Feature Article

Measurement Technique and its Application to Trace Components of Atmospheric Gas

Junji Kato

From early on, HORIBA has been developing and adopting various measurement techniques that are ideal for measuring trace atmospheric gas, as in the following examples. To measure carbon monoxide (CO), a non-dispersive infrared absorption method is used. To measure Ozone (O_3), an ultraviolet absorption method is used. For nitrogen oxides (NO_X), chemiluminescence. For sulfur dioxide (SO_2), ultraviolet fluorescence. For hydrocarbons (HC), a flame ionization method is used, and so on. In addition, HORIBA has developed a fluid modulation method, which is a method to measure gas concentrations by amplifying the difference of two signals coming from a measurement cell into which the sample gas and a reference gas are alternately introduced with a constant time interval, and has achieved absolute zero-point stability with all except SO_2 analyzer. In the case of CO measurement, HORIBA has succeeded in reducing the influence of moisture by using an interference compensation detector. In the case of O_3 and SO_2 measurement with a light source, in which light intensity variation over time is not negligible, it compensates for the influence by monitoring the light source intensity. Also, a highly productive measurement system has been developed with which it is possible to measure multiple gas components with a single detector by combining a catalyzer or convertor unit and the three-phase fluid modulation method (introducing three types of gas alternately), such as, NO_X that can measure NO and NO_2 at the same time and HC that can simultaneously measure methane (CH_4) and non-methane (non-CH_4). These various techniques for making comprehensive measurement systems have been adopted also to measure trace quantities of ammonium (NH_3) or hydrogen sulfide (H_2S) inside the clean room.

Introduction

Recently, the word "environmental pollution" has not been so frequently used and it seems that concentrations of environmental pollutants such as CO and SO_2 in the atmosphere have been surely reduced. But, the concentration of suspended particle matter (SPM), NO and NO_2 generated by moving source such as automobiles is still staying flat, and in Japan the percentage of gas emission monitoring stations that have satisfied the national environmental criteria still remains at only 85.7%. As for the ozone (O_3) concentration, there is an increasing trend. The environmental gas problem is one of the important issues to be solved globally not only in Japan but also worldwide while building a recycling-oriented society that can maintain continuous growth. Measurement of atmospheric gas is different from that emitted from a fixed source such as waste incinerator or power plants. The concentration of target substances to be measured are significantly lower because they have been diffused into the air. Therefore, in order to measure atmospheric gas components, highly sensitive and stable measurement methods are required. In this paper, we describe the features and measurement principles of the automatic atmospheric gas measurement equipment developed on the basis of HORIBA's technologies, accumulated through the company's long history. Also we will introduce application examples of measuring NH_3 and H_2S that are helpful for contamination monitoring in the clean room as an example utilizing such a feature, that is, it is possible to execute stable measurement of low concentration gas.

Air Pollution Monitoring System

Environmental pollutants that should be continuously monitored are carbon monoxide (CO), nitrogen oxides (NO_X), sulfur dioxide (SO_2), ozone (O_3) and suspended particle matter (SPM). HORIBA monitoring system corresponding to each of these pollutants is as follows.

The APMA-370 uses non-dispersive infrared absorption for measuring carbon monoxide levels. The APNA-370 uses chemiluminescence for measuring levels of nitrogen oxides. The APSA-370 uses ultraviolet fluorescence for measuring sulfur dioxide.

The APOA-370 uses ultraviolet absorption for measuring ozone.

For measuring hydrocarbon levels, there's the APHA-370 which uses a flame ionization method.

There is also SPM analyzer in the form of the APDA-361 which uses a β-ray absorption method. Figure 1 shows an external view of APXX-370 analyzer.

Figure 1   External View of APXX-370 Analyzer

Carbon Monoxide Measurement, Model APMA-370

The APMA-370 measures CO concentration using a non-dispersive infrared absorption method that is based on the nature of CO in that it absorbs special infrared light. With this method, stabilizing the output signal is usually achieved by converting the signal from detector into alternative signal by mechanically switching the light on and off. In the APMA-370, stable and highly sensitive measurement has been realized by converting the detector signal into alternative signal using *a fluid modulation* method that is based on HORIBA's proprietary methodology and by combining this with an interference compensation detector.

The fluid modulation method is a technology for measuring the concentration of a target gas component by amplifying the difference of two signals coming from a measurement cell into which the sample gas and a reference gas are alternately introduced with a constant time interval. Zero point is continuously monitored using a reference gas. Since if the sample gas does not include CO, no signal is generated, the zero point is always stable.

Structure and Measuring Principles

Figure 2 shows the structure of the analyzing unit of the APMA-370 analyzer. The analyzing unit consists of an infrared light source, a measurement cell, an optical filter and a condenser microphone detector with an interference compensation detector. The detector is comprised of two parts, a detector for measuring CO (the target component of the measurement) and an interference compensation

section for measuring the interference gas. When measuring atmospheric gas, a typical example of interference 'gas' is moisture. Reference gas and sample gas are introduced alternately into the measurement cell with an interval of 0.5 seconds through a three-way solenoid valve. Concentration of CO can be obtained by measuring the amplified modulated signal from detector. Conventionally, the sample gas and the reference gas have been switched by a rotary valve, but the method was problematic with low sensitivity due to gas mixing, resulting from the structural issue of using a rotary valve. Further, the lifetime of the motor was short. In recent equipment, since the performance of miniature solenoid valves has been dramatically improved with a high durability of over 100 million switching cycles now possible, a small solenoid valve has been adopted as shown in Figure 2. The reference gas is created by refining the sample gas with an oxidation catalyst. By changing CO in the sample gas to CO_2 using the oxidation catalyst, it becomes possible to obtain an accurate measurement by comparing and canceling out the effects of interference from other gases, even if the other gases have a large potential of interfering components.

However, when the concentration of interference gas changes, since there is a time gap for the sample gas and the reference gas to reach the measurement cell, influence due to interference gas may occur. In order to address this problem, such as a change in interference gas concentration, APMA-370 measures the concentration of interference gas component with an interference compensation detector and corrects its influence on the output signal of the measurement detector, therefore highly accurate measurements are possible.
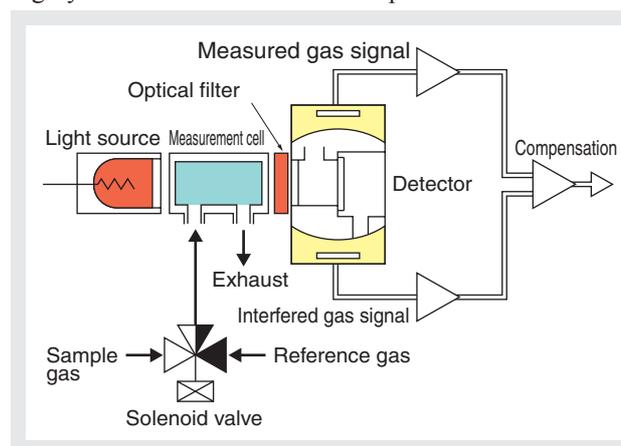

Figure 2   Structure of Analyzing Unit of APMA-370 Analyzer

Ozone Measurement, Model APOA-370

The APOA-370 measures ozone (O_3) concentration using ultraviolet absorption because it is a characteristic of ozone that it absorbs ultraviolet light. This equipment uses *a fluid modulation* method and, like the APMA-370, it is capable of highly accurate and stable measurement.

Structure and Measuring Principles

Figure 3 shows the structure of the analyzing unit of the APOA-370 analyzer. The analyzing unit consists of an ultraviolet light source, a measurement cell, an optical filter and a detector, aligned in a straight line. A pen type low-pressure mercury lamp is used as an ultraviolet light source. Glass is used as the measurement cell material because metal accelerates decomposition of ozone. So as to make use of the reflected light, a special cell which outer surface is coated with Cr by a physical deposition has been used. The optical filter is a bandpass filter that passes only light having wavelength of 254nm, which is in the absorption range of ozone. A silicon photodiode is used as the detector. Reference gas and sample gas are introduced alternately into the measurement cell with an interval of 0.5 seconds through a three-way solenoid valve. Ozone concentration can be obtained by measuring the amplified modulated signal from the detector. The Reference gas is applied after removing the ozone from the sample gas using an ozone decomposition catalyst.

Decay of light intensity is unavoidable if we use an ultraviolet lamp. In general, light intensity decrease to half of the initial intensity in just 6 to 12 months.

The detector measures the absolute intensity of light that passes through the measurement cell. Then, the detected signal is divided into an alternating current component and a direct current component. The alternating component is amplified and measured to obtain ozone concentration. The direct current component is measured to obtain the brightness of the ultraviolet lamp. Since the ozone concentration to be measured is very low, a difference of light intensity measured when the reference gas and the sample gas are introduced into the measured cell is very small compared to the absolute light intensity. Therefore, the DC component can be assumed to be in proportion with brightness of ultraviolet lamp. Based on this idea, it is possible to suppress an error in measured ozone concentration by compensating for the ozone concentration signal with the DC component, even if the brightness of the ultraviolet light source changes. HORIBA's system is different from conventional methods that measure the light intensity and the ozone concentration signal using independent detectors, since these signals are measured with the same detector. Also the influence of a drift of detector sensitivity can be compensated.
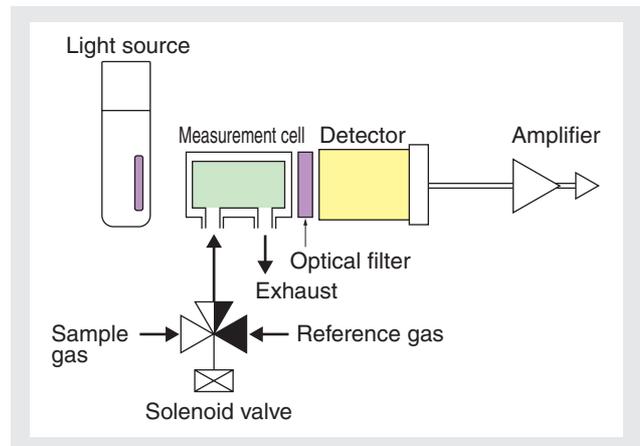

Figure 3   Structure of Analyzing Unit of APOA-370 Analyzer

Nitrogen Oxide Measurement, Model APNA-370

APNA-370 measures the concentration of nitrogen oxides by observing the light emitted when excited NO_2 molecules, which come from ozone-oxidized NO, return from the excited state to the ground state. By using a three-phase fluid modulation method, it is possible to measure NO and NO_2 concentrations at the same time with high sensibility and stability.

$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + h\nu$$
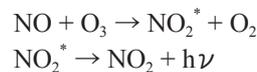
Here, it should be noted that not all the NO_2 molecules coming from the oxidation are raised up to the excitation state and the ratio of the excited NO_2 to the total number of NO_2 molecules changes with temperature and pressure.

Structure and Measuring Principles

Figure 4 shows the structure of the analyzing unit of the APNA-370 analyzer. The analyzing unit consists of a light emission cell that facilitates reaction between the ozone and the sample gas, a detector and an optical filter for selecting the wavelength to be detected. Light emitted from NO_2 has a broad bandwidth ranging from 600nm to 1000nm. In front of the detector, a bandpass filter covering wavelengths from 600nm to 1400nm is placed to eliminate the influence of light generated by reactions between hydrocarbons and ozone.

Since it's impossible to directly measure NO_2 concentrations, the NO_2 has then to be reduced to NO. For reduction of NO_2, a catalyst made of Molybdenum (Mo) supported with activated carbon is used.
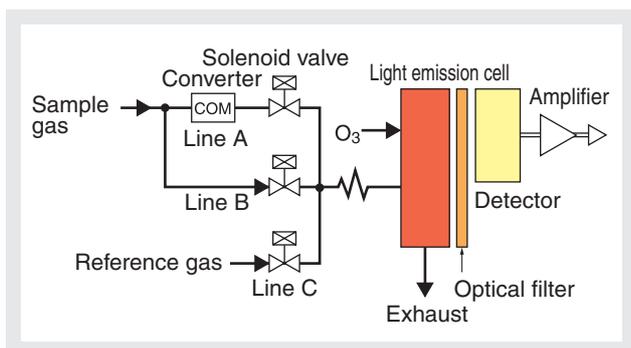
Figure 4   Structure of Analyzing Unit of APNA-370 Analyzer

To path to the light emission cell consists of line-A which includes a converter, line-B through which the sample gas is introduced, and line-C through which the reference gas for comparison is introduced, are connected by two-way solenoid valves. From each of lines -A, -B and -C, the sample gas and the reference gas are introduced into the light emission cell with a constant time interval.

So, the output signal from the detector takes a form arranged as the sequence A, B, C, A, B, C, A, B. C,….

By synchronizing the On/Off-timing to switch the solenoid valve with this output signal from the detector, it is possible to divide the output signal into a two-signal processing system as shown below.

A, _, C, A, _, C, A, _, C, A, _, C,
       …. Signal processing system (A+C) …… Figure 5(1)

_, B, C, _, B, C, _, B, C, _, B, C,
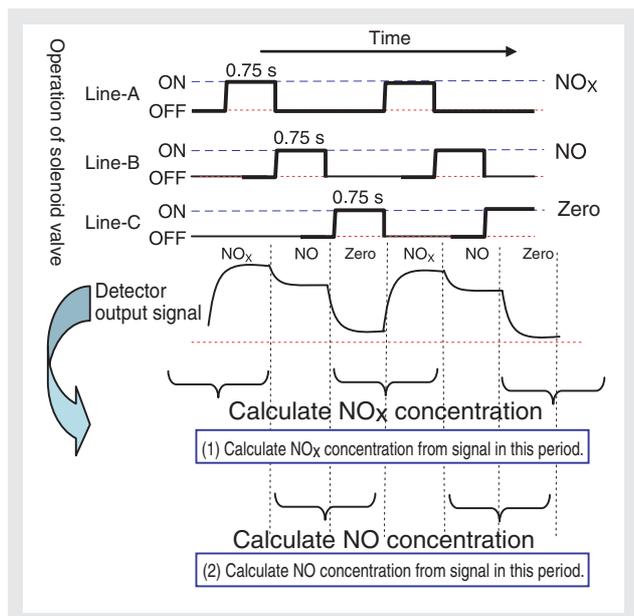   …. Signal processing system (B+C) …… Figure 5(2)

Figure 5   Conceptual Diagram of Signal Processing

In the signal processing system (A+C) corresponding to Figure 5(1), the NO_X concentration signal that is the sum of NO_2 and NO concentrations can be obtained from the

difference between line-A's signal and line-C's signal. On the other hand, the signal processing system (B+C) corresponding to Figure 5(2), NO concentration signal can be obtained from the difference between line-B's signal and line-C's signal. Since NO and NO_X concentrations are measured using the same detector, it is possible to suppress to a minimum the difference of sensitivity for NO and NO_X caused by sensitivity variations of the detector. The sample gas is utilized as the reference gas after it has reacted with ozone. Thus, it is not required to prepare special equipment for refining the reference gas. NO_2 concentration can be calculated by subtracting the NO concentration from the NO_X concentration.

Sulfur Dioxide Measurement, Model APSA-370

APSA-370 obtains SO_2 concentration with an ultraviolet fluorescence method by measuring the fluorescence intensity generated when SO_2 absorbs ultraviolet light. Since this system is equipped with an excitation light selection system composed of multiple reflection mirrors and a hydrocarbon elimination system to obtain low background noise, stable and highly accurate measurement are now possible even in the comparatively low concentration range.

Structure and Measuring Principles

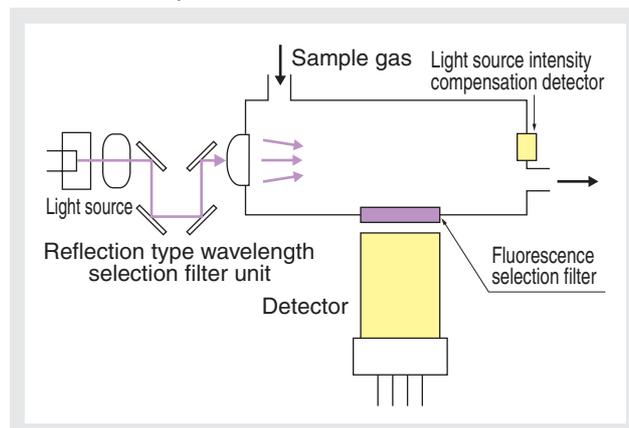Figure 6 shows a structure of the analyzing unit of APSA-370 analyzer.

Figure 6   Structure of Analyzing Unit of APSA-370 Analyzer

The analyzing unit consists of an ultraviolet source for exciting the SO_2, a reflection-type wavelength selection filter unit for selecting excitation light, a fluorescent chamber, a light source intensity compensation detector and a detector. A Xe flash lamp is used as an ultraviolet light source. The Xe lamp has a broad output spectrum including the wavelength range of the necessary bandwidth. For use as an excitation light source, it is required to eliminate unnecessary wavelength components. Otherwise, the background noise level

becomes high and the influences of temperature and noise increase. HORIBA has succeeded in fully suppressing the backlight that causes background noise, without decreasing the excitation light intensity by combining multiple reflection-type wavelength selection filters.

Although this equipment does not utilize the fluid modulation method, stable measurement has been realized by using the above-described method. The sample gas is pre-processed within the pretreatment equipment (hydrocarbon cutter) to eliminate aromatic hydrocarbons that become the interference component in SO_2 measurement. Thereafter the sample gas is introduced to the fluorescent chamber. In order to minimize a response delay owing to absorption of SO_2, etc, the inner surface of the fluorescent chamber is coated with a fluorocarbon resist. Inside the fluorescent chamber, a detector(photo-multiplier) measures fluorescent light generated when part of the SO_2 excited by ultraviolet light returns to the ground state.

The intensity of ultraviolet light from the Xe lamp decreases gradually with time. Change of intensity of the light source is measured by a light source intensity compensation detector and the SO_2 concentration data is finally corrected using this result.

Hydrocarbon Concentration Measurement, Model APHA-370

APHA-370 measures hydrocarbon concentration using a flame ionization method. This works by measuring the ion current that is generated by ionizing hydrocarbons. By combining this method with the three-phase fluid modulation method and a selective combustion method, it becomes possible to measure both of the methane and non-methane hydrocarbon concentrations with high accuracy in a single unit.

Structure and Measuring Principles

Figure 7 shows the structure of analyzing unit of the APHA-370 analyzer. The sample gas is branched to the CH_4 line including a non-methane hydrocarbon cutter and to the THC-line that connects directly to the valve. Apart from these, reference gas obtained by refining the atmospheric air which is also connected to the same gas feeding tube. Each of these gases is introduced to the detector with a constant time interval via time-controlled solenoid valves.

The non-methane hydrocarbon cutter operates utilizing the characteristic that the oxidization temperatures of hydrocarbons such as CH_4, C_2H_6, or C_3H_8 by combustive catalyst are different to each other. The oxidization

temperature of CH_4 is higher than that of C_2H_6 (there is a tendency that the greater the number of carbon atoms in the molecule, the lower the oxidization temperature). By setting the temperature of the catalyst furnace to an appropriate temperature at which CH_4 is not oxidized but C_2H_6 is oxidized, hydrocarbons other than CH_4 are oxidized and eliminated, generating CO_2 and H_2O. Gases are introduced into the flame ionization detector via three lines: line-A without the non-methane hydrocarbon cutter, line-B that includes the non-methane hydrocarbon cutter, and line-C that feeds the reference gas, alternately with a constant time interval. Ion current is measured by the flame ionization detector. The concentration of hydrocarbons ionized by the hydrogen flame can be measured as ion current that is approximately proportional to the number of carbon atoms.
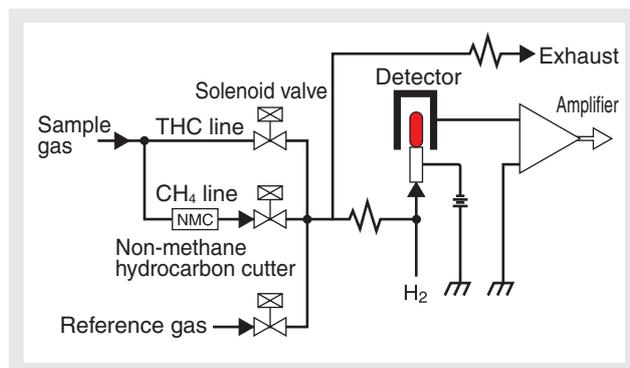

Figure 7   Structure of Analyzing Unit of APHA-370 Analyzer

Features of the APXX-370 Series

APXX-370 series is notable not only by its outstanding stability but also by easy-to-use functions due to interactive operation via a touch-panel screen. Users are not required any special knowledge about operation. Since automatic calibration and a self-diagnosis functions (alarm) are installed, anybody can easily execute continuous measurement just by connecting a calibration gas cylinder and calibration gas generator (SGGU-610). Measured data can be output as analog and digital signals (optional, RS-232C, TCP-IP). Internal data can be saved to compact flash memory (optional). Through these functions it is possible for users to remotely retrieve data and operate the equipment through a network connection and to download data onto compact flash memory.

Applications in Industry
General Description

Measurement of gas concentrations within industry is a demanding application not only for measuring the relatively high concentrations of gases emitted from fixed sources but also for monitoring clean room contamination,

or for measuring low concentrations of gases in research laboratories, on catalysts, etc.

HORIBA is applying and deploying its outstanding measurement technologies acquired through its environmental gas analysis businesses to industry.

Recently, fine patterning and multi-layering have rapidly advanced with the increase of component density in semiconductor integrated circuits. Accompanying this trend, contamination of environmental air in clean rooms has become a major problem. In this section, technology principles for measuring ammonium (NH_3) and hydrogen sulfide (H_2S) concentrations in atmospheric air will be introduced. This is achieved using HORIBA gas analyzers that are in widespread use for monitoring contamination in clean rooms and so on.

Application to Measurement of NH_3 and H_2S Concentrations

It is not easy to measure directly low concentrations of NH_3 and H_2S in atmospheric air. HORIBA is measuring NH_3 and H_2S by converting to NO and SO_2, respectively, in a pretreatment stage.

Measurement of NH_3

Figure 8 shows a gas flow diagram for NH_3 pretreatment and nitrogen oxides analyzer. The sample gas including NO_X and NH_3 is divided into two lines. One line's flow is through both the oxidization catalyst and the reduction catalyst, and the other's flow is through only the reduction catalyst. NH_3 introduced into the oxidization catalyst is decomposed to NO_2 and NO and then introduced into the nitrogen oxides analyzer via the NO_2 reduction catalyst.

In line-A, with the oxidization catalyst, NH_3 is oxidized to NO according to the following reaction equation.

$NO_X + NH_3 \rightarrow 2NO$ (Line-A)
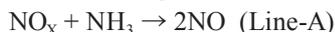
In line-B, that doesn't include the oxidization catalyst, NH_3 is not oxidized.

$NO_X + NH_3 \rightarrow NO + NH_3$ (Line-B)

In the nitrogen oxides analyzer, gas is introduced from line-A, line-B and a reference line into the detector alternately with a constant time interval. NH_3
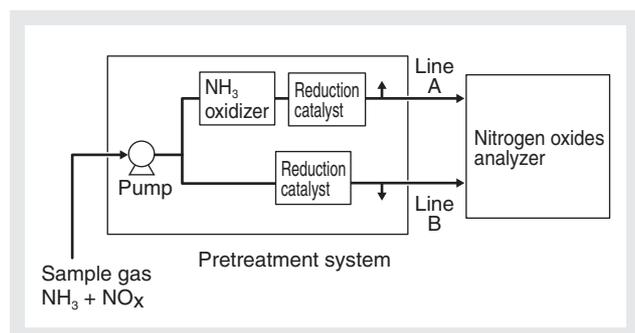

Figure 8   Gas Flow Diagram in NH_3 Pretreatment System and Nitrogen Oxides Analyzer

concentration can be obtained by subtracting the signal output when gas was introduced from line-B from the signal output when gas was introduced from line-A.

Measurement of H_2S

Figure 9 shows the structure of the H_2S analyzer. Also H_2S is difficult to measure directly. So, it is oxidized using an oxidization catalyst to produce SO_2, and then the SO_2 is measured by the sulfur dioxide analyzer. Sample gas sometimes includes SO_2 besides H_2S. Since SO_2 generates an error in H_2S measurement, it is removed by a scrubber before it is introduced into the oxidizer. For the SO_2 scrubber, sodium carbonate placed inside a hot container is used. In the oxidizer, hot Vanadium pentoxide is the catalyst. Since it has a small surface area, response time delay caused by SO_2 absorption is short.
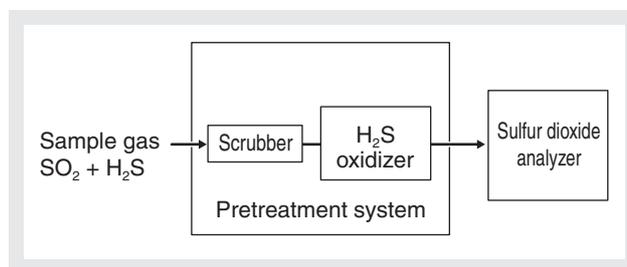

Figure 9   Structure of H_2S Pretreatment Equipment and Hydrogen sulfide Measurement Equipment

Conclusion

Today, gas measurement in the trace range has become an indispensable factor not only in the field of environmental gas measurement but also in other wide-ranging industrial fields. HORIBA will continue to advance its research and developmental activities as a leading manufacturer of analysis equipment and develop ever more sophisticated, more stable and more accurate measurement systems to contribute to development of industry and also to environmental preservation of the Earth.

Reference

[1] Norio Kada "Gas analyzer using a dual cross modulation method and its application to atmospheric air monitoring systems", *Readout*, 1, 40-46 (1990).
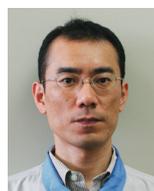
Junji Kato

HORIBA, Ltd.
Environmental & Process
Instruments Systems Division
Manager