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Tritium speciation in environmental matrices by isotopic exchange

A-L. NIVESSE^{1,2*}, N. BAGLAN³, G. MONTAVON¹, O. PÉRON¹

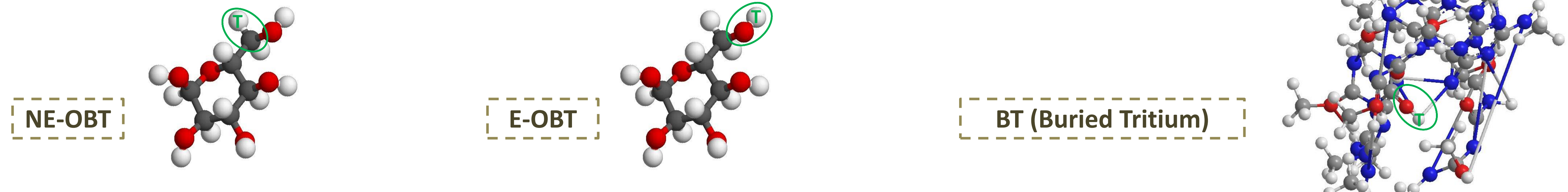
¹ Laboratoire Subatech, Groupe Radiochimie, UMR 6457, IN2P3/CNRS/IMT Atlantique/Université de Nantes, 4 rue Alfred Kastler, BP20722, 44307 Nantes Cedex 3, France (*nivesse@subatech.in2p3.fr)

² CEA, DAM, DIF, F-91297 Arpajon, France

³ CEA, DIF, DRF, JACOB, IRCM, SREIT, LRT, F-91297 Arpajon, France

Background

Tritium (³H) the radioactive isotope of hydrogen is a beta emitter with a half-life of 12.312 (25) years [1]. It can integrate organics molecules of living organisms by following the water cycle and form the organically bound tritium fraction (OBT). In 2017, the IRSN published a report on the update of knowledge on tritium in the environment [2], taking up some of the questions that have been waiting to be answered since the publication of the Livre Blanc du Tritium by ASN in 2010 [3]. Among these, those concerning the behavior, fate and speciation of this radionuclide in the environment are still relevant. The existence of two forms of OBT is commonly accepted: a non-exchangeable fraction (NE-OBT) and an exchangeable fraction (E-OBT) with the near environment. However, there is no consensus on their definition, therefore several one can be found in the literature.

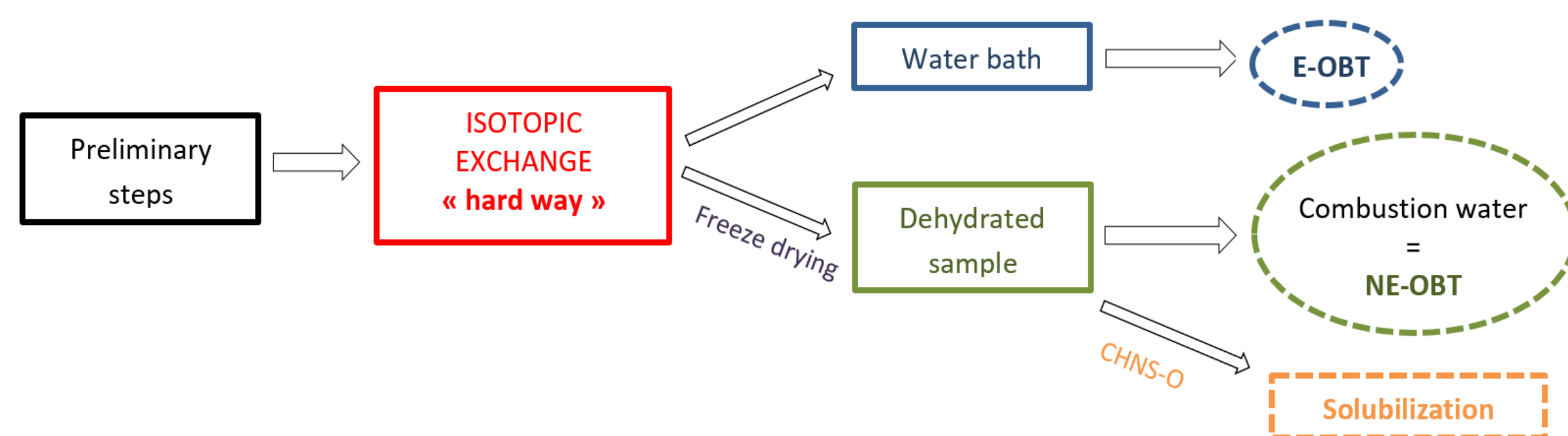


OBJECTIVE : The main goal is to improve the global understanding of tritium exchange mechanisms in environmental matrices, to validate the E-OBT and NE-OBT information and to develop the knowledge about tritium migration processes in the environment.

Experimental approach

Isotopic exchange « hard way »

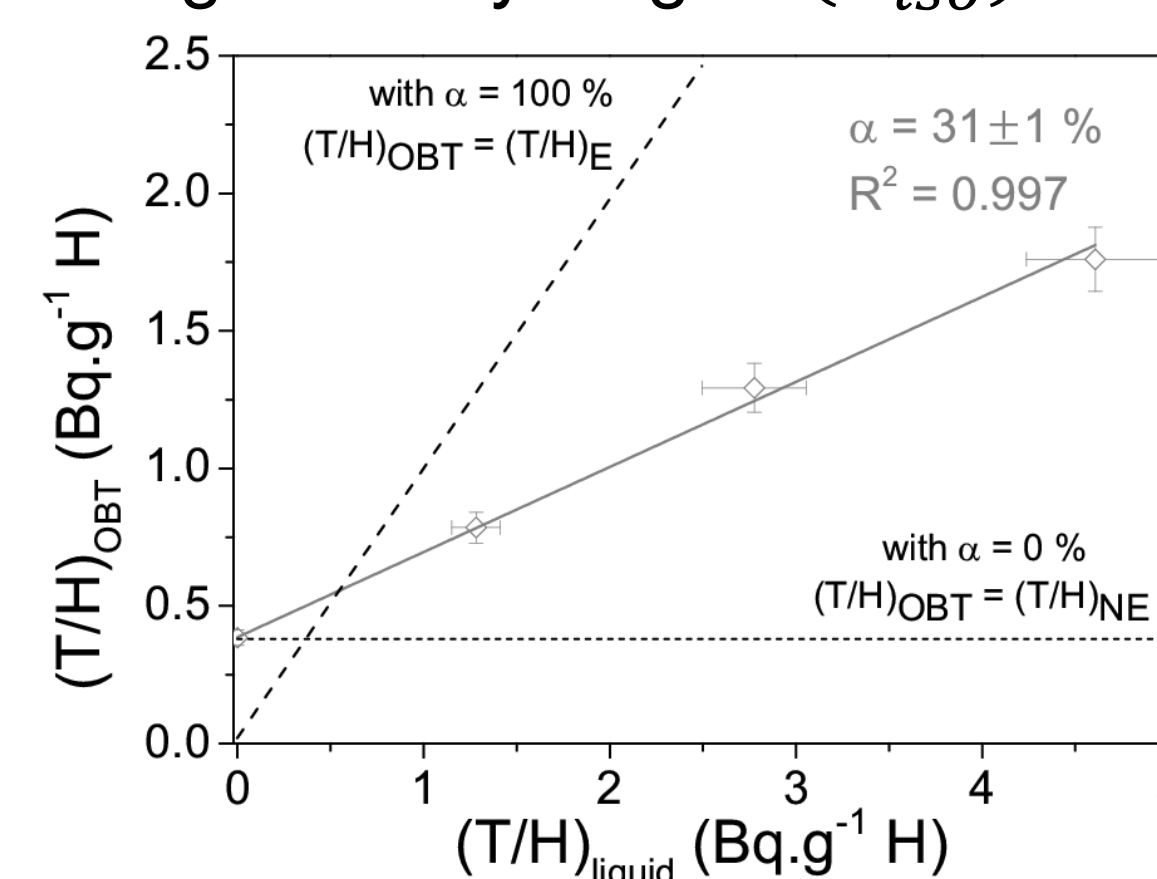
In a tritium free water bath, tritium atoms in the exchangeable position are exchanged with the hydrogen atoms of the bath : E-OBT fraction is removed from the sample. E-OBT is measured in the exchange bath and NE-OBT remaining in the sample after combustion [4].



The method leads to a potential solubilisation of a part of the sample. A proportion of the NE-OBT fraction may contribute to the E-OBT fraction measurement, which can induce an analytical bias. Solubilisation is currently estimated by elemental CHNS-O analysis of the sample before and after exchange.

Isotopic exchange « soft way »

The samples are exposed to different tritiated atmospheres in order to set up a tritium vapor phase line, with controlled and stable temperature and relative humidity parameters. This method makes it possible to determine the fraction of exchangeable hydrogen (α_{iso}) in the sample [5].



$$\left(\frac{T}{H}\right)_{OBT} = \alpha \times \left(\frac{T}{H}\right)_{E-OBT} + (1 - \alpha) \times \left(\frac{T}{H}\right)_{NE-OBT}$$

$$\left(\frac{T}{H}\right)_{NE-OBT} = \frac{\left[\left(\frac{T}{H}\right)_{OBT} - \alpha \times \left(\frac{T}{H}\right)_{liq}\right]}{1 - \alpha}$$

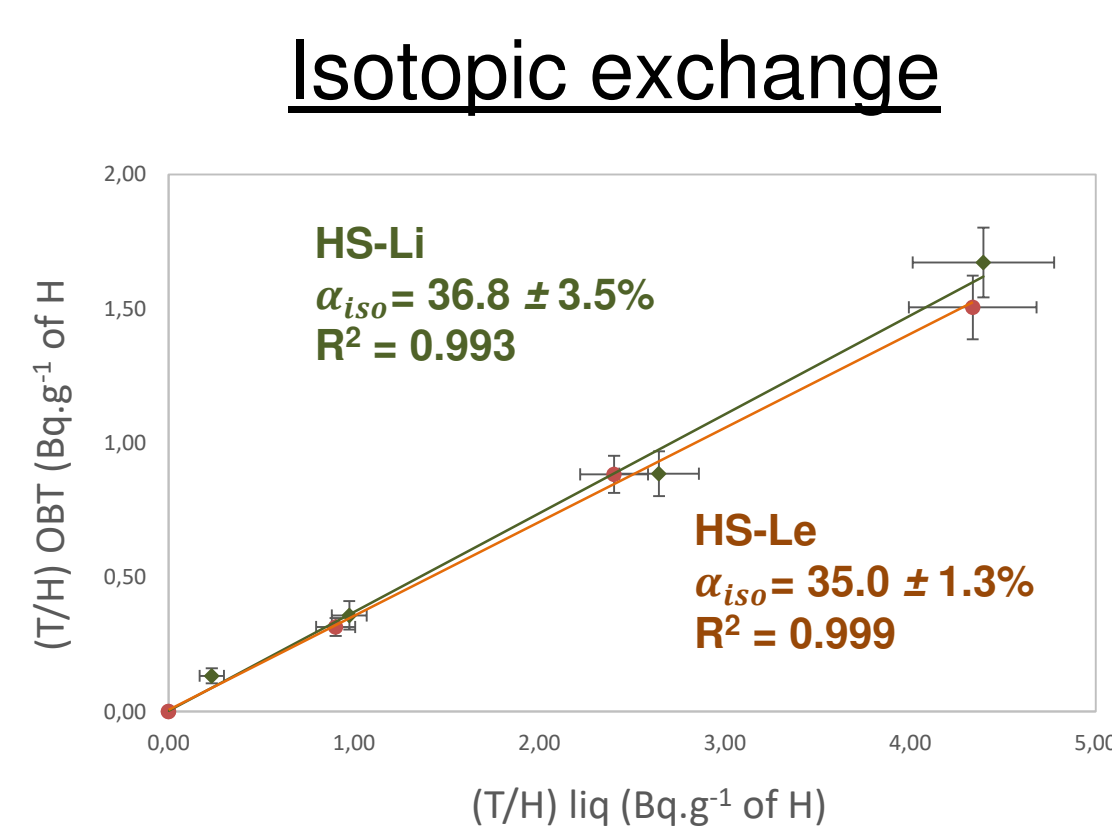


→ The (α_{iso}) parameter determination highlights the BT form in a matrix by confrontation with the ($\alpha_{theoretical}$) parameter obtained from molecular models of the matrix constituents.

Results and discussion

1. Humic substances :

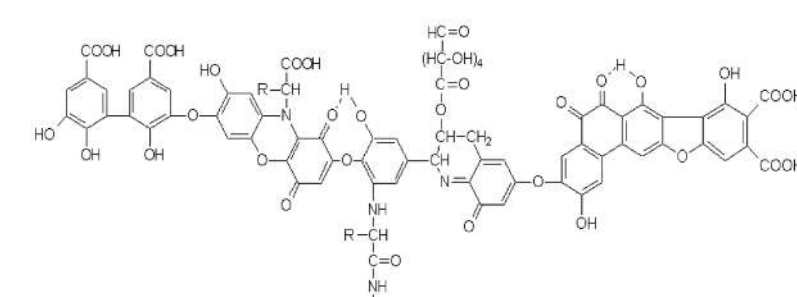
Humic substances (HS) are part of the soil organic matter. Their molecular structures complexity favors the presence of BT [6].



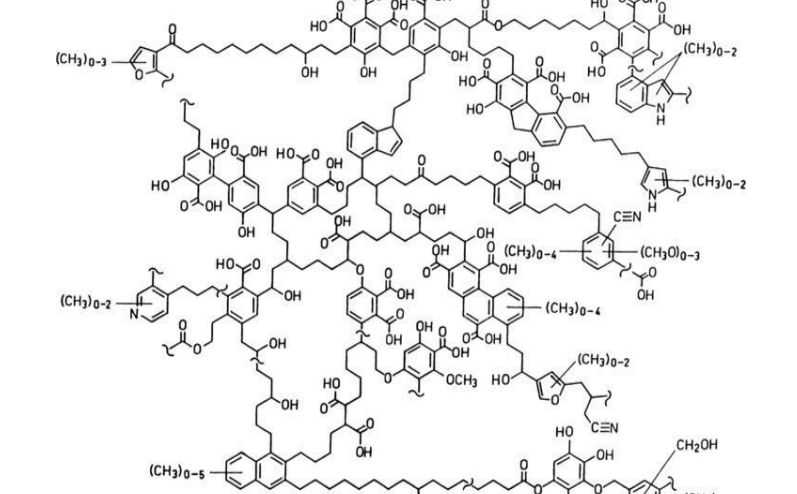
HS functional groups characterizations and contributions

	Method	HS-Li	HS-Le
$\alpha_{total\ acidity}$	Ba(OH) ₂ method	14.3 ± 2.0 %	14.5 ± 1.3 %
$\alpha_{carboxyl}$	Ca(OAc) ₂ method	0.14 ± 0.07 %	0.56 ± 0.03 %
$\alpha_{total\ OH}$	ISO14900:2017 method	15 ± 7 %	15 ± 6 %
α_{depro}	Calculated	15 ± 11 %	16 ± 7 %

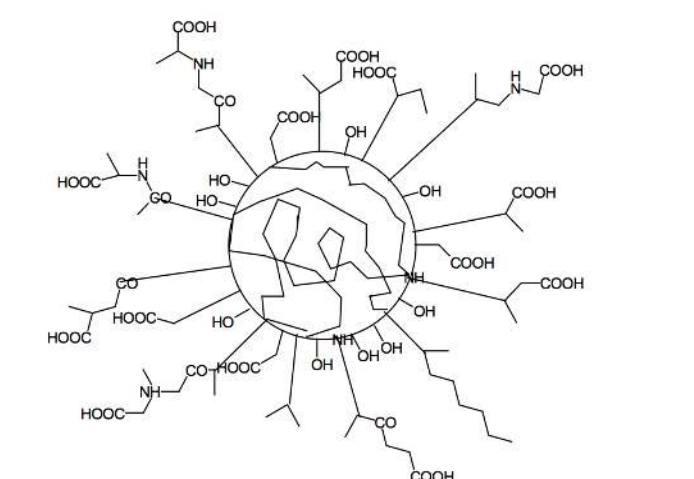
Conclusion: Humic substances (HS) isotopic exchange demonstrates a higher exchangeable capacity than characterizations of functional groups, pointing out the limitations of the standard methods in evaluating accessibility, reactivity and migration of the hydrogen element in soils.



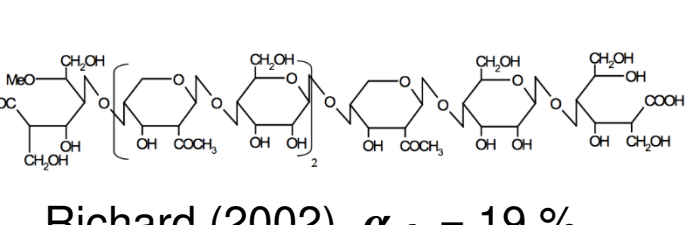
Stevenson (1982), $\alpha_{th} = 42\%$



Schulten and Schnitzer (1993), $\alpha_{th} = 13-16\%$



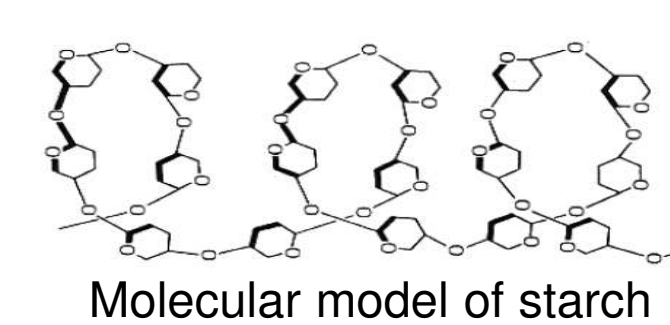
Andreux et al. (1994), $\alpha_{th} = 22-30\%$



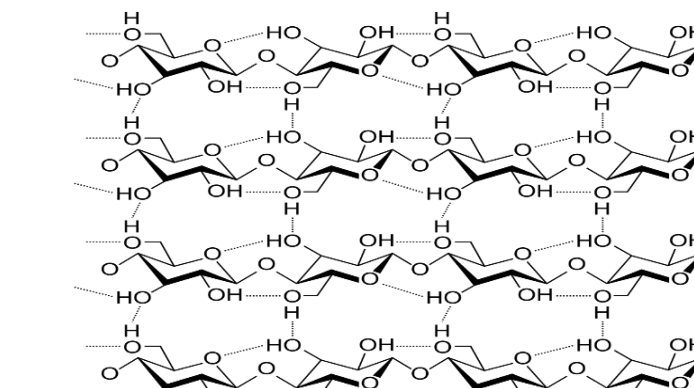
Richard (2002), $\alpha_{th} = 19\%$

2. Myriophyllum Spicatum (La Loire, France) and wheat carbohydrates (OBT WG) :

	Previous works [5]		This work	
	Wheat grains (OBT WG)	Alpha and microcrystalline cellulose	Carbohydrates* (wheat grains OBT WG)	Myriophyllum Spicatum (La Loire, France)
(α_{th})	30 %	30 %	31.6 %	30 %
(α_{iso})	31 ± 1 %	21 ± 1 % and 13 ± 1 %	31.1 ± 1.0 %	26.4 ± 0.5 %
(α_{th}) vs (α_{iso})	✓	≠	✓	≠



Molecular model of starch



Molecular model of cellulose

* Wheat carbohydrates :
- 85 % of starch ($\alpha_{th} = 30\%$)
- 15 % of maltose ($\alpha_{th} = 36.4\%$)

Conclusions:

- Exchangeable capacity model based on major constituent is validated for cereals matrices type.
- Molecular structure and conformation are responsible for the buried tritium (BT) form.

	Wheat grains (OBT WG)	Alpha and microcrystalline cellulose	Carbohydrates* (wheat grains OBT WG)	Myriophyllum Spicatum (La Loire, France)
NE-OBT (Bq.L ⁻¹) « soft way »	30.3 ± 2.6	-	24.3 ± 2.1	26.5 ± 2.3
NE-OBT (Bq.L ⁻¹) « hard way »	33.1 ± 2.6	-	32.7 ± 2.5	33.7 ± 3.1
NE-OBT deviation	8.5 ± 1.0 %	-	25.8 ± 2.9 %	21.3 ± 2.7 %

Conclusion: Analytical bias led by « hard way » isotopic exchange is verified according to the solubility properties of the studied matrix.

Perspectives

- ❑ Analytical concerns: Apple and simple carbohydrates (OBT WG)
- ❑ Speciation concerns: Evolution of the (α_{iso}) parameter depending on the degree of crystallinity of cellulose and environmental matrices applications.

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