Historical overview and current challenges in radionuclide analyses in different waste matrices and materials at SCK•CEN, Belgium

M. Vasile[1], M. Bruggeman[1], L. Adriaensen[2], A. Dobney[2], S. Boden[3],

[1]Low-level Radioactivity Measurements Expert Group, [2]Radiochemistry , [3]Dismantling & Decontamination, SCK•CEN, Boeretang 200, 2400 Mol, Belgium

mvasile@sckcen.be

SCK•CEN

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Content

- ❑ **Introduction**
- ❑ **What has been done in the past**
- ❑ **Current challenges**
  - ✓ Determination of ^{14}C, ^{36}Cl and ^{129}I (RCA)
  - ✓ Determination of ^{99}Tc in environmental samples (LRM)
- ❑ **Future plans**
- ❑ **Conclusions**

SCK•CEN

General Management

Eric van Walle: Director-General
Peter Baeten: Deputy Director-General
Hamid Aït Abderrahim: Deputy Director-General
Christian Legrain: Secretary-General

- Internal Audit
- External Medical Surveillance
- MYRRHA Management Team
- Business Development & Support
- Secretariat General Management
- Communication
- Internal Service for Prevention and Protection at Work

Institute Nuclear Materials Science

Marc Scibetta
Rachid Chaouadi
Sven Van den Berghe

Expert Groups:

- Structural Materials
- Fuel Materials
- Microstructural and Non-destructive Analysis
- Radiochemical Analysis and Processes
- Belgian Reactor 2
- Infrastructure Operation

Institute Advanced Nuclear Systems

Marc Schyns

Expert Groups:

- Nuclear Systems Physics
- Nuclear Systems Exploitation
- Nuclear Systems Design
- Primary System Design
- Design and Engineering Office
- Nuclear Systems Research
- Accelerator Project

Institute Environment, Health and Safety

Hildegarde Vandenhove
Filip Vanhavere
Christophe Bruggeman

Expert Groups:

- Molecular and Cellular Biology
- Radiological Impact and Performance Assessments
- Society and Policy Support
- Waste and Disposal
- RP Dosimetry and Calibration
- Low Radioactivity Measurements
- EURIDICE
- Dismantling, Decontamination and Waste

Institute Corporate Services and Administration

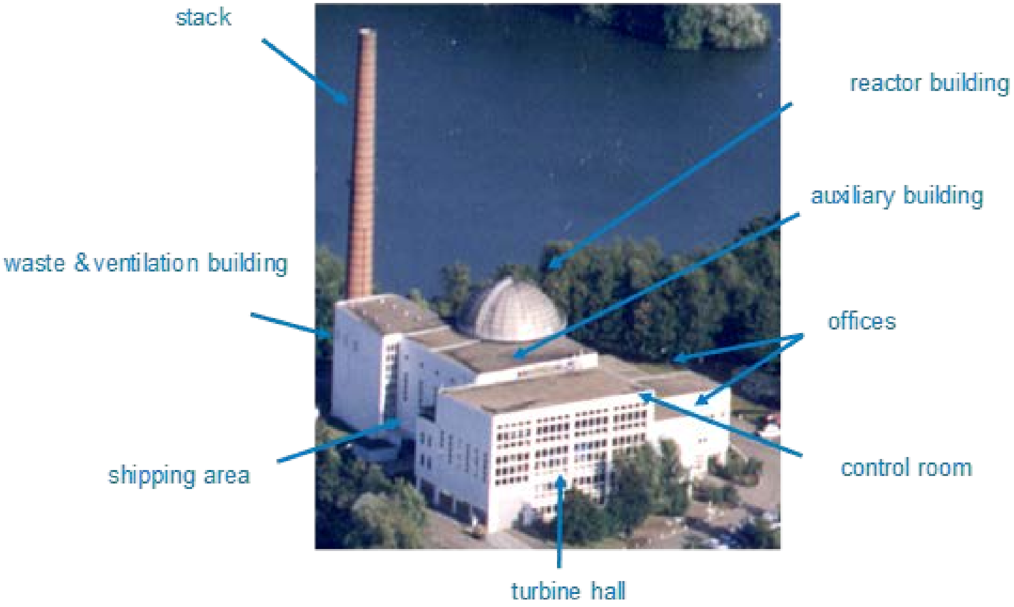
Kathleen Overmeer

Expert Groups:

- Centre for Education and Knowledge Management
- Human Resources Management
- Purchase, Accounting, Budget
- Information and Communication Technology
- Logistics
- Central Technical Services

Academy for Nuclear Science and Technology

BR3 (Belgian Reactor 3)



- ✓ **First PWR** to be built in Europe (10MW(e))
- ✓ Located at SCK•CEN
- ✓ Used for 25 years for research purposes *(testing high burn-up and gadolinium type fuels and also testing of the mixed oxide fuels)*
- ✓ Shut down in 1987
- ✓ In 1989 was selected by the EC as one of the 4 **pilot dismantling projects**

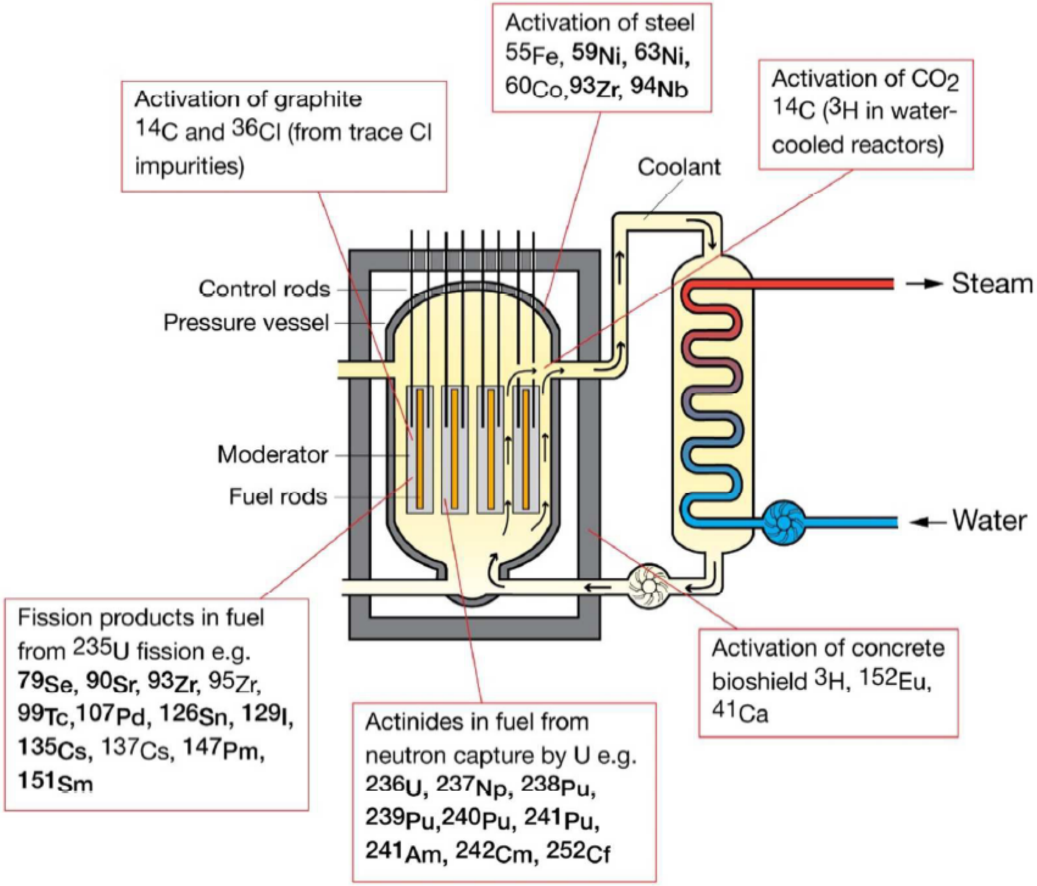
Surface repository

- In Belgium, a near surface repository for low and intermediate radioactive waste is planned for construction

- Once the repository is sealed, a monitoring plan will be implemented in order to ensure the safety of the environment and the population

- Sound environmental monitoring of nuclear sites or waste repositories also requires the measurement of the radionuclides at acceptable radioactivity concentrations

"Difficult to measure" radionuclides



- ✓ Produced during activation of different parts of a nuclear reactor
- ✓ Also during the fission of ^{235}U
- ✓ Very important for **classification of the materials** from nuclear installations
- ✓ since they are *mainly pure alpha and beta emitters* are not easy to be quantified

I. W. Croudace, B., C. Russell and P. E. Warwick, *J. Anal. At. Spectrom.*, 2016, DOI: 10.1039/C6JA00334F

How to characterize the materials resulted during decommissioning?

Combination of various characterization techniques

- ✓ Destructive Analyses (DA) ➡ '**Difficult To Measure**'
- ✓ Non Destructive Assay (NDA) ➡ Easy To Measure
- ✓ Modelling

Source: Radiological Characterization of Shut Down Nuclear Reactors for Decommissioning Purposes. Technical Report Series No. 389. (1998) International Atomic Energy Agency

Scaling factors

- ✓ The quantification of the pure alpha, beta-emitters is time consuming and expensive, so it is not feasible to perform destructive analysis on each waste batch
- ✓ Therefore, scaling factors are used
- ✓ Scaling factors relate the activity of the critical radionuclides to **Cs-137, for fission products**, and to **Co-60 for activation products**.
- ✓ Both Cs-137 and Co-60 are gamma emitters that can be easily measured in waste using non-destructive methods.
- ✓ The scaling factors can be estimated using **calculation codes**
- ✓ This calculation codes needs to be **validated**
- ✓ So, **real analyses** have to be performed on different types of samples

Past at SCK•CEN

- Focus was:
  - in optimizing sample preparation for difficult matrices, such as: concrete, resins, evaporator concentrates
  - optimizing separation of actinides using different methods
  - optimizing the measurement methods (alpha-spectrometry, mass spectrometry, LSC)

Past at SCK•CEN

- SCK•CEN + EC project 1999 + **actinides in difficult matrices**

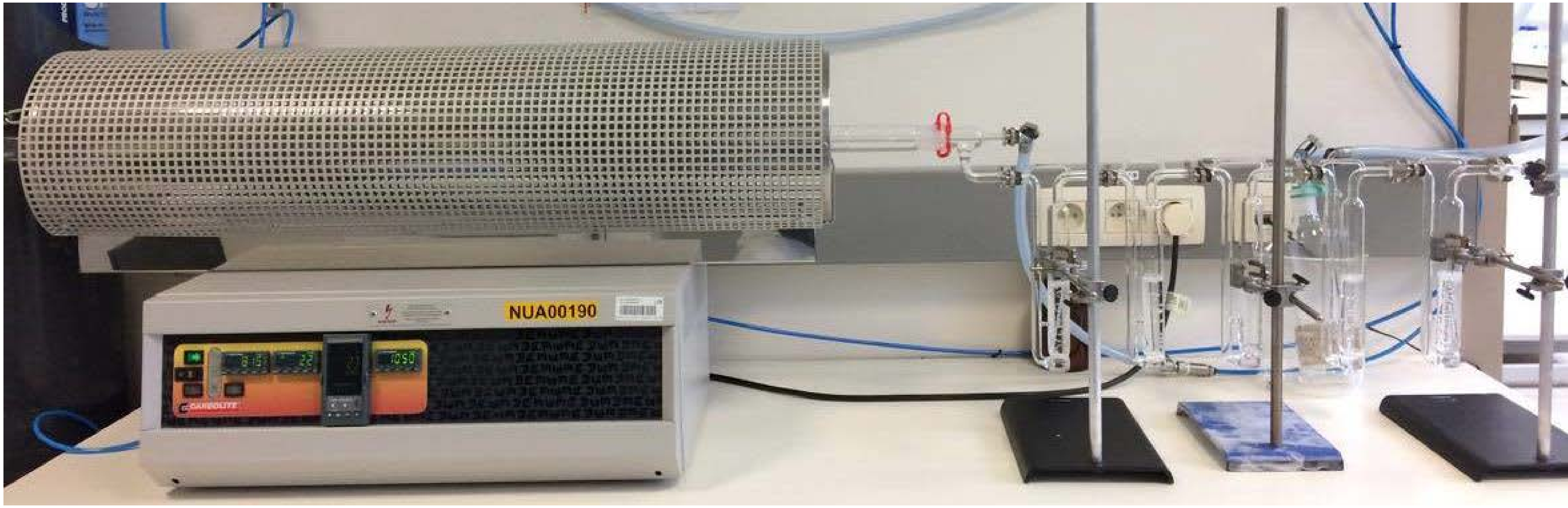
- WP1 Dissolution methods
  - *Microwave dissolution*
  - *Leaching*
  - *Fusion*
- WP2 Separation methods
  - *Ion exchange*
  - *Extraction chromatography*
- WP3 Measurement methods (source preparation)

- …

Current challenges

- RCA (high active samples)+ LRM (low active samples) collaboration for determination of other radionuclides
- actinides + **^{14}C, ^{36}Cl, ^{94}Nb, ^{99}Tc, ^{129}I, ^{63}Ni, ^{55}Fe**
- Different types of matrices: resins, evaporator concentrates, cemented waste, environmental samples
- Mass spectrometry + LSC

Determination of ^{14}C, ^{36}Cl, ^{129}I



- ✓ ^{14}C
- ✓ ^{36}Cl
- ✓ ^{129}I

}

- ✓ Graphite powder
- ✓ filter paper

?

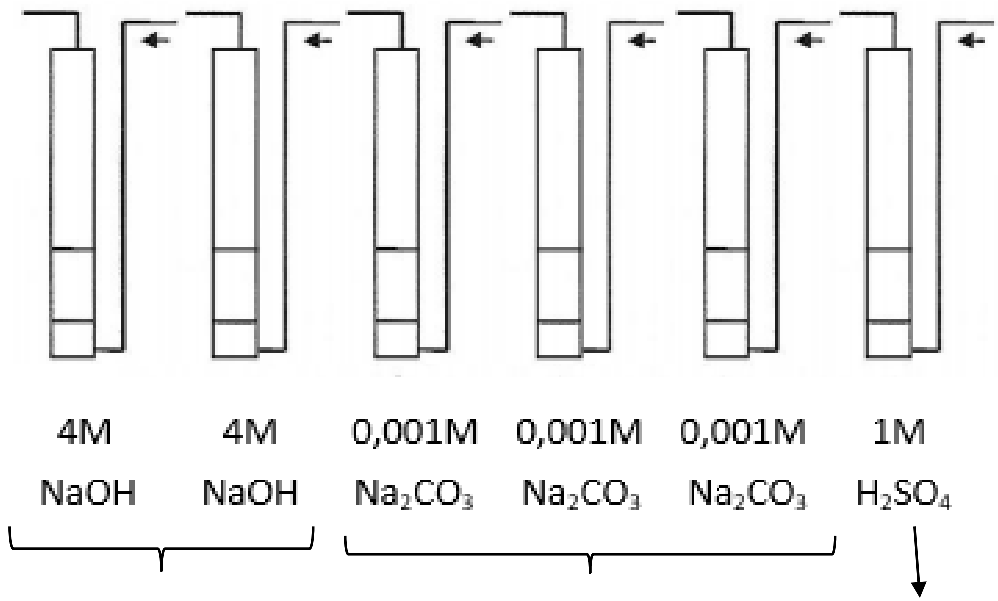
Challenges:

- ✓ Separation of the 3 radionuclides in one combustion run
- ✓ Good repeatability
- ✓ High absorption yields

Determination of ^{14}C, ^{36}Cl, ^{129}I

Challenges:

- ✓ Separation of the 3 radionuclides in one combustion run - ok
- ✓ Good repeatability – relatively ok
- ✓ **But Iodine was present in other fractions as well**



^{14}C ~61%
^{127}I ~13%

^{127}I

^{36}Cl ~87 %
^{127}I ~20%

Proposed investigations/solutions?

✓ ^{36}Cl+^{129}I can be measured together by LSC – separation using Cl-resin – results not reliable

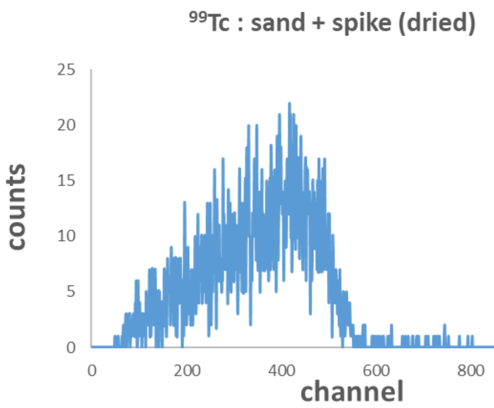
✓ ^{14}C+^{129}I is a problem – new separation by acidolize and then ^{129}I measured by ICP-MS

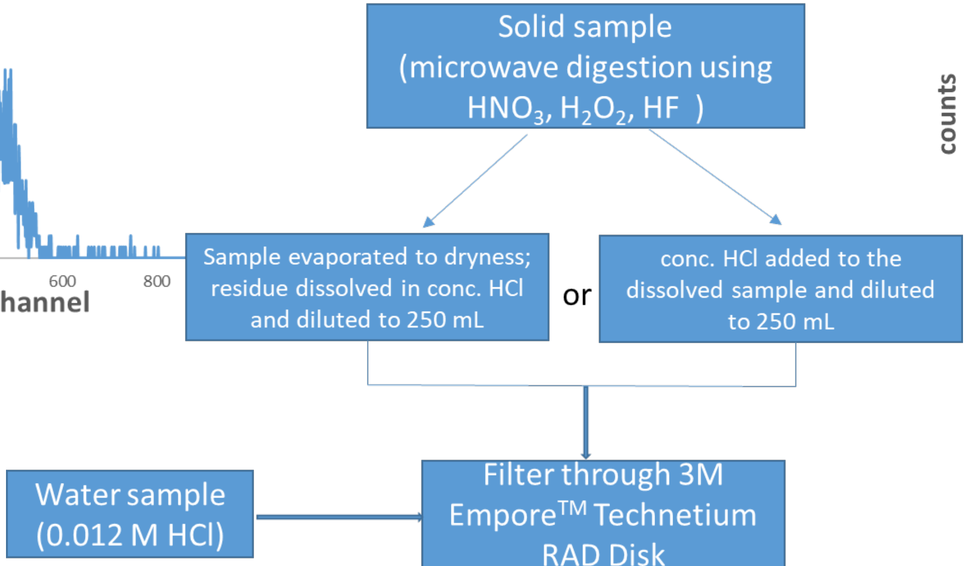
✓ keep on looking for a simpler and faster solution

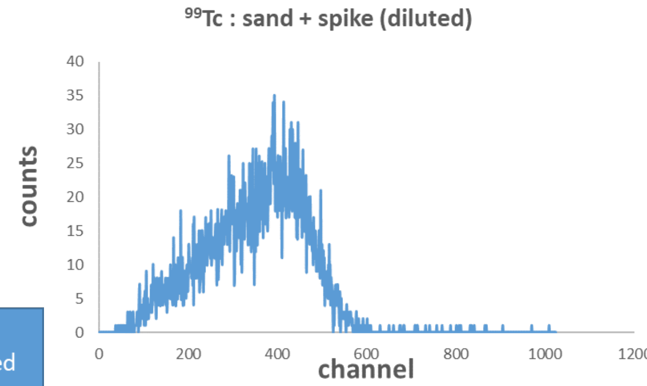
^{99}Tc quantification in environmental samples

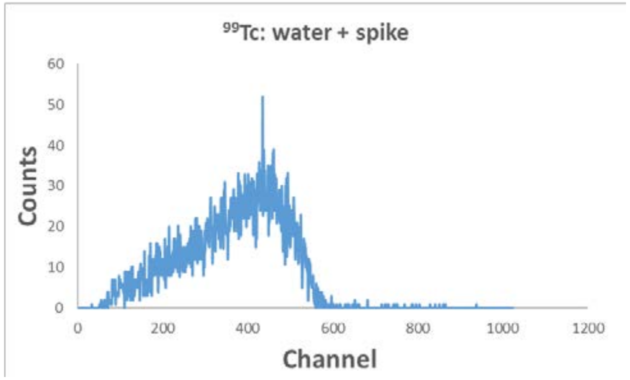
- ^{99}Tc quantification in environmental samples
- $E_{\beta max}$ = 293.8 keV
- Liquid scintillation counting as main measuring technique
- TEVA resin is used for its radiochemical separation from solid samples

^{99}Tc determination using Tc RAD discs



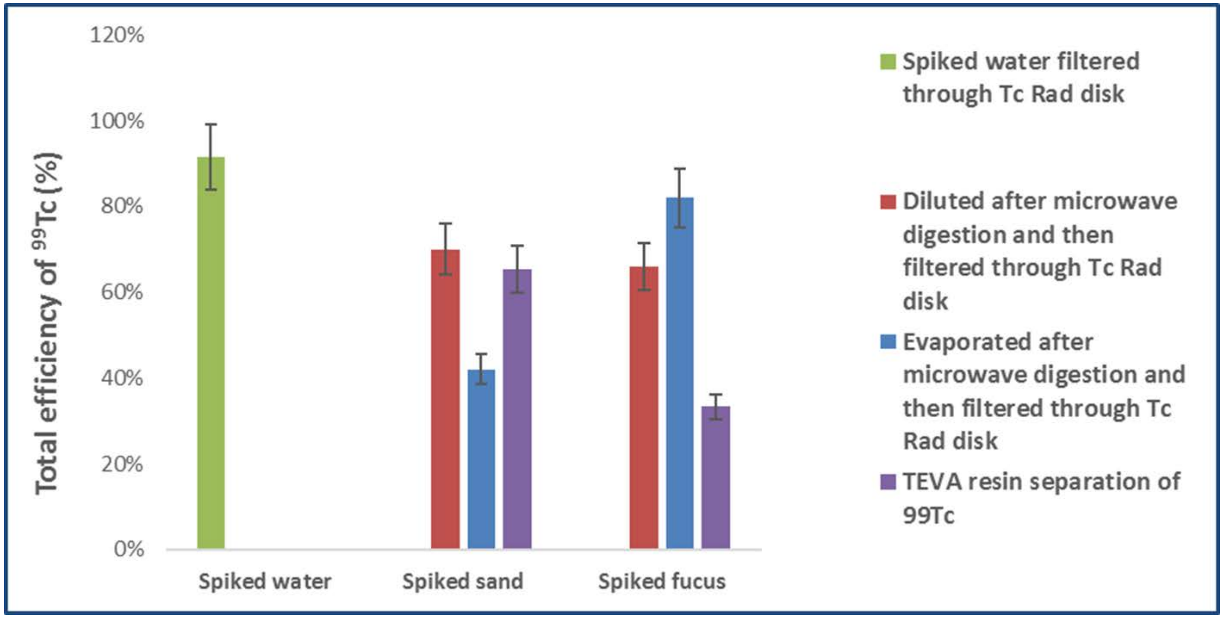






^{99}Tc determination using Tc RAD discs

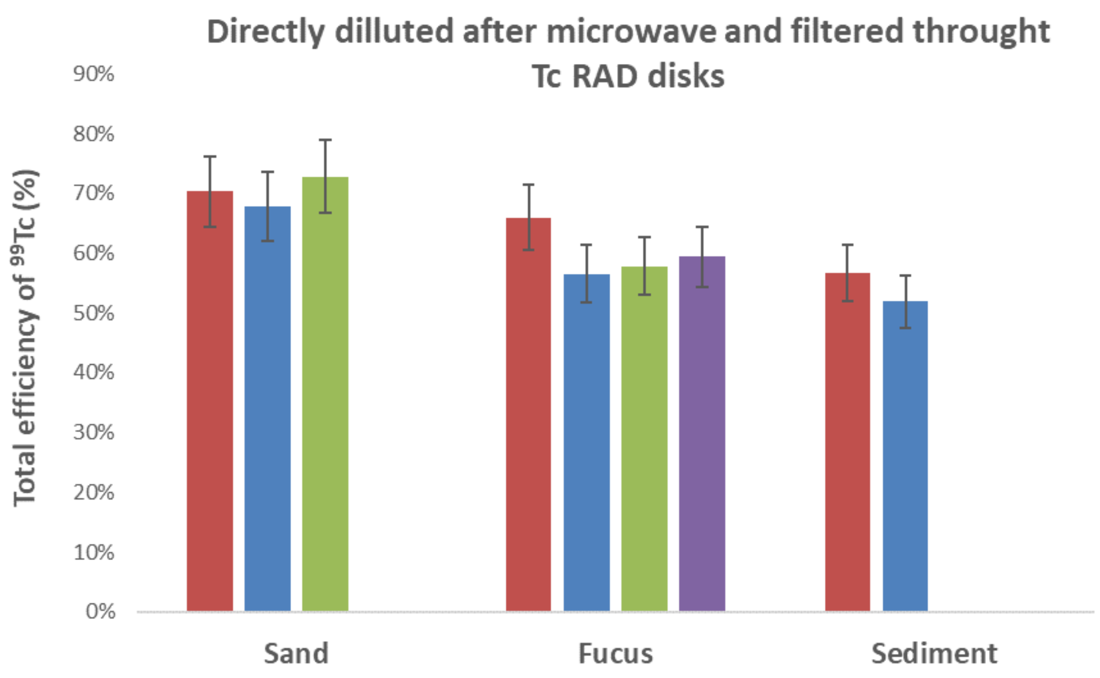
- testing the **Technetium RAD diks** for solid samples



✓ **Total efficiency** of ^{99}Tc was influenced by the **sample matrix**, lower values were obtained using spiked sand sample comparing with water sample

✓ **Dilution of the sample after digestion** with microwave, then filtration through Tc Rad disk **seems to be promising** and it makes the procedure very simple and much faster comparing with the TEVA resin separation

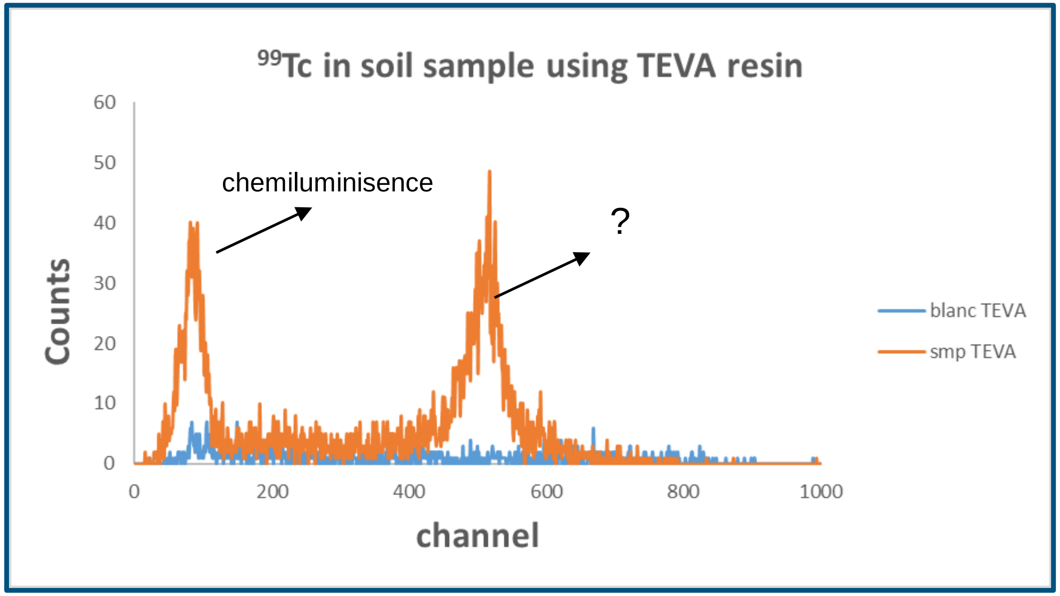
^{99}Tc determination using Tc RAD discs



- ✓ **Dilution of the sample after digestion** with microwave, then filtration through Tc Rad disk **seems to be promising** and it makes the procedure very simple and much faster comparing with the TEVA resin separation
- ✓ The total efficiency is between **60 – 70 %**

^{99}Tc determination using TEVA resin

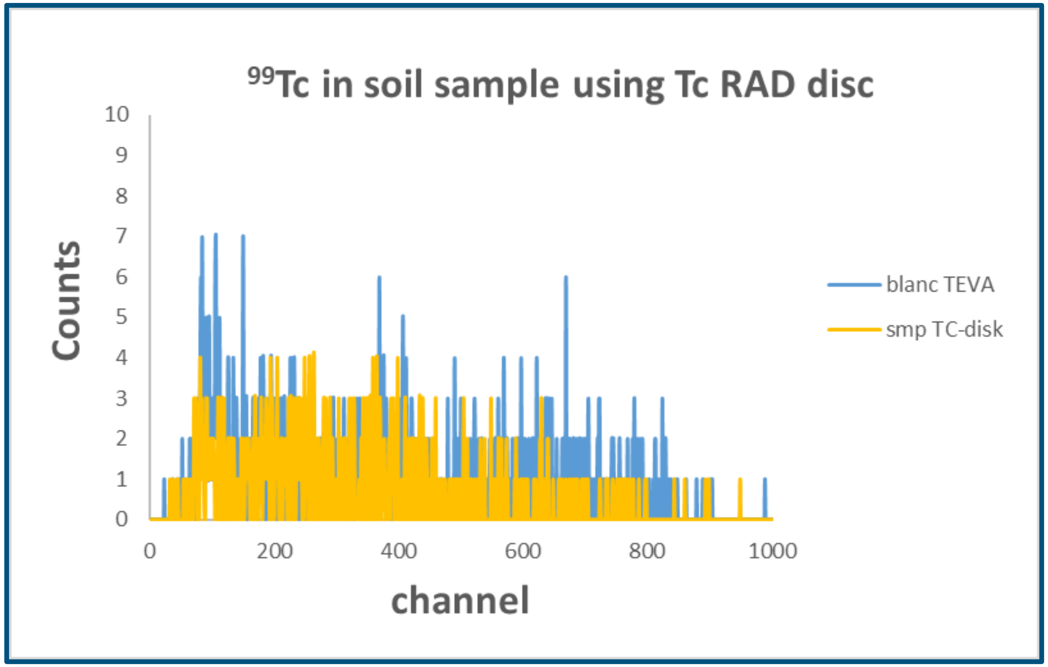
Sediment sample: ^{99}Tc separated using TEVA resin and Quantulus1220™ for its quantification



- ✓ an extra peak in the spectrum
- ✓ overestimation of the massic activity
- ✓ separation not ok?
- ✓ cross-contamination?

^{99}Tc determination using Tc RAD discs

Sediment sample: ^{99}Tc separated using TEVA resin and Quantulus1220™ for its quantification



- ✓ **No** extra peak in the spectrum
- ✓ Good separation

^{99}Tc determination using Tc RAD discs

✓**3M decided to stop with the production of the discs**

- **Perspectives/options to be investigated in the future**:

  ✓TEVA discs from Eichrom

  ✓Plastic scintillators

Future plans

- **PhD topic**:"Development of analysis methods for '*difficult to measure*' radionuclides in environmental samples around nuclear sites and in materials produced during decommissioning activities"

- **^{79}Se, ^{36}Cl, ^{129}I, ^{151}Sm, ^{147}Pm, ^{41}Ca**

- Matrices: environmental and/or nuclear materials produced during decommissioning activities (using fusion)

- LSC (Liquid Scintillation Counting)+ICP-QQQMS

Future plans

^{79}Se ($E_{\beta max}$ = 150.9 keV) **-** After a very laborious separation procedure to remove the spectrometric interferences

- LSC is the usual quantitative measurement technique employed
- The current detection limits achievable by mass spectrometry are much higher due to isobaric interference
- The ICP-QQQ-MS technique opens up the potential for using reaction chemistries

- **^{36}Cl** ($E_{\beta max}$ = 709.6 keV)
  - often measured by LSC
  - Cl-resin has been developed by Triskem
  - the use of the Pyrolyzer and Cl-resin

Future plans

- **^{151}Sm** ($E_{\beta max}$ = 76.4 keV) and **^{147}Pm** ($E_{\beta max}$ = 224 keV)
  - The use of the extraction chromatography (Ln-resin) has been reported in the literature
  - Liquid scintillation counting will be the main quantitative technique
- **^{41}Ca** (421.6 keV)
  - Very complicated and lengthy separation procedures are employed for removal of the interferences.
  - Since ^{41}Ca decays by electron capture, its quantification is achieved by LSC or X-ray spectrometry.

Conclusions

- a lot has been done in the past
- with new safety studies new nuclides of concern are considered and need to be measured
- so techniques need to be developed (and accredited when it comes to making official analyses)

Thank you for your attention!

Copyright © 2014 - SCK•CEN

PLEASE NOTE!
This presentation contains data, information and formats for dedicated use ONLY and may not be copied, distributed or cited without the explicit permission of the SCK•CEN. If this has been obtained, please reference it as a "personal communication. By courtesy of SCK•CEN".

SCK•CEN
Studiecentrum voor Kernenergie
Centre d'Etude de l'Energie Nucléaire
Belgian Nuclear Research Centre

Stichting van Openbaar Nut
Fondation d'Utilité Publique
Foundation of Public Utility

Registered Office: Avenue Herrmann-Debrouxlaan 40 – BE-1160 BRUSSELS
Operational Office: Boeretang 200 – BE-2400 MOL

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE