Environmental Technology Verification Report

IDX TECHNOLOGIES, LTD.
RIMMPA-TOFMS
(Resonance Ionization with Multi-Mirror System Photon Accumulation Time-of-Flight Mass Spectrometer)

Prepared by
Battelle

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ETV ETV ETV

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

IDX TECHNOLOGIES, LTD. RIMMPA-TOFMS (Resonance Ionization with Multi-Mirror System Photon Accumulation Time-of-Flight Mass Spectrometer)

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six verification centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AHD	adsorption and heat desorption
AMS	Advanced Monitoring Systems
APCS	air pollution control system
CEM	continuous emission monitor
dscm	dry standard cubic meter
EMS	emission monitoring system
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
HW	hot/wet
NIST	National Institute of Standards and Technology
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PE	performance evaluation
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RIMMPA	Resonance Ionization with Multi-Mirror System Photon Accumulation
RTP	Research Triangle Park
SMPB	Scotch Marine Packaged Boiler
TEQ	toxic equivalent
TOFMS	time-of-flight mass spectrometer
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the IDX Technologies Resonance Ionization with Multi-Mirror System Photon Accumulation Time-of-Flight Mass Spectrometer (RIMMPA-TOFMS) in monitoring emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the RIMMPA-TOFMS. The following is a description of the RIMMPA-TOFMS, based on information provided by the vendor. The information provided below was not verified in this test.

The RIMMPA-TOFMS (Figure 2-1) is a new laser-based mass spectrometry system that has been developed for the real-time detection and quantification of PCDD/Fs. The RIMMPA-TOFMS is based on a two-color-two-photon ionization scheme and employs a nanosecond pulse duration, which promotes isomer selective soft ionization with high sensitivity. Briefly, the technology consists of a Nd:YAG pumped dye laser including frequency doublers (tuning range between 270 – 370 nanometers, 5 – 8 nanosecond pulse width, 10 Hz repetition rate, under 0.1 centimeter^{-1} at 285 nanometer optical linewidth, 2 mJ maximum output energy) for exciting sample molecules, a frequency quintupled Nd:YAG laser (213 nm laser radiation, 3 – 5 nanosecond pulse width, 10 Hz repetition rate, 4 mJ maximum output energy) for ionizing excited molecules, and a multi-mirror system by which an optical image relaying system is constructed using 14 reflective mirrors. A pulsed valve that has been developed for operation under a high-temperature condition is used in the RIMMPA-TOFMS to produce a supersonic jet under the

 Figure 2-1. Photograph of RIMMPA-TOFMS

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choke-flow condition. This supersonic jet allows the sample gas to be cooled to cryogenic temperatures and generates uniform ordering of the gaseous molecules so that the collisions between particles are minimized, which extends the excitation lifetime of the target compounds. The supersonic molecular beam interacts with the two multi-reflected synchronous laser beams for about 40 nanoseconds in the ionization region, where the target molecules are selectively ionized and accelerated into the time-of-flight mass spectrometer.

Chapter 3
Test Design and Procedures

3.1 Introduction

EPA Method 23[1] is the certified extractive method used for quantifying PCDD/F emissions from incinerators in the United States as well as in many other countries. This method is labor-intensive, expensive, and requires an extended time for subsequent laboratory analysis of collected samples. As a result, Method 23 measurements are made infrequently only for compliance purposes and not for long- or short-term performance monitoring. Emerging technologies are being developed to provide semi-continuous monitoring or long-term sampling of PCDD/Fs and may have the potential to provide more information on PCDD/F source emissions than the relatively few samples required under federal or state regulations. However, the performance of these newly introduced technologies has not been evaluated in the United States to determine their relative operational capabilities.

The purpose of this verification test was to generate performance data on the RIMMPA-TOFMS emission monitoring system. The test was conducted at EPA's Research Triangle Park (RTP), North Carolina, campus over a period of two weeks in September 2005 and was supported by ARCADIS under a subcontract from Battelle. The accuracy and range of the RIMMPA-TOFMS were determined through comparisons to the standard Method 23 integrated sampling method for PCDD/Fs.[1] Other performance parameters such as data completeness and operational factors were determined from operator observations.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Dioxin Emission Monitoring Systems (EMSs)*,[2] and the *Quality Management Plan (QMP) for the ETV/AMS Center*.[3] As described in this report, the performance of the RIMMPA-TOFMS was to be evaluated in terms of

- Relative accuracy (RA),
- Range,
- Data completeness, and
- Operational factors (ease of use, maintenance, and consumables/waste generated).

RA and range was to be determined by comparing RIMMPA-TOFMS results to those from Method 23 reference samples collected simultaneously. Range was to be determined from measurements over a variety of defined operating conditions that produced differing levels of PCDD/Fs. Data completeness was assessed as the percentage of maximum data return achieved by the RIMMPA-TOFMS over the test period. Operational factors were evaluated by means of operator observations and records of needed maintenance, vendor activities, and expendables used.

3.2 Experimental Setup

3.2.1 Test Facility

A 2.94 thousand British thermal unit per hour, 3-Pass Wetback Scotch Marine Package Boiler (SMPB), manufactured by Superior Boiler Works, Inc., and located at the EPA RTP facility, was used for the verification test. This boiler (Figure 3-1) is capable of firing natural gas or a variety of fuel oils. In this test, the oil burner was used; this burner is a low-pressure, air-atomizing nozzle that delivered a fine spray at an angle that ensured proper mixing with the air stream. The boiler has 33 square meters of heating surface and generates up to 1,090 kilograms per hour of saturated steam at pressures up to 15 pounds per square inch. Fuel flows were measured with a liquid volume totalizer, and stoichiometric ratios were verified through dioxide (O_2) and carbon dioxide (CO_2) emission concentrations.

During this verification test, the SMPB was fully instrumented with continuous emission monitors (CEMs) for a variety of species including O_2, carbon monoxide (CO), CO_2, water (H_2O), and

Figure 3-1. Wetback Scotch Marine Package Boiler

hydrogen chloride (HCl). Continuous emission monitoring of chemical species was performed with two shared CEMs for the packaged boiler facility. One CEM bench included four gas analyzers: high-range CO, low-range CO, O_2, and CO_2. HCl was measured by a second self-contained bench-scale CEM system (Bodenseewerk), which uses an Altech Hot/Wet (HW) sampling system and a Perkin-Elmer MCS-100 Infrared Multi-Component Analyzer. The MCS is capable of measuring up to eight compounds simultaneously, using gas filter correlation and single-beam dual-wavelength techniques. The HW probe assembly samples flue gases, while maintaining temperatures at elevated levels. The flue gas from the unit passes through a manifold to an air pollution control system (APCS) consisting of a natural-gas-fired secondary combustion chamber, a fabric filter, and an acid gas scrubber to ensure proper removal of pollutants. All emission measurements are taken prior to the APCS. The SMPB facility was modified prior to testing to accommodate all the requirements of the verification test. These modifications included the addition of a section of duct equipped with several sampling ports at the exit of the

boiler to allow for the simultaneous installation of multiple dioxin EMSs and operation of duplicate Method 23 sampling trains. Figure 3-2 shows a schematic illustration of the duct, identifying the sampling locations for the reference sample trains and the RIMMPA-TOFMS. As this figure shows, one Method 23 train sampled from a port upstream in the flue gas flow from the RIMMPA-TOFMS's sampling port, and the other sampled downstream.
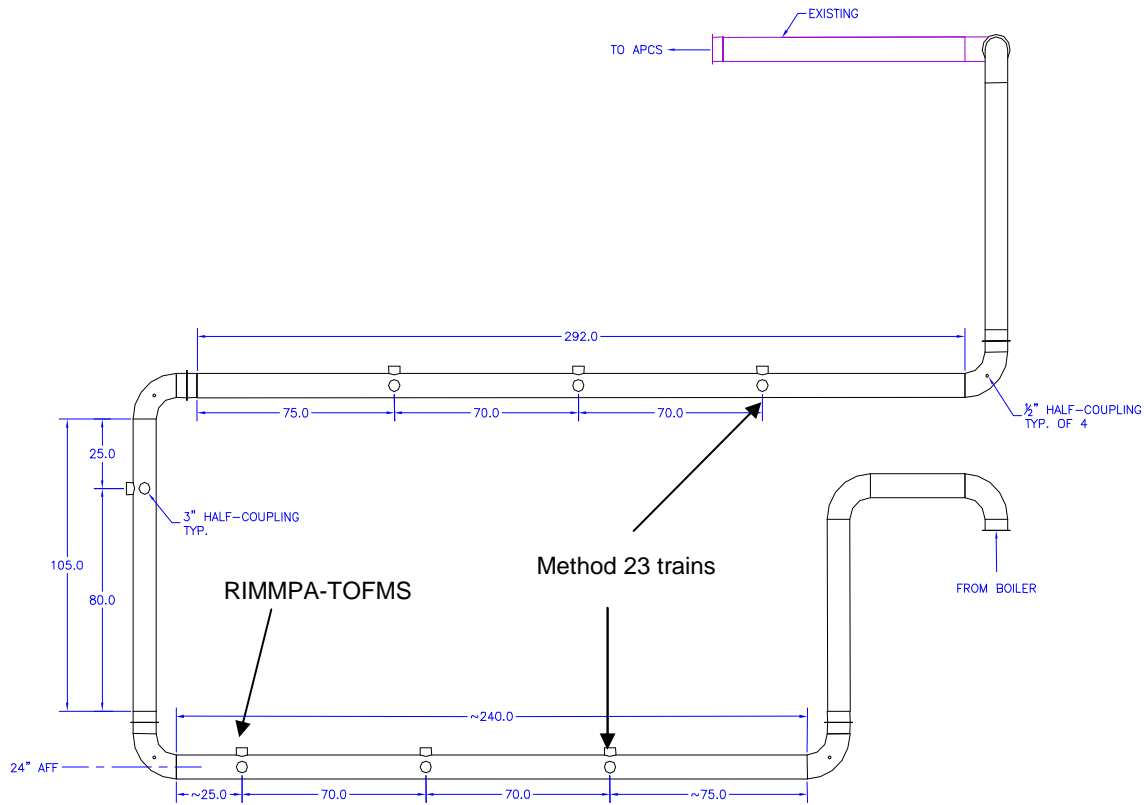
Figure 3-2. Illustration of Flue Gas Duct with Sampling Locations

A surrogate chlorinated chemical (1,2-dichlorobenzene) and a source of metal atoms (copper naphthenate) were added to the boiler fuel to promote PCDD/F formation for the emission monitoring system (EMS) testing.[4] A surrogate feed system was designed to safely tap the surrogate feed line to the fuel line just before the burner nozzle. The feed system consisted of a 37-liter pressurized stainless steel tank, in which the surrogate and the copper naphthenate were mixed.

Values for the stack gas composition from the SMPB for each test run conducted during the verification test are presented in Section 6.1 of this verification report.

3.2.2 Reference Samples

Reference samples were collected and analyzed for PCDD/F using Method 23, with the following modifications established before any sample collection took place:

- Analysis was completed by high-resolution gas chromatography/low-resolution mass spectrometry.

- Mass locking was not used with the low-resolution mass spectrometry.

- The front and back halves of the reference samples were extracted and analyzed together rather than separately.

- The internal, surrogate, and recovery standards included several that were not required in the standard method.

- Extraction procedures called for in Method 23 were modified to allow more efficient extraction of mono- through tri-chlorinated dioxins and furans.

ARCADIS collected the reference method samples and coordinated their analysis, which was conducted by EPA staff at the EPA RTP facility. To minimize potential bias caused by interlaboratory analysis differences, the RIMMPA-TOFMS samples were also analyzed by EPA staff. EPA staff ensured that the analytical instrumentation was calibrated and the samples were analyzed according to the requirements of the modified Method 23 and that the appropriate QA/quality control (QC) activities were conducted according to the method. Records of all calibrations and sample analyses were provided to Battelle and are maintained in the test files.

3.2.2.1 Reference Sample Collection

As shown in Figure 3-2, the Method 23 samples were collected at the two extreme locations of the stack gas sampling section, to bracket the locations of the technologies being evaluated in this verification test. The reference method sampling included pre-spiking the XAD-2 traps with carbon-13 labeled PCDD/F pre-sampling surrogates. Both sampling trains consisted mainly of a heated probe, heated box containing a cyclone and a filter, water-cooled condenser, water-cooled XAD-2 cartridge, impinger train for water determination, leak-free vacuum line, vacuum pump, and a dry gas meter with flow control valves and vacuum gauge. Temperatures were measured and recorded in the hot box (set at 125°C), at the impinger train outlet, at the XAD-2 cartridge outlet (maintained to be below ambient temperature), and at the inlet and outlet of the dry gas meter. Leak checks were conducted at the beginning and end of each sample run. Prior to sampling, all glassware, probe materials, glass wool, and aluminum foil were cleaned following the Method 23 cleaning procedure.

3.2.2.2 Sample Recovery

Following completion of each test run, each sampling train was recovered in a clean area, and the cleanup procedure began as soon as the probe was removed from the sample source location. During the transportation between the test facility and the designated recovery area, both ends of the heated probe and openings of the impinger assembly were sealed with aluminum foil or glass caps.

The front-half and back-half trains were recovered separately but analyzed together since no gas/solid phase PCDD/F speciation was required for this verification test. The probe and front half of the filter housing for each sample train were rinsed with acetone followed by dichloro-methane and collected in a single 250-milliliter (mL) amber jar. The probe and front-half filter housing were then rinsed with toluene and collected in a separate 250-mL amber jar. The filter was recovered and placed in a Petri dish sealed with Teflon tape.

The back-half sample trains, which consisted of an XAD-2 cartridge, the back-half filter housing, glass connection, and condenser, were recovered separately. The XAD-2 resin cartridge from each train was capped at both ends and wrapped in aluminum foil during transport. As with all sample fractions, the XAD-2 resin cartridges remained refrigerated during storage and transport. The back-half glassware was rinsed and collected in the same way as the front-half rinses. The solvent rinse jars for both the front- and back-half sample trains were capped with Teflon-lined caps, sealed with Teflon tape to prevent leakage, and stored in a refrigerated space before being sent for analysis.

3.2.3 Installation and Operation

Figure 3-2 shows an illustration of the duct indicating the locations of the Method 23 reference sampling ports and the location of the RIMMPA-TOFMS sampling port. The flue gas was exhausted through an insulated duct with an internal diameter of approximately 20 centimeters. The duct was modified prior to testing to accommodate the installation and simultaneous operation of multiple EMS technologies in addition to sampling ports for collecting Method 23 reference samples.

During testing, a sampling probe was used to draw sample gas from the duct into a heated sample line approximately 10 meters in length that was used to deliver the flue gas from the duct to the RIMMPA-TOFMS. The PCDD/Fs in the sample gas were collected on Tenax resin. After collection, the Tenax was heated, releasing the PCDD/Fs, which were subsequently introduced to the RIMMPA-TOFMS for analysis.

3.3 Test Design

Relative accuracy, range, data completeness, and operational factors for the RIMMPA-TOFMS were evaluated.

3.3.1 Relative Accuracy

The RA of the RIMMPA-TOFMS was evaluated by comparing its results to simultaneous results obtained by reference samples of the flue gas collected using Method 23. During the verification test, a series of nine Method 23 runs were conducted using duplicate Method 23 trains. The Method 23 trains sampled from ports located at each end of the sampling region where the RIMMPA-TOFMS was installed, as shown in Figure 3-2. The reference samples were recovered and submitted for analysis by the modified version of Method 23 described in Section 3.2. The PCDD/F concentrations determined by the reference methods were compared to corresponding results from the RIMMPA-TOFMS, averaged over the period of each Method 23 run. During each of the runs, the boiler operation was maintained as constant as possible. However, the duration of the sampling periods and the operating conditions of the boiler were changed from run to run to provide a range of conditions under which the RIMMPA-TOFMS was evaluated. Two sets of operating conditions were used for the runs to generate expected high and low dioxin concentrations. Runs of various durations were conducted under each set of operating conditions. Sampling periods of four hours were used to assess short-term accuracy, whereas long-term accuracy was assessed from composite samples collected over two 8-hour sampling periods on successive days (i.e., totaling 16 hours per sample). Table 3-1 shows the sampling durations and

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boiler operating conditions for each of the nine runs. Two Method 23 trains were used to collect each reference sample during each run. These trains sampled isokinetically from a single point in the gas flow, with one of the trains sampling at each end of the sampling region.

Upon completion of each run, the Method 23 trains were dismantled for sample recovery in the field by ARCADIS staff, and all collected sample fractions were logged and stored for transfer to the analytical laboratory. Subsequent to analysis, ARCADIS reviewed the data and reported final PCDD/F concentrations from all trains in units of toxic equivalents per dry standard cubic meter (TEQ/dscm), corrected to 7% O_2. The results from the simultaneously collected Method 23 trains were used to assess the degree of PCDD/F loss (if any) in the duct between the two reference method sampling ports. Unless discrepancies of greater than 30% were observed between the reference samples collected simultaneously for total measured TEQs, the results from the reference method samples were averaged together to produce the final reference data used for comparison to the RIMMPA-TOFMS results. If discrepancies of greater than 30% were observed, the data were flagged and the samples treated as independent samples for comparison to the RIMMPA-TOFMS. Discussion of the results of these comparisons is presented at the start of Chapter 6.

Table 3-1. Test Run Summary

Date	Test Run	Sampling Duration	Expected Dioxin Concentration[a]
9/12/05	1	4 hours	Low
9/13/05	2	4 hours	Low
9/14/05 & 9/15/05	3,4	16 hours (2 x 8 hours)	High
9/16/05	5	4 hours	High
9/17/05	6	4 hours	High
9/18/05 & 9/19/05	7, 8	16 hours (2 x 8 hours)	Low
9/20/05	9	8 hours	High

[a] Expected concentrations based on results of baseline testing. "High" corresponds to expected total PCDD/F TEQ of roughly 5-10 ng TEQ/dscm, and "low" corresponds to expected concentrations of roughly 1-2 ng TEQ/dscm.

3.3.2 Range

Range was to be assessed in terms of RA over the range of measured dioxin concentrations and sampling periods. The reference method samples were collected over a range of expected PCDD/F concentrations to assess the degree of agreement of the RIMMPA-TOFMS with the reference method. Based on results from baseline testing of the boiler conducted prior to the verification test, the dopant injection rate and firing conditions were changed for different test runs to achieve different expected PCDD/F concentrations (i.e., high or low concentration). Additionally, the duration of the test runs was varied to achieve a range of sampling periods from 4 to 16 hours. During each test run, the flue gas HCl level was used as an indicator of the

expected PCDD/F concentrations in the flue gas and the dopant injection rate was varied to achieve different expected PCDD/F levels for the test runs.

3.3.3 Data Completeness

Data completeness was assessed based on the overall data return achieved by the RIMMPA-TOFMS. It was reported in terms of the percentage of acceptable samples collected during the verification test and in terms of percentage of time that the RIMMPA-TOFMS system was collecting samples compared with the Method 23 sampling trains.

3.3.4 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, and repair requirements were evaluated based on observations recorded by Battelle and facility staff, and in some cases by the vendor. A laboratory record book maintained at the test facility was used to enter daily observations on these factors.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the QMP for the AMS Center[3] and the test/QA plan[2] for this verification test except as noted in Section 4.1.2.

4.1 Audits

4.1.1 Performance Evaluation Audits

A performance evaluation (PE) audit was conducted to assess the quality of the critical measurements associated with the reference sampling and analysis methods. In the PE audit, critical measurements were checked by comparing them with appropriate National Institute of Standards and Technology (NIST)-traceable standards, when available. Table 4-1 shows the critical measurements that were audited, the audit procedures and acceptance criteria for the audit comparisons, and the audit results. An initial PE audit of the Method 23 gas flow rate did not meet the acceptance criterion. However, the flow transfer standard used for the audit was found to be working improperly and therefore not appropriate for comparison. The audit was repeated using a different flow transfer standard. The results of the second audit are presented in Table 4-1.

The PE audit of the internal standard recovery was performed by spiking one blank Method 23 train with an NIST-traceable dioxin solution, provided by Battelle, and independent of the internal standards used for the reference method samples. The spiked train was not used to collect a flue gas sample, but was recovered and analyzed in the same manner as the other Method 23 trains; and the analytical results were compared with the spike amount to assess recovery. The target criteria for this PE audit were 40 to 130% recovery of the internal standards for the tetra- through hexachlorinated compounds and 25 to 130% for the hepta- and octachlorinated compounds. The actual recoveries were well within these limits, ranging from 101% to 120% for all compounds.

Table 4-1. Methods and Acceptance Criteria for PE Audit Measurements

Critical Measurement	PE Audit Method	Acceptance Criteria	Audit Results
Method 23 gas sample flow rate	Compare to independent flow measurement device	±5%	2.2 – 3.4% Pass
Method 23 stack gas temperature	Compare to independent temperature measurement device	±2% absolute temperature	0.0 – 0.55% Pass
Barometric pressure	Compare to independent pressure gauge	±1% absolute pressure	0.4% Pass
Dioxin internal standard recovery	Method spike with an independent dioxin standard	40 to 130% for tetra-through hexachlorinated compounds; and 25 to 130% for hepta- and octachlorinated compounds	101 – 120% Pass
Dioxin surrogate standard recovery	Field spike with an independent dioxin standard	70 to 130% recovery	91 – 107% Pass

The PE audit of the surrogate standard recovery was performed by spiking one blank XAD-2 cartridge with an NIST-traceable dioxin surrogate standard solution provided by Battelle, and independent of the surrogate standards used for the reference method samples. This spiked cartridge was extracted and analyzed in the same manner as the other cartridges. The target criterion for this PE audit was 70 to 130% recovery of the surrogate standards. The actual recoveries were well within these limits, ranging from 91% to 107% for all compounds.

4.1.2 Technical Systems Audits

The Battelle Quality Manager performed a technical systems audit (TSA) on September 13 and 14, 2005, to ensure that the verification test was being performed in accordance with the AMS Center QMP,[3] the test/QA plan,[2] published reference methods, and any standard operating procedures used by the test facility. In the TSA, the Battelle Quality Manager toured the test site, observed Method 23 sampling and sample recovery, inspected documentation of reference sample chain of custody, and reviewed laboratory record books. The Quality Manager also checked standard certifications and Method 23 data acquisition procedures. A TSA report was prepared, including a statement of no significant findings or corrective actions were identified.

A single deviation from the test/QA plan was documented as a result of the TSA. This deviation involved differences between the extraction procedures used by the EPA laboratory and the procedures in Method 23. The EPA laboratory used modified procedures that allowed for the extraction and quantification of lower chlorinated PCDD/PCDFs (e.g., mono- through trichlorinated PCDD/PCDFs). The modified procedures did not impact the quality of the data for this verification test.

Additionally, the EPA AMS Center Quality Officer conducted a TSA on September 14, 2005. There were no significant findings or correctives identified during that audit.

4.1.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager, or designee, traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.2 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Section 3.3.4 of the QMP for the ETV AMS Center.[3] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.3 Data Review

Data generated during this test were reviewed by a Battelle technical staff member within two weeks of generating the data. The reviewer was familiar with the technical aspects of the verification test, but was not the person who generated the data. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the RA, range, and data completeness of the RIMMPA-TOFMS during this verification test.

5.1 Relative Accuracy

The RA of the RIMMPA-TOFMS with respect to the reference sample results was assessed to be as a percent bias, using Equation (1):

$$RA = \frac{\left(\left|\bar{d}\right| + t_{0.975}\frac{S_d}{\sqrt{n}}\right)}{\overline{RM}} \times 100 \tag{1}$$

where:

$\left|\bar{d}\right|$ = the absolute value of the mean of the differences between the RIMMPA-TOFMS and reference sample results for each test run,

$t_{0.975}$ = the t-value,

S_d = the standard deviation of the differences between the RIMMPA-TOFMS and reference sample results for each test run, and

$\overline{RM}$ = the mean of the reference method results.

5.2 Range

The measurement range of the RIMMPA-TOFMS was to be reported in terms of its accuracy relative to the reference method under the variety of boiler operating conditions (i.e., PCDD/F concentrations) and sampling durations used during the test runs.

5.3 Data Completeness

Data completeness was calculated as the percentage of the total possible data return over the entire field period. The cause of any substantial incompleteness of data return was established from operator observation or vendor records and noted in the discussion of data completeness results.

5.4 Operational Factors

Operational factors were evaluated based on operator observations and information provided by the vendor. No statistical comparisons of operational factors were made.

Chapter 6
Test Results

The results of the verification test of the RIMMPA-TOFMS are presented below for each of the performance parameters. Test runs were designed to be either 4- or 8-hour periods at high or low PCDD/F concentrations. Table 6-1 presents a summary of the test runs that were completed during the verification test along with a summary of the flue gas conditions.

Table 6-1. Summary of Test Runs and Testing Conditions

Test Run	Date	Duration (hours)	Expected PCDD/F Conc.	Stack Temp. (^{o}F)	O_2 Conc. (%)	CO_2 Conc. (%)	H_2O Conc. (%)
1	9/12/2005	4	Low	312.0	4.28	12.85	11.0
2	9/13/2005	4	Low	313.5	4.72	12.77	10.8
3	9/14/2005[a]	8	High	305.5	4.30	12.98	11.1
4	9/15/2005[a]	8	High	309.5	5.38	12.22	11.0
5	9/16/2005	4	High	319.0	5.04	12.31	11.0
6	9/19/2005	4	High	316.5	5.09	12.23	10.8
7	9/20/2005[a]	8	Low	303.0	4.8	12.36	11.9
8	9/21/2005[a]	8	Low	305.5	3.12	13.35	11.7
9	9/22/2005	8	High	315.5	3.38	13.04	11.1

[a]   The samples for Test Runs 3 and 4 and 7 and 8 were collected on a single cartridge for the RIMMPA-TOFMS and analyzed as a single 16-hour test run.

Table 6-2 lists the reference method results for each test run. The results are presented for the Method 23 samples that were collected at the first sampling port (Port 1) and the seventh sampling port (Port 7). The top portion of the table shows the readings for individual dioxin and furan congeners. The lower portion of the table summarizes the TEQ values for each test run according to dioxins, furans, and the total. All results were corrected to 7% O_2.

Table 6-2. Reference Method 23 Results

Compound	Concentration [ng/dscm @ 7% O_2]																	
	Test Run 1		Test Run 2		Test Run 3		Test Run 4		Test Run 5		Test Run 6		Test Run 7		Test Run 8		Test Run 9	
	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7
2,3,7,8 - TeCDD	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
1,2,3,7,8 - PeCDD	0.2	0.2	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.1	0.1
1,2,3,4,7,8 - HxCDD	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.2
1,2,3,6,7,8 - HxCDD	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.1	0.1	0.1	0.1	0.2	0.2
1,2,3,7,8,9 - HxCDD	0.1	0.1	0.0	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1
1,2,3,4,6,7,8 - HpCDD	0.5	0.5	0.4	0.4	1.6	1.8	2.0	2.0	1.8	1.4	1.4	1.3	0.4	0.4	0.3	0.4	1.0	1.1
1,2,3,4,6,7,8,9 - OCDD	0.8	0.8	0.7	0.6	3.0	3.3	4.6	4.5	3.2	2.6	3.1	2.8	0.7	0.6	0.5	0.6	1.8	1.8
2,3,7,8 - TeCDF	0.7	0.6	0.4	0.4	2.5	2.5	2.0	2.3	1.8	1.6	1.6	1.4	0.4	0.4	0.2	0.2	1.6	1.5
1,2,3,7,8 - PeCDF	0.8	0.8	0.6	0.5	3.2	3.4	2.9	3.4	3.0	2.4	2.3	2.2	0.6	0.6	0.4	0.4	2.1	2.0
2,3,4,7,8 - PeCDF	1.8	1.8	1.3	1.1	6.8	7.2	6.2	7.1	6.5	5.2	5.4	4.9	1.3	1.2	1.0	0.9	4.6	4.4
1,2,3,4,7,8 - HxCDF	1.6	1.6	1.2	1.1	6.1	6.8	6.5	7.3	7.2	5.7	5.7	5.3	1.6	1.5	1.2	1.2	4.5	4.6
1,2,3,6,7,8 - HxCDF	1.1	1.2	0.9	0.8	4.8	5.3	4.9	5.6	5.4	4.2	4.3	4.1	1.2	1.1	0.9	0.9	3.4	3.4
2,3,4,6,7,8 - HxCDF	0.9	0.9	0.6	0.5	3.3	3.7	3.2	3.8	3.6	2.7	3.0	2.8	0.8	0.7	0.6	0.6	2.3	2.3
1,2,3,7,8,9 - HxCDF	0.1	0.1	0.0	0.0	0.3	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.2	0.2
1,2,3,4,6,7,8 - HpCDF	3.2	3.5	2.6	2.4	12.7	13.7	15.9	16.7	15.5	12.2	13.3	12.5	3.7	3.4	2.7	2.8	9.6	9.7
1,2,3,4,7,8,9 - HpCDF	0.4	0.5	0.3	0.3	2.0	2.2	2.1	2.2	2.1	1.6	1.4	1.4	0.4	0.3	0.3	0.3	1.4	1.5
1,2,3,4,6,7,8,9 - OCDF	1.0	1.3	0.9	0.9	6.2	6.5	8.6	7.9	6.7	5.3	4.8	4.5	1.1	1.0	0.9	0.8	4.3	4.1
	Concentration [ng TEQ/dscm @ 7% O_2]																	
Total PCDD	0.22	0.23	0.17	0.14	0.42	0.46	0.42	0.44	0.42	0.35	0.31	0.29	0.11	0.10	0.10	0.07	0.23	0.25
Total PCDF	1.41	1.39	1.03	0.88	5.39	5.76	5.13	5.82	5.41	4.28	4.43	4.08	1.13	1.07	0.83	0.81	3.71	3.60
Total PCDD/F	1.63	1.62	1.19	1.01	5.81	6.22	5.55	6.26	5.84	4.63	4.74	4.37	1.24	1.17	0.93	0.87	3.94	3.85

The TEQ values for each test run are also presented in Table 6-3, along with the calculated percent difference between the results from the two Method 23 trains. With the exception of the TEQ results for dioxins in Test Run 8, the results from the two trains are within 30%, indicating no substantial biases based on the sampling port locations. Even for Test Run 8, the large relative difference observed for the PCDDs originates from because of the low absolute concentrations of PCDDs in that run. Since the PCDFs for that test run agree well for the two trains, indicating that there was no substantial bias between the ports for that run, the average of the results was used in all cases for evaluation of the RIMMPA-TOFMS.

Table 6-3. Results from the Method 23 Reference Samples

Test Run	Dioxin TEQ			Furan TEQ			Total PCDD/F TEQ		
	Port #1	Port #7	% Diff.	Port #1	Port #7	% Diff.	Port #1	Port #7	% Diff.
1	0.22	0.23	-5.5%	1.41	1.39	0.3%	1.63	1.62	0.6%
2	0.17	0.14	17.7%	1.03	0.88	16.1%	1.19	1.01	16.4%
3	0.42	0.46	-7.5%	5.39	5.76	-6.8%	5.81	6.22	-6.8%
4	0.42	0.44	-5.3%	5.13	5.82	-12.0%	5.55	6.26	-12.0%
5	0.42	0.35	18.9%	5.41	4.28	23.1%	5.84	4.63	23.1%
6	0.31	0.29	6.6%	4.43	4.08	8.1%	4.74	4.37	8.1%
7	0.11	0.10	12.0%	1.13	1.07	6.1%	1.24	1.17	5.8%
8	0.10	0.07	36.4%	0.83	0.81	6.3%	0.93	0.87	6.7%
9	0.23	0.25	-10.0%	3.71	3.60	2.4%	3.94	3.85	2.3%

6.1 Relative Accuracy

No quantifiable results were obtained from the RIMMPA-TOFMS during the verification test so no estimate of relative accuracy could be made. Various difficulties associated with sampling and analysis using the RIMMPA-TOFMS arose during the verification testing. A discussion of these problems is presented in Section 6.4. Additionally, Chart 2 in Appendix A shows the congener intensities detected by the RIMMPA-TOFMS. IDX Technologies was able to detect and identify several of the highly chlorinated dioxin congeners, but was not able to get the results of the determination because of the influence of impurities that existed close to the dioxin mass numbers. Appendix A is presented as received by Battelle from IDX Technologies and has not been edited for inclusion in this report.

6.2 Range

No evaluation of range could be assessed during this verification test, for the reasons noted above under Relative Accuracy.

6.3 Data Completeness

RIMMPA-TOFMS sampling took place for a total of 42% of the total duration of the test runs. Sampling was achieved during portions of seven of the nine test runs. No RIMMPA-TOFMS sampling took place during two of the nine test runs.

Although sampling was successfully conducted during several of the sampling periods, no quantitative data were generated from the RIMMPA-TOFMS to characterize PCDD/F concentrations in the flue gas.

6.4 Operational Factors

Table 6-4 summarizes the activities performed on the RIMMPA-TOFMS system during the verification test, as well as the time required to perform those activities, and the amount of down time experienced to complete those activities. Reported times for instrument start-up, calibration, testing preparations, and instrument shut-down are approximations based on operator experience. Since these operations are relatively complex and may vary depending on day-to-day variability in instrument operation, it is difficult to quantify exactly the time required to complete the necessary activities on a daily basis. Delays in start times of individual test runs were not included in the estimated times although the RIMMPA-TOFMS operator may have continued to perform activities until each test run commenced.

6.4.1 Ease of Use

Ease of use of the RIMMPA-TOFMS was not easily established during this verification because of the difficulties encountered with the sampling system. Operation of the RIMMPA-TOFMS during this verification test was conducted by a group of four representatives from IDX. It was not apparent that the RIMMPA-TOFMS was operated under routine conditions because of problems encountered during testing. Extensive maintenance activities meant that operators were simultaneously working on separate portions of the RIMMPA-TOFMS during several periods during the test. At least one operator was required during sample collection and analysis to ensure proper operation. In general, operation of the RIMMPA-TOFMS requires extensive knowledge of sophisticated laser systems and mass spectrometers including advanced electronic data collection and manipulation equipment.

6.4.2 Maintenance

Significant maintenance activities were performed on the RIMMPA-TOFMS during this verification test. This maintenance was the result of contamination issues and failures in the sampling system employed for the verification test. These maintenance activities are not expected to be routine, but resulted in the loss of significant amount of testing data while the activities were performed.

Table 6-4. Activity Summary for RIMMPA-TOFMS

Date	Duration	Activity
9/12/05	Approximately 9 hours	• Instrument start-up, calibration, and testing preparations. • Sample collection for 240 minutes. • Sample desorption and analysis
9/13/05	Approximately 10 hours	• Signal from the RIMMPA-TOFMS indicated that the sampling system had become contaminated. • Glass wool from the sorbent tube became dislodged from the tube and was introduced into the sample delivery lines along with a portion of the TENAX resin. • Representatives from IDX technologies cleaned the sampling system and the sample delivery system, including the replacement of the pulsed nozzle for sample introduction. • No sample collected because of change of high-temperature gas valve unit.
9/14/05	Approximately 10 hours	• Signal from the RIMMPA-TOFMS still indicated contamination in the system. Sampling lines were cleaned. • Modifications were made to the sampling system to bypass the Adsorption and Heat Desorption (AHD) unit and use a temporary sampling system. • Sample collected for 90 minutes near end of test run.
9/15/05	Approximately 12 hours	• Stainless steel sampling lines and sample delivery lines were replaced. The TENAX was cleaned and replaced in the sampling system with new glass wool. • No sample collected because of change of high-temperature gas valve unit.
9/16/05	Approximately 10 hours	• Instrument start-up, calibration, and testing preparations. • Sample collection for 90 minutes. • Sample desorption and analysis. • Sample collection for 70 minutes. • Sample desorption and analysis.
9/19/05	Approximately 9 hours	• Instrument start-up, calibration, and testing preparations. • Sample collection. • Sample desorption and analysis.
9/20/05	Approximately 12 hours	• Instrument start-up, calibration, and testing preparations. • An air leak was discovered and corrected prior to testing. • Sample collection for 120 minutes. • Sample desorption and analysis. • Sample collection for 240 minutes. • Sample desorption and analysis.
9/21/05	Approximately 12 hours	• Sample inlet reconfigured to place TENAX resin closer to the filter. • Instrument start-up, calibration, and testing preparations. • Sample collection for 120 minutes. • Sample desorption and analysis. • Sample collection for 200 minutes. • Sample desorption and analysis.
9/22/05	Approximately 12 hours	• Sampling approach was modified to decrease the amount of TENAX resin used and decrease the sampling duration. • Instrument start-up, calibration, and testing preparations. • Sample collection for 15 minutes. • Sample desorption and analysis. • Sample collection for 15 minutes. • Sample desorption and analysis.

NA= Not applicable. Sample installation and recovery are performed outside of sampling period.

6.4.3 Consumables/Waste Generation

Operation of the RIMMPA-TOFMS required use of compressed helium as a carrier gas for the supersonic expansion, TENAX and glass wool for sample collection, as well as laser dye and solvent for operation of the laser system. Only one batch of dye solution was required during this verification test, which is treated as chemical waste for disposal.

Chapter 7
Performance Summary

Table 7-1 presents a summary of the results of the verification of the RIMMPA-TOFMS system during this verification test.

Table 7-1. Summary of Verification Test Results for RIMMPA-TOFMS

Parameter Evaluated	Method of Evaluation	Results
Accuracy	Comparison to Method 23 reference samples	Analysis of the collected samples could not positively quantify PCDD/PCDFs.[a]
Range	Percent difference comparison to Method 23 reference samples	Analysis of the collected samples could not positively quantify PCDD/PCDFs.
Data completeness	Ratio of number of samples successfully collected to number of potential samples that could have been collected	• Samples were collected for 42% of the duration of the test runs. • Samples were collected during portions of seven of the nine test runs.
Ease of use	Operator observations	• Routine operation of the sampling system was not observed during this test. • Extensive training and experience with advanced knowledge of mass spectrometry and laser spectroscopy techniques is required for operation of the RIMMPA-TOFMS and interpretation of the results.
Maintenance	Operator observations	• Extensive maintenance was required during the verification test to rectify a number of difficulties encountered during sampling.
Consumables/wastes generated	Operator observations	• Compressed helium was required during testing to deliver collected sample from the sorbent trap to the RIMMPA-TOFMS. • TENAX and glass wool were used in the sorbent trap for collection of the gas samples. • Laser dye and solvent were used for operation of the RIMMPA-TOFMS laser system.

[a] See Chapter 6.

Chapter 8
References

1. U.S. EPA Method 23—*Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors*, U.S. Environmental Protection Agency, February 1991. Available at: http://www.epa.gov/ttn/emc/promgate/m-23.pdf.

2. *Test/QA Plan for Verification of Dioxin Emission Monitoring Systems (EMSs)*, Battelle, Columbus, Ohio, September 6, 2005.

3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

4. George C. Clark, Michael Chu, Dahman Touati, Barry Rayfield, Jon Stone, and Marcus Cooke, "A Novel Low-Cost Air Sampling Device (AmbStack Sampler) and Detection System (CALUX Bioassay) for Measuring Air Emissions of Dioxin, Furan, and PCB on a TEQ Basis Tested With a Model Industrial Boiler," *Organohalogen Compounds*, **40** (1999), 79-82.

Appendix A
IDX Technologies Summary Test Report

NOTE: This document was prepared by IDX Technologies and is published as received. This document was not edited or verified by Battelle.

ETV REPORT

IDX-Technologies

1. Introduction

As we have reported in many occasions in the world that we have succeeded in the development of RIMMPA (Resonance Ionization with the Multi-Mirror system Photon Accumulation)-TOFMS. By the development of it, we have achieved the 2 color 2 photon resonance ionization of tetra to octa chlorinated DDs and DFs with selective soft ionization of PCDD's and PCDF's isomers.

Thus, the ETV for us is to verify the technical results on RIMMPA-TOFMS.
We have adopted two countermeasures upon this current situation. The first countermeasure is to adopt an accumulation tube as a condenser for obtaining the high density sample gas and to use helium gas for desorbing it as carrier gas.
The second is to adopt the fixed wavelength laser to make the size compact and to realize easy operation and mobile-ability.

What we had achieved in the laboratory was to detect the PCDD's and PCDF's isomers of 2,3,4,7,8-PeCDF at 410 ppq sensitivity by changing the excitation wavelength and could detect only objective parent ion without any fragmentation.

We haven't reached, however, the stage to detect the PCDD's and PCDF's isomers in the real gas. This is one of the purposes of this ETV tests for us to establish the method and verify the on-site and rapid analysis method in the real gas from boiler.

2. Target

What we have targeted through ETV test this time was that after filtering, adsorbing and accumulating the exhausting gas into a TENAX column, desorption of PCDD's and PCDF's are carried under the specifically controlled temperature and then is loaded to RIMMPA-TOFMS with helium carrier gas. We aimed at the two kinds of analysis, one was the Congener analysis and the other was the Isomer analysis.

Here, we mean that the congeners analysis is to calculate the TEQ from the relation between the sum of the total ion signals of tetra to octa chlorinated DDs and DFs and that of the Method 23(M23). The sum of the total ion signals of tetra to octa chlorinated DDs and

DFs congener's ion is calculated as follows. Selecting and fixing an appropriate wavelength of excitation laser wavelength as 310.99nm, we can get all the tetra to octa chlorinated DDs and DFs congener's ion signals and sum up the amount of time variation.

And the isomer analysis is to calculate the TEQ from the correlation between the total amount of target isomer's ion signal and that of M23 signals. Setting the excitation laser wavelength for the target isomer and getting the isomer signal and integrating it by time, we can get the total amount of target isomers.

3. Test circumstances

Terms: Sep. 12 2005 to Sep. 22 2005

Place: U.S. Environmental Protection Agency, Research Triangle Park

Test facilities: A 2.94 MBtu/hr, 3-Pass Wetback Scotch Marine Package Boiler
  manufactured by Superior Boiler Works, Inc.,

(Details are in the ETV program report)

4. Test method

The schematic diagram of sampling is shown in Fig.1

The sampling steps are briefly divided into next four steps.

4.1 Adsorption

The exhausted gas flows in the <u>A</u>dsorption and <u>H</u>eat <u>D</u>esorption (AHD) unit from sampling port in flue gas duct heated at 160 degree C through sampling probe heated at 200 degree C, glass fiber filter and 5m heated sampling line (Teflon tube). At the AHD, PCDD's and PCDF's in the exhausted gas are adsorbed in the 105 degree C heated TENAX column. The exhausted gas is disposed lastly in APCS (Air Pollutant Control System) through Silica gel, NaOH solution and pump.

4.2 Helium Substitution

To remove nitrogen, oxygen and low boiling point organic compounds that remain in TENAX column, helium gas of 120 degree C is substituted for the gases in TENAX column of 105 degree C for 5 minutes with 3L/min.

4.3 Desorption

The column is heated up to 300 degree C after closing the entrance and exit of it. Keeping it for 10 minutes after the temperature rises up to 300 degree C, the objective gas in helium carrier gas is injected to RIMMPA-TOFMS at 200 degree C.

4.4 Analysis

Analysis of congeners and isomers by RIMMPA-TOFMS are carried out.
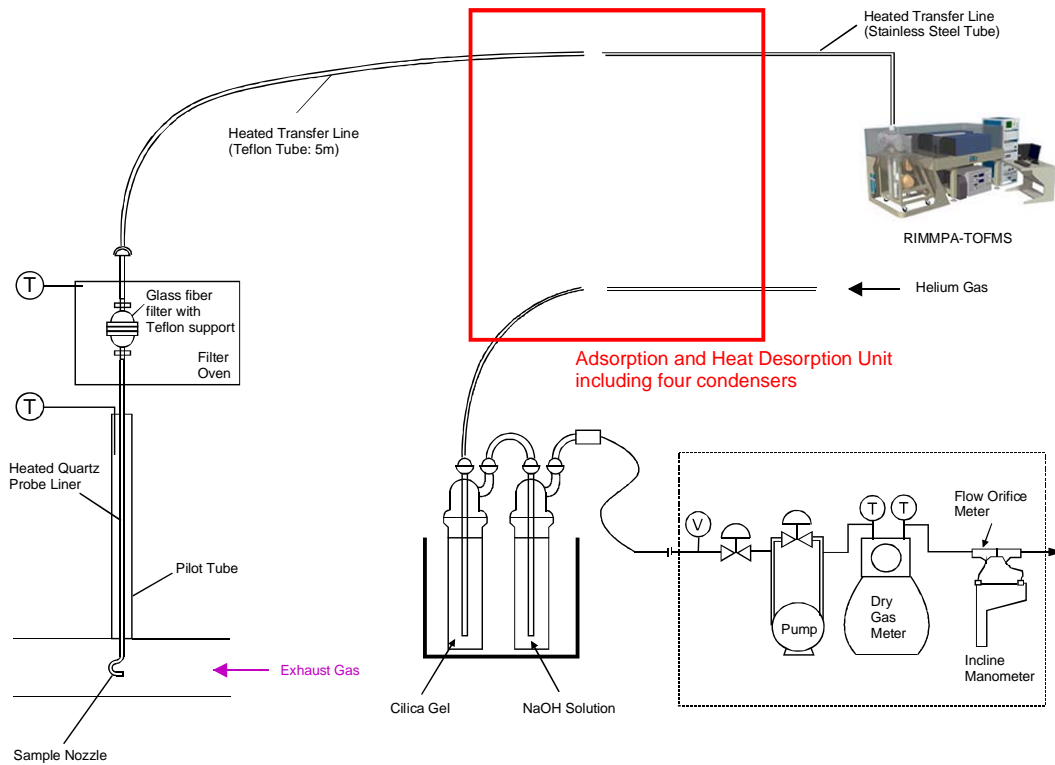
Fig.1   Schematic diagram of the sampling train, adsorption and heat
desorption unit, and measurement by RIMMPA-TOFMS

5. Test conditions

Chart 1 shows the test conditions of each day during ETV tests.

Chart 1

Test Number	Sampling			DXN-Desorption		Excitation Laser		Ionization Laser
	time [min]	rate [L/min]	volume [L]	temp. [deg.C]	flow rate [L/min]	Energy [mJ]	Wavelength [nm]	Energy [mJ]
9/12	240	2.739	657.36	300	1	3	310.99	0.1
9/14	90	4.85	436.5	280	1	3	310.99	0.1
9/16-#1	70	17.083	1195.81	300	1	3	310.99	0.1
9/16-#2	90	16.562	1490.58	300	1	3	310.99	0.1
9/19	240	15.19	3645.6	300	1	3	315.83	0.1
9/20-#1	120	13.76	1651.2	300	0.5	3	310.19	0.5
9/20-#2	240	12.51	3002.4	300	0.5	3	310.19	0.5
9/21-#1	120	17.19	2062.8	300	0.5	3	310.19	0.5
9/21-#2	200	19.3	3860	300	0.5	3	310.19	0.5
9/22-#1	15	16.19	242.85	300	0.5	3	310.19	0.5
9/22-#2	15	16.33	244.95	200-300	0.5	3	310.19	0.5

6. Test results

6.1 Congener Analysis Test Results

Chart 2 is the results of our ETV tests. The Test Number 9/19 is the result of isomer analysis and the other all are congener analysis. The values in the chart show the signal strengths of the dioxin congeners that RIMMPA-TOFMS detected. Although RIMMPA-TOFMS has succeeded in congener identification of several high-chlorinated dioxins, RIMMPA-TOFMS has not succeeded in determination of isomers due to the bad influence of impurities that exist close to dioxins in mass numbers.

Chart 2

	9/12	9/14	9/16-#1	9/16-#2	9/19	9/20-#1	9/20-#2	9/21-#1	9/21-#2	9/22-#1	9/22-#2
TeCDD						7.1		12.1			
PeCDD						6.1		5.1			
HxCDD											
HpCDD											
OCDD											
TeCDF	1.7										
PeCDF											
HxCDF											
HpCDF											
OCDF	1.3										

Blank=Not identified

6.2 Test result details

First half

The chart 3 below shows the results from Sep. 12 to Sep. 16.

Chart 3

	9/12	9/13	9/14	9/15	9/16
Sample transfer	5m Teflon tube		5m Teflon tube		5m Teflon tube
Adsorption	105 degree C	Pipe cleaning by solvent	105 degree C	Brand new pipe TENAX cleaning change of glass wool	105 degree C
Helium substitution	3L/min, 5min		3L/min, 5min		3L/min, 5min
		AHD unit cleaning		Improvement sampling unit	
Desorption	300 degree C		300 degree C		300 degree C
RIMMPA-TOFMS	310.99nm, 3mJ 213nm, 0.1mJ	New HTPD	310.99nm, 3mJ 213nm, 0.1mJ	Cleaning and change HTPD	310.99nm, 3mJ 213nm, 0.1mJ
Others	Preheating of He gas 200 degree C Congener analysis		preheating of He gas 200 degreeC Congener analysis		New He bomb Insert activate charcoal between TENAX column and He bonbe No preheating of He gas Congener analysis
Results	Fig.2-12 Lots of impurity TENAX decomposition Impossible to identify and determine	Abherence of TENAX in inside of HTPD Adherence of TENAX in the pipe	Fig13 same as 9/12 Fig14, 15 stains in the AHD unit	Higher volume of sampling rate by changing glass wool	Fig17, 18 spectrum quenching of m/z320, 345 No changes in the others Change from Helium to N_2 for cleaning Chamber baking

Sep. 12 2005

Figure 2 (Test number: 9/12) shows the mass spectrum of 270 to 500 measured by RIMMPA-TOFMS. The ion signal was obtained by integrated value of 3 minutes measurement. Although we recognized the PCDD's and PCDF's peaks, it was tough to identify and determine PCDD's and PCDF's because the spectra of other impurities overlapped the peak signals of the PCDD's and PCDF's. As indicated a and b in Fig.2, we detected the spectrum of impurities that adhere to the TENAX, the mass number of which increase by m/z 75 regularly, and the spectrum obstruct the measurements of PCDD's and PCDF's. It was thought as impurity in TENAX and it disturbs the PCDD's and PCDF's spectra.
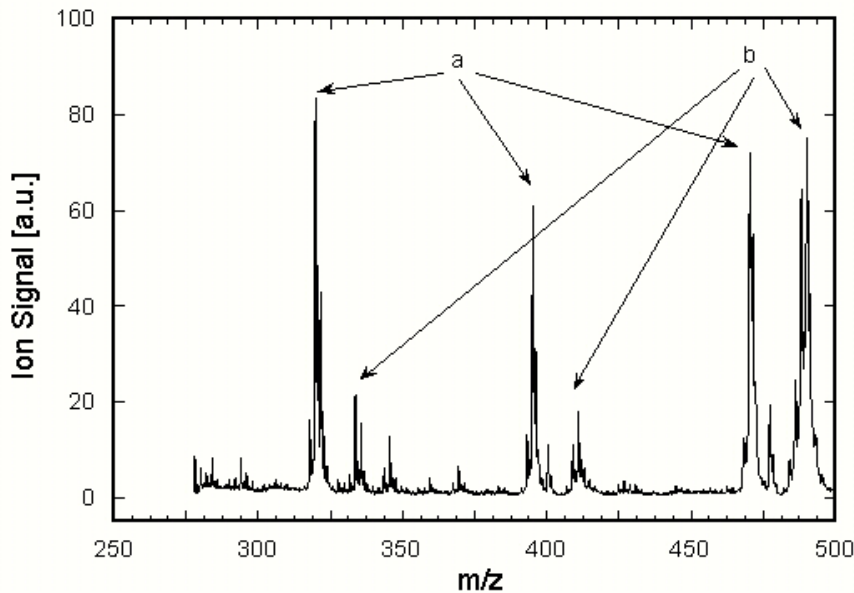
Fig.2 Mass spectrum (Test number: 9/12)

Figures 3 to 12 are the mass spectra which are expanded near PCDD's and PCDF's congeners. The indicated values are relative intensity of each peak normalized by M+2 ion signal in the case of TeCDF or M+4 ion signal in the case of OCDF. We recognized some differences in the intensity ratio between the observed one and that estimated from existence ratio of chlorine isotope. In the case of TeCDF, the observed ratios are 50.6/100 and 60.5/100, while the estimated ratios are 76/100 and 49/100. We assume that these differences might be caused by the spectra overlapping.
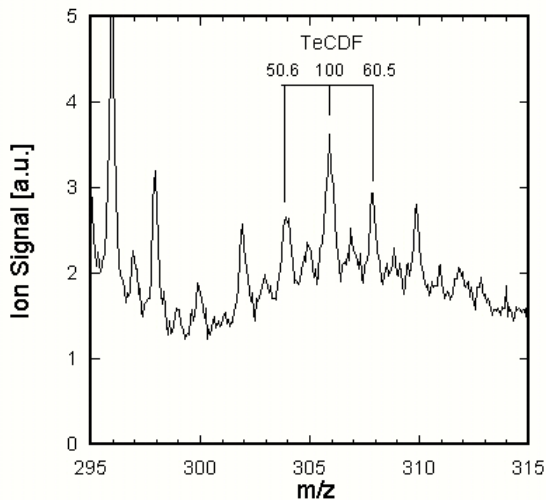
Fig.3 TeCDF

Fig.4 TeCDD

A-7
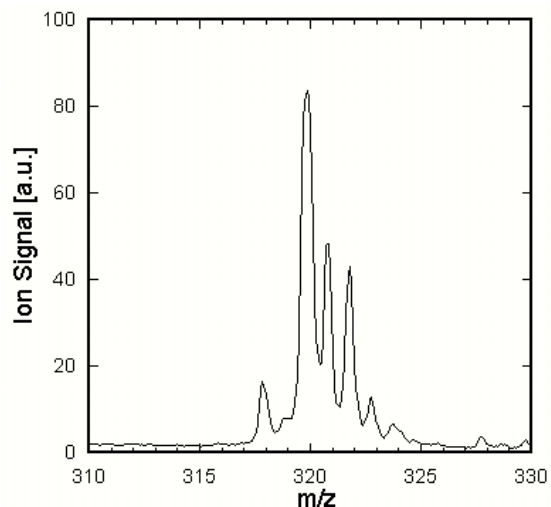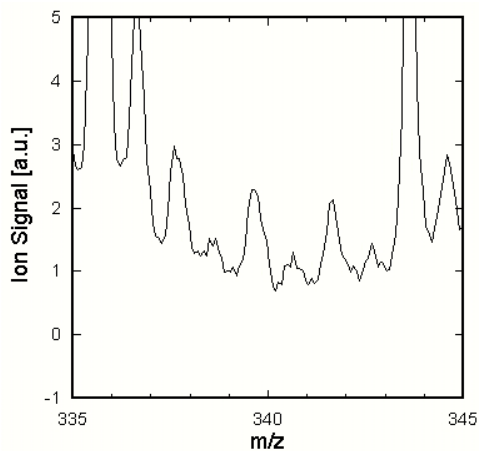
Fig.5 PeCDF
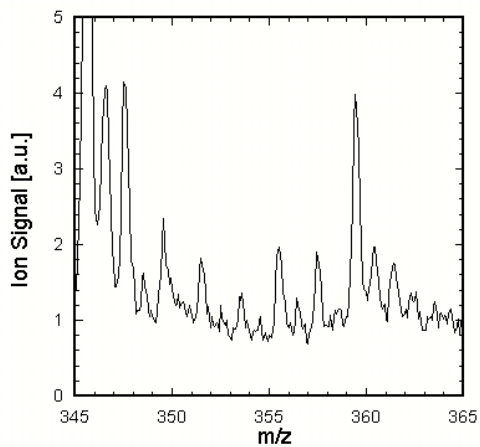
Fig.6 PeCDD
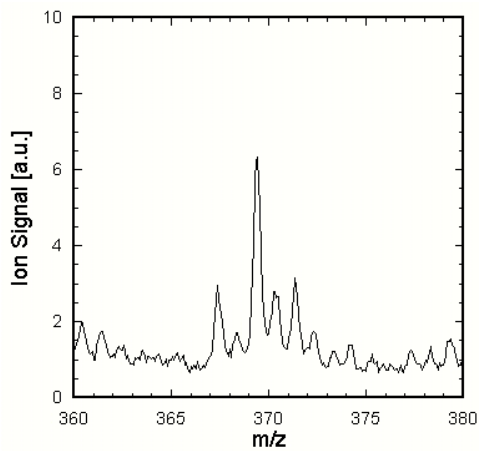
Fig.7 HxCDF
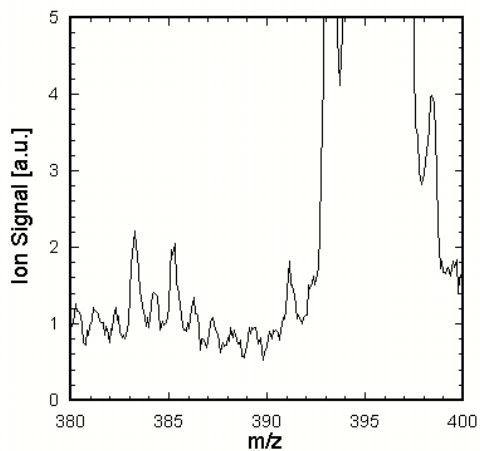
Fig.8 HxCDD
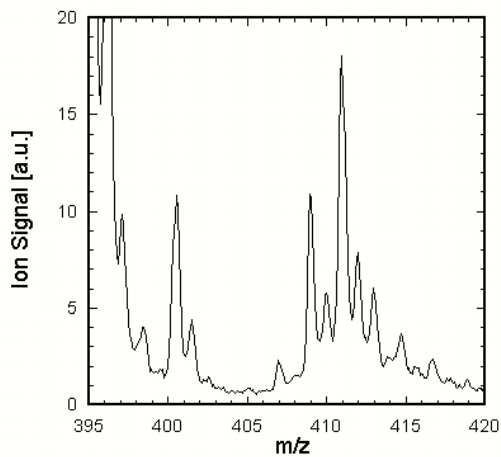
Fig.9 HpCDF
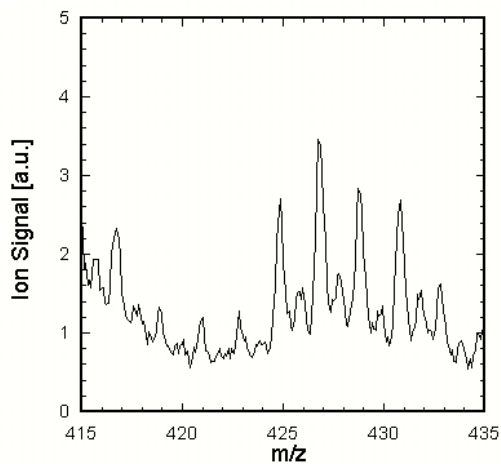
Fig.10 HpCDD
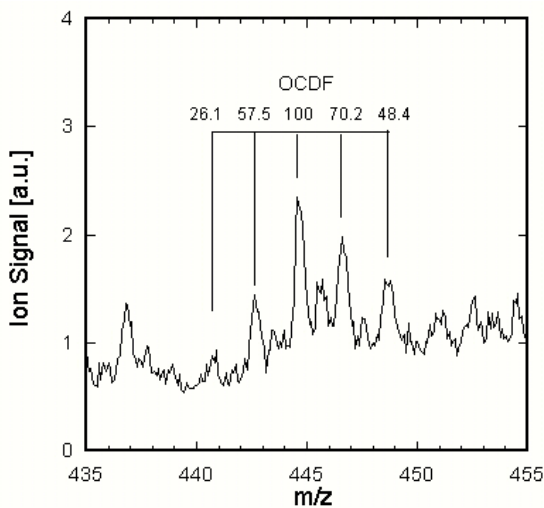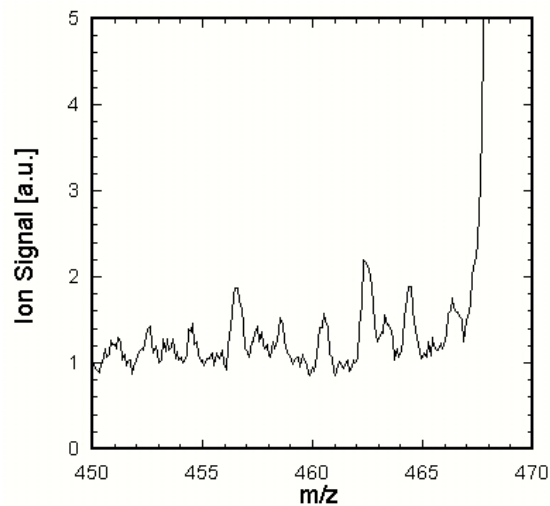
| Fig.11 OCDF | Fig.12 OCDD |

Sep. 13 2005

   To avoid the stains in the AHD unit, pipes and High Temperature Pulsed gas Device (HTPD), HTPD was changed to new one. We blow off TENAX in the AHD unit by the compressed air. And we also cleaned pipes between the AHD unit by both of compressed air and solvent.

Sep. 14 2005

   Figure 13 is the mass spectrum (mass number: 270 to 500) measured by RIMMPA-TOFMS. The ion signals are obtained by integrated value of 3 minutes measurement. The signals of impurity, however, did not disappear even after cleaning and changing of HTPD to new one. It was tough to identify and determine PCDD's and PCDF's because the spectra of the other impurity overlapped the peak signal of the PCDD's and PCDF's although we recognized the PCDD's and PCDF's peaks in our results.
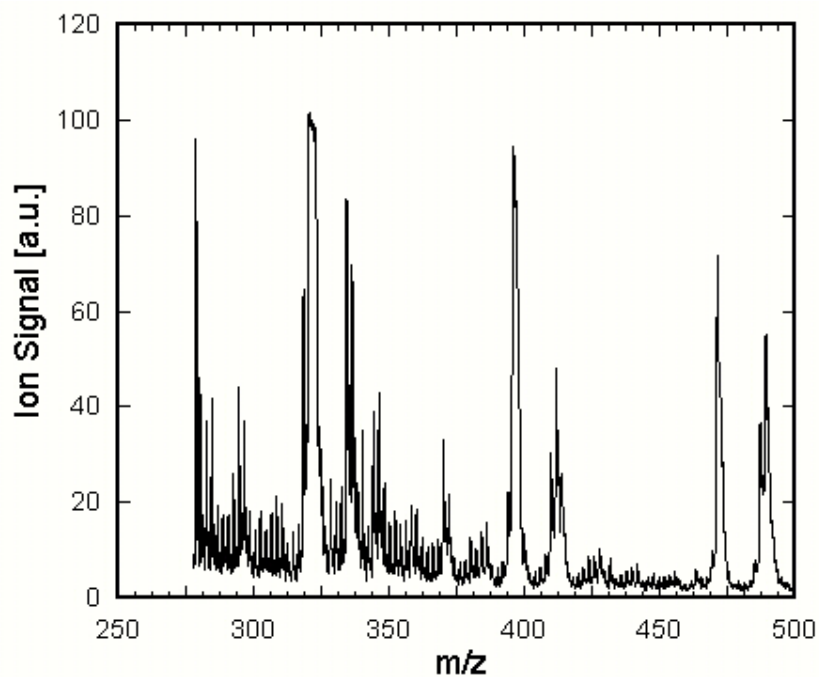
Fig.13 Mass spectrum (Test number: 9/14)

Figure 14 and 15 show the two cases of helium gas pass through the AHD unit and the case of not passes through the unit. From these results, we realized that the inside of the AHD unit has stained, so that we newly created another way of sampling without using the unit. (Refer Fig.16). And we cleaned HTPD and changed the parts of the units. Also we cleaned TENAX as well at 280 degree C for 16 hours assuming that TENAX itself has its stain.
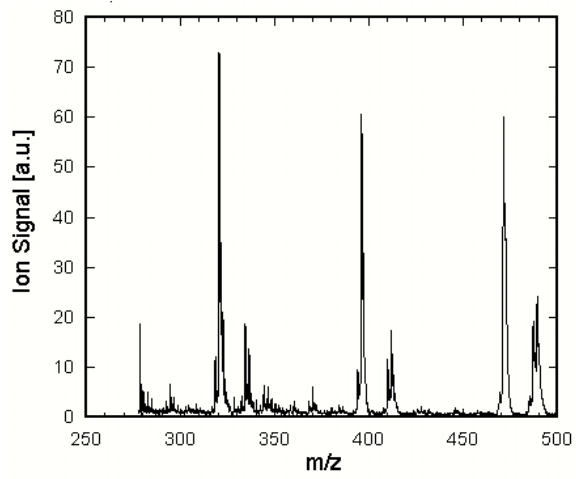
Fig.14 through the AHD unit
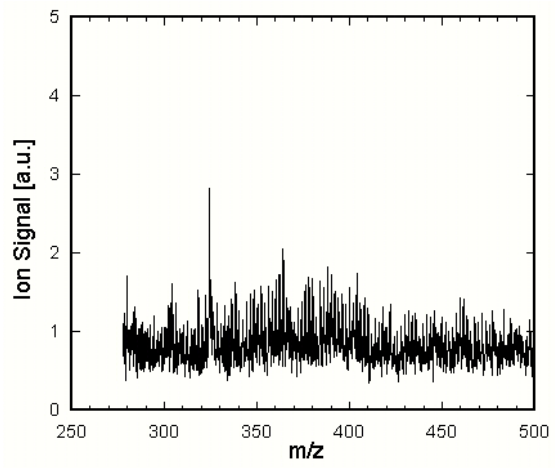
Fig.15 not going through the AHD unit
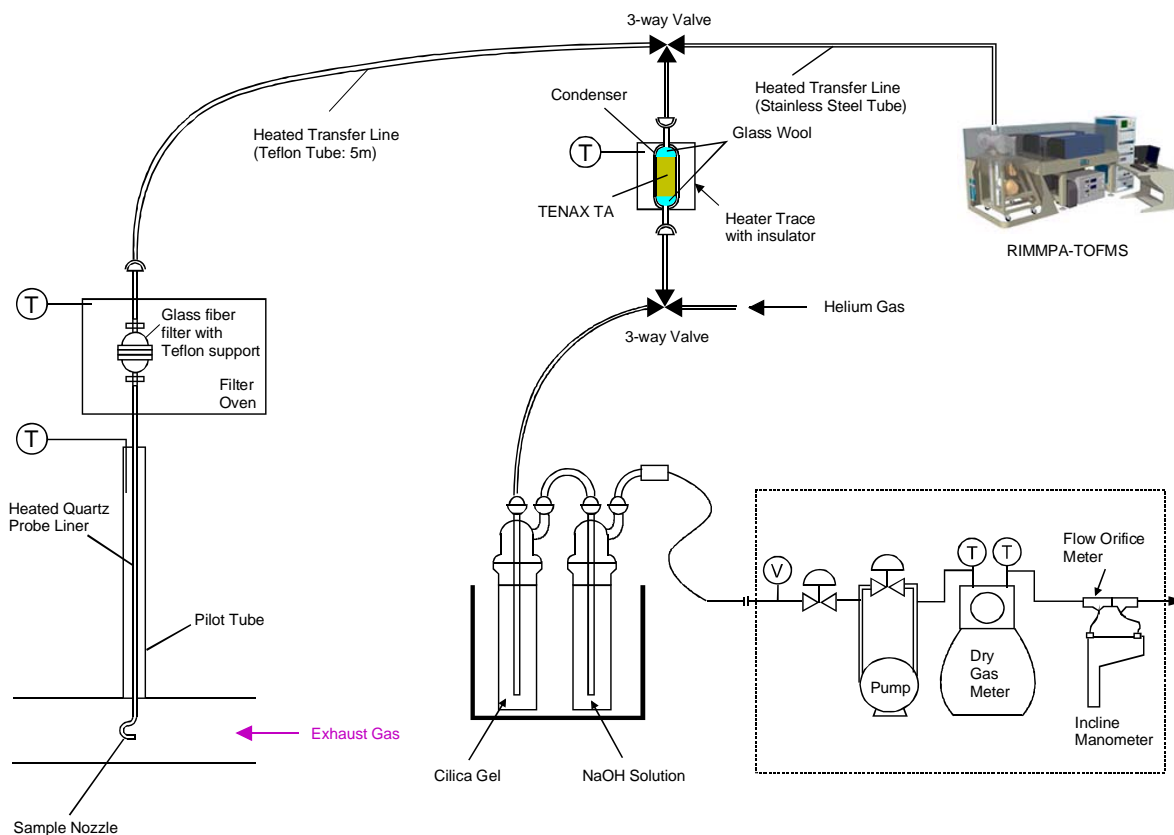
Fig.16   Schematic diagram of the sampling train, adsorption and heat desorption by single condenser, and measurement by RIMMPA-TOFMS

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We changed the glass wool to raise the sampling rate, and changed a helium cylinder to a new one as well. And we inserted the activated charcoal filter between helium cylinder and TENAX column to avoid impurity in the helium gas.

Figure 17(Test number: 9/16-#1), Fig.18 (Test number: 9/16-#2) are the mass spectra (mass number: 270 to 500) measured by RIMMPA-TOFMS and the mass spectra are obtained by integrated value of 3 minutes measurement. If we compare with the Fig.14, the ion signal of mass number 320 and 345 are decreased. However, we could not identify and determine the PCDD's and PCDF's due to the peaks of impurity.
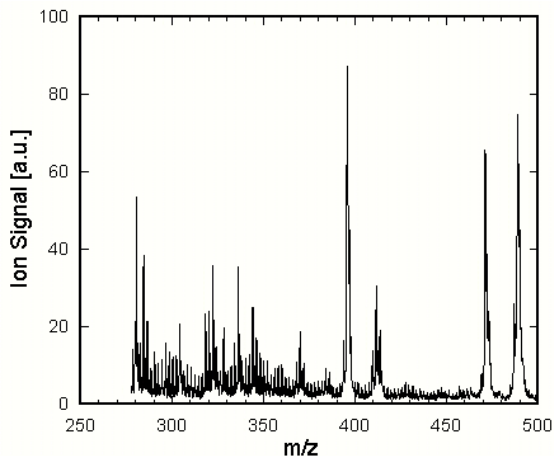
Fig.17 Mass spectrum(Test number:9/16-#1)   Fig.18 Mass spectrum(Test number: 9/16-#2)
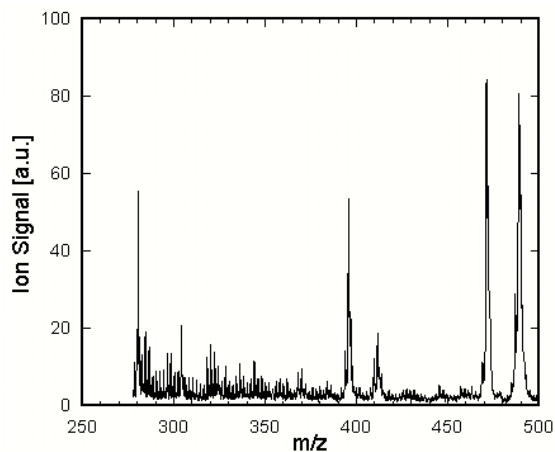
We changed the cleaning solvents from helium to nitrogen and cleaned HTPD again at 200 degree C for a day. Baking in the chamber was also done for a day. Another way that we did was to change to a 3/4 inch tube that doesn't require seal tape because we assumed that the exhausted gas from seal tape might cause the noise in the spectra of PCDD's and PCDF's.

Second half

The chart 4 below shows the summary of the results of sep. 19 thru Sep.22

Chart 4

	9/19	9/20	9/21	9/22
Sample transfer	5m Teflon tube	5m Teflon tube	No use	No use
Adsorption	105 degree C	105 degree C	105 degree C	105 degree C
Helium substitution	3L/min, 5min	3L/min, 5min	3L/min, 5min	3L/min, 5min
Desorption	300 degree C	300 degree C	300 degree C	300 degree C
RIMMPA-TOFMS	315.83nm, 3mJ 213nm, 0.1mJ	310.19nm, 3mJ 213nm, 0.5mJ Change to improve the sensitivity	310.19nm, 3mJ 213nm, 0.5mJ	310.19nm, 3mJ 213nm, 0.5mJ
Others	No preheating of He gas Isomer analysis (2,3,4,7,8-PeCDF) Change the 3/4 inch tube	No preheating of He gas Leak check of sampling line Doubled the volume the second sampling of first volume Congener analysis	No preheating of He gas Congener analysis Set TENAX column directly after the filter	No preheating of He gas Congener analysis Set TENAX column directly after the filter
Results	Fig.19 Spectrum quenching of m/z395, 410 Spectrum decreasing of m/z470, 490 Fig.20 Detect the peak signals in the m/z=338,340 and 342 2,3,4,7,8-PeCDF isomer is imposible to identify	Fig.21-32 TeCDD, PeCDD is posible to identify No detection of HpCDD, OCDF,OCDD Other congeners are imposible to identify	Fig.34-45 Same as previous day There is a possibility TENAX was broken through due to the too much sampling amount	Fig.46-56 m/z278 signal increased Congeners are imposible to identify Detection of mass spectrum m/z260, 262 Fig.57 The flow rate 0.5 to 3 L/min the ion signals increased

Sep.19 2005

Though many kinds of material are ionized because we use the shorter wavelength of the excitation laser in the congener analysis, the only selected isomers would be ionized in the isomer analysis because the longer wavelength of excitation laser is applied.

Figure 19 (Test number: 9/19) is the mass spectrum (mass number: 270 to 500) when we carried out the isomer analysis of 2,3,4,7,8-PeCDF. The ion signal is integrated value for 3 minutes measurement. The peak signals of mass number 395, 410 quenched, 470 and 490 decreased and peak signal of mass number 362 was increased. These materials are resonantly ionized by the excitation laser wavelength of 2,3,4,7,8-PeCDF.

Figure 20 is the mass spectrum near the 2,3,4,7,8-PeCDF. Although there exist the peak signals in the m/z=338, 340 and 342, we could not identify the 2,3,4,7,8-PeCDF isomer because the ionization intensity is different from the ionization intensity ratio that can be estimated by the isotope existence ratio.
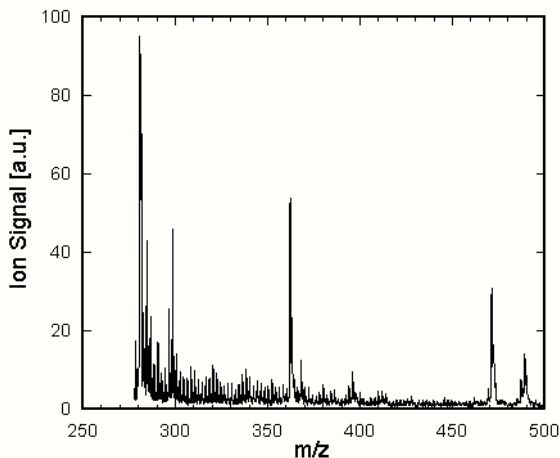
Fig.19 Mass spectrum (Test number: 9/19)
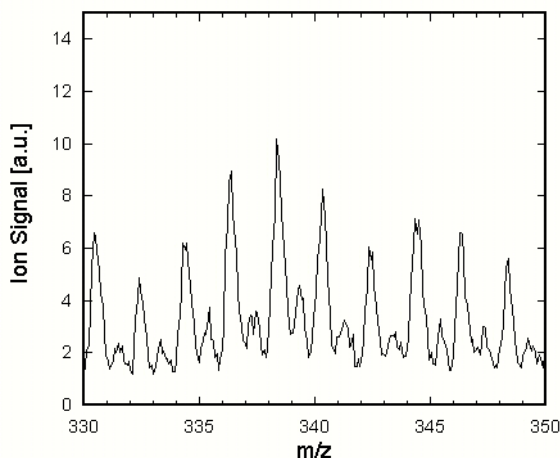
Fig.20 2,3,4,7,8-PeCDF

Sep.20 2005

We changed from isomer analysis to congener analysis because we could not identify 2,3,4,7,8-PeCDF in isomer analysis. We did leak check of sampling port before tests. To rise up the sensitivity, we changed the excitation laser wavelength to 310.19nm and ionization laser energy to 0.5 mJ because we thought the PCDD's and PCDF's density was too low to detect. We tested whether the peak signals become doubled when we sample the double volume as first sampling volume.

Figure 21 (Test number: 9/20-#1), Fig.22 (Test number: 9/20-#2) are the mass spectra (mass number: 270 to 500) measured by RIMMPA-TOFMS and the mass spectra are obtained by integrated value of 3 minutes measurement. The second sampling volume was double of the first one, however, the signals in the second sampling were lower than the first one.
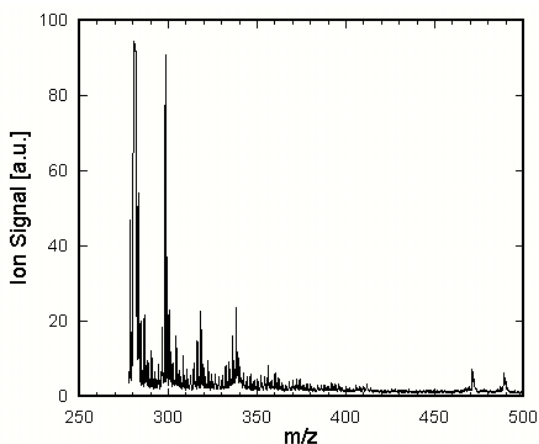
Fig.21 Mass spectrum (Test number:9/20-#1)
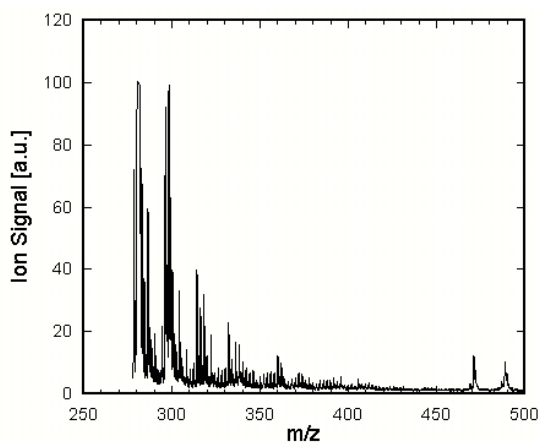
Fig.22 Mass spectrum(Test number:9/20-#2)
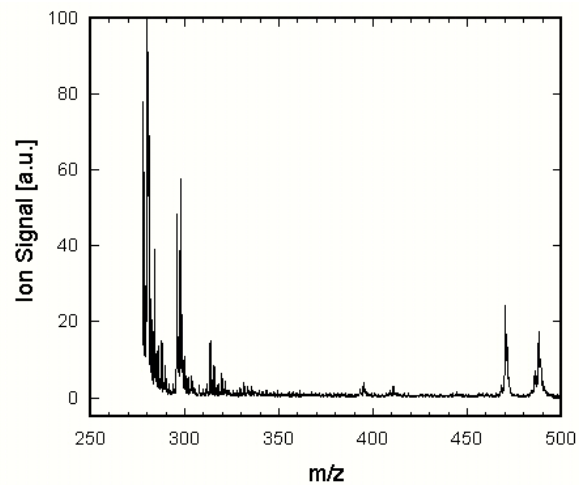
A-15

Figures 23 to 32 are the mass spectra which are expanded the near parent-ion spectrum of the tetra to octa chlorinated DDs and DFs. The indicated values are relative intensity of each peak normalized by M+2 ion signal in the case of TeCDD, PeCDD. We recognized some differences in the intensity ratio between the observed one and that estimated from existence ratio of chlorine isotope. In the case of TeCDD, the observed ratios are 71.2/100 and 57.6/100, while the estimated ratios are 77.4/100 and 48.7/100. But no detection was made on HpCDD, OCDF and OCDD or of the other congeners.
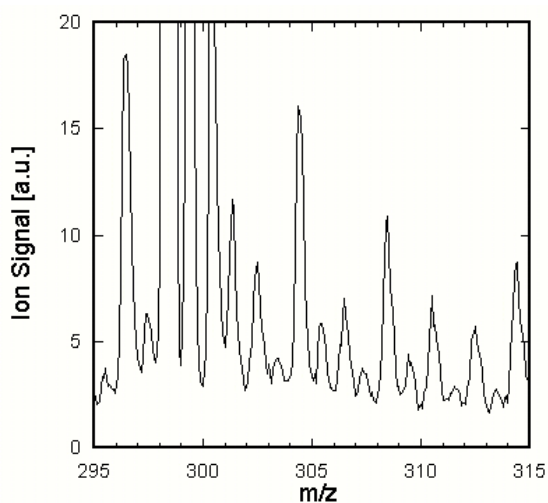
Fig.23 TeCDF
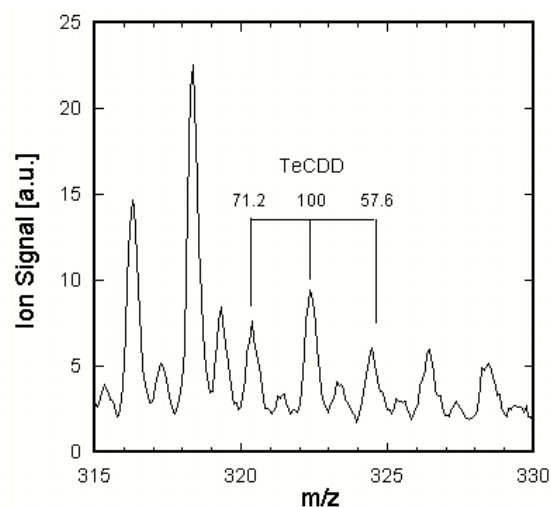
Fig.24 TeCDD
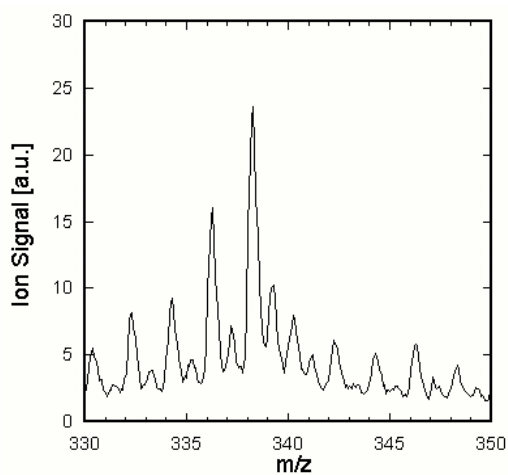
Fig.25 PeCDF
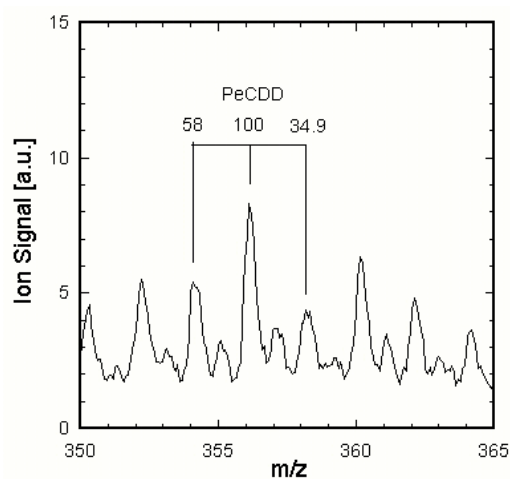
Fig.26 PeCDD
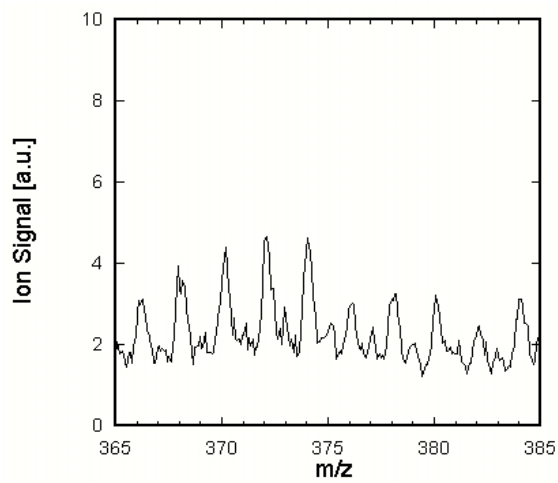
Fig.27 HxCDF
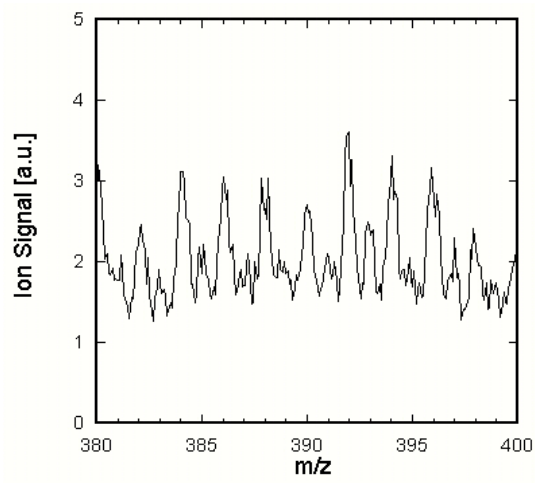
Fig.28 HxCDD
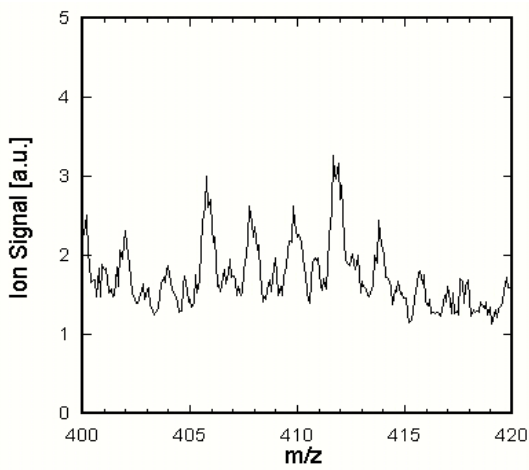
Fig.29 HpCDF
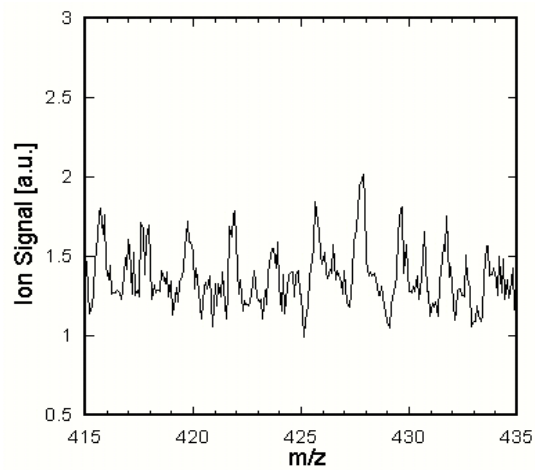
Fig.30 HpCDD
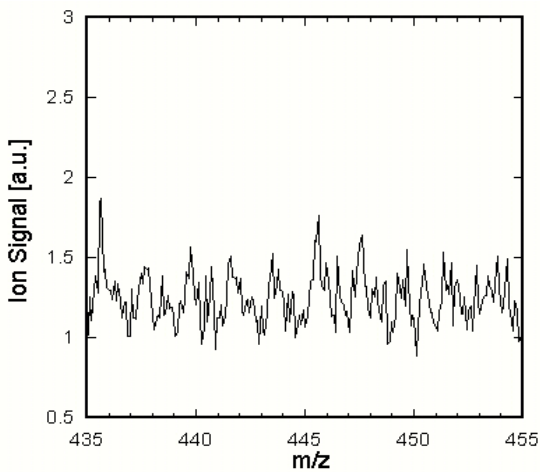
Fig.31 OCDF

Fig.32 OCDD

A-17
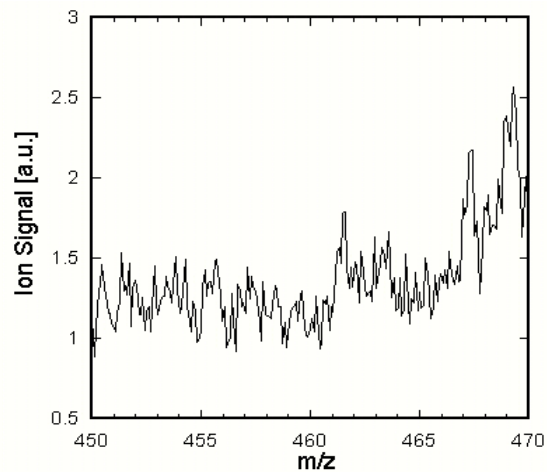
Sep.21 2005

  Knowing the fact that PCDD's and PCDF's are decreased to 1/2 during the gas moves 30cm in a 1/4 inch size Teflon tube, and that if a Teflon tube is heated at 200 degrees C, out gas will occur and PCDD's and PCDF's will be denatured, the 5m heated sampling line (Teflon tube) prepared before the experiment was removed. So the TENAX column was set directly after the filter of filter oven (Fig.33). After sampling, the temperature of the TENAX column was cooled down from 105 degree C and took it out from Filter Oven. And bringing it to the site of RIMMPA-TOFMS and going into the steps of helium substitution, desorption and analysis were curried out.

   Figure 34 (Test number: 9/21-#1), Fig.35 (Test number: 9/21-#2) are the mass spectra (mass number: 270 to 500) measured by RIMMPA-TOFMS and the mass spectra are obtained by integrated value of 3 minutes measurement. The total trend of the results of no-use of Teflon tube was not different from the case of use of it. The second sampling volume was doubled as the previous day and the signals of impurity were decreased on this day. We decided it had break through since there are too many amounts of samplings.
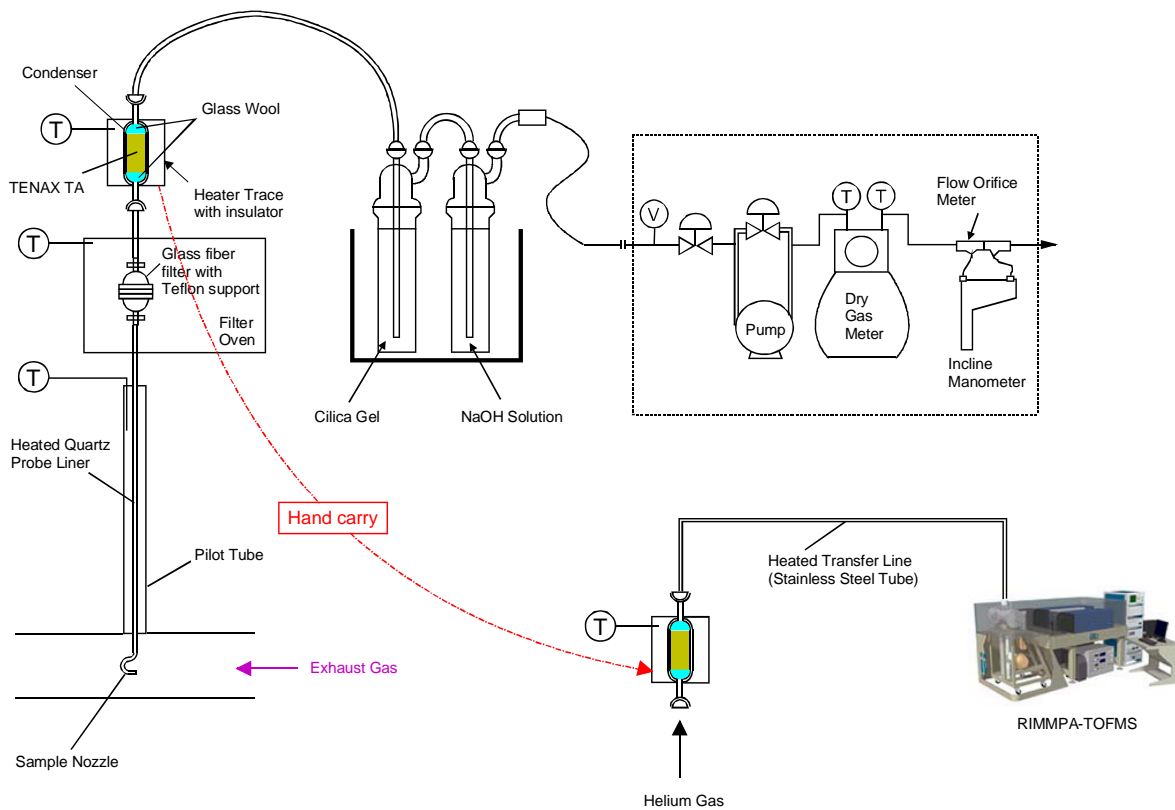
Fig.33　Schematic diagram of the sampling train, with single condenser, connected to filter directly, and measurement by RIMMPA-TOFMS
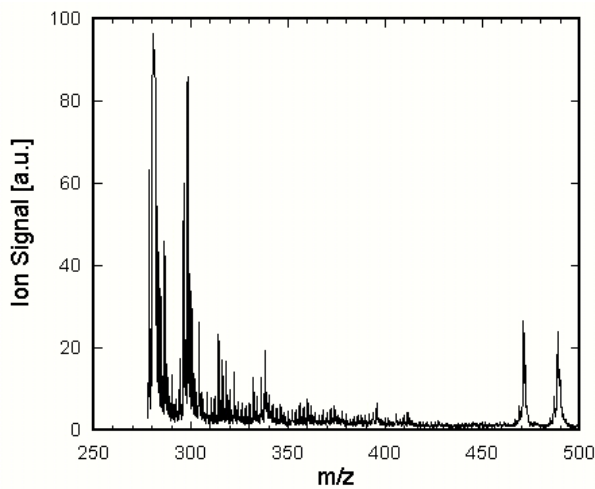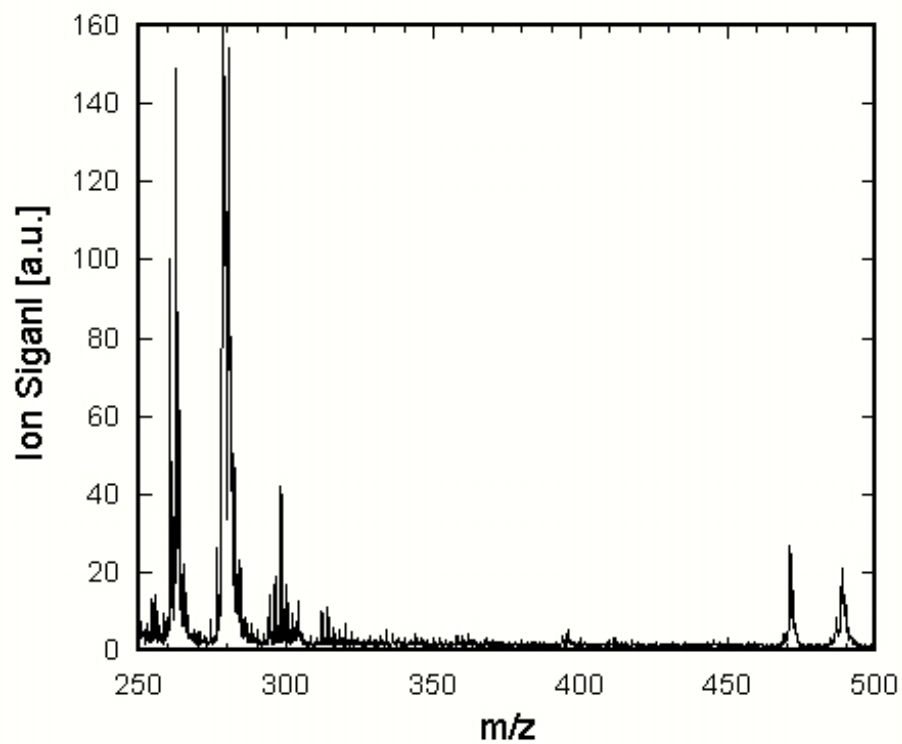

Fig.34 Mass spectrum (9/21-#1)

Fig.35 Mass spectrum (9/21-#2)

Figures 36 to 45 are the mass spectra which are expanded near parent-ion spectrum of the tetra to octa chlorinated DDs and DFs. The indicated values are relative intensity of each peak normalized by M+2 ion signal in the case of TeCDD, PeCDD. We recognized some differences in the intensity ratio between the observed one and that estimated from existence ratio of chlorine isotope. In the case of TeCDD the observed ratios are 67.2/100 and 38.8/100, while the estimated ratios are 77.4/100 and 48.7/100.
But the other congeners were impossible to identify.
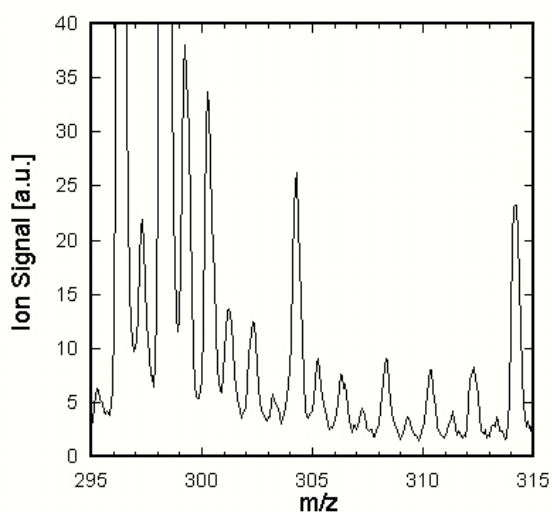
Fig.36 TeCDF
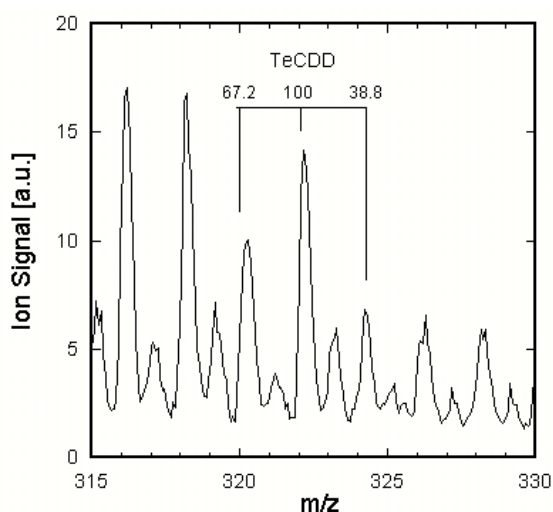
Fig.37 TeCDD
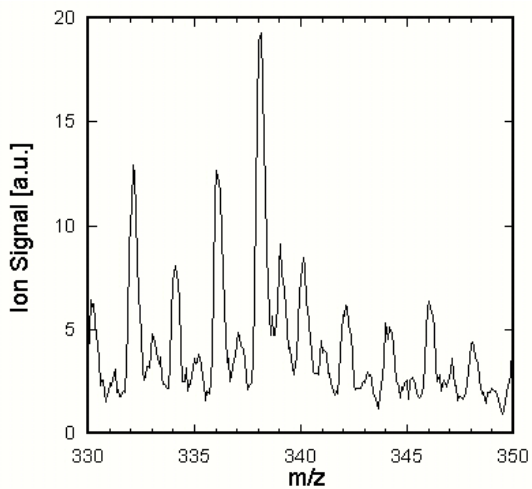
Fig.38 PeCDF
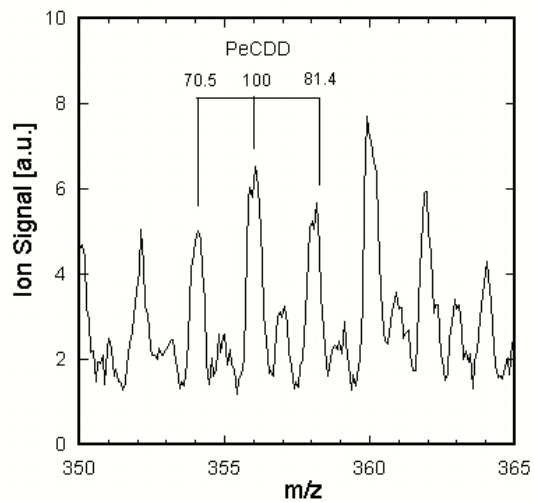
Fig.39 PeCDD
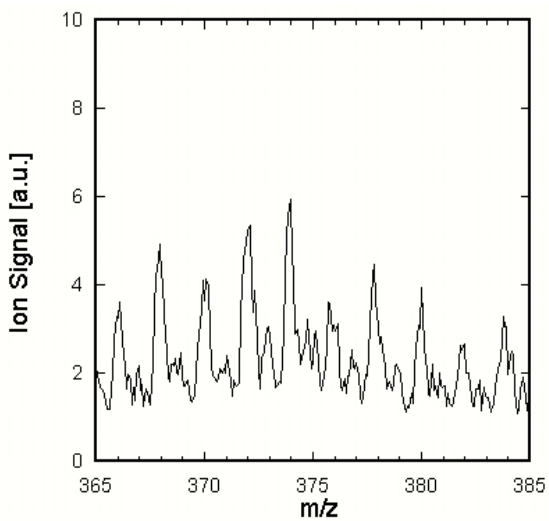
Fig.40 HxCDF
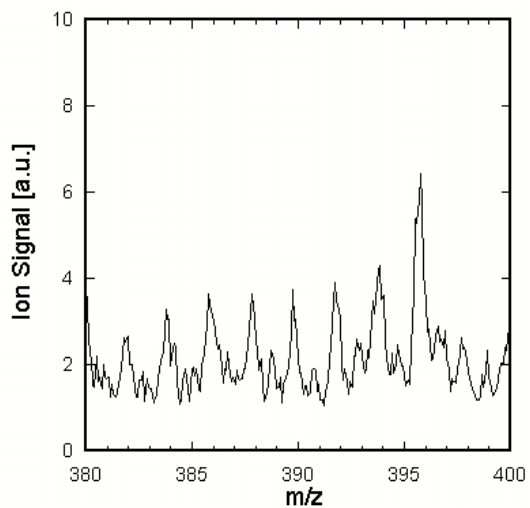
Fig.41 HxCDD
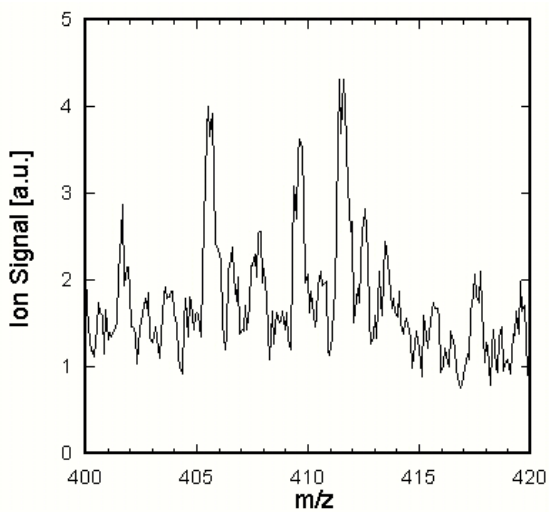
Fig.42 HpCDF

Fig.43 HpCDD

A-21
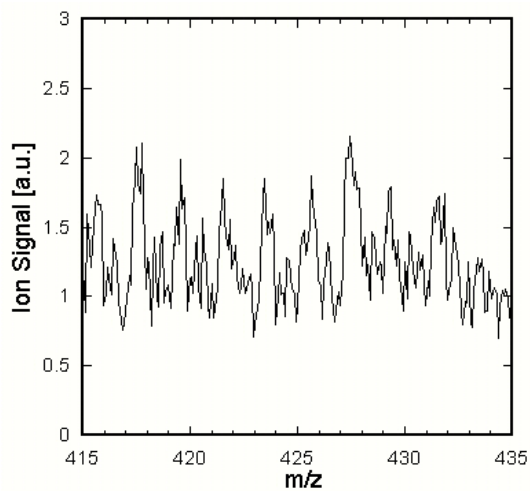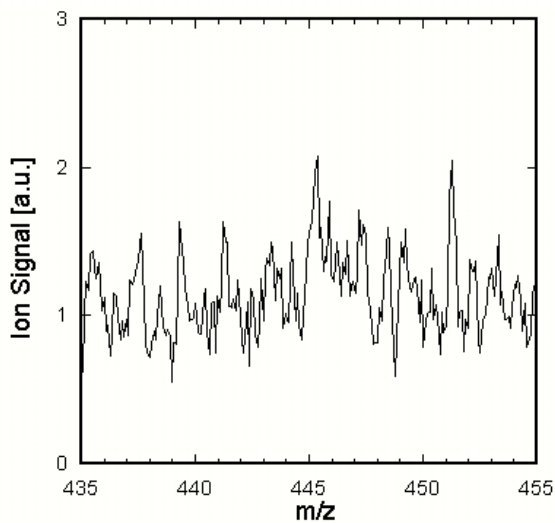
Fig.44 OCDF
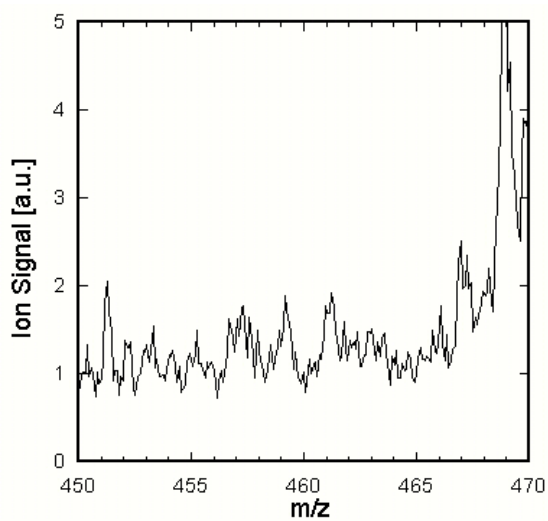
Fig. 45 OCDD

Sep.22 2005

To avoid the break through, we reduced the TENAX volume to 1 g and for the second sampling 2.5g and the volume of sampling itself were reduced.

Figure 46(Test number: 9/22-#1) is the mass spectrum (mass number: 270 to 500) measured by RIMMPA-TOFMS and the mass spectrum was obtained by integrated value of 3 minute measurements. Although the sampling volume was 1/8 of the previous day, the ion signals of mass number 278 and 280 were increased, and the other signals are decreased. We also measured the lower mass region from 250 to 270 and we recognized the spectra in mass number 260 and 262. It was assumed that the PAH or chlorinated PAH from boiler.

Fig.46 Mass spectrum (Test number:9/22-#1)

Figures 47 to 56 are the mass spectra which are expanded near parent-ion spectrum of the tetra to octa chlorinated DDs and DFs. The signals of impurity were decreased because the sampling volume was decreased and also the tetra to octa chlorinated DDs and DFs mass signals are decreased and we could not identify it nor determinate it.
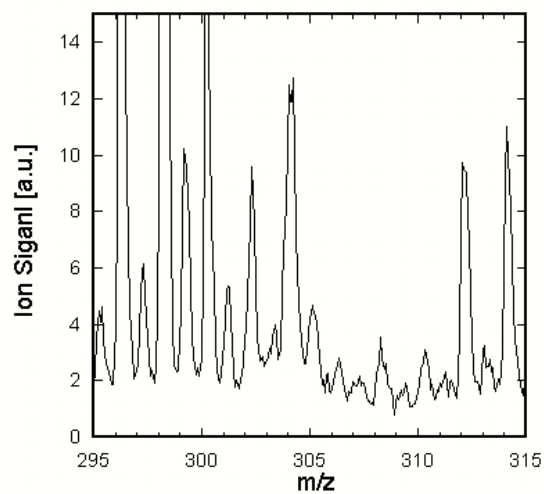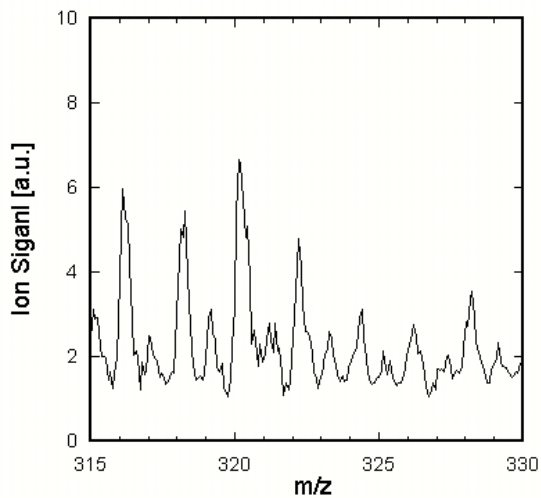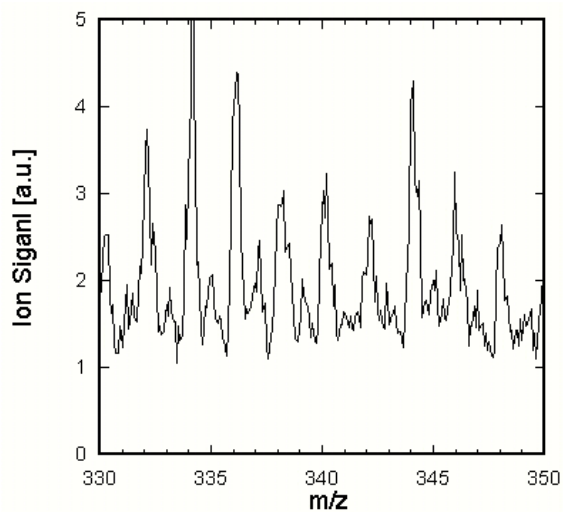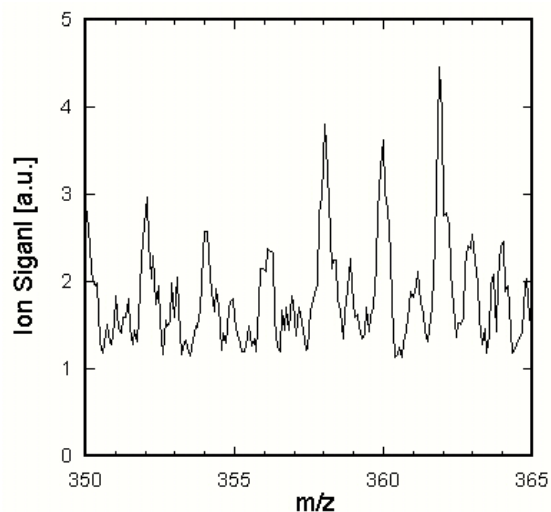
Fig.47 TeCDF

Fig.48 TeCDD

Fig.49 PeCDF

Fig.50 PeCDD
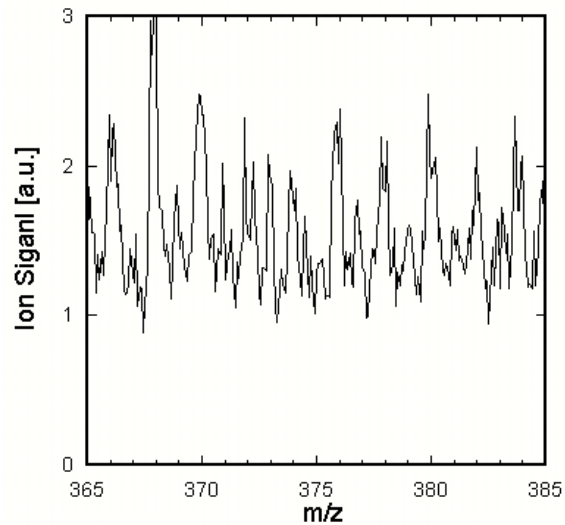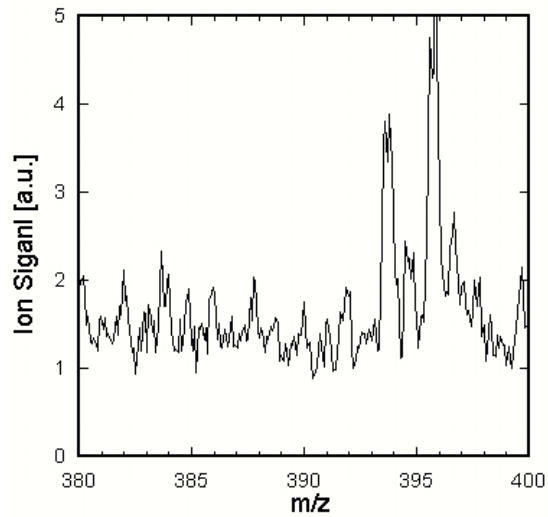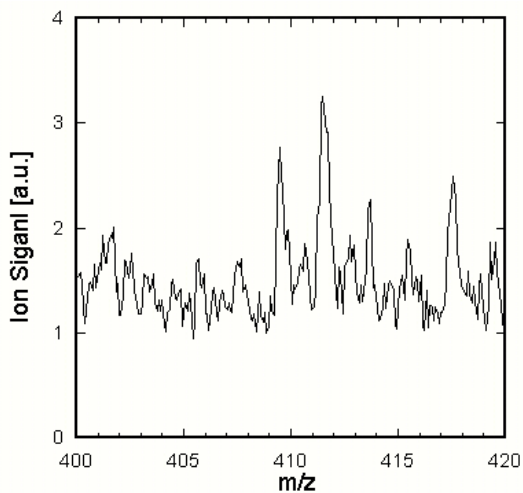

Fig.51 HxCDF

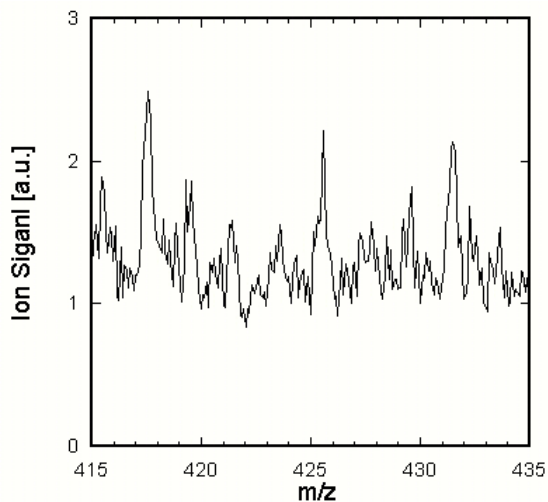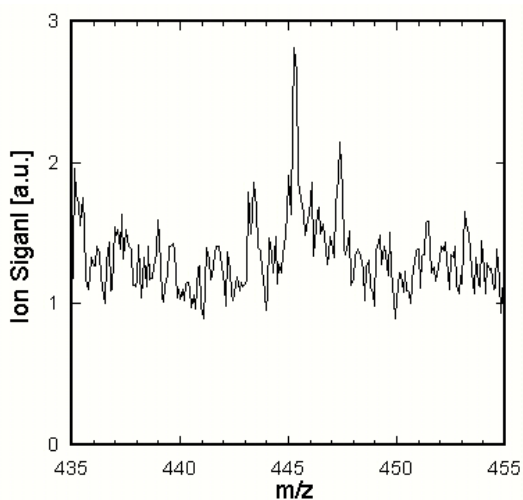Fig.52 HxCDD

Fig.53 HpCDF

Fig.54 HpCDD

Fig.55 OCDF

Fig.56 OCDD

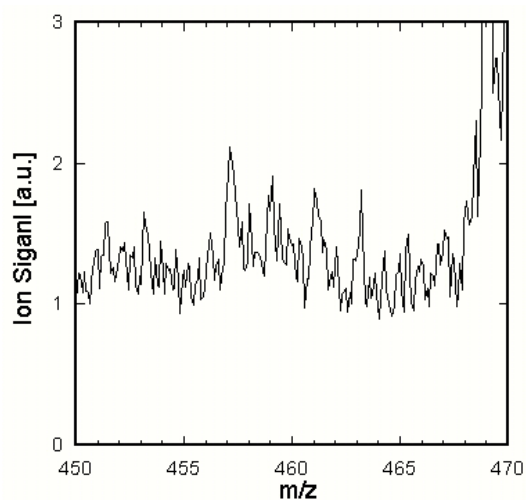It is because the some absorbed materials in TENAX were remained due to the low flow rate of helium gas.

Figure 57 is the mass spectrum obtained by RIMMPA-TOMS in the case of increasing helium flow rate to 3 L/min after the measurement end of Test number: 9/22-#2. Comparing to the data of 0.5 L/min, the ion signals increased. We thought the sample remained in the TENAX column not being pushed out.
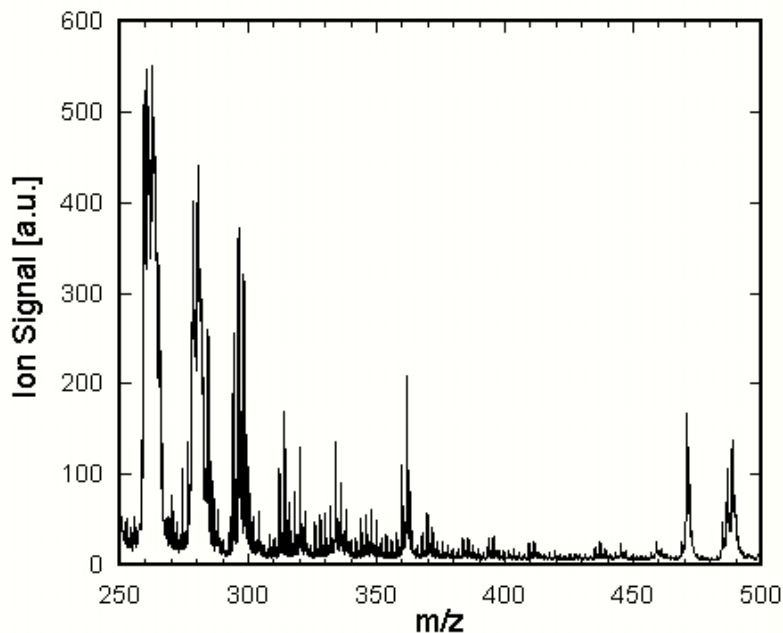
Fig.57 Mass spectrum

7. Conclusion

What we have performed this time through the test is

1. We straggled for adjusting the Adsorption and Heated Desorption.
2. It has taken us much time to get rid of unexpected occurrence of PAH & Poly-Chlorinated PAH that caused from Naphthalene Cu to generate Dioxin.
3. This PC-PAH causes the damages to break the congener ratio which is essential to identification of PCDDs/PCDFs because they overlap with those of PCDDs/PCDFs.

Even under this situation, we tried two types of analysis of congeners and isomers.

In the congener analysis, the peaks detected in the vicinity of mass of TeCDF, TeCDD, PeCDD, and OCDF were able to be identified. However, it was difficult to identify other congeners because PAH and chlorinated PAH contained in exhaust gas came in succession with spectra of PCDD's and PCDF's. With regard to the results of PAH or chlorinated PAH that we have got in the experiment, are shown in chart 5.

In the case of isomer analysis 2,3,4,7,8-PeCDF, we detected mass peaks in the mass number 338, 340 and 342. It was tough however, to identify and to measure because the intensity ratio of the isotopes 338, 340, 342 observed is different from the signal calculated by the existence ratio. It was not possible to identify the isotope signals of 2, 3, 4, 7, 8- PeCDF, because the mass spectra of impurities (PAH and chlorinated PAH etc.) that existed in the mass neighborhood of 2, 3, 4, 7, 8- PeCDF came in succession, and detection was obstructed.

Through this ETV test this time, we realized that the toughness in the real gas but at the same time we learned many things and eventually we have to the stage to convince that we are very close to be able to detect the isomer analysis in real gas in the very near future.

Chart 5

m/z	Compound		
260	$C_{18}H_9Cl$	$C_{18}H_{12}O_2Cl_4$	
262	$C_{18}H_{11}Cl$	$C_{18}H_{14}O_2$	
278	$C_{18}H_{12}OCl$	$C_{22}H_{14}$	
280	$C_{22}H_{16}$		
284	$C_{12}H_6S_2Cl_2$	$C_{12}H_6O_2SCl_2$	
286	$C_{20}H_{11}Cl$		
292	$C_{23}H_{16}$		
294	$C_{18}H_8Cl_2$	$C_{12}H_{10}Cl_4$	
296	$C_{18}H_{10}Cl_2$	$C_{18}H_{13}O_2Cl$	
298	$C_{12}H_7O_3S_2Cl$	$C_{18}H_{15}O_2Cl$	
304	$C_{20}H_{16}O_3$	$C_{24}H_{16}$	$C_{18}H_{24}O_4$
312	$C_{18}H_{10}OCl_2$		
314	$C_{14}H_{12}O_2SCl_2$		
318	$C_{21}H_{15}OCl$	$C_{12}H_5S_2Cl_3$	$C_{12}H_5SO_2Cl_3$
320	$C_{20}H_{10}Cl_2$		
328	$C_{22}H_{13}OCl$		
334	$C_{24}H_{11}Cl$		
336	$C_{20}H_{10}OCl_2$		
344	$C_{18}H_{10}O_3Cl_2$	$C_{22}H_{10}Cl_2$	$C_{18}H_7OCl_3$
346	$C_{18}H_9OCl_3$	$C_{22}H_{12}Cl_2$	
360	$C_{22}H_{10}OCl_2$		
362	$C_{28}H_{26}$	$C_{26}H_{15}Cl$	$C_{26}H_{18}O_2$
368	$C_{24}H_{10}Cl_2$		
380	$C_{18}H_8OCl_4$		
384	$C_{24}H_{10}OCl_2$		
394	$C_{26}H_{12}Cl_2$	$C_{26}H_{15}O_2Cl$	
396	$C_{26}H_{14}Cl_2$	$C_{26}H_{17}O_2Cl$	
410	$C_{26}H_{12}OCl_2$	$C_{26}H_{14}OCl_4$	
412	$C_{26}H_{14}OCl_2$		