DE LA RECHERCHE À L'INDUSTRIE

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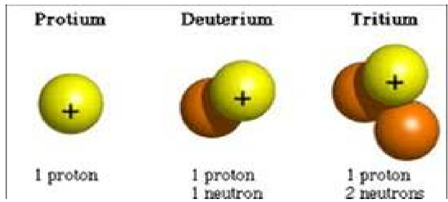
Tritium analysis strategy regarding activity concentration levels in monitoring situations.



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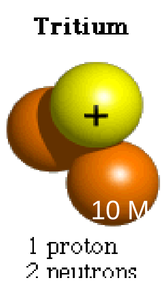
www.cea.fr

LSC 2017 – Copenhague – Mai 2017

A thought for Dan Galeriu who passed over recently



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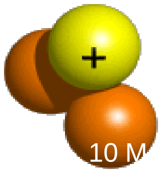


Background

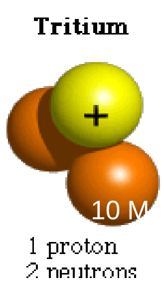
- Tritium production:
  - Natural: Effect of cosmic radiation on air component $^{14}N + n \rightarrow 3\ ^{4}He + \ ^{3}H$
  - Anthropogenic: Authorized discharge from nuclear facilities (HTO and HT mainly)
    - Past: nuclear bomb testing
    - Future: ITER and EPR

Installation

Monitoring : Discharge
Characterization : wastes and decomissionning samples

Environnement

Monitoring : waters, precipitation, biological samples
Characterization : HTO, TFWT and OBT determination



Liquid scintillation counters

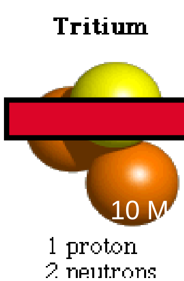
From detection limit (DL) up to the max activity concentration where linearity is assessed

Aloka LB7
(70/70 or 50/50)

Wallac Quantulus 1220
Tricarb 3170 – 3180
Quantulus GCT 6220
(10/10)

Tricarb 3100 – 2900
Tricarb 4910 – 5110
Aloka LSC 8000
(10/10)

Hidex 300 SL
(10/10)



1 Bq.kg^{-1}

5 Bq.kg^{-1}

20 Bq.kg^{-1}

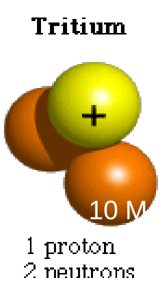
Sample type

Tritium exists under several forms in various sample types with activity concentration much lower (in normal situation) for environmental samples

	Environment (Man)	Installation
Liquid	Water, milk (urine)	Effluents
Solid	Animal, vegetal	Concretes, metals,

$10\ Bq.kg^{-1}$ — $100\ Bq.kg^{-1}$ — $1\ 000\ 000\ Bq.kg^{-1}$

Prior to liquid scintillation counting different sample treatments could be performed regarding its nature (liquid or solid), its activity concentration, possible quenching agent (chemicals, suspended matter, colour…)



Liquid sample preparation.

For monitoring with large sample variability, quench curve is often used.
The following analytical strategy is based on this assumption

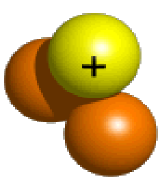
Radionuclide mixture

High quench (colour, salt…)

Distillation

Dilution

Activity concentration



Low

High

Liquid sample preparation, some recommendations.

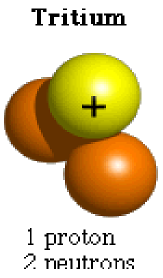
- If only two or three beta emitters coexist in the sample, quantification is possible without distillation. However, differences between beta energy emission have to be large enough (^{3}H versus ^{14}C but not ^{3}H versus ^{241}Pu), mathematical treatment is a little bit more complex (spill over correction)...

- Sample treatment could be avoided and/or simplified by using standard addition or by preparing a quench curve in the analysed matrix.

- In any case, scintillators should be suited to sample type.

- At low activity concentration, treatment blanks are advised.

- At high activity concentration, small sample volume and dilution are often a cost effective solution either on the technical and radioprotection point of view.



Solid sample preparation, definitions.

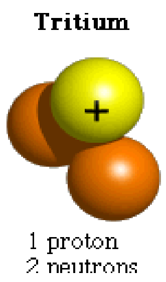
(✎) OBT definition : OBT is formed in living systems through natural or biological processes from HTO. OBT is the sum of the exchangeable and non exchangeable forms.

(✎) Kim S. B., Baglan N, and Davis P. A.; J. of Envt. 126 (2013) 83.

The different tritium containing fraction present certain similarities in terms of bond strength between hydrogen (tritium) atoms and supporting ones

	Envt. Sample	Concrete and Cements (🗎)
Liquid water	TFWT	Free and capillary water
Weakly bound tritium	E-OBT	Water of crystallisation
Tightly bound tritium	NE-OBT	Water constituent

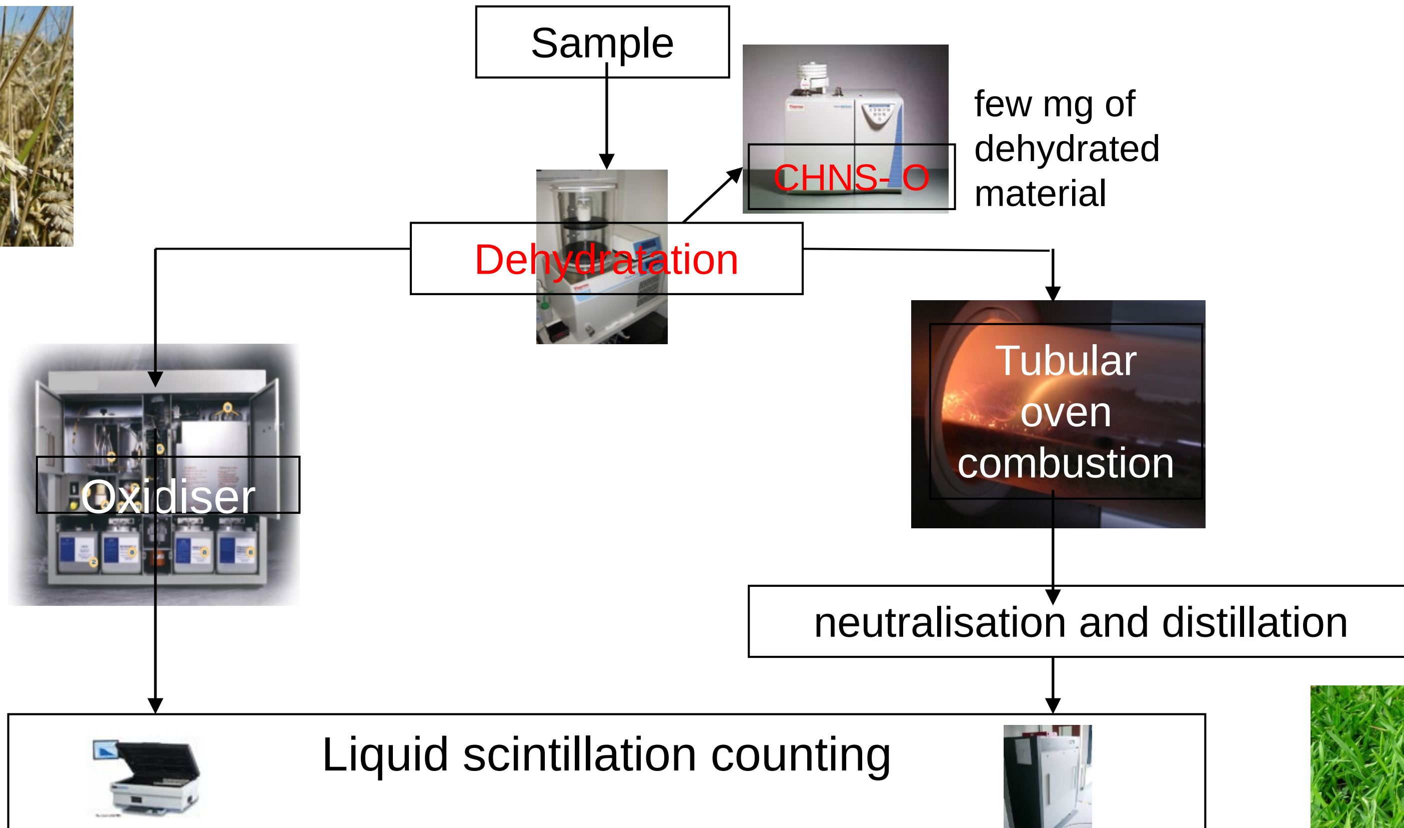
(🗎) from Kim D. J., Warwick P. E. and Croudace I. W.; Anal. Chem. 80 (2008) 5476.

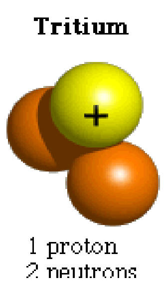


Therefore sample treatment should required similar technical processes for the different tritium fractions recovering for both types of samples.

Solid sample preparation.

Envt : consensus on OBT definition with validated methods existing in several countries and also a standard (XP M 60-824) in France .





Waste materials: a specific attention should be paid to (i) radioprotection and also to (ii) reduce losses along the analytical path. For that the main issues are (i) to decrease sample amount and (ii) to use specific tools improving tritium recovery.

Solid sample preparation

Combustion tools

Oxidiser

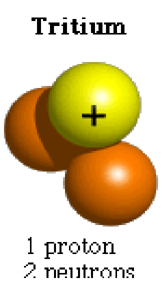
$m_s \leq 1$ g

Combustion bomb

$1\ g \leq m_s \leq 10$ g

Combustion oven

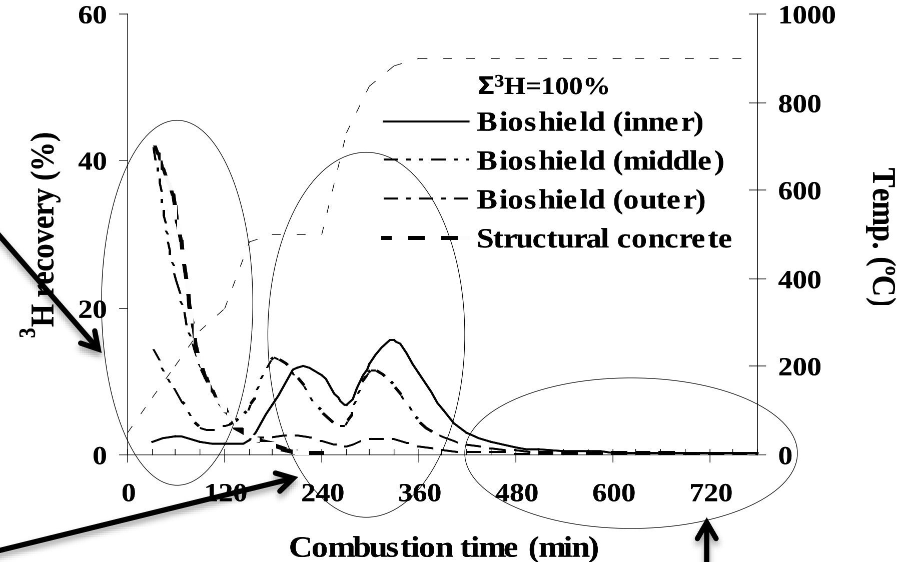
depending on tube diameter
$5 \leq m_s \leq 40$ g



Increasing masses
Improved detectable activity concentration

Solid sample preparation

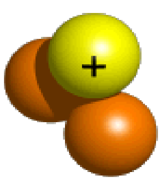
Liquid water recovery



Water of crystallization

Water constituent

Tritium

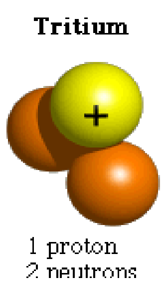


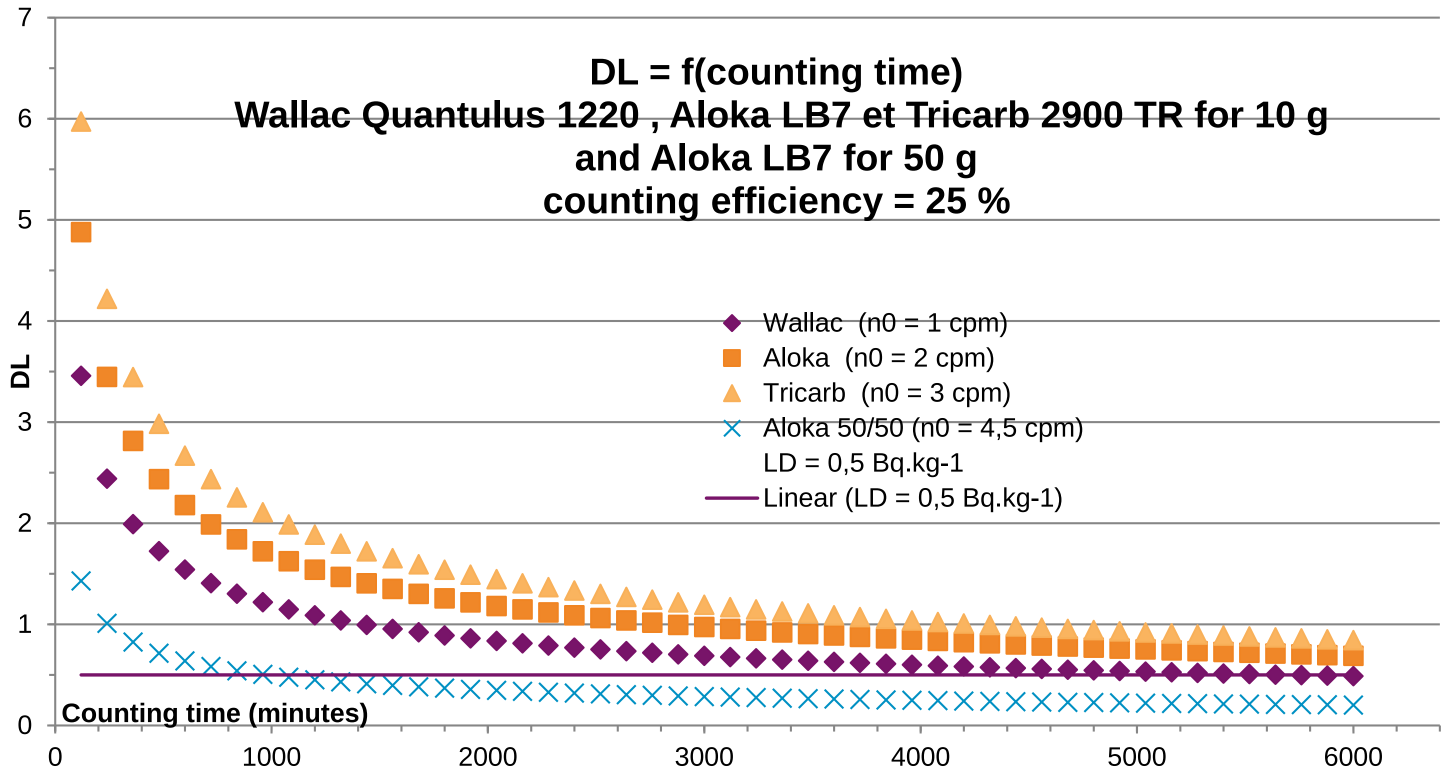
1 proton
2 neutrons

For small sample amount and a high activity concentration a single stage procedure could be interesting if tritium fractions are easy to separate.

Applicability for environmental samples ??

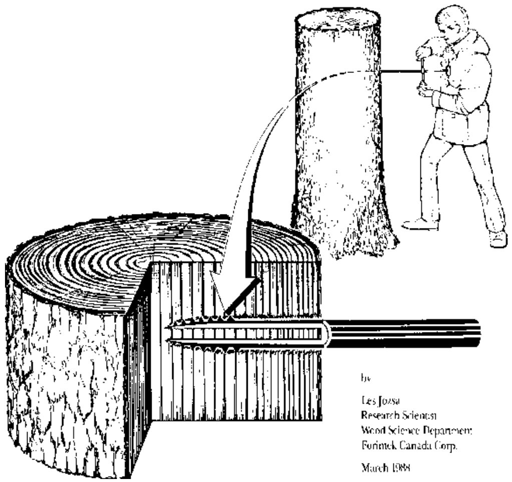
Example : low level of tritium in sea water





To reach a detection limit (DL) of about 0.5 $Bq.kg^{-1}$ Wallac Quantulus1220 (10/10) could be used with counting time in the 5000 minutes range or Aloka LB7 (50/50) in the 1200 minutes range.

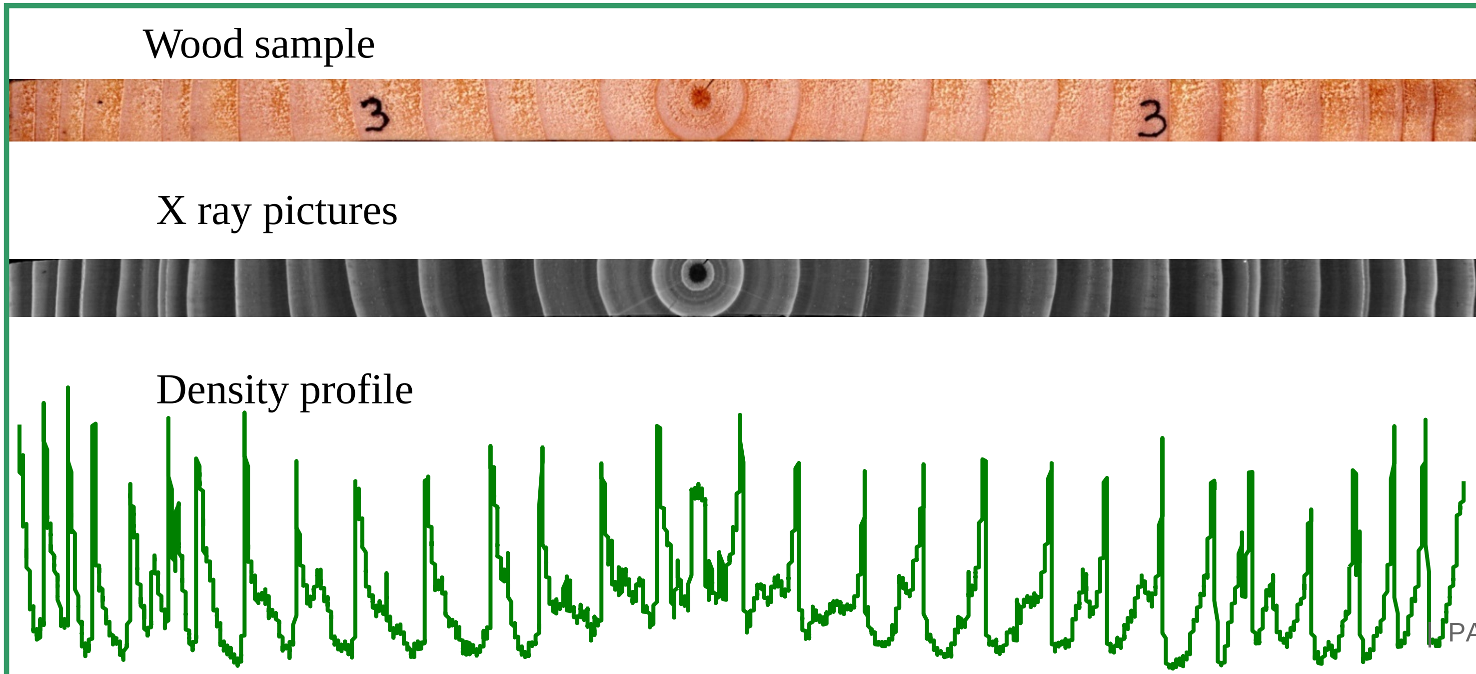
Example : Organically bound tritium (tree rings)

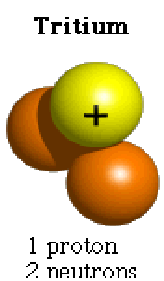


When focusing on tree rings:

❶ how samples are chosen?

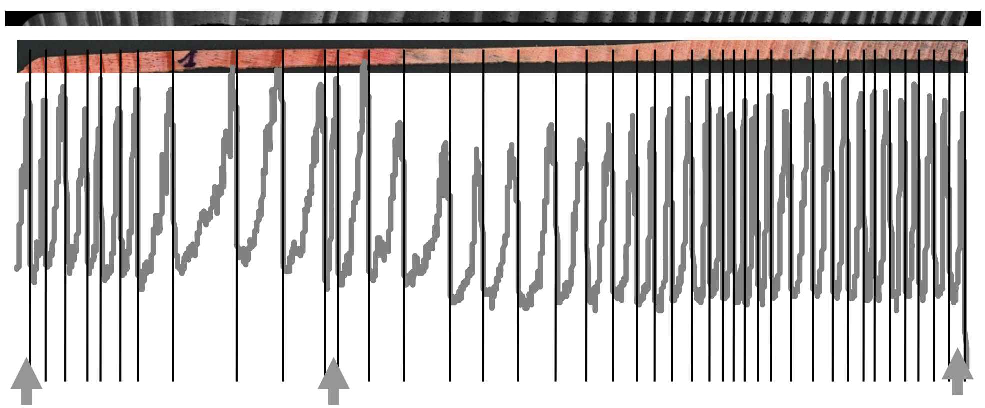
❷ how yearly rings are identified?

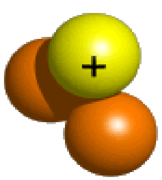




Example : Organically bound tritium (tree rings)

Rings width depends on tree type but also from its origin (location, soil, rain, sunlight…. And plays an important role to make possible yearly analysis,
Indeed, the saw used to separate rings is about 2 mm thickness.





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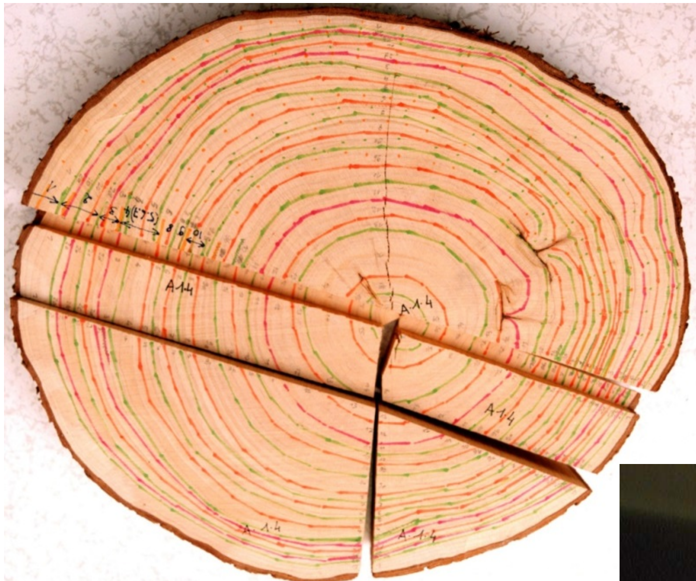
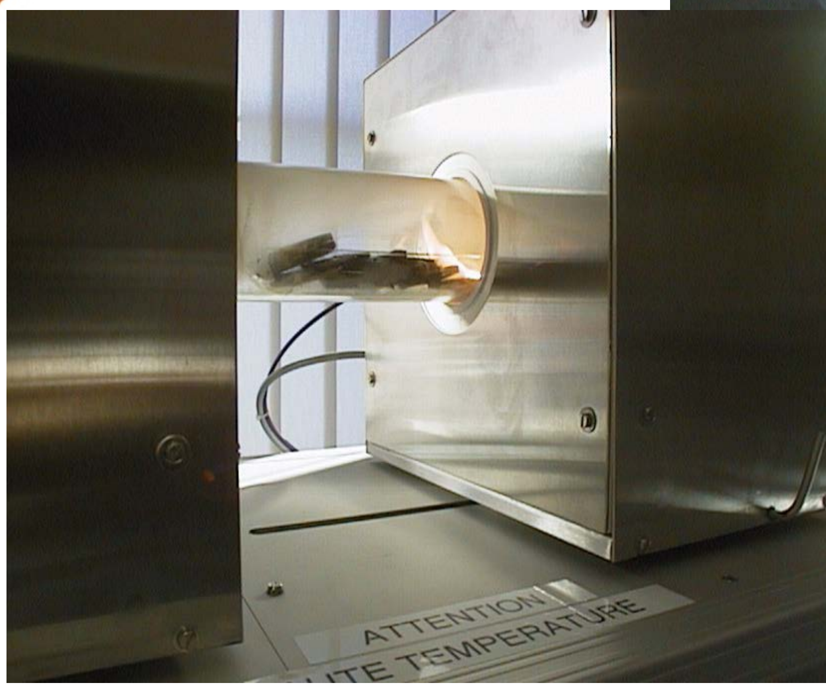
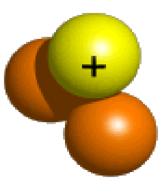


After identification tree rings are spotted on the sample and separated prior combustion.



Tritium



1 proton
2 neutrons

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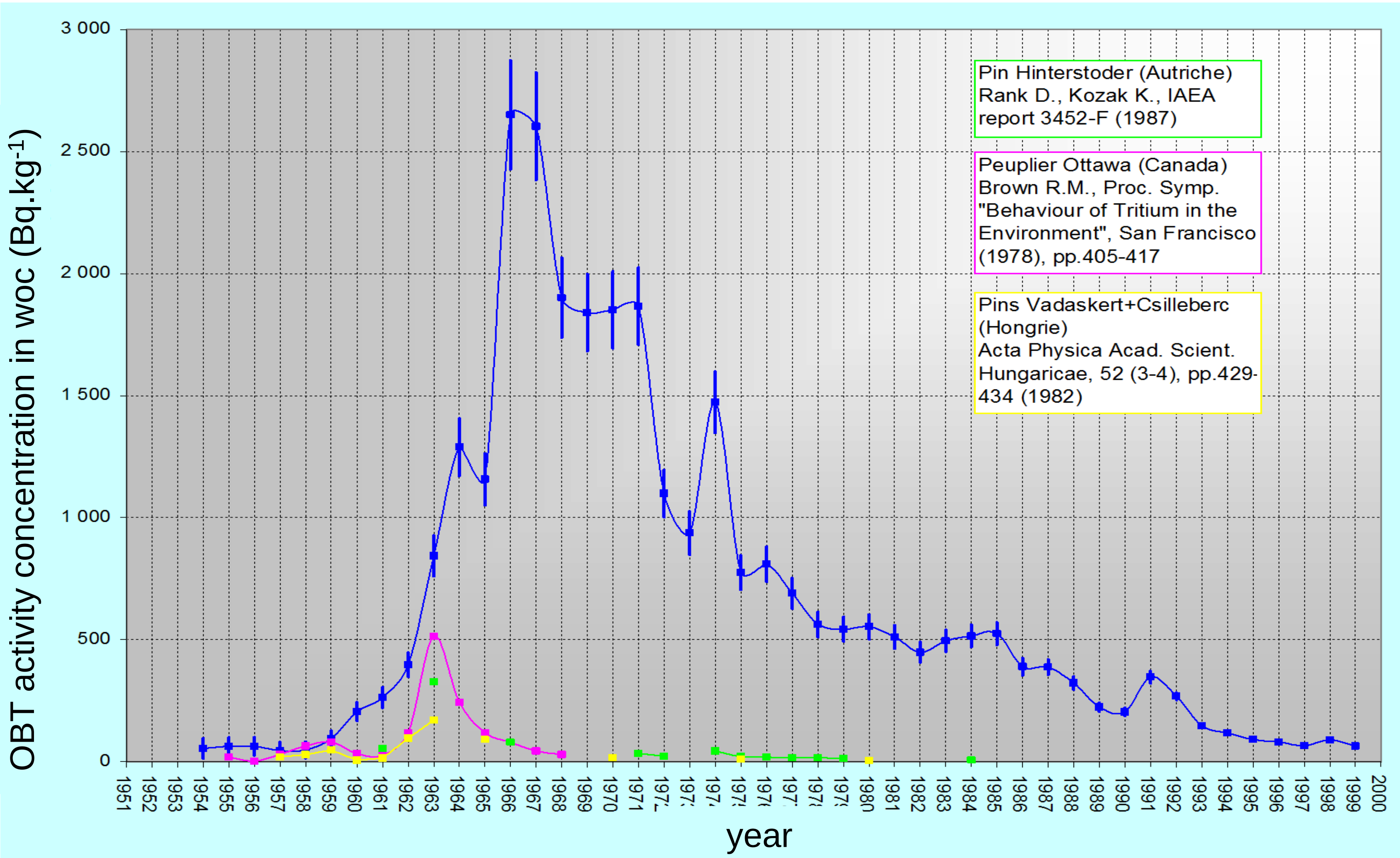
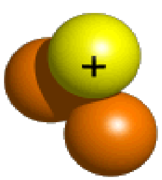


Tritium



1 proton
2 neutrons

Outlook.

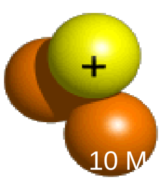
Starting from their DL to their linearity limits all counters are appropriate to determine tritium activity concentrations in environmental samples and wastes.

For effluents or waste materials, which are characterised by higher activity concentrations, decreasing sample amount should on an analytical point of view limit linearity issues and focusing on safety decrease the activity to be handled.

Using ALOKA LB 7 allows improving DL in activity concentration down to 0.2 Bq.kg^{-1} (50/50) and even to 0.1 Bq.kg^{-1} (70/70) ($n_0 \approx 4.5$ cpm, $\varepsilon \approx 25$ %, tc $\approx$ 2000 to 3000 minutes).

ALOKA LB 7 in its large vial configuration is not the best candidate to analyse liquid waste.

Tritium



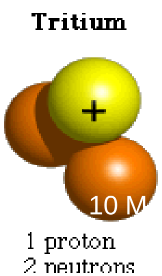
1 proton
2 neutrons

Outlook.

Using ALOKA LB 7 large vials for combustion water in the field of an OBT analysis could look promising but; to obtain 70 g of combustion water required about 150 g of dehydrated terrestrial plants which corresponds to fresh mass of about 200 g for wheat and 3 000 g for lettuce !!!

OBT analysis is more tedious and required more experienced people to deal with than HTO one.

The main concerns in OBT analytical procedure aren't LSC dependant but more related to sample treatment to avoid any modification along the process through rehydration by example.



Outlook.

dehydrated sample mass (g) to recover 70 g of woc = f(%$H_{éch}$)