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DETERMINATION OF THE BIOETHANOL RATIO IN GASOLINE FROM ^{14}C ACTIVITY CONCENTRATION BY LIQUID SCINTILLATION COUNTING TECHNIQUE IN TURKEY

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TÜRKİYE’DE BENZİNLERİN SIVI SİNTİLASYON TEKNİĞİ İLE ^{14}C AKTİVİTESİNİN BELİRLENEREK BİYOETANOL ORANLARININ BELİRLENMESİ

Abstract:

Liquid Scintillation Counting (LSC) technique is commonly applied in determining the fraction of bioethanol-gasoline blending. The basic principle of the technique is to measure the radioactivity level of ^{14}C isotope with the half-life of 5730 years, which is formed naturally and reaches to equilibrium in the bodies of all the living organisms. Gasoline is produced from petroleum, which is formed by the organisms that had died millions years ago and exposed to pressure and heat under the ground. In addition, bioethanol is a type of biofuel, obtained from fermentation of such crops like sugar beet, sugar cane, corn and sweet sorghum. Owing to the fact that the ^{14}C radioactivity level in gasoline becomes to the unmeasurable levels within millions years and the bioethanol has ^{14}C level in equilibrium with the atmosphere, it is possible to determine the blending ratios of gasoline and bioethanol.

In this study, the applicability of the determination of the ratio of biological additives in gasoline by the liquid scintillation counting technique was investigated. Gasoline-bioethanol mixture ratios were determined successfully in the commercially available gasoline and bioethanol mixtures.

Özet:

Benzin-biyoetanol karışım oranının deneysel olarak tespit edilmesinde Sıvı Sintilasyon Sayım Tekniği (LSC) yaygın olarak kullanılmaktadır. Tekniğin ana prensibi atmosferde doğal yollarla oluşan ve zamanla bütün canlıların vücudunda bir dengeye gelen ve yarı ömrü 5730 yıl olan ^{14}C izotopunun radyoaktivite seviyesinin ölçülmesidir. Benzin, milyonlarca yıl önce ölüp toprak altında kalmış olan canlıların ısı ve basınç etkisiyle dönüşmüş olduğu petrolden üretilmektedir. Biyoetanol ise şeker pancarı, şeker kamışı, mısır, tatlı sorgum gibi bitkilerin fermente edilmesi ile üretilen bir çeşit biyoyakıttır. Benzinde bulunan ^{14}C radyoaktivite seviyesinin milyonlarca yıl içerisinde yarılanarak ölçülemeyecek seviyelere gerilemesi, biyoetanolün ise atmosferle denge halinde ^{14}C seviyesine sahip olması benzin-biyoetanol karışım oranlarının belirlenmesine olanak sağlamaktadır.

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Bu çalışmada sıvı sintilasyon sayımı ile ticari olarak temin edilebilen benzin ve biyoetanol karışımLarının karışım oranları belirlenmiştir.

Key words: Liquid Scintillation Counting, ^{14}C, Bioethanol, Activity concentration, biofraction

Anahtar kelimeler: Sıvı sintilasyon sayımı, ^{14}C, Biyoetanol, Aktivite konsantrasyonu, biyofraksiyon

1. Introduction

The carbon which is trapped in the earth's crust by millions of years is revealed due to the consumption of fossil fuels. Global warming, especially formed by CO_2 emission as a result of the greenhouse effect, is an important concern for many countries. The Kyoto Protocol, signed by 181 countries, requires countries to reduce the amount of carbon released into the atmosphere to levels in 1990 (https://unfccc.int/documents). In the protocol, it is stated that instead of fossil fuels, fuels with biological origin which are relatively more costly should be used. Fossil fuels with certain amounts of biofuels added have the potential to significantly reduce CO_2 emissions (Yunoki and Saito, 2009).

The European Union (EU) encourages the use of biofuels instead of fossil fuels. According to the EU directive, the European Union aims to meet 10 percent of the transportation need from biofuels in 2020 (EC Directive, 2009). Almost all the countries encourage the production of biofuels by direct financial aid or tax reduction. As a result of these incentives, a significant increase was observed in the consumption of biofuels as seen in Figure 1 and this consumption is expected to increase in the coming years (https://www.iea.org/tcep/transport/biofuels/).

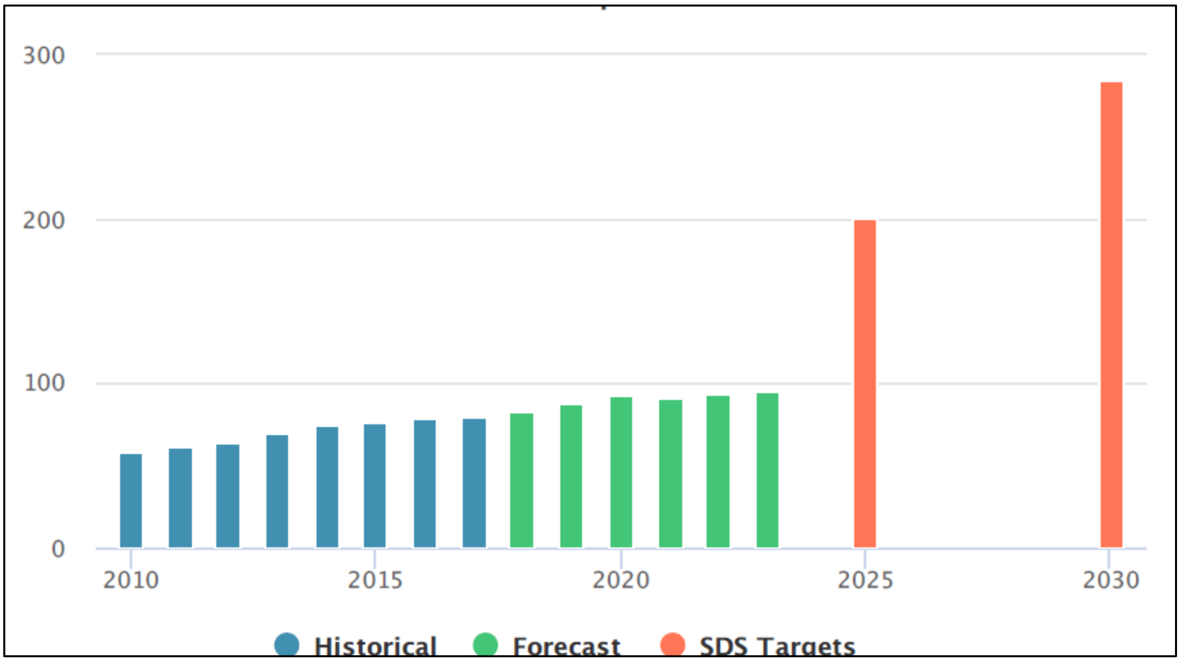

Figure 1. Global biofuel production, forecast, targets.

Biofuels are divided into two types: bioethanol and biodiesel. Bioethanol is a biofuel that can be used as fuel in gasoline-powered vehicle engines, while biodiesel is a type of biofuel that can be used as fuel for motorized vehicles that can be derived from oilseed plants or animal fats as well as vegetable and animal waste oils.

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The blending ratio of biofuels differs for each country according to the own legislation. Countries can make this ratio optional or compulsory by determining a certain limit blending rate. Thus, the need of inspection of many products produced by blending biological origin additives has arisen and also new analysis methods are needed.

Table 1. Comparison of advantages and disadvantages between methods. (Edler, 2007)

METHOD	ADVANTAGE	DISADVANTAGE
Benzene in LSC	High sensitivity, very precise, good instrument availability	More time consuming sample preparation, low capacity, benzene is a cancerogenic material.
CO_2 in LSC	Less sample preparation and low costs compared to benzene in LSC, good instrument availability	Low sample activity due to limited sample capacity of Carbosorb. Not sensitive for lowest ^{14}C activities.
AMS	High sensitivity, very precise.	High costs, therefore mainly samples with carbon content below 10%.
Direct measurement in LSC	Minimum, very fast sample preparation, good sensitivity, low costs per measurement, good instrument availability.	There is no standardized technique

In table 1 you can find the comparison of four methods used to determine the biofuel ratio of the gasoline or diesel fuels. Among these methods direct addition method is the cheapest and the fastest method.

Living things get equilibrium with the atmosphere in terms of CO_2 concentration through both nutrition and respiration during their survival. Therefore, the ^{14}C concentration of the atmosphere, the ocean and living things should be almost in balance. After the death of living things, the new ^{14}C entry stops and the ^{14}C density and radioactivity in their body decreases at a known rate. Hence, fossil fuels should not contain ^{14}C activity concentration due to long time. The ^{14}C activity concentration measured in fuels must belong to new products of biological origin added to the mixture. (Edler, 2007) Based on this assumption, direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique is one of the most efficient analysis methods for determining biofuel ratios (Idoeta, Pérez, Herranz and Legarda, 2014; Dijs, Van Der Windt, Kaihola & Van Der Borg, 2006; Edler

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and Kaihola, 2010; Norton, Cline, and Thompson, 2012; Kristof and Logar, 2013, Kristof, Hirsch and Logar, 2014; Bronić, Barešić, Horvatinčić and Sironić, 2016).

According to the National Legislation in Turkey, fossil fuels have to be mixed with certain proportions of biofuels and tax deductions are also applied for this issue (http://www.resmigazete.gov.tr/eskiler/2012/07/20120707-35.htm). For bioethanol, this ratio is 3% (v/v) for Turkey. Bioethanol is the most familiar renewable source for gasoline because of its productivity and safety.

In the present study, gasoline-bioethanol mixture ratios were determined by measuring the liquid scintillation counter in the commercially available gasoline and bioethanol mixtures. Gasoline samples should contain at least 3% (v/v) bioethanol produced from the domestic agricultural products.

2. Material and Methods

In this study, four commercially available bioethanol-gasoline mixtures were purchased from different stations in Turkey. These four samples are analyzed by using liquid scintillation technique in order to determine if they contain the relevant amount of bioethanol complying with the related legislations.

The liquid scintillation counting method is a technique for measuring the direct mixture of the sample with a scintillation cocktail in which the ^{14}C radionuclide can be homogeneously mixed. As suggested in ASTM - D6866 - 06 method, experiments were carried out with a commercially available Ultima Gold F cocktail. The sample and cocktail were blended in 20 mL glass scintillation vials. Each vial was counted for 6 hours at 4 ^{o}C and the cocktail-sample mass ratio was adjusted to 12:8. “Perkin Elmer Quantulus1220 liquid scintillation counting device at the Department of Radiation and Accelerator Technologies of Turkish Atomic Energy Authority was used for measurements (Figure 2). Technical information related to the counting system is easily accessible from elsewhere (https://www.perkinelmer.com.cn/CMSResources/Images/46-73870SPC_1220Quantulus.pdf) The Liquid Scintillation Spectrometry Laboratory has been accredited by Turkish Accreditation Agency (TURKAK) member of the International Laboratory Accreditation Cooperation (ILAC) since 2009.

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Figure 2. Perkin Elmer Quantulus1220 liquid scintillation counting device.

In order to determine the bioethanol fraction in commercially available gasoline samples, a calibration set was prepared using samples with known bioethanol fractions. For this purpose, approximately 0.5%, 1%, 2%, 3%, 5%, 10%, 50% and 100% by weight (m/m) bioethanol-gasoline mixtures were prepared and these mixtures were completed to 20 mL by adding approximately 8 mL scintillation cocktail. The vials prepared in 8 different fractions were placed in counting cells of the liquid scintillation counter and counted for six hours in the dark environment.

Based on the 100% gasoline solution count values, corresponding net CPM values for each fraction were determined. Then, the activity value per unit mass was calculated by dividing CPM values to the added fuel mass. Subsequently, a calibration curve was drawn using the net CPM / g values and fraction ratio and the curve equation was calculated. Finally, commercially available samples were counted in the liquid scintillation counter under the same conditions to determine the proportions of the samples by using calibration curve equation.

3. Results Discussion

Energy spectrum of pure gasoline, pure bioethanol and 10% bioethanol mixed gasoline are given in Figure 3, Figure 4 and Figure 5, respectively. In the given spectras, bioethanol yields peaks between 100 and 480 channel numbers.

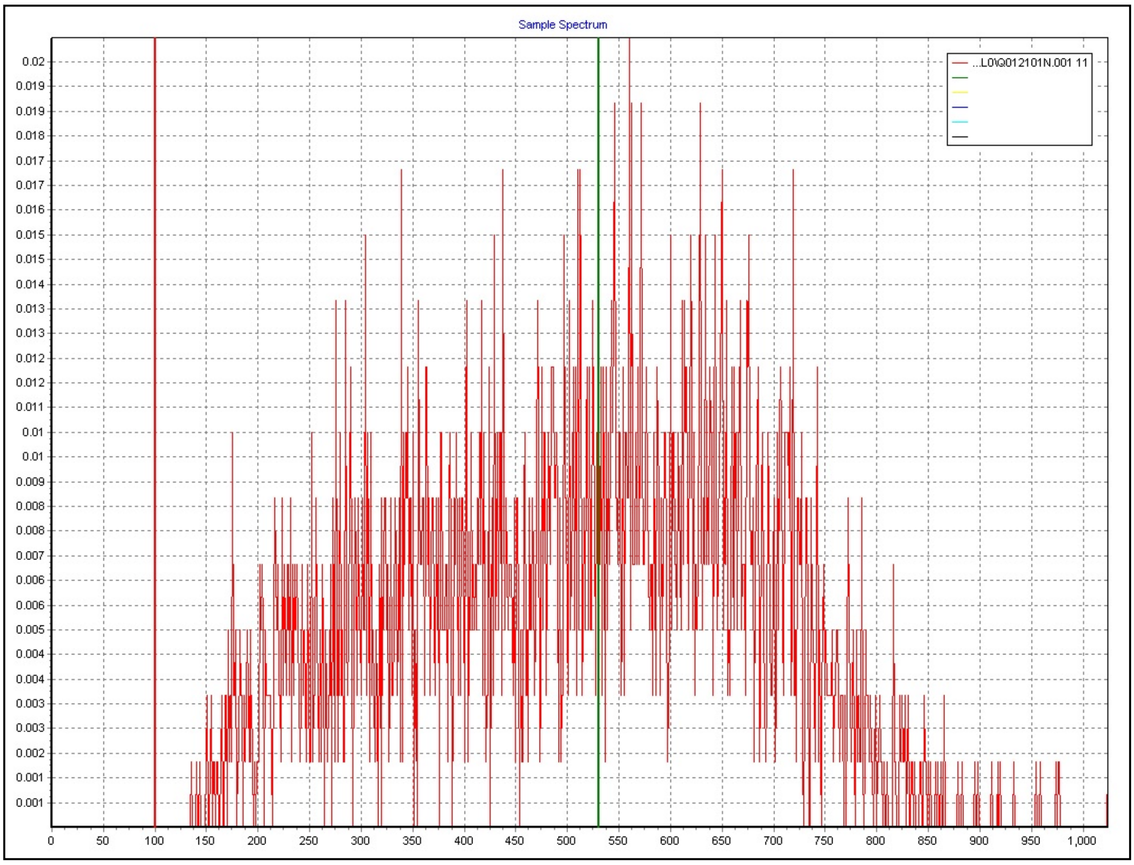

Figure 3. The energy spectrum of pure gasoline.

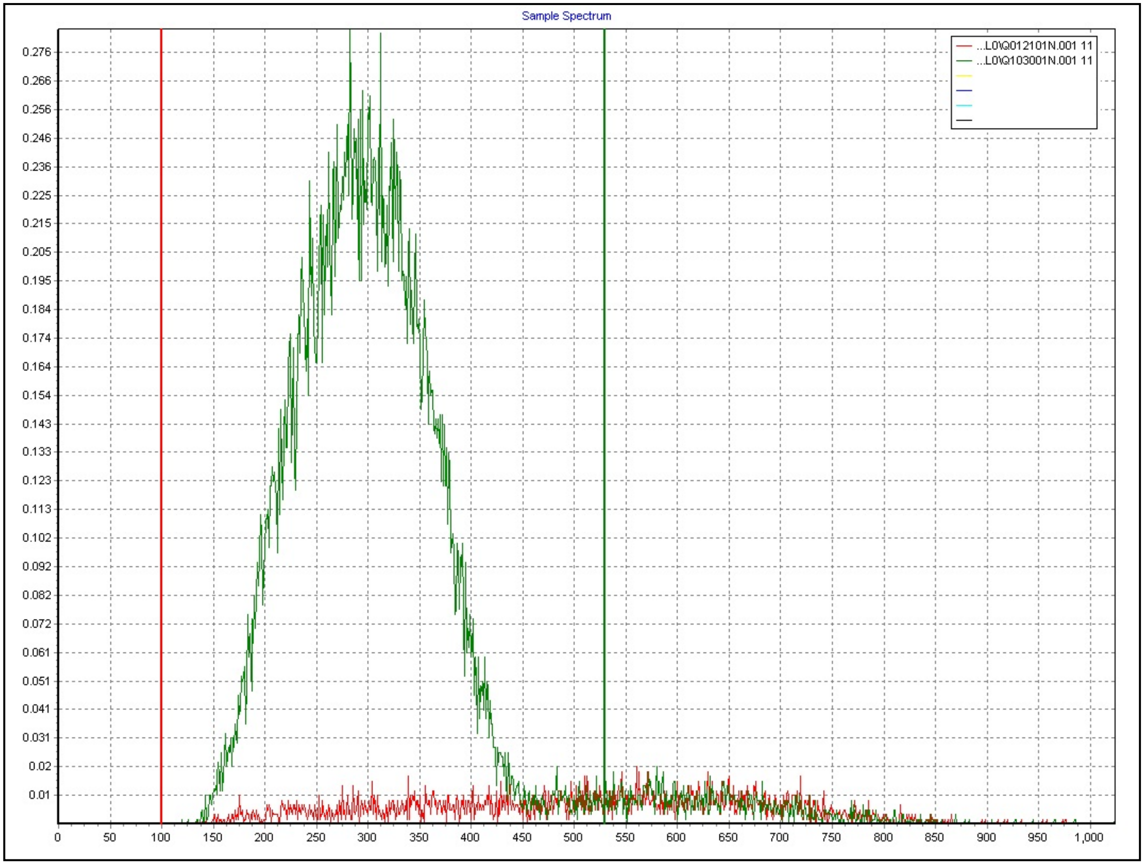

Figure 4. The energy spectrum of pure bioethanol.

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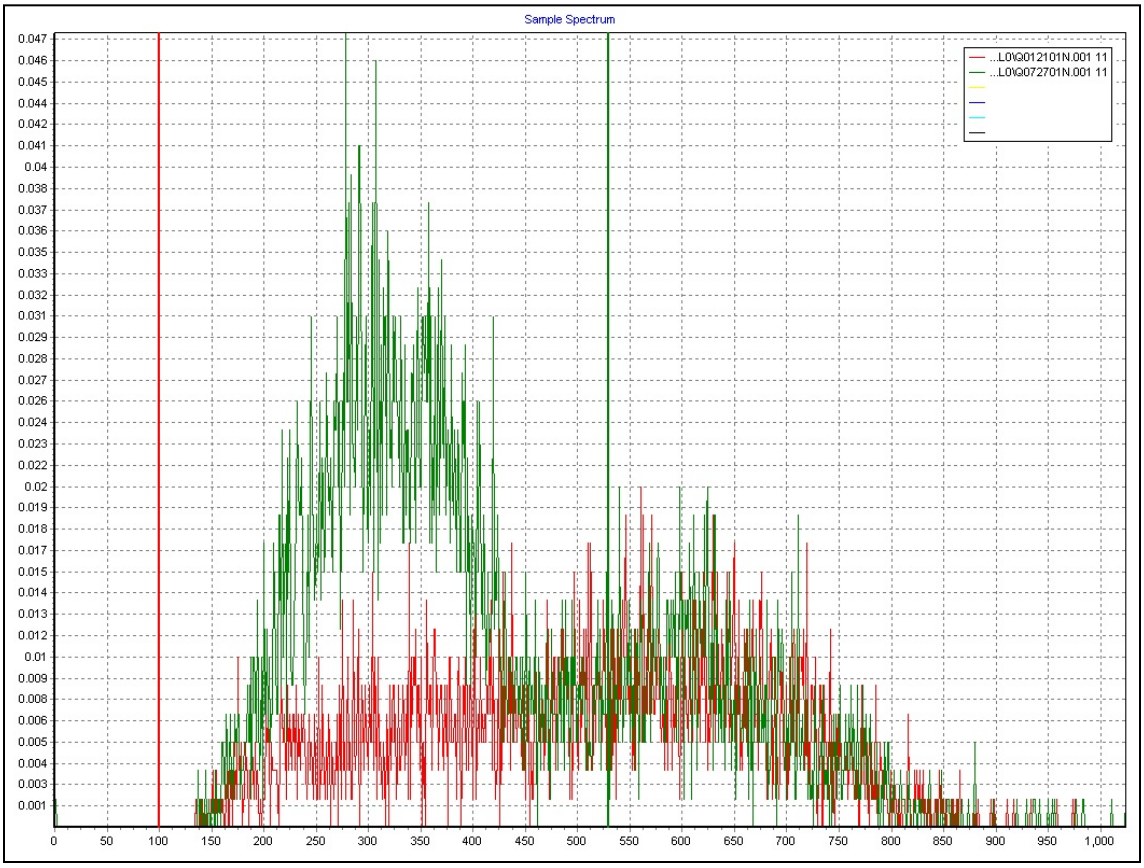

Figure 5. The energy spectrum obtained from 10% bioethanol mixed gasoline.

Curve equations were found by fitting two different calibration curves based on the counts between 1 - 1024 channels representing the entire spectrum and 130 - 540 channels that the bioethanol peaks. Relation of CPM/g and fraction values are given below in Figure 6 and Figure 7.

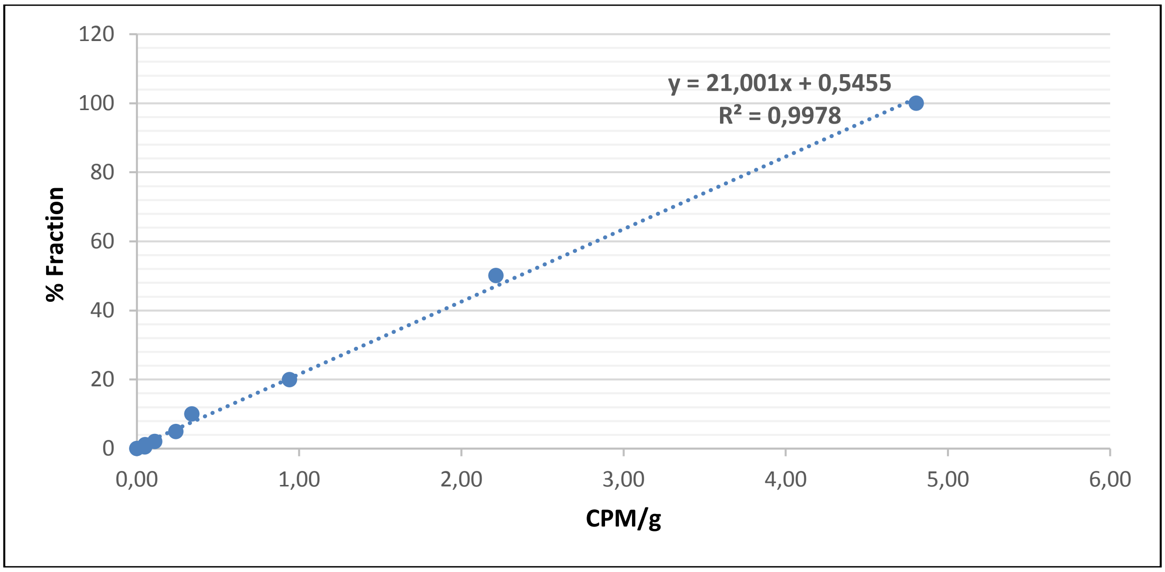

Figure 6. Relation of CPM/g and fraction values between 130 and 540 channel numbers.

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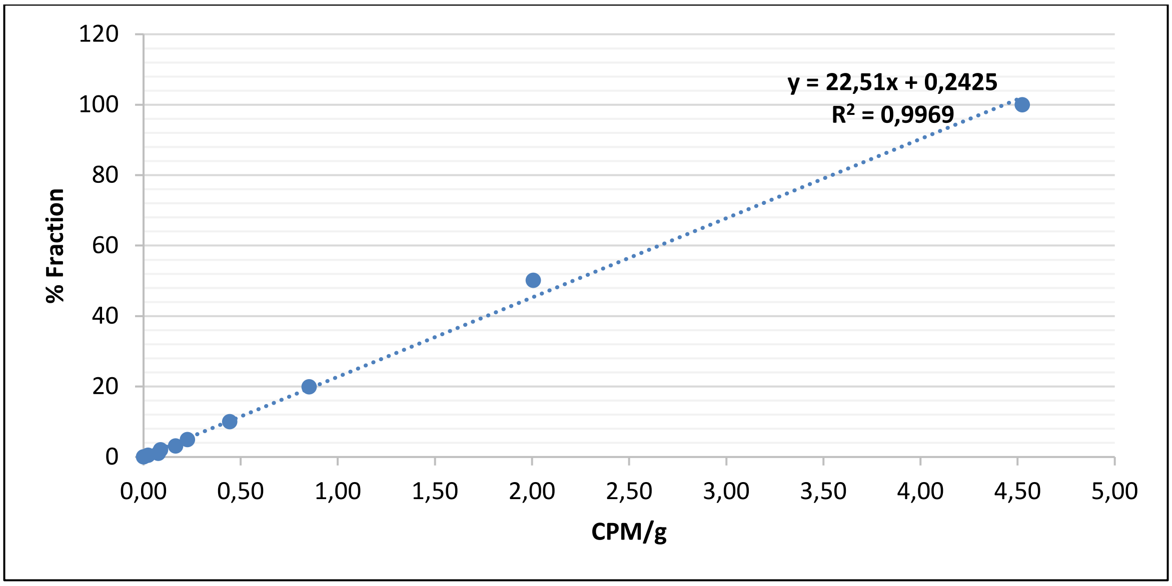

Figure 7. Relation of CPM/g and fraction values between 1 and 1024 channel numbers.

The correlation value R^2 of the curve obtained based on CPM/g values between channel numbers 130-540 is obtained closer to 1 by using the best fitted equation of the graph which is given below:

$$Y=21.001X + 0.5455$$

X and Y are refer CPM/g and % Fraction, respectively. According to the equation, the values of the fractions given in Table 2 were calculated using the obtained calibration curve equation and CPM values get from the counts of ethanol-gasoline mixture samples. In terms of commercial confidentiality, A, B, C and D letters were used instead of the original names of gasoline companies.

Table 2. Experiment results performed with real samples.

Sample	Bioethanol Mass (g)	CPM (130-540)	Net CPM (130-540)	Activity CPM/g	Experimental Fraction (%)
Background	8.33	2.41	0.00	0.00	0.55
A	8.33	4.31	1.89	0.23	5.32
B	8.35	3.94	1.53	0.18	4.39
C	8.32	3.38	0.97	0.12	2.99
D	8.33	3.57	1.15	0.14	3.45

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It was preferred to use as much gasoline as possible to determine the mixing ratio and 12:8 was determined to be ideal ratio. Calibration curve was calculated from volumetric ratios, but different amounts were observed as a result of pipetting. Therefore, it was decided to use mass ratios. Mixtures were determined to be between 8.30 and 8.34 grams, so, the adjusting errors related to the analyst that could occur during the pipetting was prevented. The calculated density levels of 95 octane gasoline and bioethanol used in the experimental processes are given in Table 3.

Table 3. Average density levels of gasoline and bioethanol

	95 Octane Gasoline (g/mL)	Bioethanol (%99.98) (g/mL)
1st measurement	0.69	0.79
2nd measurement	0.71	0.81
3rd measurement	0.70	0.79
Mean	0.70	0.79

The mass-determined ratios were converted to volumetric ratios by using this method and given in the Table 3.

Table 4. Volumetric ratios transformed from mass-ratios

	Gasoline (g)	Bioethanol (g)	Gasoline (mL)	Bio EtOH (mL)	Total Volume (mL)	Volumetric Ratio (v/v)
BKG	8.32	0.02	11.84	0.06	11.90	0.48
A	7.90	0.43	11.27	0.56	11.83	4.74
B	8.00	0.35	11.40	0.46	11.86	3.91

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C	8.09	0.23	11.54	0.31	11.85	2.65
D	8.11	0.23	11.50	0.36	11.86	3.07

According to the national regulation, it is legally obligatory to make at least 3% biofuels contribution to gasoline. When the test results given in Table 4 are examined, it is seen that the legal requirement of 3% by volume is not fully complied with.

3. Conclusions

In the current study, the applicability of the determination of the ratio of biological additives in gasoline by the liquid scintillation counting technique was investigated. By the way, bioethanol-gasoline ratios in four commercially available gasoline samples were successfully determined. The results showed that the biofraction values found in the tests were not in compliance with the legal requirement caused the emergence of other concerns. It was concluded that the additives in the products of biological origin should be inspected independently from the manufacturer. By increasing the variety of biological products, new laboratories aiming to determine the activity of ^{14}C by liquid scintillation counting technique should be established to control the products offered by the producers.

4. Acknowledgments

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