LEATHER AND ALTERNATIVE MATERIALS: A NOVEL METHOD FOR BIO-BASED CARBON QUANTIFICATION THROUGH SATURATED-ABSORPTION CAVITY RING-DOWN (SCAR) SPECTROSCOPY

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ABSTRACT

In the past years, climate change led the United Nations to define the Sustainable Development Goals Statement "blueprint to achieve a better and more sustainable future". Subsequently, the European Commission proposed the "Bioeconomy" concept followed by the Green Deal Policy, encouraging the bases for a future economy founded on renewable sources and circularity. COP 26 conference in Glasgow accelerated the decision to fight against global warming, proposing a net reduction of fossil-based fuels and materials.

Various materials were proposed in recent years claiming sustainability advantages from different points of view (animal free, waste recycled, plant based, circular, among others), without a transparent statement of the composition and proportion of renewable carbon sources used for their production. Transparency in sustainability and circularity statements needs justification by means of a robust analytical backing. Our research team individuated SCAR spectroscopy as a reliable method to quantify bio-based carbon content and thus an important identifier for biomass / fossil carbon proportions.

SCAR, capable of performing radiocarbon measurements by use of mid-infrared quantum cascade lasers, was validated against Accelerator Mass Spectrometry (AMS) on samples of materials within the range 0- 100 pMC (percent of Modern Carbon).

This paper includes the analysis of different types of leather and vegan alternatives proposed for equivalent shoe components' applications, with their intrinsic fossil / biomass carbon contents.

Keywords: Bio-based, ^{14}C quantification, quantum cascade laser, leather

1. Introduction

Global warming was internationally recognized under the Kyoto treaty protocol signed in December 1997 urging state parties to commit to the reduction of greenhouse gases. This imposed on all sectors the need for a net CO_2 reduction, to achieve the goal of keeping a global temperature rise under control. Specifically, during COP 21 the Paris agreement was adopted, establishing the goal to limit global warming to *well below 2 degrees Celsius, preferably below 1.5 degrees Celsius, above pre-industrial levels*.[1]

During the COP 26 conference in Glasgow, Paris agreement parameters were strengthened, while recognising that limiting global warming to 1.5 °C requires rapid, deep, and sustained reductions in global greenhouse gas emissions, including reducing global carbon dioxide emissions by 45% within 2030 relatively to the 2010 level and to achieve net zero around mid-century, as well as deep reductions in other greenhouse gases.[2]

These targets can only be reached by e net limitation of fossil carbon such as oil, natural gas, and coal, not only as energy resources but as raw materials for each single industrial sector.

Among the many emerging concepts, "Bioeconomy" is perfectly aligned to the net zero scope: it was defined in a 2012 document *"Innovating for Sustainable Growth - a Bioeconomy for Europe"*, as *"the production of*

renewable biological resources and their conversion and waste into products with high added value, such as food, feed, bioproducts and bioenergy".

In a more recent document, "*A sustainable bioeconomy for Europe: strengthening the connection between economy, society and the environment"* the European Commission sets the basis for a *"Sustainable European bioeconomy necessary to build a carbon neutral future in line with the Climate objectives of the Paris Agreement*". The document states *"the way to a more innovative, resource efficient and competitive society that reconciles food security with the sustainable use of renewable resources for industrial purposes, while ensuring environmental protection"*. All these concepts can be translated into the development of biomass carbon-based fuels, food and raw materials for every single sector avoiding fossil sources. In this context, a reliable method to quantify fossil / biomass carbon proportions becomes vital to the scope of measuring the circularity of the future materials.

If we consider sustainability in a cradle-to-cradle optic, it is fundamental to divide the environmental impact calculation in a series of circular events with the material to be analysed as the main reference. In this context, the intrinsic contribution of an organic material gains importance as support to understand the contribution of renewable / non-renewable carbon sources. Clearly this is not the only parameter to consider. Industrial production of materials involves energy consumption, transports, chemical intermediates, solvents, waste, and water treatment etc., all events which must be precisely measured to understand the overall impact to attribute it.

Our research team has identified radiocarbon analysis as a reliable technique to quantify bio-based carbon content in terms of biomass/fossil carbon proportions and specifically SCAR spectroscopy as a quick and effective technique for such scope.

Circularity trend in fashion materials market has experienced the proliferation of materials said to be based on natural raw materials such as "Vegea®" (grapes residues) "Piñatex®" (pineapple fibres) "Appleskin®" (apple peels and cores) "Desserto®" (cactus fibres) among others. Our first infrared spectra analysis on many leather alternative materials showed a predominance of certain polymers such as Polyurethane or PVC. For our scope of circularity analysis, it is important to understand the intrinsic contribution of bio-based / fossil carbon on each material as an important parameter for a transparent selection of the most sustainable materials. A recent paper by Meyer et al.[3] inspired us to study a method to verify biomass carbon content on the same materials and different types of leather produced with various tanning and finishing processes, so as to define a transparent method to communicate circularity claims.

Radiocarbon quantification by Liquid Scintillation Counting (LSC) or Accelerator Mass Spectrometry (AMS) are the usual methods for this quantification as specified by norms EN 16640:2017 and ASTM D6866-22. With respect to the advantages and disadvantages of the current official methods EN 16640:2017 states that LSC method instruments are cost effective, but the analysis is long, while AMS instruments are expensive, needing large installations. Regarding AMS analysis we can add that the system is highly energy- intensive, but quicker than LSC. We have identified in SCAR spectroscopy a good trade-off between cost and measurement speed with low energy consumption, as our choice for the present research.

2. The importance of ^{14}C quantification in materials' science

The carbon cycle is a perfect example of circularity: a residue of the respiration of animal beings (CO_2) becomes food for plant and bacterial organisms: atmospheric CO_2 is thus transformed into biomass by plants towards photosynthesis and later carbon transferred to animals by feed. In this way, carbon from animal or plant sources derives directly from atmospheric CO_2. Fossil carbon also derives from atmospheric CO_2 but, belonging to a very distant past biosphere equilibrium, it contributes with additional CO_2 or CH_4 upon the end of life of a synthetic material, without events that determine any absorption of environmental CO_2 during its lifetime.

Considering that materials derived from biomass, known as bio-based, are produced from plant or animal resources whose original raw material is atmospheric CO_2, their life cycle will not alter net greenhouse gas emissions. Clearly, since the sustainable production of materials is to be considered as the sum of a series of

[1] United Nations Decision 1/CP.21- Framework Convention on Climate Change – FCCC/CP/2015/10/Add.1 - "Paris Agreement" (2015).

[2] UNFCC - United Nations Framework Convention on Climate Change – Glasgow Climate Pact, Advance unedited version – downloaded from UNFCCC.int 12/04/2022 (2022)

circular events, it is essential to act on the intrinsic contribution of each material and each of its variables, and to evaluate separately the contributions due to energy, transport, natural resources, etc.

Fossil-based raw materials such as coal and petroleum derivatives produce a high contribution of greenhouse gases during the extraction of crude material (with high amounts of CH_4 release, especially if horizontal drilling techniques are applied), as well as the generation of additional CH_4 and CO_2 during the decomposition of the materials produced. Fossil carbon derivatives tend to generate substances that are difficult to digest by microorganisms, with a high release of CO_2 in case of incineration which is in many cases the only logical possibility to treat their waste.

Although it is not a rule, the trend of fossil carbon derivatives is to generate difficult and partially biodegradable materials, with probable generation of micro/nano-plastics as an intermediate degradation step. This contribution of carbon into the biosphere is one of the main causes of global warming.

3. ^{14}C: a cosmogenic origin carbon

There are three isotopic forms of carbon in nature: ^{12}C, ^{13}C and ^{14}C. Both ^{12}C and ^{13}C are stable isotopes while the radioactive isotope ^{14}C is unstable with an average decay time of 5,700 +/- 30 years. ^{14}C has a cosmogenic origin, forming naturally through the bombardment of ^{14}N present in the upper atmosphere from cosmic rays (see figure 1).

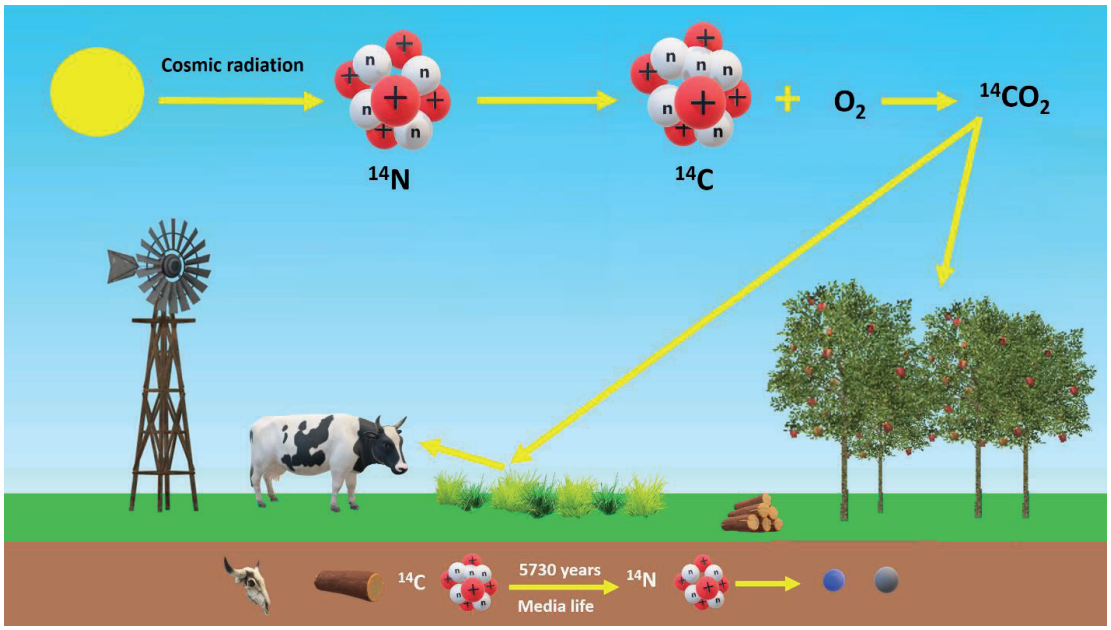


Figure 1 – ^{14}C cycle.

The ^{14}C formed combines with atmospheric oxygen to form $^{14}CO_2$ (radioactive carbon dioxide) which will subsequently be absorbed by plants and the oceans, becoming part of the life cycle. Radioactive ^{14}C converts back to ^{4}N through beta decay with emission of an electron and an antineutrino.

Following this logic, renewable carbon sources contain traces in the order of 1 part per trillion (ppt) of ^{14}C, which can be quantified with reasonable accuracy using different techniques. If we consider the average decay time of radioactive carbon, fossil or carbon mineral sources contain non quantifiable amounts of ^{14}C, and for this reason the accurate quantification of this isotope is very useful to understand the proportions of petroleum-derived carbon compared to biomass in contemporary materials and chemicals. This technique is used regularly in archaeology for dating organic finds back to 50,000 years, with reasonable accuracy.

[3] Meyer M., Dietrich S., Schulz H., Mondschein A. – Comparison of the Technical Performance of Leather, Artificial Leather, and Trendy Alternatives. Coatings 2021, 11, 226 (2021)

4. SCAR spectroscopy analysis: measurement technique

In SCAR spectroscopy, infrared radiation emitted by a quantum cascade laser (QCL) is coupled to a high- finesse Fabry-Perot cavity up to a threshold level, and then it is quickly switched off at the cavity resonance. Transmitted light during the ring-down time is detected and the decay rate is measured. If a molecular species inside the cavity absorbs the coupled light, it increases the cavity loss rate, and such variation is measured. The difference with respect to conventional cavity ring-down spectroscopy (CRDS) is that saturation effects of the molecular absorption induce a deviation of the ring-down signal from the perfectly

exponential behaviour, as expected for linear intra-cavity losses[4]. Starting from an *ab initio* theoretical model, a fitting routine was developed, taking into account the transient effects due to a changing saturation level and retrieving from each single CRD decay event both the empty-cavity and the gas-induced losses and the corresponding decay rates for the intra-cavity infrared radiation[5].

The $^{14}C^{16}O_2$ mole fraction is determined by measuring the spectral area of its (00^01-00^00) P(20) ro- vibrational transition, whose spectrum (gas-induced decay rate γ_g vs. laser frequency ν) is recorded with high spectral fidelity by scanning the laser (and cavity resonance) frequency very precisely. To this aim a

second QCL, locked to a molecular absorption line of low-pressure pure N_2O in a sealed cell, is used as a frequency reference.

By cooling the cell down to 170 K with a Joule-Thomson cryocooler, the overall intensity of the $^{13}C^{16}O_2$ interfering doublet which lies in the investigated spectral region is greatly reduced by about 2000 times, down to 1.5% of the target line.

The two-line manifold appearing in the experimentally recorded spectra consists of the target line of $^{14}C^{16}O_2$ and the interfering (01^11-01^10) Q(12)e line of N_2O, which partially overlaps with the former, thus representing most of the residual spectral interference at such a low operating temperature. A complete removal of N_2O can hardly be achieved experimentally, therefore the acquired spectrum is fitted to a two-Voigt profile[6] [7].

It is convenient to convert the measured spectral area of the $^{14}CO_2$ target line in an unknown sample to conventional ^{14}C units, such as pMC (percent of Modern Carbon) or $F^{14}C$ (fraction modern). To this aim the spectral area of the target line in the standard reference material (oxalic acid NIST SRM 4990C) must be measured with great precision (a single long-time average is enough) and the ratio between the sample and reference spectral areas must be calculated each time to get the ^{14}C content expressed in the desired units.

Due to the so-called Suess effect, the pMC value of a 100% biogenic sample is drifting towards lower and lower values at a rate of about -0.5 pMC/year. In 2019 any 100% biogenic sample reached the value of 100 pMC. Therefore, we can assume that the pMC value measured for nowadays materials nearly corresponds to their biogenic fraction in %.

5. Sample preparation

Samples of leather, artificial leather, and alternative materials were taken from areas of the original piece where the distribution of different constituents may be representative of the whole. In the case of leathers specimens were taken from the standard sampling area following EN-ISO 2418 “Leather — Chemical, Physical and mechanical and fastness tests – Sampling location” recommendations. A fine section slice was taken with a scalpel with the precaution that it should contain all the microstructural components of the material.

Alternative materials were sampled from areas far from the borders verifying their section uniformity under the microscope. In case of samples where it was difficult to obtain a uniform section, due to uneven distribution of the microstructural components, we have analysed each of them separately.

[4] G. Giusfredi, S. Bartalini, S. Borri, P. Cancio, I. Galli, D. Mazzotti, and P. De Natale, “Saturated-absorption cavity ring-down spectroscopy,” *Phys. Rev. Lett.* **104**, 110801 (2010)

[5] G. Giusfredi, I. Galli, D. Mazzotti, P. Cancio, and P. De Natale, “Theory of saturated-absorption cavity ring-down: radiocarbon dioxide detection, a case study,” *J. Opt. Soc. Am. B* **32**, 2223-2237 (2015)

[6] I. Galli, S. Bartalini, S. Borri, P. Cancio, D. Mazzotti, P. De Natale, and G. Giusfredi “Molecular gas sensing below parts per trillion: radiocarbon-dioxide optical detection,” *Phys. Rev. Lett.* **107**, 270802

[7] I. Galli, S. Bartalini, R. Ballerini, M. Barucci, P. Cancio, M. De Pas, G. Giusfredi, D, Mazzotti, N. Akikusa, and P. De Natale, “Spectroscopic detection of radiocarbon dioxide at parts-per-quadrillion sensitivity,” *Optica* **3**, 385-388 (2016)

Considering both leather and alternative materials may be split horizontally during goods manufacturing, and since the bio-based composition distribution throughout the material may suffer huge differences, it is important to record the thickness of the material analysed.

6. Sample analysis

For the analysis, the sample must be burnt to turn it into pure CO_2 gas, and its carbon content must be enough to fill the SCAR measurement cell at the optimal thermodynamic conditions of 12 mbar pressure and 170 K temperature. Considering the cell volume of 0.7 L and the additional dead volume of the filling vacuum line, at least 0.5 mmol of gas is needed, corresponding to about 6 mg of C. The sample, enclosed in a tin cup, is dropped into the high-temperature furnace (900 °C) of an elemental analyser (Elementar, mod. vario ISOTOPE cube), where it is oxidised in a pure O_2 atmosphere. The gas combustion products are carried away by a He flow, while ashes are collected in a tray. Water vapour is absorbed by a SICAPENT trap, while nitrogen oxides are reduced in a high-temperature column (550 °C) by Cu powder. N_2 is immediately released out of the elemental analyser, while CO_2 is selectively adsorbed using a proprietary purge-and-trap technology and released on demand into a glass ampoule which has been previously evacuated. The ampoule is immersed in a liquid-N_2 bath, and the CO_2 is frozen. The He carrier gas is pumped out, the liquid-N_2 bath is removed, and the ampoule is heated at room temperature. The result is an ampoule containing pure CO_2 gas, with a N_2O residual mole fraction lower than few ppb. All this procedure takes about 15 minutes to be carried out.

The ampoule is then connected to the inlet of the SCAR instrument and the measuring cell is filled with the CO_2 gas sample. After the measurement, if a long-term storage of the sample is desired for possible successive investigations, the sample can be recovered by immersing again the ampoule in a liquid-N_2 bath.

7. Validation of SCAR radiocarbon quantification against AMS

Considering that leather and alternative materials may contain fractions of fossil / bio-based carbon which can range from 0 to 100%, the validation of the SCAR spectrometer was done by analysing materials within the whole measurement range. Preliminary measurements were done on several materials, analysing nitrogen and total carbon content as shown in Table 1.

Each sample was prepared by quintuplicate and each sub-sample was measured 20 times, each of them for 6 minutes. The statistical analysis of the measured samples gave a homogeneous precision.

As an example, Figure 2 shows the complete set of 5 measurement runs (preparation + 20 measurements averaging) for one of the selected samples.

SCAR measurements compared versus AMS were linear within a very small error (<2 pMC). The plot obtained can be observed on the right of Table 1.

Sample	% N	% C	pMC Bio-based
EVA “Vegan” sole	4.6	61.6	0.2
Desserto® "Cactus leather"	4.6	61.6	24.1
Coated Patent Leather	8.4	53.5	47.1
Mix synthetic-natural fabric	7.8	50.2	60.8
Fully syntan tanned Leather	10.7	58.8	65.6
Soft milled leather "Rave®"	11.8	58.2	92.6
Vachetta Leather "Toiano"	8.9	50.9	94.7

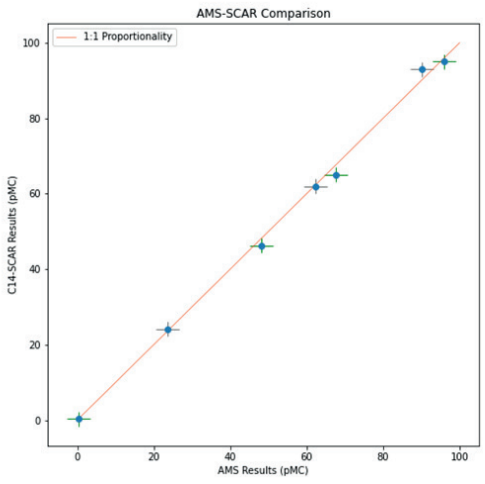


Table 1. Samples used for the validation of SCAR spectroscopic measurements against AMS

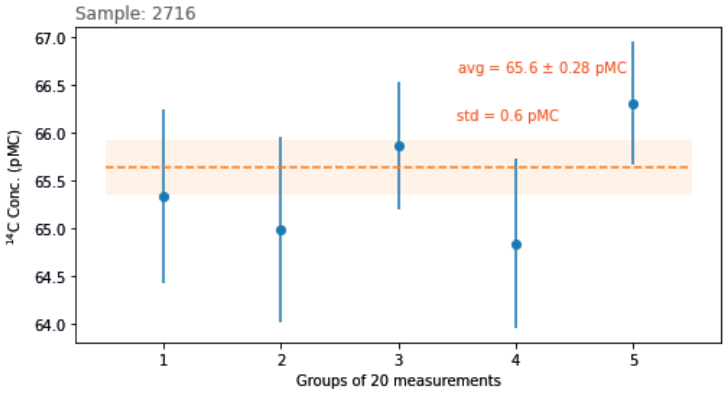


Figure 2 – Repeatability of the SCAR analysis protocol for one of the samples under study (Fully syntan tanned leather)

8. Measurement of bio-based content of different leather types and alternative materials

As a result of a first set of analysis, a series of leather types and alternative materials were measured with the scope of understanding the respective intrinsic bio-based / fossil contents.

The analytical procedure defined in this paper, will be applied as formal protocol for the future tests considering the good alignment achieved in the validation.

The results obtained were the following:

Sample	pMC Bio-based	Sample	pMC Bio-based
EVA "Vegan" sole	**0.2**	Mix synthetic-natural fabric	**60.8**
"Vegan" shoeupper	**0.4**	Fully syntan tanned Leather	**65.6**
Desserto® "Cactus leather"	**24.1**	Salmon skin	**82.4**
Appleskin®	**26.0**	Parma® Baby calf	**89.9**
Volar Bio Ultraleather®	**27.8**	Soft milled leather "Rave®"	**92.6**
Coated Patent Leather	**47.1**	Vachetta Leather "Toiano"	**94.7**

Table 2. Samples of leathers and proposed alternatives analysed using SCAR spectroscopy

9. Conclusions

SCAR spectroscopy demonstrated to be a good alternative to AMS analysis of biomass carbon content for leather and alternative materials. The results show that this system can be a useful tool to support the transparency in the communication of materials circularity claims. Validation shows that both instruments can give a perfectly aligned response. Regarding the analysed materials, so far vegan alternatives to leather are placed on the lower bio-based content area (below 30%); heavy coated leathers, high synthetic retanning and finishing leathers, as well

as mixed synthetic and natural fabrics for shoeupper, are placed between 40% and 70% biomass carbon content; real leathers are all placed above the 70% level. The presented analysis process and instrumental apparatus can be therefore considered a good first step to a future transparent labelling of materials to support circularity claims.

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Note