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Diode Laser Systems
In Gas Measurement

The application of laser diodes for improved biogas analysis

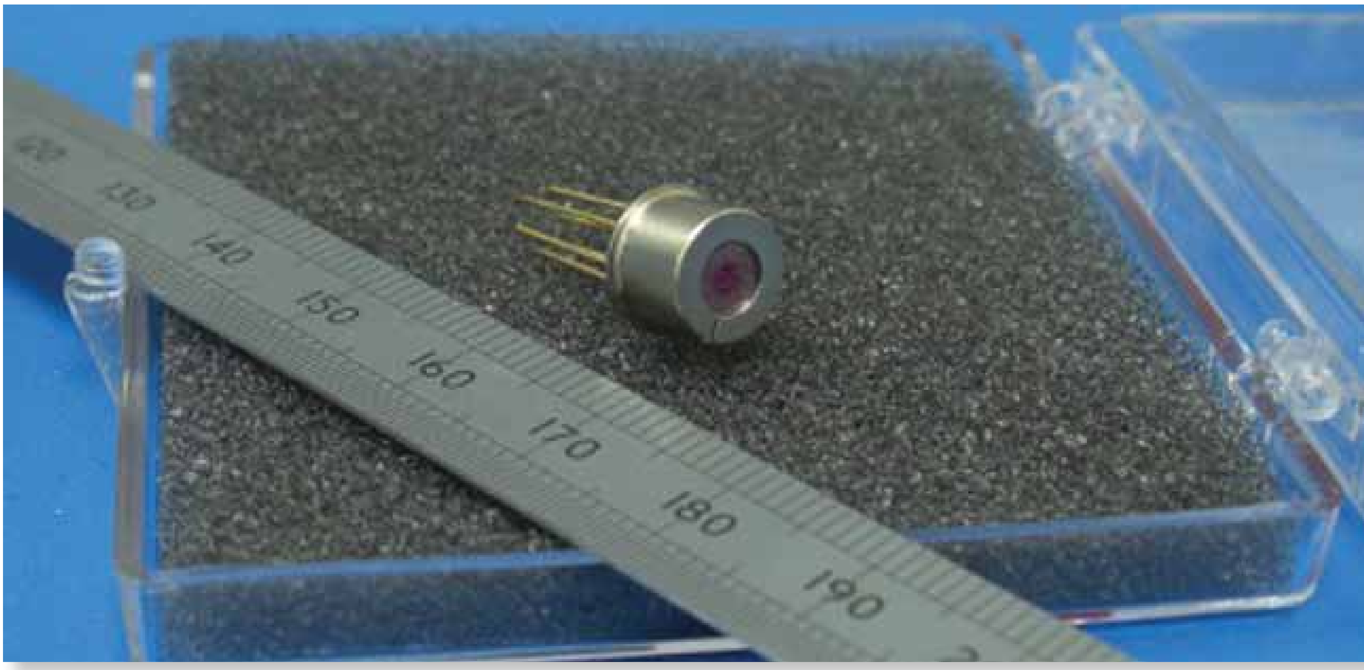


Figure 2 Tuneable diode laser measurement technique

Introduction

The online analysis of biogas has increased in importance with the increasing use of anaerobic digestion and the use of biogas to generate revenues. Fully automated gas analysis systems can help the operator maximise output, verify data, and give warnings of out of range parameters to safeguard installed plant.

Current measurement techniques can suffer from a number of problems. Cross interferences can affect readings and frequent calibration is often required. Electrochemical cells have a limited lifetime and can suffer from poisoning from other gases.

The advent of infrared (IR) diode lasers at a reasonable cost may see this situation change. Diode lasers can be tuned to measure only the gas of interest, and diode laser systems are inherently stable.

This article explains the reasons for the improved performance of diode laser systems and what this could mean for operators in the future, when diode laser systems are available.

Why analyse biogas?

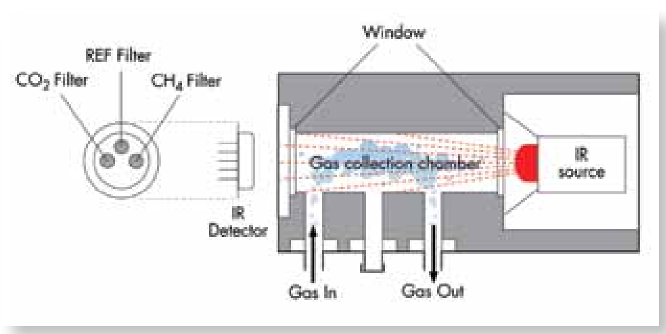
Biogas can be produced from many processes. Within the waste industry the two main processes are landfill and anaerobic digestion.

The use of anaerobic digestion for many types of organic waste is increasing rapidly and the biogas produced can be used to generate electricity that can return revenue to the operator.

The decomposition of organic waste can produce a range of gases. The two main gases are methane and carbon dioxide. Many other gases can also be produced, depending on the make up of the particular waste stream, and the environmental conditions. One of the most important lower level gases is hydrogen sulphide. This is typically produced in the range of a few parts per million (ppm) to thousands of ppm. It is important because of the damaging effect it can have on process plant and engines.

There are a number of reasons why it is important to measure the gases produced. >

Figure 1 NDIR measurement technique



Process monitoring

Measurement of methane can help to give assurance that the process is operating correctly. If the process in an anaerobic digester plant goes wrong, it can be an expensive and time consuming job to get it working again. Improved monitoring of the process will help the operator avoid problems and maximise the efficiency of the plant.
** See AWE International article June 2010, p54-55 / AEMS / BiogenGreenfinch / Westwood*

Power generation

Increasingly biogas is being used to generate electricity for use on site, CHP, or to be sold to the grid to generate revenue. Measuring the methane concentration going into the engines can help in their management and efficiency. Hydrogen sulphide is also important here as a high concentration can seriously damage the very expensive engines.

H_2S removal

H_2S is such a problem on many sites that H_2S scrubbers have to be used to remove it before the gas can be used. This is particularly true for anaerobic digesters, but high H_2S concentrations can also be found on many landfill sites. These scrubbers are expensive to run, so knowing the H_2S concentration is important in using them effectively. It is also wise to monitor the gas after the scrubber to check for correct operation.

Carbon credits

The accurate measurement of methane is required for sites within the Clean Development Mechanism (CDM) process, where carbon credits are being claimed. For large sites, even a few percent improvement in the accuracy of the methane measurement can be worth a large amount of money to the site operator.

Compliance

Gases may need to be measured for compliance or health and safety purposes, including compliance with EA requirements and pollution prevention and control (PPC).

Current technology

Methane and hydrogen sulphide are two important gases when operating a biogas plant, so we will take these as examples to compare the techniques.

Methane

Currently methane is usually measured by non dispersive infrared (NDIR). This uses a beam of IR radiation of a wavelength chosen to be absorbed by methane. By measuring the absorption, the concentration of methane can be determined.

This technique is used extensively, is relatively low cost, and robust. It was developed some 20 years ago to provide portable on-site analysis of landfill methane, prompted by the problem of 'methane migration' from landfill to surrounding properties, and at least two explosions. Since then NDIR has been used extensively for both portable and fixed methane gas analysis from landfills, CDM and increasingly anaerobic digestion.

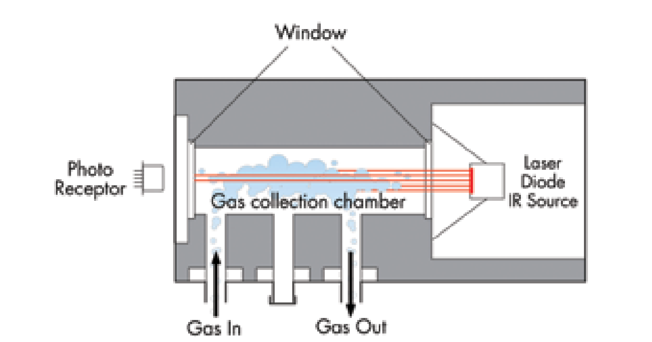
A typical NDIR sensor is shown in Figure 1. An IR source generates the IR, and this is usually a simple bulb. This IR radiation is passed through the gas, where a certain amount will be absorbed. The amount absorbed depends on the concentration of the gas. An IR detector is situated at the other end of the chamber. Because the IR source is broad band, the IR radiation needs to pass through a filter to select the wavelength of interest - the one that will be absorbed by methane in this case.

This system works well, but the NDIR technique does have a number of disadvantages.

It can have some cross interference from other gases. For example, when measuring methane there will also be a response from other hydrocarbons, which potentially can give misleading readings.

Although steps are usually taken to include a reference beam, the system can drift and therefore require frequent calibration by performing a zero and span adjustment. For portable systems this is an inconvenience, while for fixed systems it means providing an automatic calibration system with gas bottles and associated hardware. This increases the capital cost of the system and also increases the ongoing maintenance costs.

The NDIR technique is suitable for measuring percentage levels of gases where a short gas cell can be used. For measuring lower >



Diode laser diagram

levels of gas a longer path length through the gas is required, and this is difficult with the NDIR technique.

Hydrogen sulphide

Hydrogen Sulphide is usually present in the ppm to thousands of ppm range, and is difficult to measure with NDIR at these levels. The most common method of measuring hydrogen sulphide is with an electrochemical cell. Although these are low cost they have a number of drawbacks.

Electrochemical cells can be sensitive to other gases and the operator needs to be certain that none of these are present.

The cells also have a limited life, usually a year or two, and the life can be shortened by exposure to large quantities of the gas. In some situations they can also be poisoned by other gases so that the output is reduced, giving a false reading. Again it is important to know what other gases are present.

Most electrochemical cells also require a supply of oxygen, so in fixed continuous monitoring systems they need to be frequently purged with oxygen or air.

All of the above mean that while electrochemical cells are low cost, ongoing calibration and maintenance costs are high.

The advent of diode lasers

Laser light from a semiconductor diode was first demonstrated in 1962. Since then a lot of work has gone into developing diode lasers into commercial components and they are used extensively in the telecommunications industry.

"the diode laser emits an intense, forward facing beam of IR radiation. This passes through the gas and is detected by an IR detector. No IR filters are required as the diode laser only emits radiation at one wavelength"

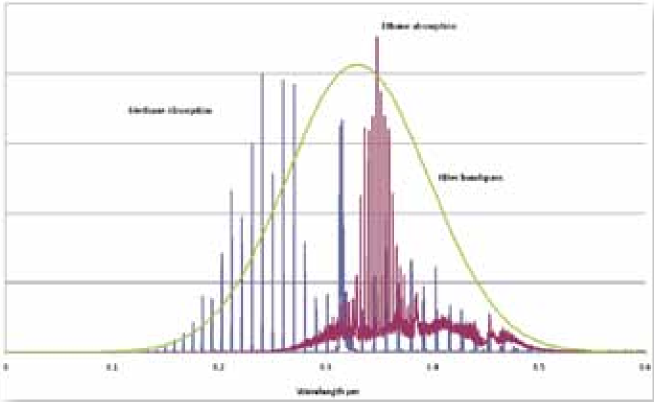
Development of IR emitting diode lasers has taken longer, but these are now available at a reasonable cost. It is now possible to use these devices as sources for IR absorption. They provide a number of benefits over the current techniques, and these will be discussed in the following sections.

A diode laser system is shown in Figure 2. The diode laser emits an intense, forward facing beam of IR radiation. This passes through the gas and is detected by an IR detector. No IR filters are required as the diode laser only emits radiation at one wavelength.

No cross gas interference

One of the problems with NDIR is that the 'bandwidth' of the IR radiation is fairly large. The bandwidth is a measure of the range of IR

Figure 3 NDIR absorption peaks and filter bandpass



wavelengths that the system responds to. For NDIR this is determined by the characteristics of the IR filter used.

Figure 3 shows the situation for NDIR. The absorption lines for methane are shown and the peak of the IR radiation passing through the gas. It can be seen that the wavelength of the IR beam has been chosen to cover the methane absorption reasonably well. However, also shown is the absorption band for ethane. This overlaps the methane absorption band, so any ethane present will also be detected and reported as methane.

"while the NDIR technique has a bandwidth of around 200nm, a diode laser has a bandwidth of 0.0006nm. This narrower bandwidth can be used to select only the gas of interest"

In fact the IR beam will be absorbed by many other hydrocarbons and the methane reading will be affected if these are present in the gas. Unfortunately it is not possible to reduce the bandwidth of the IR beam with the NDIR technique.

Thus the methane reading can be affected by the presence of other gases, particularly other hydrocarbons.

A diode laser generates IR radiation with a much narrower bandwidth. While the NDIR technique has a bandwidth of around 200nm, a diode laser has a bandwidth of 0.0006nm.

This narrower bandwidth can be used to select only the gas of interest. The overall broadband absorption of methane is actually made up of many finer individual lines as shown in Figure 3. With a diode laser source it is possible to tune the diode laser to just one of these lines.

The line of choice will depend on what other gases are present in the sample, but it is usually possible to find a line where no other lines are present from other gases within the sample. Figure 4 shows just such a region of the spectrum where a methane line is present, but there is no ethane line. Thus the diode laser technique can be made immune from interference from other gases. >

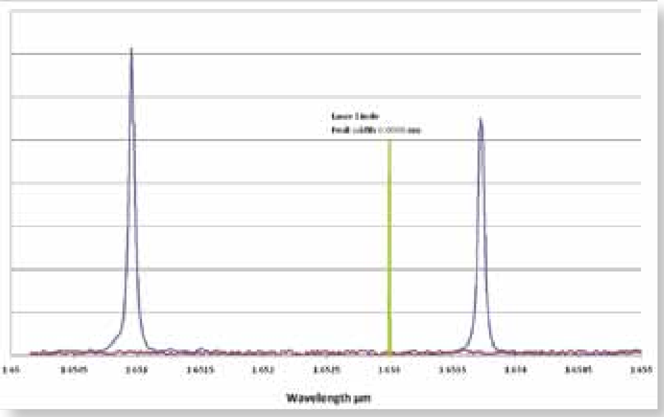


Figure 4 Absorption peaks for the tuneable diode laser technique Blue - methane absorption peaks Red - ethane background

Tuning the wavelength

Another important advantage of a diode laser is that it can be tuned over a range of wavelengths. Figure 4 shows an individual methane absorption peak. Even for this narrow peak, the diode laser bandwidth is several hundred times narrower. By controlling the current to the diode laser, the wavelength can be scanned across the absorption peak. The scanning can take place rapidly and can be carried out for each reading from an analyser, say every second.

Why is this an advantage? There are a number of advantages in being able to do this. One of the main ones is that absorption measurements are obtained ‘on peak’ and ‘off peak’. That is, a measurement is obtained at the centre of the peak where the absorption is at a maximum, and a measurement is also obtained where there is no absorption. Because of this the diode laser technique has an inbuilt reference beam - the off peak measurement. Moreover, this reference measurement is made with the same source, detector, electronics, path length, windows etc. as the main measurement. Any drift or degradation of signal due to these components will be compensated for.

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The ‘reference’ measurement is also made at a wavelength very close to the wavelength being used for the absorption measurement, whereas for NDIR the reference wavelength can be at a quite different wavelength from the main measurement. Thus any wavelength dependant changes are compensated for.

For these reasons a diode laser system inherently has excellent stability. The improved stability means that diode laser instruments should require far less frequent calibrations and user checks.

Automatic on line systems should not require the expensive addition of automatic calibration and provision of calibration gases. Another advantage of the scanning technique is that information is obtained about the shape of the line. The line shape will change depending on the gas pressure and the composition of the balance gas. By measuring the line shape these effects can be compensated for.

How is a diode laser wavelength tuned?

The wavelength output by a diode laser can be changed by two methods - altering the temperature and altering the current. Changing the temperature is usually a relatively slow process as the diode will need to stabilise at the new temperature. It is therefore normal to keep the temperature constant with a thermoelectric heater or cooler.

Scanning of the wavelength is achieved by increasing the current into the diode by feeding it a sawtooth waveform. This can be done very rapidly, many times a second if required. The sawtooth waveform will usually consist of many small steps, and a reading is taken at each of these steps. From this a scan of the absorption peak can be obtained for later processing.

Improved sensitivity

Another advantage of a diode laser is that the light is emitted in the forward direction and is much more intense than a traditional IR source. It is easy to collimate into a tight intense beam. This makes it easier to use longer path lengths and retain a reasonable light intensity at the detector. Being able to use longer path lengths enables lower gas levels to be measured. Using a diode laser, it is therefore possible to measure down to ppm levels. This would allow the measurement of ppm levels of both methane and hydrogen sulphide.

Using a diode laser system to measure hydrogen sulphide will give many advantages over the use of electrochemical cells - no cross interference, no cell replacement, no user calibration, no poisoning, less servicing, more accurate reading. Of course, a diode laser system for hydrogen sulphide will cost far more than an electrochemical cell, but it would give a more precise and reliable measurement, not be affected by other gases, and not have a limited life. The extra capital cost could be offset by the reduced maintenance costs and may be acceptable for critical applications.

Water

Biogas has a high water content and it is important that this does not affect the gas readings. With a diode laser it is possible to choose an absorption line where there are no water absorption lines. The reading should therefore not be affected by the moisture content of the Biogas.

It is still important to make sure that there is no condensation within the analyser as liquid water will absorb all IR radiation and prevent the system working. Liquid water will also cause corrosion, so the gas will still need to be conditioned before entering the analyser. >

	NDIR (for methane)	Electrochemical cell (for H_2S)	Diode Laser
Stability	Good, provided regular zero and span checks are performed	Good provided regular zero and span checks are performed	Excellent, no calibration required
Selectivity	Sensitive to other gases, particularly other hydrocarbons	Sensitive to certain other gases	Excellent, specific to chosen gas, no cross sensitivity
Lifetime	Excellent	Limited life, needs regular replacement. Can be poisoned by other gases	Excellent
Effect of high concentrations	No effect, fast recovery	High concentrations can reduce lifetime Can have long recovery time	No effect, fast recovery
Sensitivity	Suitable for percent levels	ppm levels possible	Suitable for percent or ppm levels
Cost	Medium	Low	High

One diode, many gases?

Since the diode laser wavelength can be tuned, can one diode be used to measure several gases? Unfortunately this is not usually the case. The wavelength range over which a particular diode laser can be tuned is not great and they are usually specially made to fit a particular wavelength range. In some cases it may be fortuitous that a peak for another gas of interest is present within the tuning range, but usually this will not be the case. Thus each gas will normally have its own diode laser. Unfortunately this does increase the cost somewhat for a multi gas detector.

Is this the end of the NDIR technique and electrochemical cells?

Certainly not. Diode lasers will have a role to play where the advantages discussed above are important. However, diode lasers are still relatively expensive and require more complex optics and electronics than the NDIR technique. A diode laser based instrument will cost several times as much as a NDIR based one, and this is only worthwhile if the advantages are important in the application.

Currently NDIR is low cost, reliable, robust and in use in thousands of applications worldwide. For most of these applications the disadvantages discussed above are of no consequence. NDIR instruments will continue to be developed and refined and be the mainstay for Biogas monitoring for many years to come, particularly for portable monitors.

Electrochemical cells are used extensively worldwide for many applications. Many of the gasses they measure cannot be measured by any IR technique. For H_2S, a diode laser system will be far more expensive than an electrochemical cell and will not be economical for many applications.

Conclusion

The table above summarises the advantages and disadvantages of the various techniques.

IR diode lasers have reached the stage where they can be applied to the measurement of gases.

Applying modern IR diode lasers to the measurement of biogas should give several improvements, including improved selectivity and stability, and less need for calibration checks.

The inherent stability of diode laser systems should result in a reduction in ongoing maintenance costs.

As the costs of diode lasers continue to fall and the techniques improve, we will see them in an increasing number of applications. ■

Author

Dr Roger Riley is New Products Introduction (NPI) Director at Geotech, where he has been in charge of the development team for the last 12 years.

He has been involved in all of the new products during that period, including portable and fixed landfill gas analysers, and carbon dioxide monitors.

Dr Riley's previous experience includes working for the Philips group as a project manager, developing various types of analytical instruments including gas chromatography and atomic absorption.

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