Tunable Laser Gas Analyzer TX-100

Takuya IDO

In recent years, laser gas analyzers have been introduced into various plants such as incineration plants and petrochemical plants. Since laser gas analyzers do not require the troublesome process of gas-sampling at the time of measurement, laser gas analysis provides fast response time which enables the plants to operate with high efficiency. The cross-stack laser gas analyzer is already widely used, there are several issues surrounding this device. Not only does the cross-stack analyzer have a restricted place for installation, but it also requires complicated operations to remove the analyzer from the stack for calibrated. As a response to these circumstances, HORIBA has succeeded in creating the TX-100, which is the first direct-insertion laser hydrogen chloride analyzer in Japan*1 to use a probe type optical system to overcome the prior issues. This paper will feature the principles, aspects, and examples of measurements at incineration plants.
*1: In-company investigation in August 2018

Introduction

Conventionally, an ion electrode method analyzer is used for measuring hydrogen chloride (HCl) in incineration plants and petrochemical plants, but in recent years, laser method has been adapted to these plants [1-3]. Because the laser type does not use a sample extraction and cleanup system, it provides fast response time that enables the plants to operate with high efficiency. In addition, laser method does not require maintenance or replacement of sample preparation parts such as exhaust gas sampling pump, which realizes reduction in total running cost [4, 5]. In this paper, we introduce probe type laser measurement method, calibration method and analyzer configuration. A comparative test of hydrogen chloride measurement with laser method and ion electrode method. A comparative test of moisture measurement with laser method and electrostatic capacitance type at an incineration plant. The results of these tests are also reported in this paper.

Measurement principle and optical system

The hydrogen chloride gas analyzer TX-100 is an in-situ probe type laser gas analyzer that directly measures the stack gas, by TLAS (Tunable Laser Absorption Spectroscopy) method [6]. This spectroscopic measurement method is a generic term for measuring methods using a LD (Laser Diode), QCL (Quantum Cascade Laser), or the like as a coherent light source. DAS (Direct absorption spectroscopy) and WMS (Wavelength Modulation Spectroscopy) methods are usually used in the stack gas emission measurement.

There are two methods for measuring at stack, one is the cross-stack type and probe type. The cross-stack type light emitter (laser) and a light receiver (detector) are installed on both sides of the stack. The probe type emitter and light receiver are installed on same side of the stack. **Figure 1** shows the outline of the analyzer. The characteristic of the cross-stack type is that no object is installed in the stack and the analyzer is not exposed to

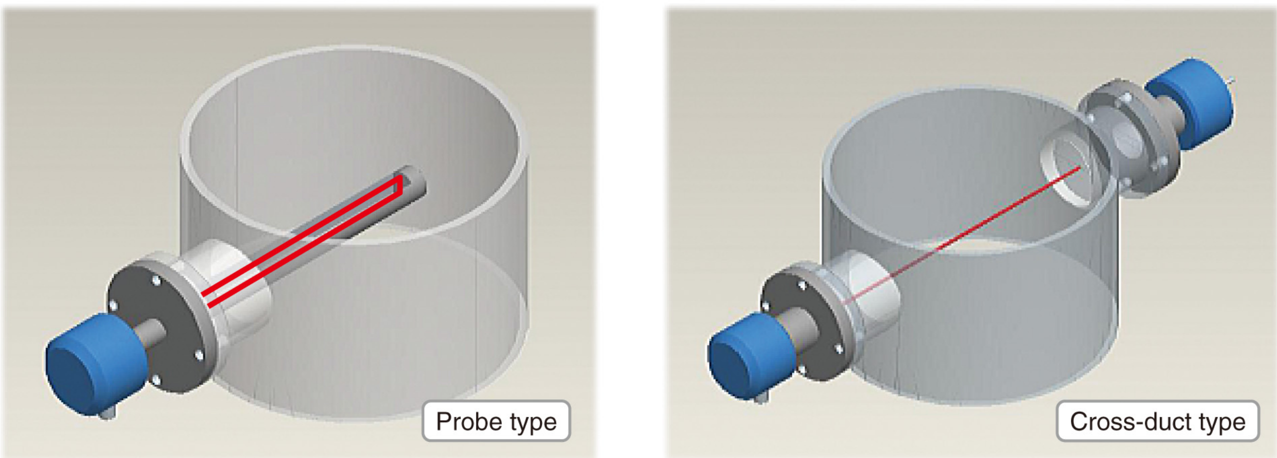

Figure 1 Comparison of probe type and cross duct type.

Figure 2 Appearance photograph of TX-100.

the exhaust gas. The benefit is that can operate with high temperature exhaust gas and corrosive conditions. The cross-stack type is being applied as a device for measuring oxygen (O_2), carbon monoxide (CO), etc. for control in a combustion furnace. The main disadvantage is that the optical axis of the analyzer depends on the state of the flue and the operating condition of the plant. The measured value tends to become unstable due to the influence of the optical axis by expansion and vibration of the stack. The characteristic of the probe type is to hold the optical axis within the probe, so it is not influenced by fluctuation of the stack. Since the optical axis is held by the probe, the influence is more unlikely than the cross-stack type. The probe type optical system is a reflection type optical system, which is better suited to plants stack with a diameter.
Attention is required when installing in a condition of 400°C or higher, including the furnace, since the installation conditions depend on the heat resistance performance of the probe. The light source is optimized for the measurement method and optical system according to the application. In accordance with its market demands a probe type optical system was adopted for laser hydrogen chloride gas analyzer.

Device Configuration

Figure 2 shows the external view of the analyzer and **Figure 3** shows the example of the overall system configuration of the equipment. The analyzer installed at the stack consists of a probe part, a CCP (Corner Cube Prism) calibration unit and an analyzer unit. The probe method realizes operation and maintenance access from one side of the stack wall. This enables easy replacement from the conventional ion electrode method and reduction of additional flange construction costs for analyzer installation and maintenance. In addition to the analyzer part described above, an optional purge unit (capable of incorporating 24 V power supply) controls air purge to protect the optical system. Operation of analyzer is via a touch panel type HMI (Human Machine Interface) unit or Windows PC HMI that operates similarly to touch panel type HMI unit. The HMI can display the trend of the acquired data as well as the operation of the analyzer such as concentration display, calibration and setting. Temperature and pressure corrections to process gas conditions are made real-time by connecting (4-20 mA) outputs of a thermometer and pressure gauge.

TX-100 original calibration mechanism [7]

By adopting probe type optical system, the TX-100 arranges both laser and detector in the same analyzer case. The laser irradiates into the flue and reflected by the CCP installed at the tip of the

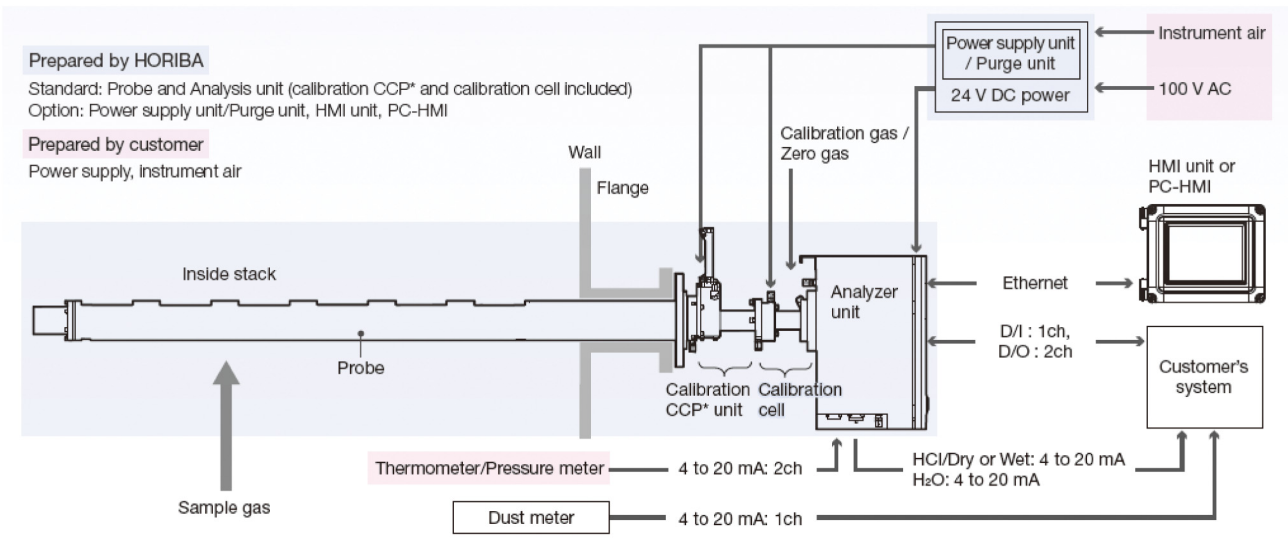

Figure 3 Example of the overall system configuration.

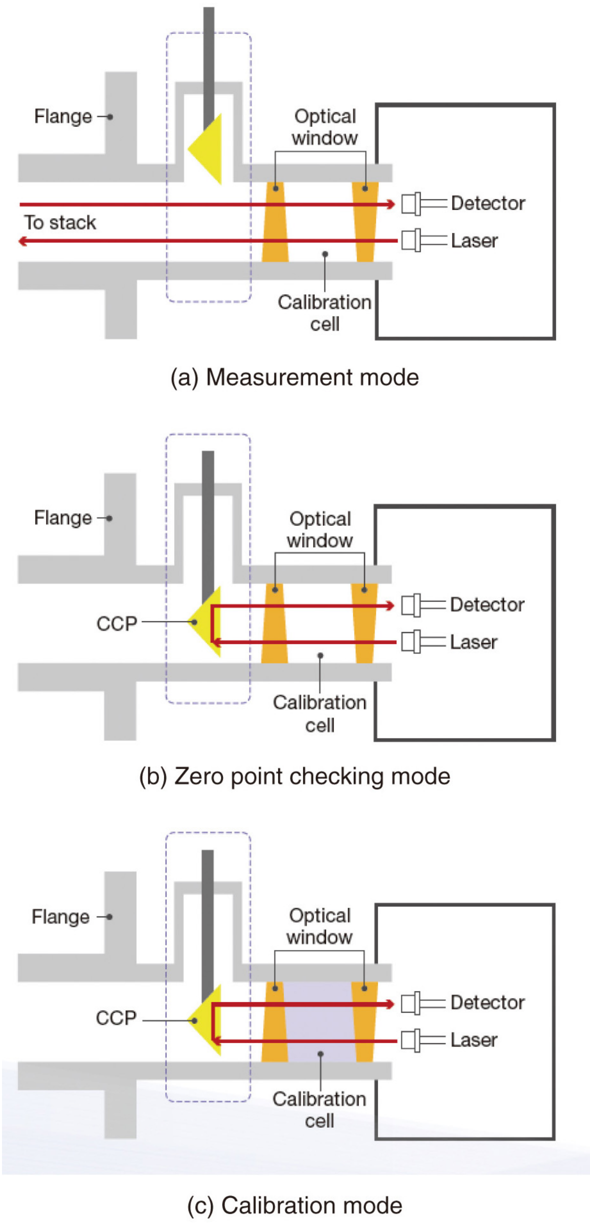

Figure 4 Calibration system.
(a) Measurement mode
(b) Zero point checking mode
(c) Calibration mode

probe, and the concentration is measured from the change of the transmitted light. This CCP is a total reflection type prism and can accurately reflect incident light in the same direction to obtain a stable signal. We developed the new differentiated gas calibration mechanism. The conceptual diagram of the calibration mechanism is shown in **Figure 4**. The calibration mechanism operates by inserting and extracting the calibration CCP, which is the same as one at the probe tip for normal continuous measurement of exhaust gas in a stack. As shown in **Figure 4** (a), the calibration CCP is out of the optical path in normal measurement. The laser light is irradiated into the stack. Then the light is reflected by the CCP at the probe tip. In **Figure 4** (b), the calibration CCP is inserted on the optical path to check the zero point signal to cancel the external environmental influences. As the result, we realize highly accurate continuous measurement. In addition, as shown in **Figure 4** (c), zero point calibration is performed with the calibration CCP inserted in the optical path while span gas is flowing through the calibration cell. This mechanism enables calibration without removing the analyzer from the stack. A calibration gas based on the ratio of the range of the analyzer is necessary because the measuring light path length and the calibration cell length are different.

For example, when the HCl full scale is 100 ppm, the necessary gas concentration for calibration is calculated from the relationship between the measurement optical path length 2 m (the reciprocating in the probe) and the calibration cell length 0.2 m (the reciprocating in the calibration cell), 100 (ppm) × 2 (m) / 0.2 (m) = 1000 (ppm). In this case, customer prepares 1000 ppm gas for calibration. Since it takes time to stabilize the gas when using gases with a high absorptivity such as HCl, it is advantageous to use a gas concentration higher than the range. This mechanism allows periodic checks of the state of the analyzer without removing the analyzer from the stack. When an out-of-tolerance alarm occurs it is possible to check whether it caused by the analyzer or the plant control.

Measurement example at an incineration plant

A comparative test of a conventional hydrogen chloride analyzer of ion electrode method and the TX-100 was carried out. The incineration plant that conducted this experiment adopts a system that reduces toxic pollutants such as HCl and sulfur dioxide (SO_2) by a combination of dry and wet scrubber systems.

In this plant, the analyzers using the ion electrode method have been installed at each outlet of the scrubber systems. In this test, the comparison of HCl concentration between laser and ion electrode methods was carried out at the outlet of the bag filter of the dry type scrubber system. HCl measurement at the outlet of the wet type scrubber system was impossible since the incineration plant removes HCl gas completely at this location. However, since a capacitance method moisture analyzer was

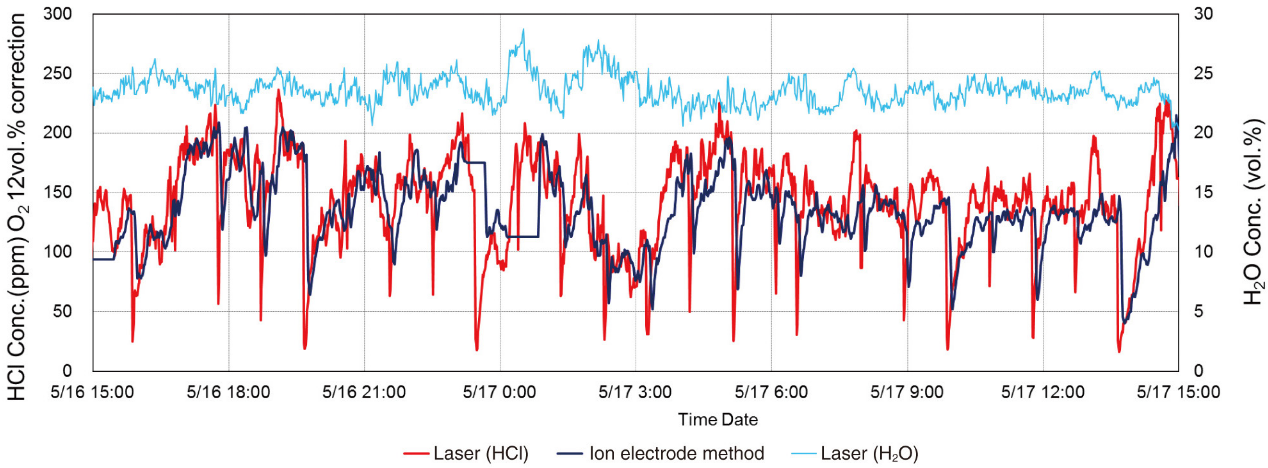

Figure 5 Comparison of HCl concentration using laser method and ion electrode method.

installed in this place, a comparative test between the laser method and the capacitance method was carried out in parallel. The TX-100 can simultaneously measure the wet value of HCl and H_2O concentration and output the dry correction value in real time. In this test, the concentrations of HCl were compared at Oxygen 12% equivalent value using the O_2 concentration measured at the same time in a sampling type analyzer for NOx gas monitoring. **Figure 5** shows the simultaneous measurement test results of the TX-100 (laser type) and ion electrode method. The TX-100 response was about 5 minutes earlier than ion electrode method, it was caused by sampling time delay and instruction response difference due to different measuring principles. The steeply decreasing concentration of HCl caused by injection of activated carbon. The analyzer of the ion electrode method shew a constant value after around 5/17. This was due to the maintenance time of the ion electrode, and the indicated value was held. A comparative test between the laser system and the electrostatic capacity system was carried out at the outlet of the wet type scrubber system. **Figure 6** shows the results with a high correlation between both methods. The electrostatic capacity method moisture analyzer, instruction hold of one hour from 7/30

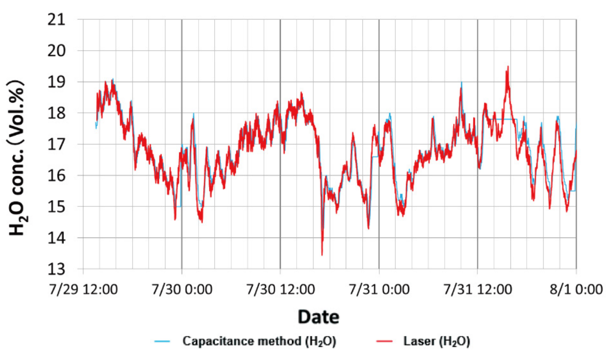

Figure 6 Comparison of H_2O concentration using laser method and capacitance method.

23: 30 was the automatic calibration time of the apparatus which was performed according to the sequence. The instruction hold from 7/31 13: 00 to 17: 00 was due to the regular maintenance of the equipment. This test was conducted for more than two years, the same instruction value as the data introduced this time has been obtained.

Conclusion

HORIBA has successfully developed the TX-100, which is the first direct-insertion laser hydrogen chloride analyzer to use a probe type optical system. The analyzer improved the stability at the plant, which over the cross-stack type laser gas analyzer. Using our unique calibration mechanism, to calibrate without removing the analyzer from the stack and the maintenance is improved. In the near future, we plan to adapt the technology to nitric oxide (NO), nitrogen dioxide (NO_2), SO_2 etc., which are difficult to measure with near-infrared laser. It is necessary to have measurement technology in the infrared region that has effective sensitivity for gas measurement. For example, a measurement system using a quantum cascade laser is capable to obtain laser oscillation in various regions of the infrared spectrum. We are planning to develop a new measurement analyzer that combines this technology and the TX-100 unique technology.

References

[1] M. Webber, D. Baer, R. Hanson: Applied Optics, Vol. 40, Issue 12, p2031-2042 (2001)
[2] I. Linnerud, P. Kaspersen, T. Jager: Appl Phys B, Vol.67, p297-305 (1998)
[3] H. Teichert, T. Fernholz, V. Ebert: Applied Optics, Vol. 42, Issue 12, p2043-2051 (2003)
[4] S. Mukaihara: Kangikyou, P17-18 (2011.7)
[5] J. Madabushi, C. Heinlein, D. Fahle: International Society of Automation 55th Analysis Division Symposium (2010)
[6] Y. Deguchi: Industrial applications of Laser Diagnostics, p167-208 (2011)
[7] T. Ido, T. Ohnishi, T. Mori, "Gas analyzer", Japan patent No.6386607 (2018. 8. 17)

Takuya IDO

Process & Environmental Instruments R&D Dept.
HORIBA, Ltd.