DE LA RECHERCHE À L'INDUSTRIE

# IMPROVEMENT OF DIFFERENT ANALYTICAL TECHNIQUES TO CHARACTERISE RADIONUCLIDES DIFFICULT TO MEASURE AND TOXICS IN NUCLEAR WASTE AT LASE LABORATORY

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# CONTEXT OF THE STUDIES

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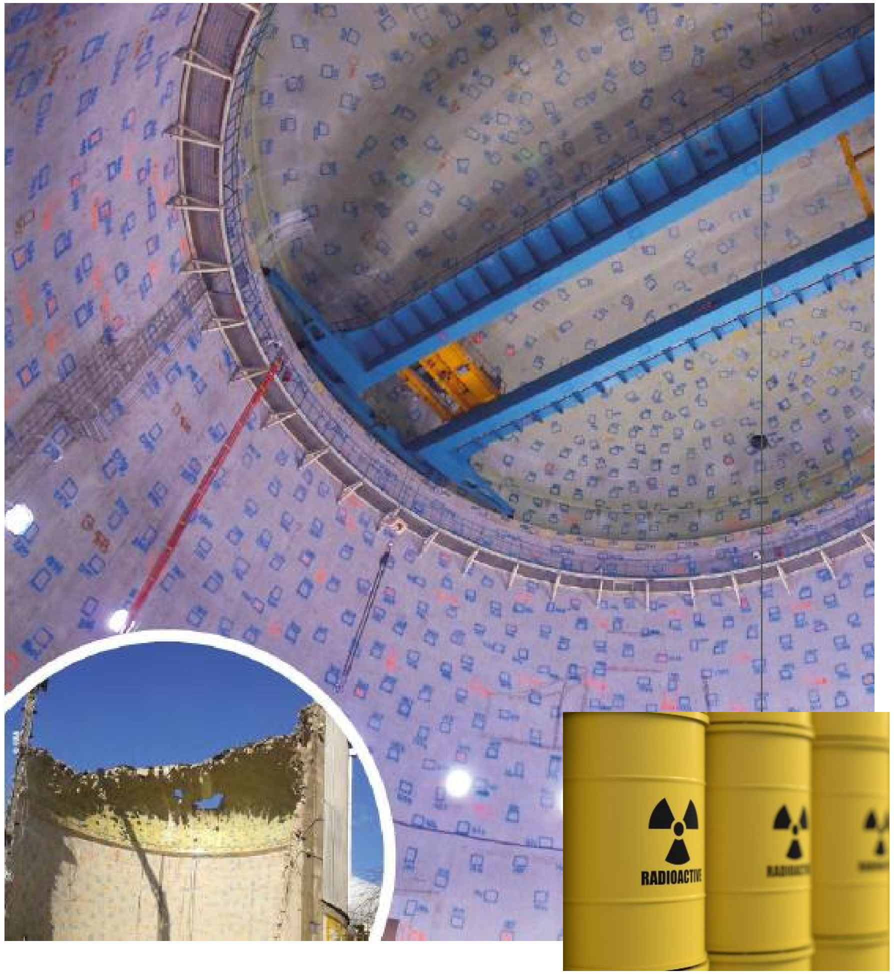
# CONTEXT OF THE STUDIES

## Decommissioning and dismantling of nuclear facilities

- The decommissioning and dismantling (D&D) of nuclear facilities is a global challenge to be addressed in the future, particularly in France.
- In 2015, around 150 nuclear power plants were stopped or were under D&D operations. By 2050, more than half of the world nuclear capacity is scheduled to be shut down for dismantling.



ð **High volumes of radioactive wastes are and will be produced.**

ð **Their management and their characterisation is a key issue to be studied.**

# CONTEXT OF THE STUDIES

## Characterisations of low and intermediate nuclear wastes in France

- In France, the National Radioactive Waste Management Agency **ANDRA** requests **chemical and radiochemical characterisations of nuclear wastes**.
  - **Chemical characterisations**: 11 toxic elements, 21 complexing compounds (organic or inorganic substances) to be declared
  - **Radiochemical characterisations**: 143 radionuclides to be declared

| Chemical compound | Declaration threshold ($\mu g.g^{-1}$) for ANDRA surface disposal |
|---|---|
| Pb | 100 |
| Ni | 20 |
| As | 10 |
| Hg | 1 |
| Chloride | No threshold |
| Nitrate | No threshold |
| **EDTA, DTPA** | **No threshold** |
| Citrate | No threshold |

| Radionuclide | Declaration threshold ($Bq.g^{-1}$) - Acceptance limit ($Bq.g^{-1}$) for ANDRA surface disposal | |
|---|---|---|
| $^{3}H$ | $10 \rightarrow 2 \times 10^{5}$ | |
| $^{60}Co$ | $10 \rightarrow 1 \times 10^{8}$ | Half-life |
| $^{137}Cs$ | $10 \rightarrow 3 \times 10^{5}$ | ≤ 31 years |
| **$^{55}Fe$** | **$10 \rightarrow 6 \times 10^{9}$** | |
| $^{14}C$ | $10 \rightarrow 9 \times 10^{4}$ | Half-life |
| $^{36}Cl$ | $10^{-2} \rightarrow 5$ | > 31 years |
| $^{63}Ni$ | $1 \rightarrow 3 \times 10^{6}$ | |
| Σ alpha-emitters | $4 \times 10^{3}$ | |

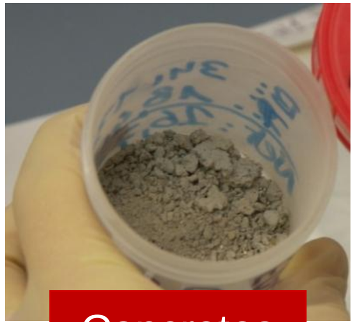
# CONTEXT OF THE STUDIES

## Characterisations of nuclear wastes

- High variety and complexity of matrices

Graphites

Metals



Concretes

Ion exchange resins embedded or not

Muds

Sludges

**ð For analytical laboratories (such as LASE at CEA Saclay), there is a challenge to develop robust and selective methods to characterise all the various matrices encountered in radwastes.**

# NEW DEVELOPMENTS FOR RADIOCHEMICAL CHARACTERISATIONS OF NUCLEAR WASTE AT LASE LABORATORY

## In situ technique: MAUD project

- Before any analytical measurement in laboratories, a sampling process has to be implemented. In this framework, in situ techniques are of prime interest to optimize the sampling step, to localize the radioactivity and to find hot spots.

- As part of a project called “MAUD”, the LASE laboratory has developed an industrial device with ARL-Laumonier company for dismantling applications so as to provide:
  - In situ measurements on solids
  - Real time measurements
  - Mappings of radionuclides
  - Quantitative measurements (a, b, g)
  - Sensitive detection for a and b emitters

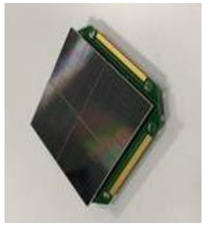
INVESTIR L'AVENIR

ANDRA
Agence nationale pour la gestion des déchets radioactifs

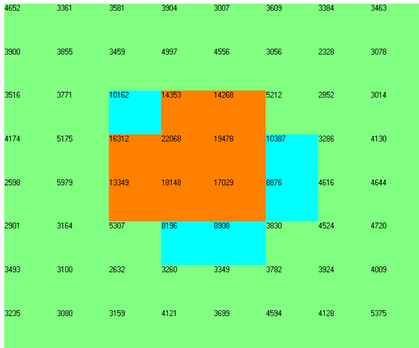
Laumonier
INNOVATION & INDUSTRY

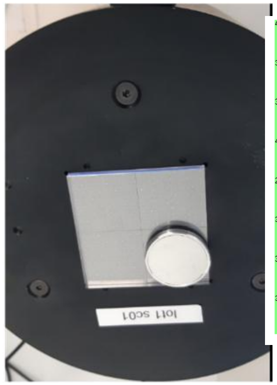
## In situ technique: MAUD project

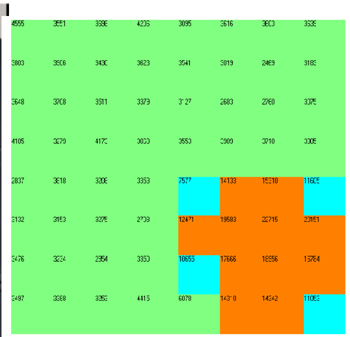
- The industrial device is composed of:
  - A cheap solid scintillator



  - A sensitive detector based on Silicon PhotoMultipliers (SiPM)
    - Use of a 64 SiPM array to ensure a large mapping





*Images obtained with a Pu-239 sealed source (~ 150 Bq)*

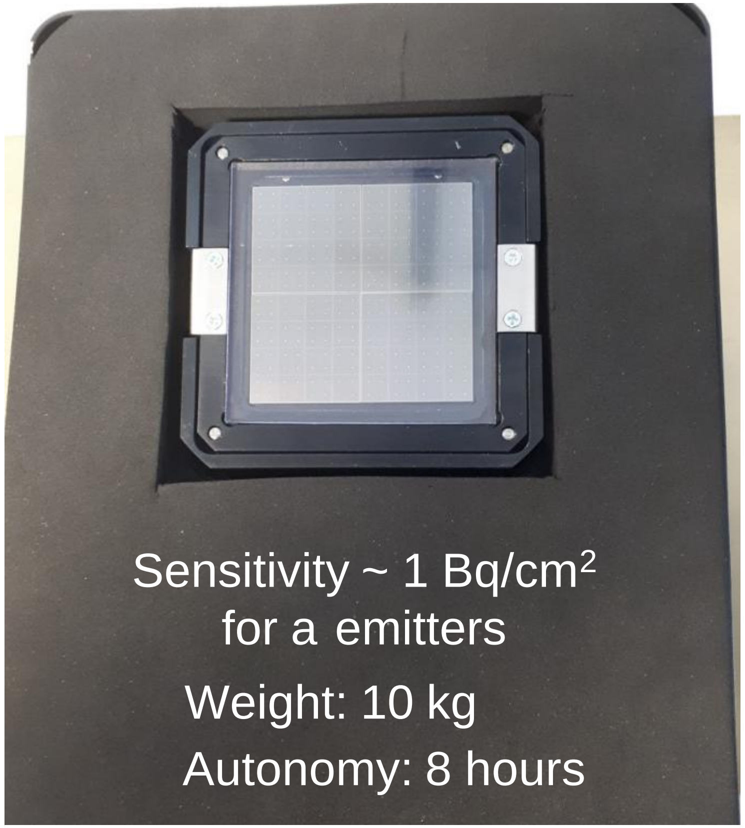
## In situ technique: MAUD project

- In site measurements with the system planed before the end of 2019

Laumonier INNOVATION & INDUSTRY

https://www.at-laumonier.fr/

https://international.andra.fr/sites/international/files/2019-08/Fiche%20projet%20MAUD%20VF-UK.pdf



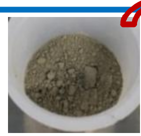

& S. Billon et al., JNRC, Vol. 320 (3), 643-654 (2019)

# RADIOCHEMICAL CHARACTERISATION

## Gamma spectrometry on solids

- After the arrival of samples in analytical laboratories, aliquoting has to be performed. Gamma spectrometry directly applied to solids is of prime interest to verify the homogeneity of the samples and the representativity of test portions and also to increase the sensitivity in comparison to gamma spectrometry applied to digested samples.

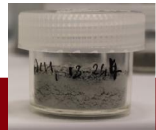
Concrete



Acid digestion with ~ 0.3 g
Gamma spectrometry in the classical setting

Powder ~ 30 g
Gamma spectrometry in the « LABSOCS » setting

| RN | Measured activity (Bq/g) | Detection limit (Bq/g) |
|---|---|---|
| Co-60 | | ≤ 1.3 |
| Sb-125 | | ≤ 2.0 |
| Cs-134 | | ≤ 0.8 |
| Cs-137 | 1.2 | ≤ 1.0 |
| Am-241 | | ≤ 0.6 |



| RN | Measured activity (Bq/g) | Detection limit (Bq/g) | Gain in detection limit |
|---|---|---|---|
| Co-60 | 0.7 | ≤ 0.1 | 14 |
| Sb-125 | | ≤ 0.04 | 50 |
| Cs-134 | | ≤ 0.02 | 40 |
| Cs-137 | 1.1 | ≤ 0.1 | 11 |
| Am-241 | 0.8 | ≤ 0.05 | 11 |

**ð Increase in sensitivity: between 10-fold and 50-fold factors**

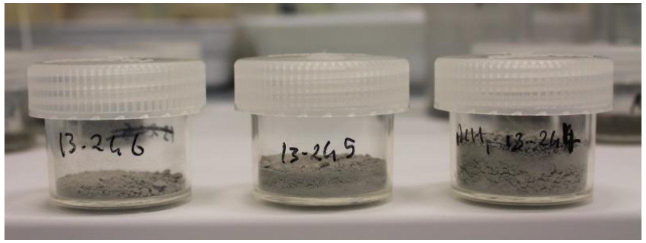
# RADIOCHEMICAL CHARACTERISATION

## Gamma spectrometry on solids

- Validation step of « LABSOCS » modelling by applying the experimental design described in the French NF T90-210 validation standard
- Necessity to evaluate the accuracy but a few commercialised standards
- Preparation of 2 home-made concretes to obtain standards with different levels of radioactivity

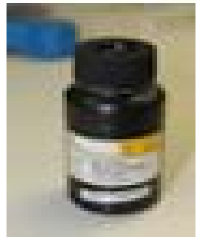
concrete mortar

non-radioactive simulated sludge

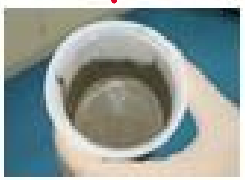



Mixing of both concretes

concrete mortar

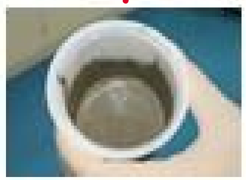


mixed gamma standard



wet concrete 1

Drying and crushing of both concretes

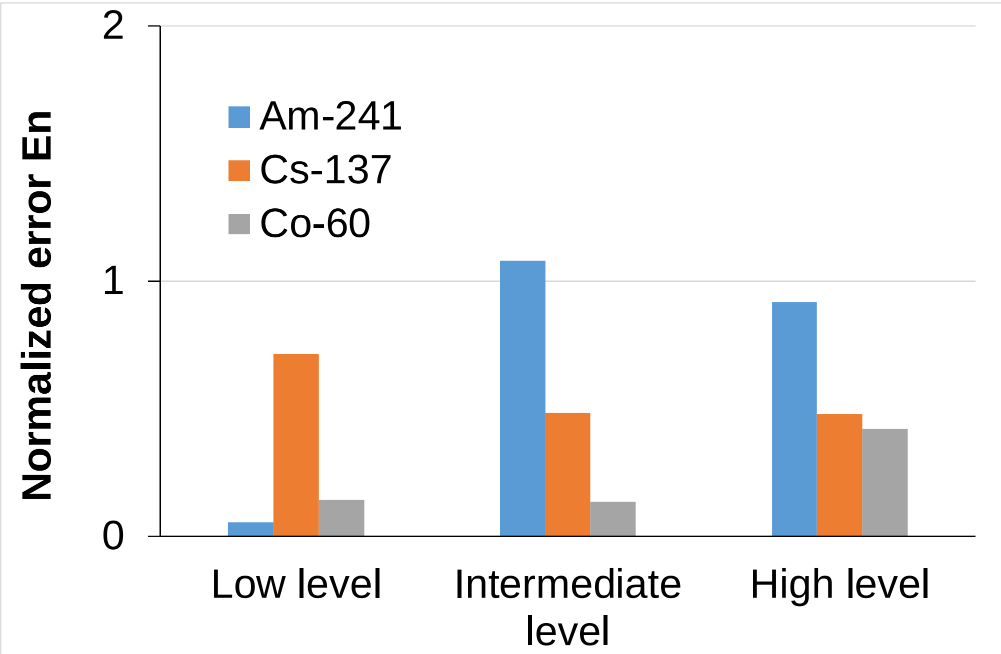


wet concrete 2

# RADIOCHEMICAL CHARACTERISATION

## Gamma spectrometry on solids

- Comparison of the results obtained with gamma spectrometry on solids concretes and gamma spectrometry on digested concretes by calculating a normalized error $E_n$




Home-made concrete standards

Acid digestion and classical gamma setting

Direct « LABSOCS » gamma setting

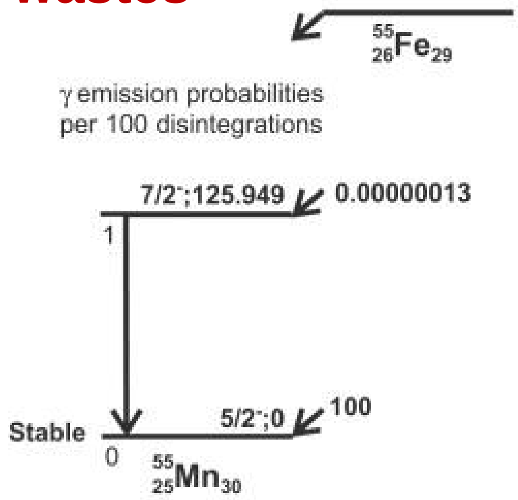
Whatever the radionuclide and the radioactivity level : │En│< 2

ð The « LABSOCS » modelling is validated for concretes

## Determination of $^{55}Fe$ in radioactive wastes

- $^{55}Fe$ is a short-lived radionuclide (half-life of 2.7 years).

- $^{55}Fe$ decays by electron capture to $^{55}Mn$ with emission of Auger electrons and X-rays (5.89, 5.90 and 6.51 keV).




- $^{55}Fe$ is produced from neutron activation of stable Fe.

- $^{55}Fe$ can be present in steels, but also in nuclear graphites, ion exchange resins, effluents and sludges.

- As the energies of Auger electrons and X-rays emitted from $^{55}Fe$ are very low, $^{55}Fe$ needs to be isolated from the matrix elements and the interfering radionuclides ($^{60}Co$, $^{63}Ni$) through radiochemical procedures prior to analysis, often liquid scintillation counting (LSC).

# Determination of $^{55}Fe$ in radioactive wastes in France

- Literature review: most of the radiochemical procedures are based on the complexing agent of **cupferron** or **MIBK** (Methyl IsoButyl Ketone).

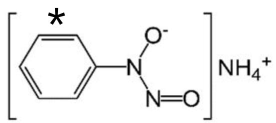
Digestion of the sample

Addition of carriers: Fe, Ni and Co

Addition of ammonia

Liquid chromatography on anion-exchange resin

**Liquid-liquid extraction with chloroform and cupferron***



**ICP, AAS:** stable Fe measurement
ð Radiochemical yield

**Liquid scintillation counting (LSC):** $^{55}Fe$ measurement
ð Massic activity, $Bq.g^{-1}$

**2 procedures depending on Fe quantity**

French NF M60-322 Standard (2005)

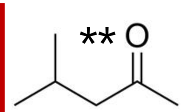
Fe < 700 mg/L

Digestion of the sample

Addition of carriers: Fe, Ni and Co

Evaporation and dissolution of residue in HCl 6M

**Liquid-liquid extraction with MIBK****



**ICP, AAS:** stable Fe measurement
ð Radiochemical yield

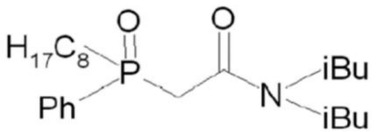
**Liquid scintillation counting (LSC):** $^{55}Fe$ measurement
ð Massic activity, $Bq.g^{-1}$

## Determination of $^{55}$Fe in radioactive wastes in France

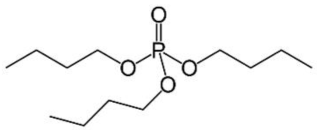
- **Aim:** to develop an alternative procedure to measure $^{55}$Fe in radwastes without toxic REACH compounds (chloroform)

- Literature review: implementation of **TRU® resin** (impregnated with CMPO dissolved in TBP)

CMPO

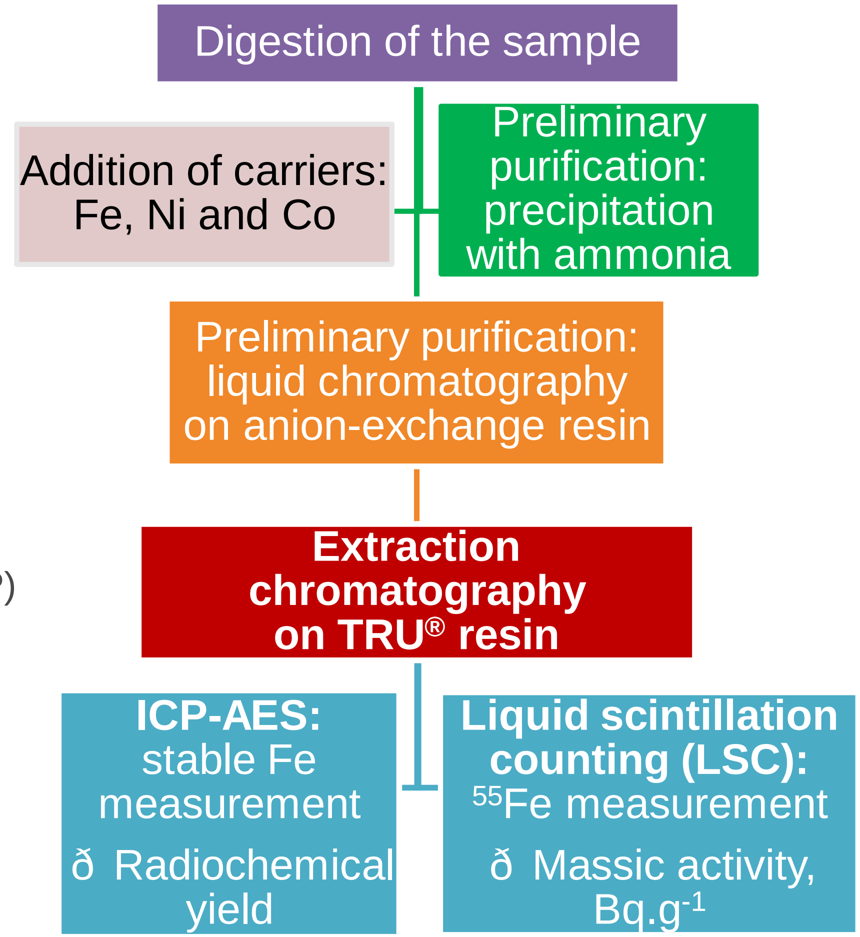



TBP




octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO) dissolved in tri-n-butyl phosphate (TBP)

- Comparisons between the reference LASE procedure and the TRU-based procedure on different samples



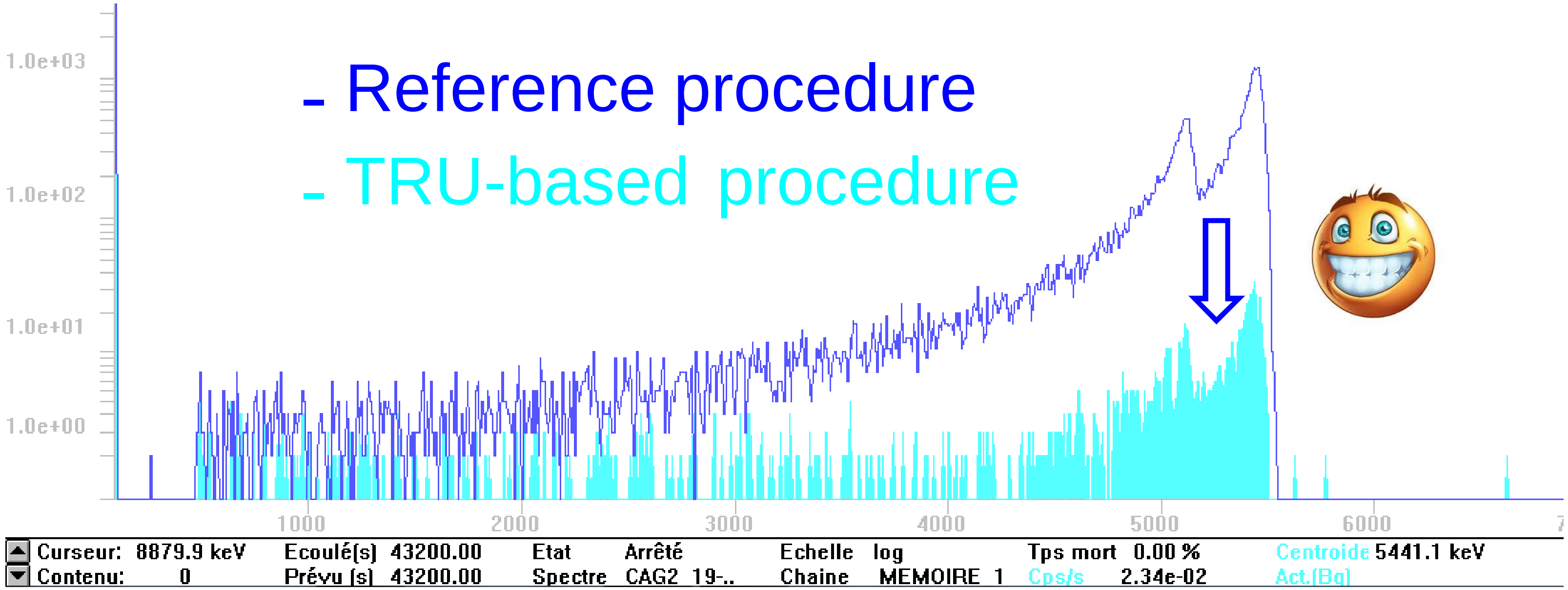
# Determination of $^{55}Fe$ in radioactive wastes in France

| Matrix | Massic $^{55}Fe$ activity (Bq/g) with reference procedure | Yield (%) with reference procedure | Massic $^{55}Fe$ activity (Bq/g) with TRU-based procedure | Yield (%) with TRU-based procedure | Difference in % | Normalized error $E_n$ |
|---|---|---|---|---|---|---|
| Ion exchange resin | 2.6E+04 | 74 | 2.5E+04 | 86 | - 5 | -0.74 |
| Ion exchange resin embedded in polymer | 3.5E+03 | 73 | 3.7E+03 | 88 | 4 | 0.42 |
| Muds embedded in concrete | 4.3E+03 | 65 | 4.6E+03 | 57 | 8 | 0.95 |
| Steel | 3.8E+03 | 23 | 3.7E+03 | 80 | - 2 | -0.19 |
| Aluminium | 3.7E+05 | 72 | 3.6E+05 | 82 | -2 | -0.19 |
| Sludge | 3.4E+01 | 70 | 1.0E+01 | 81 | **- 69** | **-3.3** |

**ð No significant difference except for a sludge sample containing high amounts of alpha emitters**

## Determination of $^{55}Fe$ in radioactive wastes in France

- Alpha spectrometry applied to purified $^{55}Fe$ fractions with both LASE procedures




ð **Improvement of the decontamination factors towards alpha emitters (ex: up to a 30-fold factor for Pu) with TRU-based procedure**

ð **Validation of the new procedure with interlaboratory comparison**

ð **Revision of the French NF M60-322 Standard within the French standard authority**

# NEW DEVELOPMENTS FOR CHEMICAL CHARACTERISATIONS OF NUCLEAR WASTE AT LASE LABORATORY

DE LA RECHERCHE À L'INDUSTRIE

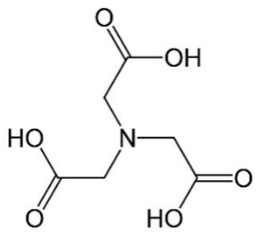
# CHEMICAL CHARACTERISATION

## Determination of complexing agents in French radioactive wastes

- Complexing agents such as polyhydroxycarboxylic acids can be present in nuclear effluents and wastes due to their use in **decontamination processes**.

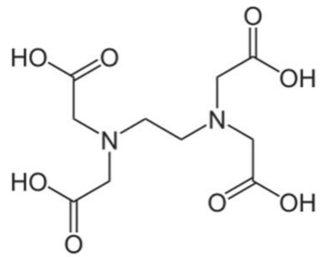
- Those compounds can form stable complexes with actinides and toxic metals and may favour their migration in the environment ð **risk for the safety of waste repositories**

- ANDRA requires the determination of 4 organic compounds in priority:



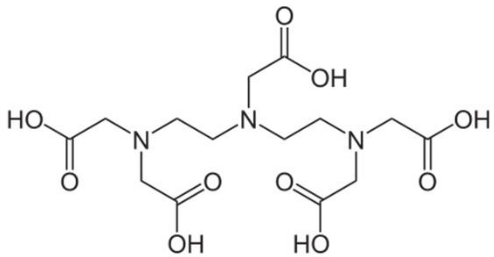
NTA

NitriloTriacetic Acid



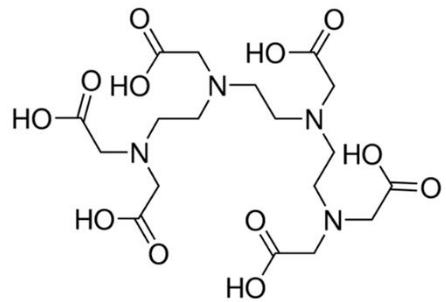
EDTA

EthyleneDiamineTetraacetic Acid



DTPA

DiethyleneTriaminePentaacetic Acid



TTHA

Triethylenetetramine-N,N,N',N'',N''',N'''-hexaacetic acid

# CHEMICAL CHARACTERISATION

## Determination of EDTA, DTPA, NTA, TTHA by HPLC-MS

**Ion-pair chromatography with TBA in Water/MeOH eluent**

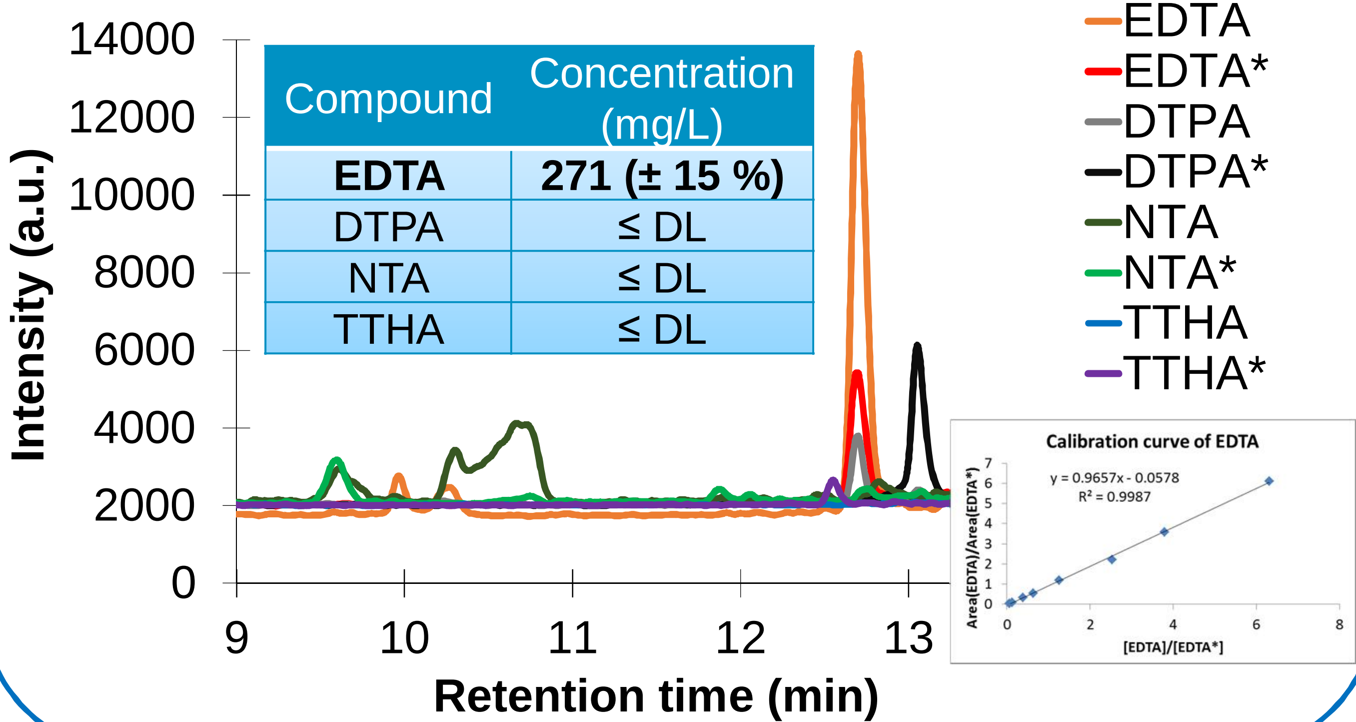
**φA** : $H_2O$ 100%, 0.3 mM MeOH, 1.2 mM TBA

**φB** : $H_2O$/MeOH (10/90 v/v), 1.05 mM MeOH, 1.2 mM TBA

- Sample spiked with internal standards
- Filtration
- Addition of $NH_3$ (pH = 9-10)
  Precipitation of several metal hydroxides
- Centrifugation
  Collection of supernatant
- Addition of $Ni^{2+}$ in excess
- HPLC-MS analysis

Luna Phenyl Hexyl
(150 x 2.00 mm ; 3 µm)

### Real radioactive sludge




| Compound | Concentration (mg/L) |
|---|---|
| **EDTA** | **271 (± 15 %)** |
| DTPA | ≤ DL |
| NTA | ≤ DL |
| TTHA | ≤ DL |

& L. du Bois de Maquillé et al., J. Chrom. A, Vol. 1276, 20-25, (2013)

# CHEMICAL CHARACTERISATION

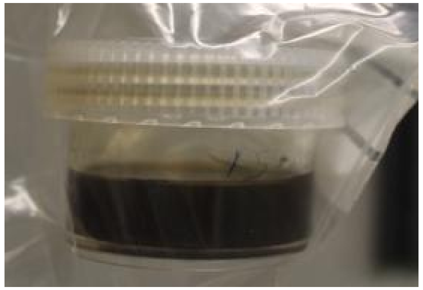
## Determination of toxic elements in French radioactive wastes

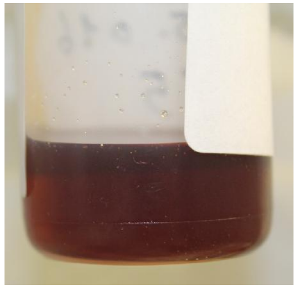
- ANDRA requires the determination of 10 toxic elements in priority: Pb, B, Ni, Cr, As, Sb, Se, Cd, Hg, Be

- At LASE laboratory, toxic elements are measured by ICP-AES or ICP-MS




- Recently, a new demand has emerged for the characterisation of toxics in oils





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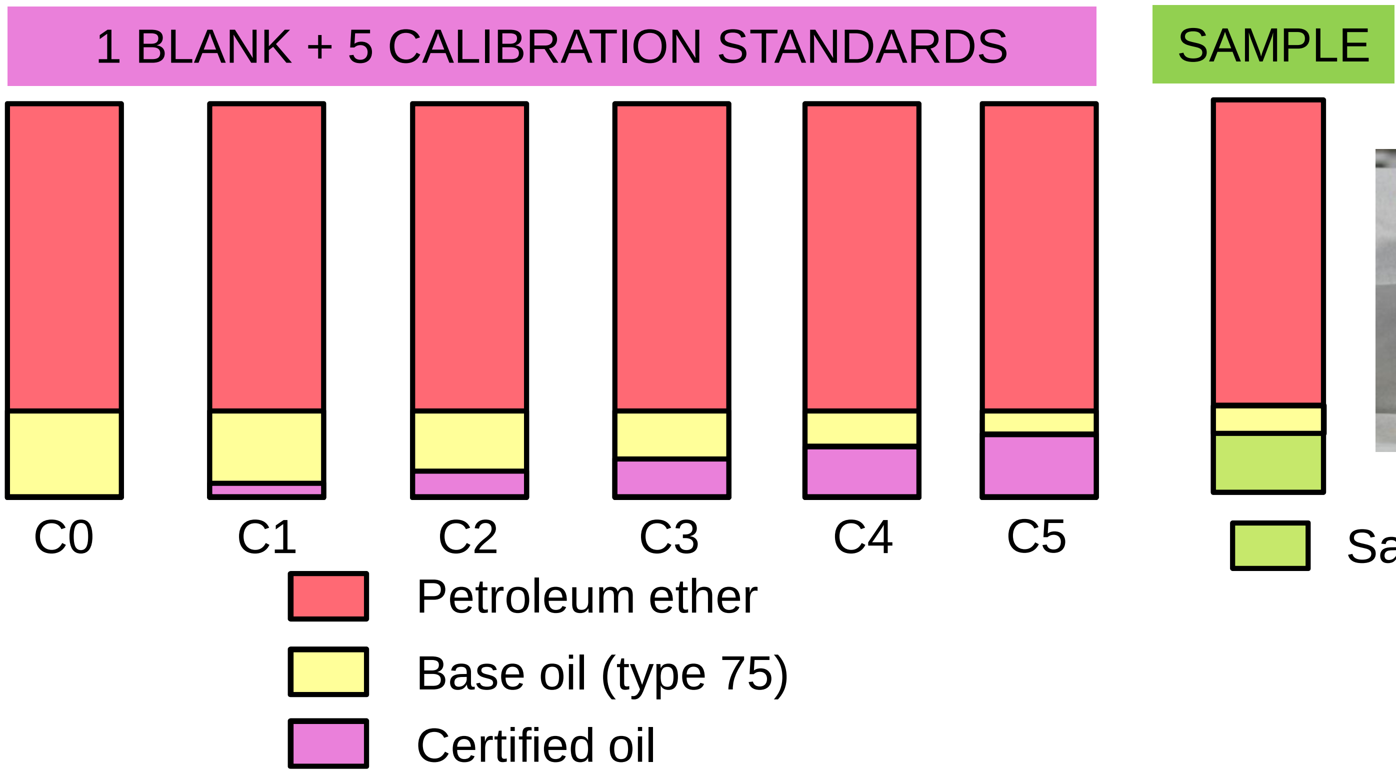
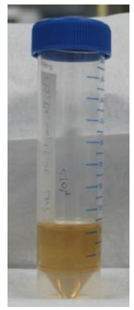
# CHEMICAL CHARACTERISATION

## Determination of toxic elements in oils

- Development of a procedure to analyse toxic elements directly by ICP-AES without any digestion step so as to achieve a high sensitivity

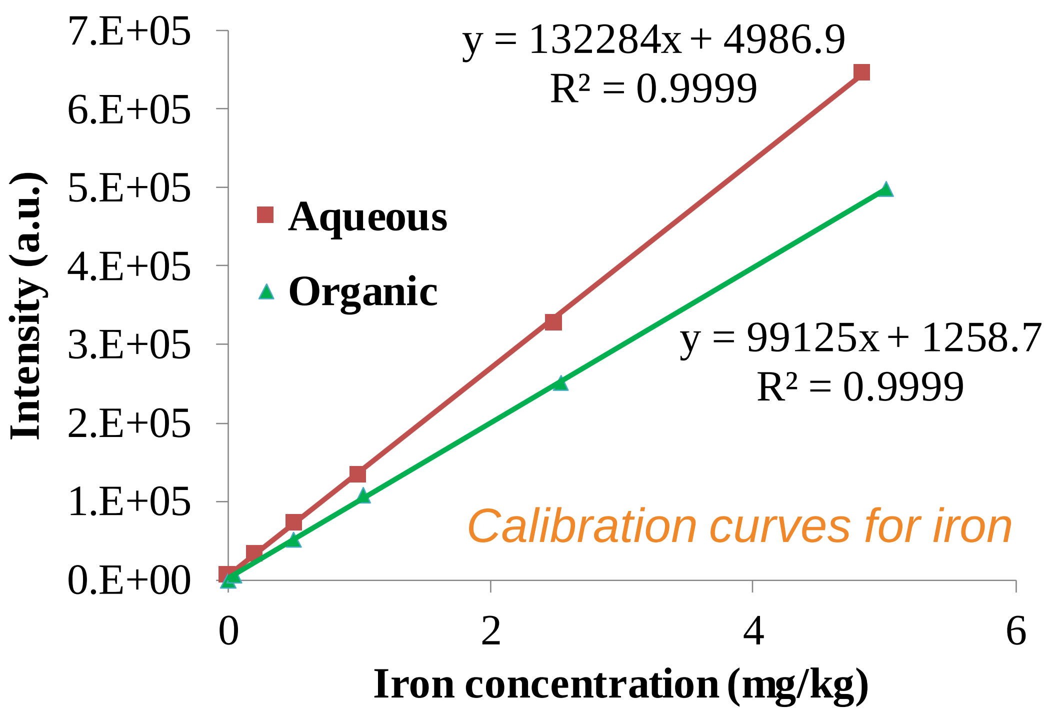
- Preparation of calibration standards and samples in a mixing solution based on petroleum ether (kerosene) and base oil (3/4-1/4)



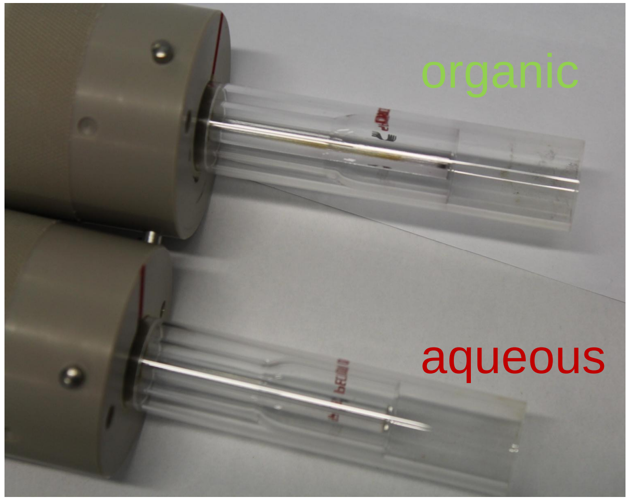



## Determination of toxic elements in oils

- Comparison of the sensitivity between aqueous and organic matrices




*Calibration curves for iron*




Direct analysis of toxics in oils:
J Lower detection limit
L Deposits of coal in torch

- Validation of the developed method by participating to interlaboratory comparisons organized by LGC on engine oil lubricants

# CONCLUSIONS

# AND

# PROSPECTS

# CONCLUSIONS AND PROSPECTS

## Improvement of different analytical techniques to characterise radionuclides and toxics at LASE laboratory

### CONCLUSIONS

- New developments for many techniques: in-situ device with SiPM for alpha and beta emitters, gamma spectrometry applied to solids, radiochemical Fe-55 procedure, analysis of complexing agents and toxics
- But, also for C-14 speciation, detection of DTM radionuclides at low level with AMS, such as Cl-36, I-129, Ca-41
- Importance to participate to proficiency tests and interlaboratory comparisons so as to check the accuracy of the developed methods: LNHB, NPL, CETAMA, LGC, AGLAE, BIPEA…

### PROSPECTS

- Implementation of coupling techniques between HPLC and ICP-MS to analyse long-lived RN

SYP2019

Thank you for your attention



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