

Ultra-sensitive High-speed Monitoring Technology for Trace-level Toxic Halogenated Hydrocarbon Compounds

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Mitsubishi Heavy Industries, Ltd. (MHI) has further improved its original high-speed analysis technology developed by combining vacuum ultraviolet light ionization, ion trapping, and time-of-flight type mass spectrometry with the aim of monitoring trace-level toxic substance in exhaust gas from incinerator furnaces in an attempt to increase the analytical sensitivity and extend the applicability of the technology to actual plants. As a result, the technology has made it possible to analyze trichlorobenzene (T3CB), a dioxin precursor, in a gaseous state in twenty seconds with a sensitivity of 80 ng/m³N, and pentachloro-dibenzofuran (P5CDF), a type of dioxin, in a solvent in sixteen minutes with a sensitivity of 1 pg using the selective accumulation of target substances and separation of interfering substances in the ion trap. These results show that higher speed and higher sensitivity in analyzing toxic substances than had been previously possible can be achieved and the adverse effects of impurities contained in actual gas reduced. In addition, MHI has developed a cleaning procedure for the vacuum ultraviolet light irradiating window to contribute to extending the service life of the analyzing system.

1. Introduction

Many products that MHI produces often need to have compatibility between their mechanical performance and environmental performance. Recently, there has been a strong trend toward requiring ever better improvement of the latter. In particular, the emissions of dioxins (hereafter referred to as DXNs) and gaseous substances that exert green house effects on the atmosphere burden the environment with heavy loads, so that the measurement, monitoring and reduction of these emissions have become an issue of major social concern.

MHI considers the development of highly sensitive environment-monitoring technology to be an important theme coping with these social concerns. To this end, MHI has been focusing much effort on developing various measurement methods that use advanced technologies in the field of applied physics and chemistry, in addition to promoting the advancement of combustion control and exhaust gas treatment techniques.

For instance, MHI has already developed laser ionization mass spectrometry as a method for monitoring toxic substances existing in ppt (parts per trillion) and ppb (parts per billion) levels for use in plants that dispose of polychlorobiphenyl (PCB), which is a highly toxic compounds. MHI has succeeded in putting this system into practical use as a super high sensitive exhaust gas

monitoring system, for the purpose of checking whether PCB concentrations in exhaust gas and the working environment are lower than required safety standard levels⁽¹⁾.

In addition, MHI has developed a tunable diode laser spectrometry capable of real-time- measurement of the spatial distributions of CO, CO₂, and NO_x existing in ppm (parts per million) levels in the atmosphere and is promoting its application in monitoring the interior of incinerator furnaces and the local surrounding atmosphere, as a compact, easily maintainable, and highly sensitive gas monitoring system⁽²⁾.

In this paper, technical aspects of the vacuum ultraviolet (hereafter abbreviated as VUV) ionization mass spectrometry system are described in detail. The system has been developed by MHI as a fast monitoring system for measuring DXNs and their precursors, which are reactants that lead to the formation of DXNs, in exhaust gas, in order to reduce trace-level organic chlorine compounds emitted from incinerator furnaces. The technology used for the system is characterized by being applicable and effective in monitoring various target substances present in ppt to ppb levels. Further information regarding the results of the field tests of this technology can be found by referring to a previous report⁽³⁾.

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2. Principle of measurement and improvement of performance

Fig. 1 shows the configuration of the system. This analysis system originally developed by MHI consists of (1) ionizing a target substance contained in exhaust gas by VUV light, (2) accumulating the target ions in an ion trap, and (3) identifying the accumulated target ions using time-of-flight mass spectrometry (hereafter abbreviated as TOF). The basic principle has already been described in a previous report⁽⁴⁾. This time, the selective accumulation of a target substance and separation of interfering substances in the ion trap have been added to increase the sensitivity and extend the practical applicability of the system to being able to handle actual gases containing various interfering substances.

2.1 VUV ionization

Since VUV light has a shorter wavelength and stronger photon energy than usual ultraviolet light, it can directly and efficiently ionize a target molecule with photons. In addition, since this ionization process using VUV is simple, the affect of coexisting molecules on ionization efficiency is small. An ionization process with these useful characteristics contrasts with other ionization processes such as laser ionization and atmospheric pressure chemical ionization that have such problems as reduced ionization efficiency in multi-chlorine molecules or the impact of oxygen concentration on ionization efficiency.

Furthermore, since the ionizing potential of Lyman light (wavelength: 121.6 nm, photon energy: 10.1 eV), which is irradiated from hydrogen plasma and is used for this ionization process, is a slightly higher in photon energy than the 8.5 to 10 eV of DXN and their precursor ionization energy, it can be used to perform ionization efficiently without the occurrence of any dissociation. Thus, VUV light is an excellent ionization source. However, because of the following problems, it has not been used practically in high sensitive analysis until now.

- (1) Since VUV light is difficult to produce in sufficiently large quantities at a time, the amount of ion-generation that can be realized per unit time is limited.
- (2) Since the VUV light can ionize all molecules whose ionization energies are lower than the VUV photon energy, selectivity of this method in the ionization is low. Therefore if there are a lot of interfering molecules that have the same mass number as that of the target molecules and the lower ionization energy than the photon energy, the measurement accuracy is deteriorated. This is often the case in actual exhaust.
- (3) Since the window material is damaged quickly, frequent maintenance is required.

With regard to Item (1), the VUV ionization technology described in this paper can first be characterized by

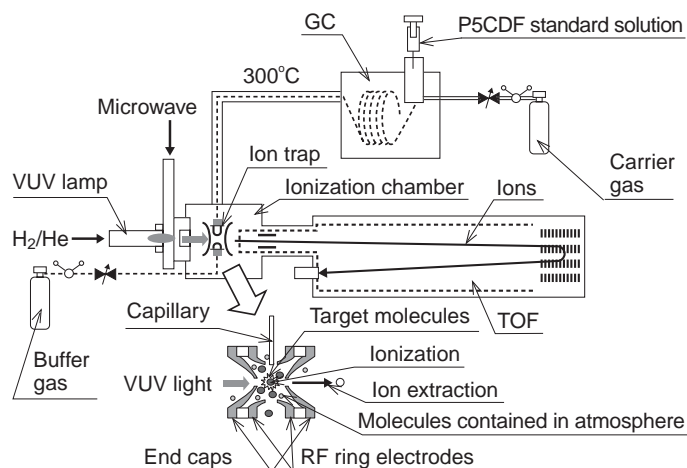


Fig. 1 Real-time measurement system for trace-level organic chlorine compounds

This system consists of a vacuum ultraviolet light lamp, ion trap, and TOF. The figure shows system configuration with a gas chromatography installed to measure P5CDF. Gas chromatography is not used when measuring T3CB.

performing ionization successively using a lamp that generates light continuously, accumulating the ionized ions in the trap, and ensuring a sufficient number of ions.

2.2 Selective accumulation in ion trap and fragmentation of accumulated ions

The problem mentioned in Item (2) above was solved as described below. **Fig. 2** shows the timing chart for each process. The following is a description taking T3CB as an example. When ions are accumulated in the ion trap under continuous ionization using a VUV lamp and a selective signal is applied to the ion trap, only these ions with the same mass number as that of T3CB are accumulated; other ions with different mass numbers are simultaneously eliminated (selective accumulation)⁽⁵⁾.

The selecting signal has an inverse Fourier transform waveform of a continuous frequency spectrum in which only the secular frequency of T3CB to be accumulated is not included. (The secular frequency is given by the mass number of T3CB and the trap frequency [1MHz for instance] applied to the RF ring electrode.)

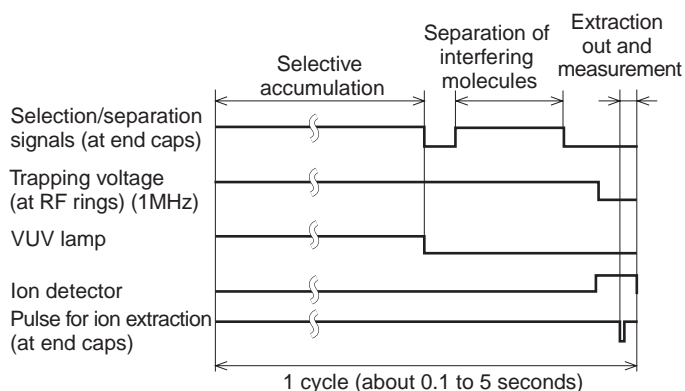


Fig. 2 Timing chart

This figure shows the timing chart of the lamp, trap, and TOF.

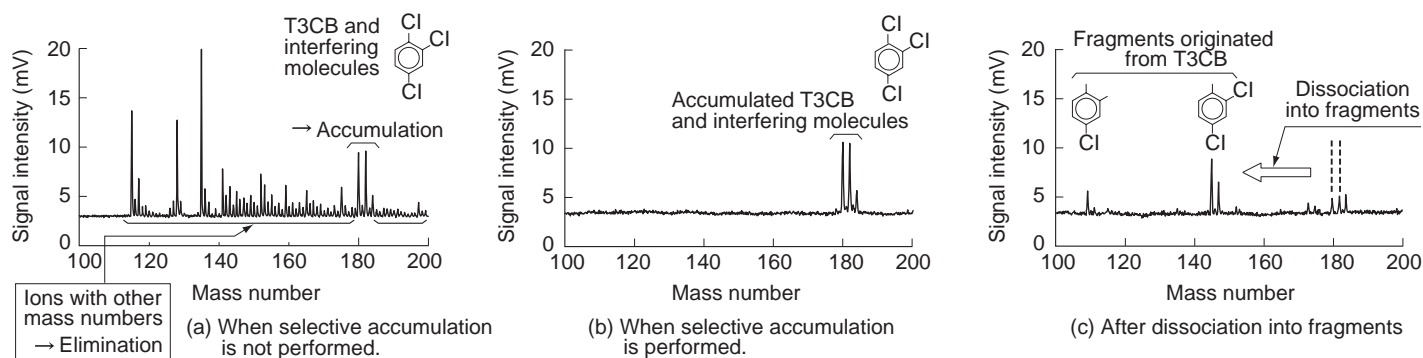


Fig. 3 Mass spectrum of T3CB

Interfering molecules are separated through the selective accumulation of molecules with mass numbers of 180, 182, and 184 and their subsequent fragmentation.

Fig.3 (a) shows the mass spectrum of a typical gas sample when the selective accumulation is not performed, while Fig.3 (b) shows the mass spectrum when a selective accumulation is performed. The latter shows that ions with mass numbers 180, 182, and 184, which are the isotopic ions of T3CB, can be selectively accumulated.

Then, T3CB and its interfering molecules that have the same mass number as T3CB, which are selectively accumulated together with the T3CB, are separated. In this procedure, the ions of T3CB that have been accumulated are given a strong shake by a wave with the secular frequency of T3CB (previously described) applied to the end caps, so that the ions of T3CB are made to collide with the ambient buffer molecules at which point they are dissociated into fragments (hereafter referred to as fragmentation). As shown in Fig.3 (c), T3CB is dissociated into molecules with mass numbers of 145 and 147, which have lost one chlorine atom, respectively, and the molecules with a mass number of 109, which have lost two chlorine atoms and one hydrogen atom. Interfering molecules (which are supposed to consist of straight chain hydrocarbons) can then be separated from the T3CB molecules since they are dissociated nearly at random. Thus, by detecting the separated T3CB molecules in the TOF, it becomes possible to realize a highly sensitive analysis that is not influenced by interfering molecules.

2.3 Improvement of life of the VUV window

A MgF₂ window through which the VUV light is irradiated is used in order to partition the VUV lamp and ionization chamber. However, the material is easily deteriorated. The reasons for its short life have been identified and the following countermeasures have been taken to improve the performance and longevity of the window as follows.

(1) Effect of hydrocarbons in the ionization chamber

We found that trace amounts of hydrocarbons contained in gas in an ionization chamber adhere to the inner surface of the window as carbon, due to the photochemical reaction of VUV. On the other hand, we also found that the carbon is eliminated if oxygen or water vapor is present inside the chamber when VUV is irradiated in the chamber. Accordingly, the phenomena was

used as a cleaning procedure in which oxygen or steam is injected and applied to the surface of the window during normal operation or maintenance service.

(2) Deterioration of MgF₂ due to production of color center

We found that color centers that absorb light with a wavelength of 121.6 nm are produced near the lamp side surface of the window substrate by the VUV light containing various wavelengths generated by the lamp. On the other hand, it has been also found that the production rate of the color center can be reduced by decreasing the temperature of the window. Consequently, the window and its vicinity are to be cooled during operation as a means of preventing the formation of a color center.

In addition to the countermeasures described above, a design in which eight windows can be used in turn without exposing the vacuum system to the air has been developed in order to prevent time loss to obtain high vacuum after the air exposure. This makes it possible for the system to run continuously with maintaining a high level of sensitivity for about six months.

3. Configuration of system

Fig. 1 shows the configuration of the monitoring system tested in this study. The sample of gas to be analyzed was led into the interior of the ion trap through a capillary column. The sampling tubing and the capillary column were kept at high temperatures between 100 to 300°C, so as to minimize the possible loss of any of the DXNs and their precursors due to adhesion and time lags since they adhere easily to any walls they come in contact with and because their concentrations are extremely low. In addition to above, the ionization chamber was also kept at a temperature of 200°C.

The quadrupole type electrodes were adopted for use as the ion trap. The VUV light from the source lamp was irradiated onto the target molecules that were led into the trap. The higher the pressure in the trap, the greater was the amount of ionized molecules present. However, excessively high pressure results in gas breakdown. As a result of optimization, appropriate internal pressure of the ionization chamber was determined to be 10⁻² Pa.

The selecting signal applied to carry out the selective accumulation was generated at an arbitrary waveform generating board installed in a computer, amplified by an amplifier, and applied to the trap through a filter that protects the flow back of pulse voltage applied for the ion extraction. Since one cycle of the selecting signal is about 3 ms, for instant, the signal was repeatedly applied during an accumulation time of 0.1 to several seconds. On the other hand, for the fragmentation, a wave with the secular frequency explained previously was given from the same system described above.

Ions dissociated into fragments were led to the TOF with the timing shown in Fig. 2, and mass-analyzed. Then, the concentration of the target molecules was calculated from the total number of fragments originated from the target molecules. A series of these procedures was repeated multiple times during twenty second period and the integrated values were adopted as the calculated value.

In order to improve the sensitivity of the system, such parameters as the frequency and voltage of the high frequency wave applied to the trap, the spectrum waveforms of the selecting signal and fragmenting signal (including the range of mass numbers to be eliminated, the range to be selected, and amplitude distributions), time for trapping (accumulating), time required for each process, voltage for the ion extraction, accelerating voltage at TOF, and selection of fragments included in measurement were all optimized.

Furthermore, the sensitivity of the system was increased by lighting the VUV lamp only during accumulation. This was done in order to prevent the following two problems from arising. (1) Ions produced during the fragmentation become noise. (2) VUV light that leaks into the TOF and enters the detector becomes noise.

In the case of pentachloro-dibenzofuran (P5CDF), the sample was in a form of a solution. (Details regarding P5CDF are described in Section 4.2.) Therefore, gas chromatography was added to extract P5CDF from the

solvent and concentrate it in order to improve the level of sensitivity. In addition, a buffer gas (N₂ at a pressure of 3×10^{-3} Pa) was introduced into the trap in order to improve the efficiencies of the selective accumulation and fragmentation of the ions/molecules.

4. Results and discussion

4.1 Measurement of T3CB

In order to check the combustion conditions of an incinerator furnace, the study focused on T3CB, which is a DXN precursor, because its concentration is relatively high and is said to correlate closely to the amount of DXNs created.

First of all, the system was calibrated. As a sample, the standard gas with $80 \mu\text{g}/\text{m}^3_{\text{N}}$ of T3CB was further diluted with nitrogen gas. Fig. 4 shows the calibration line. The Y-axis intercept point, i.e. the count number of ions at the zero point of the X-axis, was 4.2 (corresponding to noise component) and the coefficient was 0.052 (count number of ions)/(ng/m³_N) with respect to the least square approximate straight line. Hence, the lower detecting limit was determined to be $80 \text{ ng}/\text{m}^3_{\text{N}}$ (=10 ppt). At a concentration of $80 \text{ ng}/\text{m}^3_{\text{N}}$, the count number was found to be 8.4, which is sufficiently larger than the noise component. The longer the trapping time, the larger is the count number. However, excessively longer trapping time leads the accumulation of ions to a point of saturation in high concentration. The trapping time was optimized to be 0.3 seconds. Integration time was 20 seconds.

The monitoring system was then applied in the measurement of actual exhaust gas at the outlet of a waste incinerator furnace⁽³⁾. Since the monitoring system was installed upstream of the after-treatment unit such as a dust collector, the combustion conditions inside the furnace could be monitored directly. After eliminating solid materials such as ash, the exhaust gas quickly cooled to about 200°C and was led to the system. The fragment spectrum obtained by this procedure is shown in Fig. 5. In addition to the same fragments as those originated

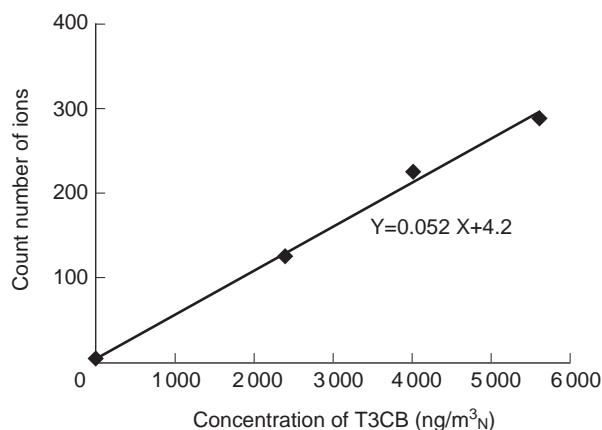


Fig. 4 Calibration line using T3CB as standard gas
Linearity is maintained over a wide range of T3CB concentration.

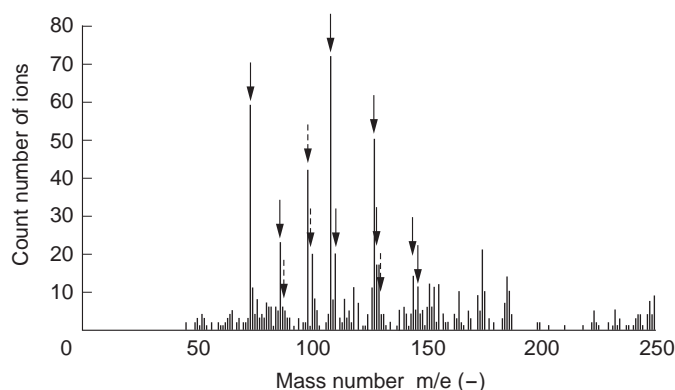


Fig. 5 Mass spectrum of fragments of T3CB in actual exhaust gas
In addition to the fragments (indicated by solid line arrow marks) in the standard gas, new fragments (indicated by dotted line arrow marks) are generated.

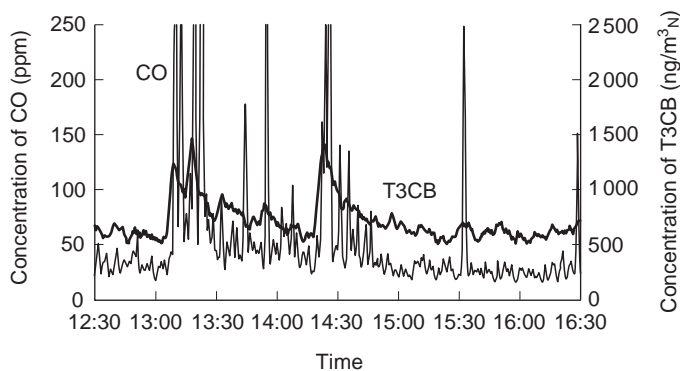


Fig. 6 Time history of T3CB concentration at outlet of actual incinerator furnace

Since measured T3CB value follows the change of CO concentration, it is believed that the monitoring system properly measures T3CB concentration.

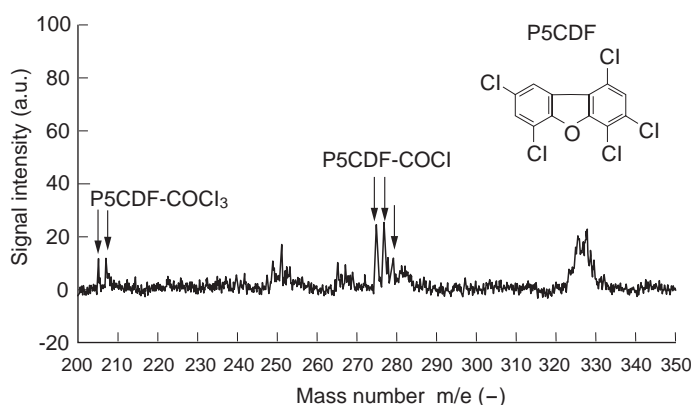


Fig. 7 Spectrum after fragmentation of P5CDF

The figure shows a spectrum of P5CDF measured using the system with gas chromatography. The measured values are calculated by the time integration of the signal of all the fragments.

from the standard gas, which are indicated by solid line arrows, the fragments indicated by dotted line arrows are also thought to originate from T3CB. Although the production processes of these fragments are unknown, they are thought to be produced by any action due to water vapor contained in the actual exhaust gas. This assumption was confirmed by an experiment in which H₂O was added into the standard gas. The concentration of T3CB was then calculated taking into consideration these fragments together. The fragments corresponding to other mass numbers are thought to originate from interfering molecules other than T3CB.

Fig. 6 shows the concentration of T3CB changed with the lapse of time, compared with that of CO. As can be seen from the figure, the concentration of T3CB increases with that of CO when the concentration of CO is high. Therefore, it can be seen that the monitoring system can monitor the state of combustion in an incinerator furnace. It is believed that in regions where the concentration of CO is low, the concentration of CO is not suitable as an index for the generation of DXNs, and instead of CO, DXN precursors such as T3CB are said to have a better correlations with the state of combustion in the furnace. Consequently, the application of the sys-

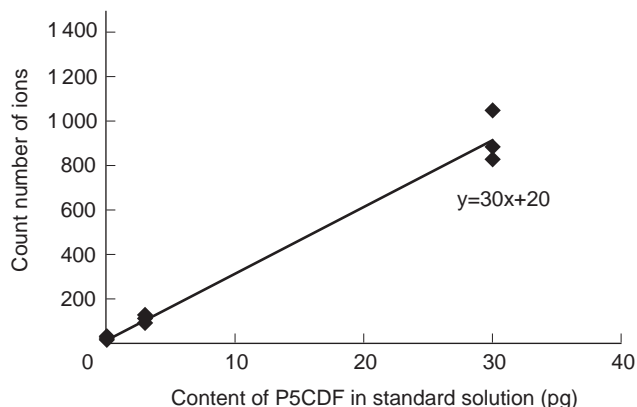


Fig. 8 Calibration line of P5CDF

Linearity is obtained over a wide range of P5CDF concentration.

tem should be quite useful to monitor the condition of the combustion and reduce the DXN generation.

4.2 Measurement of P5CDF

As one of the indices of DXN emissions in the exhaust gas from incinerator furnaces, P5CDF, a type of DXNs, was chosen for a measuring target. In previous study, MHI has revealed that the concentration of P5CDF is relatively high in exhaust gas. In addition, P5CDF has a strong correlation with the TEQ (Toxicity Equivalency Quantity) value of DXNs as a whole⁽³⁾.

First, the detecting sensitivity of the system was calibrated using a commercially available standard solution. **Fig. 7** shows the mass spectrum of P5CDF after the fragmentation. Based on other reports, it has been known that the mass numbers 275, 277, and 279 indicate the fragments in which C, O, and Cl have been eliminated from P5CDF, respectively, and 205 and 207 indicate the fragments in which C, O, and 3Cl have been eliminated. The other fragments seem to have originated from the liquid phase components that have eluated from the capillary. **Fig. 8** shows the calibration line in a solution containing 0 to 30 pg of P5CDF.

From this figure, the lowest detectable limit was determined to be 1 pg, based on the indication that the Y-axis-intercept point, i.e. the count number of ions at the zero point of the X-axis, was 20 (corresponding to noise components) and the coefficient was 30 (count number of ions/pg) with respect to the least square approximate straight line. The count number 50 at 1 pg is sufficiently larger than 20 corresponding to the noise component. The required time for the measurement was 16 minutes, including the time required for the gas chromatography. The trapping time was 0.1 seconds after optimization in the same way as was the case with T3CB.

The system was then applied to the monitoring of P5CDF contained in the actual exhaust gas emitted to the atmosphere, being installed downstream from the bag filter (dust collector) of the incinerator furnace. Since the concentration of P5CDF here was as low as

0.1 ng/m³N or less, P5CDF was concentrated using solvent extraction with an automatic concentration device before being introduced into the monitoring system. The concentration procedure takes 2 to 6 hours to complete. The detailed result of this actual exhaust measurement was described in the previous report⁽³⁾ and it confirmed that this system is practically usable.

5. Conclusion

The vacuum ultraviolet ionization ion trap mass spectrometry system described above has been developed in order to monitor the state of combustion in and the emission of trace-level organic chlorine compounds from an incinerator furnace. As a result, sensitivities of 80 ng/m³N (measuring time: twenty seconds) and 1 pg (measuring time: sixteen minutes) for T3CB (standard gas) and P5CDF (standard solution), respectively, were achieved. In addition, the applicability of the mass spectrometry system to actual incineration plants was extended by adding a process to eliminate interfering molecules and a means for extending the lives of the irradiating windows. MHI intends to utilize this analytical technology to improve the performance of waste incinerator furnaces, in the future.

The measurement technologies, developed by MHI, in-

cluding the technology described in this paper, are applicable not only in improving the environmental performance of various plants, but also to various fields such as protecting against atmospheric and soil pollution, the development of new materials and processes, and the creation of suitable countermeasures against crimes and terrorisms. Accordingly, MHI intends to utilize the full potential of this system and related processes widely in the future.

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