

# Biogas Market Segment

Biogas as renewable source of energy is becoming increasingly important since biogas has some ecological advantages mainly being CO<sub>2</sub> neutral and hence reducing the formation of greenhouse gases. Biogas is formed by anaerobic micro-organisms that feed off carbohydrates and fats producing methane and carbon dioxide as metabolic waste products.

The main components of biogas are methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), but it also contains significant quantities of undesirable compounds such as hydrogen sulphide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>) and siloxanes. These trace components can be very harmful if they become adsorbed by the oil as they may destroy the engine, e.g., due to corrosion.

Biogas engines for power generation are usually deployed in so called CHP (combined heat and power generation) units where the heat generated is used to optimise the fermentation process of wastes or biodegradable materials. Typically temperatures between 35-60°C are required. The biogas generated during the fermentation process is then used to produce electricity.

Biogas engines are typically designed to operate on different types of biogas. The gas engines are linked to an alternator to produce electricity. Biogas engines are available with different capacities ranging from hundreds of kW to several MW capacity.

Gases derived from biological processes such as fermentation will contain contamination such as water, hydrogen sulphide and siloxanes. All these contaminants can have detrimental effects on the lifetime and the efficiency of the engines as they degrade the oil in the biogas engine.

Water is present in biogas in form of water vapour due to the nature of the feedstock. The amount of water within the biogas depends on the temperature and where the biogas originates from. If the water content within the biogas becomes too high the combustion of the biogas can be very challenging and, in combination with hydrogen sulphide can condense into sulphuric acid.



Hydrogen sulphide (H<sub>2</sub>S) originates from the feedstock which is usually high in sulphur such as amino acids and proteins. H<sub>2</sub>S reacts with water to form sulphuric acid which is a very corrosive component and can cause damage to the gas engine itself.

Typical life-times of lubricants for biogas engines are 1500 h and it is important to manage the lifetime of the lubricant effectively as the downtime of the engine during oil change has significant costs associated with it.

During the combustion of the biogas within the biogas engine the products are absorbed by the engine oil. Especially the effects of water and H<sub>2</sub>S on the engine oil have to be monitored to ensure that the engine lubrication is guaranteed.

The key parameters that should be monitored in the engine oil are the oxidation of the base oil, the pH value of the oil and the Total Base Number of the oil.

Applications notes for these parameters can be found on our website:

- Oil oxidation
- I-pH value
- Total Base Number

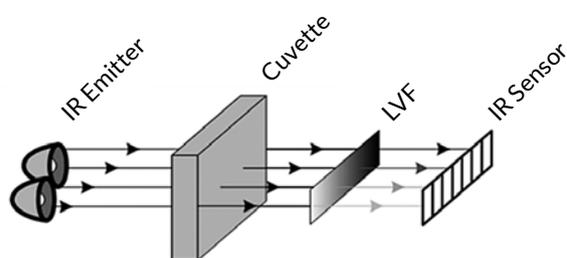
## Mid-infrared spectroscopy

Mid infrared spectroscopy (Mid IR) is a powerful technique for measuring the concentration of organic molecules. Mid-IR spectroscopy covers the absorption of light by a sample in the range from 2000 nm to 12000 nm. In this wavelength range the absorption of light at a specific wavelength can be linked unequivocally to a certain molecular structures that subsequently identifies the molecule.

In the Mid-IR wavelength region each molecule absorbs light at a molecule characteristic wavelength and the amount of light absorbed is a measure of the concentration of the particular molecule in a sample.

As different molecules absorb light at different characteristic wavelength in the Mid-IR wavelength region the measurement of a mid-infrared absorption spectrum from 5500 nm to 11000 nm can be used to identify the existence and the concentration of a multitude of different molecules in a sample.

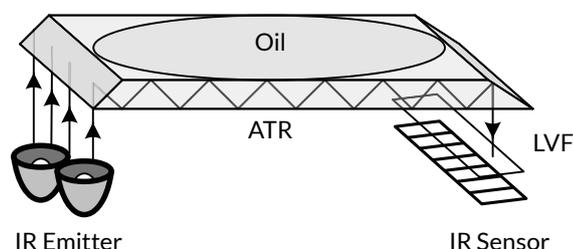
Mid-infrared spectroscopy is either carried out in transmission mode or in ATR mode where ATR stands for Attenuated Total Reflection.



In transmission mode (see picture above) the light from a broadband emitter is directed through a cuvette (which contains the sample) onto a grating. The grating splits out the light into more discrete wavelength (similar to a rainbow) and the light then falls onto an infrared sensor (line array) where each pixel corresponds to a specific wavelength. A mid-infrared absorption spectrum is recorded by first recording the signal levels of each of the pixels of the line array without a sample being present in the cuvette. This is called a background measurement. Subsequently the measurement is repeated but with a sample being

present in the cuvette. This is called the sample measurement. The difference between the background measurement and the sample measurement originates from the light that is absorbed by the sample and it is called the absorption spectrum of the sample.

The working principle of the ATR mode is shown below. Light from a broadband emitter is coupled into an ATR crystal. The geometry of the crystal is designed in such a way that the light bounces through the ATR crystal (total internal reflection) and is coupled out on the other side where the light is again split up into discrete wavelengths by a grating and detected by an infrared line array.



If now a sample is placed on top of the ATR crystal the refractive index of that sample is different to that of air resulting that the light penetrates which each bounds a certain distance into the sample before it is reflected back into the ATR crystal (evanescent waves). Which each bounce certain wavelength of the light are absorbed by the sample sitting on top of the ATR crystal.

An absorption spectrum of a sample in ATR mode is obtained in the same way as in transmission mode. First a measurement is taken without a sample being present on the ATR crystal (background measurement). Subsequently a sample is placed onto the ATR crystal and the sample measurement is taken. The difference is again called the absorption spectrum of the sample.

In principle both transmission mode and ATR mode provide exactly the same absorption spectrum of the sample and it depends on the exact application which measurement mode is best suited.

## Oil conditioning monitoring based on Mid-IR spectroscopy

Many different substances can be used to lubricate a surface. Oil and grease are the most common. Grease is composed of oil and a thickening agent to obtain its consistency, while the oil is what actually lubricates. Oils can be synthetic, vegetable or mineral-based as well as a combination of these. The application determines which oil, commonly referred to as the base oil, should be used. In extreme conditions, synthetic oils can be beneficial. Where the environment is of concern, vegetable base oils may be utilized.

Lubricants containing oil have additives that enhance, add or suppress properties within the base oil. The amount of additives depends on the type of oil and the application for which it will be used. Typical additives are anti-foam additives, anti-wear additives and anti-oxidants. The only problem with additives is that they can be depleted, and in order to restore them back to sufficient levels, generally the oil volume must be replaced.

As such a replacement of the lubricants can be very expensive (either directly due to the high costs of the lubricant or indirectly due to downtime of the engine and lost earnings) it is desirable to have a cost effective oil conditioning monitoring sensor that provides accurate and reliable information about the condition of the oil.

Mid-IR spectroscopy is well suited to oil condition analysis. During the aging of the oil, different decomposition and conversion processes occur at the molecular level resulting in changes in the absorption spectrum. As these aging processes introduce changes in the absorption spectra at many different characteristic wavelengths one IR spectrum of an oil sample can provide accurate and conclusive information about the status of the oil and about it can help to identify the root cause of the aging mechanism as the characteristic wavelength, where the change in absorption is observed, is linked to one specific and uniquely identifiable molecular structure.

The oil aging or degradation process can be attributed to three key aging mechanisms:

- oil degradation
- additive depletion
- contamination

Base oil degradation is predominantly driven by an oxidation processes. It can be viewed as the chemical breakdown of the base oil molecules with oxygen as a reagent. The principle source of oxygen is air. There are a number of parameter that accelerate the oxidation process such as high temperature, wear particles, water and other contaminants. The breakdown of the base oil involves a number of chemical reactions that produce acid compounds which undergo further reactions to form polymeric compounds resulting in varnish, sludge and other deposits. Typical oil condition parameters related to base oil degradation are: Oxidation, Total Acid Number (TAN), Total Base Number (TBN), nitration and sulphation.

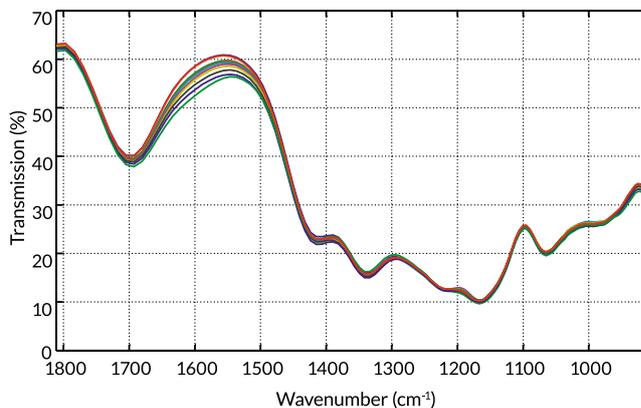
Additives are part of any modern lubricant solution. Additives are functional groups, usually with central ions such as zinc, molybdenum, magnesium etc. that are suspended into the base oil to enhance the overall performance of the lubricant. Typical additives are used to combat the main degradation mechanism of the base oil and they address areas such as anti-foam additives, anti-wear additives and anti-oxidants additives.

During the oil ageing process the concentration of additives within the lubricant decreases and once the additive concentrations have reached a lower threshold concentration the degradation of the lubricant becomes inevitable. Monitoring the concentration levels of the different additives is therefore very important to get a good understanding of the current condition of the oil.

Typical additives used to neutralise the key degradation mechanisms are molecules with central ions of

zinc, molybdenum, phosphorus, calcium, magnesium, barium or sodium. Again these molecules have uniquely identifiable characteristic absorption wavelength and by way of measuring the infrared absorption spectrum of an oil sample the respective concentrations of each of the additives can be determined.

Oil contamination is often caused by foreign substances such as water, glycol, diesel, petrol or foreign oils. Each of these substances have unique characteristic absorption wavelength and can therefore easily being identified. This is shown in the figure below for water contamination of a oil between 250–5000 ppm. A characteristic water absorption peak at  $1644\text{ cm}^{-1}$  develops as the water concentration in oil increases.



Mid-IR spectroscopy is able to provide information (qualitatively and quantitatively) about the three different aging mechanism. By a detailed analysis of the mid-infrared absorption spectrum of an oil sample the oil condition can be characterised and specific degradation mechanism can be identified and analysed.

## Oil Condition Sensors based on Mid-IR spectroscopy

The oil condition sensor of the IR Sphinx series detects the three major oil degradation mechanism simultaneously. The standard oil condition parameters, that are commonly obtained by laboratory based analysis, are calculated from the measured IR spectra.

The sensor is based on a spectral apparatus that is constructed with no moving parts, which makes it durable and virtually maintenance free. Meaningful oil condition parameters are calculated from the recorded spectra by a previously built oil-specific calibration (chemometric model).

The sensor also does not require any consumables or wet chemistry which significantly enhances the safety aspect and reduces long term operation costs.

One sensor can be configured to measure all parameters that are relevant to the oil condition monitoring and maintenance of marine engines.

In addition to portable systems for rapid on-site analysis, device models for use in the laboratory are available – as well as rugged field installations for

In addition to portable systems for rapid on-site analysis, device models for use in the laboratory are available – as well as rugged field installations for inline operation.

## IR Sphinx ATR product portfolio and technical specification

Spectrometer	IRSphinx ATR Lab		IRSphinx ATR Portable		IRSphinx ATR Industrial			
								
Spectral range	2.5–5.0 $\mu\text{m}$ 4000–2000 $\text{cm}^{-1}$		5.5–11.0 $\mu\text{m}$ 1800–900 $\text{cm}^{-1}$		2.5–5.0 $\mu\text{m}$ 4000–2000 $\text{cm}^{-1}$		5.5–11.0 $\mu\text{m}$ 1800–900 $\text{cm}^{-1}$	
ATR Crystal Material	ZnS	ZnSe	ZnS	ZnSe	ZnS	ZnSe	ZnS	ZnSe
ATR Frame Material	Stainless steel							
Spectrometer Housing Material	Anodized aluminium							
Number of Sample Reflections	9							
Dimensions (L x W x H)	165 x 74 x 35 mm							
Protection Class	IP64							
Battery	–		Lithium polymer (LiPo) 1300 mAh				–	
Power Requirement	5 Volt DC, 5 W		5 Volt DC, 5 W				5 Volt DC, 10 W	
Standalone Operation	–		–				yes	
Interface	USB, Ethernet		USB, Ethernet, Bluetooth				USB, Ethernet, CANopen	
Weight	~700 g		~710 g				~750 g	

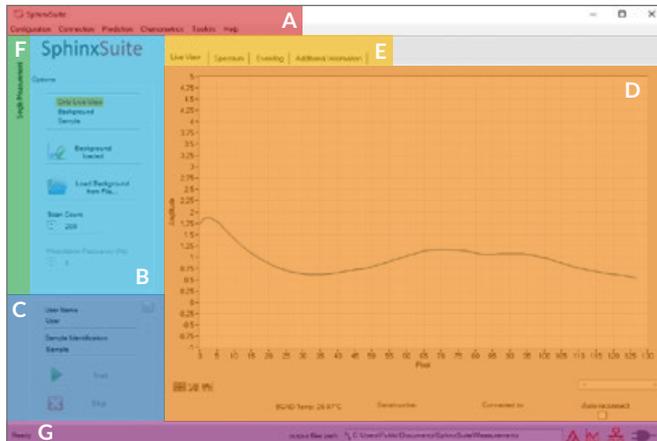
## IR Sphinx Transmission product portfolio and technical specification

Spectrometer	IRSphinx Transmission Lab		IRSphinx Transmission Portable		IRSphinx Transmission Industrial			
								
Spectral range	2.5–5.0 $\mu\text{m}$ 4000–2000 $\text{cm}^{-1}$		5.5–11.0 $\mu\text{m}$ 1800–900 $\text{cm}^{-1}$		2.5–5.0 $\mu\text{m}$ 4000–2000 $\text{cm}^{-1}$		5.5–11.0 $\mu\text{m}$ 1800–900 $\text{cm}^{-1}$	
Cuvette	Aluminium		Aluminium		Stainless steel + fluid channels			
Spectrometer Housing Material	Anodized aluminium							
Dimensions (L x W x H)	85 x 99 x 97 mm		165 x 74 x 97 mm				85 x 99 x 97 mm	
Protection Class	IP44		IP64				IP44	
Battery	–		Lithium polymer (LiPo) 1300 mAh				–	
Power Requirement	12 Volt DC, 5 W		5 Volt DC, 5 W				12 Volt DC, 10 W	
Standalone operation	–		–				yes	
Thermal Stabilisation	–		–				yes	
Interface	USB, Ethernet		USB, Ethernet, Bluetooth				USB, Ethernet, CANopen	
Weight	~430 g		~720 g				~460 g	

## Sphinx Suite-Software

All Spectrolytic's products come with a proprietary software called Sphinx Suite. The software is modular and can be customised as required. The software also has the option to interface directly with commonly used data processing software such as Unscrambler.

By default all spectrometers are delivered with the Basic software option. The Basic software module allows the customer to perform measurements, save data, export data etc.



**A: Menu bar with configuration options**

**B: Measurement options and import/export configuration**

**C: Start & Stop measurement button**

**D: Graphic display**

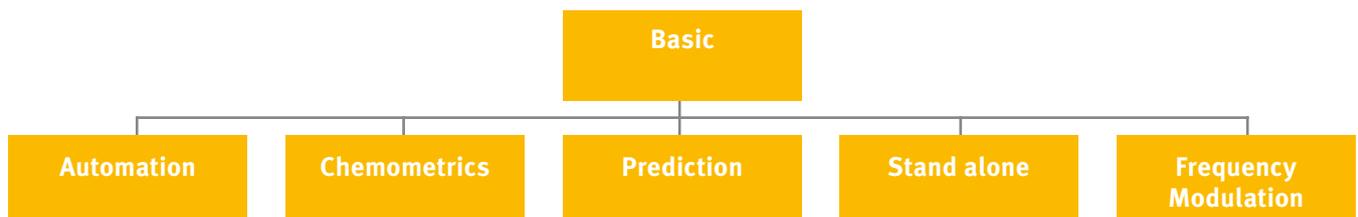
**E: Data selection tabs**

**F: Measurement selection**

**G: Status bar with information about battery charge level, connection and folders**

## Sphinx Suite-Software Modules

The picture below depicts the available software modules that are available within Sphinx Suite.



### Basic software

Measuring and capturing spectral data, saving data, exporting data to Excel etc.

### Automation module

Definition of measurement routines, Continues execution of measurement routine, automatic data capture, automated reconnect after computer restart, trigger modus, control of extension interface

### Chemometric module

ANN model builder (classification), PLS1 model builder (quantification), SIX model builder (similarity index), band pass filter model builder, Definition of control parameters, saving of models, analysis of historic data

### Prediction module

Integration in Automation module, automatic evaluation of measured IR spectra, visualisation of control values, saving of the analytical results, generation of customised reports

### Stand alone module

OCOM interface (allows user to control spectrometer via external interface), transfer of automation sequences onto spectrometer, autonomous measurement by spectrometer without computer

**Frequency Modulation module** Optimisation of emitter modulation frequency between 5–20 Hz