

# DETERMINATION OF BIOGENIC FRACTION IN USED CAR TYRES AND IN LIQUID FUELS BY $^{14}\text{C}$ METHOD

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## CONTENT

*Measurement of  $^{14}\text{C}$  activity of various types of samples that can be used as fuels for energy production and transport can be used to determine the fraction of biogenic component within the samples. The method is based on different  $^{14}\text{C}$  signatures of the biogenic and the fossil components. Here we present two examples: determination of the biogenic fraction in used car tyres and in liquid fuels. Various measurement methods are discussed in terms of their advantages or main drawback.*

## 1. Introduction

Intensive use of fossil fuels for energy production and transport during 20<sup>th</sup> century caused an increase of  $\text{CO}_2$  concentration in the atmosphere [1]. The increase of  $\text{CO}_2$  concentration can be slowed down by the use of biogenic materials for energy production and/or transport. The "environmentally kind politics" of the European Union stimulates the use of biogenic fuels by lower excise and income tax relief. Thus, there is a need for independent determination of the fraction of the biogenic component in various types of fuels by reliable and accurate methods. One of such methods is the  $^{14}\text{C}$  method, which is based on different content of  $^{14}\text{C}$  in biogenic and in fossil components.  $^{14}\text{C}$  is a cosmogenic isotope, formed in the atmosphere by interaction of cosmic rays (neutrons) with atmospheric  $^{14}\text{N}$ . Together with other carbon isotopes (stable isotopes  $^{12}\text{C}$ ,  $^{13}\text{C}$ )  $^{14}\text{C}$  combines with atmospheric oxygen forming carbon dioxide, which is used by plants in the photosynthesis, and animals then acquire  $^{14}\text{C}$  by eating the plants. In such a way, a uniform distribution of  $^{14}\text{C}$  in the atmosphere and biosphere is attained. When the animal or plant dies, carbon exchange with the environment is stopped while the radioactive decay continues. This is the basis of the radiocarbon dating method [2]. A pure biogenic material reflects the modern atmospheric  $^{14}\text{C}$  activity, while no  $^{14}\text{C}$  is present in fossil fuels (oil, coal). Therefore, a biogenic fraction of any material of interest is proportional to its  $^{14}\text{C}$  content [3]. The  $^{14}\text{C}$  method is the most reliable method of determination of the biogenic fraction in fuels and it can be applied to various types of fuels used, such as solid communal waste, used car tyres, liquid fuels. It can be used also to determine the biobased content of various manufactured products (e.g., solvents and cleaners, lubricants, construction material, carpets, etc.) [4]. Alternatively, the  $^{14}\text{C}$  method can be applied to determine  $^{14}\text{C}$  content of the  $\text{CO}_2$  produced by combustion of various fuels in waste-to-energy plants [3,5]. Any measuring technique used in  $^{14}\text{C}$  laboratories could be used [6]. Here we present comparison of characteristics (precision, complexity, and price) of various techniques for biogenic fraction determination by the  $^{14}\text{C}$  method. An example of the application of the  $^{14}\text{C}$  methods to the used car tyres will be presented, and a special case of liquid fuels will be discussed.

## 2. $^{14}\text{C}$ measurement techniques

Different measurement techniques can be applied for  $^{14}\text{C}$  activity measurement [2,6,7,8]. Radiometric measurement techniques are based on counting  $^{14}\text{C}$  decay rate by liquid

scintillation counters (LSC), while the accelerator mass spectrometry (AMS) technique counts the number of  $^{12}\text{C}$ ,  $^{13}\text{C}$  and  $^{14}\text{C}$  atoms. For LSC measurement a sample can be prepared in form of benzene or as  $\text{CO}_2$  absorbed in a cocktail [7,8], while for AMS graphite targets are prepared [e.g., 9].

The main characteristics of the mentioned  $^{14}\text{C}$  measurement techniques – sample type, required mass of carbon, complexity, precision, price, main drawback – are compared in Table 1. Advantages of AMS over LSC techniques are: smaller sample size needed (as little as 20 mg of a sample) and higher precision than radiometric techniques. However, the AMS analysis is more expensive, sometimes the representativeness of a sample may be questionable, and it is more sensitive to any contamination during sample preparation. The LSC-benzene technique has a time-consuming and complex benzene synthesis but gives lower uncertainties than the much simpler technique of  $\text{CO}_2$  absorption in absorption-scintillation cocktails [7,8]. The simplest method of direct LSC measurement of liquids mixed with the appropriate scintillation cocktail is applicable only to liquid fuels [10,11] and will be discussed later.

**Table 1. Comparison of different techniques for  $^{14}\text{C}$  measurement**

Measurement technique	Sample types	Required mass of carbon	Complexity *	Precision *	Price *	Main drawback
AMS	all	~1 mg	3	4	4	representativeness of the sample
LSC-benzene	all	~4 g	4	3	3	time-consuming
LSC- $\text{CO}_2$	all	~0.6 g	2	2	2	high uncertainty
LSC-direct	liquid fuels	10 ml of liquid	1	1	1	quenching

\* The higher the number, the more complex the method / the lower the uncertainty / the higher the price

### 3. Presentation of the results

Results of measurement are presented as relative specific  $^{14}\text{C}$  activity,  $a^{14}\text{C}$ , expressed in percent of modern carbon (pMC), where 100 pMC is equivalent to the specific activity of 226 Bq/kgC. In further text we use the term " $^{14}\text{C}$  activity" for  $a^{14}\text{C}$ .

A material can be composed of a biogenic component (of fraction  $f_{bio}$ ) and a fossil component ( $f_f$ ), where  $f_f + f_{bio} = 1$ . The measured  $^{14}\text{C}$  activity of such a mixed material,  $a^{14}\text{C}_{mix}$ , can be presented as a combination of the biogenic and fossil components:

$$a^{14}\text{C}_{mix} = f_f a^{14}\text{C}_f + f_{bio} a^{14}\text{C}_{bio} \quad (1)$$

Since in fossil fuels all  $^{14}\text{C}$  had been decayed, and  $a^{14}\text{C}_f = 0$  pMC, it follows that the fraction of the biogenic component can be determined as

$$f_{bio} = a^{14}\text{C}_{mix} / a^{14}\text{C}_{bio} \quad (2)$$

The value of  $a^{14}\text{C}_{bio}$  must be known. Generally,  $a^{14}\text{C}_{bio}$  refers to the biogenic  $^{14}\text{C}$  activity of the year when the plant grew reflecting the  $^{14}\text{C}$  content of atmospheric  $\text{CO}_2$  during biomass growth. Before the anthropogenic activities disturbed the natural distribution of  $^{14}\text{C}$  in the atmosphere and biosphere during the 20th century [2], the value of  $a^{14}\text{C}_{bio}$  was 100 pMC. The  $a^{14}\text{C}_{bio}$  has been changing in the second half of the 20th century

approaching almost twice the natural  $a^{14}\text{C}_{\text{bio}}$  in the early 1960s due to atmospheric bomb tests, and declining since then. The ASTM 6866 [6] recommends the use of 105 pMC for biogenic material originating from last several years. The monitoring of  $^{14}\text{C}$  activity of the atmosphere and biosphere performed in our laboratory showed that the atmospheric and plant  $^{14}\text{C}$  activities have been almost constant during last 10 years, ranging from 103 pMC to 106 pMC (annual mean values) at clean-air sites, i.e., sites not influenced by industry or intensive traffic. In the city of Zagreb the atmospheric  $^{14}\text{C}$  activity is lower, ranging from 101 pMC to 105 pMC, due to intensive use of fossil fuels in industry and traffic, as well as for heating during winter [2]. Therefore, to calculate the fraction of biogenic component (eq. 2) the value  $a^{14}\text{C}_{\text{bio}}$  of 105 pMC will be used. It should be noted that the value of 105 pMC can be safely used for short-lived biomass that grew during last  $\sim 10$  years. When the wood, wooden products or wooden pellets produced from a wood grown in the second half of the 20<sup>th</sup> century are used as fuels,  $^{14}\text{C}$  activities may lie in the range between 105 pMC and even  $\sim 190$  pMC, depending of the year of growth. Such values would yield unrealistic  $f_{\text{bio}}$  values of  $>100\%$ , if the correct  $a^{14}\text{C}_{\text{bio}}$  values were not used.

#### 4. $^{14}\text{C}$ activity of used car tyres

Certain industries use end-of-life-tyres as fuel to reduce the consumption of traditional fuels and also to reduce their energy bills. The cement industry uses more scrap tyre fuels than any other industry. Tyres provide a heat output equivalent to that of petroleum coke and coal, but also make it possible to reduce fossil  $\text{CO}_2$  emissions due to combustion significantly because of their biomass fraction of 18.3 % and 29.1 % in passenger car tyres and truck tyres, respectively [12]. Car and truck tyres represent a heterogeneous material, and the sampling is a critical step of the complete process of determination of the biogenic fraction in tyres by the  $^{14}\text{C}$  method.

In the radiocarbon laboratory of the RBI we measured several car tyre samples obtained from cement industries. The samples submitted to the laboratory were non-homogeneous bulk samples of  $\sim 1$  kg and consisted of several types of tyres/plastic material. We explored all 3 sample preparation and measurement techniques. The bulk samples were pre-treated by an acid-base-acid method usually applied in radiocarbon dating laboratories for removal of impurities [8,13]. About 90 g of homogenized tyre scraps was carbonized for 15 min at 400 °C followed by 15 min at 600 °C. An aliquot of 7.5 g (out of  $\sim 30$  g obtained after the carbonization) was taken for combustion if benzene synthesis followed, while for the  $\text{CO}_2$ -absorption technique an aliquot of  $\sim 5$  g produced enough  $\text{CO}_2$  to prepare duplicate  $\text{CO}_2$ -cocktails. Once the  $\text{CO}_2$  was obtained, further preparation and measurement procedure was the same as for any other sample [7,8]. For AMS, about 14 mg of pre-treated and homogenized tyre scraps was taken for combustion and subsequent graphite synthesis [9,13].

In Table 2 we present the  $^{14}\text{C}$  activities of several car tyre samples obtained by different measurement techniques, as well as the fraction of biogenic component in these samples determined by equation (2). As expected, the AMS gave the smallest and LSC- $\text{CO}_2$  the highest measurement uncertainties. The AMS subsample (14 mg) may not represent a perfectly homogenized mixture of various types of material in a composed sample which may cause somewhat different  $a^{14}\text{C}$  value from that obtained by the LSC method. Both LSC techniques gave consistent results, although we have not determined  $^{14}\text{C}$  activity of the sample by both LSC techniques. Generally, all obtained  $f_{\text{bio}}$  fractions are lower than the global average of biomass fraction of car tyres [12].

**Table 2.  $a^{14}\text{C}$  and fraction of biogenic component  $f_{bio}$  in several car tyre samples determined by different measurement techniques.**

Sample	AMS		LSC-benzene		LSC-CO <sub>2</sub>	
	$a^{14}\text{C}$ (pMC)	$f_{bio}$ (%)	$a^{14}\text{C}$ (pMC)	$f_{bio}$ (%)	$a^{14}\text{C}$ (pMC)	$f_{bio}$ (%)
A	4.32 ± 0.05	4.11 ± 0.05			8.3 ± 1.5	7.9 ± 1.4
B					8.7 ± 0.9	8.3 ± 0.9
C					6.2 ± 1.0	5.9 ± 1.0
D			5.8 ± 0.2	5.5 ± 0.2		
E					6.0 ± 0.9	5.7 ± 0.9

## 5. Liquid fuels

According to the EU Directive 2009/28/EC [14] all (liquid) fuels have to contain at least 10 % of bio-fuel, i.e., blend of biogenic origin, by 2020. Fossil matrix of the fuels is either gasoline (benzine) or diesel (gas oil), while biogenic blends are usually bioethanol, fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others. A technique of direct measurement of the  $^{14}\text{C}$  content in liquid fuel is simple and fast but has a main disadvantage that different liquid colours cause different quenching properties of samples and thus change the measurement efficiency. Various methods have been suggested to overcome this problem (e.g., decolourization, separate quenching curves for various combinations of the fossil matrix and biogenic blends). Some of them resulted in rather complicated data evaluation techniques depending on the type of a sample, both of the fossil matrix and biogenic blend [10,11].

We proposed a new technique that uses liquids of different colours to construct modern and background calibration curves [15]. The proposed technique takes advantage of otherwise main drawback of the method, i.e., quenching parameter of various samples is used as the calibration parameter. In the first step we used various biogenic liquids having different quenching properties to construct “modern calibration curve” (MCC). We apply the conclusion about the constant  $a^{14}\text{C}_{bio}$  during last 10 years, as discussed above, so it was not critical to know exactly the year of production of the biogenic material, as long as it is “recent”. Materials used for MCC construction resemble the biogenic blends added to fossil matrix: various brands of domestic oil (vegetable, sunflower, olive and pumpkin oils) and bioethanol, as well as modern benzene of exactly known  $^{14}\text{C}$  activity (~1050pMC) measured in our laboratory for other purposes. The MCC curve relates the count rate of biogenic materials with their SQP values, where SQP is the standard quench parameter determined by the  $^{152}\text{Eu}$  external source in the LSC Quantulus. In the region of SQP values between 500 and 900 the MCC can be described by a quadratic function (with  $R^2 = 0.997$ ), while for  $\text{SQP} > 700$  it can be approximated by a linear function ( $R^2 = 0.98$ ). Intensive colours of olive and pumpkin oils resulted in low SQP values and lower count rates than other oil brands although all these samples were of recent biogenic origin. At the SQP values below 570, the count rate of the biogenic samples became indistinguishable from the background count rate, so the MCC is valid for the range  $570 < \text{SQP} < 900$ .

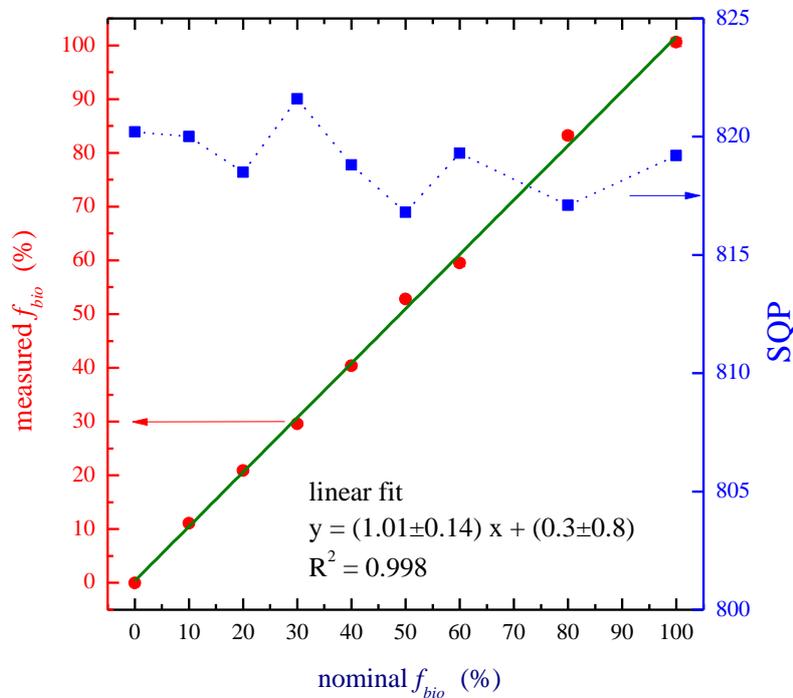
The background calibration curve (BCC) related the SQP and count rates of various background samples, i.e. samples that do not contain  $^{14}\text{C}$ , which can be considered as “fossil” samples. For construction of BCC we used several 100 % fossil fuel samples, pure benzine and benzene, as well as distilled water. Among the benzene samples, we

used  $^{14}\text{C}$ -free benzene used as background sample in our routine  $^{14}\text{C}$  dating measurements. The background count rate was linearly correlated with the SQP values in the range of SQP values from 400 (water) to 900 (benzene),  $R^2 = 0.94$ .

The procedure of data evaluation for the unknown sample consists of measurement of SQP and count rate, determination of background count rate corresponding to the measured SQP value by using BCC, and determination of the count rate of the biogenic sample corresponding to the measured SQP values by using MCC. The fraction of the biogenic component in the sample is then simply calculated as the ratio of net count rates of the sample to the biogenic material [15].

All samples, including modern and background standards, should be measured under the same conditions. Our experiments showed that the optimal measurement conditions are the following: low-potassium glass vials of 20 ml, scintillation cocktail UltimaGoldF (UGF), the ratio sample:UGF of 10 ml : 10 ml, spectra recorded by LSC Quantulus evaluated in the window 124 – 570 channels [15]. The lowest detectable biogenic fraction is 0.5 % for measurement duration of 600 minutes.

To test the method we prepared various mixtures of fossil and biogenic liquids in the nominal concentration ranges of the biogenic component from 0 % to 100 %. The following sets of mixture were analysed: vegetable oil and fossil fuel that both have approximately the same value of the SQP parameter, bioethanol and fossil fuel with different SQP values, bioethanol and  $^{14}\text{C}$ -free benzene. In all case, the calculated biogenic fraction agreed well with the nominal fraction. As an example, in Figure 1 we show the results for mixtures of vegetable oil and fossil fuel. The measured  $f_{bio}$  values determined by the described data evaluation technique agree very well with the nominal  $f_{bio}$  values (linear correlation shown in Figure 1 with  $R^2 = 0.998$ ), while the SQP values of all mixtures remained more-or-less constant.



**Figure 1.** Comparison of the measured biogenic fraction  $f_{bio}$  (left ordinate) in prepared mixtures of vegetable oil and fossil fuel with the nominal fraction shown on x axis. The SQP values of the mixtures are shown also (right ordinate).

In addition, mixtures of two different biogenic liquids (vegetable oil and bioethanol, vegetable oil and olive oil) having different quenching properties were studied to examine the reliability of the method when the mixture components have different SQP values, while both are of biogenic origin. Both SQP values and count rates changed continuously as the mixture composition changed, and the measured biogenic fraction ranged from 97 % to 120 %. These results indicate that the method should be improved. Several cocktails of both biogenic liquids and fossil fuels were measured repeatedly during 90 days after preparation of the cocktails with UGF. No change in either SQP or count rate was observed, proving that the prepared cocktails are stable during at least 3 months after preparation.

The obtained results were in good agreement with those obtained by different evaluation technique, both for the benzene and diesel as the fossil matrix and various biogenic blends [15]. Our method depends neither on the fossil matrix or the biogenic additive type, it does not require  $^{14}\text{C}$  spikes or other expensive standards, and furthermore, one does not need to know the qualitative composition of the fuels, as it is the case for other evaluation techniques.

## 6. Conclusion

Determination of the fraction of the biogenic component in various materials has become recently a very interesting topic both for the scientists and for various industries. It is also important for the global environment, because the use of biogenic materials for energy production and transport may lower the increase of atmospheric concentration of  $\text{CO}_2$  of fossil origin. The  $^{14}\text{C}$  method is a very powerful method for determination of the biogenic fraction.

Different measurement techniques have been developed mainly for the radiocarbon dating application, and they can be successfully applied also for the purpose of biogenic fraction determination. Methods differ in complexity and the required mass of a sample. The AMS method requires about 1000 times less sample than the LSC techniques, and has a lower measurement uncertainty, which makes it the best choice for the dating application in e.g. archaeology or art history. However, it is quite expensive and the small sample (range of mg) may not be a representative sample of a non-homogeneous composed mixtures, such as used car tyres or communal waste. The LSC techniques (benzene synthesis and  $\text{CO}_2$ -absorption), although of different complexity and uncertainties, gave consistent results for the biogenic fraction in car tyres.

The innovative data evaluation technique of the direct measurement of  $^{14}\text{C}$  activity of liquid fuels in LSC is presented and discussed. The method still needs some improvements, especially for highly quenched liquids, but it gives comparable results with other data evaluation techniques, and does not depend on the type of the fuel mixture.

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## ABSTRACT

Intensive use of fossil fuels for energy production and transport during 20<sup>th</sup> century caused an increase of  $\text{CO}_2$  concentration in the atmosphere. The increase of  $\text{CO}_2$  concentration can be slowed down by the use of biogenic materials for energy production and/or transport. One of the method for determination of the fraction of the biogenic component in any type of fuel or waste is the  $^{14}\text{C}$  method, which is based on different content of  $^{14}\text{C}$  in biogenic and in fossil component: while the biogenic component reflects the modern atmospheric  $^{14}\text{C}$  activity, no  $^{14}\text{C}$  is present in fossil fuels. The  $^{14}\text{C}$  method is the most reliable method of determination of the biogenic fraction in various materials. It can be applied to various types of fuels used, such as solid communal waste, used car tyres, liquid fuels, even to the  $\text{CO}_2$  produced by combustion of various fuels. Any measuring technique used in  $^{14}\text{C}$  laboratories could be used. Here we present comparison of characteristics (precision, complexity, and price) of various techniques for biogenic fraction determination by the  $^{14}\text{C}$  method in used car tyres, based on our experience.

Determination of biogenic fraction in liquid fuels is of special interest because all (liquid) fuels have to contain at least 10 % of bio-fuel, i.e., blend of biogenic origin, by 2020 (EU Directive 2009/28/EC). A technique of direct measurement of the  $^{14}\text{C}$  content in liquid fuel is simple and fast but has a main disadvantage: different liquid colours cause different quenching properties and changes in the measurement efficiency. Various methods have been suggested to overcome this problem (e.g., decolourization, separate quenching curves for various combinations of the fossil matrix and biogenic blends). We have proposed a new technique that uses liquids of different colours to construct modern and background calibration curves. The technique depends neither on the fossil matrix or the biogenic additive type. Lowest detectable biogenic fraction is 0.5 %. A case/problem of highly quenched samples still remains to be solved.