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Determination of biogenic component in liquid fuels by the ^{14}C direct LSC method by using quenching properties of modern liquids for calibration ☆

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HIGHLIGHTS

- Radiocarbon method is applicable for biogenic component determination.
- Biogenic component in liquids determined by direct measurement in LSC.
- New evaluation technique is proposed for liquid fuels.
- Quenching of modern liquids is used for calibration.
- Quenching curve does not depend on chemical composition of the liquid.

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ABSTRACT

The fraction of biogenic component within various types of materials that can be used as fuels for energy production and transport can be determined by measuring their ^{14}C activity. The method is based on different ^{14}C signatures of the biogenic and the fossil components: while the biogenic component reflects the modern atmospheric ^{14}C activity, no ^{14}C is present in fossil fuels. A direct measurement of the ^{14}C content in liquid fuel by liquid scintillation counter is a simple and fast technique but has a main disadvantage: different liquid colors cause different quenching properties and affect the measurement efficiency. We propose a new evaluation technique that uses liquids of different colors to construct modern and background calibration curves. Various binary mixtures of biogenic liquids have been used to verify the relation between the count rate and the quenching parameter. Mixtures of a biogenic and a ^{14}C-free liquid demonstrated the potential of the proposed technique for determining the biogenic fraction of a mixture.

1. Introduction

Intensive use of fossil fuels for energy production and transport during 20th century caused an increase of CO_2 concentration in the atmosphere (Dijs et al., 2006). The increase of 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 (European Commission, 2003). 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. The European Standard EN 15440:2011 (European Committee for Standardization, 2011) specifies three normative methods for the determination of the biogenic fraction in solid recovered fuel (a mixture of biogenic and non-biogenic substances): the selective dissolution in a hydrogen peroxide/sulfuric acid mixture, the manual sorting method, and the ^{14}C method based on different content of ^{14}C in biogenic and in fossil components. American Society for Testing and Materials (2012) defines standard test methods (i.e., measurement techniques) for determining the biobased content of solid, liquid and gaseous samples using radiocarbon analyses.

^{14}C is a cosmogenic isotope, formed in the upper atmosphere by interaction of neutrons produced in various transformations of cosmic rays that enter the atmosphere with atmospheric ^{14}N.

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Together with other carbon isotopes (stable isotopes ^{12}C and ^{13}C) ^{14}C combines with atmospheric oxygen forming carbon dioxide, which is used by plants in the photosynthesis, and animals then acquire ^{14}C by eating the plants. In such a way, a uniform distribution of ^{14}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 (Libby et al., 1949; Arnold and Libby 1949; Libby 1955) that can be used for dating organic material of up to 60,000 years old.

A pure biogenic material reflects the modern atmospheric ^{14}C activity, while no ^{14}C is present in fossil fuels (oil, coal). Therefore, the biogenic fraction of any material of interest is proportional to its ^{14}C content (Mohn et al., 2008). The ^{14}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 for energy production or transport, such as solid communal waste, used car tyres and liquid fuels. It can be used also to determine the bio-based content of various manufactured products (e.g., solvents and cleaners, lubricants, construction material, carpets, etc.) (Norton and Devlin, 2006). Alternatively, the ^{14}C method can be applied to determine ^{14}C content of the CO_2 produced by combustion of various fuels in waste-to-energy plants (Mohn et al., 2008; Muir et al., 2015). Any measuring technique used in ^{14}C laboratories could be used (American Society for Testing and Materials, 2012). In Section 2 (^{14}C measurement techniques) we present comparison of characteristics (precision, complexity, and price) of various techniques for biogenic fraction determination by the ^{14}C method. Accuracy of the ^{14}C method, irrespective of the used measurement technique, has been regularly checked by international radiocarbon intercomparison studies (e.g. Scott et al., 2010) and is not a subject of this paper. Section 3 gives a brief definition of the quantities and units used. A new evaluation technique for direct measurement of 14C activity in liquids by liquid scintillation counting is presented in Section 4.

2. Comparison of ^{14}C measurement techniques

Different measurement techniques can be applied for ^{14}C activity measurement (e.g., American Society for Testing and Materials, 2012). Radiometric measurement techniques are based on counting ^{14}C decay rate by gas proportional counters (GPC) (Nydal et al., 1975) or liquid scintillation counters (LSC) (Noakes et al., 1965; Kojola et al., 1984; Polach et al., 1988; Theodorsson, 1991), while the accelerator mass spectrometry (AMS) technique counts the number of ^{12}C, ^{13}C and ^{14}C atoms (Nelson et al., 1977; Bennett et al., 1977). Before being measured, a sample has to be prepared in a form suitable for the measurement, and the first step is combustion of organic samples or hydrolysis of carbonate samples to obtain CO_2. For GPC measurement CO_2 is then usually converted to methane and for LSC measurement to benzene. Alternatively, CO_2 can be absorbed in a cocktail (Qureshi et al., 1989; Woo et al., 1999). For AMS measurements graphite targets are usually prepared (e.g., Noakes et al., 2006). In the Radiocarbon Laboratory of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia, the AMS and two LSC measurement techniques can be performed (Horvatinčić et al., 2004; Krajcar Bronić et al., 2009, 2010a).

The main characteristics of the mentioned ^{14}C measurement techniques – sample type, required mass of carbon, complexity, precision, price, main drawback – are compared in Table 1. Note that the GPC measurement technique is not discussed because it has been replaced by either LSC or AMS techniques. The main advantages of the AMS technique are smaller sample size needed than for the radiometric techniques (as little as several mg of a sample, depending on the type of a sample) and higher precision. However, the AMS analysis is more expensive, so not all laboratories can purchase the AMS machine. In the application of bio-based product analysis, sample size is not typically a limiting factor, but samples frequently exhibit heterogenic compositions (Noakes et al. 2006). If LSC techniques are at disposal, and if the mass of the sample is large enough, it may be advisable to use the LSC for certain types of samples for monitoring purposes or hydrogeological applications (Krajcar Bronić et al., 2010b). The LSC-benzene technique includes a complex and time-consuming benzene synthesis but gives lower uncertainties than the much simpler technique of CO_2 absorption in absorption-scintillation cocktails. Due to relatively high measurement uncertainty of the LSC-CO_2 technique, it is usually not applied for archeological samples, although technically all samples can be prepared in the form of absorbed CO_2. The simplest method of direct LSC measurement of liquids mixed with an appropriate scintillation cocktail is applicable only to liquid fuels (Krištof and Kožar Logar, 2013; Idoeta et al., 2014). The method does not require special sample pretreatment, but the measurement efficiency depends on the sample color (Edler and Kaihola, 2007).

3. How to calculate biogenic fraction

Results of measurement of ^{14}C activity are presented as relative specific ^{14}C activity, $a^{14}C$, expressed in percent of modern carbon (pMC), where 100 pMC is equivalent to the specific activity of 226 Bq/kgC (Mook and van der Plicht, 1999). In further text we use the term "^{14}C activity" for $a^{14}C$. (Recently, it has been proposed to use a dimensionless quantity F, fraction of modern carbon (van der Plicht and Hogg, 2006), which is equivalent to $a^{14}C$, with the difference that F is dimensionless, and $a^{14}C$ is expressed as percentage. However, we rather use $a^{14}C$, not to confuse F with f, defined in Eq. (1).).

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

$$a^{14}C = f_f\, a^{14}C_f + f_{bio}\, a^{14}C_{bio} \quad (1)$$

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

Table 1
Comparison of some characteristics of different techniques for ^{14}C measurement: sample types, required mass of carbon, complexity, precision, price and the main drawback.

Measurement technique	Sample types	Mass of carbon	Complexity*	Precision*	Price*	Main drawback
AMS	all	~1 mg	3	4	4	expensive instrument
LSC-benzene	all	~4 g	4	3	3	time-consuming
LSC-CO_2	all	~0.6 g	2	2	2	high uncertainty
LSC-direct	liquid fuels	10 ml of liquid	1	1	1	color quenching

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

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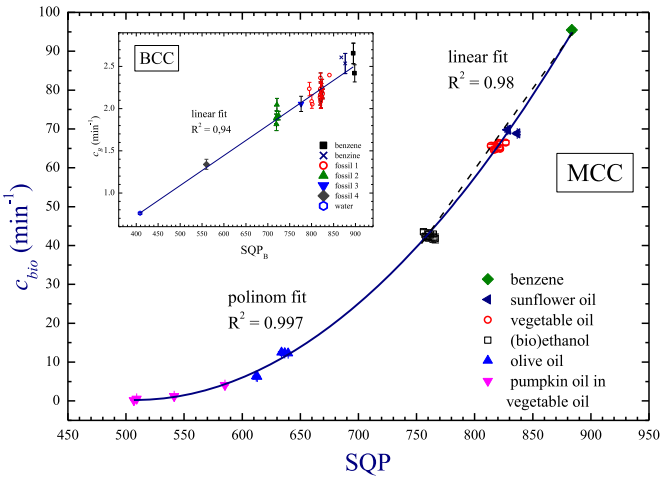

Fig. 1. Modern calibration curve (MCC) with a quadratic fit in the whole range of SQP values and a linear fit for SQP > 740. Inset: background calibration curve (BCC) with a linear fit.

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

Generally, $a^{14}C_{bio}$ refers to the biogenic ^{14}C activity of the year when the plant grew reflecting the ^{14}C content of atmospheric CO_2 during biomass growth. Before the anthropogenic activities disturbed the natural distribution of ^{14}C in the atmosphere and biosphere during the 20th century, the value of $a^{14}C_{bio}$ was 100 pMC (Levin et al., 2008). The $a^{14}C_{bio}$ has been changing in the second half of the 20th century approaching almost twice the natural $a^{14}C_{bio}$ value in the early 1960s due to atmospheric bomb tests and declining since then (Levin et al., 2008; Hua et al., 2013). The ASTM 6866 standard test method (American Society for Testing and Materials, 2012) recommends the use of 105 pMC for biogenic material originating from last several years.

The monitoring of ^{14}C activity of the atmosphere and biosphere performed in our laboratory showed that the atmospheric and plant ^{14}C activities have been almost constant during last 10 years (i.e., since 2005), 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}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 (Krajcar Bronić et al., 2010b). Therefore, to calculate the fraction of biogenic component (Eq. 2) the value $a^{14}C_{bio}$ of 105 pMC can be safely used for short-lived biomass that grew during last ~10 years. When the wood, wooden products or wooden pellets produced from a wood grown in the second half of the 20th century are used as fuels, ^{14}C activities may lie in the range between 105 pMC and even ~190 pMC (Levin et al., 2008; Krajcar Bronić et al., 2010b; Hua et al., 2013), depending on the year of growth. Such values would yield unrealistic f_{bio} values of >100%, if the correct $a^{14}C_{bio}$ values for the year of wood growth were not used.

4. Liquid fuels

According to the European Parliamed Council (2009; Directive 2009/28/EC) all (liquid) fuels have to contain at least 10% of biofuel, i.e., blend of biogenic origin, by 2020. Fossil matrix of the fuels can be gasoline (benzine), diesel (gas oil), kerosene, or naphtha, while biogenic blends are usually bioethanol, fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others (Krištof and Kožar Logar, 2013). A technique of direct measurement by the liquid scintillation counting of the ^{14}C content in liquid fuel is simple and fast and does not require any sample preparation procedure. However, some vegetable oils produced from the most common materials such as rapeseed, sunflower, soybean or animal fat, have more or less intense mostly yellowish colors. The different liquid colors cause different quenching properties of samples and thus change the measurement efficiency (Edler and Kaihola, 2007). Various methods have been suggested to overcome this main disadvantage of the direct method, such as decolorization (ter Wiel et al., 2010), or separate quenching curves for various combinations of the fossil matrix and biogenic blends resulting in rather complicated data evaluation techniques depending on the type of a sample, both of the fossil matrix and biogenic blend (Krištof and Kožar Logar, 2013; Idoeta et al., 2014) assuming that the sample composition is known.

Our laboratory received from a customer a set of liquid fuel samples of not known composition in which the fraction of biogenic component had to be determined. The set was completed with several different, but not identified, samples of pure fossil origin intended to be used as background samples. Since the type of the sample was not identified either, we could not apply the technique of different quenching curves (Krištof and Kožar Logar, 2013) and we needed a different approach to data evaluation.

A good correlation between the count rates of various fossil (i.e., background) samples and their SQP values was observed. The SQP is the standard quench parameter determined by the ^{152}Eu external source in the LSC Quantulus: the SQP value represents the channel dividing the ^{152}Eu spectrum into two regions containing 99% and 1% of the total counts. To check the relation, we included also benzine (gasoline) of analytical purity, distilled water and the ^{14}C-free benzene that is used as background sample in our routine ^{14}C dating measurements (LSC-benzene technique). The background count rate of all samples linearly correlated with the SQP values in the range of SQP~400 (water) to 900 (benzene), R^2=0.94 (Fig. 1. inset). The relation we call the "background calibration curve" (BCC). The BCC relates the SQP and count rates of various background samples, i.e. samples that do not contain ^{14}C, which can be considered as "fossil" samples.

Various biogenic liquids that are readily commercially available having different quenching properties are then used to construct "modern calibration curve" MCC (Fig. 1). We apply the conclusion about the constant $a^{14}C_{bio}$ values during last 10 years, as discussed in Section 3. Therefore, it is 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 have been used: vegetable (a mixture of sunflower and soybean oil, commercially available as "vegetable oil"), sunflower, two brands of olive oil, pumpkin oil, and bioethanol in addition. Although benzene is not used as a blend in fuels, our study included also modern benzene prepared from a sample of recent atmospheric CO_2 having ^{14}C activity of 104.5 ± 0.5 pMC, as measured by the standard LSC-benzene protocol (Horvatinčić et al., 2004). The MCC curve (Fig. 1) relates the count rate of biogenic materials with their SQP values. Benzene, known as the good medium for radiocarbon dating, gave the highest SQP value and the highest count rate among the studied liquids. Sunflower and vegetable oil samples of light yellow color gave surprisingly higher SQP values and count rates than the transparent bioethanol sample. Intensive colors of both olive oil brands resulted in low SQP values and lower count rates than other oil brands although all these samples are of recent biogenic origin. Pure pumpkin oil has a dark, almost black, color resulting in very low SQP value of 506. Addition of 10% of pumpkin oil into vegetable oil reduced the SQP value significantly, from ~830 to ~585, while addition of 20% of pumpkin oil reduced the SQP further to ~540. Addition of 30% of pumpkin oil reduced the SQP value of the mixture to ~510, i.e., almost to the value of pure

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pumpkin oil. The mixtures of vegetable and pumpkin oil gave also low count rates that are used for construction of MCC in low SQP region (Fig. 1).

The shape of the obtained MCC (Fig. 1) does not depend on the chemical composition of the liquid, i.e., on the number of carbon atoms in a molecule. This fact is rather surprising and enables the calibration of various modern samples irrespective on the exact chemical composition. In the whole region of SQP values the MCC can be described by a quadratic function (with $R^2=0.997$), while for SQP > 740 it can be approximated by a linear function ($R^2=0.98$). At the SQP values below 570, the count rate of the biogenic samples becomes indistinguishable (within measured uncertainties) from the background count rate, so the MCC is valid for the range 570 < SQP < 900.

With the BCC and MCC curves, we can now propose a new evaluation technique of data collected by liquid scintillation counter. The proposed technique takes advantage of otherwise main drawback of the method, i.e., color quenching, in such a way that the quenching parameter is used as the calibration parameter separately for modern and ^{14}C-free samples.

The procedure of data evaluation for the unknown sample consists of (1) measurement of SQP and count rate c of the unknown sample, (2) determination of background count rate c_B corresponding to the measured SQP value by using BCC, and (3) determination of the count rate of the biogenic sample c_{bio} corresponding to the measured SQP value 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 (compare Eq. (2))

$$f_{bio} = \frac{c - c_B}{c_{bio} - c_B} \quad (3)$$

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 were evaluated in the window between channel 124 and 570. Setup of the Quantulus parameters were the same as for other ^{14}C measurements, i.e. high coincidence bias and the pulse amplitude comparison (PCA) value of 100. Measurement duration of 600 min was divided into 20 intervals of 30 min each, and the SQP value was measured in each cycle. The average count rate and its uncertainty were calculated by using EasyView1.0 spectra evaluation software.

The critical level L_c and the detection limit L_d, as defined by Currie (1968), are determined for the case of "well known blank" and both α and β (probabilities of an error of the first and second kind) values of 0.05 and the corresponding k value (the quartile of the standard normal distribution for a 95% confidence level) of 1.64. In this case the critical level is expressed as $L_c=k\sigma_B$ and the detection limit as $L_d=2k\sigma_B$ (Currie, 1968), where σ_B is the background count rate uncertainty (shown in Fig. 1, inset). Table 2 summarizes the typical σ_B values obtained at three SQP values, and

Table 2
Critical levels and the detection limits of f_{bio} at three SQP values derived from background uncertainty σ_B after Currie (1968). The uncertainties of f_{bio} estimated from the typical uncertainties of count rates giving this f_{bio} values at the given SQPs.

SQP	σ_B	f_{bio} (%) critical level	f_{bio} (%) detection limit	uncertainty (%) at $f_{bio}=5\%$	uncertainty (%) at $f_{bio}=50\%$
820	0.08	0.23	0.46	0.17	0.6
700	0.07	0.5	1.0	0.4	0.9
600	0.06	2.0	4.0	1.6	2.0

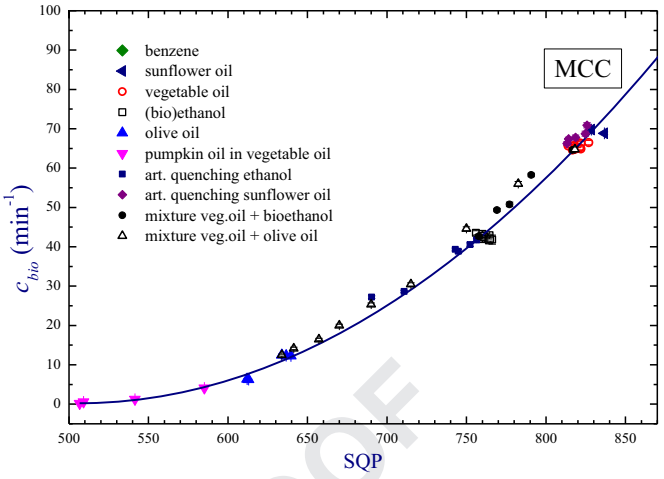

Fig. 2. Modern calibration curve (MCC) with results of artificial quenching of vials with sunflower oil and bioethanol, and mixtures of two biogenic liquids (vegetable oil and olive oil, vegetable oil and bioethanol, vegetable oil and pumpkin oil).

the corresponding critical levels and detection limits of f_{bio}. The detection limit of the proposed method is therefore < 1% of biogenic fraction for moderately quenched samples (SQP > 700). For highly quenched samples the detection limit is higher because the difference between count rates of the modern and fossil liquids decreases and at SQP < 570 the count rate of modern liquids becomes indistinguishable from the count rate of the ^{14}C-free samples. The uncertainties of the measured f_{bio} values of 5% and 50%, also shown in Table 2, are calculated from the uncertainties in count rates (600 min measurement) that would result in such f_{bio} values at the given SQP values.

To see whether quenched modern samples lie on the MCC curve, we performed two sets of tests. First, the vials with bioethanol and sunflower oil were artificially quenched by covering the vials with increasing number of layers of semitransparent tape (1–5 layers). Both the SQP values and the count rates were lower for taped vials and the values moved along the MCC (Fig. 2). The second set consisted of mixing two biogenic liquids having different SQP values, such as vegetable oil and bioethanol, and vegetable and olive oil, while highly quenched mixtures of pumpkin oil in the vegetable oil have already been described. Mixtures of vegetable oil with bioethanol and olive oil resulted in data points positioned along the MCC curve (Fig. 2), justifying previous conclusion that the MCC is not sensitive to the exact chemical composition of the liquid.

To test the proposed evaluation technique we prepared two sets of mixtures of fossil and biogenic liquids in the nominal concentration range of the biogenic component from 0% to 100%. In the first set of experiment both liquids had similar SQP values. The measured f_{bio} values of mixtures of vegetable oil and "fossil 1" (Fig. 3) determined by the described data evaluation technique agree very well with the nominal f_{bio} values (linear correlation shown in Fig. 3 with $R^2=0.998$), while the SQP values of all mixtures remained constant with the median 819.2 and the mean 819.1 ± 1.5. Similar results were obtained also for a mixture of bioethanol and the "fossil 2" sample having SQP values of 750 and 720, respectively.

Finally, the set of mixtures of bioethanol, that is often used as a biogenic blend, and the analytically pure benzine was prepared (Fig. 4). These liquids have different both SQP values and ^{14}C contents. The SQP values of mixtures showed a continuous change with the mixture composition. The measured f_{bio} values correspond well to the nominal biogenic fractions below 5% and about 80%. However, the measured biogenic fraction f_{bio} slightly

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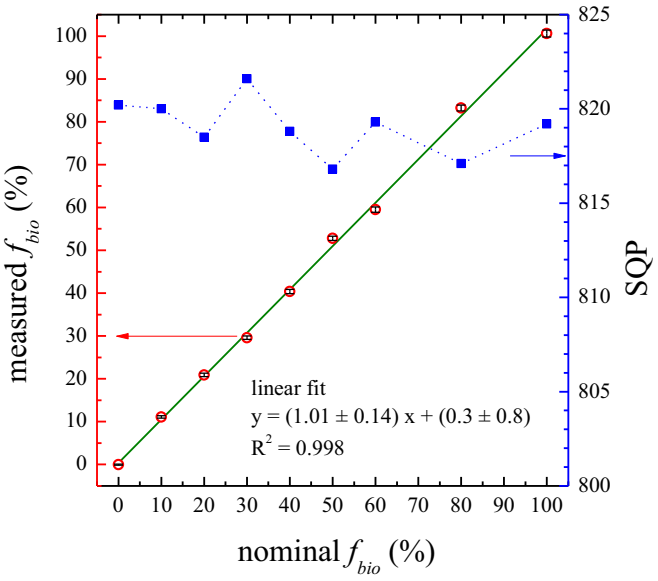

Fig. 3. Comparison of the measured biogenic fraction f_{bio} in prepared mixtures of vegetable oil and fossil fuel ("fossil 1") with the nominal fraction of the vegetable oil shown on *x* axis. The SQP values of the mixtures are shown also (right ordinate). Note that the uncertainties in f_{bio} lie within the symbols.

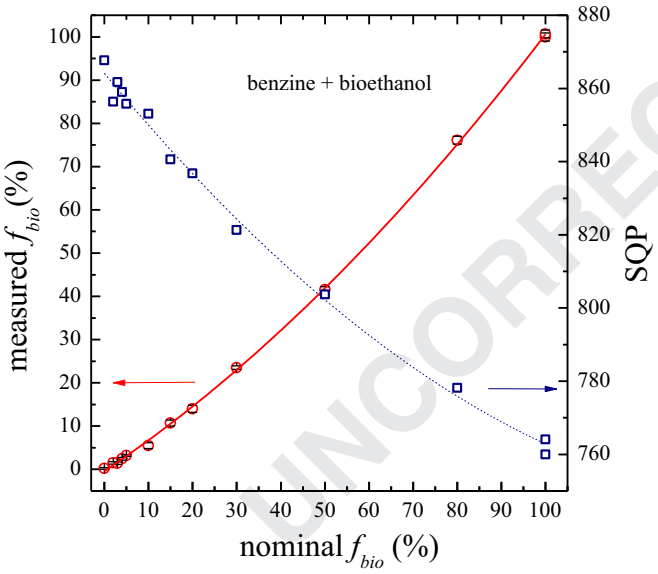

Fig. 4. Comparison of the measured biogenic fraction f_{bio} in prepared mixtures of bioethanol and analytically pure benzine with the nominal fraction of the bioethanol shown on *x* axis. The SQP values of the mixtures are shown also (right ordinate).

underestimates the nominal biogenic fraction in the region between.

5. Conclusion

Different measurement techniques developed mainly for the radiocarbon dating application can be successfully applied also for the purpose of biogenic fraction determination. In case of organic liquids, including liquid fuels, a simple method of direct measurement by liquid scintillation counting has been recently developed for determination of the biogenic fraction. The main problem associated with the LSC-direct method is variable quenching due to different colors of liquids.

The innovative data evaluation technique of the direct measurement of ^{14}C activity of liquid fuels in LSC is presented here. It utilizes the color quenching of various types of liquids having the same ^{14}C activity, to construct calibration curves for modern and ^{14}C-free samples. Modern calibration curve has been obtained by different modern liquids, such as various brands of domestic oil, bioethanol and benzene of the known ^{14}C activity, while for the background calibration curve various ^{14}C-free liquids have been used. All modern liquids and their mixtures form a single curve so we conclude that the method does not depend on the exact chemical composition of the liquid. The method was successfully applied to mixtures of vegetable oil and bioethanol with ^{14}C-free liquids. We suggest that the data evaluation method could be used for determining the biogenic fraction in various types of organic liquids, including liquid fuels of unknown chemical composition.

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