6. APPENDICES

APPENDIX A

MEASUREMENT METHODS

CONTENTS

1. Measurement Method of CFC-11, CFC-113, Carbon tetrachloride, and 1,1,1-Trichloroethane

(GC Analytical Method 1)

(1) Analytical System

A schematic diagram of the analytical system assembled for this method is shown in **Figure 1**. The analytical system can be roughly divided into two sub-systems, a sample introduction system and a gas chromatograph. The sample introduction equipment is a system which introduces a certain volume of air sample from a sample container into an analytical column through a measuring loop. The sample introduction system was assembled in the JESC laboratory. The gas chromatograph is a Shimadzu GC-14A gas chromatograph equipped with an electron capture detector (ECD).

Stainless steel tubes with 1/8 inches of outside diameter (OD) connect the pressure gauges, the sampling container, the valves and other components. The measuring loop is made of approximately 4 m long glass tube with 5 mm inside diameter (ID). The volume of the measuring loop is 75.73 ml. The whole of the volume of the measuring loop associated with the measurement of sample volume including tubing and other components was estimated to be 80.0 ml. The dryer tube is a stainless steel tube with 3 mm ID, 10 cm long filled with Chromosorb W 30-60 mesh column packing coated with 5w/w% of magnesium perchlorate (Mg(ClO4)2). The dryer tube can be re-generated by bake-out at 150 ℃ for 20 min with a inert gas flow inside. The stop valves are U.S. Nupro Type SS-4H metal bellows valves.

The sample concentration tube is a U-shaped stainless steel tube with 3 mm ID, 20 cm long filled with 0.1g of Chromosorb W 60-80 mesh column packing. Four-port valve 1 is equipped to prevent degradation of the analytical column or the detector by oxygen that passed the sample concentration tube during the sample concentration procedure mentioned below.

The nitrogen carrier gas is introduced to the GC after decompressed from a cylinder and refined via the two gas purifying tubes that are respectively filled with Molecular sieve 5A and Molecular sieve 13X. The carrier gas streams which flow from the flow controllers of the GC are again refined through another two gas purifying tubes.

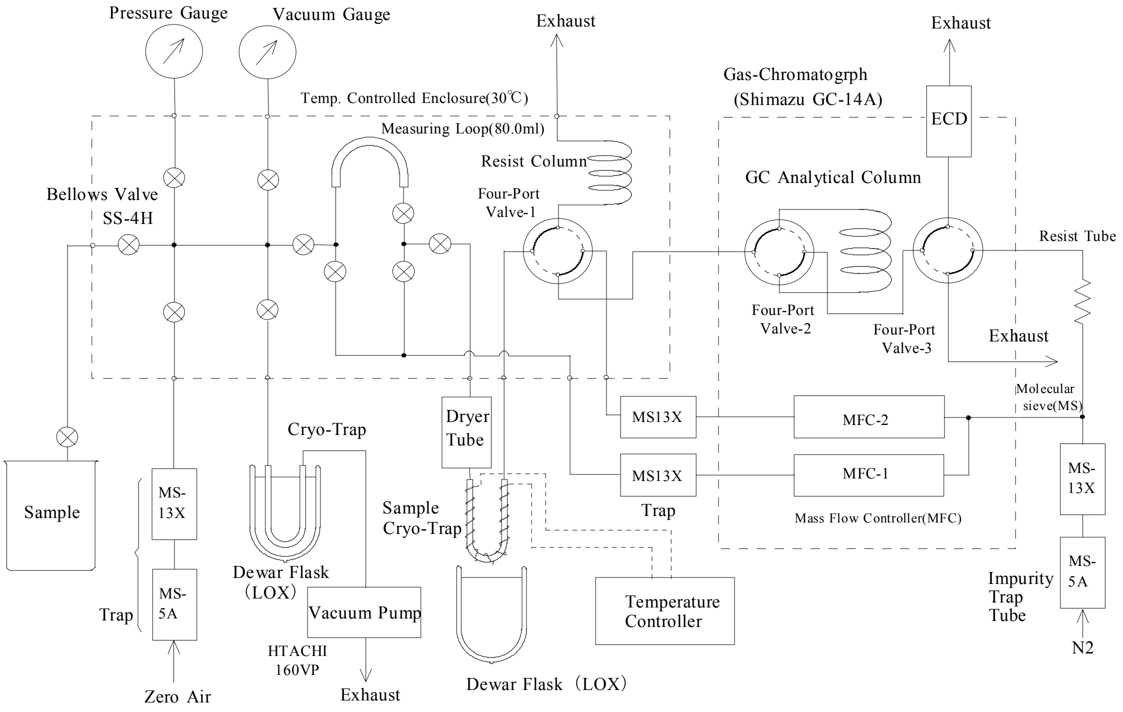

Figure 1. CFCs analytical system (SYSTEM I)

The analytical conditions for the gas chromatography are shown in **Table 1**.

Table 1. Analytical conditions of GC analytical method 1

Term	Condition
Gas chromatograph	Shimadzu GC-14A
Column	DC-550 25 %, Shimalite 101, 60-80 mesh, 3mm ID, 4 m long, stainless steel +OV-101 25%, Shimalite 101, 60-80mesh, 3mm ID, 2 m long, stainless steel
Column oven temp.	30 ℃ (5 min) to 90 ℃, 2 ℃/min
Carrier gas	N2, 50 ml/min
Detector	ECD (370 MBq, Ni 63, 220 ℃)
Sample volume	28.4 ml (STD)

(2) Analytical Procedures

A sample container was connected to the sample introducing port of the sample introduction equipment, and the sample introduction line and the measuring loop were evacuated to 0.1 mmHg (13 Pa) or less. Approximately 28 ml of the air sample in the sampling container was removed to the measuring loop until the pressure in the loop reached a fixed value (i.e. 300 mmHg or 40 kPa). The sample concentration tube was immersed in liquid oxygen. After the temperature of the tube reached the liquid oxygen temperature, the sample air in the measuring loop was introduced into the sample concentration tube through the operation of the valves. A period of four minutes was necessary to whole of the sample passed the concentration tube by the carrier gas flow. Four-port valve 1 was kept in the bypass position during this procedure. After the concentration procedure was completed, four-port valve 1 was changed to the analysis position and the next procedure was held till the fluctuation of the pressure in the carrier gas settled. The liquid oxygen flask was removed from the sample concentration tube, and the tube was heated to 50 ℃. After the gas chromatographic analysis accomplished, the analysis system was left until tetrachloroethylene eluted from the analytical column.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

2. Measurement Method of CFC-114 (GC Analytical Method 2)

(1) Analytical System

A schematic diagram of the analytical system assembled for this method is shown in **Figure 2**. The analytical system can be roughly divided into two sub-systems, a sample introduction system and a gas chromatograph. Several components in the sample introduction equipment are common to the measuring method of CFCs (**Figure 1**). Sample concentration tube 1, four-port valve 1, and refining of carrier gas and others are the same as GC analytical method 1.

Sample concentration tube 2 is similar to sample concentration tube 1 in the structure and the packing contained with. Four-port valve 2 ejects unnecessary compounds which have been introduced into the precolumn outside of the system by reversion of the gas flow in this column. Four-port valve 3 distributes the eluants from the precolumn into the sample concentration tube 2 or outside. The eight-port valve releases the pressure in the end of the precolumn to the ambient during the re-concentration procedure.

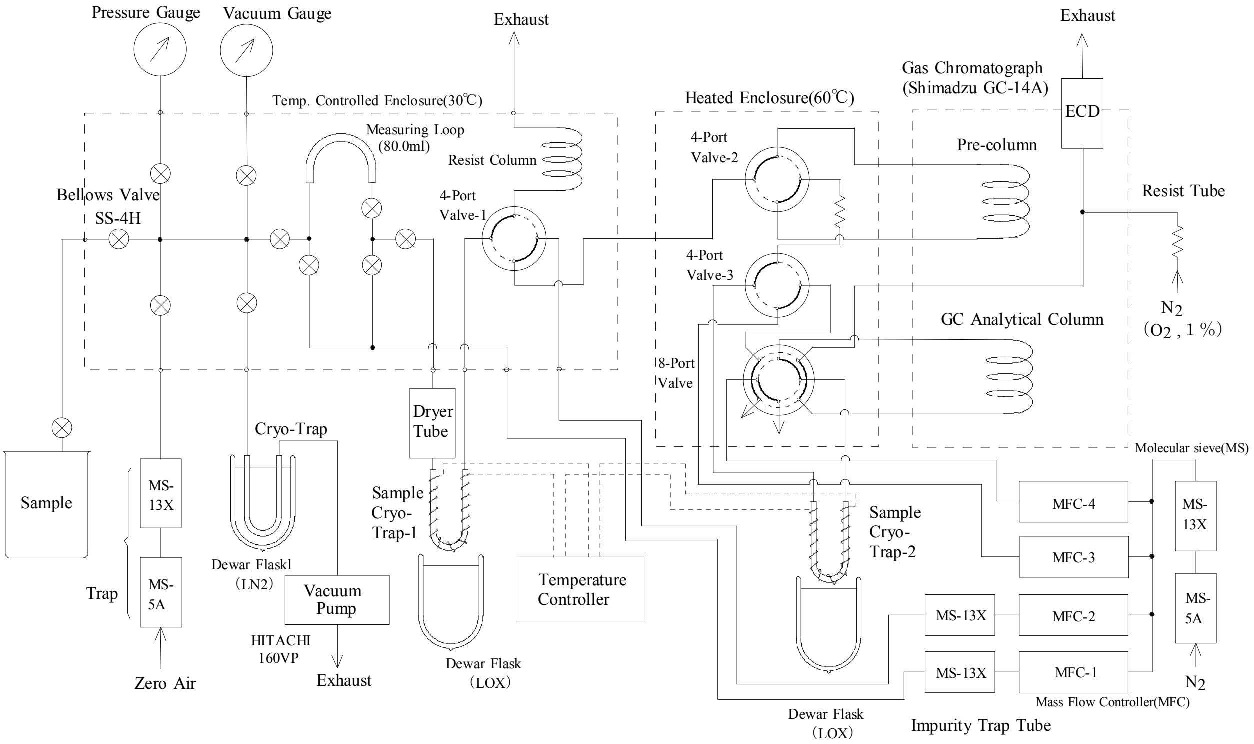

Figure 2. CFC-114 analytical system（SYSTEM II）

The analytical conditions for the gas chromatography are shown in **Table 2**.

Table 2.　Analytical conditions of GC analytical method 2

Term		Condition
Pre-treatment	Precolumn	DC-550 25 %, Shimalite 101, 60-80 mesh, 3 mm ID, 4m long, stainless steel
	Column temp.	25 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	113.8 ml （STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	GS-Alumina, 0.53 mm ID, 50 m long
	Column temp.	60 ℃
	Carrier gas	N2, 5 ml/min
	Make-up gas	N2, 45 ml/min
	Detector	ECD （370 MBq, Ni 63, 220 ℃）

(2) Analytical procedures

(A) Sample Concentration Procedure

A sample container was connected to the sample introducing port of the sample introduction equipment. The sample introduction line and the measuring loop were evacuated to 0.1 mmHg (13 Pa) or less. Approximately 56 ml of volume of the air sample in the sample container was removed to the measuring loop until the pressure in the measuring loop reached a fixed value (i.e. 600 mmHg or 80 kPa). Sample concentration tube 1 was immersed in liquid oxygen. After the temperature of concentration tube 1 reached the liquid oxygen temperature, the sample air in the measuring loop was introduced into concentration tube 1 through the operation of the valves. This procedure was carried out twice to accumulate the sample volume to approximately 114 ml (STD).

(B) Re-concentration and Analysis Procedure

After the concentration procedure was accomplished, four-port valve 1 was turned to the analysis position. The liquid oxygen flask was removed from sample concentration tube 1, and the tube was heated to 25 ℃. Time-check was started at the same time, and sample concentration tube 2 was immersed in the liquid oxygen. Four-port valve 3 was turned to the trapping position at the time CFC-12 finished to elute from the precolumn to again concentrate CFC-114 and CFC-114a on sample concentration tube 2. Four-port valve 3 was again turned to the ejecting position at the time CFC-114 and CFC-114a finished to elute from the precolumn. Thus the re-concentration procedure was accomplished. Approximately four minutes was necessary for the re-concentration procedure under the conditions shown in **Table 2**. The liquid oxygen flask was removed from sample concentration tube 2, and sample concentration tube 2 was heated to 25 ℃ and the gas chromatographic analysis was started. CFC-114 and CFC-114a were eluted at approximately 25 minutes in order of the description.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

3. Measurement Method of CFC-115 (GC Analytical Method 3)

(1) Analytical System

Since the typical atmospheric concentration of CFC-115 is minute and ECDs have poor sensitivity for this substance, the amount of sample should be enlarged to about 500 ml or more in analysis of this substance. The measuring loop technique which was adopted in GC analytical method 1 and 2 is not adequate to handle a sample with a volume of 500 ml or more. To precisely measure a greater volume of a sample, we installed an evacuated flask to the end of the sample concentration tube which sucks the sample air to concentrate and also determines the sample volume extracted. A schematic diagram of the system is shown in **Figure 3**. (SYSTEM III). Several components and the GC are common to the analytical system used in GC analytical method 1 and 2 (SYSTEM I and SYSTEM II). The calibration gas is introduced to the GC in the similar manner of GC analytical method 2 through the measuring loop mentioned in analytical method 2.

The measuring flask which functioned as a sample suction pump and a measure for sample volume is made of stainless steel with 1,960 ml of inner volume. The whole of the volume of the measuring flask which associated with the measurement of the sample volume including tubing and other components is 1,996 ml. The measuring flask is not installed in a temperature-maintained enclosure, but the room temperature was maintained at 23 ℃ while the measurements was being conducted.

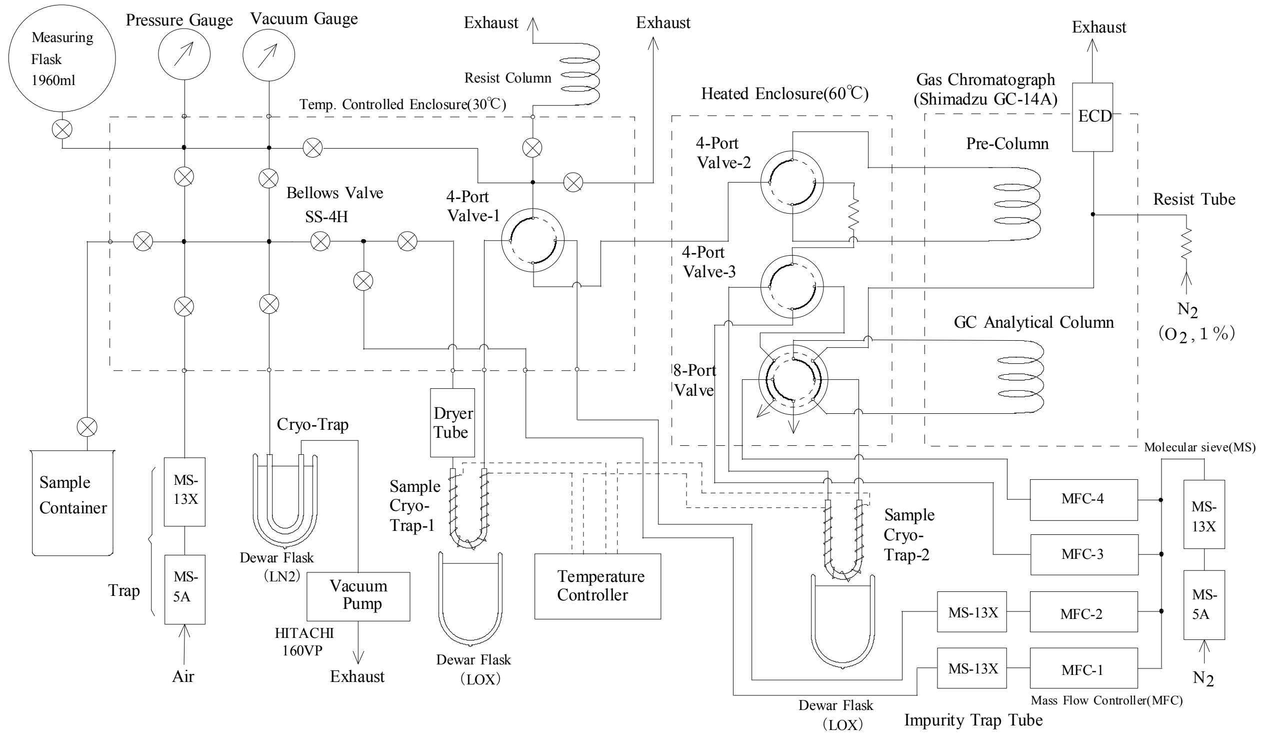

Figure 3. CFC-115 analysis system（SYSTEM III）

The analytical conditions for the gas chromatography are shown in **Table 3**.

Table 3. Analytical conditions of GC analytical method 3

Term		Condition
Pre-treatment	Precolumn	Carbopack B 1% SP1000, 60-80 mesh, 3 mm ID, 2 m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	284.5 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	GS-Alumina, 0.53 mm ID, 50 m long
	Column temp.	30 ℃
	Carrier gas	N2, 5 ml/min
	Make-up gas	N2, 45 ml/min
	Detector	ECD（370MBq, Ni 63, 220 ℃）

(2) Analytical Procedures

(A) Sample Concentration Procedure

The measuring flask was evacuated to 0.1 mmHg (13 Pa) or less. A sample container was connected to the sample introducing port of the sample introduction equipment, and the sample introduction line was evacuated to 0.1 mmHg(13 Pa) or less. Sample concentration tube 1 was immersed in liquid oxygen. Approximately 284 ml of volume of the air sample in the sample container was removed to the measuring flask through cryo-cooled sample concentration tube 1 until the pressure in the flask reached a fixed value (i.e. 117.4 mmHg or 15.6 kPa). The calibration gas was concentrated on sample concentration tube 1 in the similar manner of GC analytical method 2.

(B) Re-concentration and Analysis Procedure

Re-concentration and analysis procedure were similar to the procedures of GC analytical method 2. CFC-115 eluted from the precolumn at approximately five minutes and eluted from the analytical column at approximately 13 minutes under the conditions shown in **Table 3**.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

4. Measurement Method of Halon-1211 and Halon-1301 (GC Analytical Method 4)

(1) Analytical System

The analytical system was the same as described in GC analytical method 2. The analytical conditions are shown in **Table 4**.

Table 4. Analytical conditions of GC analytical method 4

Term		Condition
Pre-treatment	Precolumn	DC-550 25%, Shimalite 101, 60-80 mesh, 3mm ID, 4m long, stainless steel
	Column temp.	50 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	56.9 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	Carbopack B 1% SP1000, 60-80 mesh 3 mm ID, 2 m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Detector	ECD（370 MBq, Ni 63, 220 ℃）

(2) Analytical Procedures

The analytical procedures were the same as described in GC analytical method 2. Halon-1211 and halon-1301 eluted from the precolumn at approximately two minutes and approximately four minutes, respectively, and eluted from the analytical column at approximately four minutes and approximately 13 minutes, respectively, under the conditions shown in **Table 4**.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

5. Measurement Method of Halon-2402 (GC Analytical Method 5)

(1) Analytical System
The analytical system was the same as described in GC analytical method 3. The analytical conditions are shown in **Table 5**.

Table 5. Analytical conditions of GC analytical method 5

Term		Condition
Pre-treatment	Precolumn	OV-17 25%, Shimalite 101, 60-80 mesh, 3 mm ID, 5m long, stainless steel
	Column temp.	60 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	284.5 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	Carbopack B 1% SP1000, 60-80 mesh 3 mm ID, 1.5m long, stainless steel
	Column temp.	60 ℃
	Carrier gas	N2, 50 ml/min
	Detector	ECD（370 MBq, Ni 63, 220 ℃）

(2) Analytical Procedures
The analytical procedures were the same as described in GC analytical method 3. Halon-2402 eluted from the precolumn at approximately eight minutes and eluted from the analytical column at approximately 15 minutes under the conditions shown in **Table 5**.

(3) Calculation
A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

6. Measurement Method of CFC-12 and HCFC-22 (GC Analytical Method 6)

(1) Analytical System

The analytical system was the same as described in GC analytical method 2 with the exception that a branch-off between the analytical column and the ECD was installed. 0.03% of oxygen was added to the carrier gas by introducing nitrogen which contained 1% of oxygen through the branch at a flow rate of 1.5 ml/min. The analytical conditions are shown in **Table 6**.

Table 6. Analytical conditions of GC analytical method 6

Term		Condition
Pre-treatment	Precolumn	DC-550 25%, Shimalite 101, 60-80 mesh, 3 mm ID, 4m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	56.9 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	Carbopack B 1% SP1000, 60-80 mesh 3 mm ID, 4 m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Detector	ECD（370 MBq, Ni 63, 220 ℃, 0.03 % O2 doped）

(2) Analytical Procedures

The analytical procedures were the same as described in GC analytical method 2. CFC-12 and HCFC-22 eluted from the precolumn at approximately three minutes and CFC-12 eluted from the analytical column at approximately 12 minutes and HCFC-12 eluted at approximately five minutes under the conditions shown in **Table 6**.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

7. Measurement Method of HCFC-141b (GC Analytical Method 7)

(1) Analytical System
The analytical system was the same as described in GC analytical method 3. The ECD was doped with O2 the same as GC analytical method 6. The analytical conditions are shown in **Table 7**.

Table 7. Analytical conditions of GC analytical method 7

Term		Condition
Pre-treatment	Precolumn	DC-550 25%, Shimalite 101, 60-80 mesh, 3 mm ID, 3m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50ml/min
	Sample volume	284.5 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	Supelco Vocol, 0.53mm ID, 3um, 100 m long
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Detector	ECD（370 MBq, Ni 63, 220 ℃, 0.03 % O2 doped）

(2) Analytical Procedures
The analytical procedures were the same as described in GC analytical method 3. HCFC-141b eluted from the precolumn at approximately 10 minutes and eluted from the analytical column at approximately 22 minutes under the conditions shown in **Table 7**.

(3) Calculation
A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

8. Measurement Method of HCFC-142b and Methyl Bromide (GC Analytical Method 8)

(1)Analytical System

The analytical system was the same as GC analytical method 7. The analytical conditions are shown in **Table 8**.

Table 8. Analytical conditions of GC analytical method 8

Term		Condition
Pre-treatment	Precolumn	DC-550 25%, Shimalite 101, 60-80 mesh, 3 mm ID, 4m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	56.9 ml（STD）
Analysis	Gas chromatograph	Shimadzu GC-14A
	Analytical column	Carbopack B 1% SP1000, 60-80 mesh 3 mm ID, 4 m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Detector	ECD（370 MBq, Ni 63, 220 ℃, 0.03 % O2 doped ）

(2) Analytical Procedures

The analytical procedures were the same as described in GC analytical method 3. HCFC-142b and methyl bromide eluted from the precolumn at approximately three minutes and HCFC-142b eluted from the analytical column at approximately 11 minutes and methyl bromide eluted at approximately seven minutes under the conditions shown in **Table 8**.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

9. Measurement Method of HFC-134a (GC/MS Analytical Method)

(1) Analytical System

A schematic diagram of the analytical system for HFC-134a measurement is shown in **Figure 4**. This system can be roughly divided into two sub-systems, a sample introduction system and a gas chromatograph-mass-spectrometer (GC-MS). The sample introduction equipment which was assembled for CFC-115 measurement was used for sample concentration and sample refinement. See GC analytical method 3 for the detail of the sample introduction equipment.

The GC-MS is a JEOL JMS-GCmate gas chromatograph-mass-spectrometer. The GC-MS consists of a HP-6890 gas chromatograph and a double focusing magnetic field mass-spectrometer. The sample concentration tube shown in **Figure 4** is a U-shaped stainless steel tube with 3 mm ID, 20cm long filled with Chromosorb W column packing with 30-60 mesh. The four-port valve (GL Science Type UMF-4) changes the carrier gas flow to the sample concentration tube or to the analytical column. Helium gas (Nippon Sanso, 99.9999% in purity) is introduced to a flow control device after decompressed from a cylinder and refined via an oxygen removal tube (U. S. Alltech OXY-TRAP) and a gas purifying tube filled with molecular sieve 13X (laboratory made). The helium carrier gas flow is controlled by a mechanical flow control device with stainless steel diaphragm (U.S. Porter Type VCD1000) and finally refined through an impurity trap tube immersed in liquid nitrogen.

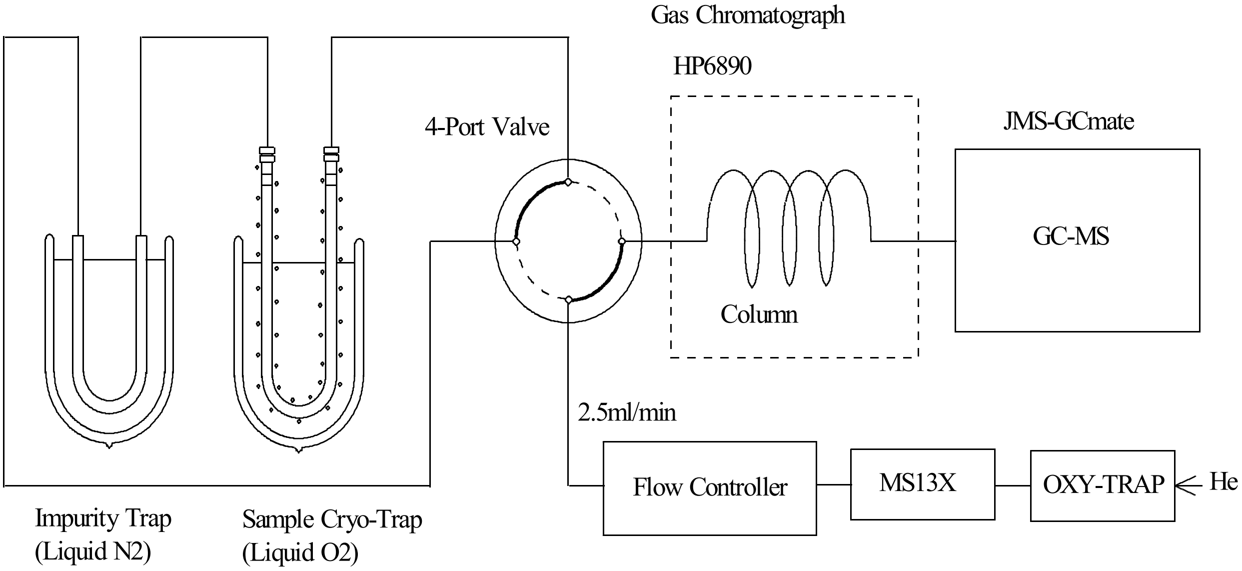

Figure 4. HFC-134 analytical system（GC/MS analysis ）.

The analytical conditions are shown in **Table 9**.

Table 9. Analytical conditions of GC-MS analytical method (HFC-134a)

Term		Condition
Pre-treatment	Precolumn	DC-550 25%, Shimalite 101, 60-80 mesh, 3 mm ID, 4m long, stainless steel
	Column temp.	30 ℃
	Carrier gas	N2, 50 ml/min
	Sample volume	300 ～ 350 ml
Analysis	Gas chromatograph	HP 6890
	Analytical column	Carbopack B（+1% SP1000） 60/80 mesh 0.8 mm ID, 3 m long
	Column temp.	30 ℃
	Carrier gas	He, 2.5 ml/min
	Concentration temp.	Liquid O2 temp.
	Desorption temp.	25 ℃
MS	Mass Spectrometer	JEOL JMS GC-Mate
	Ionization	EI（70 V, 300 uA）
	SIM	69（m/z）

(4) Analytical Procedures

(A) Sample Concentration Procedure

The sample concentration procedure was the same as described in GC analytical method 3.

(B) Re-concentration and Analysis Procedure

The re-concentration procedure was similar to the re-concentration procedure of GC analytical method 2. HFC-134a eluted at approximately three minutes from the precolumn under the conditions shown in **Table 9**.

Sample concentration tube 2 which contained HFC-134a fraction, kept in Liquid O2, was subsequently connected to the GC-MS, then the route of the carrier gas flow was changed to the sample concentration tube. The tube was then heated to 25 ℃, and a single mass ion monitoring (SIM) analysis with a mass number of 69 amu was initiated to run. HFC-134a eluted from the analytical column at approximately seven minutes under the conditions.

(3) Calculation

A relation curve must once be created beforehand to verify the linearity in the response of the detector in an expected range that would cover a dispersion of sample concentrations. See Chapter **2. METHOD** in the text of the report for the calibration gas, calculation method of concentrations and others.

APPENDIX B

HCFCS AUTOMATIC MEASURING APPARATUS

1. Outline of the HCFCs Automatic Measuring Apparatus

(1) HCFCs Automatic Measuring Apparatus

A schematic diagram of the HCFCs automatic measuring apparatus (hereinafter referred to as "the apparatus") is shown in **Figure 5**. The apparatus mainly consists of a sample introduction system and a GC-MS.

The sample introduction system was assembled in the JESC laboratory. The pneumatic valves (U.S. Nupro Type 6LVV) and metal bellows valves (U.S. Nupro Type SS-4H) are used in the system where the valves are exposed to the sample air. The three pneumatic rotary valves are GL Type AR-UMF-4 and Type AR-UMF-6. The electronic mass-flow controller which maintains constant sample air flow is a Kofloc Type 3650. The freezer is a Nippon Freezer Type MYBIO which has inner volume of 70 L. The nominal operation temperature of this freezer is -80 ℃. The cold trap tube 1 is a made of stainless steel with 3 mm ID, 200 mm long filled with 0.4 g of Carbopack B 60-80 mesh + 1% SP-1000 (U.S. Supelco). The cold trap tube 2 is a made of stainless steel with 2 mm ID, 100 mm long filled with 0.06 g of same packing mentioned above. The dryer tube is a made of stainless steel with 3 mm ID, 200 mm long filled with 0.3 g of Chromosorb W 30-60 mesh coated with 5 w/w% of Mg(ClO4)2. The cold trap tubes and the dryer tube are equipped with heating wires and thermocouples.

The GC-MS is a Shimazu 2010. The analytical column is a Chrompack CP-Sil 5CB (0.53 mm ID, 5 μ m film thickness, 100 m long) capillary column. Helium gas (99.9999%) is used as the carrier gas at a flow rate of 5mL/min and as the purge gas at a flow rate of 20mL/min. The Shimazu 2010 GC/MS has an

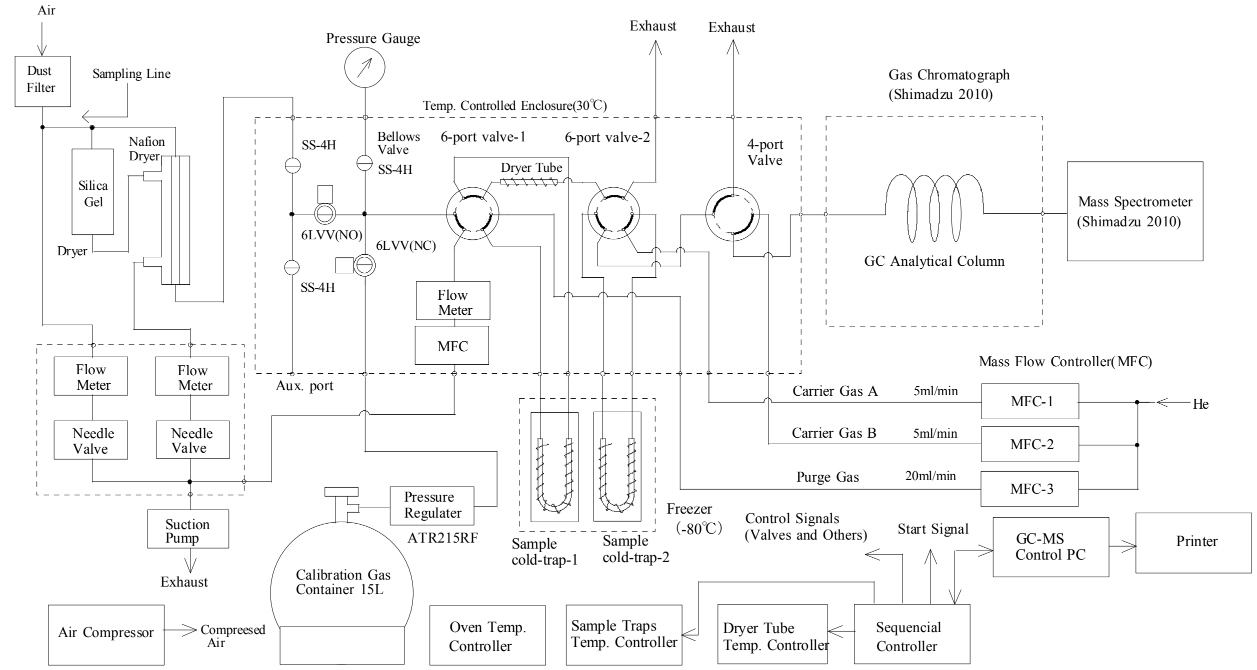

Figure 5. HCFCs automatic measuring apparatus

electric carrier gas control system designed for split/split-less injection. This flow control system is not available for this analysis because the control software of the GC-MS does not permit any carrier gas leakage that may occur during the analysis. Additional three mechanical carrier gas flow controllers therefore were required (U.S. Porter Type VCD1000 for the carrier gas and Koflock Type 2203 for the purge gas).

(2) Operation

The sample air was first dehumidified via the Nafion dryer tube (U.S. Perma Pure Type MD-110-48P-4). The sample air was passed through the sample concentration tube kept at -80 ℃ in the freezer. Then, the compounds are separated from the air. During the sampling procedure, the sample air was drawn at a rate of 0.1 L/min over the sampling period of 10 min. 1L of sample air was concentrated on the concentration tube as a result. Then the sample concentration tube was heated from -80 ℃ to 150 ℃ in a short period of time in the helium gas flow, the compounds collected on the concentration tube packing were vaporized. The released analytes were dehumidified via the Mg(ClO4)2 dryer tube and again concentrated on the small secondary cold trap tube to enhance chromatographic resolution of the individual sample components. The secondary cryo-concentration tube was heated to 150 ℃, then the compounds collected on the tube packing were again vaporized and carried onto the analytical column by the helium gas flow. The analytical column temperature was raised from 30 ℃ up to 120 ℃ at a rate of 2 ℃/min.

(3) Concentration Procedure

Among analytical methods of CFCs or HCFCs, since these substances have low boiling temperatures, the typical concentration procedures are performed under around liquid oxygen temperature. However, a continuous feed of liquid oxygen or other cryogen to an automatic measuring apparatus would obviously take much efforts. We employed a commercial freezer instead of the cryogen. Since the nominal lowest temperature of this freezer was -80 ℃, a possible error may occur during the concentration cycle for the target substances that have extremely low boiling temperatures. As HCFC-22 has the lowest boiling temperature of -40 ℃ among the target analytes, this substance was considered to possess the greatest difficulty in concentration procedure. Therefore, we adopted a cold trap tube filled with Carbopack B 60-80 +1% SP-1000 to improve the adsorptiveness. The break through capacity of this cold trap tube for HCFC-22 was estimated to be over 10L at -80 ℃. As a concentration tube filled with adsorbent generally has a difficulty in the recovery of compounds which have high boiling temperatures, in the operation of this apparatus, the directions of the gas flows in the concentration tubes were replaced between the concentrating procedure and the eluting procedure to ease the elution of the compounds (back-flush).

2. Introduction of the Sample Air

A stainless steel tube with 8 mm OD, approximately 30 m long was extended from the apparatus through the wall to the sampling point at the rooftop of the JESC building. Ambient air from the sampling point was drawn through this tubing to the apparatus. The outline of the sample line is shown in **Figure 6**. The inside of the sample line was kept ventilating with an ambient air flow at a rate of 0.3L/min using a diaphragm pump.

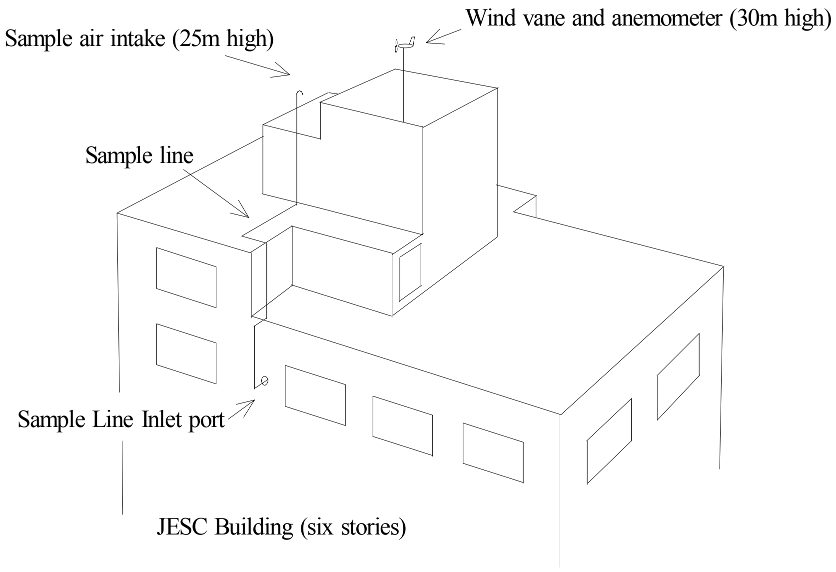

Figure 6. Sampling line for automatic measurement

APPENDIX C

CHROMATOGRAMS

Typical gas chromatograms obtained in this work are shown in **Figure 1 - Figure 9**.

Figure 1 is a typical chromatogram of CFC-11 and others / GC analytical method 1 (Nemuro, 11:00, January 18, 2007). **Figure 2** is a typical chromatogram of CFC-114 / GC analytical method 2 (Wakkanai, 15:00, January 15, 2007). **Figure 3** is a typical chromatogram of CFC-115 / GC analytical method 3(Wakkanai, 13:00 January 15, 2007). **Figure 4** is a typical chromatogram of halon-1211 and halon-1301 / GC analytical method 4 (Wakkanai, 13:00, January 15, 2007). **Figure 5** is a typical chromatogram of halon-2402 / GC analytical method 5 (Nemuro, 11:00, January 17, 2007). **Figure 6** is a typical chromatogram of HCFC-22 / GC analytical method 6 (Nemuro, 12:00, January 17, 2007). **Figure 7** is a typical chromatogram of HCFC-141b / GC analytical method 7 (Wakkanai, 15:00, January 15, 2007). **Figure 8** is a typical chromatogram of HCFC-142b / GC analytical method 8 (Wakkanai, 13:00, January 15, 2007). **Figure 9** is a typical chromatogram of HFC-134a / GC/MS analytical method (Wakkanai, 11:00, January 16, 2007).

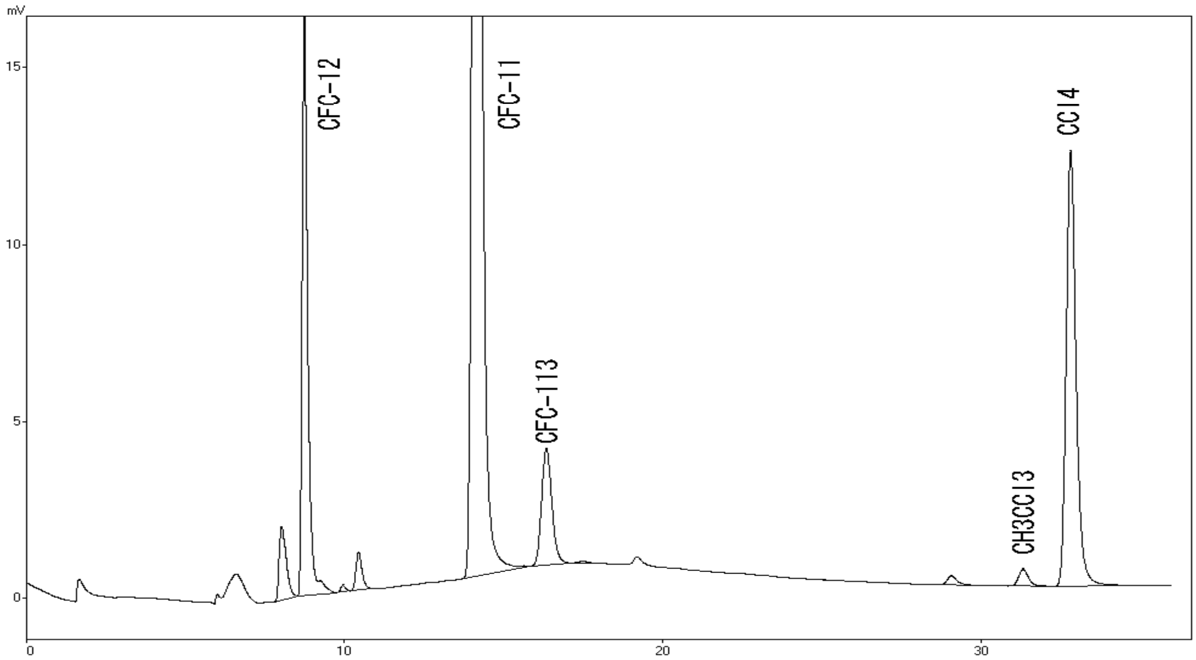

Figure 1. Typical chromatogram from GC method 1 of a sample collected in Hokkaido. CFC-11, CFC-113, CH3Cl3, and CCl4 measured.

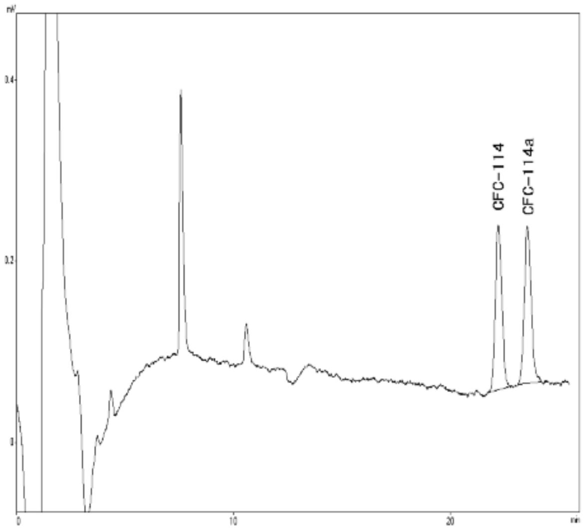

Figure 2. Typical chromatogram from GC method 2 of a sample collected in Hokkaido
CFC-114 measured

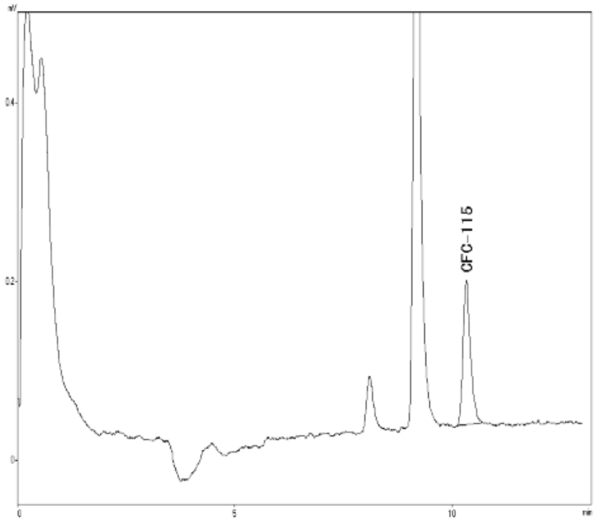

Figure 3. Typical Chromatogram from GC method 3 of a sample collected in Hokkaido
CFC-115 measured

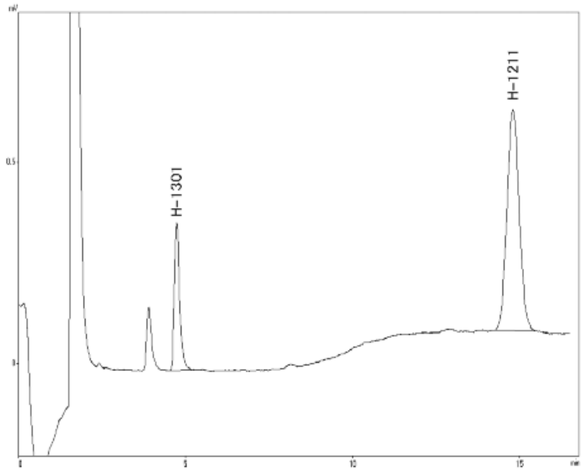

Figure 4. Typical chromatogram from GC method 4 of a sample collected in Hokkaido Halon-1211 and halon-1301 measured

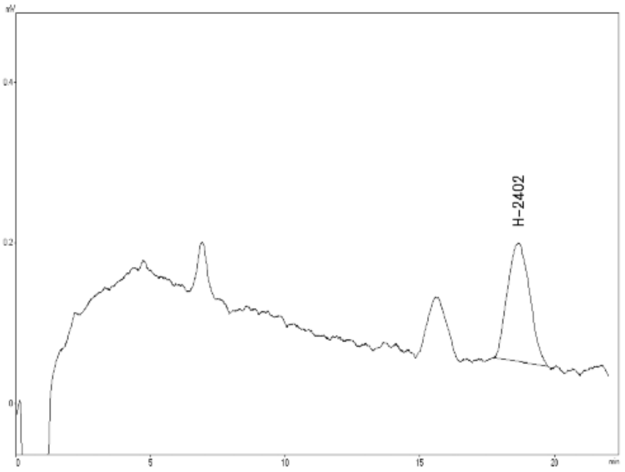

Figure 5. Typical Chromatogram from GC method 5 of a sample collected in Hokkaido Halon-2402 measured

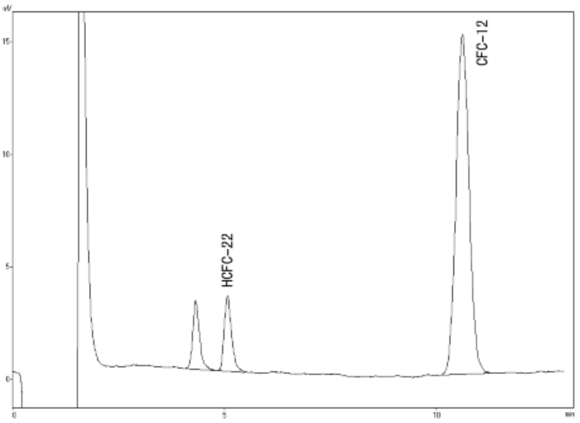

Figure 6. Typical chromatogram from GC method 6 of a sample collected in Hokkaido HCFC-22 measured

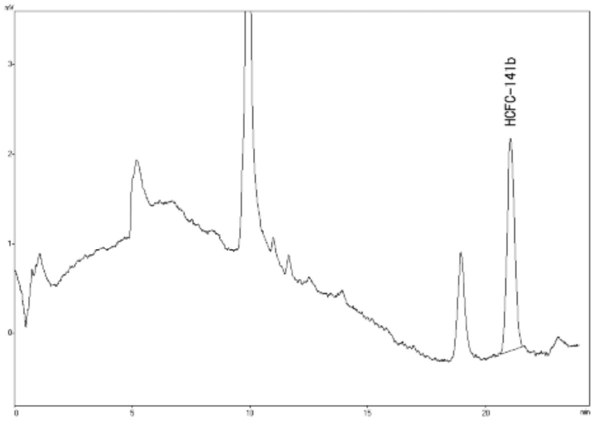

Figure 7. Typical Chromatogram from GC method 7 of a sample collected in Hokkaido HCFC-141b measured

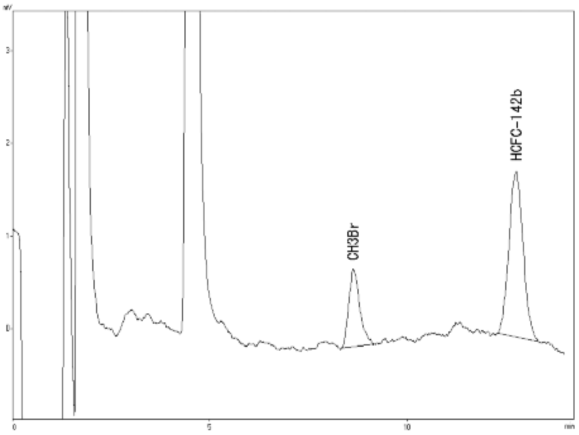

Figure 8. Typical chromatogram from GC method 8 of a sample collected in Hokkaido HCFC-142b and CH3Br measured

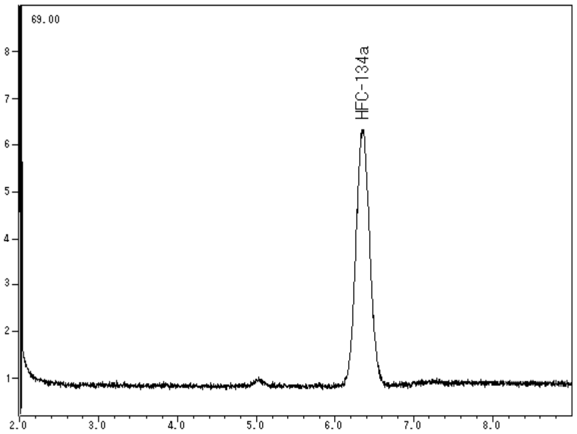

Figure 9. Typical Chromatogram from GC-MS method of a sample collected in Hokkaido HFC-134a measured