A Simple Interface for a Gas Chromatography System for Air Samples in Sub-Ambient Pressure

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Introduction

In recent years, concentrations of many atmospheric components have undergone rapid changes especially in association with human activities.[1] Increases in concentrations of greenhouse gases such as CO_2, CH_4, N_2O, and Chlorofluorocarbons (CFCs) in the atmosphere are typical examples, which have resulted from activities such as fossil fuel consumption, agricultural revolutions, deforestation and refrigeration and air conditioning industries. Considering the importance of these changes on the global climate, much effort to continuously monitor these gases has been expanded worldwide.[2-4] An important operating mode of many continuous monitoring stations is the collection of air samples in the field and their delivery to laboratories for analysis.

One frequently used method to collect air samples is the filling of pre-evacuated sampling flasks with air samples up to the ambient pressure.[5] In order to analyze air samples with a gas chromatography system (GC), however, a positive pressure above the ambient pressure of the samples is required to flush the injection loop with air samples before sample injection into the system. A frequently used technique is to connect a transfer pump between a sampling flask and the injection loop of the GC system.[6] Some researchers fill up sampling flasks above ambient pressure with a pump in order to utilize this “excess” pressure to flush the injection loop.[7] However, addition of the pump into the analysis procedure can introduce the possibility of contamination and also an excess usage of samples for the analysis.

We have developed a simple interface system to introduce air samples in flasks with sub-ambient pressure into the injection loop and to pressurize the samples to ambient pressure without any contamination prior to their injection into GC for analysis. The system has been successfully used to monitor the concentrations of CFC-12 and CFC-12, important greenhouse gases and also ozone-depleting chemicals[8,9] in background air samples collected at Gosan, Jeju Island. In this paper, we describe the essential attributes of the interface system.

Analytical Method

The schematic diagram of the interface system is shown in Figure 1. It consists of a vacuum manifold with appropriate vacuum gauges, a sampling bottle, the injection loop of the GC system, and a three-way valve connecting the vacuum line to the atmosphere. The principle of the step-wise operation is shown in Figure 2. The interface system including the injection loop is first evacuated to vacuum (2a); a gas sample is expanded from the sample flask into the pre-evacuated injection loop by opening the sample valve (2b); then, the sample in the injection loop under sub-atmospheric pressure is pressurized to the ambient pressure avoiding any contamination by introducing the ambient air from the back through the 52 mL (1/8” O.D., 15 m) isolation coil by switching the position of the three-way valve (2c). The sample in the injection loop, then, can be injected into a GC system for analysis. The long isolation coil is essential for preventing any contamination of samples from intruding air.

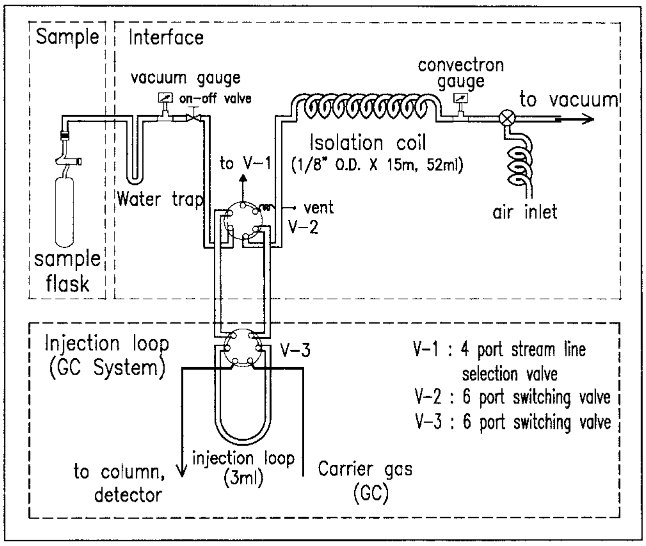

Figure 1. A schematic diagram of the interface manifold constructed for the analysis of CFC-12, CFC-11 and N_2O from flask samples. The manifold was constructed to transfer air samples left in the flask with sub-atmospheric pressure into the injection loop of GC system.

Results and Discussion

System integration. This interface system was assembled

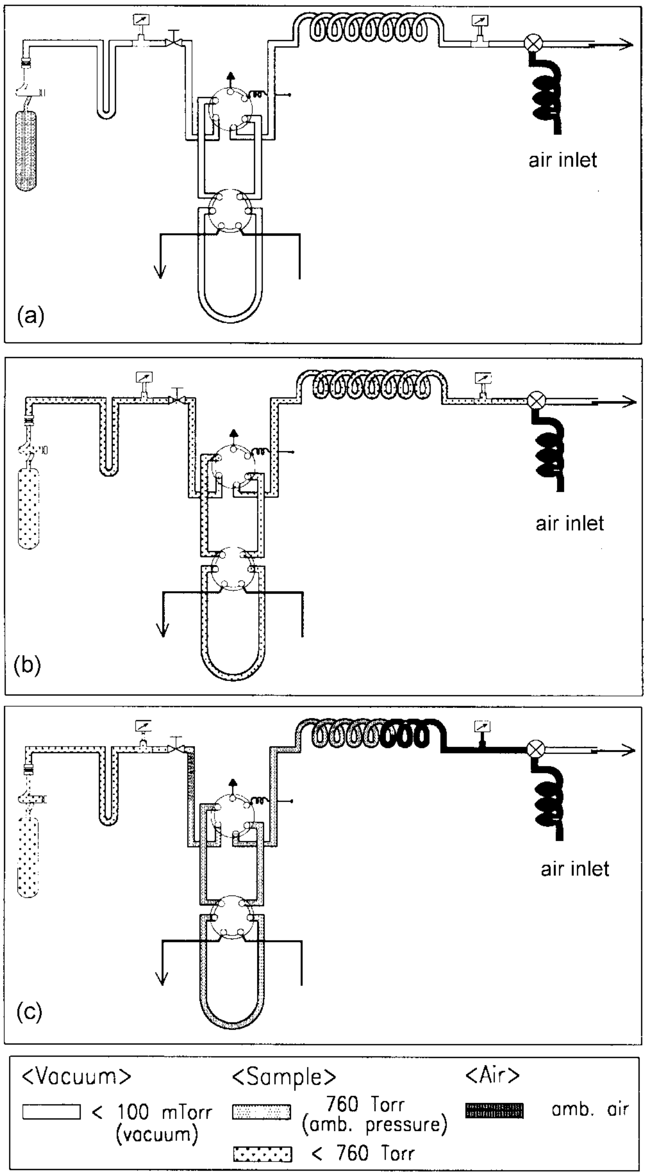

Figure 2. A schematic diagram of the analytical method for CFC-12 and CFC-11 measurements from flask samples. The interface system including the injection loop is first evacuated to vacuum (2a), a gas sample is expanded from the sample flask into the pre-evacuated injection loop by opening the sample valve (2b), then, the sample in the injection loop with sub-atmospheric pressure is pressurized to the ambient pressure avoiding any contamination by introducing the ambient air from the back through the 52 mL (1/8" O.D., 15 m) isolation coil by switching the position of the three-way valve (2c).

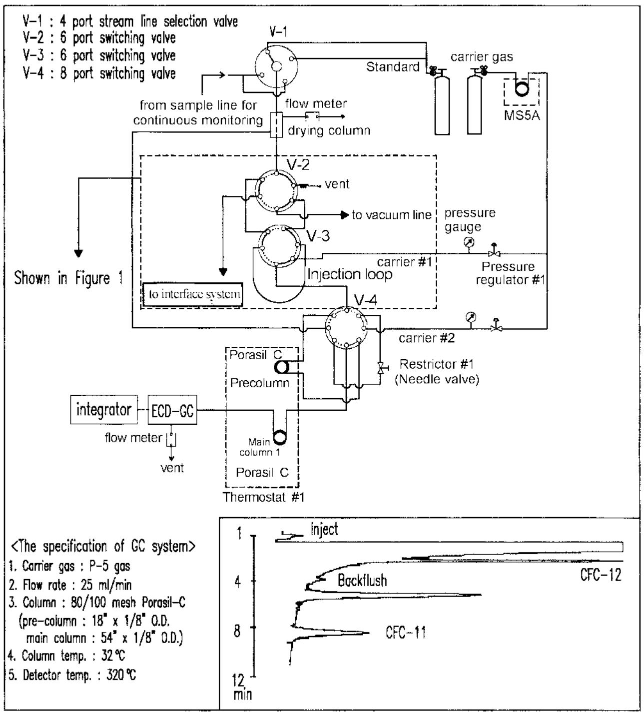

Figure 3. A schematic diagram of ECD-GC system with a typical chromatogram. CFC-11 and CFC-12 were separated by two Porasil-C columns (a pre-column: 80/100 mesh Porasil-C column, 18” × 1/8” O.D. and a main column: 80/100 mesh Porasil-C column, 54” × 1/8” O.D.) maintained at 32 °C. When both CFC-11 and CFC-12 passed through the pre-column, the flow direction of the carrier gas in the pre-column was reversed by switching the system into a back-flushing mode in order to maintain the columns clean from other long-residing CFC compounds present in the samples.[10]

with an ECD-GC system (HP5890 Series II), which was developed for analyzing CFC-11 and CFC-12 in the air samples and is shown in Figure 3. A P-5 gas (a mixture gas of Ar 95% and CH_4 5%) at a flow rate of 25 mL/min was used as a carrier gas for the GC system. CFC-11 and CFC-12 were separated from other components by passing gas samples through two Porasil-C columns (a pre-column: 80/100 mesh Porasil-C column, 18” × 1/8” O.D. and a main column: 80/100 mesh Porasil-C column, 54” × 1/8” O.D.) maintained at 32 °C. When both CFC-11 and CFC-12 passed through the pre-column, the flow direction of the carrier gas in the pre-column was reversed while the flow in the main column was still maintaining the normal direction for the further separation by switching the system into a back-flushing mode in order to maintain the columns clean from other long-residing CFC compounds present in the samples. And the typical chromatogram for CFC-12 and CFC-11 are shown in Figure 3. Details of the GC system is further described elsewhere.[10]

Validation of the system. In order to validate the system operation, the initial test was carried out with a CFC-free clean air sample. The CFC-free clean air was prepared by passing the ambient air through the liquid nitrogen trap at –195.8 °C. The test was conducted using samples with varying pressure in the manifold and the results are shown in Figure 4. The figure clearly shows that the samples are not contaminated at all with the ambient air during the pressurizing step of the sample in the injection loop to the ambient pressure as long as the initial sample pressure in the manifold is over 200 mmHg above vacuum.

Precision and accuracy. The precision of the analysis was determined by repeated measurement of standard air samples of known concentration. The overall precision of the analysis was 0.4% for CFC-12 and 1.0% for CFC-11,

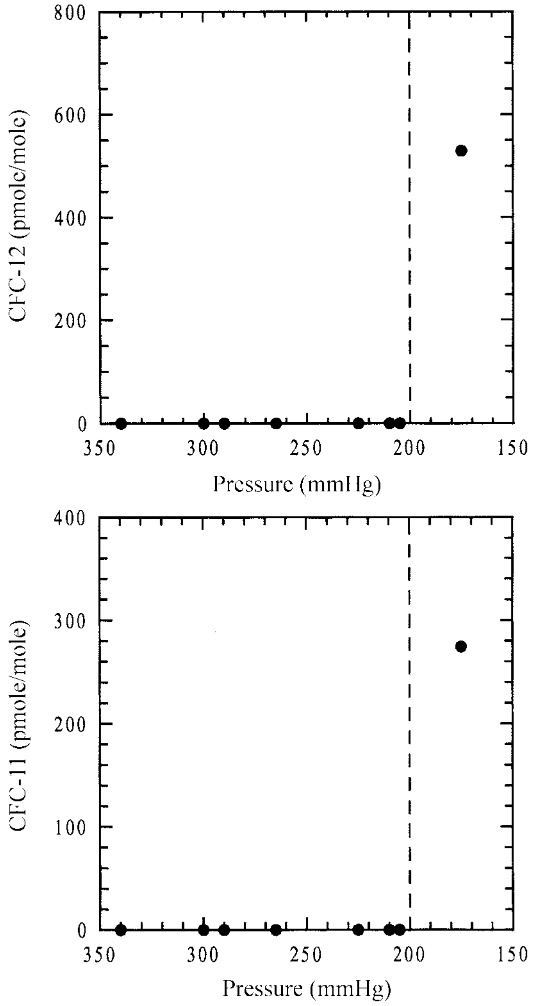

Figure 4. A graph showing an effect of pressure about concentrations of CFCs. It clearly shows that the samples are not contaminated at all as long as the sample pressure in the manifold is over 200 mmHg above vacuum.

respectively.

The standard for CFC-11 and CFC-12 used in the experiment was prepared at the Scripps Institution of Oceanography, according to the scale used for global monitoring program, AGAGE (Weiss, SIO 1995 scale).[11] The concentration of the CFC-11 and CFC-12 in the standard air was 267.17 pmole/mole and 523.53 pmole/mole, respectively.

In the actual analysis, one standard air sample was analyzed for every 4 air samples to keep the accuracy of the data within the precision of the analysis.

Application: Gosan, Jeju Island. The system has been used since 1995 to analyze CFC-11 and CFC-12 in 3-liter flask samples, collected regularly once a week at Gosan, Jeju Island, a background monitoring station in Korea. The flasks with samples in the atmospheric pressure were first analyzed for CO_2 with an NDIR analyzer and the rest of the samples in the flask with sub-atmospheric pressure were analyzed for CFC-11 and CFC-12 with the GC system. The CO_2 results at the Gosan Station, shown in Figure 5, clearly reveal that the air at the Jeju Island is typical of background

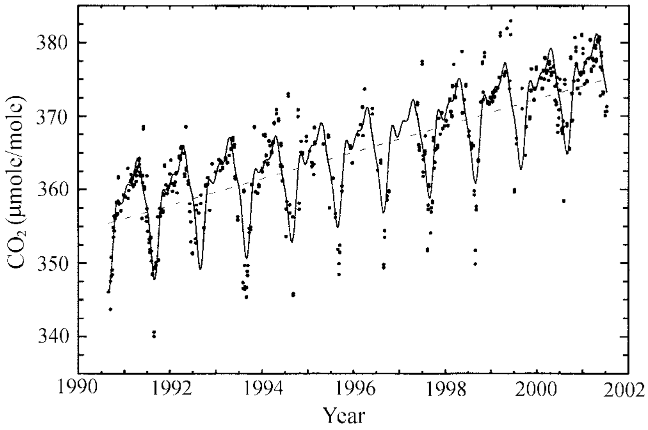

Figure 5. Concentrations of atmospheric CO_2 at Gosan Station, Jeju Island.

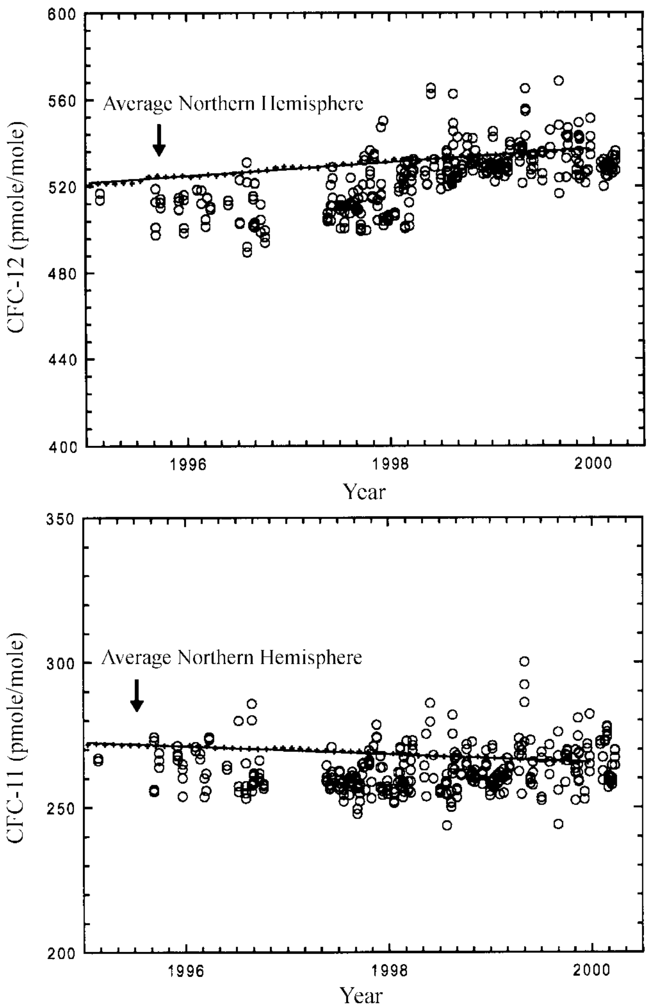

Figure 6. Concentrations of CFC-12, CFC-11 from air samples collected in 3-liter glass flasks at Gosan station (1995. 1.-2000. 3.). The results clearly show that the concentrations in the area are highly comparable to global average values for these gases in the mid-latitude Northern Hemisphere.

clean atmosphere characteristics.

The CFC-11 and CFC-12 results are shown in Figure 6. The global average concentrations in the Northern Hemisphere are also shown in the figure. The studies from global monitoring networks show that the increase rate of CFC-11 and CFC-12 concentrations in the clean atmosphere has been reduced markedly in recent years especially since the initiation of global reduction campaign according to the 1987 Montreal Protocol.[9] The results in Figure 6 show that the concentrations in the atmosphere near Jeju Island highly comparable to the global average values in the mid-latitude Northern Hemisphere, further showing that Jeju Island may serve as a background monitoring station in Korea.[4]

Conclusion

An interface for a GC system was developed in order to analyze gas samples in sampling flasks with sub-atmospheric pressure and was applied successfully to monitor important greenhouse gases such as CFC-11 and CFC-12 at Gosan, Jeju Island. This interface system can be applied to any GC system and thus could be useful to monitor many other important components in the atmosphere.

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