Agri - Food

Chemicals

Geo - Environment

Energy

Application Note

Isotope analysis in biofuel samples

Instrument: COMPACT IDmicro, 14C – SCAR, ECS 8024 – C14

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Innovative Elemental Analysis

Biofuel: definition

Biofuels are fuels derived directly or indirectly from biomass.

Biomass is organic, non-fossil material of biological origin (plants and animals). It includes wide range of materials harvested from nature or biological portion of waste.

Biofuels can be split up into three categories:

- solid biofuels (fuelwood, wood residues, wood pellets, animal waste, vegetal material, ...)
- liquid biofuels (biogasoline, biodiesel, bio jet kerosene, ...)
- biogases (from anaerobic fermentation and from thermal processes)

In particular:

liquid biofuels includes all liquid fuels of natural origin (e.g. produced from biomass and/or the biodegradable fraction of waste), suitable to be blended with or replace liquid fuels from fossil origin. In energy statistics, liquid biofuels is a product aggregate equal to the sum of biogasoline, biodiesels, bio jet kerosene and other liquid biofuels.

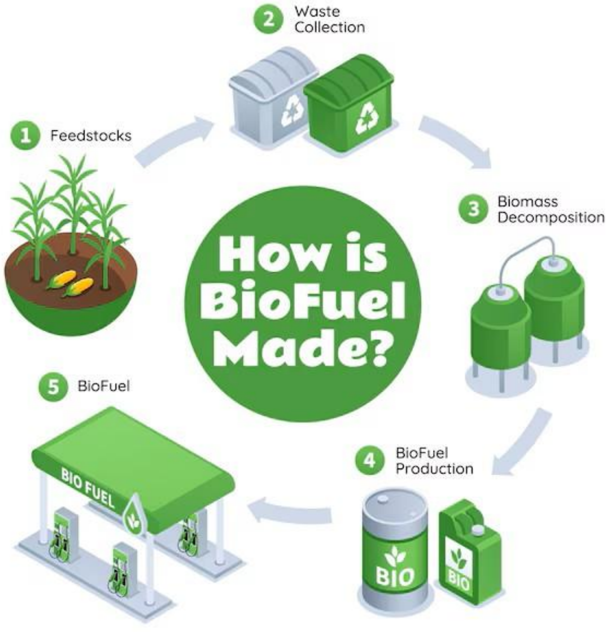
Biomass feedstock is a key source of renewable energy, essential for generating sustainable electricity, heat and transport fuels.

It is matter of *Green Deal*

In the context of the Green Deal, renewable energy represents a fundamental pillar of the transition towards cleaner energy.

Biofuels, bioliquids, and biomethane are among the renewable sources covered by the European Directive, provided they meet specific sustainability requirements. These requirements serve to distinguish which biofuels and bioliquids produce a genuine environmental benefit, such as through the reduction of greenhouse gases, respect for the land, etc.
The sustainability criteria must be met by all economic operators in the biofuel, bioliquid, and biomethane production chains, such as growers, presses, refineries, traders, waste and by-product producers, and production plants.

These alternative energy sources plays a major role in the transition away from greenhouse gas-intensive fuels toward a more sustainable, low carbon future.



Within the fuel sector, the manufacturing of biofuel blends using biomass resources lessens the impact of carbon dioxide (CO2) on the environment, while also allowing fuel manufacturers to receive tax credits and demonstrate compliance with regulatory initiatives.

Not only cars

Maritime sector

The IMO has already launched new short, medium and long-term measures, investments and incentives within the framework of the Initial Strategy:

- Extension of the ETS regulation to the shipping sector
- Payment of carbon credits
- Promotion of sustainable alternative fuels
- Review of the directives on energy taxation

FuelEU Maritime is the European regulation that aims to decarbonise the maritime sector.

Aviation sector

ICAO's CORSIA program requires the aviation industry to offset growth-related greenhouse gas emissions starting in 2021. CORSIA, currently voluntary, includes a second mandatory phase (2027-2035), which will directly affect most airlines.
RefuelEU Aviation is the European regulation aimed at decarbonizing the aviation sector.

Automotive sector

European legislation has imposed specific requirements for the entire biofuel, bioliquid, and biomethane supply chain in the automotive transport sector. To demonstrate compliance with the sustainability requirements of the Directive (and related delegated acts) and, where applicable, to access concessions, economic operators must obtain specific certification.

Application Note – Isotope analysis in biofuel samples

Biofuel certification

Large-scale production of biofuels raises concerns about their sustainability: real greenhouse gas emissions, loss of biodiversity, changes in land use, social aspects, competition with food.

Biofuels must be sustainable

Many biofuels are blended with their corresponding fossil fuel to ensure compatibility and performance.

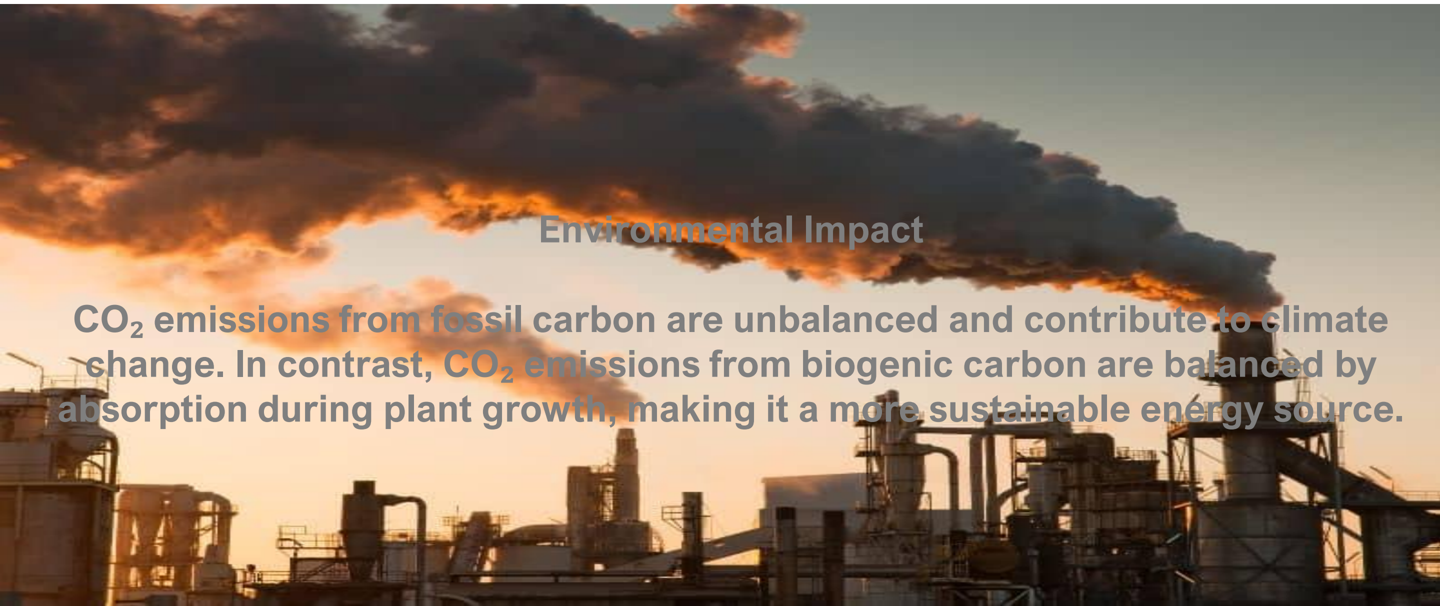
Mixing percentages depend on both technological limitations and regulatory regulations.

When biofuels are blended with fossil fuels, the sustainability information and GHG (GreenHouse Gases) characteristics assigned to the blend must reflect the physical share of biofuels in the blend.

Fossil or biogenic carbon?

Fossil carbon is found in fossil fuels such as oil, coal, and natural gas, which were formed millions of years ago by the decomposition of organic material under high pressures and temperatures.

Biogenic carbon comes from recent biological sources, such as plants and animals, and is part of the natural carbon cycle.



Environmental Impact

CO_2 emissions from fossil carbon are unbalanced and contribute to climate change. In contrast, CO_2 emissions from biogenic carbon are balanced by absorption during plant growth, making it a more sustainable energy source.

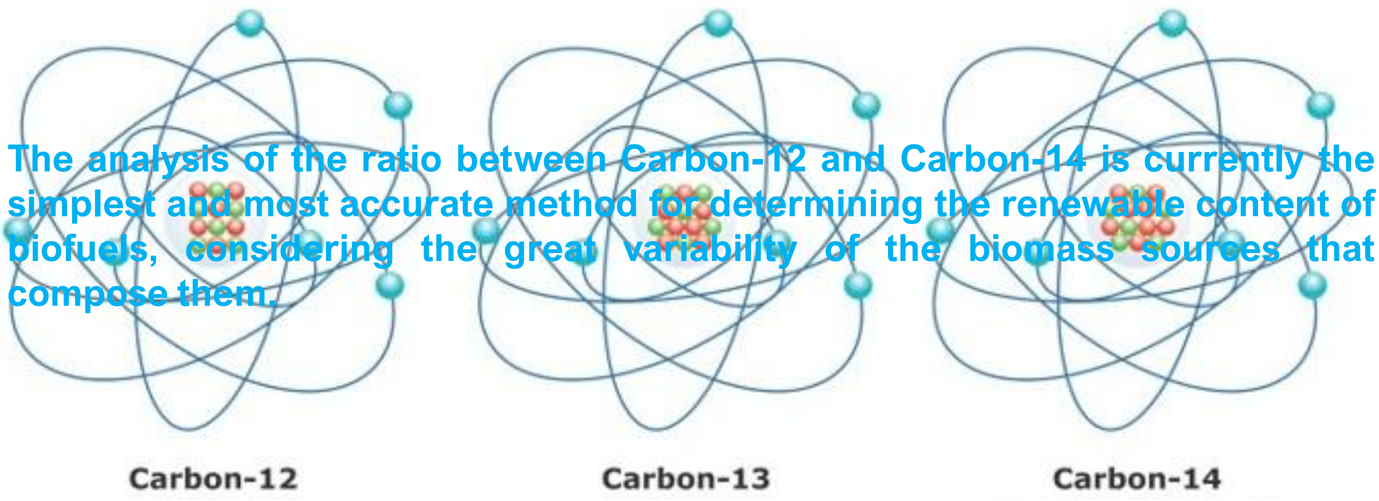
The importance of isotopic analysis

Carbon on Earth exists in three main isotopic forms, namely carbon-12 (stable isotope), carbon-13 (stable isotope), and carbon-14 (weakly radioactive).

As the world moves towards more sustainable energy sources, the accurate identification and quantification of bio-based content in feedstocks and fuels have become increasingly important. One of the most reliable methods for this purpose is Carbon-14 (C-14) testing.

C14 analysis, or radiocarbon dating, is a method for determining the age of organic materials by measuring the remaining amount of the radioactive isotope carbon-14 (14C). It works because living organisms take in 14C from the atmosphere, and when they die, the 14C stops being replenished and begins to decay at a known rate (its half-life is about 5,730 years). By comparing the ratio of 14C to stable carbon-12 in a sample to the ratio in the atmosphere, scientists can estimate how long ago the organism died.

During its life, a plant or animal is in equilibrium with its surroundings by exchanging carbon either with the atmosphere or through its diet. It will, therefore, have the same proportion of 14C as the atmosphere, or in the case of marine animals or plants, with the ocean. Once it dies, it ceases to acquire 14C, but the 14C within its biological material at that time will continue to decay, and so the ratio of 14C to 12C in its remains will gradually decrease. Because 14C decays at a known rate, the proportion of radiocarbon can be used to determine how long it has been since a given sample stopped exchanging carbon – **the older the sample, the less 14C will be left.**



The analysis of the ratio between Carbon-12 and Carbon-14 is currently the simplest and most accurate method for determining the renewable content of biofuels, considering the great variability of the biomass sources that compose them.

Example

Measurement report on the determination of the 14CO2 content in 5 samples provided by a primary petrochemical company*

CO2 extraction

The liquid samples were received already weighted and collected in silver cups. Each sample was processed by an elemental analyzer: ECS 8024 – C14 model.

The CO2/He mixture is fluxed through a ceramic molecular sieve (Zeolite 13X) and the CO2 is trapped by the Zeolite material, so that He can be pumped out.

The isotopic mixture of the extracted CO2 is then sent to the C14-SCAR system to perform the measurement of the 14CO mole fraction in static condition.
The following table summarizes the relevant parameters of the preparation routines of the samples:

Sample	Volume (ul)	Total prep. time (min.)	Date
1	13.0	15	08/04/2025
2	13.0	15	08/04/2025
3	13.0	15	09/04/2025
4	13.0	15	10/04/2025
5	13.0	15	10/04/2025

Measurement Method

The C14-SCAR instrument used for the measurements.
The radiocarbon mole fraction (M) of an unknown sample is retrieved by referencing the result (R) of the SCAR measurement to the oxalic acid standard calibration result (R_S) (NIST, SRM 4990C, 14C content = 134.06 pMC[1]):

$$M = R/R_S \cdot 134.06\ pMC$$

*due to confidential information, we can not show the company name

[1] The unit used for radiocarbon mole fraction is pMC, "percent of Modern Carbon", with modern (100 pMC) defined as the 14C mole fraction in the atmosphere in 1950.

A periodical calibration on the standard is performed with a few-hours measurement, and the typical relative error $\Delta R_S / R_S$ is:

$$\frac{\Delta R_S}{R_S} \approx 0.15\%$$

For a correct estimation of the overall uncertainty of the mole fraction, the uncertainty of the calibration is also considered, by taking the quadrature sum of the two relative errors:

$$\left(\frac{\Delta M}{M}\right)^2 = \left(\frac{\Delta R}{R}\right)^2 + \left(\frac{\Delta R_S}{R_S}\right)^2$$

In the following, the results M for each sample are reported, as given by the C14 SCAR instrument upon the averaged measurement.

A 2-h-long measurement is performed for each sample, corresponding to 6 individual scans of 20 minutes each. The acquisitions are then averaged and fitted in order to obtain the final result.

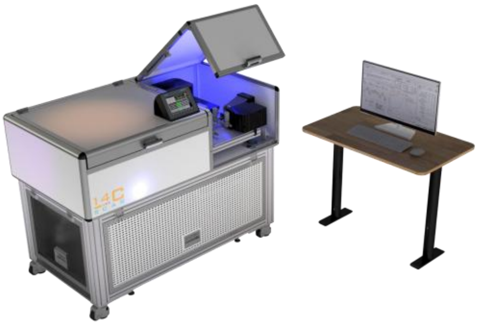
The overall uncertainty ΔM* on the final result is cited as ±0.5 pMC (1 σ), and takes into account the repeatability uncertainty.

In order to obtain the biogenic fraction of the material, the ratio with the atmospheric 2024 reference value (99.7 pMC) has been taken from the updated 2024 version of the ASTM D6866-24 Standard.

The result only applies to relative carbon content, not to relative mass content.

No correction for any possible fractionation effect has been applied, since the C14-SCAR can not, at present, measure the 13C/12C molar fraction.

ECS 8024 – C14 elemental analyser



C14 - SCAR

Results

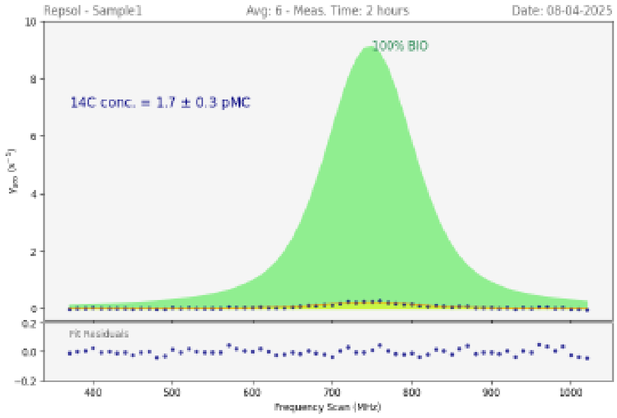
Sample 1

Averaging time: ~2h

SCAR result: 1.7 ± 0.5 pMC

Biobased carbon content: 1.7 %

Fir of average data



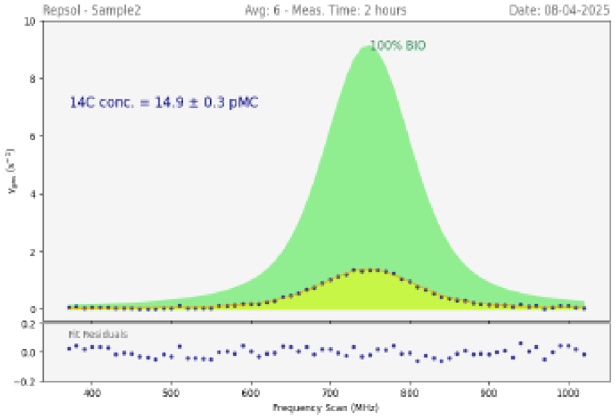
Sample 2

Averaging time: ~2h

SCAR result: 14.9 ± 0.5 pMC

Biobased carbon content: 14.9 %

Fir of average data



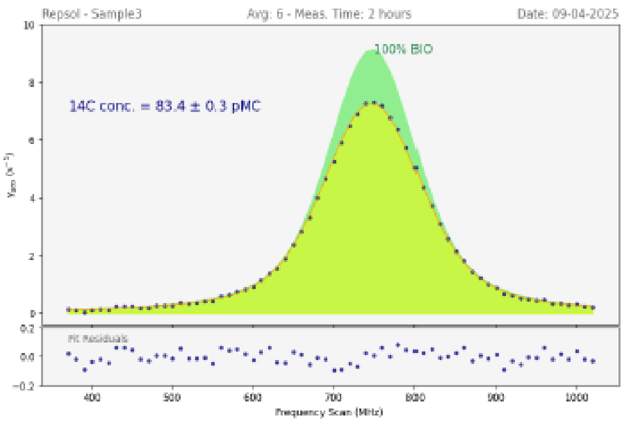
Sample 3

Averaging time: ~2h

SCAR result: 83.4 ± 0.5 pMC

Biobased carbon content: 83.4 %

Fir of average data



Results

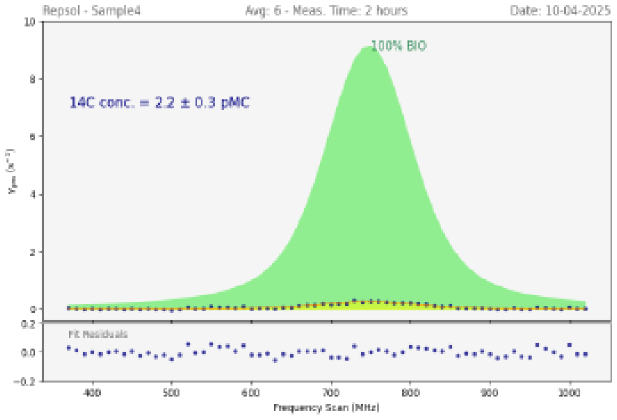
Sample 4

Averaging time: ~2h

SCAR result: 2.2 ± 0.5 pMC

Biobased carbon content: 2.2 %

Fir of average data



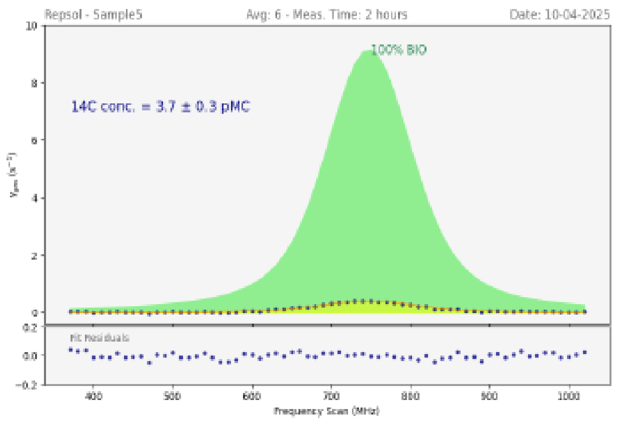
Sample 5

Averaging time: ~2h

SCAR result: 3.7 ± 0.5 pMC

Biobased carbon content: 3.7 %

Fir of average data



The following table summarizes the results with their total uncertainty:

Sample	M (pMC)	ΔM (pMC)	ΔM^* (pMC)
Sample 1	1.7	0.3	0.5
Sample 2	14.9	0.3	0.5
Sample 3	83.4	0.3	0.5
Sample 4	2.2	0.3	0.5
Sample 5	3.7	0.3	0.5

To send your samples: sales@nctechnologies.it

For analytical and technical questions: customerservice@nctechnologies.it

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