PROBLEMS WITH STORAGE OF SAMPLES FOR OBT ANALYSIS

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- ^{14}C dating of archaeological samples
- geochronology
- monitoring ^{3}H in precipitation and ^{14}C in the atmosphere and biosphere
- monitoring ^{14}C in biological samples in the vicinity of nuclear power plant
- determination of the biogenic fraction in liquid fuels
- various applications of isotope methods (^{3}H, ^{14}C, stable isotopes ^{2}H, ^{18}O, ^{13}C)

Motivation

- Involved in monitoring ^{14}C in biological samples (and atm. CO_2) around the nearby nuclear power plant and it would be desirable to implement OBT determination in the same samples
- Croatia (and RBI) taking active part in DONES project (testing materials for fusion power plants → tritium is produced and should be monitored)

We took part in the 4th, 5th and 6th OBT inter-comparison studies (grass, fish, quinces)

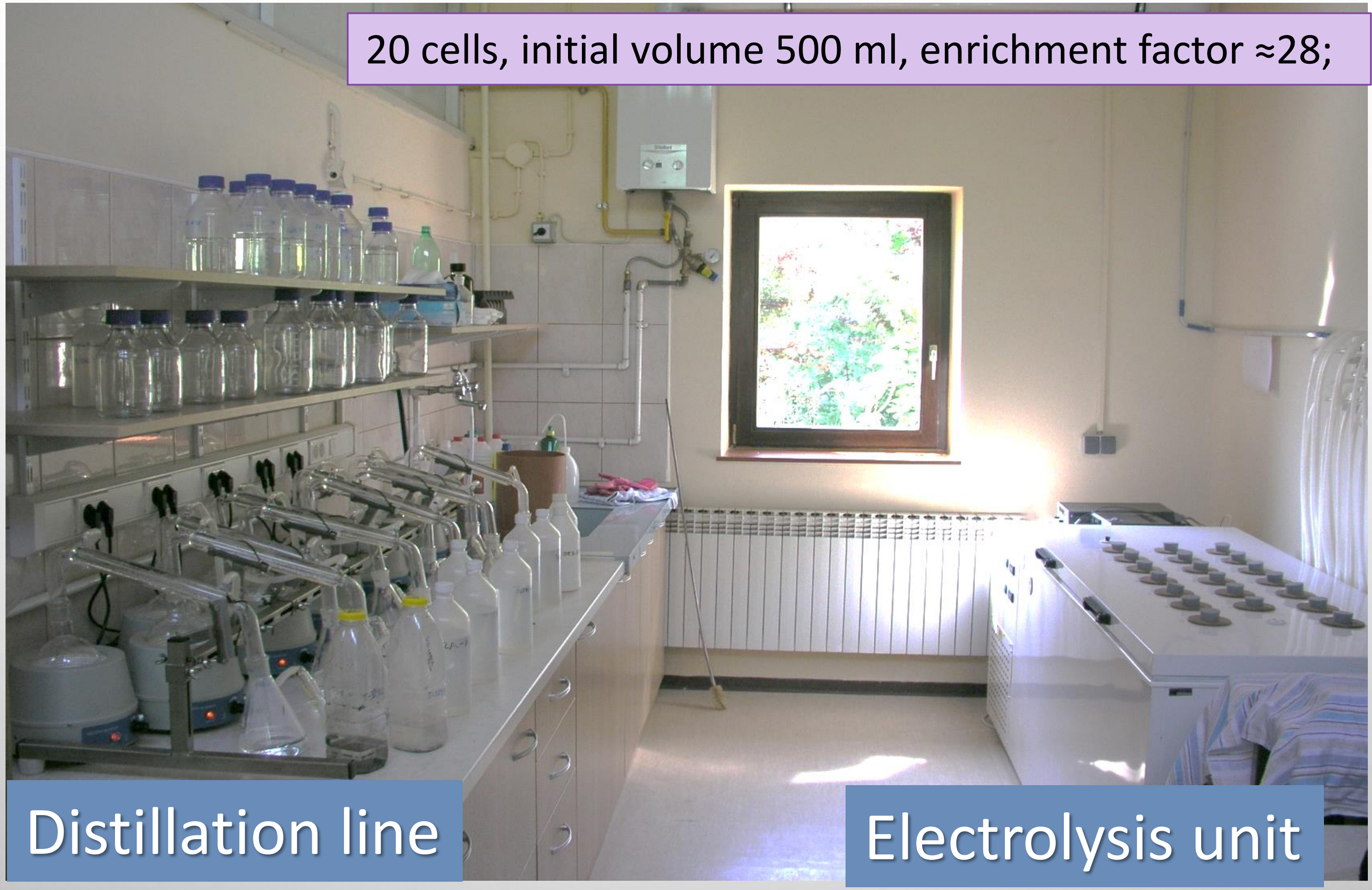


Methods

Activity concentration of ^{3}**H** was measured by gas proportional counting technique from 1976 until 2010 (CH_4 - measurement gas)

and since 2008 by liquid scintillation counting after electrolytic enrichment (or without it).

RBI – Electrolythic enrichment



Methodology of Tritium Determination in Aqueous Samples by Liquid Scintillation Counting Techniques , I. Stojković, N. Todorović, J. Nikolov, I. Krajcar Bronić, J. Barešić , U. Kozmidis Luburić, In TRITIUM - ADVANCES IN RESEARCH AND APPLICATIONS, ISBN: 971-1-53613-507-7 (e-Book), Nova Science Publisher 2018

RBI – LSC Measurement

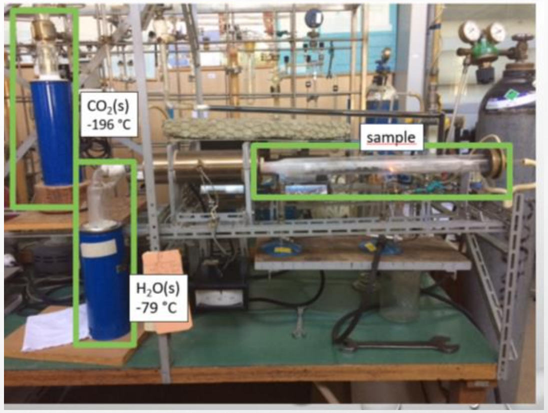
^3H – direct measurement
^3H – with el. enrichment
8 ml **H_20** + 12 ml UG LLT

*LSC-A ^{14}C – **absorbed CO_2**
*LSC-B ^{14}C – **C_6H_6**
LSC-F ^{14}C – **liquid organic fuels** (biogenic fraction)

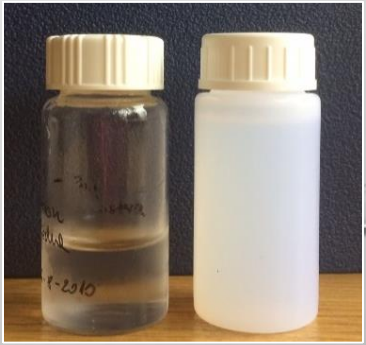
*ISO 17025/2017 since 2021

LSC-Quantulus 1220

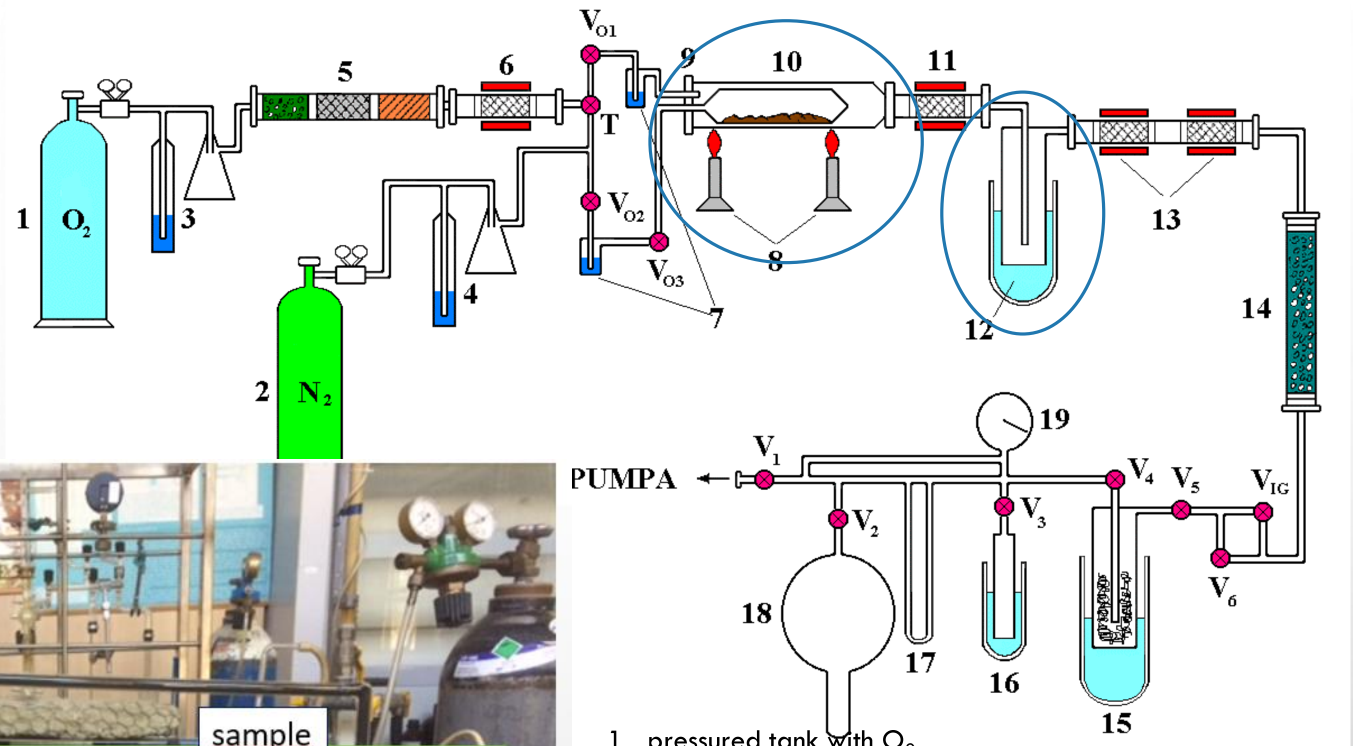
Sample preparation for OBT

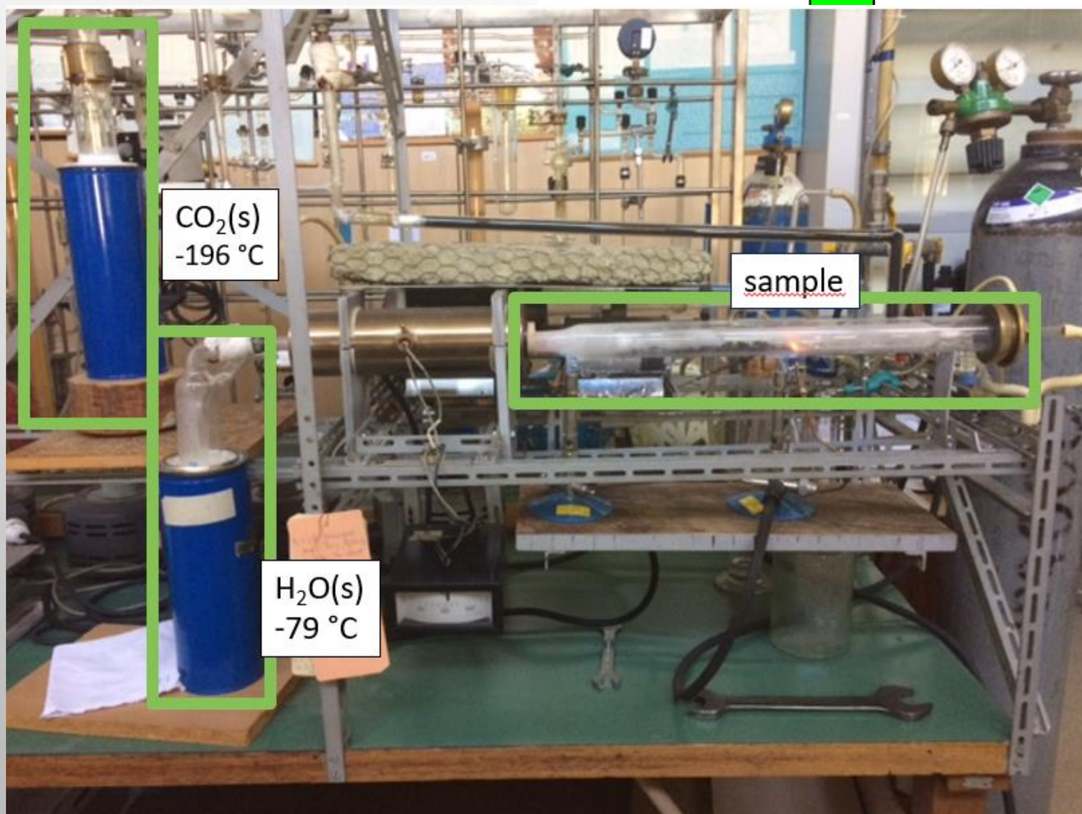


1. Cut the sample
2. Dry at 80 °C
3. Sample combustion
4. Collect water
5. Purification (Na_2O_2, $KMnO_4$)
6. Distillation
7. Cocktail preparation



Combustion line for organic samples





1 pressured tank with O_2
2 pressured tank with N_2
3 flow-rate indicator – bubbler, O_2
4 flow-rate indicator – bubbler, N_2
5 absorption tube for purification of O_2
6 furnace for purification of O_2 (filled with Ag wool, 450 °C)
7 bubblers for O_2/ N_2 flow indication in inner and outer tubes
8 burners
9 metal cap
10 quartz tube with the sample
11 oxidation furnace (filled with quartz wool, 750 °C)
12 water trap (-80 - -100 °C)
13 furnace for purification of CO_2 (filled with Ag wool, 450 °C)
14 absorption tube for purification of CO_2 (filled with MnO_2)
15 trap for CO_2 (filled with, Cu cuttings, -196 °C)
16 metal reservoir for CO_2 collection and storage
17 Hg-manometer for measurement of CO_2 pressure
18 glass bulb for CO_2 collection, volume of 12 L
19 digital pressure-meter

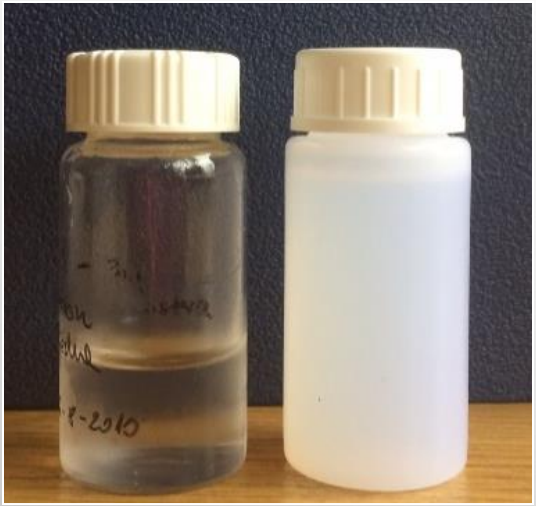
Purification and distillation

Distillation line

- Na_2O_2 ,
  - pH >8
  - ~2 mg/g
- $KMnO_4$,
  - colour of red wine
  - 2-10 mg/g
- distillation

Cocktail preparation and LSC measurement:

8 ml of **sample** with **12** ml of **UG LLT**
Measurement 400 minutes (in 8 cycles x 50 min)



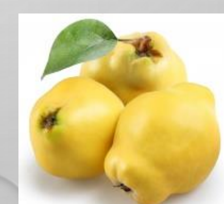
Sample storage

Samples of “grass” (2017 intercomparison) and “quinces” (2019 intercomparison) were analyzed after four and two years, respectively, as a part of laboratory quality control.

Grass (T-4832)
RBI result – 435 Bq/l
(2s = 90; 2u = 9)
Assigned value – 479 (15) Bq/l

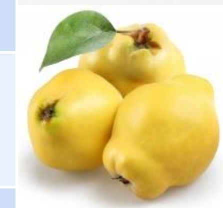
Quinces (T-5160)
RBI result – 50.2 Bq/l
(2s = 1.8; 2u = 2.2)
Assigned value – 48.6 (4.4) Bq/l

The samples had been kept in their original storage package, plastic bag sealed with tape, at room temperature.

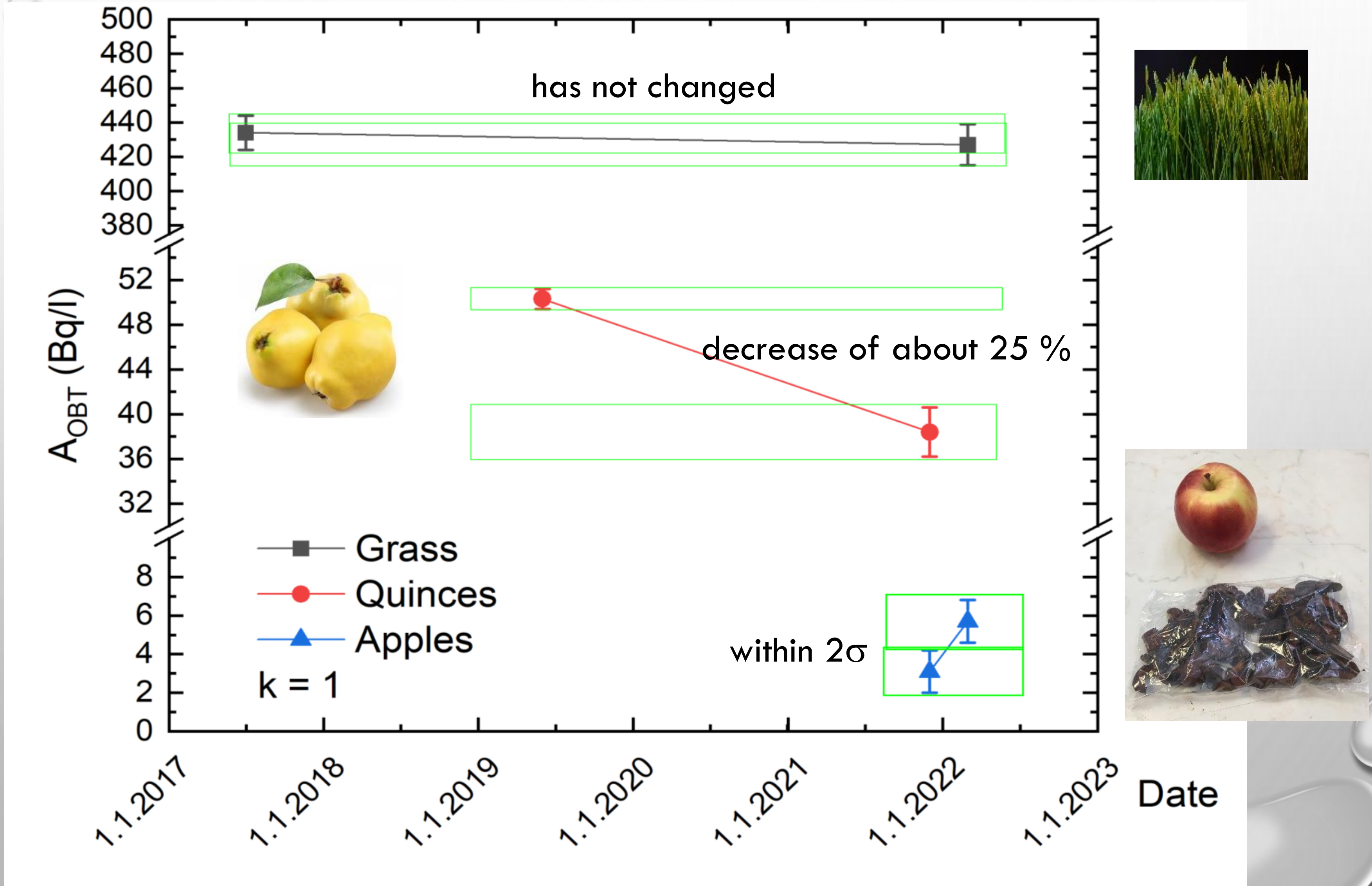


Issue with sample storage
Results

	First	Second
Grass T-4832	434 ± 20 Bq/l in July 2017	427 ± 24 Bq/l in March 2022
Quinces T-5160	50.3 ± 1.8 Bq/l in June 2019	38.4 ± 4.4 Bq/l in December 2021
Apples T-5551	3.1 ± 2.2 Bq/l in December 2021	5.7 ± 2.2 Bq/l in March 2022



Issue with sample storage
Results



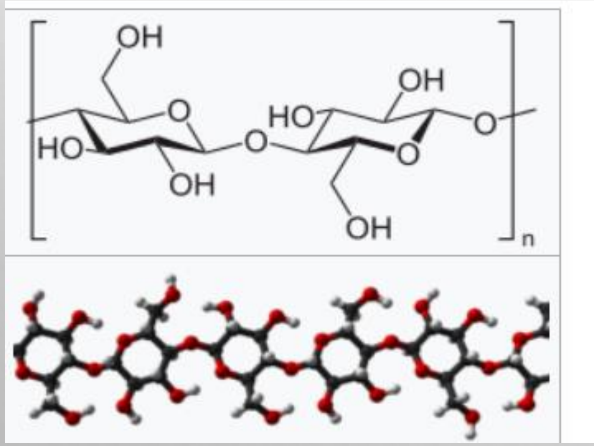
Disscusion

Cellulose and sucrose

Grass -

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a **polysaccharide** consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units.

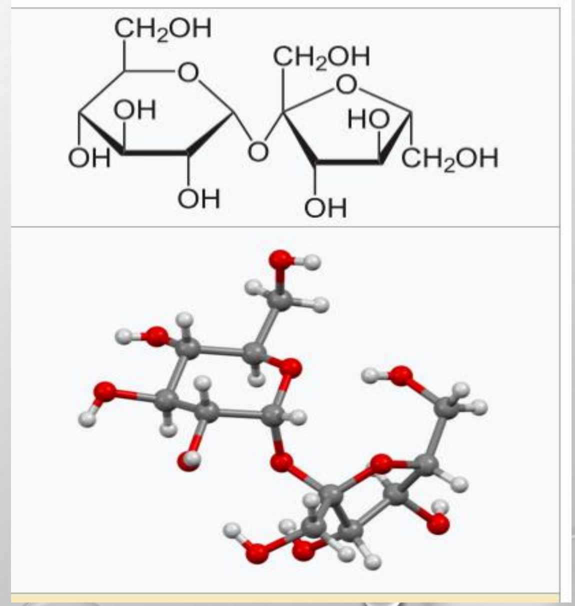
-Stable, difficult to decompose.



Quinces (fruit)

Sucrose is a **disaccharide** sugar composed of glucose and fructose subunits. It is produced naturally in plants and is the main constituent of white sugar. It has the molecular formula $C_{12}H_{22}O_{11}$.

-Soluble in water

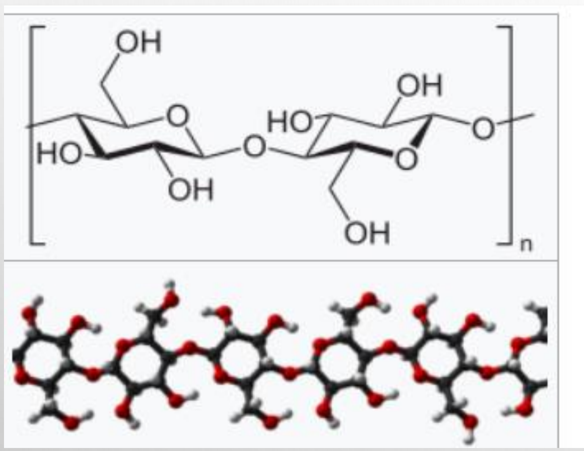


Disscusion

Cellulose and sucrose

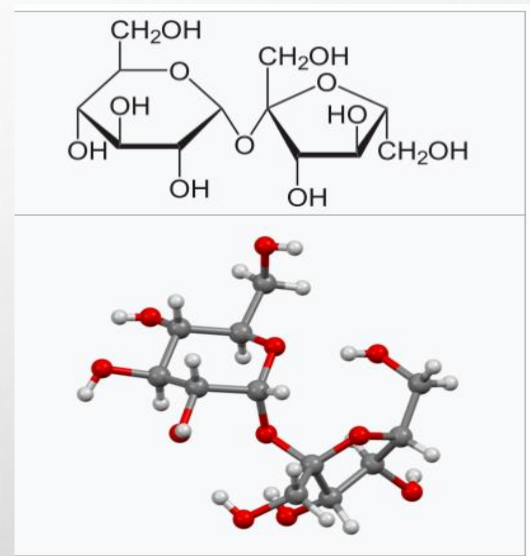
Cellulose (grass)

Sucrose (fruit)



-Cellulose is more stable.

-Sucrose prone to exchange on -OH groups with atmospheric water? (Precipitation 0.4 – 1.0 Bq/l)



Conclusions

- Samples for OBT analysis may overgone changes that influence result if not stored properly
- The susceptibility to change may depend on the composition of the sample

What to do next?

- Store samples in vacuum plastic bags in freezer?

Thank you for listening!
Questions and suggestions?

for listening

Sample preparations:

4th OBT int - separated fractions done with pyrolysis and oxidation

$+KMnO_4$ – only for colored samples

5th - both fractions analyzed together, dilution only in one analysis

$+Na_2O_2$ and $KMnO_4$ - always

6th – the same as 5th, no dilution required

$+Na_2O_2$ and $KMnO_4$ - always

Cocktail preparation and LSC measurement:

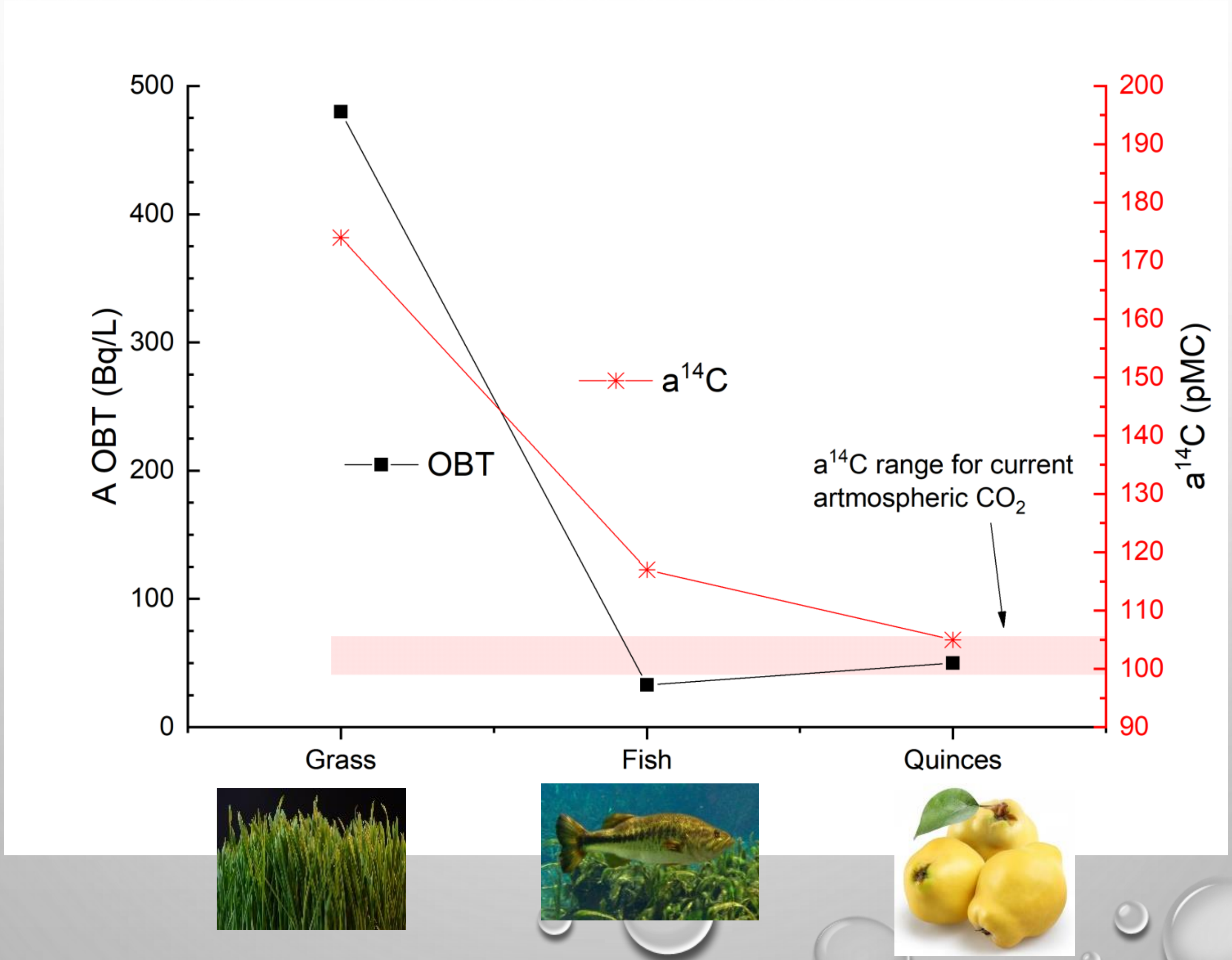
8 ml of **sample** with **12** ml of **UG LLT**

Measurement 400 minutes (total time, in 8 cycles)

Channels 25-253 (92% tritium and 82% background)

Efficiency 23.6 %

OBT and ^{14}C activity in the intercomparisons samples



4th OBT intercomparison exercise 2017 - grass

Repli-cate	Sample mass used for combustion (g)	Mass of combustion water recovered (g)	Activity in **Bq L^{-1}** of combustion water + uncertainty (k =2)	Activity in **Bq kg^{-1}** of dehydrated sample + uncertainty (k =2)*
1 2-Py	19.10	4.62	373 ± 8	190 ± 4
2 2-Ox		2.62	494 ± 8	252 ± 4
3 3-Ox	18.64	2.33	462 ± 8	235 ± 4
4 4-Py	17.99	5.89	434 ± 9	221 ± 5
5 4-Ox		0.91	412 ± 10	210 ± 5
mean ± 2s			**435 ± 90**	**222 ± 46**
mean ± 2u			**435 ± 9**	**222 ± 4**
Arithmetic mean all data			459 ± 30	237 ± 15
Assigned value - Arithmetic mean without outliers			**479 ± 15**	**247 ± 15**
Percentage deviation			-9 %	-10 %
Z score			-2.9	-3.3
Zeta score			-0.9	-1.0
^{14}C activity			**174 ± 4 pMC** **393 ± 10 Bq/kgC**	

* Hydrogen concentration provided by the organizers

5th OBT intercomparison exercise 2018 - fish

Replicate	Sample mass used for combustion (g)	Mass of combustion water recovered (g)	Activity in **Bq L^{-1}** of combustion water + uncertainty (k =2)	Activity in **Bq kg^{-1}** of dehydrated sample + uncertainty (k =2)*
1	10.25	5.84	30.3 ± 2.6	20.9 ± 1.8
2	10.50	6.50	30.8 ± 2.8	21.3 ± 1.9
3	10.13	6.19	30.3 ± 2.7	20.9 ± 1.9
4	1st comb. 8.95 2nd comb. 9.32	1st - 5.00 2nd - 5.92 P=1	29.1 ± 3.0	20.1 ± 2.1
5	same as No4	Dilution P=3.649	30.2 ± 2.0	20.8 ± 1.4
mean ± 2s			**30.1 ± 1.3 Bq L^{-1}**	**20.8 ± 0.9 Bq kg^{-1}**
mean ± 2u			**30.1 ± 2.6 Bq L^{-1}**	**20.8 ± 1.8 Bq kg^{-1}**
Arithmetic mean all data			40.3 ± 23.7	27.7 ± 15.7
Assigned value - Arithmetic mean without outliers			**32.8 ± 3.7**	**22.6 ± 5.5**
Percentage deviation			-8 %	-8 %
Z score			-0.7	-0.3
Zeta score			-0.7	-0.3
^{14}C activity			**117 ± 2 pMC 264 ± 6 Bq/kgC**	

* Hydrogen concentration provided by the organizers

6th OBT intercomparison exercise 2019 - quinces

Repli-cate	Sample mass used for combustion (g)	Mass of combustion water recovered (g)	Activity in **Bq L^{-1}** of combustion water + uncertainty (k =2)	Activity in **Bq kg^{-1}** of dehydrated sample + uncertainty (k =2)*
1	21.90	9.87	49.75 ± 2.11	25.57 ± 1.12
2	20.75	9.65	51.16 ± 2.87	26.29 ± 1.50
3	18.35	8.00	49.41 ± 2.03	25.39 ± 1.08
4	20.56	7.70	51.23 ± 2.00	26.33 ± 1.06
5	20.02	8.63	49.66 ± 2.07	25.52 ± 1.10
mean ± 2s			**50.24 ± 1.76**	**25.82 ± 0.90**
mean ± 2u			**50.24 ± 2.24**	**25.82 ± 1.18**
Arithmetic mean all data			49.1 ± 1.8	25.2 ± 1.5
Assigned value - Arithmetic mean without outliers			49.1 ± 1.8	25.2 ± 1.5
Percentage deviation			2.3 %	2.4 %
Z score			1.2	1.0
Zeta score			0.5	0.4
^{14}C activity			**105 ± 1 ‰** **238 ± 2 Bq/kgC**	

* Hydrogen concentration provided by the organizers