

2. METHODS

2.1. SAMPLE CONTAINERS

Two types of containers with a volume of 2 L (1) and 12 L were used in the sample collections. The respective external appearance of each type of container is shown in **Figure 2.1** and **Figure 2.2**. The sampling containers were made of stainless steel and had valves with a stainless steel body and metal bellows (U.S. Nupro Type SS-4H).

The containers were prepared (see note) by JESC and sent to the NS Environmental Science Consultant Corporation, Sapporo division which conducted the field sampling. This division carried the containers in its own vehicle to the sampling locations and then used them for the sampling.

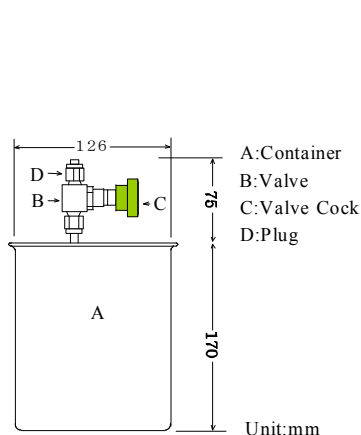


Figure 2.1. 2 L container

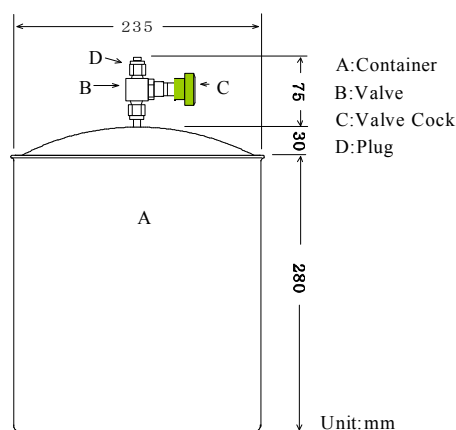


Figure 2.2. 12 L container

2.2. SAMPLE COLLECTION

In the background area (Wakkanai and Nemuro, Hokkaido), the observer selected a seashore location that was suitable for the sampling where the wind was blowing from the sea onto the land. In the sampling procedures, the observer removed the plug of the sampling container beforehand, and held the container against the wind and then opened the valve. The observer closed the valve when the sound of inflowing air stopped and then tightened the plug. Either 2 L containers or 12 L containers were used for the air collections. The air samples were collected at ambient pressure. The observer recorded the wind direction, wind speed, air temperature, and humidity at the time of the sampling using a propeller anemometer, a wind vane, and an Assmann hygrometer. In both locations, the observer collected five samples over two consecutive days. The observer considered the intervals between the samplings to be equal to an hour or longer as far as possible. The observer apportioned the number of samples between the two days.

An outline of the sampling method for the automatic measurement apparatus in the urban area observation (JESC, Kawasaki-shi) is given in section 2.5 and the details of the automatic measuring apparatus are also described in Appendix B.

Note) The preparation of the containers was as follows: The interior of the containers was cleaned using boiling water, then dried and evacuated to a pressure of 0.1 mmHg (about 13 Pa) or less. Next, they were heated for about 1 hour at 120 °C, filled with pure air, immediately evacuated, and then filled with pure air with approximately 1% humidity. The containers were left to stand for a few days, and finally evacuated.

2.3. CALIBRATION GAS

(1) Calibration Gas for Dominant CFCs and Other Dominant Hydrocarbons

The calibration gas for the CFC-11, CFC-12, CFC-113, carbon tetrachloride, and 1,1,1-trichloroethane measurements was prepared through the dilution of the raw gases or concentrated liquids with synthetic air using the dilution system shown in **Figure 2.5** (July 1989). The calibration gas was saved in a 6 L stainless steel container, which was manufactured according to our specifications. The calibration gas contained 0.2 ppbv of carbon tetrachloride and 0.5 ppbv of the other substances.

(2) Calibration Gas for CFC-114, CFC-115, Halons, HCFCs and Methyl Bromide

The calibration gas for the CFC-114, CFC-115, halons, HCFCs, and methyl bromide measurements was prepared through the dilution of the raw gases or concentrated liquids with synthetic air using the dilution system shown in **Figure 2.5** (October 2003). The calibration gas was saved in a 15 L stainless steel container (U.S. Scientific Instrumentation Specialist Inc.). The calibration gas contained 0.1 ppbv of CFC-114, 0.05 ppbv of CFC-115, halon-1211, halon-1301, and halon-2402, 0.2 ppbv of HCFC-22, and 0.1 ppbv of HCFC-142b and methyl bromide.

The calibration gas also contained approximately 0.5 % of water for the purpose of stabilizing the concentrations of the substances, however, the effect of adding water for the improvement of the stability of these substances in a stainless steel container is not well understood (4). The stability of these substances in a stainless steel container kept for a long period of time is also not well understood.

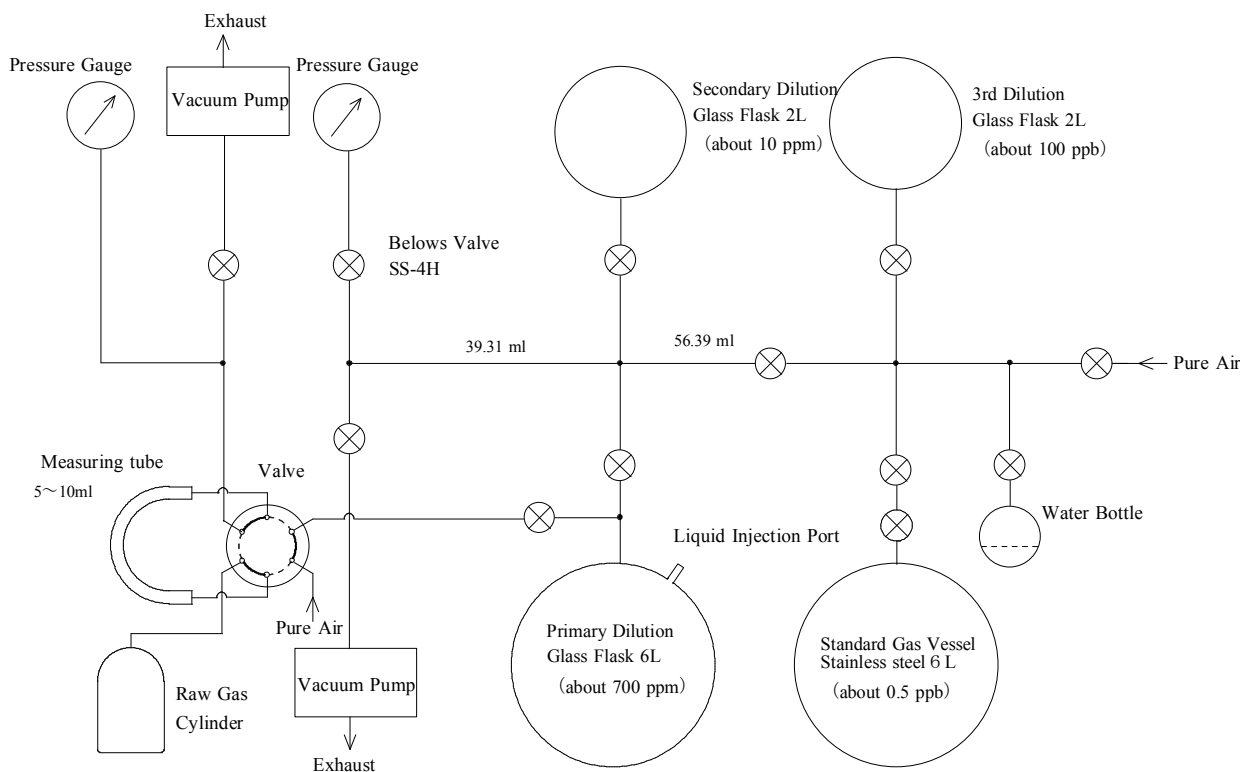


Figure 2.5. Calibration gas dilution system

(3) Calibration Gas for HCFC-141b and HFC-134a

The calibration gas for the HCFC-141b and HFC-134 measurements was purchased from Taiyo Toyo Sanso Inc (December 2001). The calibration gas contained 20.8 pptv of HCFC-141b and 20.8 pptv of HFC-134 diluted with nitrogen, and was pressured in a 10L aluminum alloy cylinder. The stability of HCFC-141b and HFC-134a kept for a long period of time in an aluminum alloy cylinder is not well understood.

(4) Calibration Gas for Daily Measurements

An air sample collected at Wakkanai in March 2000 (a 32L stainless steel container, U.S. BRC) was used as the standard gas for the daily measurement of CFC-11, CFC-12, CFC-113, CFC-114, halon-1211, halon-1301, carbon tetrachloride, 1,1,1-trichloroethane, and HCFC-22. The concentrations of these substances in the daily standard were determined through comparison with the calibration gas mentioned above. The calibration gases mentioned above were used for the daily measurement of CFC-115, halon-2402, HCFC-141b, HCFC-142b, methyl bromide, and HFC-134a.

2.4. ANALYTICAL METHOD

(1) Outline of Analytical Method of CFCs and Other Dominant Substances

Since an electron capture detector (ECD) well responds to many CFCs and other halocarbons (halons, carbon tetrachloride, 1,1,1-trichloroethane) specified as the subject substances for measurement in this program, these substances were measured by gas chromatography using an ECD (hereinafter referred to as the "GC analytical method"). These substances were divided into five groups according to their physical characteristics, typical atmospheric concentrations, and the existence of interfering compounds and suitable analytical conditions were established for each group. The grouping of the substances and the five analytical methods are summarized in **Table 2.1**.

GC analytical method 1 shown in the table was an analytical method that concentrated the compounds in a small amount of the sample air through the introduction of the sample on a cryo-concentration tube kept at an extremely low temperature and with the immediate introduction of the compounds onto the analytical column. This method was applied to the measurement of CFC-11, CFC-12, CFC-113, carbon tetrachloride, and 1,1,1-trichloroethane which exist in high concentrations in the atmosphere.

GC analytical method 1 was not applicable to the precise analysis of the other substances due to the extremely low concentrations of these substances in the atmosphere. Therefore, these substances excluding the above five substances were measured by several methods based on the dual column separation technique to completely separate these substances from other compounds. As shown in the table, GC analytical method 2 was applied to the measurement of CFC-114, GC analytical method 3 was applied to the measurement of CFC-115, GC analytical method 4 was applied to the measurement of halon-1211 and halon-1301 and GC analytical method 5 was applied to the measurement of halon-2402.

Table 2.1. Grouping of CFCs and other halocarbons, and analytical methods

Method	Detector	Analytical column / Precolumn	Substance
GC analytical method 1	ECD	DC-550 25% 4m + OV-101 25% 2m	CFC-11, CFC-113, Carbon tetrachloride, 1,1,1-Trichloroethane
GC analytical method 2	ECD	Alumina PLOT 50m / DC-550 25% 4m	CFC-114
GC analytical method 3	ECD	Alumina PLOT 50m / Carbopack B +1% SP1000 3m	CFC-115
GC analytical method 4	ECD	Carbopack B +1% SP1000 2m / DC-550 25% 4m	Halon-1211, Halon-1301
GC analytical method 5	ECD	Carbopack B +1% SP1000 1.5m / OV-17 25% 5m	Halon-2402

(2) Outline of Analytical Method of HCFCs, Methyl Bromide, and HFC-134a

Although an ECD scarcely responds to HCFCs and methyl bromide in comparison with CFC-11 and carbon tetrachloride, the addition of a small amount of oxygen into the carrier gas fairly improves the sensitivity of the detector to these substances (8). In addition, the measurement method using GC-ECD generally gives a higher accuracy than that using a gas chromatograph mass spectrometer (hereinafter referred to as "GC-MS"). A method using GC-MS was applied to the analyses of urban air in the series of measurements in this survey during 1992-1995. These substances were measured using GC-ECD with the carrier gas flow doped with oxygen. Since it was difficult to precisely measure these substances simultaneously due to the problem of separation, the three HCFCs and methyl bromide were divided into three groups, and suitable analytical conditions were established for each group. CFC-12 could also be analyzed by GC analytical method 1. Since the precision of the measurement was in principle better than that of GC analytical method 1, the concentrations of CFC-12 were determined by this method. Since an ECD is insufficiently responsive to HFC-134a, even when modified by O₂ doping, a GC-MS was applied to the measurement of this substance (see note). The grouping of the substances and the four analytical methods are summarized in **Table 2.2**. The details of each of the measuring methods mentioned above are reported on in Appendix B.

Note) The response of the O₂-doped ECD to HFC-134a did not exceed 1/70 of that of HCFC-142b.

Table 2.2. Grouping of HCFCs, methyl bromide, and HFC-134a and analytical methods

Method	Detector	Analytical column / Precolumn	Substance
GC analytical method 6	ECD (O ₂)	Carbopack B +SP1000 1% 3m / DC-550 25% 4m	HCFC-22, CFC-12
GC analytical method 6	ECD (O ₂)	Carbopack B +SP1000 1% 3m / DC-550 25% 4m	HCFC-142b, Methyl bromide
GC analytical method 6	ECD (O ₂)	Carbopack B +SP1000 1% 3m / DC-550 25% 4m	HCFC-141b
GC/MS analytical method	MS	Carbopack B +SP1000 1% 3m / DC-550 25% 4m	HFC-134a

(3) Calibration of Sensitivity and Calculation of Concentration

The atmospheric concentrations of the subject substances measured were determined by comparison of the areas or heights of the peaks of the substances between the samples and the reference (an air sample in which the concentrations were known or the calibration gas, see Section 2.3) both measured under the same conditions. The reference gas was measured once while the sample analyses were conducted twice or three times. The atmospheric concentrations of the subject substances measured were finally calculated as a value with respect to dry air (volume/volume) through compensation for the humidity observed at the time of the air collection. The resulting concentrations were expressed in parts-per-trillion by volume (pptv, 10^{-12}) or parts-per-billion by volume (ppbv, 10^{-9}). All the concentrations obtained from the background survey are expressed in pptv. The concentrations observed in the urban area in past surveys frequently reached the ppbv level or higher, thus concentrations obtained from the urban area survey are principally expressed in ppbv.

(4) Detection Limit

The detection limits of subject substances measured using the manual analytical methods are shown in **Table 2.3**. The detection limits were calculated from the heights of the peaks equivalent to three times the noise level for the typical sample volumes (see Appendix A).

Table 2.3. Detection limits of subject substances measured using manual analytical methods

(Unit: pptv)

Substance	Detection limit	Substance	Detection limit	Substance	Detection limit
CFC-11	0.5	CFC-115	2	1,1,1-Trichloethane	2
CFC-12	5	Halon-1211	0.2	HCFC-22	10
CFC-113	2	Halon-1301	0.2	HCFC-141b	1
CFC-114	0.5	Halon-2402	0.05	HCFC-142b	1
CFC-114a	0.05	Carbon tetrachloride	1	Methyl bromide	0.5

2.5. AUTOMATIC MONITORING IN URBAN AREA

(1) Monitoring by Automatic Measurement

Since concentrations of the specified substances in urban air vary widely, only a large number of measurements can yield typical values at a sufficient level of confidence through averaging of the results. However, it was difficult to perform such a sufficient number of measurements with manual operations. Therefore, continuous monitoring with an automatic measuring apparatus (hereinafter referred to as the "CFCs automatic measuring apparatus") had been conducted since 1990 (7).

The concentrations of CFCs, carbon tetrachloride, and 1,1,1-trichloroethane in air that had been measured using the "CFCs automatic measuring apparatus" declined and were recently approaching the background levels due to the control of these substances under the ozone layer protection law (7). However, concentrations in air of HCFC-22, HCFC-141b, HCFC-142b, and HFC-134a that emerged as substitutes for CFCs have been continuously increasing (7), and the large amount of emissions of these substances in urban or industrial areas has become of concern.

The "CFCs automatic measuring apparatus" was not applicable to these new substances. Therefore, these substances were measured by analytical methods with air collection using containers and manual operation during 1993-2003, and this survey revealed that the concentrations of these substances in urban air were considerably higher than those in the background area, however, manual measurements could not be performed for more dense surveys or monitoring in detail (8).

A new automatic measuring apparatus (hereinafter referred to as the "HCFCs automatic measuring apparatus" or "the new automatic measuring apparatus" or "the apparatus") that is able to measure these CFC-substitute substances was installed and began operation. This apparatus is equipped with a mass spectrometer as the detector and a sample concentration procedure is adopted that "CFCs automatic measuring apparatus" did not have, thus this apparatus is able to sensitively determine concentrations in air of HCFC-22, HCFC-141b, HCFC-142b, methyl bromide, and HFC-134a, as well as the conventional CFCs and halocarbons. Among the substances that had been measured by the "CFCs automatic measuring apparatus" CFC-11 and CFC-12 will be continuously observed by the new automatic measuring apparatus since the concentrations of these substances are prevalent and emissions of them in urban or industrial areas are of concern.

(2) Measurements by Using of "HCFCs Automatic Measuring Apparatus"

As mentioned above, the HCFCs automatic measuring apparatus (assembled in the laboratory) was used to analyze air samples by gas chromatography with a mass spectrometer. This apparatus analyzed air samples by concentrating a sample of air on a concentration tube that was cooled to -80 °C in a freezer with the subsequent desorption of the concentrated compounds and the introduction of the compounds into the GC-MS for selected ion monitoring detection (SIM). This apparatus operated automatically, including the calibrating operation. The apparatus is installed in a temperature-controlled room. The ambient air was introduced from the sampling air intake (approximately 25 m from the ground) to the apparatus through a stainless steel pipe. The air intake is installed on the rooftop of the building. The concentrations of CFC-11, CFC-12, HCFC-22, HCFC-141b, HCFC-142b, methyl bromide, and HFC-134a in air were determined. The apparatus analyzed the ambient air every five hours. The apparatus operated continuously with the exception of short periods of time due to maintenance, mechanical problems, power failures, or other reasons.

(3) Calibration of Sensitivity

The calibration gas used for the daily calibration was reserved in a 15L stainless steel container, the

interior of which was coated with SiO₂. The calibration gas contained 250 pptv of CFC-11, 500 pptv of CFC-12, 200 pptv of HCFC-22, and 100 pptv of HCFC-141b, HCFC-142b, methyl bromide, and HFC-134a.

(4) Detection Limit

The detection limits for the subject substances measured by the HCFCs automatic measuring apparatus are shown in **Table 2.4**. The detection limits equal to three times the standard deviations obtained from the results of five times repeated measurements of a sample with low concentrations. Of all the subject substances measured, the detection limit was below the current background level.

Table 2.4. Detection limits of subject substances measured using automatic measuring apparatus (Unit: pptv)

Substance	Detection limit	Background level
CFC-11	2	244
CFC-12	4	549
HCFC-22	2	190
HCFC-141b	0.5	21.0
HCFC-142b	1	18.4
Methyl bromide	1	9.4
HFC-134a	1	46.8

Note) Background levels shown here were obtained in January 2007.

(5) Observation of the Weather

Observation of the weather conducted simultaneously with the measurements was necessary since it was expected that the degree of variation of the concentrations of the measured substances in air would considerably depend on the meteorological conditions of the surrounding area as well as the level of emissions. Therefore, in consideration of their importance, the wind direction and wind speed have continuously been observed at the rooftop of the JESC building.