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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



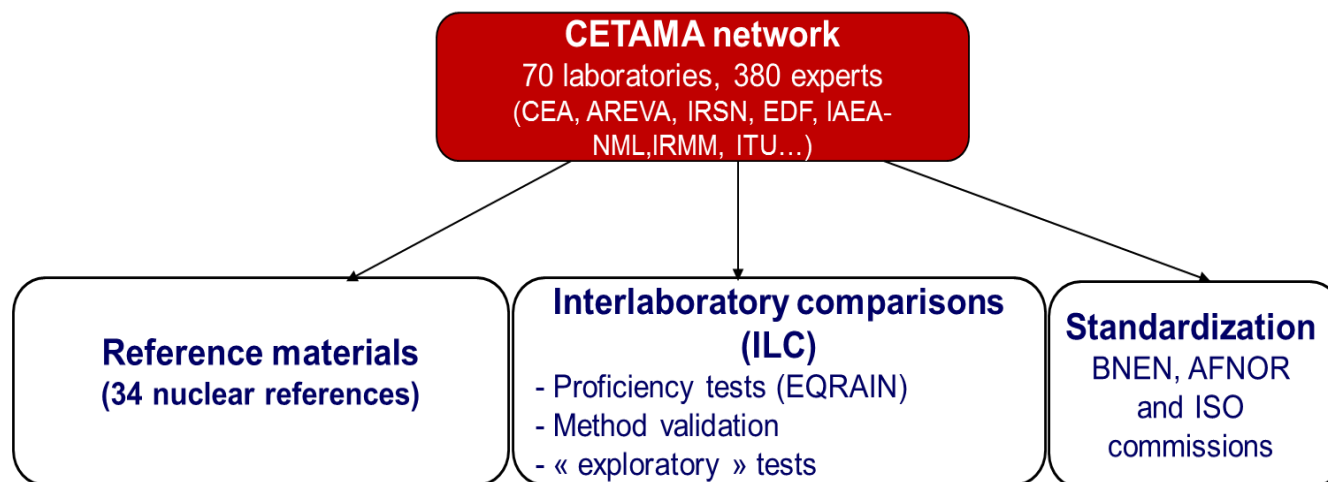
CEA Marcoule Center



CRM : 3 new CETAMA standards in 2016

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





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),

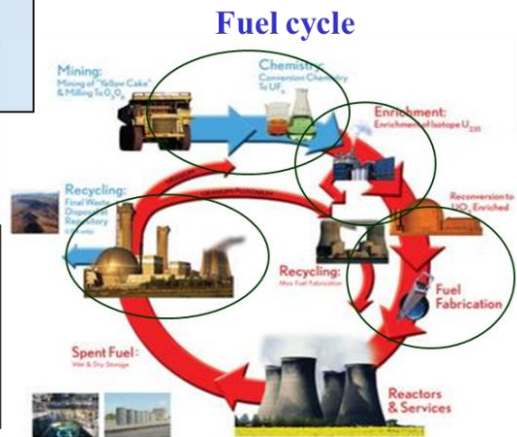


High chemical purity Pu metal MP2 renewing: MP4
PuO₂ pellets

U matrix CRMs

MIN x &
Gems series
(Uranate)

MP2-MP4
MIRF
242Pu
237Np
HDBP



MU2, OU1, OTU1
Mushrooms &
Opera series

MIRF 02
CETAMIR
Viognier
Syrha
PuO₂

Isotopic composition
(U, Pu)



²⁴³Am 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

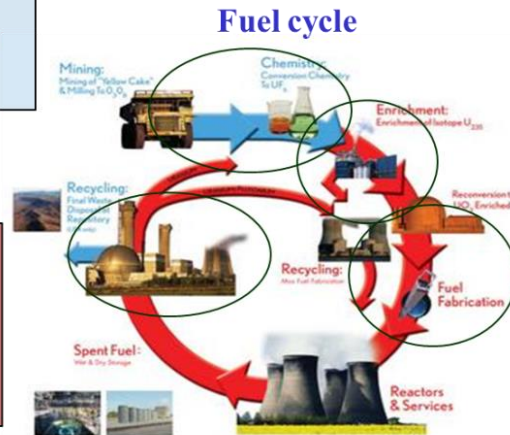
matrix CRMs
& impurities



- 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

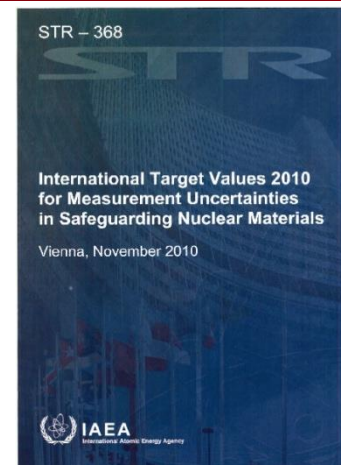
Extension to safeguards problematics

- ✓ **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

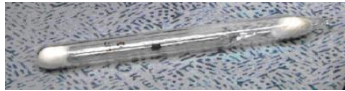
Real matrix reference materials



Use of reference materials (ISO Guide 33)

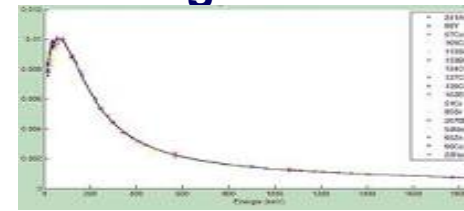
Material for instrument calibration

- High chemical purity RM
- Standard solutions
- Sources

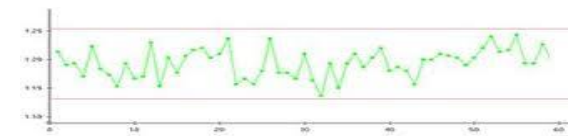


} 2 main uses

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)



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, PO₄, SO₄

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

CERTIFICAT DE MATERIAU DE REFERENCE
CONCENTRE URANIFERE - URANATE DE MAGNESIUM
« CALCEDOINE »
Lot 1989f

Le matériau de référence, objet du présent certificat, se présente sous la forme de granulats fins versés 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 ± 0,85 |
| Zr | 2,86 ± 0,09 |
| Mo | 1,53 ± 0,09 |
| PO ₄ ³⁻ | 1,25 ± 0,66 |
| V | 0,684 ± 0,025 |

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

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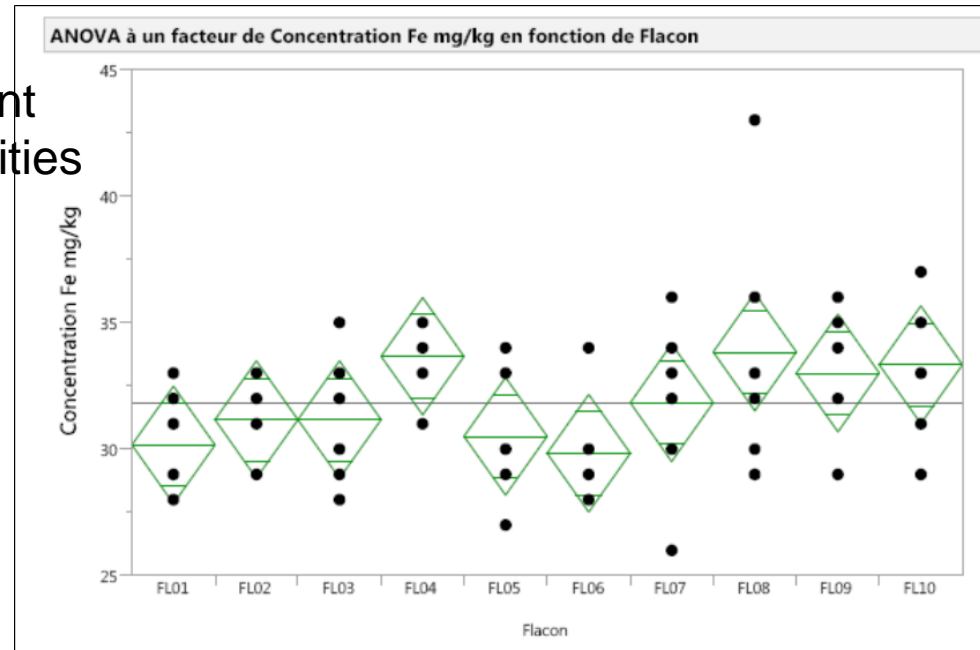
- Both certification and PTS ILC
- Excess variance approach to take into account the spread of the results and the uncertainties of the laboratories



$$x_{CRM} = x_{char} + \delta x_{hom} + \delta x_{stab}$$

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

- 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)



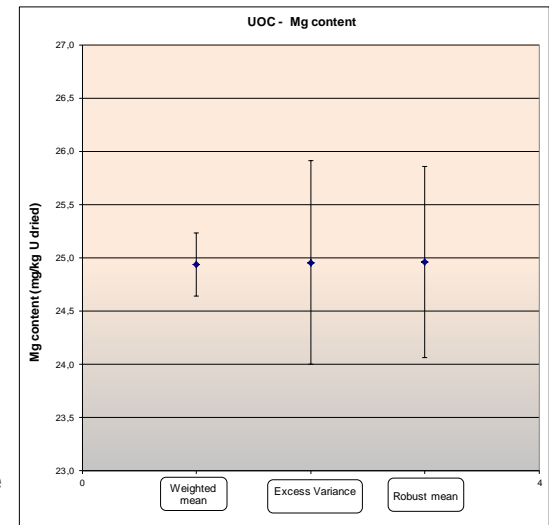
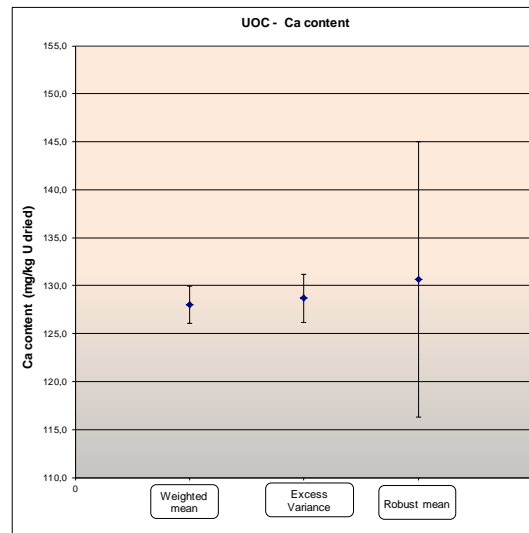
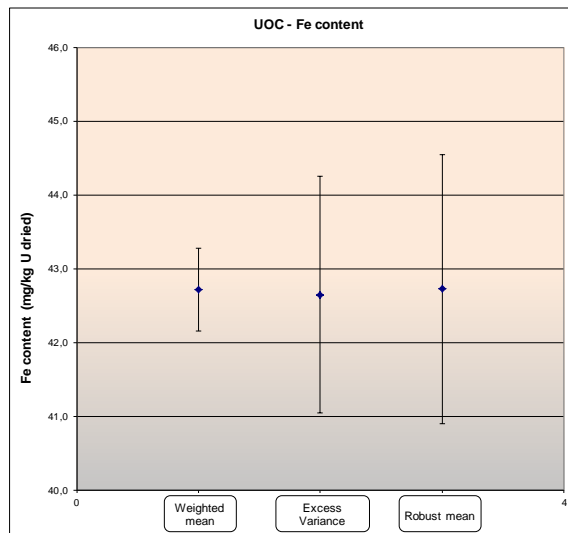
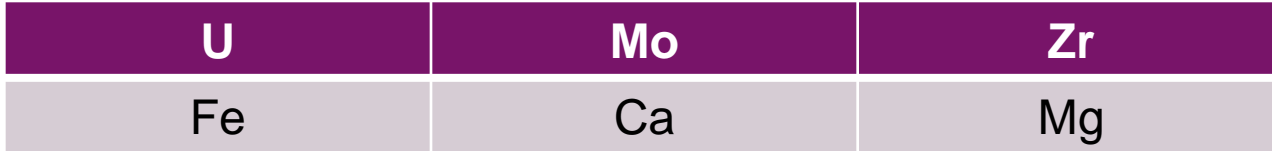
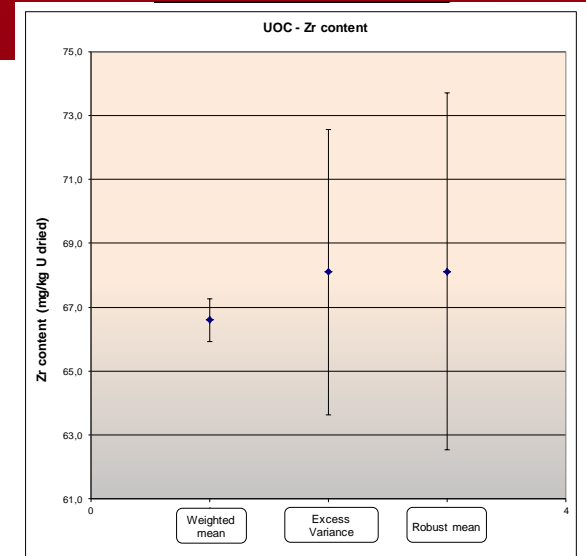
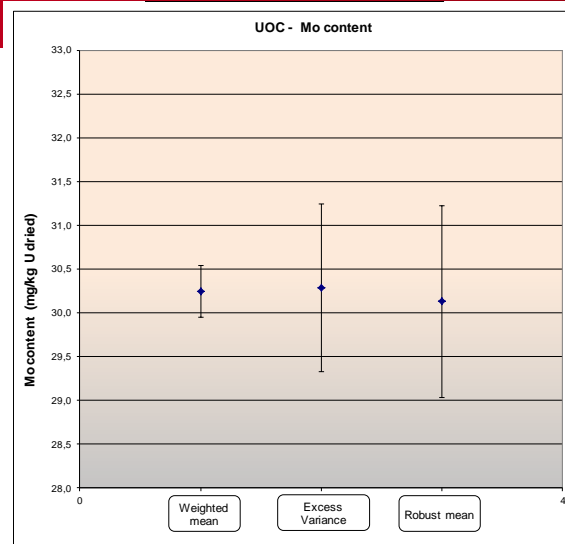
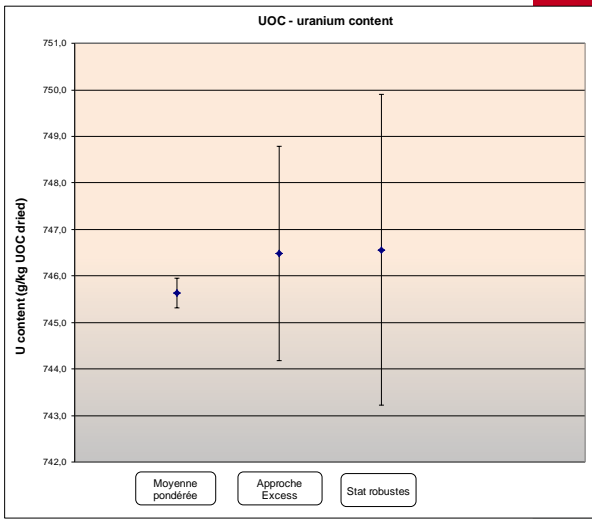
Anova à un facteur

| 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 | | | |

| 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 |

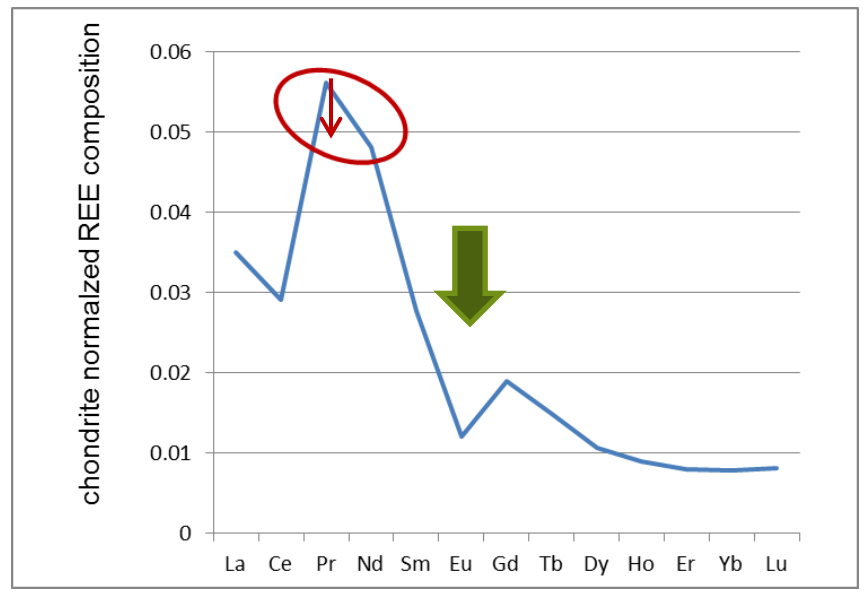
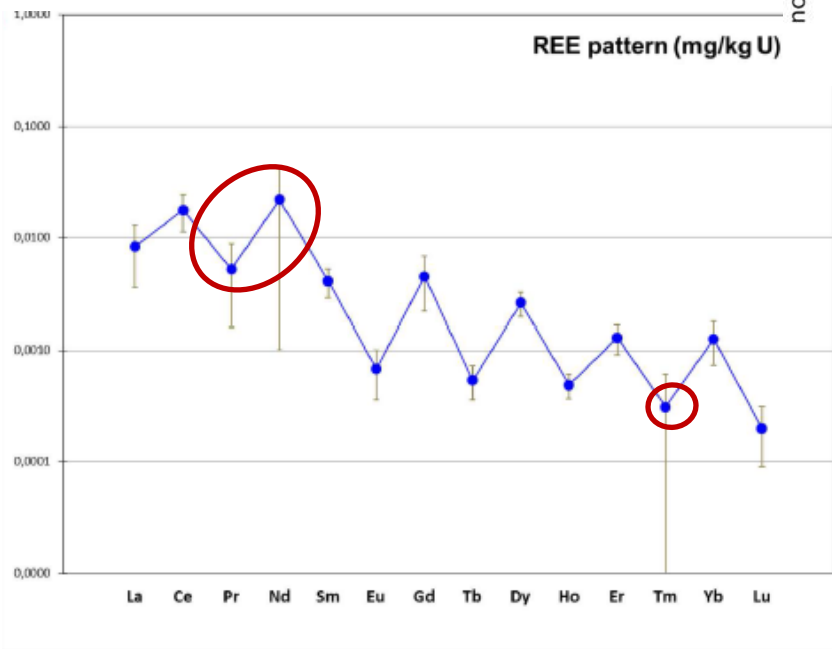
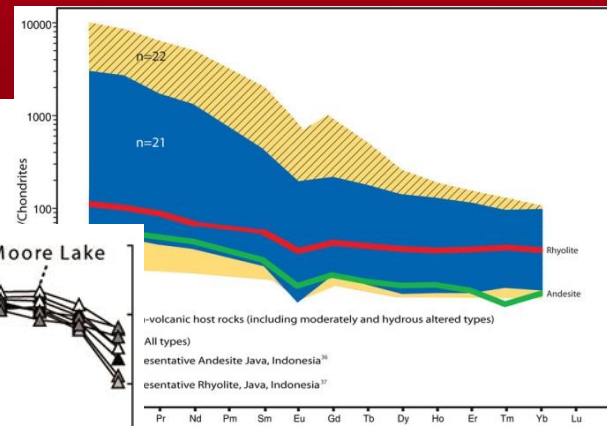
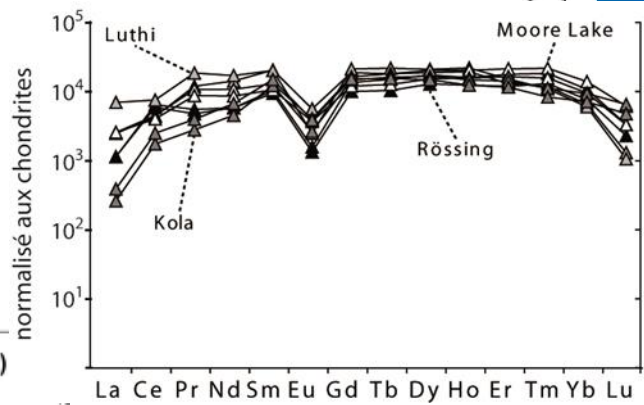
CONCENTRATION OF THE MAJOR IMPURITY CERTIFIED VALUE



riaux de

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

| Éléments 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)

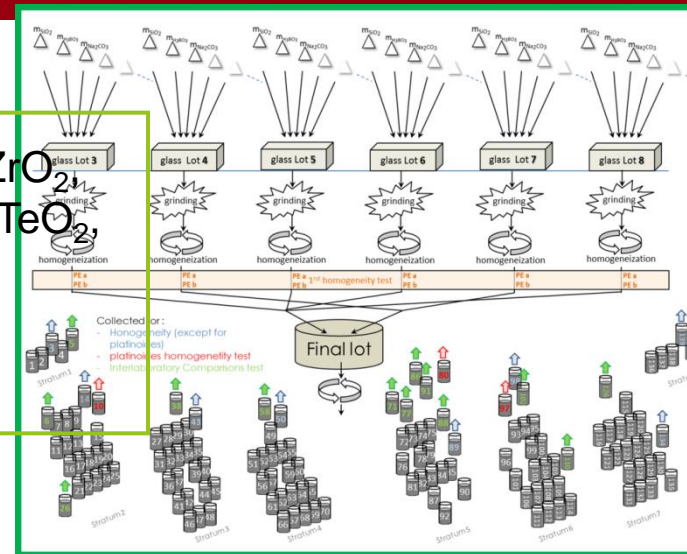
M. Crozet et al. ASTM workshop 2016 (Vienna, June)

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

Precursors: SiO_2 , B_2O_3 , Na_2O , Al_2O_3 , 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)

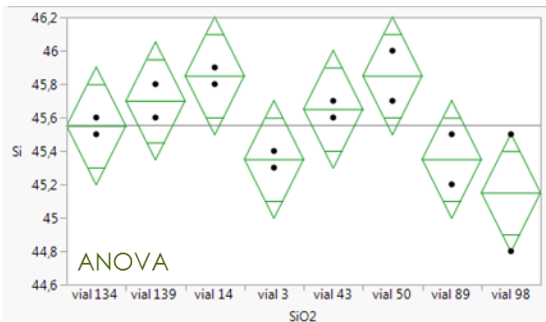
$$x_{CRM} = x_{char} + \delta x_{hom} + \delta x_{stab}$$

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

$$\frac{m_{ox,glass}}{m_{glass}} = \frac{m_B \text{ precursor} - m_B \text{ lost}}{m_{glass}(\text{precursors}) + m_{impurities} - m_{lost \text{ glass}}}$$

F grinding
K $m_B \Rightarrow m_{B2O3}$

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



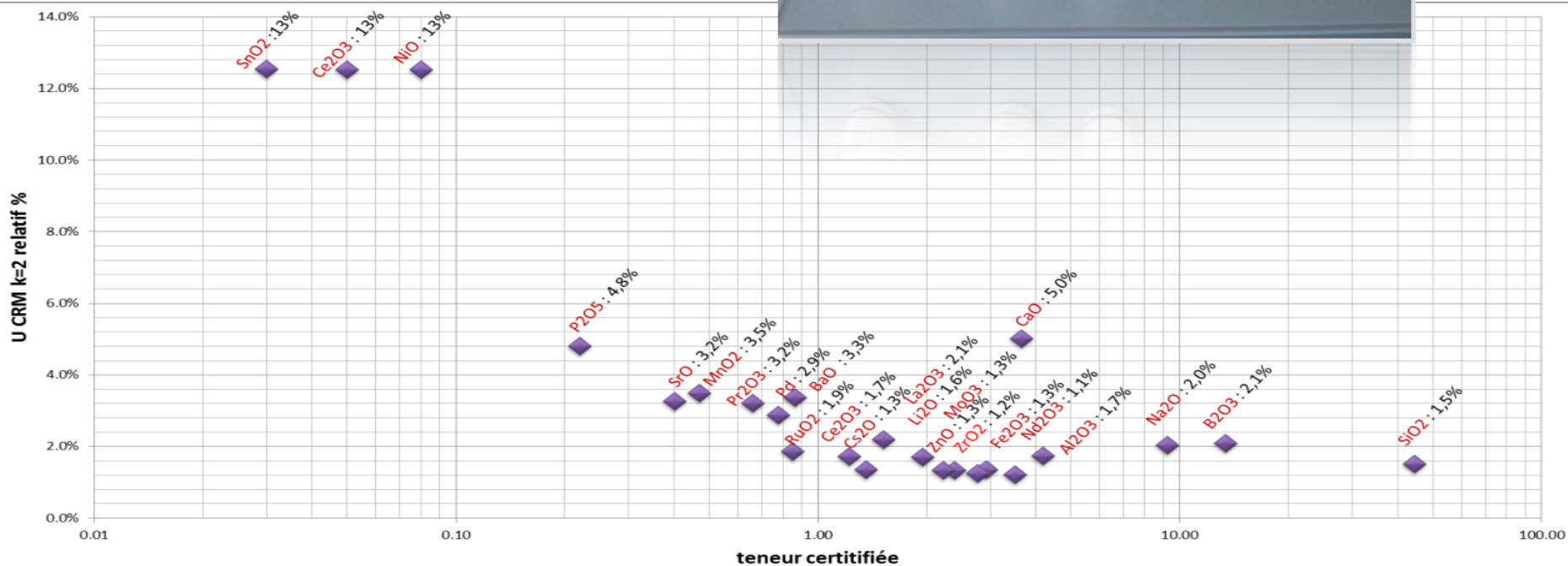
$$u_{hom} = \sqrt{u_{between}^2 + u_{within}^2}$$

- 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



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 ₂ O ₃ | 13,38 | 0,28 | 2,1% |
| | Na ₂ O | 9,23 | 0,19 | 2,0% |
| | CaO | 3,66 | 0,19 | 5,0% |
| | Nd ₂ O ₃ | 3,512 | 0,042 | 1,2% |
| | Fe ₂ O 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 ₂ O | 1,951 | 0,034 | 1,7% |
| | La ₂ O ₃ | 1,521 | 0,034 | 2,2% |
| | Cs ₂ O | 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 ₂ O ₃ | 0,660 | 0,021 | 3,2% |
| | MnO ₂ | 0,470 | 0,016 | 3,5% |
| | SrO | 0,402 | 0,013 | 3,3% |
| | P ₂ O ₅ | 0,220 | 0,011 | 4,8% |
| | NiO | 0,080 | 0,010 | 13% |
| | Cr ₂ O ₃ | 0,0501 | 0,0063 | 13% |
| | SnO ₂ | 0,0300 | 0,0038 | 13% |
| indicative values | | % w/w | U k = 2 % w/w | U rel k = 2 % of % w/w |
| | TeO ₂ | 0,205 | 0,017 | 8,5% |
| | Al ₂ O ₃ | 4,183 | 0,072 | 1,7% |
| | Ce ₂ O ₃ | 1,221 | 0,021 | 1,7% |

CETAMA

U metal Floralties serie

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



IMPURITIES IN U METAL (FLORALIE)

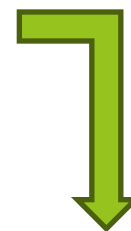
- ❑ Cutting of U metal stored in oil
- ❑ Isotopic composition of natural uranium
- ❑ Devoted to the calibration for SQ impurity analysis:
 - ❑ mainly metal and alkali metal
 - ❑ Different range of concentrations
- ❑ Certification by ILC
 - ❑ ICP AES and molecular or atomic spectrophotometry measurement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



Improvement of the certified composition assessment?

FLORALIE SERIE CERTIFICATE

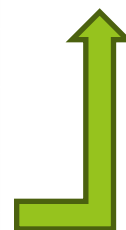
| Ref. SAMPLE | ELEMENTS | | | | | | | | | | | | | |
|-------------|----------|-----|------|----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|
| | Ag | Al | B | Co | Cr | Cu | Fe | Mn | Mo | Ni | Pb | Si | Sn | Zr |
| Bleuet | <0,5 | 40 | ≤0,2 | 4 | 5 | 12 | 70 | 6 | 7 | 24 | 1,5 | 70 | ≤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 |



- **“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*

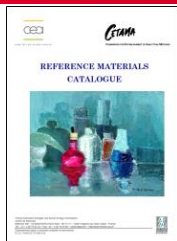


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Direction de l'énergie nucléaire
Département de radiochimie et procédés
Commission d'ETAbblissement des Méthodes
d'Analyse

Nuclear Reference Materials producers



CETAMA

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

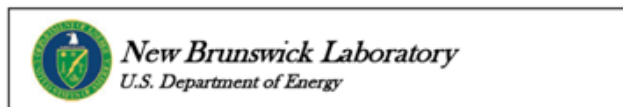
LNHB

<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>

http://www.nbl.doe.gov/html/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>