Development of a Gas Analysis Technology "IRLAM" Using Quantum Cascade Laser and Unique Concentration Calculation Method

~ Realization of High-Sensitivity, Low-Interference, and Fast-Response Gas Analysis ~

SHIBUYA Kyoji

HORIBA's newly developed gas analysis method using a quantum cascade laser (QCL), infrared laser absorption modulation (IRLAM), dramatically reduces calculation time compared to conventional spectral fitting methods by extracting information important for concentration determination from the absorption signal of the sample gas as features (patent registered). By combining this method with QCLs manufactured in-house and a uniquely structured Herriott cell with a small volume and long optical path length, we have completed a gas analyzer with high sensitivity, small influence of interfering gases, and fast response. IRLAM has succeeded in greatly expanding the industrial application range of gas analysis using QCL, realizing the world's first QCL-based onboard exhaust gas measurement and real-time monitoring of petrochemical processes.

Keywords
gas analysis, infrared absorption spectroscopy, quantum cascade laser, spectral analysis, features

Introduction

HORIBA has long applied gas analysis technology using infrared absorption to automotive and factory exhaust gas measurement, atmospheric environment measurement, and process monitoring and control, and has contributed to reducing environmental impact and improving productivity in various industrial fields. A conventional infrared gas analysis technique called non-dispersive infrared absorption (NDIR) has been widely used.[1] NDIR uses thermal radiation from a light source such as a heated filament, cuts out the wavelength band to be used with an optical bandpass filter to match the absorption band of the target gas and determines the concentration of the target gas from the amount of absorbed infrared light. Because the wavelength resolution of the light source is not high in NDIR, it is difficult in principle to remove the influence of interfering gases whose absorption bands overlap with those of the target gas. Therefore, the use of a pneumatic detector[2] that detects infrared light in a cell filled with the target gas can provide a certain degree of gas selectivity. The gas analysis method using Fourier transform infrared spectroscopy (FT-IR) can acquire the absorption spectrum of the entire infrared region of a sample gas. This makes it possible to simultaneously measure many gas components by applying multivariate analysis. The FT-IR method is widely used for automotive emission gas measurements.[3] On the other hand, quantum cascade laser infrared spectroscopy (QCL-IR), a gas analysis method using a single wavelength quantum cascade laser (QCL) as a light source, can considerably suppress the interfering gas influences by selecting a suitable wavelength for the measurement with high wavelength resolution. Moreover, the QCL-IR method can provide higher sensitivity than NDIR and FT-IR because of the high energy density per unit wavelength of the light source and the straightness of the laser beam facilitating the use of a multipass cell to obtain a long optical length. HORIBA was the first company in the world to apply gas analyzers using QCL-IR to automotive emission gas measurements.[4,5] However, in applications such as automotive emission gas measurement, where many interfering gases coexist and their concentrations change dynamically, it is difficult to completely eliminate interfering gas influences by wavelength selection alone. In conventional QCL-IR, the concentration of the target gas corrected for interfering gas influences is calculated by curve fitting between the measured absorption spectrum of the sample gas and the model spectra of the target gas and interfering gases prepared in advance. In addition to interfering gas influences, various other disturbances such as fluctuations in environmental temperature and pressure, drifts in laser oscillation wavelength, and spectral broadening due to interactions with coexisting gases can change the absorption spectrum. Since a complex fitting process involving repetitive operations is required when these nonlinear disturbances are included in the correction, a high-performance and bulky computer has to be installed in the equipment to perform such operations in real time. However, such requirements not only increase the cost and size of the device, but also limit the scope of application for industrial instruments, which are required to operate stably even in harsh environments.

To address this, we came up with the idea of applying the concept of "features" used in a field such as machine learning to the QCL-IR concentration calculation algorithm. By extracting features of target gas, interfering gas and other disturbances from the absorption signal obtained in the measurement, the number of explanatory variables is greatly reduced while maintaining the amount of information necessary for concentration quantification. Thereby the load on the concentration calculation process is dramatically reduced. This has made it possible to achieve sufficiently high-accuracy and real-time measurement with even a board-embedded general-purpose microcomputer while eliminating various disturbances that affect the measurement accuracy. We have named this gas analysis method Infrared Laser Absorption Modulation (IRLAM™*1)[6] and have successfully commercialized a gas analyzer based on this principle. The following describes the principle and configuration of IRLAM, compares it with conventional technologies, and introduces examples of products in which IRLAM has been applied.

*1: IRLAM is a registered trademark or trademark of HORIBA, Ltd. in Japan and other countries.

Principle and configuration of IRLAM

Gas analysis by absorption spectroscopy, including IRLAM, uses a basic principle based on Lambert-Beer law that the absorbance A, defined as the logarithm of the ratio of the incident light intensity I_{in} to the sample gas and the transmitted light intensity I_{out} is proportional to the gas concentration c and the optical path length L, which is expressed by the following equation.

$$A = -\log\left(\frac{I_{out}}{I_{in}}\right) = \varepsilon \cdot c \cdot L$$

Here, ε is a gas-specific constant called the absorption coefficient.

Figure 1 shows a schematic diagram of the basic configuration of an IRLAM gas analyzer. In the IRLAM gas analyzer, a light from the QCL is incident on an analysis cell into which sample gas is introduced, called a Herriott cell, and the emitted light after transmission through the sample gas is received by an infrared detector to acquire absorption signals. The concentration of the target gas is then calculated from the obtained absorption signal using a unique concentration calculation algorithm with feature extraction. There are three important elements that characterize the IRLAM gas analyzer: the QCL, the Herriott cell, and the concentration calculation algorithm, each of which is described below.

Quantum cascade laser

QCLs are a relatively new type of semiconductor lasers capable of room-temperature laser oscillation in the mid-infrared region (with wavelengths ranging from 4 to 12 μm).[7] Since most gas molecules show the strongest absorption in the mid-infrared region, the QCL, which can oscillate in this wavelength region, is the most suitable light source for gas analysis. A QCL consists of a multilayer semiconductor thin film with several hundred layers, and its feature is that the oscillation wavelength can be arbitrarily designed by controlling the material composition and film thickness. HORIBA has established the technology to manufacture QCLs in-house with optimal wavelengths according to the type and concentration range of the target gas. This enables to flexibly response to a variety of gas analysis needs.

Herriott Cell

In gas analyzers using absorption spectroscopy, the longer the distance that light penetrates the sample gas (optical path length), the greater the absorbance and the higher the sensitivity, as shown by Lambert-Beer law. Therefore, the IRLAM gas analyzer employs a gas cell called Herriott cell, as shown in Figure 1, in which light is multiply reflected by opposing mirrors installed inside to obtain a long optical path length.

Conventional Herriott cells generally use circular spherical mirrors,[8] but we use elongated spherical mirrors to significantly reduce the internal volume of the cell while ensuring a sufficient optical path length.[9] Reducing the internal volume of the cell improves the response time of

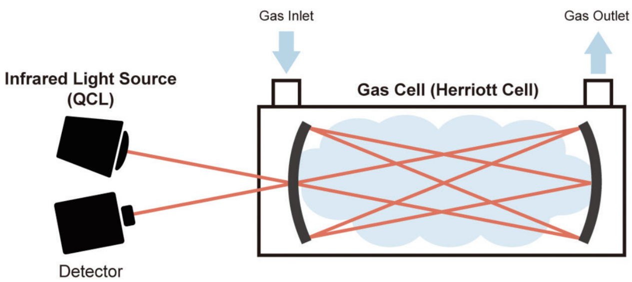

Figure 1 Schematic diagram of the basic configuration of the IRLAM gas analyzer.

the analyzer, which is dictated by the gas displacement time. In the Herriott cell with the elongated spherical mirrors, a 5 m optical path length can be achieved with an internal volume of only 40 mL. This contributes to the improved response time and the downsizing of the IRLAM gas analyzer.

Concentration calculation algorithm

The most distinctive element of the IRLAM gas analyzer is the concentration calculation algorithm.

IRLAM's concentration calculation algorithm applies the concept of "features" used in a field such as machine learning. Figure 2 shows a schematic of the gas analysis procedure in IRLAM. When the wavelength of QCL is modulated at a certain period around a peak of the absorption spectrum of the target gas, a periodic absorption signal reflecting the shape of the absorption spectrum is obtained from the detector. By correlating this absorption signal with multiple reference signals prepared in advance according to the features to be extracted, features quantities are extracted, and the obtained feature quantities are compared with the reference feature quantities obtained in advance using the calibration gas to determine the concentration using the least-squares method.[6,10]

In machine learning, the algorithm automatically determines the features to be extracted by learning from a large amount of training data, but in IRLAM, the designer selects the factors important for concentration quantification based on experience and determines the features to be extracted by understanding their influences on the absorption signal based on their physical properties. Specific factors important for concentration determination include the shape of the absorption signal of the target gas and the interfering gases, the influence of QCL oscillation wavelength drift, and the influence of spectral broadening caused by changes in pressure or coexisting gas concentration. In actual gas analysis applications of IRLAM, concentration quantification is performed using about 10 features related to these factors.

The advantage of the concentration calculation procedure using features is that by compressing spectral information through feature extraction, concentration calculations with correction functions for interference gas influences and other disturbance can be performed with significantly fewer explanatory variables than in the conventional case of direct curve fitting to absorption spectra. In general spectral curve fitting, since absorption spectral data consists of several hundred points, it is necessary to perform a least-squares method consisting of several hundred simultaneous linear equations. In the case of IRLAMs, on the other hand, the number of simultaneous linear equations is only a few to 10, so the computational load is reduced to 1/10 to 1/100. Therefore, even when high-speed real-time measurement is required, a high-performance computer is not necessary; a general-purpose embedded processor is sufficient. This allows the IRLAM to be configured without the need for a PC, facilitating downsizing and expanding its range of applications as an industrial instrument capable of stable and continuous operation even in harsh environments.

Performance comparison between IRLAM and conventional technologies

IRLAM has significantly improved from conventional gas analysis technologies using infrared absorption in terms of detection sensitivity and interference gas influence. The following is a comparison between IRLAM and conventional technologies based on specific measurement examples.

Detection sensitivity

Figure 3 compares the results of simultaneous measurement of formaldehyde (HCHO) in automotive exhaust gas by an IRLAM gas analyzer and a conventional FT-IR gas analyzer. The red line shows the FT-IR measurement results, and the blue line shows the IRLAM measurement results. The right figure shows that the overall trend of concentration change is consistent between the two methods. However, it can be clearly seen that the magnitude of the noise is very different. As shown in the left figure, which is an enlarged version of the right figure, the noise of IRLAM is less than one-tenth that of FT-IR. IRLAM can accurately measure even slight concentration

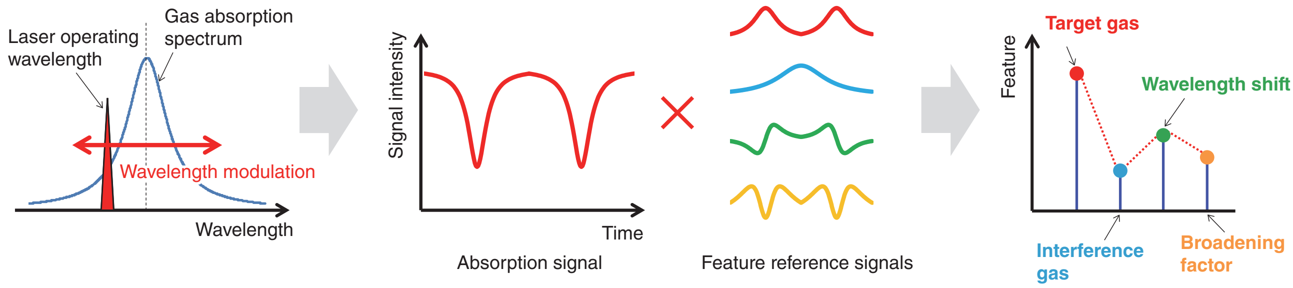

Figure 2 Conceptual diagram of the gas analysis procedure in IRLAM.

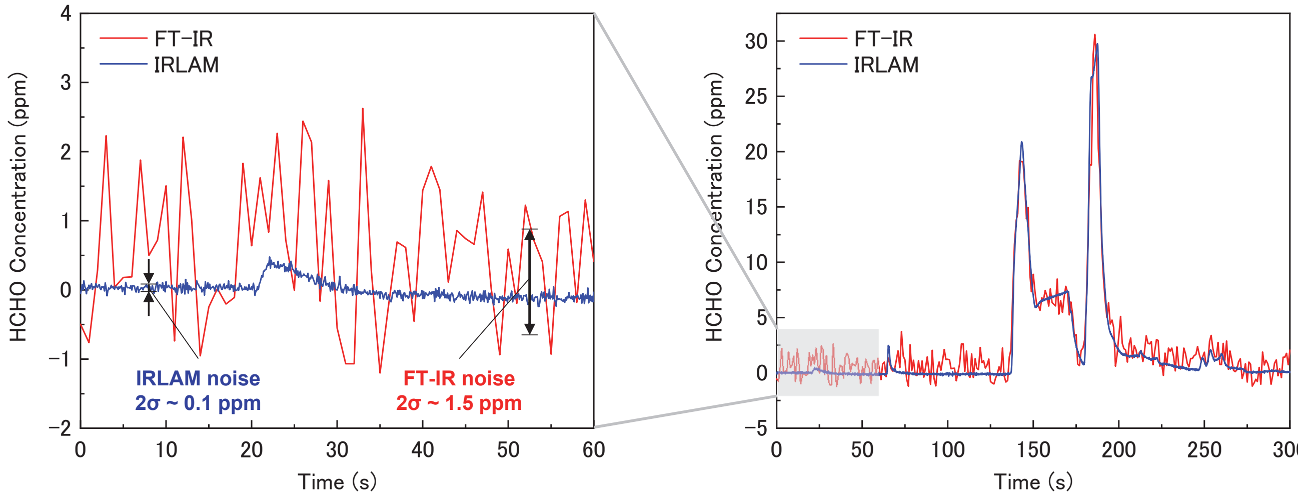

Figure 3 Comparison of detection sensitivity between IRLAM and FT-IR for HCHO measurement (the left figure is enlarged from 0 to 60 s in the right figure).

changes that is undetectable with FT-IR because they are buried in noise. Thus, IRLAM showed more than 10-fold improvement in detection sensitivity compared to conventional FT-IR.

Interfering gas influence

Figure 4 compares the changes in the concentration readings of an IRLAM gas analyzer and a conventional NDIR gas analyzer when the target gas, dinitrogen monoxide (N_2O), and the interfering gas, carbon dioxide (CO_2), were introduced into the analyzer cell in sequence. The red line graph in the left figure shows the measurement result by NDIR, and the blue line graph in the right figure shows the measurement result by IRLAM. The NDIR measurement result on the left shows that the concentration readings change significantly not only when N_2O, the target gas is introduced, but also when CO_2, the interfering gas, is introduced. This indicates that the concentration of N_2O cannot be measured correctly when CO_2 is mixed with the sample gas because it is greatly affected by the interfering gas of CO_2. On the other hand, the IRLAM measurement result shown on the right indicates that no interfering gas influence was observed, even though CO_2 was introduced at a concentration 10 times higher than in the NDIR test. This shows that the IRLAM can accurately measure the concentration of N_2O even when CO_2 is mixed at high concentration. Thus, IRLAM has achieved almost zero interfering gas influences, which was not possible with conventional NDIR technology.

Examples of products to which IRLAM is applied

IRLAM with the features described above are already used in fields requiring highly accurate, real-time measurement, such as automotive exhaust gas measurement and petrochemical processes. In the following, we will introduce some of the IRLAM gas analyzers that are currently in the market.

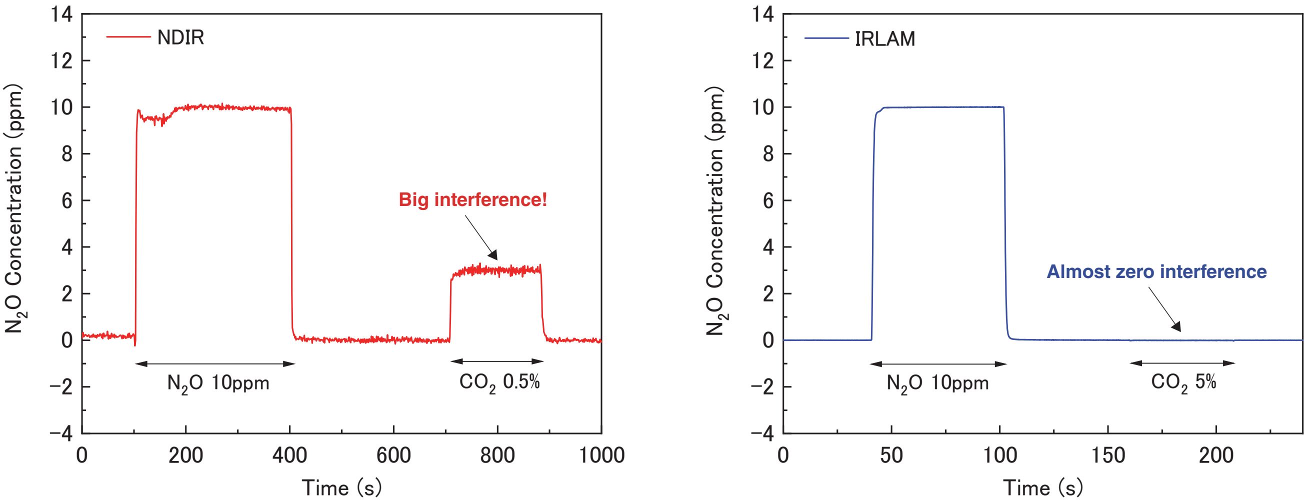

Figure 4 Comparison of interfering gas influence between IRLAM and NDIR for N_2O measurement (left: NDIR, right: IRLAM).

Engine Exhaust Gas Analyzer, MEXA-ONE IRLAM

MEXA-ONE IRLAM is an IRLAM gas analyzer for stationary automotive exhaust gas measurement. The lineup includes a type installed in the MEXA-ONE engine exhaust gas analyzer (XLA-11, XLA-13H) and a standalone unit type (MEXA-ONE-XL-NX), which are used for exhaust gas certification testing of completed vehicles and research and development to improve the environmental performance of engines.

The XLA-11 is designed to measure N_2O, a regulated greenhouse gas, with ppb-level measurement accuracy for dilution measurements using a constant volume sampling system, which is a certified test method. The MEXA-ONE-XL-NX can simultaneously measure four nitrogen compounds (NO, NO_2, N_2O, and NH_3) in real time with high accuracy, including nitrogen oxides (NOx), which have long been regulated substances, and ammonia (NH_3), which has recently been attracting attention as one of the substances causing PM2.5. It is widely used by automobile manufacturers and others as an indispensable product for the development of low environmental impact vehicles.

The XLA-13H is designed to measure HCHO, a hazardous substance that is already regulated in the United States and other countries and is being considered for regulation in Europe, and enables highly accurate continuous measurement in automotive exhaust gas test cycles, which has been difficult with conventional technology.[11] This product was also evaluated by the Joint Research Centre (JRC) of the European Commission, which provides guidelines for emission control and other policies in Europe, and its performance was shown to be sufficient for actual emission gas measurement.[12]

Onboard Emissions Measurement Systems, OBS-ONE IRLAM

In recent years, the real driving emission (RDE) regulation which measures emissions while driving on a real road has been introduced in Europe. In order to perform RDE testing, a compact and environmentally resistant analyzer called a Portable Emission Measurement System (PEMS) is required. In particular, unlike analyzers in a laboratory, on-board analyzers must be able to perform stable measurements even under severe environmental conditions, such as severe vibration and fluctuations in temperature and atmospheric pressure. IRLAM's highly robust concentration calculation algorithm and robust hardware design enabled us to meet such stringent requirements, and we succeeded in commercializing the world's first QCL-based gas analyzer dedicated for onboard emissions measurement (OBS-ONE-XL). Figure 5 shows a photograph of the OBS-ONE-XL.

In this product, N_2O and NH_3, which are under consideration for introduction in the next European automotive emission regulation Euro 7, are the measurement targets. Thanks to the aforementioned compact Herriott cell using a elongated spherical mirror and PC-free concentration calculation algorithm, the product is compact enough to withstand onboard use.[13] The product then attracted the attention of the JRC of European Commission and was evaluated for consideration for Euro 7. The results showed good correlation with stationary analyzers and sufficient performance for practical use as a PEMS.[14,15]

Process Laser Gas Analyzer, PLGA-1000

The PLGA-1000 is an IRLAM gas analyzer for real-time monitoring and control of petrochemical processes. Figure 6 shows a photograph of the analyzer. In the past, process monitoring using gas chromatography (GC) has been the mainstream, but GC lacks real-time performance, resulting in delays in detecting process abnormalities, which in some cases can lead to large raw material losses and reduced productivity. Therefore, a more real-time measurement method was required. However for the petrochemical process, it was difficult to measure with methods other than GC that do not involve gas separation because the influences of interfering gases and broadening are strong due to the presence of many hydrocarbons at high concentrations.

Figure 5 Photograph of the on-board emission measurement system, OBS-ONE-XL.

Figure 6 Photograph of the petrochemical process gas analyzer, PLGA-1000.

In spite of such difficult gas conditions, it has been demonstrated that PLGA-1000 can accurately measure the target gas in real-time by eliminating influences of the interfering gases and broadening with its unique concentration calculation algorithm. This achievement has been recognized by a major petrochemical manufacturer, which has adopted the PLGA-1000 to measure impurities such as acetylene (C_2H_2) in the ethylene (C_2H_4) production process.

Contribution to a carbon neutral society with IRLAM

Various applications of the IRLAM gas analysis technology are being considered for the utilization of carbon-neutral alternative energy sources centered on hydrogen. For example, when hydrogen is used in fuel cells, there is a demand to control impurities in hydrogen at the ppm to ppb level during hydrogen production and use because impurities in hydrogen affect the performance and life of fuel cells. In addition, direct combustion of hydrogen and NH_3, one of the hydrogen carriers synthesized from hydrogen, as a carbon-free fuel is being considered for utilization. When hydrogen and NH_3 are combusted, CO_2 is not generated, but NOx and unburned NH_3 can be emitted, so combustion control is important to suppress these emissions. Furthermore, in the Carbon Capture and Utilization (CCU) initiative to achieve carbon neutrality by capturing and reusing emitted CO_2, gas analysis plays an important role in controlling the purity of the captured CO_2 for reuse and in controlling the methanation process to synthesize methane (CH_4), which is useful as energy, from the captured CO_2 and hydrogen. IRLAM can provide solutions to these requirements and challenges through high-sensitivity and low-interference continuous gas analysis.

Conclusion

As described above, IRLAM has realized highly accurate real-time measurement under difficult conditions to measure with conventional technologies by using a QCL manufactured in-house as a light source, a Herriott cell with a unique structure and an original concentration calculation algorithm based on the feature extraction from the absorption signal. As the result, IRLAM has succeeded in greatly expanding the industrial application range of gas analysis using QCL.

The features of IRLAM can be summarized as follows

(1) High sensitivity and low interference: The fundamental features of QCL-IR and our unique concentration calculation algorithm enable highly sensitive measurement without being affected by various interfering gases contained in the sample gas.

(2) Direct and real-time: No sample gas pretreatment is required. Highly accurate real-time measurement is possible due to fast gas displacement by the small volume Herriott cell and fast concentration calculation algorithm.

(3) High stability and reliability: The unique concentration calculation algorithm and robust hardware design enable stable and accurate measurements even in harsh operating environments (large temperature and pressure fluctuations, large vibrations).

IRLAM is expected to continue to meet the gas analysis needs of all industries and contribute significantly to reducing the environmental impact of each industry, improving productivity, and realizing a carbon-neutral society. Readers who wish to deepen their understanding of the details discussed in this paper are referred to a review article[16] in which the author comprehensively summarizes the IRLAM technology.

*Editor’s note: Unless otherwise indicated, the information in this article is based on our own research as of the year of publication of this article.

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SHIBUYA Kyoji
Advanced R&D Department,
Technology Innovation Center, R&D Division
HORIBA, Ltd.
Ph.D.