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## Plutonium mass content accurate determination by controlled potential coulometry at CETAMA

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S. Picart. Plutonium mass content accurate determination by controlled potential coulometry at CETAMA. Plutonium futures 2018, Sep 2018, San Diego, United States. cea-02338711

**HAL Id: cea-02338711**

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Submitted on 24 Feb 2020

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# Plutonium Futures— The Science 2018



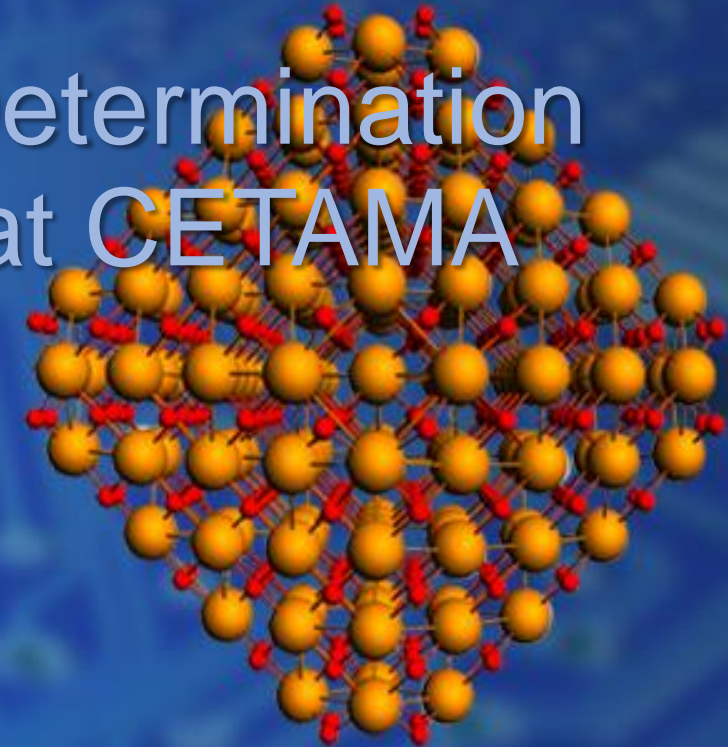
A Topical Conference on Plutonium and Actinides

Plutonium Mass Content Accurate Determination  
by Controlled Potential Coulometry at CETAMA

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# Outlines

- CETAMA: who are we?
- Metrology of plutonium: what for?
- Highly accurate determination of Pu content: what are the most appropriate techniques?
- Controlled potential coulometry of Pu: what performance can we expect?
- Implementation of coulometry: what are the difficulties?
- Uncertainty evaluations: which best approach?
- Perspectives of coulometry: what challenge for this technique?



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# Presentation of CETAMA

- Commission for establishment of analytical methods
- CEA, Nuclear division, located in Marcoule (south of France)
- Commission created in 1961 for diffusion of good practice in analytical science within the nuclear field



- Main activities:
  - Organization of working groups for exchanging information on analytical techniques and methods (15 working groups, 380 members in Europe)
  - Fabrication, certification and marketing of Certified Reference Materials (CRM)
  - Organization and interpretation of interlaboratory comparisons
  - Writing of methods, draft standards and reference documents [1]

- Laboratory of Metrology of Nuclear Materials in Atalante facility (Marcoule)
  - fabrication of CRM
  - development of analytical tools dedicated to actinides metrology



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[1] Validation of method for ICP-AES; from sample to results, EDP sciences, (2017).



# Metrology of Plutonium

- Control of nuclear fissile materials
- Knowledge of quantity and grade of Pu matter
- Guarantee of fissile material accountancy
  - for safety in nuclear facility as regards criticality
  - to prevent diversion of matter (proliferation risk)
- Need of reference material
  - to ensure validation of analytical methods and calibration of equipment
  - to perform reliable and accurate plutonium content determination



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# Best analytical tools for determining Pu mass content with high accuracy



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- ID-TIMS (Isotope Dilution-Thermoionization Mass Spectroscopy):

- with the use of spikes enriched in Pu<sup>239</sup>
- low uncertainties for Pu amount determination : 0.17-0.28% [1,2]

[1] Plutonium Handbook, "Analytical Techniques for the Detection of Plutonium", 2<sup>nd</sup> edition, edited by DL Clarck, DA Geeson, RJ Hanrahan Jr, ANS.

- Redox Titrimetry :

[2] International target values 2010 measurement uncertainties in safeguarding nuclear materials, IAEA STR-368, (2010).

- based on potentiometric method (Waterbury&Metz [3] or Mac Donald&Savage [4])
- level of uncertainty: 0.21-0.28% [2]

[3] G. R. Waterbury and C. F. Metz, Anal. Chem. 31,1144,(1959).

[4] A. Mac Donald and D. J. Savage, IAEA-SM-231/52 (1978).

- Coulometry

- based on controlled potential coulometry [5,6,7]
- lowest level of uncertainty: 0.10-0.14% [2,7,8,9]

[5] F. A. Scott, R. M. Peekema, Second U.N. International conference on the Peaceful Uses of Atomic Energy, A/CONF.15/P/914, p. 573, (1958)

[6] W. D. Shults,, Talanta, vol. 10, p. 833, (1963).

[7] Holland, M. K., Weiss, J. R., and Pietri, C. E., proceedings of the 3rd ESARDA Symposium, Karlsruhe, Germany, May 6-8, 1981.

[8] Ruas A., Leguay N., Sueur R., Vedel N., Dalier V., Moisy Ph., Radiochim. Acta, 102(8) : 691-699 (2014).

[9] ISO 12183, Controlled-potential coulometry assay of plutonium, (2018).



# Controlled potential coulometry of Pu

- Principle:
  - based on the measurement of quantity of electricity during an electrochemical reaction
  - on the reversible reaction involving Pu(IV)/Pu(III) redox pair:



- Faraday Law:
  - relates the quantity of electricity  $Q$  to the amount of Pu,  $m_{\text{Pu}}$ ,

$$m_{\text{Pu}} = \frac{Q}{nF} M_{\text{Pu}}$$

F: Faraday constant,  $F=96485.34 \text{ C/mol}$

M: molar mass of Pu,  $M=239.076 \text{ g/mol}$

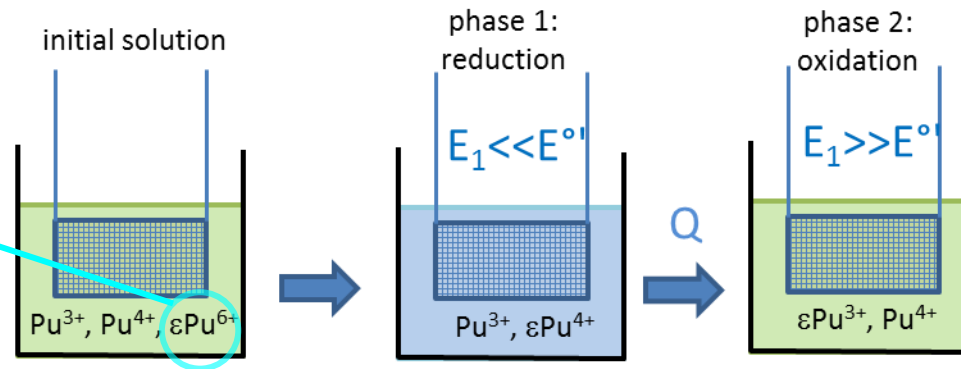
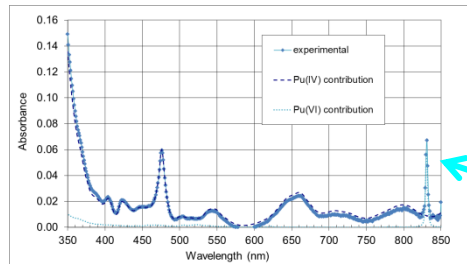
n: exchanged electron = 1

- within a range of potentials with no competing reactions
- Primary measurement:
  - calibration against physical standards of high level of accuracy
    - time (s) and electric current (A)
  - absolute method



# Protocol of measurement

- Phase 1: preliminary reduction to the Pu<sup>3+</sup> oxidation state
- Phase 2: oxidation of Pu<sup>3+</sup> to Pu<sup>4+</sup>



$E^{\circ}$  = formal potential of Pu<sup>4+</sup>/Pu<sup>3+</sup> redox pair

$$E^{\circ} \pm 230 \text{ mV}$$

$\epsilon \text{ Pu}^{4+}$  = fraction of Pu<sup>4+</sup> not reduced at first stage  
 $\epsilon \text{ Pu}^{3+}$  = fraction Pu<sup>3+</sup> not oxidized at second stage

Nernst equation:  $E_1 = E^{\circ'} + \frac{RT}{nF} \ln \left( \frac{\epsilon \text{Pu}^{4+}}{\text{Pu}^{3+}} \right)$      $E_2 = E^{\circ'} + \frac{RT}{nF} \ln \left( \frac{\text{Pu}^{4+}}{\epsilon \text{Pu}^{3+}} \right)$

- Calculation of the fraction of plutonium electrolysed,  $f$  [1]:

- $f$  = correction factor <1:

- depends on  $E^{\circ'}$ ,  $E_1$  and  $E_2$
- calculated from the Nernst Equation describing equilibrium after phase 1 and 2

[1] Holland, M. K., Weiss, J. R., and Pietri, Anal. Chem., 50, 236, (1978).

$$m_{\text{Pu}} = \frac{Q}{nFf} M_{\text{Pu}}$$

$$f = \frac{\exp\left(\frac{n \cdot F \cdot (E_2 - E^{\circ'})}{R \cdot T}\right)}{1 + \exp\left(\frac{n \cdot F \cdot (E_2 - E^{\circ'})}{R \cdot T}\right)} - \frac{\exp\left(\frac{n \cdot F \cdot (E_1 - E^{\circ'})}{R \cdot T}\right)}{1 + \exp\left(\frac{n \cdot F \cdot (E_1 - E^{\circ'})}{R \cdot T}\right)}$$





# Implementation of coulometry

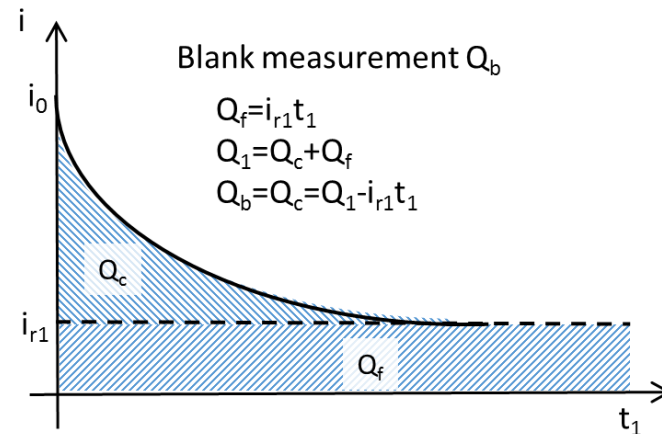
- Step 0: Dilution of sample (optional)
  - with dilution factor  $DF = m_2/m_1$

$$m_{Pu} = \frac{Q}{nFf} M_{Pu} DF$$

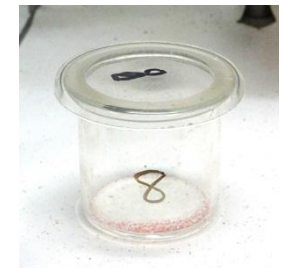
- Step 1: weighing of sample and fuming to dryness
  - addition of  $H_2O_2$  to reduce Pu(VI) to Pu(IV) [1]
  - addition of  $H_2SO_4$  to stabilize Pu(IV) in the form of crystals of  $Pu(SO_4)_2$

- Step 2: blank measurement  $Q_b$ 
  - $HNO_3$  0.9M + sulfamic acid (to prevent nitrous acid interference)
  - same sequence as coulometric titration  $E_1$  (reduction),  $E_2$  (oxidation)
  - measurement of total charge  $Q_1$ , sum of the charge attributed to double layer capacitive current  $Q_c$  and to reversible reactions in the electrolyte  $Q_f$  (residual current  $i_{r1}$ )
  - Expression of net blank charge  $Q_b$  :

$$Q_b = Q_1 - i_{r1} t_1$$



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# Coulometric titration of Pu

- Step 3 : Pu measurement

- dissolution of  $\text{Pu}(\text{SO}_4)_2$  with blank
- reduction/oxidation sequence:  $E_1, E_2$
- measurement of  $Q_2$  during oxidation step, residual current  $i_{r2}$  and duration  $t_2$

- Expression of results :

- net charge  $Q_s$  of Pu titration :

$$Q_s = Q_2 - i_{r2}t_2$$

- effective charge  $Q$  after correction of the blank

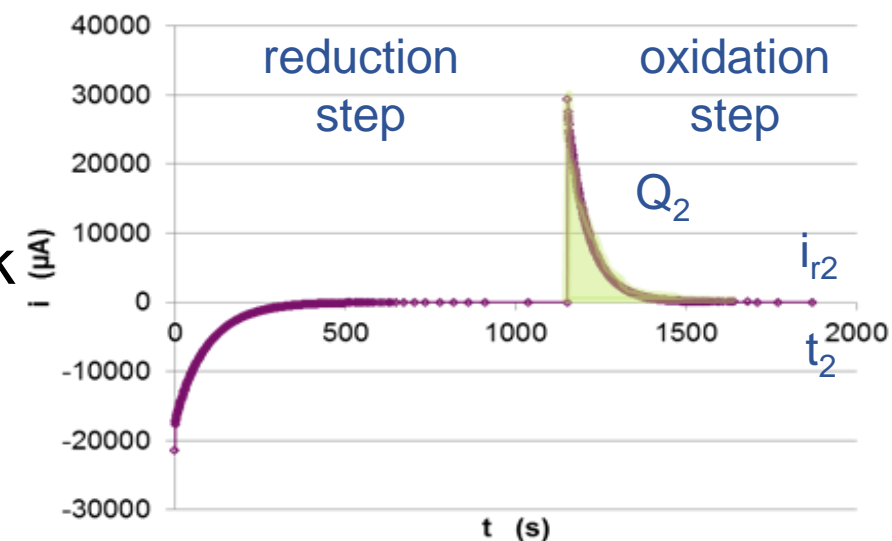
$$Q = Q_s - Q_b$$

- plutonium mass

$$m_{\text{Pu}} = \frac{Q}{nFf} M_{\text{Pu}} = \frac{(Q_2 - Q_1 - i_{r2}t_2 + i_{r1}t_1)}{nFf} M_{\text{Pu}}$$

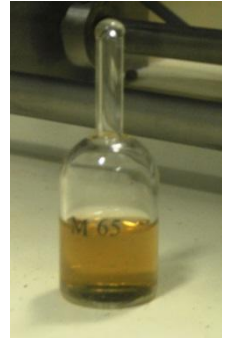


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# EQRAIN Pu Standard characterization

- Titration of one vial of EQRAIN Pu 14 standard
- Measurement of bias and fidelity:
  - 5 replicates
  - expression of relative difference  $D(\%)$  :  $D(\%) = \frac{(m_{exp} - m_{ref})}{m_{ref}}$
  - calculation of standard deviation for Pu concentration



## • Results

Exp.	m Pu ref. (mg)	m Pu coulo. (mg)	D (%)	S [Pu] (%)
LF04	6.2932	6.2952	+0.03	0.064
LF 05	6.2832	6.2785	-0.08	
LF 06	6.3168	6.3191	+0.04	
LF 07	6.3011	6.2952	-0.09	
LF 08	6.2983	6.2936	-0.07	



# EQRAIN Pu Standard characterization



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- Trueness analysis:

- expression of normalized deviation  $E_n$ :

$$E_n = \frac{|X_{mean} - X_{ref}|}{\sqrt{u_{(exp)}^2 + u_{(ref)}^2}}$$

$X_{mean}$ , concentration mean value of experimental replicates;  
 $X_{ref}$ , concentration reference value;  
 $u_{(exp)}$ , standard uncertainty on experimental concentration;  
 $u_{(ref)}$ , standard uncertainty on the reference concentration.

- critical values:  $E_n \geq 2$ , significant bias;  $E_n < 2$ , non significant bias.

$$E_n = 0.4 < 2$$

$$\frac{|X_{mean} - X_{ref}|}{X_{ref}} = 0.035\%$$
$$u_r(\text{ref}) = 0.060\%$$
$$u_r(\text{exp}) = 0.064\%$$

→ no bias observed for the series of results (5 replicates)





# EQRAIN Pu Standard characterization

- Fidelity analysis:

- ① First approach: application of the law of the propagation of variances
    - mathematical expression of Pu concentration in g/kg:

$$[Pu] = \frac{Q}{nFf} \frac{M_{Pu}}{m_{sample}} DF$$

- hypothesis: uncertainties on  $M_{Pu}$ ,  $F$  and  $f$  neglected.
  - combined uncertainty :

$$u_r^2([Pu]) = u_r^2(Q) + u_r^2(DF) + u_r^2(m_{sample})$$

normal distribution for Q

$$u_r(Q) = \sqrt{2} * \frac{u(Q_b)}{Q} = \sqrt{2} * \frac{0,7}{2500} = 0.040\%$$

uniform distribution for weighing

$$u_r(m_{sample}) = \frac{\sqrt{2}}{\sqrt{3}} * \frac{u(m)}{m} = \frac{\sqrt{2}}{\sqrt{3}} * \frac{1}{4500} = 0.018\%$$

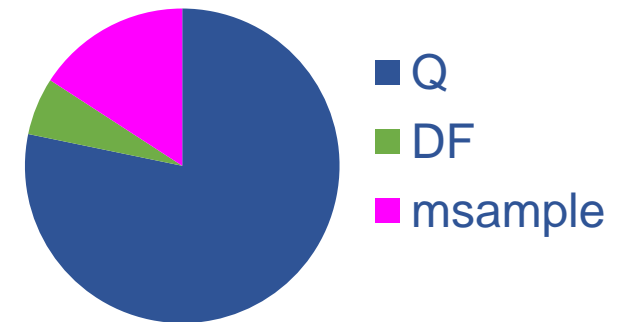
$$u_r(DF) = \frac{\sqrt{2}}{\sqrt{3}} * \sqrt{\left(\frac{u(m)}{m_1}\right)^2 + \left(\frac{u(m)}{m_2}\right)^2} = \frac{\sqrt{2}}{\sqrt{3}} * \sqrt{\left(\frac{2}{15000}\right)^2 + \left(\frac{2}{50000}\right)^2} = 0.011\%$$

$$u_r([Pu]) = \sqrt{0.040^2 + 0.018^2 + 0.011^2} = 0.045\%$$

$$U_r([Pu]) = 2 \times 0.045\% = 0.090\%$$



## Uncertainty Budget



→ major contribution = Q measurement



# EQRAIN Pu Standard characterization

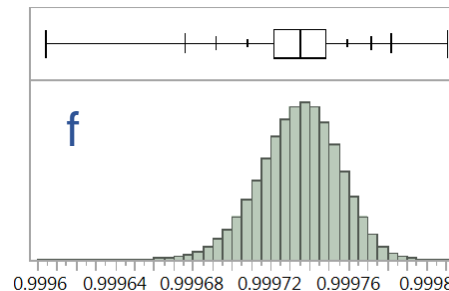
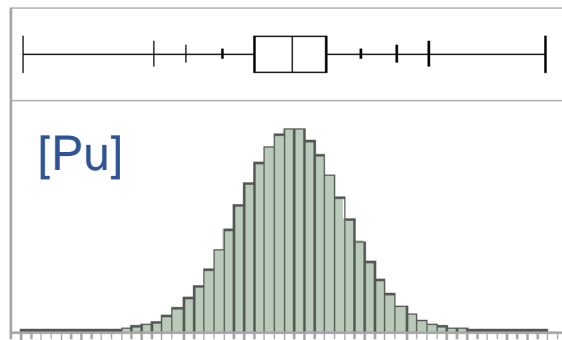


- Fidelity analysis:

- ② Second approach: Monte Carlo Method (MCM)
  - calculation based on propagation of probability distribution
  - pertinent when [1]:
    - the measurand mathematical model is complicated (non linear expressions)
    - the uncertainties of the input are not of the same order of magnitude
  - appropriate to estimate uncertainties for  $f$  and  $m_{Pu}$  or  $[Pu]$ ;
  - sampling of a great number  $N$  of values of input quantities at random and according to their probability distribution ( $N \approx 10^6$ ) (JMP®13 SAS institute Inc.)

$$[Pu] = \frac{Q_s - Q_b}{nFf} \frac{M_{Pu}}{m_{sample}} DF$$

$$[Pu] = f(Q_2, Q_1, t_2, t_1, i_{r2}, i_{r1}, F, E_2, E_1, E', R, T, M_{Pu}, m_{sample}, m_2, m_1)$$



$$u_r([Pu]) = 0.047\%$$

$$* CI([Pu])_{95\%} = 0.093\%$$

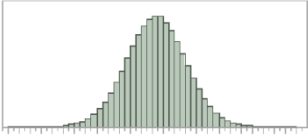
\*CI coverage interval

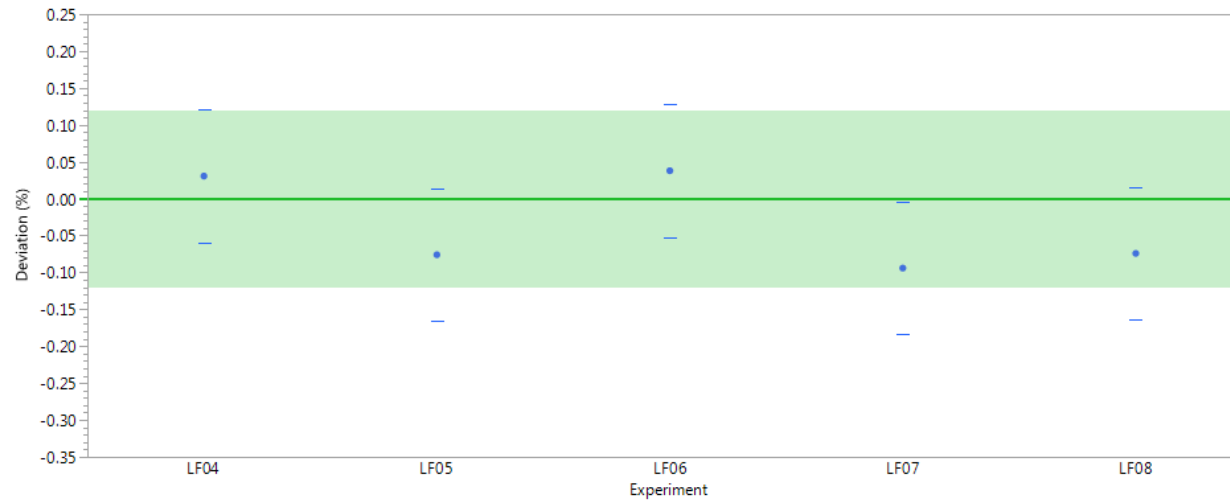


[1] M. Crozet, C. Rivier, *Journal of Radioanalytical and Nuclear Chemistry* **302**, 103-115 (2014)

# Uncertainty evaluation

- Coherence of Classical and Monte Carlo Method approach

	GUM approach		Monte Carlo Method approach		
	$u_r$ ([Pu]) GUM	$U_r$ ([Pu]) GUM $k = 2$	$u_r$ ([Pu]) MCM	$Cl_r^*$ ( $m_{Pu}$ ) MCM 95%	probability density function of $m_{Pu}$
$m_{Pu}$	0.045%	0.090%	0.047%	0.094%	



- coulometry = accurate method for determining Pu amount in solution
- performance of Coulometry at LAMMAN in accordance with ITV ( $u(r)=0.1\%$  to be compared with  $u_r([Pu])=0.045-0.047\%$ )



# Conclusion and perspectives

- Coulometry
  - robust technique for determining Pu amount
  - with high accuracy
  - well adapted for metrology laboratories working on actinides
- Challenge for our lab
  - coulometric titration of Pu in presence of uranium
  - coulometric titration of uranium
  - upgrading of our equipment



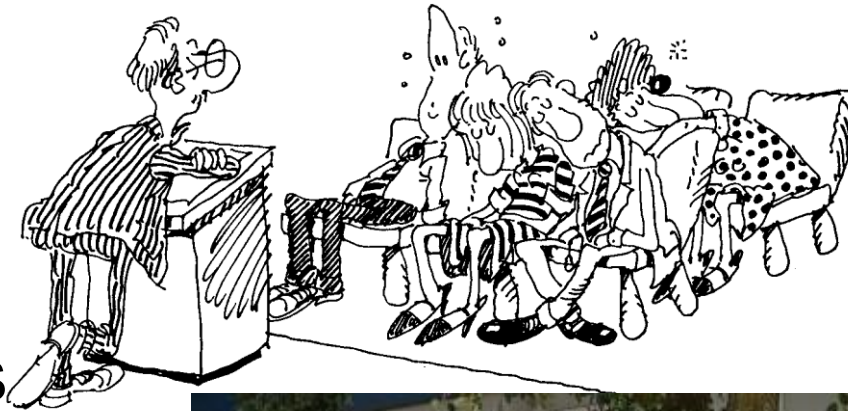
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# Thanks

- for your kind attention
- to my CETAMA colleagues
  - Marielle CROZET (1)
  - Danièle ROUDIL (2)
  - Véronique BELIN (3)
  - Caroline BERTORELLO (4)
- to our trainees
  - Ygor DAVRAIN (5)
  - Louis FAURE (6)



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