » CRM

First step : fabrication (CEA/DEN/DTCD–LCV)

- Precursors: SiO_2, B_2O_3, Na_2O, Al_2O3, CaO, Nd_2O_3, Fe_2O_3, ZrO_2, ZnO, MoO_3, Li_2O, La_2O_3, Cs_2O, Ce_2O_3, BaO, Pr_2O_3, MnO_2, SrO, TeO_2, P_2O_5, NiO, Cr_2O_3, SnO_2 , RuO_2, Pd
- Grinding
- Homogeneization



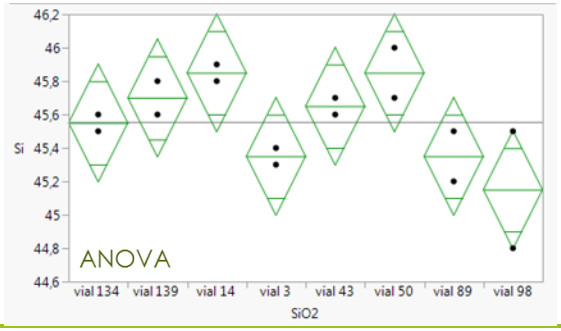
Second step : certification (CETAMA)

$$x_{CRM} = x_{char} + \delta x_{hom} + \delta x_{stab} \qquad u_{CRM} = \sqrt{u_{char}^2 + u_{hom}^2 + u_{stab}^2}$$

$$\frac{m_{ox,glass}}{m_{glass}} = \frac{m_B \text{ precursor} - m_B \text{ lost}}{m_{glass\,(precursors)} + m_{impurities} - m_{lost\,glass}} \; F_{grinding} \; K_{m_B \Rightarrow m_{B2O3}}$$

$$u_{stab} = u_{SLT}$$

$$u_{hom} = \sqrt{u_{between}^2 + u_{within}^2}$$



- Stratified random sampling
- ANOVA 1 factor

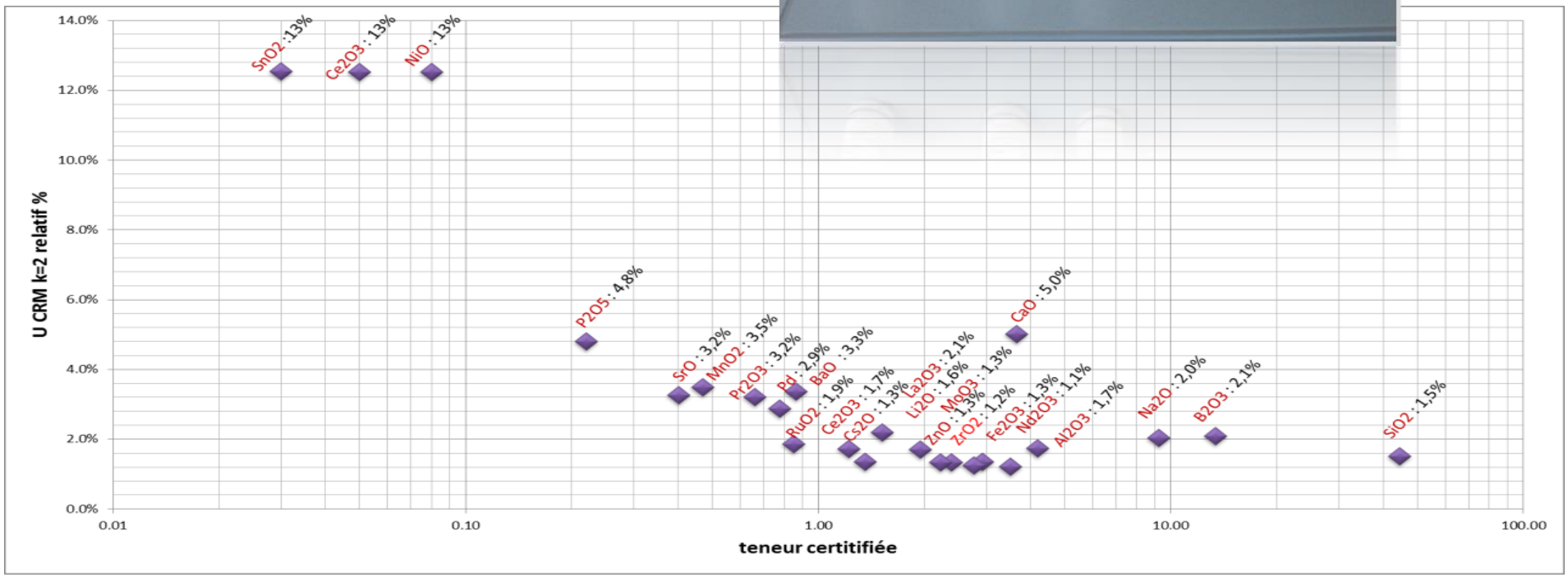
UOX GLASS CERTIFICATION PROCESS

Third step : verification (CETAMA)

- Confirmation by ILC
- XRF Q and SQ
- ICP OES and MS







FINAL UOX COMPOSITION GLASS CERTIFICATE

CRM UOx Glass : 25 components

- 22 certified mass contents
- 3 indicative mass contents



		% w/w	U CRM k=2 % w/w	U CRM rel k=2 % of % w/w
certified values	SiO_2	44,52	0,67	1,5%
	B_2O_3	13,38	0,28	2,1%
	Na_2O	9,23	0,19	2,0%
	CaO	3,66	0,19	5,0%
	Nd_2O_3	3,512	0,042	1,2%
	Fe_2O_3	2,921	0,040	1,3%
	ZrO_2	2,771	0,035	1,3%
	ZnO	2,383	0,032	1,3%
	MoO_3	2,221	0,030	1,3%
	Li_2O	1,951	0,034	1,7%
	La_2O_3	1,521	0,034	2,2%
	Cs_2O	1,361	0,019	1,3%
	BaO	0,865	0,029	3,4%
	RuO_2	0,853	0,016	1,9%
	Pd	0,776	0,022	2,9%
	Pr_2O_3	0,660	0,021	3,2%
	MnO_2	0,470	0,016	3,5%
	SrO	0,402	0,013	3,3%
	P_2O_5	0,220	0,011	4,8%
	NiO	0,080	0,010	13%
	Cr_2O_3	0,0501	0,0063	13%
	SnO_2	0,0300	0,0038	13%

		% w/w	U k = 2 % w/w	U rel k = 2 % of % w/w
indicative values	TeO_2	0,205	0,017	8,5%
	Al_2O_3	4,183	0,072	1,7%
	Ce_2O_3	1,221	0,021	1,7%

CETAMA

U metal Floralies serie

- Impurity in uranium matrix
- Complementary of “Champignon” series (U_3O_8)
- Renewing of old CETAMA CRM







IMPURITIES IN U METAL (FLORALIE)

- Cutting of U metal stored in oil
- Isotopic composition of natural uranium
- Devoted to the calibration for SQ impurity analysis:
  - mainly metal and alkali metal
  - Different range of concentrations
- Certification by ILC
  - ICP AES and molecular or atomic spectrophotometry measurement
  - Without uncertainty value assessment nor confidence interval ?





Improvement of the certified composition assessment?

FLORALIE SERIE CERTIFCATE

Ref. SAMPLE	ELEMENTS													
	Ag	Al	B	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Si	Sn	Zr
Bleuet	<0,5	40	≤0,2	4	5	12	70	6	7	24	1,5	70	≤2	25
Capucine	0,5	40	0,55	4	32	55	140	25	20	190	5	22	4	55
Dahlia	0,6	90	0,8	8	140	72	450	32	30	290	2	40	7	70
Eglantine	1,2	120	0,25	15	15	7	38	4	50	50	15	13	20	110
Fuschia	1,3	150	0,35	26	17	23	200	60	95	110	25	110	20	150
Géranium	10	210	2,15	55	115	100	480	120	210	320	23	230	50	240

	Al	B	Co	Cr	Cu	Fe	Mn	Mo	Ni	Si	Sn	Th	Zr
Verveine	1020	1,5	45	95	105	510	95	420	130	360	400	≤ 50	110

- Unit :mg.Kg_U^{-1}
- Homogeneity >2 g samples

Ref. SAMPLE	ELEMENTS															
	Al	B	Be	Bi	Ca	Cr	Cu	Fe	In	Mn	Nb	Ni	Si	Th	Ti	V	W
Hortensia	60	1	<0,1	<1	≤2	140	80	460	1	15	≤5	340	34	5	5	4	<5
Iris	100	-	0,2	≤1	4	27	35	130	6	6	≤10	115	13	<5	10	3	≤5
Kentia	120	1,3	-	-	5	9	130	110	-	12	20	480	40	<5	40	3	5
Lys	40	-	1,5	1,2	≤2	155	5	450	9	10	80	100	35	17	90	50	≤5

PERSPECTIVE : MATRIX CRM FOR D&D

- **"Matrix" and impurities RM** lead to complex developments but are of paramount importance for safeguards and D&D analysis

- **The fabrication of homogenised real samples** well characterised thanks to ILC data processing approaches is a suitable solution:

  - from synthetic doped sample to real sample

❖ Future European project proposal devoted to D&D waste analysis

❖ 4 main topics and challenges

- Sampling methodology extension to HA and MA waste
- NDA /in situ current techniques performance assessment, new development
- DA adaptation in laboratory – performance assessment
- Matrix CRM

❖ Call for partners : danielle.roudil@cea.fr or cetama@cea.fr



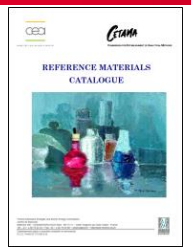
Thank you for your attention

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Département de radiochimie et procédés
Commission d'ETAblissement des Méthodes d'Analyse

Nuclear Reference Materials producers



CETAMA

http://www-cetama.cea.fr/

LNHB

http://www.nucleide.org/



Institute for Reference Materials and Measurements

http://irmm.jrc.ec.europa.eu/reference_materials_catalogue/catalogue/Documents/isotopicrm_catalogue_jun2008.pdf



NIST

http://www.nist.gov/srm/index.cfm

New Brunswick Laboratory
U.S. Department of Energy

http://www.nbl.doe.gov/htm/certified_reference_materials.htm

CERCA-LEA (Activity standards lab)

http://www.lea-cerca.com/fr/catalogue/

NUCLITEC

http://www.ezag.com/home/products/isotope-products.html