Real-time PCB Gas Monitoring System (MOHMS-21GP)

SHINSAKU DOBASHI*1
YOSHIHIRO DEGUCHI*1
MASAHARU KIRA*2
RYUICHIRO TANAKA*3
YOSHINORI IZAWA*3

This report describes the technical characteristics and measurement results of a real time PCB gas monitoring system (MOHMS-21GP) developed by Mitsubishi Heavy Industries, Ltd. (MHI). The characteristics of the gas direct-introduction type laser ionization TOFMS (Time of Flight Mass Spectrometry), which indicates the measuring principle of this device, are described. A detecting sensitivity of 0.01 mg/m^{3}N, equivalent to 1/15 of the limit specified by regulatory requirements, was achieved. The measurement test results obtained using the exhaust gas from a PCB disposal plant (MHI) are also presented.

1. Introduction

PCB (Polychlorobiphenyl), which had been widely used as insulating oil for condensers and other equipment up to 1970s, is suspected at present of being one relative of environmental chemical adversely influencing organisms and environment(1). Thus, in order to make all domestically existing PCBs completely harmless, the Japanese PCB Treatment Special Equipment Law came into force from June 2002. One result of this new law is that the construction of PCB disposal plants is being accelerated. In order to dispose PCBs completely, it is essential to monitor the concentration of PCB at all times, so as to prevent any PCB leakage and to ensure the safety of personnel.

Table 1 Specifications of PCB gas monitoring system (MOHMS-21GP)

Trade name	MOHMS-21GP
Measuring principle	Gas direct-introduction type laser ionization TOFMS method
Lower limit of quantitative analysis of PCB	0.01 mg/m^{3}N
Measuring time	One minute

However, since conventional analysis methods require two or three days to analyze a sample, the development of a real-time analytical method has been eagerly sought. In order to meet this need, MHI has developed a PCB gas monitoring system (MOHMS-21GP) using laser ionization TOFMS (time of flight mass spectrometry). This system is capable of measuring PCB gas in one minute with a sensitivity of 0.01 mg/m^{3}N (equivalent to 1/15 of the limit specified by law). MHI has verified the applicability of this system to the exhaust gas and the atmosphere of the work environment in PCB disposal processes, in the MHI's PCB disposal plant.

2. Characteristics of PCB gas monitoring system

Table 1 shows the specification of the PCB gas monitoring system (MOHMS-21GP). As shown in the table, this system is characterized by its capability of measuring PCBs with a sensitivity of 0.01 mg/m^{3}N.

The measuring principle used for this monitoring system is known as the gas direct-introduction type laser ionization TOFMS method. **Fig. 1** shows the measuring

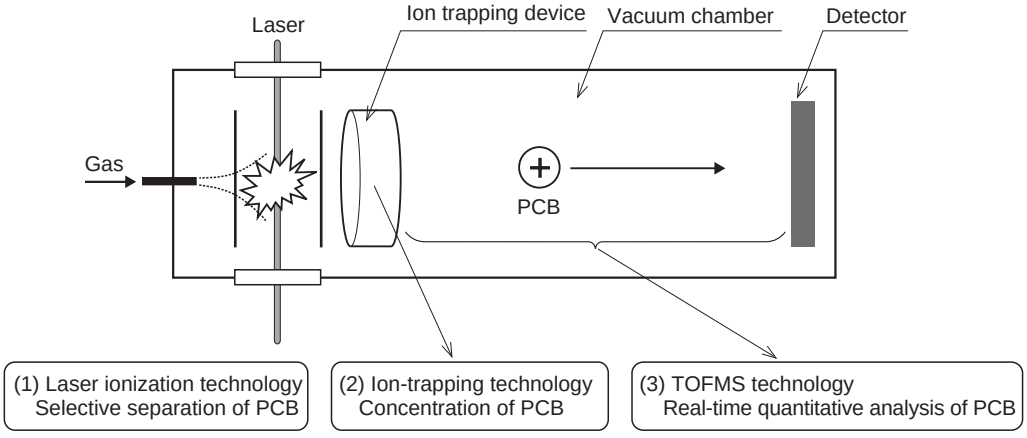


Fig. 1 Measurement process of PCB gas monitoring system (MOHMS-21GP)
After PCB ions are generated by irradiation with a laser and the PCB ions are concentrated in an ion trap, PCB is identified and quantitatively analyzed by TOFMS.

*1 Nagasaki Research & Development Center, Technical Headquarters
*2 Machinery Headquarters
*3 Nagasaki Shipyard & Machinery Works

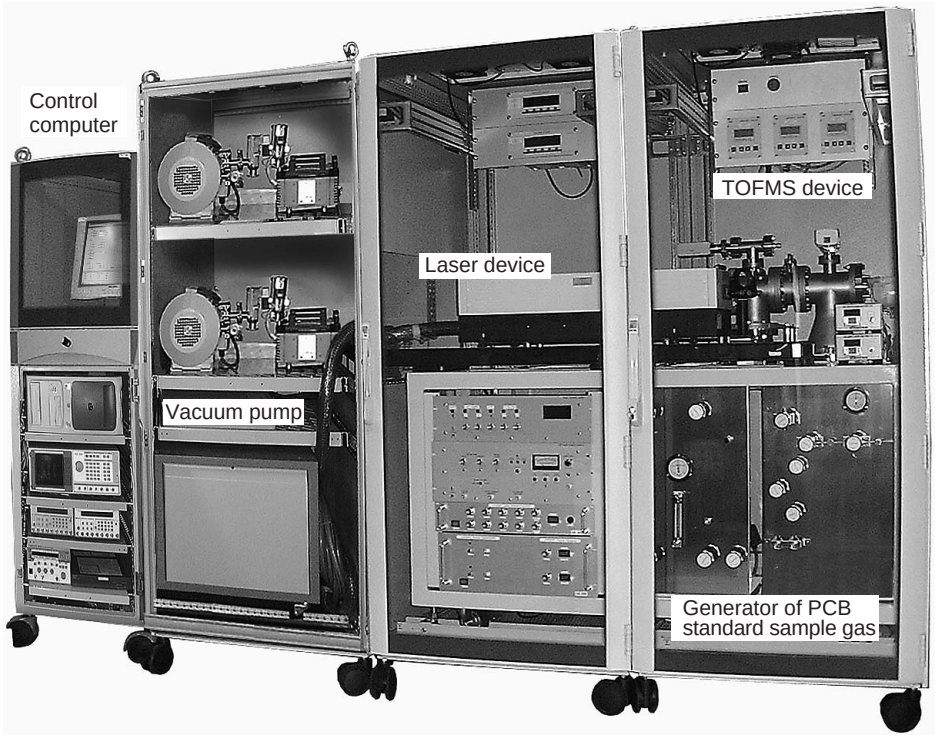


Fig. 2 Photograph of PCB gas monitoring system (MOHMS-21GP)
The PCB gas monitoring system consists of a laser device, TOFMS device, vacuum pump, control computer, and a generator of PCB standard sample gas.

principle of this system[(2)–(5)]. As can be seen in the figure, the system introduces the sample gas directly into the vacuum chamber, where (1) laser ionization[(2)], (2) ion-trapping, (3) TOFMS[(2)] are performed to identify and quantitatively analyze PCBs concentration.

Gas contains many molecules other than PCB. In order to monitor trace amounts of PCB contained in gas while on-line, it is essential to be able to separate and concentrate PCBs in a short time. Accordingly, the following three technologies has been developed and been proven successful in overcoming this essential requirement. The most important characteristic of this development is the capability of measuring PCB to a high level of sensitivity, while maintaining the analysis accuracy of PCB even in the exhaust gas and the atmosphere of the work environment.

(1) Laser ionization: Extensive original research work has made it possible to determine the optimum laser-irradiating condition (wavelength: 266 nm, laser pulse duration: 100 picoseconds) for selectively ionizing PCBs and to separate PCBs selectively.
(2) Ion-trapping: Extensive research work has also made it possible to develop effective methods for concentrating PCBs and highly sensitivity.
(3) TOFMS: Real-time quantitative analysis of PCBs has been made possible by combining the benefits of mass spectrometry into the process.

These developed technologies enable for this system to analyze trace amounts of PCBs, while maintaining a high level of selectivity in one minute, even in the exhaust gas and the atmosphere of the work environment containing various kinds of molecules.

3. Composition of PCB gas monitoring system

Fig. 2 shows the photograph of the PCB gas monitoring system. This system consists of a TOFMS device, a laser device, vacuum pumps, a generator of PCBs standard sample gas, and a control computer.

The TOFMS device is kept at a vacuum of approximately 10^{-7} Torr, which makes mass spectrometry possible by TOFMS, in which is vacuumed using a vacuum pump (turbo molecular pump). The laser device irradiates UV light (wavelength of 266 nm and a pulse time length of 100 picoseconds) to achieve the highly efficient ionization of PCB. The generator of PCBs standard sample gas makes it possible to use for the correction of the PCBs concentration.

In this system, PCBs reference sample gas with a concentration of 0.001 to 1 mg/m^{3}N (the concentration of PCB introduced varies according to the number of chlorine atoms in the PCB molecule) can be introduced, with the vapor of the PCB standard sample mixed together with balance gas (nitrogen gas). The control computer controls the operation of the system, and sends the data with the computed results to the central control room of the PCB disposal plant.

The gas sampling line can be switched using automatic switching valves so that it can be connected to many different sampling points in the PCB disposal plant. In the MHI's PCB disposal plant, a total of five

sampling points are provided in the exhaust gas line of the PCB hydrothermal decomposition process and the lines of atmosphere of the work environment in the PCB container treatment process so that PCB levels in each gas sample can be monitored.

4. Measuring results of PCB

4.1 Evaluation of measuring sensitivity of PCB

Fig. 3 shows the results obtained by measuring PCBs introduced from the PCB standard sample gas, applying laser ionization TOFMS method. The PCB standard sample KC-300 (Kaneka Corporation) was used as the sample, which contains 2, 3, and 4 chlorine PCBs as the main components. The measuring time was one minute. The concentrations of these PCBs were determined by analysis [gas sampling + GC-MS (Gas Chromatography Mass Analysis)]. As a result, concentration values of 0.20, 0.69, and 0.16 mg/m^{3}N were obtained for the 2, 3, and 4 chlorine PCBs, respectively. The x-axis and y-axis in Fig.2 indicate mass number and signal intensities, respectively. As can be seen from the figure, it could be confirmed that the 2, 3, and 4 chlorine PCBs can be measured to an excellent degree. The theoretical detection limits converted by S/N = 3 are 0.0001 mg/m^{3}N (about 100 pptv) for 2 chlorine PCB, 0.00048 mg/m^{3}N (about 40 pptv) for 3 chlorine PCB, and 0.00080 mg/m^{3}N (about 60 pptv) for 4 chlorine PCB, respectively.

Fig. 4 shows the evaluation test results for accuracies obtained by analysis (gas sampling + GC-MS). The x-axes in the figures indicate the results analyzed using the GC-MS method, while the y-axes indicate the measured results of the concentration of PCB obtained using the PCB gas monitoring system (MOHMS-21GP). As shown in the figures, it can be confirmed that the measured results of the concentration of PCB using this monitoring system has a good correlation with the results analyzed using the conventional method, with an accuracy within 30% of the standard deviation. As a result, it could be verified that a sensitivity of 0.01 mg/m^{3}N equivalent to 1/15 of the limit, 0.15 mg/m^{3}N specified in statutory regulations, can be perfectly achieved.

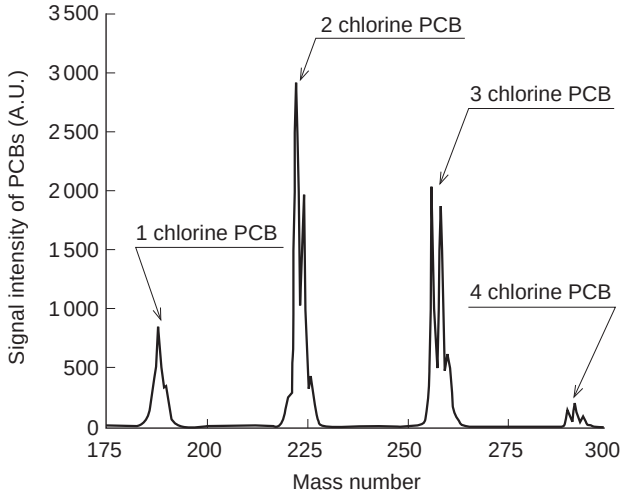


Fig. 3 Measured result of PCB standard sample (KC-300)
It could be confirmed that PCB can be measured without noise signal and with an excellent sensitivity using this system.

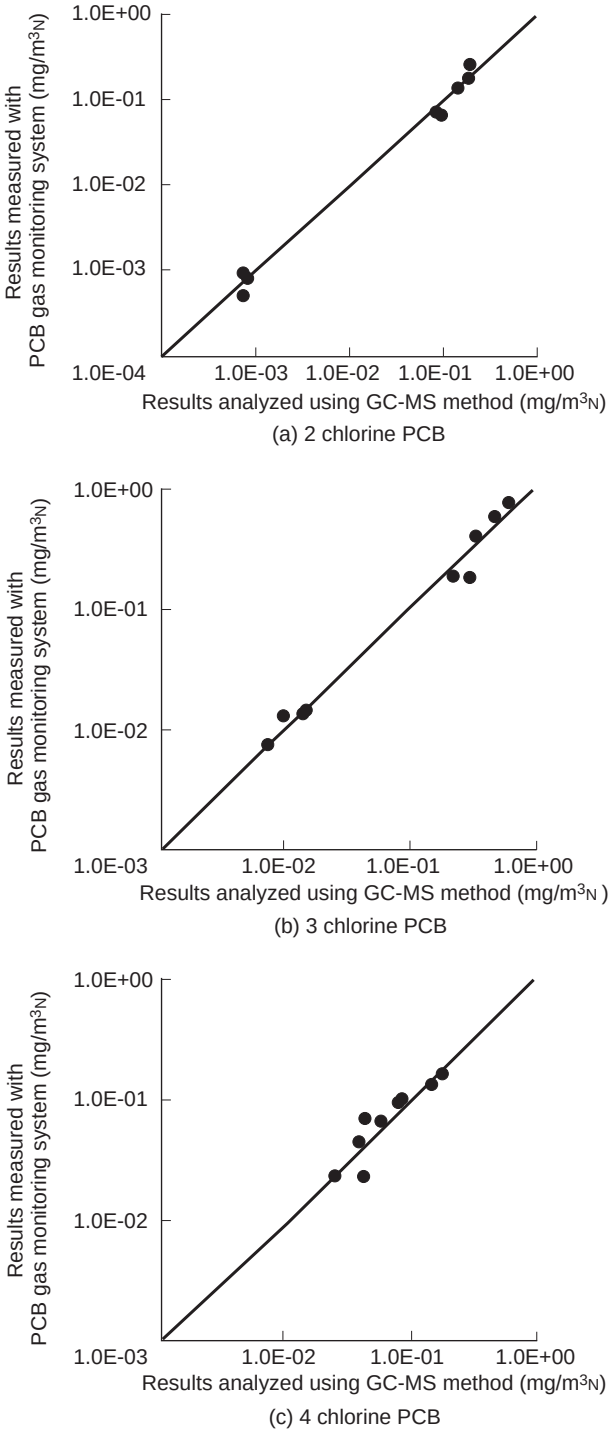


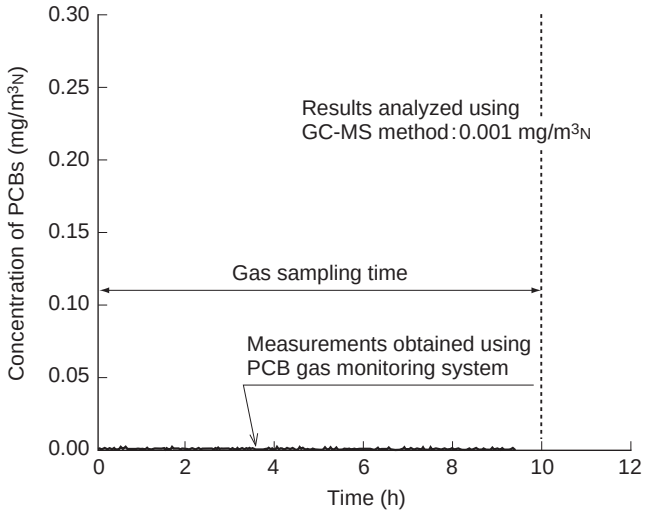
Fig. 4 Comparison of analysis results by the method (gas sampling + GC-MS)
As a result of measurements of reference gas sample using the PCB gas monitoring system (MOHMS-21GP), it could be confirmed that the measurements have a good correlation with those obtained using the conventional method, with an accuracy that is within 30% of the standard deviation.

4.2 Measured results of actual gas from PCB disposal plant

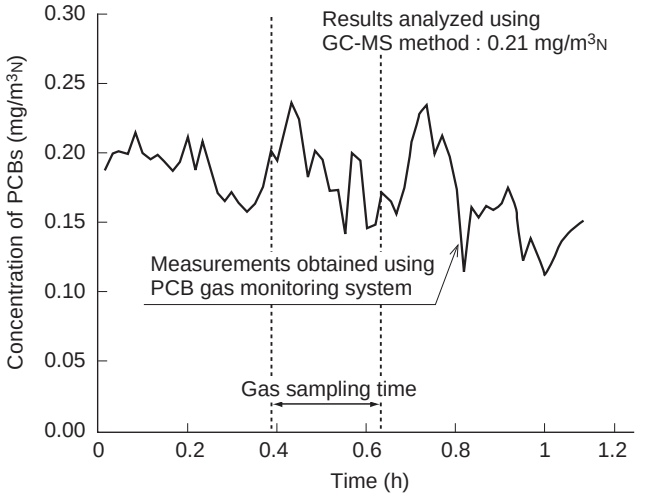
4.2.1 Comparison with GC-MS method

Fig. 5 shows a comparison of both results of measurements obtained with the PCB gas monitoring system (MOHMS-21GP) and results obtained by analysis (gas sampling + GC-MS) for the exhaust gas examined from the PCB disposal plant (MHI). The x-axis in the figures indicates measurement time, while the y-axis indicates monitored PCB concentrations. In the gas measurements, both the PCB gas monitoring system and GC-MS method must conform with each other in both low concentrations and high concentrations of PCBs. As can be seen from the figure, it could be confirmed that the results measured using the MOHMS-21GP conform with the results obtained with the GC-MS method, for both high and low concentrations and high concentrations of PCB.

As noted above, since it could be confirmed that PCB measurement is possible even in actual gas containing main gases mixed with various substances, it could be verified that use of the PCB gas monitoring system (MOHMS-21GP) is practical.



(a) Measurement of the exhaust gas containing low concentration PCB



(b) Measurement of the exhaust gas containing high concentration PCB

Fig. 5 Comparison with measured results of the exhaust gas using conventional method
Results measured using the PCB gas monitoring system were found to be in good agreement with results measured using the conventional method in both low and high concentration zones of PCB.

4.2.2 Measurement test results of the gas in the PCB disposal plant

Fig. 6 shows an example of the exhaust gas and the atmosphere of the work environment measurement results of the PCB disposal plant (MHI). The exhaust gas from the PCB hydrothermal decomposition process and the atmosphere of the work environment in the PCB container treatment process were analyzed using the PCB gas monitoring system (MOHMS-21GP). The results of the analysis are shown in the figure. The x-axis of the figure indicates the measuring time, while the y-axis indicates the concentration measured using MOHMS-21GP. As can be seen from the figure, it was confirmed that the concentration of PCB in the environmental gas, which is remarkably lower than the 0.15 mg/m^{3}N specified by statutory regulations, can be measured in real time. As a results, it could be verified that the MOHMS-21GP is a very useful tool for being able to check whether a PCB disposal process is performed safely and well; that is, the MOHMS-21GP is a very useful device for ensuring safety in a PCB disposal process.

5. Conclusion

The technical characteristics and measurement test results of a PCB gas monitoring system (MOHMS-21GP) were indicated, and the effectiveness of real time measurement of PCB was verified. The following major results could be verified.

(1) The gas direct-introduction type laser ionization TOFMS method was applied as a real time PCB gas

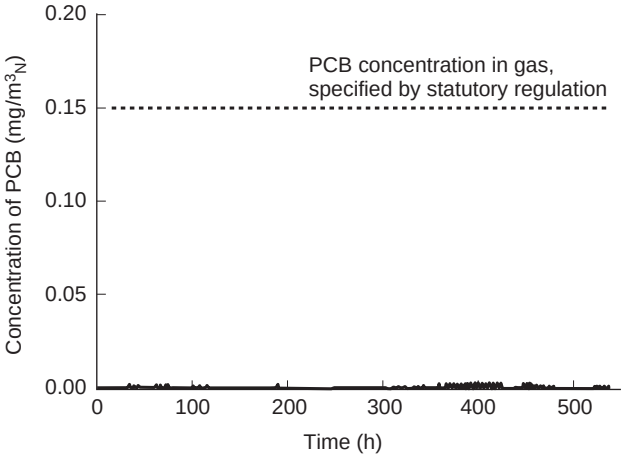


Fig. 6 Measured result of the gas in the PCB disposal plant
It could be confirmed that the concentration of PCB in the gas, which is lower than 0.15 mg/m^{3}N specified by statutory regulation, can be measured in real time during an actual PCB disposal process. Accordingly, it could be verified that the PCB gas monitoring system (MOHMS-21GP) is a very useful tool capable of checking whether a PCB disposal process is safely and excellently performed. In other words, the MOHMS-21GP is a very useful device for ensuring safety during a PCB disposal process.

monitoring system. As a result, a measuring sensitivity of 0.01 mg/m^3_N PCB could be fully achieved.

(2) The PCB gas monitoring system (MOHMS-21GP) was capable of measuring PCB levels without being influenced by main gas components and coexistent various substances, even under the exhaust gas and the atmosphere of the work environment conditions from the PCB disposal plant (MHI). Accordingly, the MOHMS-21GP could be evaluated as being a very useful tool for confirming the safety and excellent operation of a PCB disposal plant.

As mentioned above, the PCB gas monitoring system is believed to play an important role in ensuring safety in PCB disposal procedures. Further details can be obtained by contacting the Environmental Solution Department, Machinery Headquarters, MHI (Tel.81-3-6716-3735).

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Shinsaku Dobashi


Yoshihiro Deguchi


Masaharu Kira


Ryuichiro Tanaka


Yoshinori Izawa