

HIDEX

Hidex Biofuel Method

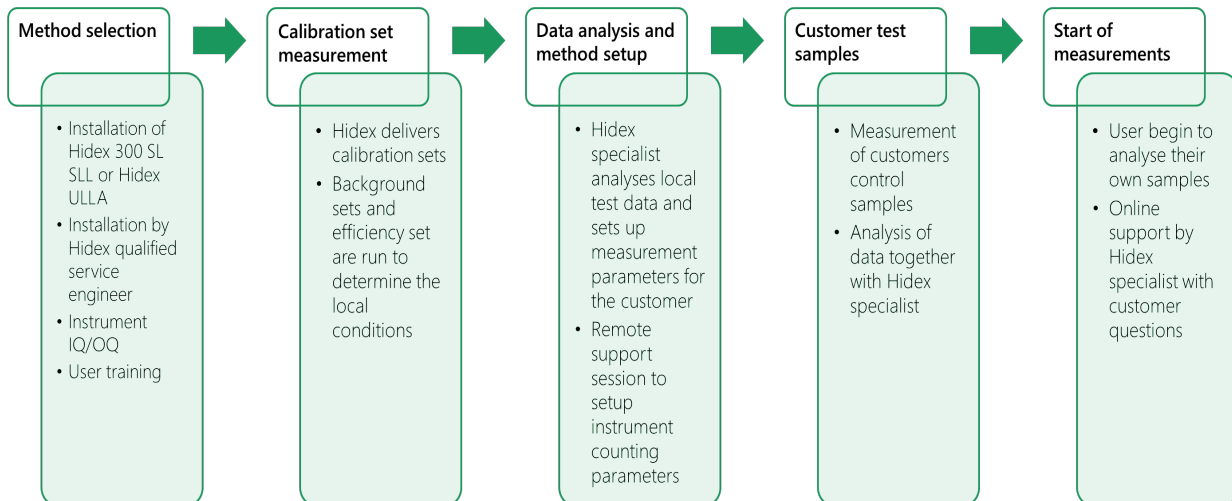


INTRODUCTION

Fossil based fuels are increasingly replaced by fuels of biologic origin, such as hydrotreated vegetable oil (HVO). In June 2023, the European commission delegated regulation on the methodology to determine the percentage of biogenic carbon component in fuels with either AMS accelerator mass spectrometry or LSC Liquid Scintillation Counting. These methods are based on ^{14}C dating principle. Conventional procedures provide accurate results but require costly, complex, and time-consuming sample preparation prior to the measurement.

Direct detection by LSC is an attractive alternative as an in-house method. Liquid fuel samples can be measured directly after mixing with scintillation cocktail. The main limitation of the direct method is the requirement of a fossil-carbon based background calibration sample with similar quench level as the unknown samples. Such a sample is often difficult to find as fuels, especially mixtures, vary by color and by the content of aliphatic hydrocarbons. This affects background CPM and counting efficiency. Hidex has developed a biofuel method that overcomes these shortcomings.

BIOFUEL METHOD SETUP PROCESS



WHAT IS REQUIRED FROM THE CUSTOMER?

Customer laboratories must fulfil certain requirements to use Hidex Biofuel Method

- Hidex LSC compatible with the Hidex Biofuel Method
- Service and support contract with Hidex or Hidex authorised distributor
- Total carbon content of the fuel samples
- Trained laboratory technician capable to analyse samples

WHAT IS INCLUDED IN THE HIDEX BIOFUEL METHOD?

As part of the method Hidex delivers materials required for calibration of Hidex instruments to be used with the method.

- Two background quench sets
- Two efficiency calibration sets
- 10 L of MaxiLight+ liquid scintillation cocktail from the same production batch with calibration sets
- Vials for unknown samples 500 pcs



Background and efficiency calibration samples.

WHAT SERVICES ARE INCLUDED?

As part of the Hidex method we provide the following services

- Hidex prepares and test individual calibration sets which are tested at Hidex. If a new instrument is order Hidex will test the calibration sets with the specific unit.
- Online support to measure and analyse the background and efficiency calibration sets
- Setup of measurement parameter files with local measurement conditions and user training to analyse data
- Online support to analyse customer control samples
- Online support to analyse first set of customers samples
- 12 months online support for troubleshooting and customer questions

WHICH HIDEX INSTRUMENT IS RIGHT FOR YOUR LABORATORY NEEDS?

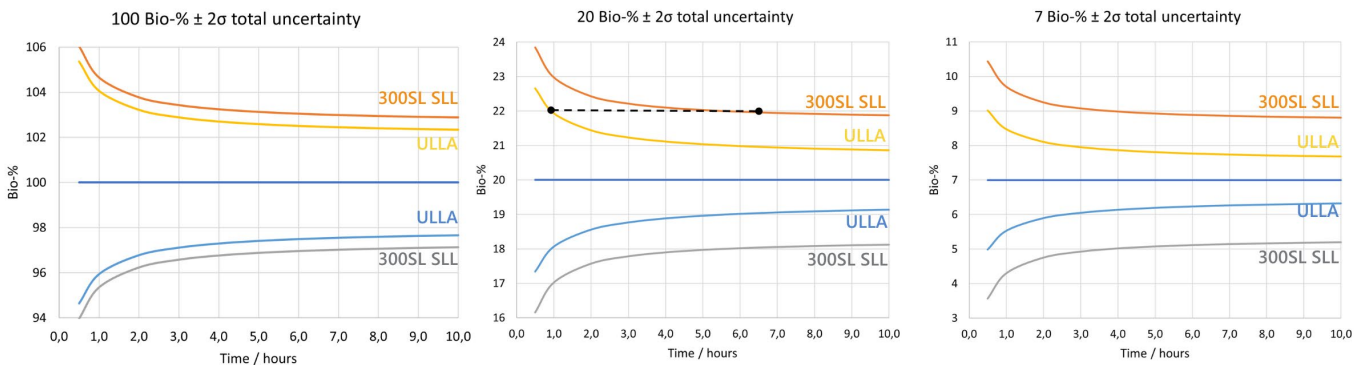
HIDEX ULLA



HIDEX 300SL SLL



Hidex offers two compatible instruments for the Biofuel Method. The Hidex 300SL SLL and Hidex ULLA. The main advantage of Hidex ULLA is the reduced counting time. The shorter counting time reduces sample turnaround time and significantly improves laboratory's efficiency.



Depending on the user requirements, 300SL SLL may be enough for the highest bio-content assays (e.g. 100% HVO). The time saved becomes apparent using ULLA the lower the measured bio-% gets. As an example, at 20% bio-content, the same uncertainty ($20 \pm 2\%$) reached with 300SL SLL in 6-7 hours, and in ULLA in under 1 hour. Time saved is 6-7-fold. This is represented with a horizontal bar in the graph for 20% biofuel. When bio-% gets even lower, it is apparent from the 7% biofuel graph, that 300SL SLL may not ever reach similar accuracy than is reachable with ULLA in just 1 hour ($7 \pm 1.5\%$).



HIDEX BIOFUEL METHOD APPENDIX

ABSTRACT

A novel method based on radiocarbon dating and liquid scintillation counting (LSC) was developed to determine the biocarbon content in biofuels without fuel specific background sample. Hidex biofuel method is an easy-to-use measurement that requires no sample preparation making it well suitable for fast in-house detection needs. It uses a patent pending algorithm to find the background count rate and counting efficiency of unknown biofuel samples with variable colour. Hidex biofuel method employs a liquid scintillation counter with triple-double coincidence ratio (TDCR) output and an external standard. The performance of the method was demonstrated by analysing several different types of biofuels with a bio-% ranging from 1 to 100%. Results showed an excellent correlation between Hidex biofuel method and accelerator mass spectrometry (AMS), with detection limit down to 1% biocarbon.

INTRODUCTION

Fossil based fuels are increasingly replaced by fuels of biologic origin, such as hydrotreated vegetable oil (HVO) and bioethanol. Percentage of biogenic component in fuel can be determined with accelerator mass spectrometry (AMS) and LSC measurement with benzene synthesis (ASTM D6866 and EN 16640 guidelines), both based on ¹⁴C dating principle. These methods provide accurate results but require expensive and time-consuming sample preparation. Direct detection by LSC is an attractive alternative as liquid fuel samples can be measured directly after mixing with scintillation cocktail (DIN 51637, ASTM D8473-22 guidelines and Hurt et.al., Energy Fuels, 35, 2, 1503–1510, 2021). Fuel samples are often highly variable and intense in colour, which is affecting both counting efficiency and background CPM. This is a challenge especially with fuel blends, as a fossil-based background sample with similar quenching properties is rarely available.

Hidex biofuel method is an improvement on the direct LSC measurement. The method includes an algorithm, that uses a combination of two different types of quench parameters (external standard TDCR = eTDCR and QPE) to detect simultaneously both colour and chemical quench in the sample. It calculates the background count rate without a fuel specific background sample. The same algorithm finds also counting efficiency for each sample. The method employs a 3-PMT LS counter enabling triple-double coincidence ratio (TDCR) output and an external standard. The biofuel algorithm is derived from background and efficiency quench curves with chemical and colour quenchers. TDCR and external standard quench parameters are used for the calculation of background and counting efficiency of unknown samples.

MATERIALS AND METHODS

LSC measurement

- Hidex automatic TDCR liquid scintillation counter
 - o 300 SL super low level, 600 SL super low level or ULLA ultra low level models
 - o Temperature control unit
 - o Eu-152 external standard source

Calibration of the biofuel method

The biofuel method requires TDCR counter equipped with cooling and Eu-152 external standard source. The counter used in this study was Hidex 300SL super low level (425-020) instrument. The algorithm is derived from background and counting efficiency quench curves which are measured on-site. Each quench set includes 7 standards with variable amount of nitromethane for chemical quenching and 7 standards with variable amount of Sudan1 for colour quenching. Quench curve sets are available in Teflon coated plastic vials or in glass vials. The quench curve measurements should be started as soon as possible, preferably within two weeks of arrival but no earlier than two days after installation. Counting efficiency measurement (14 samples: Ef 1-14) takes about three hours. Background measurement (14 samples: Bg 1-14) takes about 4.5 days. After the calibration the algorithm is installed as MikroWin template (.par file) and is ready to use for routine analysis of the biofuel samples.

Note! The algorithm is specific:

- for the instrument
- for the quench curves
- for the location of the instrument. Recalibration is required if the instrument is moved to another laboratory.
- for the materials i.e. vial type and MaxiLight+ cocktail. Glass vials should be ordered from the same manufacturer to keep the background constant due to the possible variations of K-40 in the glass material.

Use of the method is limited to samples within the quench range of the algorithm calibration.

Sample preparation

Add 10 ml MaxiLight+ scintillation cocktail to 20 ml Teflon coated plastic vial or glass vial. Samples are always prepared in the same type of vials as used in the quench curves measurements. Use polycone lined caps with glass vials. Tare the weight of the vial on analytical balance. Add 10 ml biofuel sample directly to the cocktail. Measure and record the mass of the biofuel sample on analytical balance. Perform all weighing with vial cap on. Gently mix the sample with the cocktail. Enter the sample mass in grams to the biofuel para file. Very volatile samples (for example naphtha and gasoline) can be difficult to weigh. To ease the sample preparation, such samples can be cooled before weighing.

Wipe each vial with an antistatic wipe or with a moist cloth just before placing the vials on a tray inside the instrument. Check that the cooling is on (target temperature 17°C), and the temperature is 16-17°C. Let the samples cool down on the tray in dark at least for an hour or two before starting the measurement. Store the samples in a dark and cool place, preferably at 15-20°C.

Long measurement times (5-7 hours) are recommended for low activity biofuel samples, i.e. for fossil and mid to low bio-% samples. Shorter measurement time (for example 1h) can be used for scanning purposes. Check that Use External standard and Use Guard are both selected in advanced options. All samples are counted twice, first with the external standard automatically positioned under the detector chamber for the selected time (use 60 seconds for external standard counting time).

Note! External standard quench parameter QPE should be >600 and the predicted counting efficiency >30%. If these values are below the optimized range, the quenching can be reduced using less sample. Reduce the sample to cocktail ratio from 10 + 10 ml to 8 + 12 ml to 5 + 15 ml, or experimentally even lower. The algorithm template will indicate with red flags if some of the samples have too low QPE and/or counting efficiency and need more dilution.

Quick QPE scan of the samples is suggested to ensure that all samples are in the optimal quench level before starting the long measurements. Quick QPE scan uses only 60 seconds counting time for external standard and a few seconds for sample avoiding hours counting of overly quenched samples.

Calculation of bio-%

All results are calculated in the MikroWin biofuel algorithm template (.par file). The counts are collected from optimized luminescence free triple coincidence ROI. Background count rate and counting efficiency are predicted using the algorithm and are found in Results-tab. The fuel mass and the carbon content are entered to the corresponding matrices in the biofuel para file before or after the measurement. Background count rate (Background) is subtracted from the count rate of the samples (CPM) and converted to absolute activity (DPM) by dividing with counting efficiency (Efficiency).

$$DPM = \frac{(CPM_{sample} - CPM_{bg})}{Efficiency} \quad (1)$$

Biobased carbon content (Bio-%) is calculated using carbon mass-% of the biofuel (grams of biofuel * carbon content, cc) and assuming that the specific ¹⁴C activity of carbon is 13.56 DPM/g.

$$Bio \% = \frac{DPM \text{ measured}}{fuel \text{ mass} * cc * 13.56} * 100 \quad (2)$$



DPM comes from the biocomponent only, so

$$DPM\ measured = m_{bio} * cc_{bio} * 13.56 \quad (3)$$

where m means mass (g). The carbon content cc is determined with Total Organic Carbon (TOC) analyzer. In Hidex biofuel method, biomaterials are assumed to be from 2019 or later. Instructions for bio-% correction of older biomaterials can be found in ASTM D8473-22 section 14.3.1.1. For example, biofuels manufactured from tens of years old wood-based material could result bio-% >100%. In this case the specific activity is higher than 13.56 DPM/g, probably near 15 DPM/g (see table 2.).

RESULTS AND DISCUSSION

Hidex biofuel method has been tested with various types of fuels and their blends. Here we present results from in-house prepared HVO-diesel samples (Table 1.) and from biofuel samples received as unknowns (Tables 2. and 3.). The samples were prepared by mixing 10 ml of fuel with 10 ml of MaxiLight+ cocktail and analysed for 7h. Some of the kerosene samples were diluted due to the very intense colour. Bio-% was calculated according to equation 2.

Table 1. Comparison of HVO-diesel blends: expected bio-% versus bio-% determined using Hidex biofuel method (with $\pm 1\sigma$ uncertainty).

Expected Bio-%	LSC Hidex Bio-%*
100	99.0 \pm 0.7
78.8	76.8 \pm 0.6
57.7	57.7 \pm 0.6
38.5	37.7 \pm 0.5
19.2	18.9 \pm 0.4
13.9	13.8 \pm 0.3
9.4	9.8 \pm 0.3
4.6	4.3 \pm 0.3
2.7	2.7 \pm 0.3
0.9	1.2 \pm 0.3
0	-0.2 \pm 0.2

Table 2. Biofuel comparison study with AMS and Hidex biofuel method. All samples were received as unknowns. *The specific activity of very old wood-based material is higher than 13.56 DPM/g used in the calculation. **If fossil methanol is used in the production of FAME, the bio-% is 93-95% of expected. For more information see chapter Notes on FAME.

Composition	Expected bio-%	AMS University	LSC Hidex
100% HVO	100	101.2 \pm 1.2	100.2 \pm 0.8
100% HVO	100	100.9 \pm 1.2	99.6 \pm 0.8
100% HVO	100	100.7 \pm 1.2	100.4 \pm 0.8
100% HVO	100	100.1 \pm 1.2	103.1 \pm 1.0
100% HVO (woody biomass)	100*	111.0 \pm 1.4	106.4 \pm 0.7
70% diesel 7% FAME, 23% HVO	30**	25.3 \pm 0.3	26.7 \pm 0.9
70% diesel 7% FAME, 23% HVO	30**	28.6 \pm 0.4	25.7 \pm 0.9
70% diesel 15% FAME, 15% HVO	30**	29.8 \pm 0.4	30.1 \pm 0.4
100% diesel	0	0	0.1 \pm 0.3
100% FAME	100**	95.4 \pm 1.2	95.6 \pm 0.9
100% GTL (fossil)	0	0	-0.1 \pm 0.3
90% diesel, 10% HVO	10		9.8 \pm 0.3
95% diesel, 5% HVO	5		5.0 \pm 0.3

100% bio-naptha	100		96.6 ± 0.9
80% petrol, 10% ethanol, 10% bionaptha	20		17.1 ± 0.4

Table 3. Low bio-% kerosene samples were analysed with AMS and Hidex biofuel method. All samples were received as unknowns.

Low bio-% kerosene samples	AMS Bio-%	Hidex Bio-%	Cocktail to sample ratio
Fossil / "0%"		0.29 ± 0.31	10+10 ml
Unknown sample	1,87	1.50 ± 0.33	10+10 ml
Unknown sample	0,72	0.76 ± 0.29	10+10 ml
Unknown sample *Too dark (extreme colour quench)	1,25	N/A*	0.5+19.5 ml
Unknown sample	3,98	5.49 ± 0.46	10+10 ml
Unknown sample	3,04	4.3 ± 0.63	5+15 ml

Role of carbon content in bio-% of blends

Sometimes when measuring blends of low-carbon content biocomponents, e.g. FAME (cc 0.77) and bioethanol (cc 0.522), the bio-% result is lower than that expected from their masses in blend. A possible reason is that the carbon content of the total blend (cc_{tot}) is used in bio-% calculation which yields pMC = percent modern carbon = percent biocarbon of all carbon in blend. With low-cc biocomponents pMC is lower than mass-bio-% because the biocomponent brings less carbon per weight to the blend than high-cc fossil component. To get the mass-bio-%, only the cc of biocomponent (cc_{bio}) should be used.

Mass Bio-% = percent of biocomponent mass of all fuel mass.

Carbon content = cc_{bio} = cc of biocomponent only.

Inserting equation 3 to equation 2 leads to

$$Bio \% = \frac{m_{bio} * cc_{bio} * 13.56}{fuel\ mass * cc_{bio} * 13.56} * 100 \quad (4)$$

Most terms cancel out and

$$Bio \% = \frac{m_{bio}}{fuel\ mass} * 100 = \frac{m_{bio}}{m_{bio} + m_{fos}} * 100 = mass\ Bio\ \% \quad (5)$$

pMC = percent modern carbon = percent of biocarbon of all fuel carbon.

Carbon content = cc_{tot} = carbon content of blend.

This can be written

$$cc_{tot} = \frac{(m_{bio} * cc_{bio}) + (m_{fos} * cc_{fos})}{m_{bio} + m_{fos}} \quad (6)$$

In equation 6 cc_{fos} means the carbon content of fossil component. Inserting equation 6 to equation 2 leads to cancellation of fuel mass $m_{bio}+m_{fos}$, leaving

$$Bio \% = \frac{m_{bio} * cc_{bio}}{(m_{bio} * cc_{bio}) + (m_{fos} * cc_{fos})} * 100 = pMC \quad (7)$$

Bio-% calculation example

8 g of blend containing 50 m-% bioethanol ($cc_{bio} = 0.522$) in fossil fuel ($cc_{fos} = 0.86$) was measured, i.e. there is 4 g of bioethanol and 4 g of fossil fuel.

$$cc_{tot} = (0.5 * 0.522) + (0.5 * 0.86) = 0.691 \quad (8)$$

$$4 \text{ g of bioethanol} = 4 * 0.522 * 13.56 = 28.31 \text{ DPM} \quad (9)$$

So, if an unknown bioethanol sample of 8 g gave 28.31 DPM, following calculations could be done.

$$mass \text{ Bio \%} = \frac{28.31}{8 * 0.522 * 13.56} * 100 = 50\% \quad (10)$$

➔ Interpretation 1: 50% of blend mass was bioethanol.

$$pMC = \frac{28.31}{8 * 0.691 * 13.56} * 100 = 38\% \quad (11)$$

➔ Interpretation 2: 38% of blend carbon was biocarbon as it should be:

$$\frac{4 * 0.522}{(4 * 0.522) + (4 * 0.86)} * 100 = 38\% \quad (12)$$

Unknown carbon content

If the carbon content of the fuel is unknown or cannot be determined, the proportion of the biocomponent can be reported as biocarbon mass of all sample mass. This is much more informative than just a CPM or DPM value.

$$\frac{\text{Biocarbon mass (g)}}{\text{Sample mass (g)}} \% = \frac{\text{DPM}/13.56}{\text{Sample mass (g)}} * 100 \quad (13)$$

From the equations 13 and 14 it is easy to see the relation between the mass ratio and bio-%.

$$\text{Bio \%} = \frac{1}{cc} * \frac{\text{Biocarbon mass (g)}}{\text{Sample mass (g)}} \% \quad (14)$$

Carbon content summary

- If carbon content of the biocomponent cc_{bio} is used in the calculation, the bio-% is biocomponent mass-% of all blend mass, i.e. mass-bio-%, m-bio-%.
- If carbon content of total blend cc_{tot} is used in the calculation, bio-% is pMC, percent modern carbon, or percent of biocarbon of all carbon in blend.
pMC = biobased carbon content
- If blend is totally unknown and cc measured separately, it produces cc_{tot} and hence bio-% is pMC.
- If $cc_{\text{bio}} < cc_{\text{fos}}$, pMC < m-bio-%.
- If $cc_{\text{bio}} = cc_{\text{fos}}$, pMC = m-bio-%.
- AMS results are reported as pMC → lower than m-bio-% in blends of low-cc biocomponents such as bioethanol and FAME.

Notes on FAME

FAME (Fatty Acid Methyl Ester) is the generic chemical term for biodiesel derived from renewable sources. FAME is produced by transesterification of vegetable oils with methanol. Recently it has come to our attention that the FAME production uses likely petroleum sourced methanol. The ester methyl of FAME comes from methanol. So, if this methanol is fossil, and assuming FAME molecules are typically 15-20 carbon atoms, biocarbon-% is 93-95% of expected.

A carbon content 0.77 is generally used for calculating the bio-% of FAME. If one of the FAME carbon atoms is fossil based, 0.77 is not the carbon content of the biocomponent c_{bio} only, but rather the total carbon content c_{tot} of blend. This could explain why some LSC bio-% results are often slightly too small for FAME.

According to DIN 51637:2014-02 section 10.3, knowing the average molecular chain length (l_{av}) of 17.71, the carbon content of biocomponent can be calculated using equation 13.

$$cc_{bio} = \frac{l_{AV} - 1}{l_{AV}} * cc_{tot} = \frac{17.71 - 1}{17.71} * 0.77 = 0.73 \quad (13)$$

If the exact type of FAME (fatty acid distribution or average chain length) is known, this value can be used in the calculation (e.g. for rapeseed methyl ester RME $l_{AV} = 17.80$).

Bioethanol and biomethanol

Hidex biofuel method is based on non-polar MaxiLight+ cocktail. It is therefore applicable for bioethanol and its blends as well as for all non-polar biobased fuels. Methanol, on the other hand, is polar molecule that does not dissolve in MaxiLight+ cocktail, so Hidex biofuel method is not suitable for pure biomethanol applications as such.

However, the direct LSC method is well suited for bioethanol and biomethanol, since fuel specific fossil background samples are available for both. The counting efficiency can be determined with C-14 radioactive spiking. If the background and efficiency are constant (all samples are similar), the same values can be used in all measurements and there is no need to define them again in every measurement. For biomethanol applications we recommend AquaLight+ cocktail, which is a general-purpose scintillation cocktail for aqueous and non-aqueous samples.

Here is the procedure for biomethanol in short:

Efficiency:

- Add 10 ml of AquaLight+ cocktail in a vial.
- Add small volume (20-200 μ l) of C-14 solution for example in toluene, preferably 5000 - 10 000 DPM. Exact C-14 activity needs not to be known.
- Set coincidence time 35 ns to ensure exact DPM determination.
- Measure the activity in open window 5-650 for 10 min.
Calculate the DPM with TDCR: $DPM = CPM/TDCR$.
- Add 10 ml of methanol to the same vial.
- Set coincidence time 20 ns to reduce background and get robust measurements.
Keep the coincidence time 20 ns henceforth.
- Measure the activity in triple ROI T100-400 for 10 min.
- Calculate the $Eff = CPM \text{ ROI T100-400} / DPM \text{ ROI 5-650}$.

Background:

- Background sample: Add 10 ml AquaLight+ cocktail + 10 ml fossil methanol in a vial.
- Measure the background sample in triple ROI T100-400 for 5-7 hours (if possible, do several repeats and use the average value).

Unknowns:

HIDEX

- Unknown sample: Add 10 ml AquaLight+ cocktail + 10 ml unknown biomethanol sample in a vial. Weigh the mass of the biomethanol sample.
- Measure the biomethanol sample in in triple ROI T100-400 for 5-7 hours.
- Calculate the biomethanol DPM = (biomethanol CPM T100-400 - background CPM T100-400) / Eff
- Calculate the bio-% = biomethanol DPM / (mass of biomethanol * carbon content * specific activity) * 100.



CONCLUSIONS

Our aim was to develop a new, easy-to-use, direct LSC measurement for determining the bio-% of biofuels. The Hidex Biofuel Method was tested with different types of fuels whose bio percentage varied between 1 and 100%. The method is based on an algorithm which is derived from background and efficiency quench curves with chemical and colour quenchers. The algorithm uses TDCR and external standard quench parameters for finding the background and counting efficiency of unknown samples. A fuel-specific background sample is not required. The Hidex Biofuel Method expands the applicability of direct LSC. The results presented here show that it is suitable for a wide range of fuel types and their blends, as well as for coloured fuels. The bio percentages determined with the Hidex Biofuel Method were very well in line with the corresponding AMS results.

SUMMARY

- Direct in-house measurement of bio-%
- No need for a fuel specific background sample
- Minimal sample preparation
- Suitable for wide variety of fuel types, and their blends with variable colour
- No luminescence interference
- Detection limit down to 1 % biogenic content
- Dilution recommended for the highest colour intensity samples



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HIDEX LSCs COMPATIBLE WITH BIOFUEL METHOD



Hidex ULLA



Hidex 300SL SLL

ADDITIONAL SERVICES



LSC Cocktails



Sample preparation for LSC



Standards

HELPING SCIENTIFIC RESEARCH AND SAFETY OF EVERYDAY LIFE

At Hidex scientific development is at the core of our values. We believe in the scientific advancement and continued improvement of our products. Our passion is to develop and optimise instrument sensitivity, streamline measuring operation, and make usability as smooth as possible.

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