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Direct LSC method for measurements of biofuels in fuel

Romana Krištof [a,b], Jasmina Kožar Logar [b,*]

[a] AMES d.o.o., Brezovica pri Ljubljani, Slovenia
[b] Jožef Stefan Institute, Ljubljana, Slovenia

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ABSTRACT

Direct liquid scintillation counting (LSC) for quantification of biofuels content in fuels was implemented and validated on three liquid fossil fuel matrices—ethanol, gasoline and diesel. Fatty acid methyl esters (FAMEs), hydrogenated vegetable oils (HVO) and bio-ethanol were used as biofuels. The method is applicable in the range up to 100% for all tested combinations of bio components. The sensitivity and precision of the method are suitable for determination of bio component content in the blends which is appearing on the global market. The method does not require special equipment for sample preparation.

1. Introduction

Transportation is one of the main reasons for elevating consumption of energy [1]. Several countries of the world encourage the production of energy from renewable sources. The EU Member States reduced the taxes for the bio components in fuels because the production costs of bio-fuels are higher than the price of fossil fuels [2,3]. The testing methods are therefore needed to control the presence of bio components in fuels and to prove the eligibility for tax reimbursement.

Different substances of distinct origin can be used as bio-fuels, for example bio-ethanol, ethyl tertiary butyl ether (ETBE), fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others. Several techniques are therefore applied for monitoring purposes, taking into consideration different bio-fuels characteristics. Nuclear magnetic resonance [4], gas chromatography [5], accelerator mass spectrometry (AMS) [6–8] and infra-red spectrometry [9] which are also standardised by EN 14 078 and ASTM D7371, can be used for characterisation of specific bio-components related to diesel, usually for FAMEs. Time-consuming analytical techniques usually require skilful operators for complex sample preparation and expensive equipment. Distinction between bio-ethanol and ethanol, for example, cannot be determined by many of the above mentioned methods. AMS and Liquid Scintillation Counting (LSC) are able to distinguish between these two components.

In LSC, the quantity of ^{14}C in the sample is the criterion for bio-fuel presence in the fuel taking into account that the concentration of ^{14}C in the recent-grown bio component is the same as in the atmosphere, while there is no ^{14}C in the fossil component because it has already disappeared given its decay half-life of 5700 years [10].

Different approaches regarding LSC are performed for measurements of bio components in fuels: one of the LSC methods is described also in the ASTM D6866 standard [11]. The method has excellent accuracy and can be performed on all types of bio components, but need extensive pre-treatment and is time consuming. Namely, the first step of the sample preparation for ^{14}C determination by LSC generally goes through transformation of the organic matter to CO_2 by combustion. The produced CO_2 is transformed into benzene and then mixed with the scintillation cocktail.

In search for fast, accurate and sensitive determination procedure for the mass percentage of bio-fuels in fuels, the so called

* Corresponding author. Tel.: +386 14773293.
E-mail address: jasmina.logar@ijs.si (J.K. Logar).

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direct LSC methods were proposed for specific bio components in the single fossil matrices. The methods use a liquid scintillation counting without usual sample pre-treatment; LSC samples are prepared by simply mixing the fuel sample and the scintillation cocktail. Dijs et al. [10] and Edler [12] worked with mixtures of bio-ethanol and ethanol or gasoline, while Norton et al. [13,14] used direct LSC method for bio components in diesel samples. Usage of commercially available [10,12] and specific in-house [13,14] scintillation cocktails are reported.

Characterisation and validation of a general direct method for quantification of various bio-fuels in mixtures with different fossil fuels by liquid scintillation are presented and discussed in this article. Criteria for successful performance of the method such as the limits of quantification, repeatability, selectivity, linearity and reproducibility are discussed. The article therefore covers generally used mixtures of fuels in the global market as well as newcomers: bio-ethanol and FAMEs as representatives of commonly used bio-fuels, and HVO which belongs to the so called second generation of bio-fuels. The proposed method can be used in the measurement range from 0 to 100% for all tested combinations of blends. The commercially available scintillation cocktail was used for all described samples.

2. Experimental

2.1. Fuel samples

Multiple specimens of three different types of fossil fuels were taken as a basis of the samples: ethanol, gasoline and diesel. They were also used in measurements for background correction. Bio-ethanol, hydrogenated vegetable oil (HVO) and several different fatty acid methyl esters (FAMEs) were used as bio components. The following combinations of blends were prepared: bio-ethanol with ethanol, bio-ethanol with gasoline, HVO with gasoline, FAME with diesel and HVO with diesel. LSC samples were prepared as a mixture of fuel blend and scintillation cocktail Ultima Gold^{TM}F (PerkinElmer) in a volume ratio 1:1 as proposed by Dijs [10] and Edler [12]. High performance glass vials of 20 mL were used (PerkinElmer) for all measured LSC samples. All components were pipetted and weighted. In order to facilitate further data processing all results refer to the weighted values. Two sets of samples were prepared for each combination of bio and fossil components. One set was used for determination of a calibration curve while the other was served for validation purposes. Calibration curves were determined by sets of seven samples with different and known ratios of fossil and bio component within the range from pure fossil fuel to 100% of biofuel. Sets of three samples with different quantities of bio-fuel were prepared for validation purposes and measured in accordance with the method's procedure. They were treated as samples with unknown ratio of bio and fossil components. Validation samples covered the whole range of calibration curve.

Samples with an unknown ratio of bio and fossil components were sampled and analysed with the presented method as well as with an adequate standard method in a Customs Administration's laboratory. Measured samples were ethanol and diesel based. Four inter-laboratory comparison samples were measured for confirmation of the accuracy and applicability of the method. Samples were unknown blends of ethanol with bio-ethanol, gasoline with bio-ethanol, gasoline with HVO and ethanol, and the sample of diesel with HVO.

2.2. LSC measurements and determination of counting efficiency

All measurements were performed on ultra low-level liquid scintillation counter Quantulus 1220 (PerkinElmer) at least 24 h after preparation. Each sample was measured for 1000 min through 5 cycles. Producer's settings for ^{14}C measurements were considered with high coincidence bias and no pulse amplitude comparison. Due to the quench related shift of spectra, low coincidence bias was used for measurements of FAMEs in quantities larger than 10%. The temperature in the LS counter was set at 18 °C.

For determination of counting efficiency the external standard method was performed through the measurement of SQP(E) (Standard Quench Parameter of the External standard) for 1 min at each counting cycle. The SQP(E) value was then used as the argument in the fitted quench curve, based on the commercially available ^{14}C Ultima Gold^{TM} Low Level Quenched Standard Set (PerkinElmer).

Quantulus 1220 sorts counts in logarithmically scaled channels which are related to the energy of beta decay from ^{14}C. Counts with energies between 3.50 and 27.72 keV (channel window: 150–400) were used for bio-ethanol, 3.50–79.77 keV (channel window: 150–550) for HVO blends and 1.93–27.72 keV (channel window: 100–400) for FAME blends. The channel window was chosen with respect to the figure of merit [15].

2.3. Determination of bio component mass percentage ($\%_m$) in the blends

Mass percentages of calibration blends were calculated as the ratio of biofuel's mass to the sum of bio and fossil components. Two different types of calibration curves for determination of bio component mass percentage in the blends were prepared for each fuel type and specific bio-fuel. The so called one-step calibration curves were fitted through measured specific count rates (in cpm/g) and known mass percentages of the bio component. This approach was shown as applicable for the samples with chemically identical bio and fossil components. In our case this was ethanol.

Activity concentration (in dpm/g) appears instead of specific count rate in two-step calibration curves. The additional step, conversion of count rates to activity, is performed through the quench curve. This type of calibration curve is more general and can be applied for all of the above mentioned combinations of bio components and fossil matrices, while it is indispensable in the cases where different ratios of bio and fossil components affect liquid scintillation counting.

2.4. Uncertainty evaluation

Uncertainty of the measurement was calculated according to the law of propagation of uncertainty using $k=2$ for a level of confidence of 95%. We evaluated the contribution of variable uncertainties to the total uncertainty by GUM guidelines [16]. The results are directly burdened with uncertainties of balance, sample and background counting, counting efficiency, repeatability and uncertainty of calibration. Pipetting, temperature measurement and luminescence of samples make indirect contributions to uncertainty and are manifested in the above mentioned uncertainties.

2.5. Validation of the method

Validation of the method was executed in accordance with standard EN 17 025 where in Section 5.4.5.3 of the standard suggests an evaluation of detection limit, selectivity of the method, linearity, repeatability and sensitivity [17]. Precision and accuracy were also evaluated. All listed parameters except limit of quantification are understood as the general terms in metrology [18].

Detection limit: Limits of quantification (Lq) by Curie [19] and ISO11929 [20] were chosen for characterisation of the level at which the measurement precision is satisfactory for a quantitative determination of the bio-component content in the fuel

blends. Lq were calculated for 1000 min of the background counting time.

Selectivity: SQP(E) is an essential measurement parameter to distinguish among different bio-components and matrix type.

Linearity was demonstrated by the least-square method and the correlation coefficient R^2 which is actually the square of the Pearson product moment correlation coefficient.

Repeatability was evaluated as a dispersion of calculated mass percentage of bio components, which was obtained through 10 consecutive counting cycles. The same measurement values were analysed by one and two-step calibration curves.

Reproducibility was verified through different aspects. Replicates of the same sample were prepared and measured. Each sample had been measured twice in a period of a week. The second evaluated aspect was changed in the measurement conditions. These samples were measured in a period of 1 month when samples were exposed to the temperature change during the measurement.

Sensitivity: The slope of the calibration curve was used for evaluation of the sensitivity.

Precision was determined through the width of the calibration curve which is defined by uncertainty of the measured counting rate.

Accuracy was evaluated by taking part in an inter-laboratory comparison of European Customs Laboratories. In addition results of some blind test samples of ethanol and diesel were also verified by Customs Administration Laboratory.

3. Results and discussion

3.1. Determination of the blend percentage ($\%_m$) by radiocarbon analysis

Mixtures of bio-ethanol and ethanol or gasoline were measured in blends up to 100% of biofuel as presented in Table 1. One-step calibration curves were made for both matrices. The SQP(E) values of bio-ethanol blends were between 758 and 766 for the ethanol/bio-ethanol blends while values from 765 to 825 were observed for the gasoline/bio-ethanol blends. Efficiency correction was therefore needed and activity concentration was used for all bio-ethanol calibration samples due to the significant differences in the SQP(E) values of the gasoline/bio-ethanol blends. A two-step calibration curve was prepared for both fuel combinations due to the similarities in the sample activity and the proximity of both calibration curves. Linear calibration curve was obtained with coefficient R^2 larger than 0.99 for the whole calibration range.

Hydrogenated vegetable oil (HVO) was also measured in two matrices: in gasoline or diesel with up to 100% of biofuel (see Table 2). Counting efficiency changed in correlation with the amount of biofuel; we observed that the increase of SQP(E) value from 777 in fossil gasoline or 801 in fossil diesel to SQP(E) of 838 when 100% HVO was measured. The two-step calibration curve was therefore applied. Activity concentrations related to mass per cents of the bio component were plotted. In the case of HVO blends one calibration curve was sufficient and covered both matrices. The HVO calibration curve shows a linear correlation of the activity to the mass per cent of biofuel with a high correlation coefficient R^2 0.99, which is comparable with the blends containing bio-ethanol. However, the HVO calibration curve is not the same as that for bio-ethanol, because of different total activities of the bio component with larger density of C atoms.

FAMEs of bio origin were measured only in blends with diesel. Measurements on the whole range (0–100%) of FAMEs indicated SQP(E) values from 817 for fossil diesel to 550 in FAMEs from bio sources (see Table 3). Change of colour was also observed during sample preparation [21]. Due to the shifting of the spectra only blends up to 10% of FAMEs can be measured with the same protocol as bio-ethanol and HVO. For blends above 10% we changed measurements protocol to lower coincidence bias and repeated measurements. The SQP(E) values showed no significant difference from those observed with high coincidence bias. The activity of the measured samples showed linear correlation to the mass percentage of measured bio component. As in the cases of bio-ethanol and HVO correlation coefficient is greater than 0.99.

3.2. Uncertainty evaluation

Uncertainty for measurements near the detection limit (Lq), at 10% and at 100% of biofuel were calculated and evaluated. Data

Table 1
Calibration data of bio-ethanol blends. Activity concentrations are specified per gram of sample.

Sample	**Ethanol/bioethanol blends**			**Gasoline/bioethanol blends**		
	Biofuel quantity ($\%_m$)	Activity concentration (dpm/g)	Efficiency (%)	Biofuel quantity ($\%_m$)	Activity concentration (dpm/g)	Efficiency (%)
1	0	0	71.6	0	0	80.1
2	1.81 ± 0.01	0.11 ± 0.01	71.5	1.75 ± 0.01	0.1 ± 0.01	81.1
3	3.79 ± 0.01	0.22 ± 0.01	71.6	3.63 ± 0.01	0.21 ± 0.01	77.6
4	9.80 ± 0.01	0.59 ± 0.01	71.6	10.16 ± 0.01	0.51 ± 0.01	76.1
5	20.48 ± 0.02	1.13 ± 0.02	71.9	21.25 ± 0.02	1.11 ± 0.02	74.1
6	58.66 ± 0.06	3.49 ± 0.05	71.7	59.00 ± 0.06	3.35 ± 0.05	72.1
7	100	6.01 ± 0.11	71.5	100	6.08 ± 0.11	72.1

Table 2
Calibration data for HVO blends. Activity concentrations are specified per gram of sample.

Sample	**Gasoline–HVO blends**			**Diesel–HVO blends**		
	Biofuel quantity ($\%_m$)	Activity concentration (dpm/g)	Efficiency (%)	Biofuel quantity ($\%_m$)	Activity concentration (dpm/g)	Efficiency (%)
1	0	0	81.1	0	0	79.7
2	2.01 ± 0.01	0.13 ± 0.01	81.1	1.91 ± 0.01	0.14 ± 0.01	77.9
3	4.01 ± 0.01	0.36 ± 0.01	78.7	3.78 ± 0.01	0.35 ± 0.01	77.9
4	6.09 ± 0.01	0.60 ± 0.01	78.6	5.64 ± 0.01	0.52 ± 0.01	78
5	10.26 ± 0.01	1.03 ± 0.02	79.7	9.37 ± 0.01	0.88 ± 0.02	78.4
6	41.18 ± 0.04	4.36 ± 0.07	81.4	38.26 ± 0.04	3.98 ± 0.07	80.7
7	100	11.15 ± 0.2	86.4	100	11.21 ± 0.2	86.4

are presented in Table 4. Uncertainties of balance, variability of background and counting efficiency were nominally equal for all cases. Background stability and sample counting were evaluated as combined uncertainty; it represents the largest contribution to total uncertainty. Second important uncertainty source is the uncertainty of the standard solution for the determination of the quench curve and counting efficiency. Uncertainty of balance represents negligible portion of the evaluated uncertainty. Compared to the long half-life of ^{14}C, biofuels are made from the contemporary sources. We do not use half-life in our calculations and therefore associated uncertainty is not accounted. Uncertainties of calibration and repeatability add up to 2.3% to uncertainty of activity (data not shown).

3.3. Validation of the method

Detection limit: Calculated limits of detection (Lq) are presented in Table 6. Limits calculated according to Curie [19] are the highest of his proposed limits. Although calculated values differ they fulfil the request of authorities [2] and are low enough to determine the amount of bio components which is usually found in a real field sample obtained from the fuel stations [22]. The calculated Lq is comparable to those reported by other authors [10,12–14]. Background count rate substantially affects calculated limits of detection, so the improvement of a counting protocol and settings can improve the value of Lq to some extent. Our background counting rate was obtained in 1000 min of the counting time and the length of counting time enables us measurement uncertainty of 3% also near the limit of quantification.

Selectivity of the method: The content of bio component in the blends is determined through one of the three different two-step calibration curves. The type of fossil fuel matrix in the sample is usually labelled so the choice is reduced to two of them. Accompanying measurement data provide additional information on which curve should be chosen for certain unknown sample. One of such is SQP(E) value which offers distinctive differences between bio components. A diminishing value is observed in ethanol and FAMEs, while addition of HVO leads to an increase of SQP(E). The value of SQP(E) can be therefore applied as a trigger for choosing the corresponding calibration curve. Fig. 1 shows graphical presentation of our trigger and how it works. When the SQP(E) value of diesel sample is in the area (A) additional measurement by the UV/VIS spectrometer is needed. UV/VIS spectrometer differs between bio component's colours; FAMEs containing sample is yellower than the HVO containing sample. Decision is therefore made according to the absorption region. If the SQP(E) value of gasoline samples is in area (B), differentiation is made with addition of deionised water to the original sample. Activity of the deionised water and decanted water with ethanol is measured. The solubility of ethanol in water is used as a trigger.

Linearity: The regression lines are fitted through each calibration set from Tables 1 to 3. The calibration curves for all bio components are linear with correlation coefficients greater than 0.99 (see Table 5). As expected for the case of one-step calibration curves, linearity was achieved only in ethanol/bio-ethanol blends. Other one-step calibration curves failed in demonstration of linearity due to the changes of matrices through blends.

Repeatability: Dispersion of counting rates which were obtained in successive counting cycles was within one standard deviation of the results as shown in Table 6. Repeatability of the results exceeded two standard deviations in the case of one-step calibration curves. Only bio-ethanol obtained repeatable results by using both one and two-step calibration curves. Since

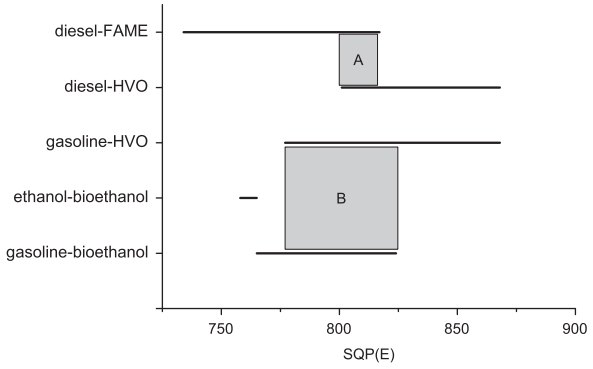

Fig. 1. Selectivity of the method. When the SQP(E) value in area (A) additional spectrometry measurement is needed. In area (B) choice is based on the solubility of ethanol.

Table 3
Calibration data for FAME blends. Activity concentrations are specified per gram of sample.

Sample	Biofuel quantity ($\%_m$)	Activity concentration (dpm/g)	Efficiency (%)
1	0	0	80.0
2	10.46 ± 0.01	1.24 ± 0.02	75.4
3	20.81 ± 0.01	2.30 ± 0.06	73.59
4	40.77 ± 0.01	4.75 ± 0.13	69.09
5	60.85 ± 0.01	7.80 ± 0.22	63.31
6	80.19 ± 0.01	10.65 ± 0.31	59.32
7	100	13.50 ± 0.40	59.5

Table 5
The coefficients of the calibration curves and coefficients of determination. Activity concentration in dpm per gram of sample is used as variable.

Bio component	Slope	Intercept	Correlation coefficient (R^2)
Bio-ethanol	17.63	−0.032	0.997
HVO	9.156	0.712	0.998
FAME	12.546	0.315	0.999

Table 4
Uncertainties sources as per cent of total uncertainty.

Source	Uncertainty					
	Near Lq		At 10 $\%_m$		At 100 $\%_m$	
	% of total	Absolute	% of total	Absolute	% of total	Absolute
Balance	2×10^{-9}	0.0001 g	1×10^{-05}	0.0001 g	4×10^{-05}	0.0001 g
Background stability	99.99	0.041 cpm	76.23	0.041 cpm	38.74	0.041 cpm
Sample counts		0.05 cpm		0.2 cpm		0.87 cpm
Counting efficiency	0.004	1.3%	23.77	1.3%	61.26	1.3%

Table 6
Results of validation parameters calculation. Repeatability and limit of detection were calculated for the calibrated range. Presented values refer to two-step calibration curves and are the worst which were obtained.

Bio component	Repeatability	Lq Currie (%$_m$)	Lq ISO11929
Bio-ethanol	0.54	0.65	0.11
HVO	0.34	0.98	0.76
FAME	0.41	0.67	0.38

Table 7
Results of inter-laboratory comparison for four samples. The last two lines refer to the same mixed sample.

	Reported value (%$_m$)	Calculated value (%$_m$)	Z-score[a]	Target value (%$_m$)	Z-score
Bio-ethanol in ethanol	79.80 ± 2.7	79.77 ± 1.02	0.03	79.98	−0.06
Bio-ethanol in gasoline	5.80 ± 0.3	5.82 ± 0.84	−0.02	6.19	−1.3
HVO in diesel	18.71 ± 0.59	18.67 ± 0.43	0.09	18.88	−0.29
HVO in gasoline	12.10 ± 0.5	10.94 ± 1.78	0.65	10.13	3.94
Bio-ethanol in gasoline	10.20 ± 0.4			10.34	−0.35

[a] *Z*-score calculated from reported and calculated values, *z*-score calculated from reported and target values.

repeatability is a major indicator for quality of biofuel determination, one-step calibration curves were discarded.

Reproducibility: We tested reproducibility by preparing and measuring two LS samples for each calibration curve in a period shorter than one week. The results of all tested samples were reproducible within measurement uncertainty. Second test of reproducibility was obtained by changes of measurement conditions. LS samples were exposed to controlled temperature change and measured. The change of count rate and the SQP(E) value was observed, but since we used activity of the sample and two-step calibration curve, changed temperature conditions did not affect the determination of biofuel quantity.

Sensitivity: The steepest linear regression curve is the most sensitive and vice versa. The method is the most sensitive for determination of bio-ethanol content in both matrices as calibration curve slope is 17.63. The least sensitive calibration curve was shown to be the HVO calibration curve with a curve slope of 9.16.

Precision: In order to determine which calibration curve is the most precise, we looked for the slope of the calibration curve and its uncertainty. This evaluation was chosen because we already considered the uncertainty of the individual calibration point when determining calibration curve. Results show that the HVO calibration curve is the most precise; as expected FAME calibration curve is the least precise.

Accuracy: The accuracy of the method was proved in an inter-laboratory test organised by the German Customs Laboratory on behalf of the European Union Group of Customs Laboratories [23]. Nine of 15 participating laboratories performed the LSC technique. Measurements were done on four samples of different compositions. HVO and/or bio-ethanol were used as bio component. Results were reported with expanded uncertainty for coverage of 95%. Values calculated by organisers were robust mean and standard deviation of the reported values of all participating laboratories. *Z*-score was calculated for each set of results. The limit for acceptability was set to 2. All our reported results were therefore declared as successful what can be seen also in Table 7 with the summary of the obtained results. In addition we calculated *z*-score with target value obtained gravimetrically by organisers. In the comparisons with gravimetrically determined target values the uncertainties of organiser's values were set to 0 since they were not reported. In these calculations sample with HVO and bio-ethanol in gasoline (for HVO in gasoline) was not acceptable. Result of HVO for the sample with HVO and bio-ethanol in gasoline was obtained after separation of the ethanol from the original sample. The separation was made with the addition of water. Nevertheless compared to other laboratories which performed the LSC techniques we were one of the laboratories with the most consistent and accurate results.

The accuracy was evaluated also by comparing measurements of some samples of ethanol and FAMEs to standardised methods used in the laboratory of Customs Administration of Republic of Slovenia. The laboratory uses densitometry for ethanol and modified SIST EN14078 method for FAMEs. The ethanol samples were in the range of total bio component content; the *z*-score of results was −0.20. The FAMEs were measured in the range of market fuels; the *z*-score for FAMEs measurements was −1.38. Therefore results of both laboratories are comparable in the frame of the reported uncertainties.

4. Conclusions

Direct LSC method for determination of the bio component content in fuels was implemented, tested and evaluated for five different combinations of three bio-fuels and three fossil matrices. Two-step calibration curves, where the activity of the sample is obtained from universal fitted quench curve and then transferred to the mass percentage of bio component, are the most appropriate approach. Three calibration curves are sufficient to cover all measured blends. The fossil matrix is not the critical or crucial parameter since there is one single calibration curve for two different matrices and one sort of the bio component. The method is operational in the range up to 100% of bio-fuel for all discussed combinations. The method is the most sensitive in the case of bio-ethanol. All presented calibration curves show linear correlation of activity concentration to percentage of bio-fuel. The method was approved with the international inter-comparison test and comparison of the results with the partner laboratory. The extent of obtained limits of detection, uncertainty as well as accuracy, precision, repeatability and sensitivity allow the usage of the method for the surveillance of bio component quantity in blends with fossil fuels in accordance with market and authority demands.

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