Laser-based radiocarbon analyzer

Saverio Bartalini - InnovHub - 29 Nov 2023

Outline

Il Radiocarbonio e la tecnica SCAR

- Potenzialità e limiti della rivelazione del radiocarbonio
- La tecnica SCAR

Lo strumento C14-SCAR

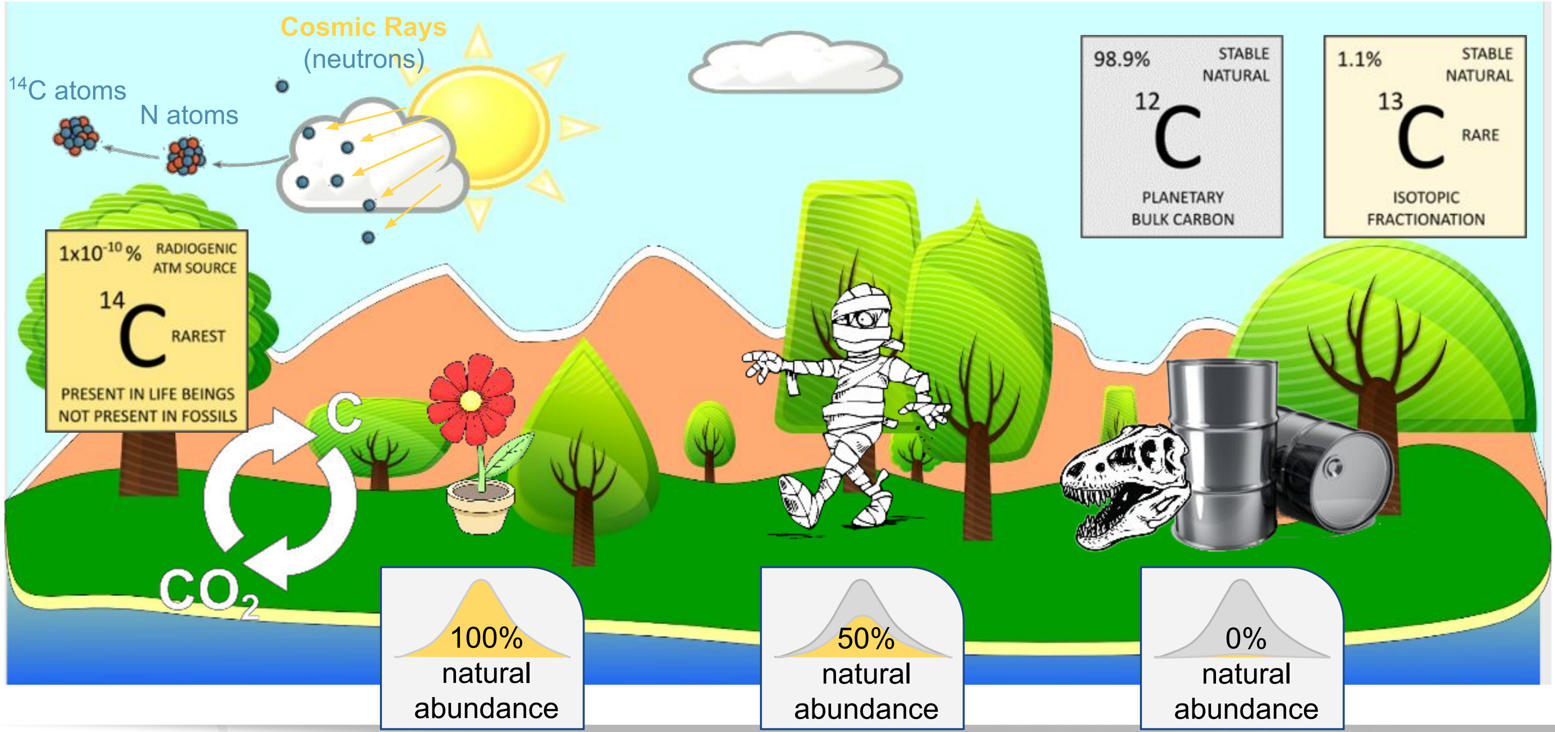
- Descrizione dello strumento
- Descrizione del processo di misura
- Futuri sviluppi

Applicazioni e prestazioni

- Biogenic content in fuels and textiles
- Performances attuali e future

PPQ SENSE

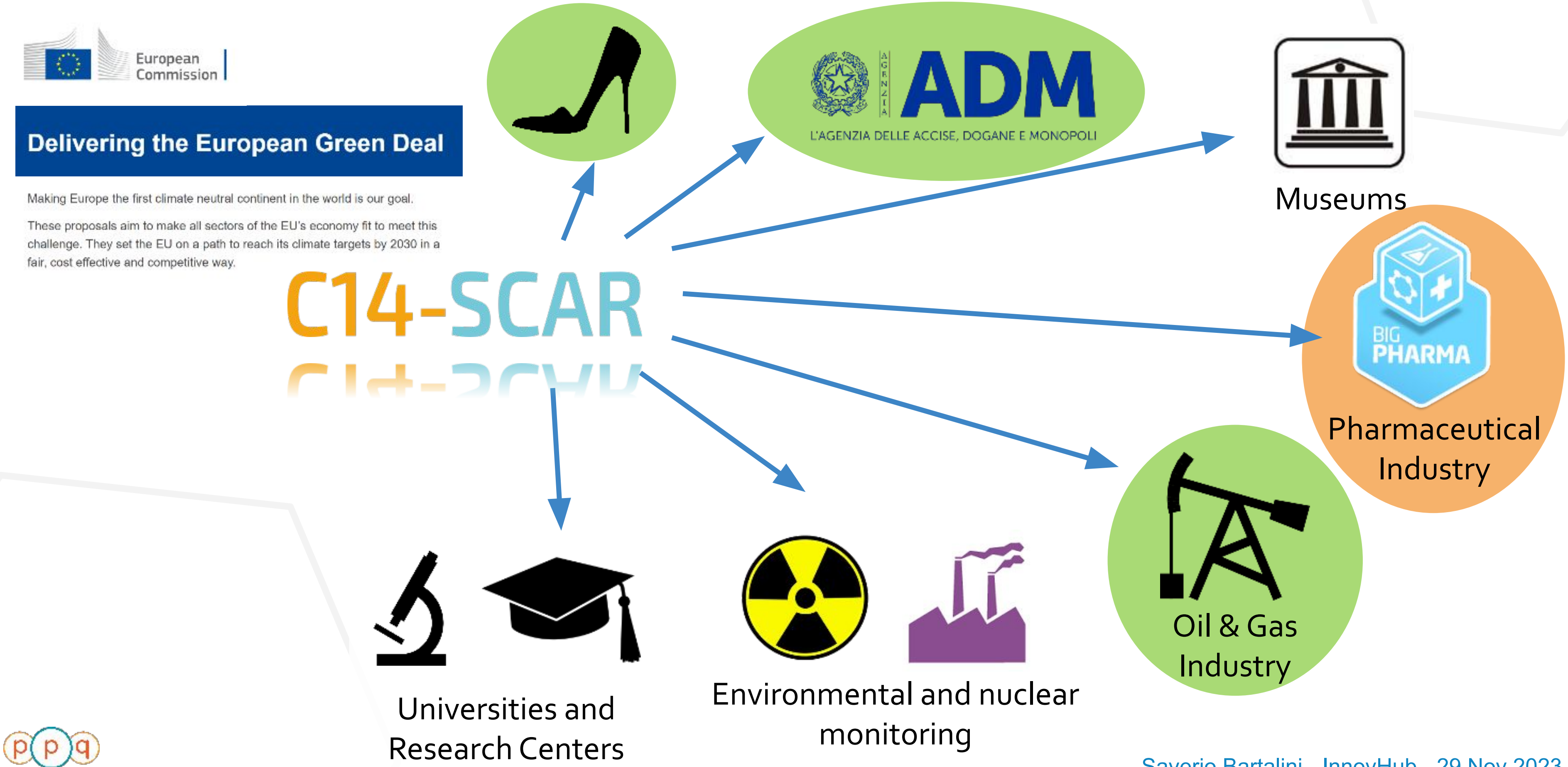
Introducing radiocarbon (^{14}C): **the marker of life.**



Modern - Bio | **Ancient** | **Fossil**

Application Example: Measuring the radiocarbon content of a fuel (or plastic) allows to determine if it is produced from **fossil oil** or from **renewable biogenic source** material.

Analysis of bio-based content in any material.



New directives in EU

COMMISSIONE
EUROPEA

Bruxelles, 5.6.2023
C(2023) 3513 final

REGOLAMENTO DELEGATO (UE) …/... DELLA COMMISSIONE

del 5.6.2023

sulla metodologia per determinare la quota di biocarburanti e di biogas per il trasporto derivanti da biomassa trattata con combustibili fossili in un processo comune

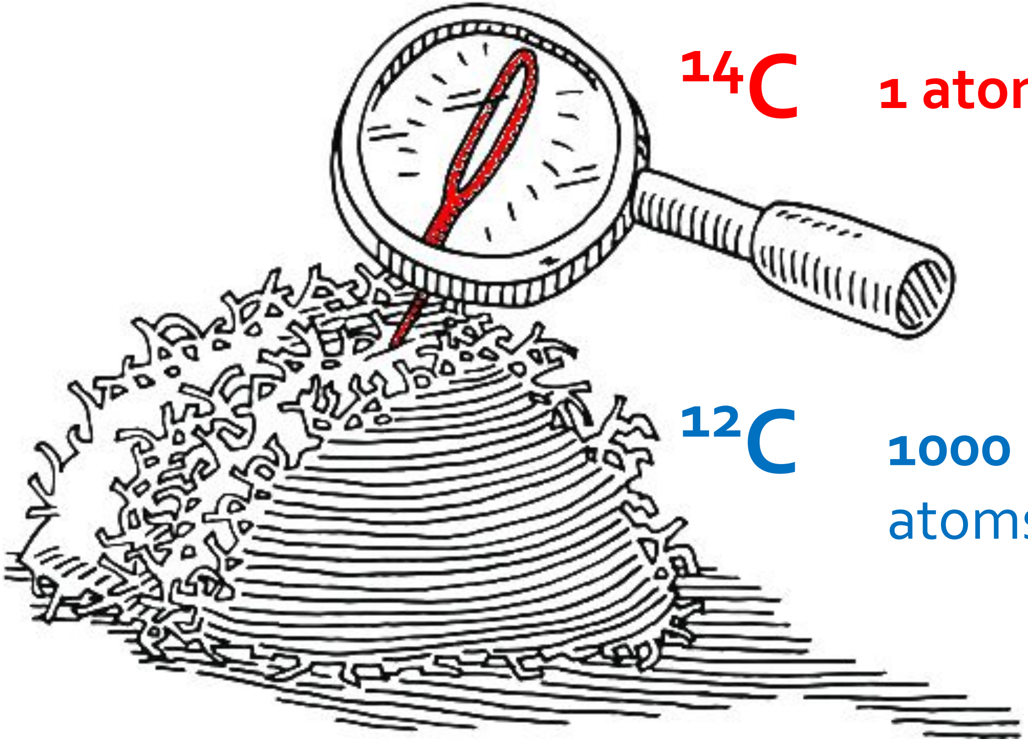
Per trovare un equilibrio tra i costi di verifica e la precisione delle prove, l'atto delegato consente agli operatori economici di usare un metodo di prova armonizzato comune basato sul radiocarbonio (14C), o di usare metodi di prova propri, caratteristici dell'impresa o del processo. Tuttavia, per garantire l'applicazione di un metodo di prova comune sul mercato, gli operatori economici il cui metodo principale è diverso da quello del radiocarbonio (14C) dovrebbero applicare periodicamente quest'ultimo agli output per verificare la correttezza del metodo principale. Inoltre, per consentire agli operatori economici di abituarsi a usare il metodo del radiocarbonio (14C) insieme a un altro metodo di prova principale, nel primo anno di applicazione di questa metodologia è previsto un certo grado di flessibilità in merito alla percentuale accettabile di deviazione tra i risultati delle prove di verifica principali e secondarie,

The challenge of measuring radiocarbon concentration

1x10^{-10} % RADIOGENIC ATM SOURCE

^{14}C RAREST

PRESENT IN LIFE BEINGS
NOT PRESENT IN FOSSILS



^{14}C 1 atom

^{12}C 1000 billions atoms

The detection of radiocarbon (^{14}C) is really difficult, due to its extremely low concentration in nature.

The problem: a technology bottleneck

The detection of ^{14}C is **really challenging**, due to its extremely **low concentration** in nature.

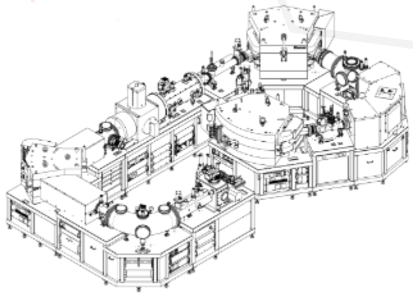
The required sensitivity is of **1 part in 10^{15}**

Currently used technologies have been conceived 40 year ago

AMS: Accelerator Mass Spectrometry

LSC: Liquid scintillation counting

LSC cocktail



AMS facility

AMS and LSC **cannot support** the **future market needs** driven by the **green revolution**:

Expensive

> 2M€ (AMS)
Consumables (LSC)

Bulky

>10m^2 footprint (AMS)
> 3 tons

Complex

High maintenance (AMS)
Carcinogens (LSC)
High Voltages (AMS)

Slow

> 12h wait
from sample to result

Fact1: AMS facilities are just ~20 in EU and ~100 worldwide

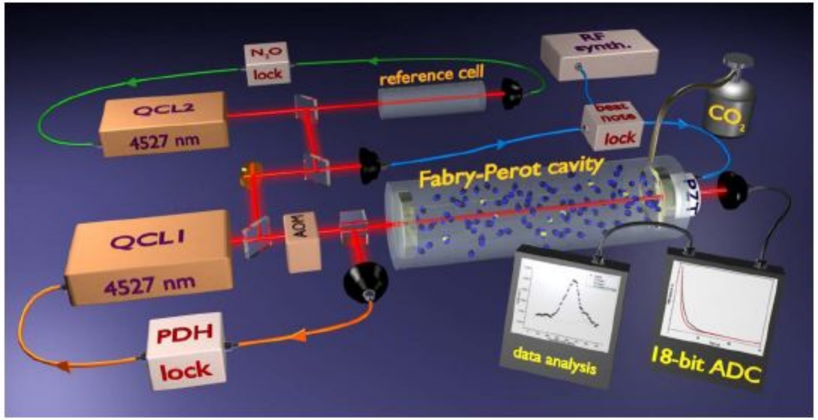
Fact2: a single LSC measurement on a small sample can take up to 10 hours

The solution:
Saturated-absorption CAvity Ring-down (SCAR) spectroscopy

ppqSense has developed an highly innovative, efficient, **laser-based** technique for measuring ^{14}C concentration.

SCAR sets the **world record** in the detection sensitivity for a given molecular specie ($^{14}CO_2$) with any spectroscopic technique.

SCAR exploits the latest photonics solutions, such as **Quantum Cascade Lasers** (QCLs), provides room-temperature operation with **no moving parts**.



High-reflectivity supermirrors

Ultra-low-noise electronics

Gas-phase storable sample

Patent WO2014170828A1, "Apparatus and method for measuring the concentration of trace gases by SCAR spectroscopy".

Patent WO2017055606A1, "Method for measuring the concentration of trace gases by SCAR spectroscopy"

Patent WO2016067241A1 ,"Low-noise current source"

PATENTED

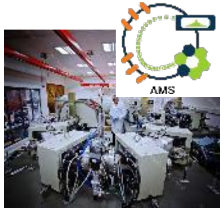
The product: the world first radiocarbon spectrometer

ppq SENSE

14C SCAR

- ✔ Compact and transportable Equipment
  < $2m^2$ footprint; <500kg weight
- ✔ Low power consumption (< 1kW)
- ✔ Maintenance-free operation
- ✔ The best sensitivity (<1 pMC)
- ✔ Unprecedented dynamic range
  from fossil to highly enriched samples
- ✔ Fast measurements
  10 minutes, 30 minute with sample preparation
- ✔ Works with any solid or liquid material

The competition: C14-SCAR provides the best precision with a fraction of cost and size



Accelerator Mass Spectroscopy (AMS) detects isotope ratio of ^{12}C, ^{13}C, ^{14}C ions. The use has increased, but its **economic and energy costs** make only ~20 instruments available in Europe.

Liquid Scintillation Counting (LSC) uses β-decay counting, but with **insufficient precision** for monitoring applications, thus requiring large sample amounts, high isotope doses and difficult measure automation.

SCAR detects absorbed IR photons. It is demonstrated and sold for ^{14}C quantification for many applications. Qualification for spread use require **less sample needs, better modularity and automation.**

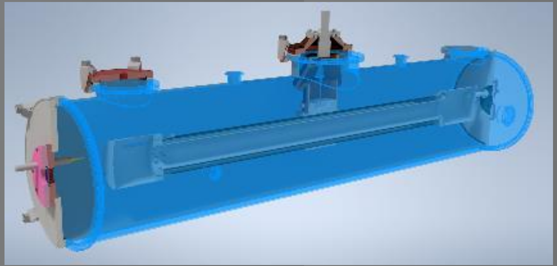
	14C SCAR	Ionplus AMS	HIDEX LSC
Size	✓	✗	✓
Weight	✓	✗	✓
Minimum sample needs	✓	✓	✗
Precision measurement	✓ **HIGH**	✓ HIGH	✗ LOW
Dynamic range	✓ **VERY HIGH**	✗ LOW	✓ HIGH
Cost (€)	✓ **< 600 k**	✗ 1.5 – 5 M	✓ 150 k
Sample handling and preparation	✓ **Fully automatic**	✓ automatic	✗ manual

The instrument

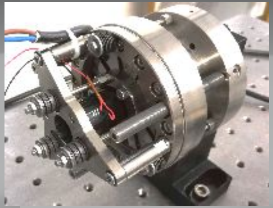
14C SCAR

PPQ SENSE

The development of the instrument.



Completely re-designed SCAR
high-finesse optical cavity

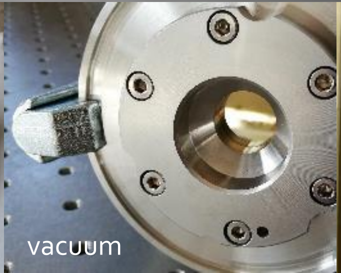


3 QubeCL systems control
most of the instrument
1 QubeDT is employed

QUBE CL SYSTEM

hundreds of hours
of testing

cryogenic



vacuum

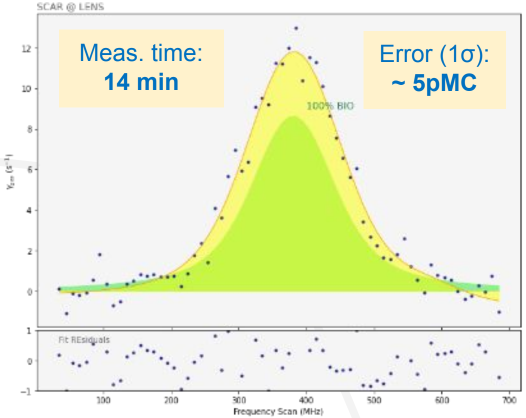
mechanical
stability

heat
management

ppq SENSE

3 SCAR generations

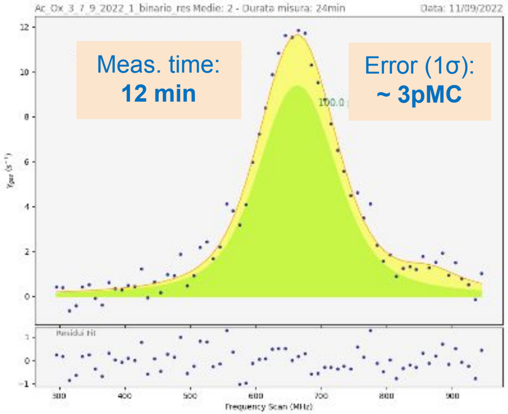
2015 SCAR**2**



Meas. time:
14 min

Error (1σ):
~ 5pMC

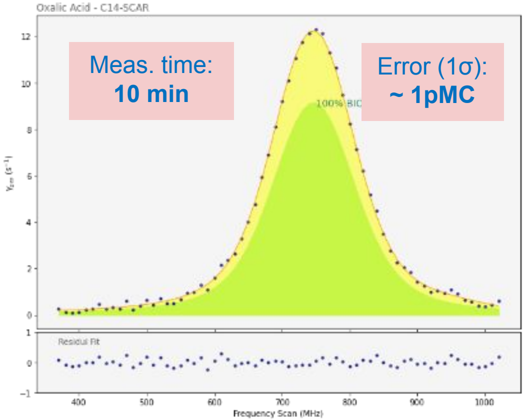
2019 SCAR**3**



Meas. time:
12 min

Error (1σ):
~ 3pMC

2021 SCAR**4**

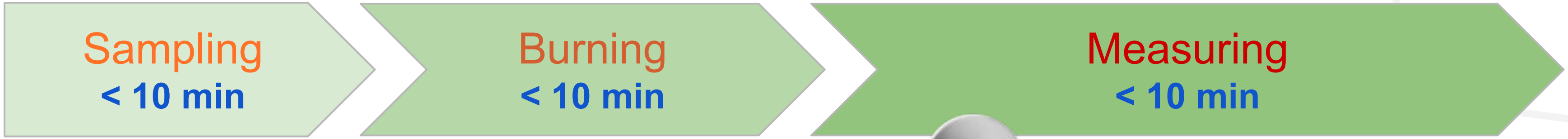


Meas. time:
10 min

Error (1σ):
~ 1pMC

ppq SENSE was born in 2016 — C14-SCAR hits the market

Sample preparation and measurement

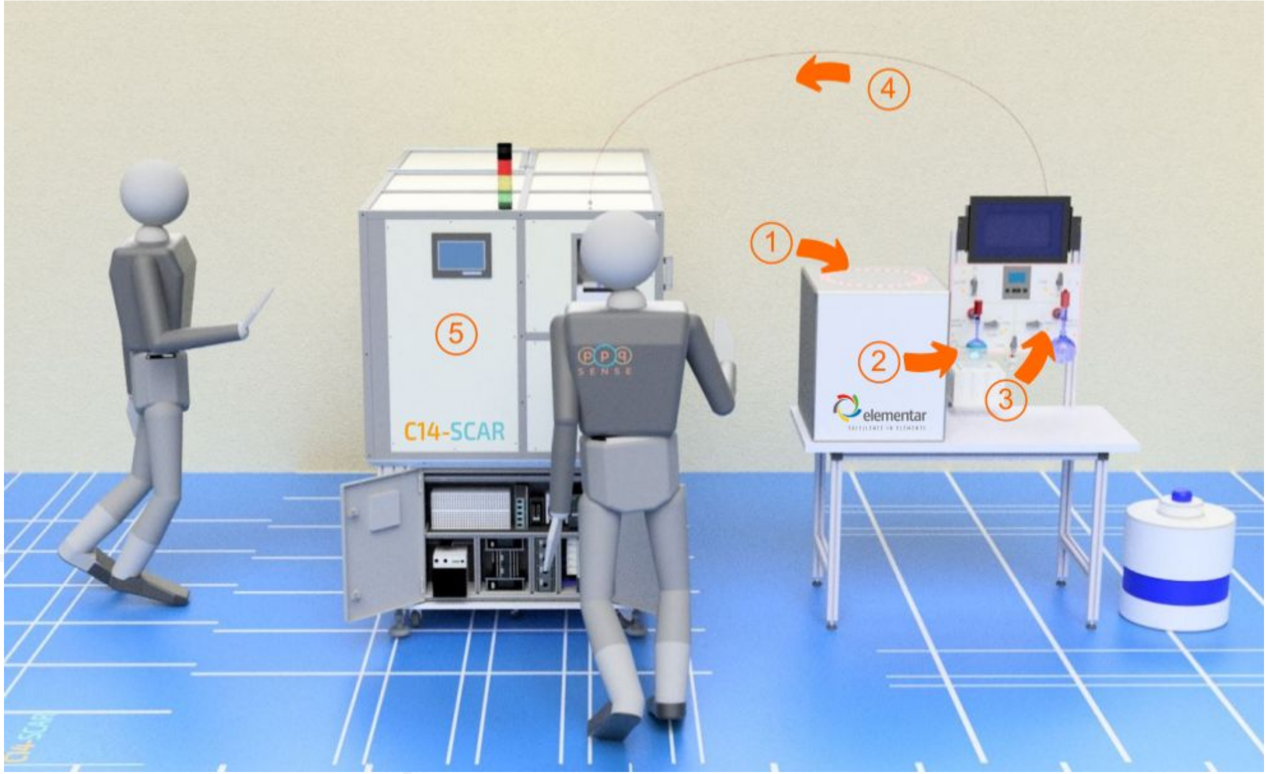


Elemental Analyzer
Vario EL cube

CO_2 gas

Solids	Liquids	Gases
Plastics Wood Fabrics	Fuels Ethanol ...	CO_2 CH_4 ...

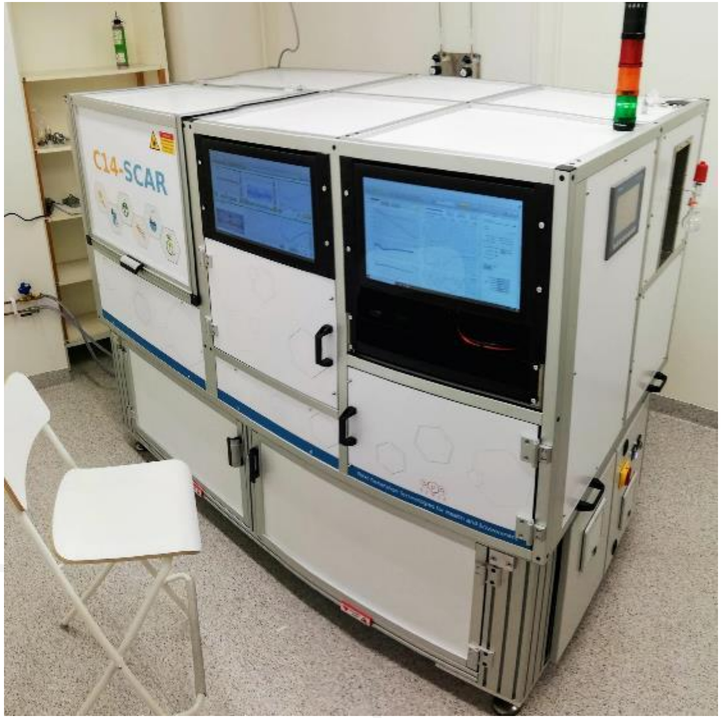
The measurement process



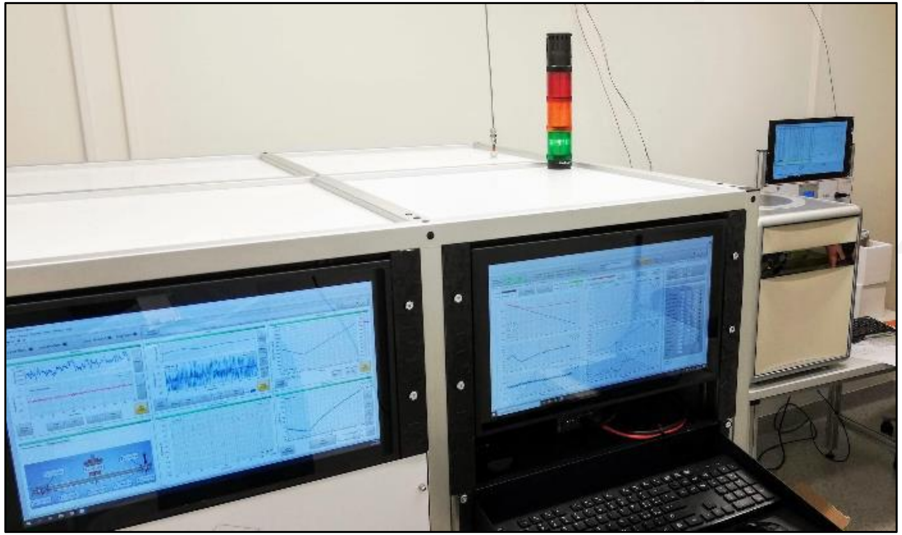
Process description and consumables

1. Sample preparation
   Tin cups
1. Sample Combustion
   He, O_2 (purity level 5.0)
1. Separation of CO_2 from He
   Present: LN (5 litres/day)
   Future: LN-free automatic process
1. Filling of the C14-SCAR cavity
2. Measurement

C14-SCAR001 is now working.



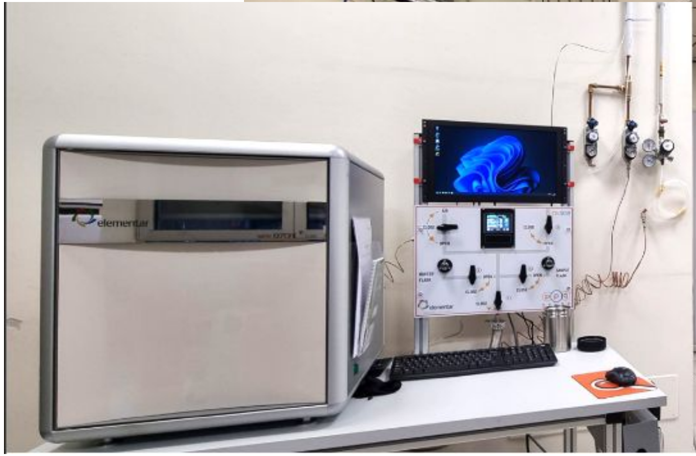
RI.
SE



ppq
SENSE

C14-SCAR s/n003
@ ArsTinctoria

ARS TINCTORIA



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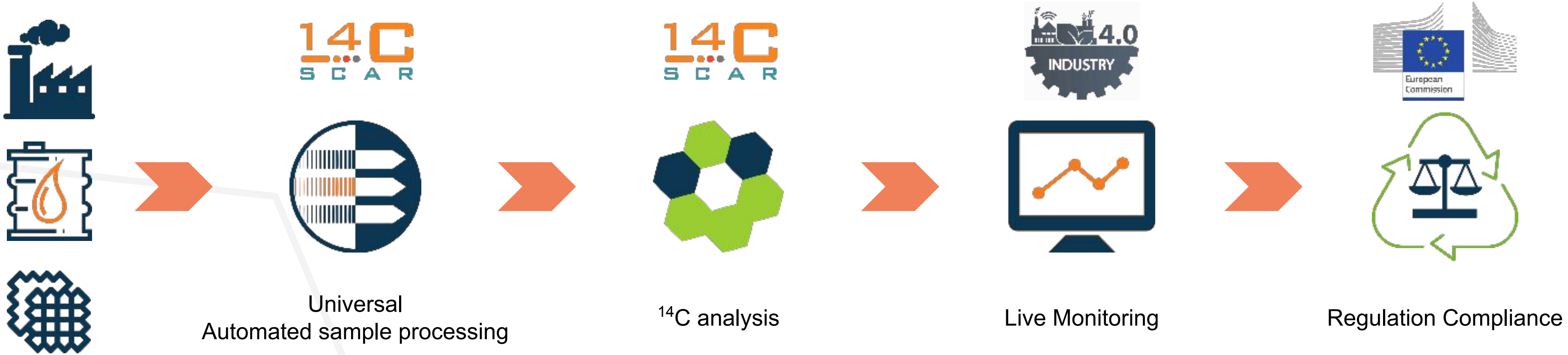
New developments (1/3): Fully automated analysis

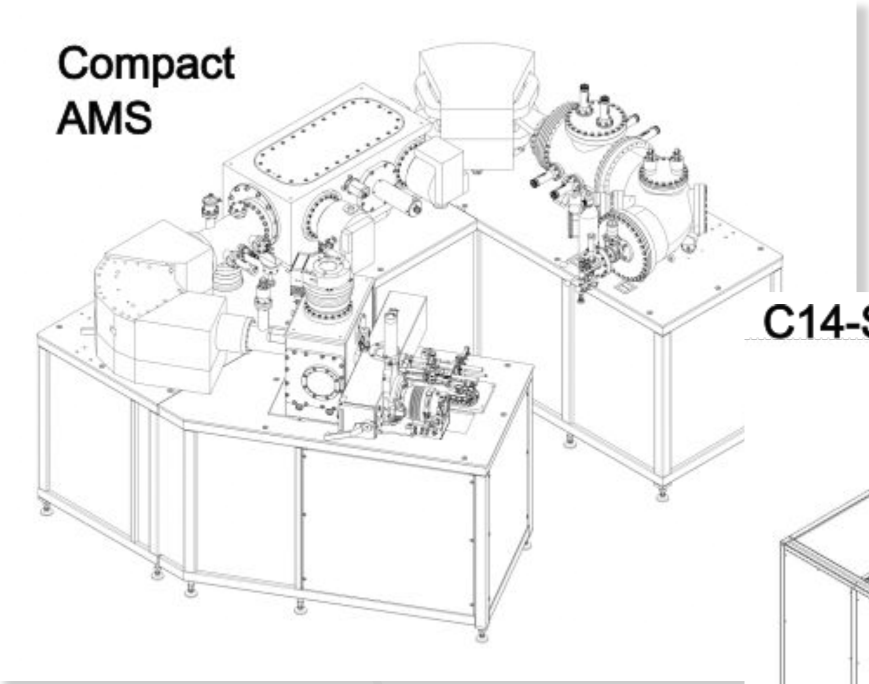
We plan to develop the first universal and fully automated process for biogenic fraction measurement

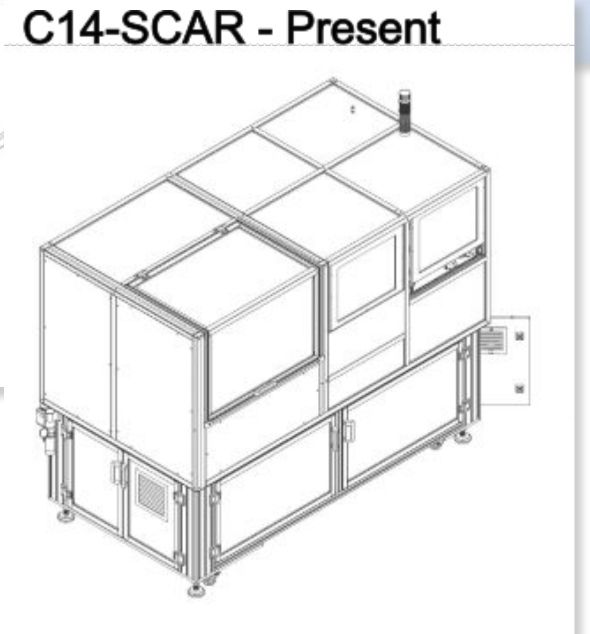
- ✔ From sample to result in < 30 min
- ✔ Continuous sample loading
- ✔ Maintenance-free non-stop operation over weeks
- ✔ Data sharing for live monitoring



A seamless process from sample to certified result

New developments (2/3): Compact Version





New features:

10x smaller optical cavity volume

Required ^{14}C mass < 500µg

Total weight < 300 kg

Cryogen-free operation

Really **deployable on the field**

Price **< 500k€**

ppq SENSE

New developments (3/3): Integrated systems for radiocarbon analysis

NC TECHNOLOGIES

ppq SENSE

EC 8020

CHNS Organic Elemental Analyzer

8070 Air CO2 + Portable Sampler

Atmospheric CO_2 analysis

IDMicro EA

IRMS for **C**, N, O and S isotopic and elemental analysis.

δ13C Analysis

14C SCAR

^{14}C Analysis

Complete solution for $^{12}C/^{13}C/^{14}C$ isotope ratio in liquids and solids

Complete solution for $^{12}C/^{13}C/^{14}C$ isotope ratio in atmospheric air

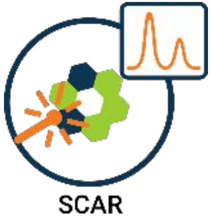
In progress: Method Accreditation

EN 16640:2017 regulates measurement methods for the bio-based carbon content determination using the radiocarbon method. The standard currently includes 3 methods:

- AMS - Accelerator Mass Spectroscopy
- LSC - Liquid Scintillation Counting
- BI - Beta Ionization

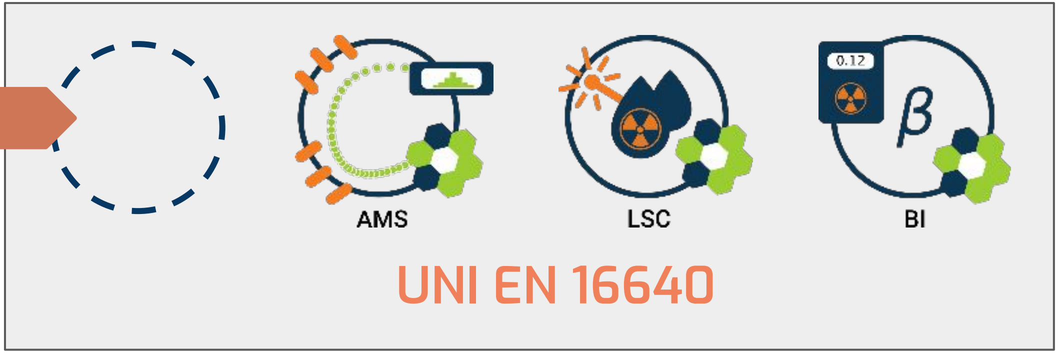
- ✔ Gives a **legal validity** to the SCAR method
- ✔ Enables SCAR for forensic use
- ✔ Makes SCAR a **reference method** for calibrating other techniques

We have activated the process to include the SCAR method in the EN 16640 standard



Method D - Saturated-absorption CAvity Ring-down (SCAR)

Integration Proposal to EN 16640



Applications

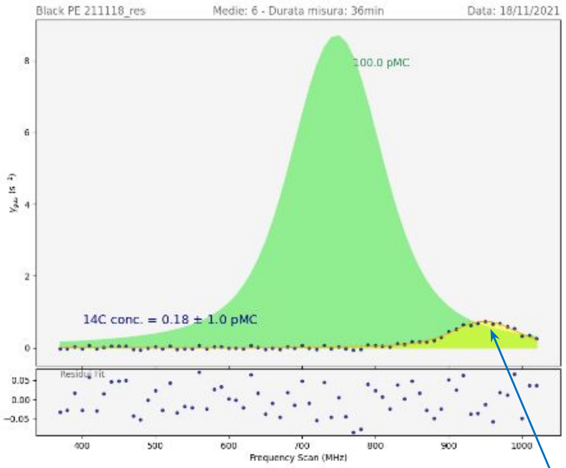
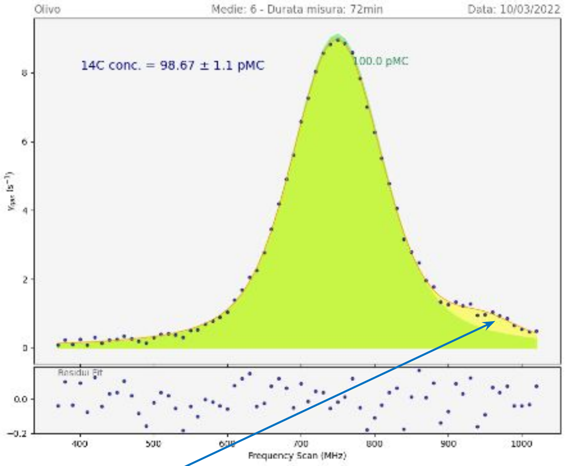
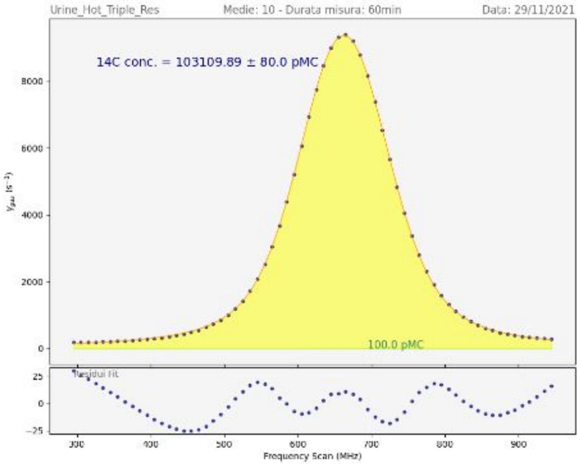
14C

SCAR

pp q
SENSE

Measuring in the 0…1 Modern range, and beyond

The method is linear across a wide dynamic range: highly enriched samples (up to 1000 modern) can be measured without any significant memory effect.

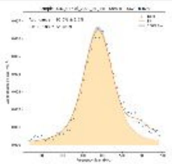
Fossil material: 0 pMC	Modern biogenic material: 100 pMC	Enriched human urine: ~10^5 pMC
		

Interfering N_2O line

The presence of the interfering N_2O line can systematically bias low-mole-fraction measurements

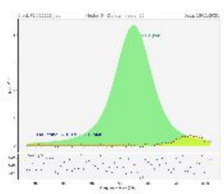
C14-SCAR

RI. SE
Research Institutes of Sweden



Biodiesel/Diesel Mixtures

Plastics

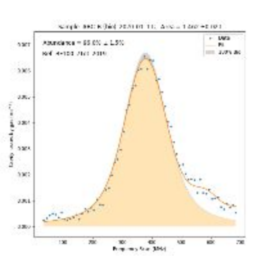


Italian Ministry for Environment

Consiglio Nazionale delle Ricerche

MINISTERO DELL'AMBIENTE
E DELLA TUTELA DEL TERRITORIO E DEL MARE

Bio-cherosene
for aviation

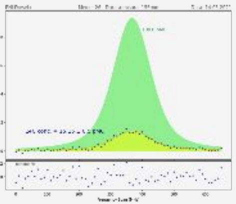


E-RIHS.it
EUROPEAN RESEARCH INFRASTRUCTURE
FOR HERITAGE SCIENCE

ICOS
INTEGRATED CARBON OBSERVATION SYSTEM

eni

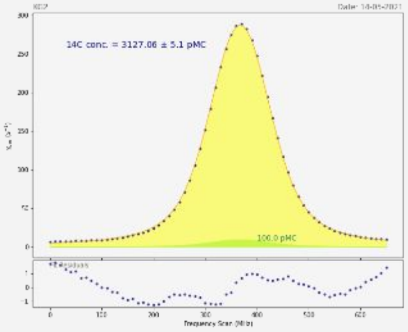
Analysis of
commercial
bio-fuels



European Commission

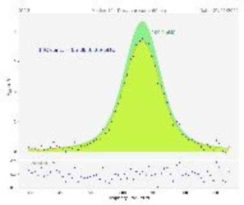
European Commission
DG Joint Research Centre – JRC
Directorate G
Nuclear Safety & Security

Graphite from
nuclear
power plant



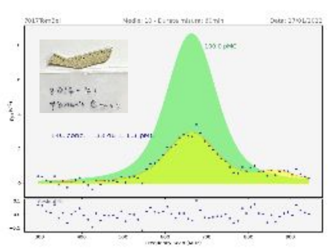
Bio-fuel
for aviation

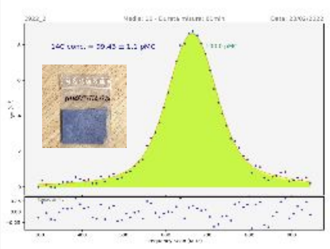
NESTE



Determination
of biogenic
carbon
content in
fashion
materials

ARS TINCTORIA





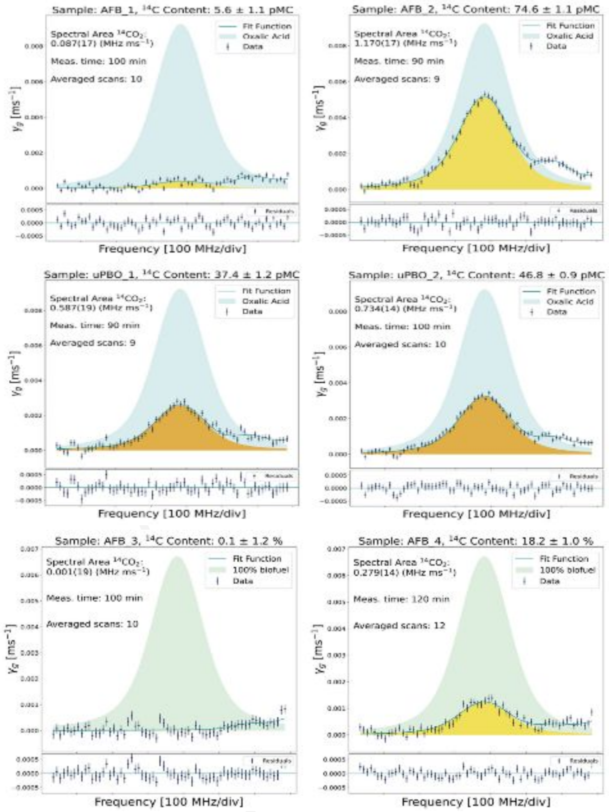
Biogenic Fraction Determination in Fuel Blends

Giulia, M., Santi, D., Bartalini, S., Cancio, P., Galli, I., Giusfredi, G., Haraldsson, C., Mazzotti, D., Pesonen, A., & de Natale, P., "Biogenic Fraction Determination in Fuel Blends by Laser-Based $^{14}CO_2$ Detection", *Advanced Photonics Research*, ***2*** (3), 2000069 (2021).

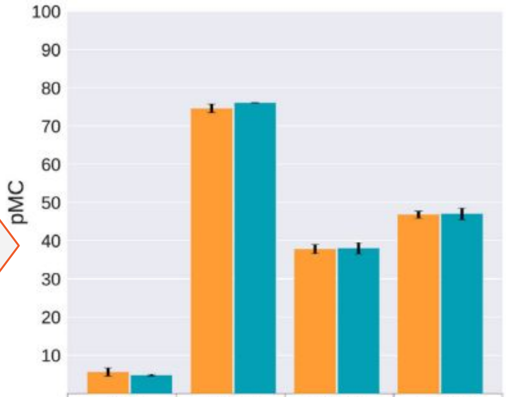
HEFA fuel
Jet A-1 fossil
blend
(Neste Corp.)

Upgraded
pyrolysis
bio-oil
(RISE Inst.)

HEFA fuel
Jet A-1 fossil
blend
(Aeronautica
Militare)

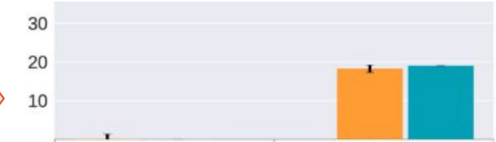


AMS
intercomp.



	AFB_1	AFB_2	uPBO_1	uPBO_2
SCAR	5.6 ± 1.1	74.6 ± 1.1	37.8 ± 1.2	46.8 ± 0.9
AMS	4.74 ± 0.20	76.04 ± 0.08	38.0 ± 1.5	47.0 ± 1.5

mass
mixing
ratio



	AFB_3	AFB_4
SCAR	0.1 ± 1.2	18.20 ± 1.0
MMR	0.0 ± 0.0	18.98 ± 0.01

Instrument:
SCAR2

Meas. time:
140 min

Uncertainty:
~ 1 pMC

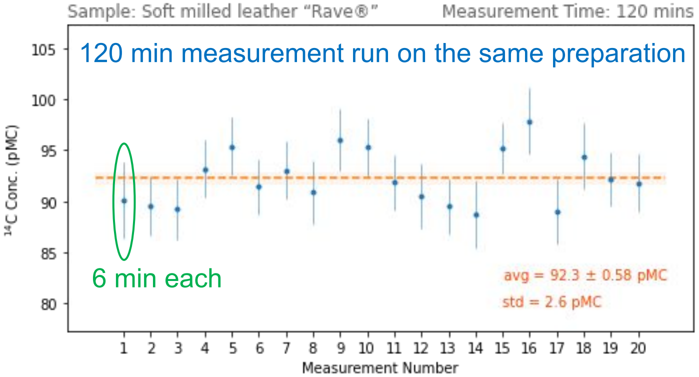
Biobased Carbon Quantification Technique on Leather, Artificial Leather, and materials used in the fashion industry

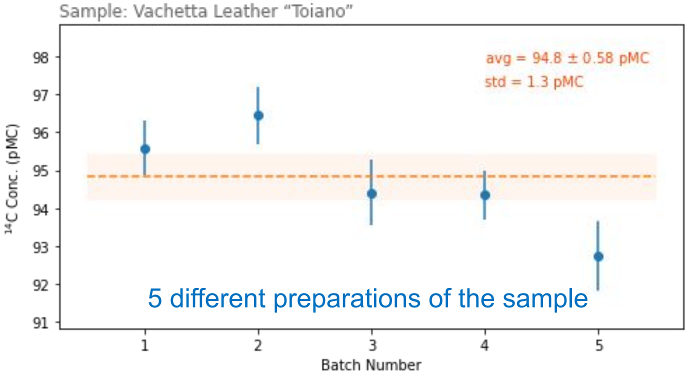
Carcione, F., Defeo, G. A., Palomino, E., Galli, I., Bartalini, S., and Mazzotti, D., "Material Circularity: A Novel Method for Biobased Carbon Quantification of Leather, Artificial Leather, and Trendy Alternatives", *Coatings* **13** (2023).

7 different materials have been analyzed (SCAR3). In this case, due to the typical **sample dishomogeneity**, the repeatability of the overall process, including the sample preparation (5 times), is also studied.

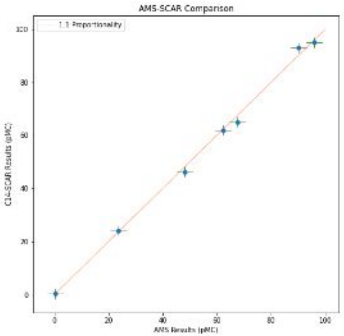
LVMH

CHANEL





Sample	SCAR			AMS		AMS-SCAR
	^{14}C content (pMC)	Uncertainty (pMC)	Repeat. σ (pMC)	^{14}C content (pMC)	Uncertainty (pMC)	Discrepancy (pMC)
EVA "Vegan" sole	**0.2**	0.4	0.6	**<0.44**	**--**	<0.24
Desserto® "Cactus leather"	**24.1**	0.3	0.6	**23.6**	**0.1**	-0.5
Coated Patent Leather	**47.1**	1.1	2.4	**48.1**	**0.2**	+1.0
Mix synthetic-natural fabric	**61.0**	0.6	1.2	**62.3**	**0.2**	+1.3
Fully syntan tanned Leather	**65.6**	0.3	0.6	**67.6**	**0.2**	+2.0
Soft milled leather "Rave®"	**92.6**	0.5	1.0	**90.1**	**0.3**	-2.5
Vachetta Leather "Toiano"	**94.8**	0.6	1.3	**96.0**	**0.3**	+1.2

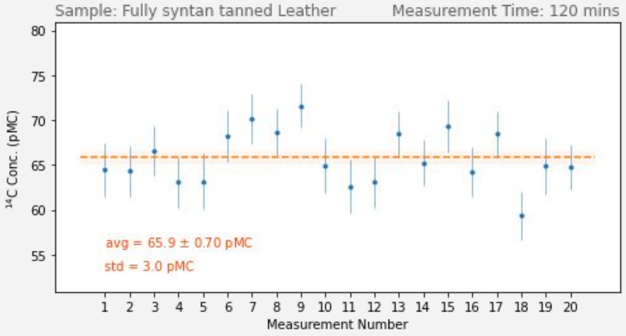


C14-SCAR consolidated performances

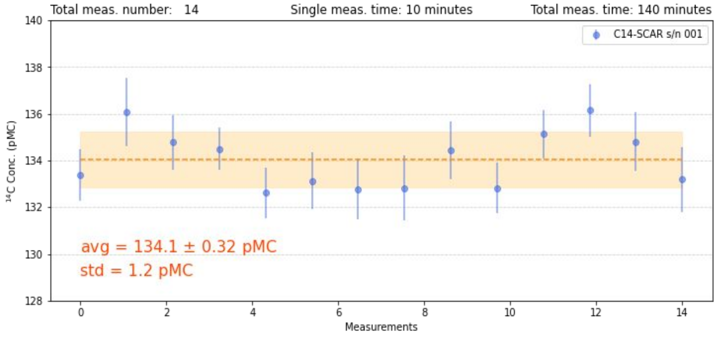
C14-SCAR is a newborn instrument: its performances are yet improving

Averaging time (min)	Achieved Precision (pMC)	
	Prototype	C14-SCAR
12	3.3	1.5
24	2.3	1.1
60	1.4	0.8
240	0.9	0.3

SCAR3 (prototype)



SCAR4 (C14-SCAR instrument)



Short-term

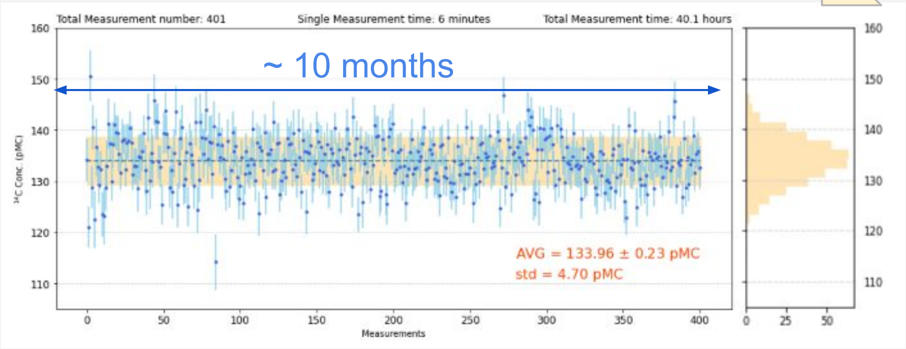
single sample prep

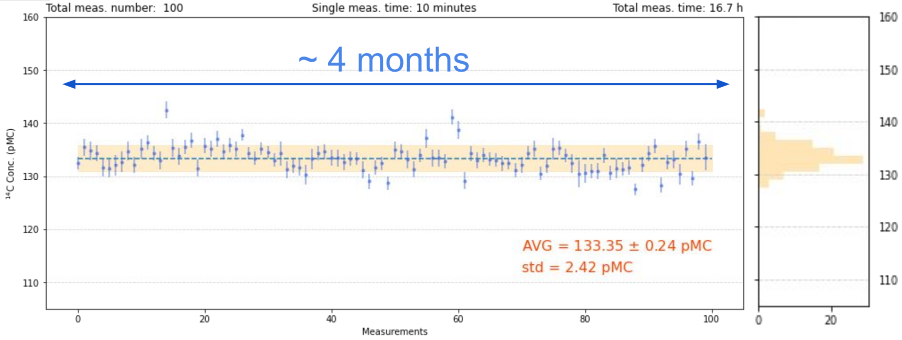
single meas run (h)

Long-term

multi sample prep

multi meas run (months)



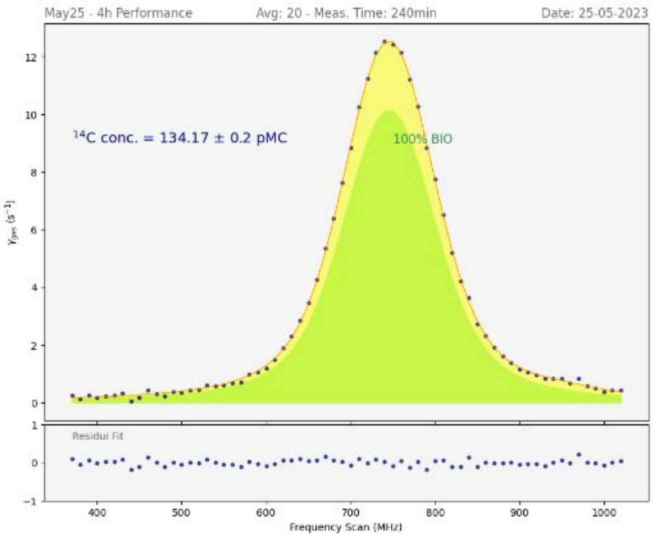


Progresses on performances

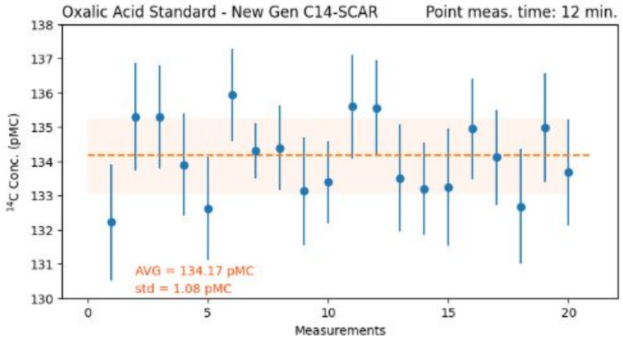
Analysis on a series of 20 measurements on Oxalic Acid.
Each measurement takes 12 minutes.
Total measurement time: 4 hours.

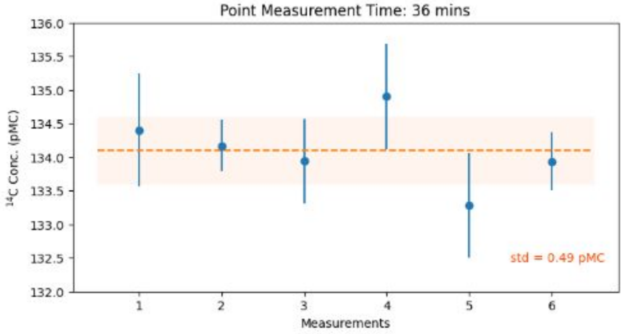
Right:
Data are analyzed singularly or in groups,
evidencing the effects of averaging in terms of precision

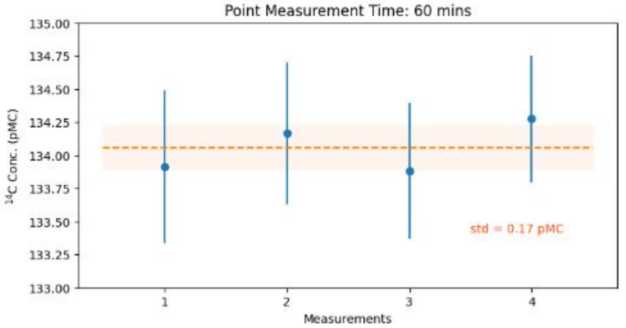
Below:
Data are averaged in a single trace and analyzed



Meas time (minutes)	precision (pMC)
12	1
36	0.5
60	0.2







Thank you!

14C SCAR

by

ppq SENSE