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Automated Analysis of Persistent Organic Pollutants in the Gas Phase by Laser Ionization Mass Spectrometry

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Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. The detection and evaluation of small amounts of POPs require methods with both high precision and high chemical selectivity. Conventional methods involve a number of preparatory steps and time-consuming analysis and are not suitable for the abovementioned purposes. Hence, new automated analysis methods are required for on-line detection and rapid analysis of POPs. In this paper, mass spectrometry with resonance-enhanced multi-photon ionization (REMPI) is performed to obtain information about the automated analysis of POPs in the gas-phase with on-line detection. Dynamic trapping time-of-flight mass spectrometry (TOFMS) was performed with sufficient selectivity and sensitivity for rapid analysis of polychlorinated biphenyls (PCBs) in the gas phase. Compared to normal trapping, the use of dynamic trapping enabled ion signal intensity to be increased by a factor of greater than 10. The detection limit at 1 min was < 1 ppbV, and the accuracy also correlated well with the results of conventional analysis. Based on these results, an automated monitoring system was developed for automated analysis of PCBs. It was confirmed that this monitoring system was capable of analyzing PCB concentration without being influenced by main gas components or various coexisting substances, even under conditions characterized by exhaust gas and the work environment atmosphere. PCB concentration in PCB waste plants, which is substantially lower than the 0.10 mg/m3N specified in statutory regulations, could be analyzed within 1 min. It was possible to make continuous long-term analysis for over 2,000 h (120,000 points).

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1. Introduction

Modern systems of mass production, consumption, and disposal have caused many environmental issues such as air and water pollution, global warming, and ozone layer destruction. International conventions and legal regulations have been reinforced in order to reduce environmental load without restraining production and consumption activities. However, worldwide environmental pollution by persistent organic pollutants (POPs) is still a serious social problem. POPs are toxic chemicals that adversely affect human health and the environment around the world. Therefore, governments in many countries have taken measures to eliminate or reduce the release of POPs into the environment.

It is essential to strictly guard against leakages of POPs, especially in waste-treatment facilities, giving a strong imperative for automated, rapid, and continuous analysis of POPs in the gas phase. Evaluating a small quantity of POPs requires methods with both high precision and high chemical selectivity. As conventional methods involve several preparatory steps and time-consuming analysis, and they do not meet the abovementioned requirements. Given this background, new methods are needed for the automated analysis of POPs with on-line detection. One of the most powerful tools in the automated analysis of molecules is laser radiation. Lasers have high intensities and enable us to detect the nonlinear responses of molecules12-14. Laser radiation consists of monochromatic light, by which well-controlled and well-defined excitation of selected molecules can be achieved.15-17 Recent years have seen considerable research devoted to the use of laser spectroscopy for a rapid analysis of atoms and molecules. The growth of laser spectrometry has, in part, been the result of advances in laser technology, including the advent of high-powered, ultrashort-pulsed, narrow-bandwidth, tunable lasers that can produce wavelengths ranging from the infrared to the vacuum ultraviolet.18,19 This significant advance enables many automated analytical methods to be developed, including laser-induced breakdown spectrometry (LIBS),20-23 laser-induced fluorescence spectrometry (LIF),20-23 laser-induced fluorescence spectrometry (LIF),20-23 laser-induced fluorescence spectrometry (LIF),20-23 laser-induced fluorescence spectrometry (LIF),20-23 laser-induced fluorescence spectrometry (LIF),20-23
sorption spectrometry, Raman spectrometry, and mass spectrometry with resonance-enhanced multi-photon ionization (REMPI). In particular, the use of REMPI in mass spectrometry, which features molecular selectivity and enables fragment-free ionization in a short time, has become the automated analysis method of choice for the environmental trace analysis of POPs.

In this report, mass spectrometry with REMPI is performed to obtain information about the automated analysis of POPs in the gas-phase with on-line detection. It is mechanically possible to analyze POPs very quickly in the gas phase, without requiring multiple preparatory steps, including gas sampling, purification, and condensation. This may become a useful automated analytical tool for addressing important problems including environmental trace analysis, industrial quality control, and safety management of chemicals in the gas phase.

The authors have previously developed trace analysis of polychlorinated biphenyls (PCBs) with on-line detection through the use of picosecond laser ionization/ion-trap/time-of-flight mass spectrometry (LI-IT-TOFMS). The LI-IT-TOFMS was developed by combining an ion-trap function with direct gas introduction-type laser ionization (offering molecular selectivity and a fragment-free operation), and consideration was given to the high sensitivity required for the rapid analysis of di-, tri-, and tetra-chlorinated biphenyls. It was confirmed that a laser with a pulse duration of 100 ps clearly generated a stronger PCB ion signal than a 5 ns pulse laser, by a factor of more than 10. New findings presented here include the efficient trapping of laser-ionized PCB ions using the dynamic trapping time-of-flight mass spectrometry (TOFMS), as well as the simulation of electric field control conditions for efficient trapping, and observation of the effectiveness of reducing the speed of the ions introduced into the trap apparatus. Evaluations of accuracy based on comparisons with the results of the conventional method (gas sampling/gas chromatography mass spectrometry; gas sampling/GC-MS) demonstrated a coefficient of variation of 30% in terms of the R=O transition. 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-monitoring system online. We used the internal standard gas (2,4-di-chlorinated toluene) in order to check the correct operation of the monitoring system. It was confirmed that the PCB concentration in the environmental gas (which is substantially lower than the value of 0.10 mg/m³N as specified by statutory regulations), can be analyzed within 1 min. We also confirmed that it is possible to perform continuous long-term analysis for over 2,000 h.

In summary, it was verified that the LI-IT-TOFMS is a highly useful automated analysis method for determining whether the PCB disposal processes are performed safely and well. In other words, the PCB monitoring system is a very useful method for ensuring safety in PCB disposal processes.
states, thus enabling selective ionization of the target sample molecules.

The efficiency of ionization increases according to the value of the rate constants, "a" and "b." The number $N_i$ for state C in the ionization process, as shown in Fig. 2, is expressed as follows:

$$N_i = \frac{bX_0}{b+k_{ia}} \left( 1 + \frac{L}{K-L} \exp(-Kt_i) - \frac{K}{K-L} \exp(-Lt_i) \right).$$

(1)

Here, $t_i$ represents the laser-pulse duration, while $X_0$ represents the number of molecules in the ground state. $K$ and $L$ are determined as follows:

$$K = \frac{1}{2}( (2a+b+k_{ia}) + (2a+b+k_t+k_{ia})^2 - 4a(b+k_{ia})^2 )^{1/2},$$

(2)

$$L = \frac{1}{2}( (2a+b+k_{ia}) + (2a+b+k_t+k_{ia})^2 - 4a(b+k_{ia})^2 )^{1/2}. $$

(3)

Equation (1) can generally be approximated as shown below with $a$, $b$, $k_{ia} \leqslant t_i^{-1}$ in the resonance-enhanced two-photon ionization process for aromatic compounds, using a pulse laser with a duration of 10 ns or less:

i) $k_{ia} \leqslant t_i^{-1}$

$$N_i = \frac{1}{2} \frac{abX_0}{k_{ia}} \exp(2\pi t_i L).$$

(4)

ii) $k_{ia} \geqslant t_i^{-1}$

$$N_i = \frac{abX_0}{k_{ia}} \exp(2\pi t_i L).$$

(5)

In cases of a large $k_{ia}$ value appearing in chlorinated aromatic compounds, $N_i$ is in inverse proportion to $k_{ia}$, as shown in Eq. (5). This induces a substantial decrease in the detection limit. In contrast, Eq. (4) suggests that by reducing the laser-pulse duration, $N_i$ values tend to be unrelated to $k_{ia}$. It was reported by Matsumoto et al. that applying a laser-pulse duration of 500 fs to halogenated benzene gave higher $N_i$ values than in the case of a 15 ns duration.

### 2.2 Dynamic trapping

The ion-trap device is a type of quadrupole mass spectrometer. It features two hyperboloidal end cap electrodes (the entrance end cap and the exit end cap), with a ring electrode sandwiched between the end cap electrodes. Application of a radiofrequency (RF) high-frequency field to the ring electrode creates a circumferential trajectory for retaining the ions inside the ion trap. The region of trapped ions is determined by the Mathieu formula.

In cases where the phase differential between the end cap electrode and the ring electrode is substantial, it is difficult to introduce the ions into the trap, resulting in poor trapping efficiency. In particular, with laser ionization, where ionization is performed using laser pulses, it is necessary to time the introduction of the ions so that the phase differential is small. Accordingly, the dynamic trapping method was selected as an effective means of resolving this issue.

In the dynamic trapping method, the RF voltage applied to the ring electrode when ions are introduced to the trap is either off or set to a low level. The voltage is then gradually raised in order to trap the ions. Figure 3 presents RF waveform diagrams for an ordinary trap and for a dynamic trap. As indicated in the figure, ions can be introduced into the dynamic trap when the RF voltage value is low, enabling highly efficient ion trapping.

In addition, in cases where the velocity of ions introduced into the trap is high, the circumferential trajectory inside the trap becomes unstable, and sufficient trapping efficiency cannot be obtained. Velocity reduction would allow a stable trajectory, with greater efficiency. A method was therefore devised for reducing velocity and achieving greater efficiency by applying a direct voltage to the exit end cap electrode.

### 3. Experimental

#### 3.1 Automated analysis system of PCBs

Figure 4 provides an illustration of the setup and a photograph of the automated analysis system of PCBs in the gas. The ion trap-type time-of-flight mass spectrometer (R. M. Jordan Co., Inc., Ion Trap Angular Reflectron D-1450) houses a vacuum chamber. Internal pressure of approximately $1.0 \times 10^{-6}$ Pa was achieved and maintained using a rotary pump (Compagnie Financière Alcatel, 1015-SD) and a turbo molecular pump (Pfeiffer Vacuum Technology AG, TCP-521). The measurement sample was supplied to the interior of the apparatus as an effusive molecular beam.

The sample was ionized by laser irradiation using a YAG laser (TOKYO INSTRUMENTS INC., PL-2240). The pulse duration was 100 ps, with a pulse repetition rate of 500 Hz. After passing the fundamental light of the YAG laser through a KDP crystal (K$_2$HPO$_4$), to generate second harmonic (wavelength of 532 nm), a BBO crystal (β-BaB$_2$O$_4$) was used to obtain 266 nm laser irradiation. Output for the 266 nm wavelength was 300 mW.

After accelerating the ions by applying 10 V to the electrode, the ions were introduced into the ion-trap apparatus (R. M. Jordan Co., Inc., Quadrupole Ion Trap
C-1251) by means of dynamic trapping. In order to cool the ions, helium gas (pressure: about $3.0 \times 10^{-6}$ Torr) was introduced into the trap. Following ion concentration using the ring electrode (RF frequency of 1 MHz, and RF voltage of 1,600 V) inside the trap, a pulse voltage was applied to the end cap electrode using a high voltage pulse generator (Directed Energy, Inc., PVM-4140). In addition, SIMION 7.0 (Tech Science) was utilized as a simulation tool for the ions inside the trap device. In this manner, the concentrated ions were released into the flight tube. The released ions were subjected to uniform motion in the flight tube, and, after being reflected by the reflector, were detected by the MCP detector. The signal of the detector was amplified, counted by the ion counter, and then stored as data in a computer. (Reprinted with permission from ref. 42, ©2004, The Japan Society for Analytical Chemistry.)

Fig. 4. (a) Experimental setup of the automated analysis system of PCBs in the gas. The sample (PCBs gas) was introduced as an effusive molecular beam, and ionized by laser irradiation. After ions were accelerated by an electrical potential and concentrated by the ion trapping device, they were subjected to uniform movement inside the flight tube. Ions were detected by the MCP detector. The signal of the detector was amplified, counted by the ion counter, and then stored as data in a computer. (Reprinted with permission from ref. 42, ©2004, The Japan Society for Analytical Chemistry.) (b) Photograph of the the automated analysis system of PCBs in the gas. This system consists of the ion trap-type time-of-flight mass spectrometer, the laser device, vacuum pumps, and a control computer. (Reprinted with permission from ref. 45, ©2007, The Japan Society of Mechanical Engineers.)

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Fig. 5. Diagram of the gas-sampling system of the conventional method. The sampling tube transporting the PCB gas was bifurcated so that the gas was conveyed simultaneously to the time-of-flight mass spectrometer and the gas sampling system. Gas sampling used an n-hexane solvent absorption method to collect PCBs. After collection, gas quantities were measured by a gas meter, and then exhausted. The PCBs collected by the n-hexane solvent were then analyzed by GC-MS. (Reprinted with permission from ref. 46, ©2007, The Society of Chemical Engineers, Japan.)
containers and held at around 300–325 K to produce PCB vapor. This vapor was mixed with balance gas (nitrogen), and the PCB-gas concentration was quantified using a cross-checking system (gas chromatography mass spectrometer (SHIMADZU CORPORATION, GCMS-QP2010)).

### 3.2 Internal standard introduction

Standard gas was used in order to verify the correct operation of the monitoring system. The standard gas was supplied from a cylinder (Sumitomo Seika Chemicals Co., Ltd.) containing 2,4-di-chlororinated toluene (concentration, 1 ppmV; balanced gas, nitrogen). As indicated in Fig. 1, the standard gas and the sample gas were mixed and introduced in the monitoring system. The quantity of the standard gas was 1/10 of the sample gas.

### 3.3 Cross-checking system (gas sampling/GC-MS)

Concentration of the PCB gas was analyzed by gas sampling/GC-MS. Figure 5 shows a diagram of the gas sampling system. As illustrated in the figure, the sampling tube transporting the PCB gas was bifurcated so that the gas was conveyed simultaneously to the time-of-flight mass spectrometer and the gas sampling system. Gas sampling used an n-hexane solvent absorption method to collect PCBs. After collection, gas quantities were measured using a gas meter, and then exhausted. The PCBs collected by the n-hexane solvent were then concentrated and analyzed by the gas chromatography mass spectrometer.

### 3.4 PCB Disposal plants

Figure 6 shows the container treatment process and the hydrothermal decomposition process in the PCB disposal plant (Mitsubishi Heavy Industries, Ltd.). The container treatment process disassembles and washes contaminated containers in order to separate PCB pollutants. The hydrothermal decomposition process decomposed the PCB pollutants into inorganic substances. (Reprinted with permission from ref. 45, ©2007, The Japan Society of Mechanical Engineers.)

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Fig. 6. (a) The container treatment process and (b) the hydrothermal decomposition process in the PCB disposal plant. The container treatment process disassembles and washes contaminated containers in order to separate PCB pollutants. The hydrothermal decomposition process decomposed the PCB pollutants into inorganic substances. (Reprinted with permission from ref. 45, ©2007, The Japan Society of Mechanical Engineers.)
composes the PCB pollutants into inorganic substances. The container treatment process consists of three stages: preprocessing, disassembly, and cleaning.

### 3.5 Gas sampling system of the PCB disposal plants

The gas sampling line can be switched with valves in order to connect to various sampling points in the PCB disposal plant, as shown in Fig. 7. In this study, a total of five sampling points were provided, including the exhaust gas line of the PCB-hydrothermal decomposition process and the atmosphere of the work environment in the PCB container-treatment process, thus allowing monitoring of PCB measurement for each gas sample.

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### 4. Results and Discussion

#### 4.1 PCB ionization properties according to laser-pulse duration

Figure 8 presents the TOFMS spectra for PCBs at laser-pulse durations of (a) 100 ps and (b) 5 ns using the LI-IT-TOFMS method. The vertical axis represents the signal intensity of ions, while the horizontal axis shows mass number. KC-300 was used as the measurement sample. Analytical time was 1 min. As indicated in the figure, the PCB spectra were characterized by multiple peaks, because the isotopic abundance ratio of Cl atoms (Cl^{35} : Cl^{37}) was 3 : 1, while that of C atoms (C^{12} : C^{13}) was 99 : 1. Furthermore, the picosecond laser-ionization method was successfully used for measuring the mass spectra attributed to di-, tri-, and tetra-chlorinated biphenyls. The signal amplification rates were more than 10 times greater with 5 ns laser. This observation indicates that the use of laser irradiation with a short pulse duration also encourages the ionization of PCBs. With respect to PCB ionization, it was considered that ionization is more dominant than spontaneous emission and nonradiative relaxation processes in the exited state when the laser pulse duration is 100 ps. In one of the nonradiative relaxation processes, molecules undergo intersystem crossing. Intersystem crossing is important when a molecule contains a moderately heavy atom such as Cl, because then the spin-orbit coupling is large and the molecule easily undergoes nonradiative relaxation.27, 28 In other words, when laser irradiation with a 5 ns pulse duration is used, a small quantity of PCB is ionized because nonradiative relaxation processes become the major process. When laser irradiation with a 100 ps pulse duration is used, the efficiency of PCB ionization is increased and it is possible to perform high-sensitivity measurement of PCBs. POPs include many halogenated aromatic compounds such as polychlorinated dibenzo-furans (PCDFs), polychlorinated dibenzo-p-dioxins (PCDDs), and polybrominated biphenyls (PBBs). Most halogenated aromatic hydrocarbons can be ionized by resonance-enhanced two-photon ioniza-
tion. Therefore, it is considered possible to analyze many POPs rapidly through the use of the picosecond laser-ionization method.

4.2 Optimal injection of PCB ions into the ion-trap

4.2.1 Dynamic trapping results

Figure 9 presents the TOFMS mass spectra for PCBs with and without the use of the dynamic trapping method. The vertical axis represents signal intensity, while the horizontal axis shows mass number. KC-300 was used as the measurement sample. As indicated in the figure, di-, tri-, and tetra-chlorinated biphenyls were confirmed to have been detected. Compared with ordinary trapping, it was confirmed that the signal intensities for di-, tri-, and tetra-chlorinated biphenyls increased when the dynamic trapping method was applied. The intensities for di-, tri-, and tetra-chlorinated biphenyls were increased by factors of 11.6, 11.2, and 12.1, respectively. In the case of ordinary trapping, because the phase difference between the end cap electrode and the ring electrode is large, the efficiency at which ions are introduced into the ion trap is reduced. By contrast, dynamic trapping features the timed introduction of ions into the apparatus when the phase differential is small, enabling greater efficiency. This results in an improved signal intensity when using dynamic trapping, in comparison with ordinary trapping.

4.2.2 Improved ion trapping efficiency through ion simulation

Figure 10 presents the electrical field distribution when a positive voltage of 20 V is applied to the exit end cap of the ion trap, with the contour of the electric field shown at 2 V intervals. The ions are introduced through the hole in the entrance end cap electrode, before being slowed by the resistance caused by the field applied to the exit end cap, and then start to move in the opposite direction. In order to raise the ion trapping efficiency of the apparatus, it would be desirable for the ion trajectories to converge near the center of the trap. In other words, it is necessary for the ion movement near the center of the trap to be zero. In order to address this, the timing of ion introduction into the trap was changed, and conditional optimization was performed by simulating the ion trajectories. Figure 11 shows results of this simulation. In Fig. 11(a), because the timing is appropriate, the amount of ion movement near the center is zero. Accordingly, it can be confirmed that the ion trap trajectories are satisfactorily converged at the center. By comparison, in Fig. 11(b), because the amount of ion movement near the center is not zero, the trajectory convergence is poor. Figure 11 also shows the time-of-flight mass spectra corresponding to the simulation conditions for (a) and (b). In the case of (a), where the trajectories are converged near the center, the PCB measurement signal intensity was confirmed to increase. Comparing the rate of increase to results for the application of dynamic trapping indicated in Fig. 11, the signal intensity for di-, tri-, and tetra-chlorinated biphenyls increased by factors of 2.5, 2.9, and 4.4, respectively. It was also ascertained that the mass resolution of the measurement signal also increased. This suggests that the ions are appropriately converged in the trap. Based on the foregoing, optimized ion simulation enabled improved ion-trapping efficiency for the ion trap device.

4.3 Evaluation of the results in analysis by conventional methods

Figure 12 shows a comparison between the measurement data obtained by LI-IT-TOFMS and that by conventional analysis (gas sampling/GC-MS). The horizontal axis represents the result of the conventional GC-MS, and the vertical axis shows the results of the LI-IT-TOFMS. The measurement sample consisted of PCBs containing the di-, tri-, and tetra-chlorinated biphenyls. As shown in the figure, the results of the measurements by LI-IT-TOFMS were highly correlated with those from the conventional chemical analysis. Correlation showed a standard deviation of 30% compared with the results of the chemical analysis. Figure 13 shows the results of the chemical analysis of di-, tri-,
and tetra-chlorinated biphenyls in comparison with the results of LI-IT-TOFMS. The horizontal axis represents the results of the conventional analysis (gas sampling/GC-MS), and the vertical axis shows the mass spectra of the LI-IT-TOFMS. By using standard PCB gases (KC-300 and KC-500), the concentration in each of the gaseous PCBs species was adjusted to 1–1000 μg/m³. As the figure indicates, the results for each of the PCB species also correlated well with the results of the conventional analysis. Calculations of the accuracy showed a standard deviation of 30%. We also confirmed that the signal intensities of the di-, tri-, and tetra-chlorinated biphenyls were sufficient for the analysis. The theoretical detection limits at 1 min calculated for S/N=3 were 0.001 μg/m³ for di-chlorinated biphenyls, 0.005 μg/m³ for tri-chlorinated biphenyls, and 0.034 μg/m³ for tetra-chlorinated biphenyls. The above results demonstrate that it is possible to achieve the PCB quantitative limit (10 μg/m³) for 1 min using the LI-IT-TOFMS.

4.4 Environmental monitoring of the exhaust gas and the atmosphere of the work environment

4.4.1 Applicability of the internal standard

Figure 14 shows the measurement resulting from the laser-ionization TOFMS when a standard gas (2,4-di-chlorinated toluene, 1 ppmV) was added to the PCB standard gas sample, KC-300 (Kaneka Corp.). As the quantity of the standard gas was 1/10 that of the sample gas, the concentration of the standard gas was around 100 ppbV. The concentration of the PCB sample was 362 μg/m³. The horizontal axis represents the time-of-flight of the ions, and is equivalent to the mass number. The vertical axis represents the signal intensity. Analytical time was 1 min. As shown in the figure, and similar to the findings with di-, tri-, and tetra-chlorinated biphenyls, an adequate signal intensity was obtained for 2,4-di-chlorinated toluene. This result indicates that 2,4-di-chlorinated toluene can be used as a standard gas for online checking of the operation in the system. Figure 15 presents the measurement results (trends) when the standard gas was added to the exhaust gas and the atmosphere of the work environment from PCB processing. Measured concentrations of di-, tri-, and tetra-chlorinated biphenyls are shown in Fig. 15(a), while Fig. 15(b) shows the signal intensity of 2,4-di-chlorinated toluene. The horizontal axes of Figs. 15(a) and (b) both represent the same time. The measurement time for each measure-
ment point was 1 min. As is clear from Fig. 15(a), the concentration of di-, tri-, and tetra-chlorinated biphenyls in the flue gas was at the 1 μg/m³ level. At the same time, as seen in Fig. 15(b), the signal intensity for 2,4-di-chlorinated toluene remained steady. These results demonstrated on an online basis (1 min) that the monitoring system was functioning appropriately, and confirmed that the measurements of PCB concentrations shown in Fig. 15(a) were reliable.

4.4.2 Applicability of the exhaust gas and the atmosphere of the work environment

In the exhaust gas of the hydrothermal decomposition processes and the workplace atmosphere, the main components were N₂, CO₂, O₂, and H₂O and air. These gases were contaminated by several trace components attributed to insulating oils, cleaning chemicals, and their decomposition products to the order of mg/m³. The concentrations of these trace components were dependent on the plant operating conditions and varied by several orders of magnitude. Some trace components have masses that are similar to those of PCBs, and our method can separate PCBs from most of these components using resonance-enhanced two-photon ionization. On the other hand, the conventional method requires a time-consuming process for the separation of PCBs from these components. Figure 16 shows the mass spectra of the exhaust gas from a PCB treatment plant for high and low PCB concentrations. The “high” PCB concentration was 0.2–0.3 mg/m³, and the “low” PCB concentration was below 0.01 mg/m³. The horizontal axis in the figure represents mass number, while the vertical axis shows signal intensity.
As can be seen from the figure, it was confirmed that the LI-IT-TOFMS enables us to analyze the exhaust gas from the PCB treatment plants, for both high and low PCB concentrations. At high PCB concentration, contaminants have been detected in the spectrum, but there is no interference with the mass range of di-, tri-, and tetra-chlorinated biphenyls. As noted above, since it was confirmed that PCB measurement is possible even in the exhaust gas containing main gases mixed with various substances, use of the LI-IT-TOFMS was verified as being practical.

4.4.3 Long-term reliability

Figure 17 shows examples of the work environment atmosphere analysis results for the PCB disposal plant. The atmosphere of the work environment in the PCB-container treatment process was analyzed using the laser mass spectrometer for PCBs. The horizontal axis indicates time, while the vertical axis represents the PCB concentration as measured by the LI-IT-TOFMS. It was confirmed that the concentration of PCBs in the environmental gas (which is substantially lower than the 0.10 mg/m³ specified by statutory regulations) can be analyzed within 1 min. Accordingly, it was verified that the LI-IT-TOFMS is highly useful for the automated analysis of whether PCB disposal processes are performed safely and well. In other words, the LI-IT-TOMS is very useful for ensuring safety of the work environment in a PCB disposal plant.

Fig. 15. Results when the standard gas was added to the exhaust gas and the atmosphere of the work environment from PCB processing, (a) the concentrations of di-, tri-, and tetra-chlorinated biphenyls, (b) the signal intensity of standard gas (2,4-di-chlorinated toluene). Horizontal axes show the same time. The online basis (1 min) that the monitoring system was functioning appropriately confirmed that the measurements of PCB concentrations shown were reliable. (Modified with permission from ref. 46, ©2007, The Society of Chemical Engineers, Japan.)

Fig. 16. Mass spectra of the exhaust gas from PCB treatment plants. It was confirmed that the LI-IT-TOFMS method enabled us to measure the exhaust gas from the PCB treatment plants. PCB concentration was (a) 0.2–0.3 mg/m³ and (b) below 0.01 mg/m³. (Reprinted with permission from ref. 45, ©2007, The Japan Society of Mechanical Engineers.)

Fig. 17. Examples of the work environment atmosphere analysis results for the PCB disposal plant. The concentration of PCBs in the work environment of the PCB disposal plant, which is substantially lower than the 0.10 mg/m³ specified by statutory regulations, could be analyzed within 1 min. It was possible to make continuous long-term measurements for over 2,000 h (120,000 points). (Reprinted with permission from ref. 47, ©2009, Japan Society of Material Cycles and Waste Management.)
As indicated in Fig. 17, the present study was also performed in order to evaluate the reliability of the LI-IT-TOFMS in mechanically analyzing PCB concentrations in environmental gases. It was possible to make continuous long-term analysis for over 2,000 h (120,000 points). We confirmed that the laser mass spectrometer had long-term reliability for automated analysis.

5. Conclusion

The applicability of the laser-ionization dynamic-trapping time-of-flight mass spectrometry for environmental monitoring was evaluated, and the following results were obtained.

1) Compared with ordinary trapping, the use of dynamic trapping enabled increased ion signal intensity by a factor of more than 10.

2) The application of ion-simulation enabled the optimization of conditions such that the ion-trap trajectories converged near the center of the apparatus, thereby raising ion trapping efficiency.

3) PCB measurement sensitivity was calculated based on the results noted in 1) and 2) above, and sufficient sensitivity (i.e., in the pptV range) was obtained with a measurement duration of 1 min. PCB-measurement accuracy was also evaluated, and good agreement was found with the results of the gas sampling/GC-MS (accuracy of 30% standard deviation).

4) We undertook the automated analysis of the exhaust gas and the work environment atmosphere in PCB treatment plants using the LI-IT-TOFMS, confirming that the automated analysis system could be operated appropriately by the introduction of an internal standard gas (2,4-dichlorinated toluene), and that it was possible to make continuous long-term analysis for over 2,000 h. The method was capable of automated analysis of PCB concentration without being influenced by main gas components and various coexisting substances, even under conditions characterized by exhaust gas and the work environment atmosphere.

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