Supporting Information

A Detachable Trap Preconcentrator with a Gas Chromatograph-Mass Spectrometer for the Analysis of Trace Halogenated Greenhouse Gases

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ST 1. Measurement procedure for airborne NF_3

The procedure for measuring ambient level NF_3 consists of 11 steps in total. The position states of V1, V2, V3, V4, V5, linear motion 1, and linear motion 2 are defined and expressed in coordinates. (on/off, on/off, on/off, on/off, 1/2/3, on/off, and on/off, respectively) V5 is controlled to set three types of gas flow pathways. (Figure S1) The default coordinates are given in Figure 1. Henceforth, if the flow direction is toward the GC-MS, fore-flush will be recalled to define the flow direction. In case of back-flush, the gas flow goes to vent 1. Regarding the coordinate definition of the linear motion, piston push, namely, the trap attachment is denoted as the "on" state. The 11 steps involved in the measurement of NF_3 at the ambient concentration are as follows. Step 1: The sample was flown in the line before the concentration trap, in order to flush the inner surface of the gas line. Purified He was flowed in the last part of the line to maintain the inert conditions (on, on, on, off, 1, on, on). Step 2: V3 was maintained in the on-state for 10 min and the sample was flowed at 200 mL/min and concentrated at T1, which was maintained below −135°C (on, on, off, off, 2, on, on). Step 3: The sampling line was cleaned by flushing with He for 1 min (off, off, off, off, 2, on, on). Step 4: The temperature of T1 was adjusted to −75°C through the PID control of the cartridge heater. In this step, the trap was attached on the baseplate. In order to prevent desorption loss of the adsorbed gas sample due to overshooting in the rapid temperature transition during the initial heating, the temperature was increased while V3 was closed (off, off, on, off, 3, on, on). Step 5: To reduce the transfer efficiency of CO_2, which is a dominant interfering substance of NF_3 analysis, the temperature of T1 was maintained at −75°C, the sublimation point of CO_2 (at 1 atm). The fore-flushing of T1 at 90 psi of He for 3 min allowed the preconcentrated analytes to be transferred to T2 (off, off, off, off, 3, on, on). At this moment, the temperature of T2 was maintained at −135°C. While Arnold used an MS-4A precolumn to backflush CO_2,[15] our study aimed at eliminating CO_2 from the analyte stream by efficient ventilation with precise temperature control of T1. Since Hisiv-3000 removes NF_3 very efficiently, it had to bypass the MS-4A/Hisiv 3000 precolumn. It should be mentioned that the CO_2 removal was not perfect for mass-filter penetration at m/z = 45 tuned for NF_3 measurement (Figure 3 (a)). On the other hand, CF_4 measurement could be accomplished by using the MS-4A/Hisiv 3000 precolumn while tuning the target m/z to 69 (CF_3^+). (ST 4 and Figure S10). For the simultaneous measurement of CF_4 and NF_3 with less interference, the Gaspro column (used as the replacement to Hisiv-3000) must ensure better separation of these gases from air-borne interferences such as N_2, O_2, Ar, CH_4, and Kr.[14] When analyzing CO_2-free samples, it was necessary to immediately transfer the concentrated analytes to T2 after increasing the temperature to 100°C in Steps 4 and 5 (Figure S4). Step 6: With V5 closed, the temperature of T2 was increased to −115°C. Simultaneously, the temperature of T1 was increased to 100 °C in preparation to clean the residual analytes (off, off, on, off, 2, off, on). Step 7: V5 was opened, and N_2, O_2, Ar, CH_4, and Kr were significantly removed by the fore-flush of T2 at −115 °C for 20 s (on, off, off, on, 3, off, on). At this moment, T1 was maintained at 100 °C for cleaning in the subsequent step. Step 8: With T2 closed, the temperature was increased to 80 °C to enable desorption of the analytes over 1 min (off, on, off, off, 2, off, off). If T2 was opened before increasing the temperature of T2, peak broadening with substantial tailing was observed in the chromatogram due to the retention of the analytes in T2. This step would help improve the resolution, which might have worsened by the retention of the analytes at the low temperature in T2. This phenomenon will be discussed

in detail in Section 4.1. Step 9: T1 was opened and the gas flow derived by EPC1 was applied to clean T1 and inject the preconcentrated analytes, which were carried by He. The injection did not take the route via T2. This state was maintained for 2 min (off, on, off, off, 1, off, off). The temperature of the GC front inlet was maintained at 250°C, the GC inlet gas pressure was 4.2 psi, and the split ratio was 0.5:1. High-temperature (over 80 °C) flushing in this step ensured a concentrating volume size in the next step, which might lead to high precision during preconcentration. Step 10: After the injection of the analytes, T2 was maintained at a high temperature, and cleaning was conducted for 2 min while cooling T1 (off, on, off, off, 2, off, on). Step 11: T2 was cooled for 14 min while proceeding with the GC/MSD analysis (off, on, on, off, 2, on, on). The total time of the NF_3 analysis depended more strongly on the trap cooling time than on the retention time in the main column. The total run time was ~35 min. The oven temperature was maintained at 50 °C and then increased up to 150°C after the appearance of the NF_3 peak, in order to bake out the remaining substances in the main column. At this time, the inlet module automatically adjusted the He flow pressure to maintain a flow rate of 5 ml/min, as the temperature of the oven increased. After Step 10, the pressure of EPC3 was increased to clean the precolumn. This cleaning process was unnecessary for NF_3 measurement. The m/z of the target ion for analyzing NF_3 was 52 and that of the qualifier was 71. The m/z of the target ion for analyzing CF_4 was 69 and that of the qualifier was 50. The dwell time was set to 20 ms for each m/z.

ST 2. Measurement procedure for airborne HFCs

The procedure for measuring HFCs also consists of 11 steps (Figure S3). Note that it is possible to measure CFCs, PFCs, and hydrofluoroolefins (HFOs) by same method described here. Step 1: Prior to sampling, the sample was flown through the line for 20 s (on, on, on, off, 2, on, on). Step 2: V3 was opened, and a total of 2 L of the sample was collected with a sampling flow of 200 mL/min for 10 min. The temperature of T1 was maintained at −135°C (on, on, off, off, 2, on, on). Step 3: T1 was heated to −64°C for 1 min. T1 was closed to prevent sample bleeding due to temperature overshoot (off, on, on, off, 2, on, on). This is done to ensure a quantitative desorption process. During this study, no overshoot was observed. Step 4: T1 was heated at −64°C and fore-flushed with 50 psi for 25 s to vent substances such as N_2, O_2, Kr, Xe, and CO_2 (off, on, off, off, 2, on, on). At −64°C, the SF_6 remains in the trap for some time, while Xe (b.p. = −108 °C), which strongly interferes with SF_6, is removed from the trap with high efficiency. If the time of Step 4 is long, the target analytes might escape due to constant flow; therefore, this step needs to be controlled carefully. Step 5: T1 was closed and heated at 200°C for 1 min (off, on, on, off, 3, off, on). Step 6: The analytes were transferred from T1 to T2 by back-flush at a pressure of 50 psi for 5 min. At this moment, the temperature of T2 was −135°C (off, on, off, off, 3, off, on). Miller et al. set the temperature of the trap at 100°C when transferring substances and injecting them into the main column. However, in this study, T2 was set to 200°C, which is advantageous in terms of increased transfer rate and peak shape improvement during injection. The special structure of this detachable device made it possible to use an analytical method that lasted longer at higher temperatures. Step 7: T2 was heated to −115°C and vented for 20 s (off, on, off, off, 3, off, on). This enabled the removal of highly volatile substances that were not of interest (N_2, O_2, Xe, Kr, and CH_4) from T2. In contrast, T1 continued to backflush at a pressure of 50 psi to induce the complete transfer of the

analytes. Step 8: With T2 closed, it was heated to 200°C and maintained there for 7 min (off, on, off, off, 2, off, off). This step uses a higher setting temperature and longer waiting time than those in Step 8 of NF_3 measurement because the analytes are less volatile than NF_3 and therefore require more time to heat to a higher temperature. In addition, while heating and maintaining T2 at 200°C in Step 8, the flow pressure of the front inlet was increased to 60 psi to prepare for pulsed injection in Step 9. The pulsed injection allowed analytes to be injected to the GC-MS at a high pressure, thus improving the shape of the peaks. Step 9: The analytes heated to 200°C in the T2 were injected into the main column for 2 min without passing through the precolumn (off, on, on, off, 1, on, off). The pressure of EPC was maintained at 60 psi for 1.5 min and then decreased to 6.3 psi for 0.5 min. When the injection pressure was maintained at 60 psi for more than 1.5 min, the injection peak tended to chromatographically interfere the analytes. In contrast, T1 was maintained at 200°C and then back-flushed to be cleaned. Step 10: The cooling of trap was started by attaching the closed T1 to the baseplate and T2 was fully cleaned with 50 psi He from EPC1 for 3 min (off, on, on, off, 3, on, off). Step 11: Both T1 and T2 were attached to the baseplate and cooled for 12 min (off, on, on, off, 2, on, on). The target ions (qualifier) of HFC-134a, HCFC-22, and HCFC-142b, which are of major interest in this study, are 83(33), 67(50), and 65(85), respectively, and the dwell time is 20 ms.

ST 3. Measurement procedure for NF_3 in synthetic air (N_2/O_2)

Figure S3 is a procedure for the analysis of NF_3 or CF_4 in controlled matrix composition, i.e. O_2 and N_2. The main difference from the original procedure (Figure S2) is in Step 5. V3 is opened while the T2 temperature is maintained at -135 ℃ and T1 is 100℃ so that the concentrated substances are transferred to T2. This is because selective desorption of CO_2 is not needed. The total run time is reduced, and the transfer efficiency of NF3 is sufficiently guaranteed.

ST 4. Difference from Medusa GC-MS

Supplement Table 1 compares the Medusa GC-MS to the instrument developed in this study. The purpose of AGAGE Medusa GC-MS is in situ measurement, and the purpose of KRISS's instrument is laboratory precision management. Therefore, Nafion Dryer used in Medusa is not necessary in this study. Instead, only dry gas can be used in this set-up. The lower cooling efficiency of the cold-end KRISS instrument (PT-14, Polycold Division of Brooks Automation, Petaluma) compared to Medusa (PT-16, Polycold Division of Brooks Automation, Petaluma was discussed) and improvement of the cooling efficiency by using detachable trap re discussed in the main text. Other details regarding instrumentation are tabulated in Supplementary table 1. Experimental results show that the sample stability was better when installed in the front portion. Even if the sampling flow is 200ml/min, stable sampling is possible. The amount of adsorbent filled in Trap 1 is 120 mg due to the limit of the trap design. This is 80 mg less than the amount entering the AGAGE Medusa System. The amount of adsorbent entering Trap2 was 10 mg, twice the amount of AGAGE Medusa. The higher inner diameter of the trap compared to Medusa enabled the adsorbent to be filled in a shorter section. This might be the reason for the more uniform adsorption of the analyte along the trap length and smaller loss during desorption/transfer process as compared to the Medusa. This eventually helped improve the measurement precision.

ST 5. Evaluation of calibration uncertainty

The area of the measured signal peak is denoted by Eq. 1 to calculate the $C_{unknown}$ in Figure S8. Reference is D015147, and unknown is D985596. For drift correction, reference-unknown-reference (RUR) was used, and one-point calibration was performed assuming that this measurement method maintained linearity within the measurement concentration range (Supplement Eq. 1).

$$C_{unknown} = (\frac{R_{unknown}}{R_{ref}}) \cdot (C_{ref}), \qquad \text{(Supplement Eq. 1)}$$

where C is the mole fraction of the analytes and R is the response area of the chromatogram. The subscripts refer to each of the RUR methods.

$R_{unknown}$ and R_{ref} are measured values and correspond to Type A evaluation. Standard uncertainty was calculated by dividing the standard deviation of each measurement set by $\sqrt{n}$ to calculate u ($R_{unknown}$) and u (R_{ref}), whose values are the standard uncertainty (u). The measurement was performed in the following order: four-time measurement of reference, three-time measurement of unknown, and five-time measurement of reference.
D015147 used as a reference is a gas prepared by the gravimetric method, so type B evaluation was applied for the concentration of gas (C_{ref}). The u (C_{ref}) value was determined from the uncertainty through the gravimetric method (C_{grav}).
Sensitivity coefficient (S_i) is obtained from Supplement Eq. 2.

$$S_i = \frac{\partial C_{unknown}}{\partial x_i} \qquad \text{(Supplement Eq. 2)}$$

The standard uncertainty and sensitivity coefficient obtained for each factor were combined using the propagation of uncertainty, Supplement Eq.3.

$$u_c^2 = \sum_{i=element}^{N} S_i^2 u^2(C_i) \qquad \text{(Supplement Eq. 3)}$$

The expanded uncertainty (U) was calculated by multiplying the combined standard uncertainty and the coverage factor (k) (value=2) (k=2, confidence level 95%) (Supplement Eq. 4).

$$U = k \cdot u_c \qquad \text{(Supplement Eq. 4)}$$

ST 6. Measurement procedure of CF_4

The measurement of CF_4 is similar to the measurement of NF_3. The main difference between the two methods is

the valve position in Step 8 for NF_3 measurement. The precolumn includes HISIV-3000 to separate CF_4 from analytical interfering substances. However, loss of NF_3 occurs when passing through HISIV-3000. Therefore, when analyzing NF_3, we injected it into the main column, bypassing the precolumn in Step 8, to avoid loss of analytes. However, when analyzing CF_4, the analytes passed through the precolumn. Figure S10 is the chromatogram of CF_4 obtained by the analysis method described.

Table S1. Difference between Medusa GC-MS and this work

		Medusa	This work
Purpose		In-situation measurement	Laboratory measurement
Gas Dryer		Nafion	Only use Dry gas
Cooler		PCC Cryotiger PT-16	PCC Cryotiger PT-14
Pressure Control		EPC only	Front Inlet, EPC
Sample Source		Air Pump Module	Cylinder
Mass Flow Controller (MFC)	**location**	End portion	Front portion
	Type	MEMS-Flow (Redwood Microsystems Inc.)	5850E Thermal (Brooks Instruments Inc.)
Sampling flow		100 ml/min	200 ml/min
Mass Spectroscopy		Agilent 5973/5975	Agilent 5975C
Temperature		-165 ~ 100 ℃	-135 ~ 200 ℃
Precolumn		40 mg of 100/120 mesh molecular sieve 4 Å (MS 4 Å) followed by 160 mg of 100/120 mesh HiSiv-3000 (HiSiv, UOP, Des Plaines, IL) in a 80 cm long by 0.75 mm i.d. stainless steel column (Restek Corp., Bellefonte, PA)	50 mg of 100/120 mesh molecular sieve 4 Å (MS 4 Å) followed by 200 mg of 100/120 mesh HiSiv-3000 (HiSiv, UOP, Des Plaines, IL) In a 30cm long by 2.18 mm i.d. stainless steel column (Restek Corp)
Main column		CP- PoraBOND Q fused silica PLOT main column (25 m long, 0.32 mm i.d., 5 µm film thickness, Varian Inc., Palo Alto, CA).	CP- PoraBOND Q fused silica PLOT main column (75 m long, 530 µm i.d., 10 µm film thickness, Varian Inc.,)
Trap 1	**Length**	76.8 cm	10.0 cm
	Amount of Adsorbent	Hayesep D 100/120, 200 mg	Hayesep D 100/120, 120 mg
Trap 2	**Length**	81.9 cm	10.0 cm
	i.d.	0.51 mm	1.6 mm
	Amount of Adsorbent	Hayesep D 100/120, 5.5 mg	Hayesep D 100/120, 10 mg

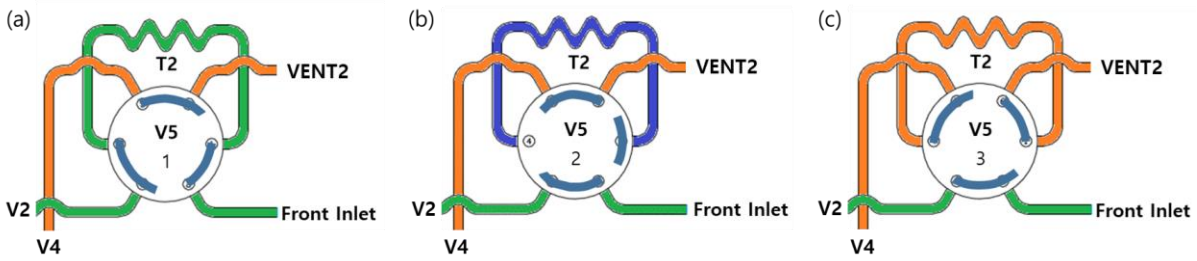

Figure S1. Gas flow pathways of V5. The position coordinates (1 or 2 or 3) given underneath of the symbol V5 correspond to (a), (b), and (c), respectively. For eye guide, connected lines are identically colored.

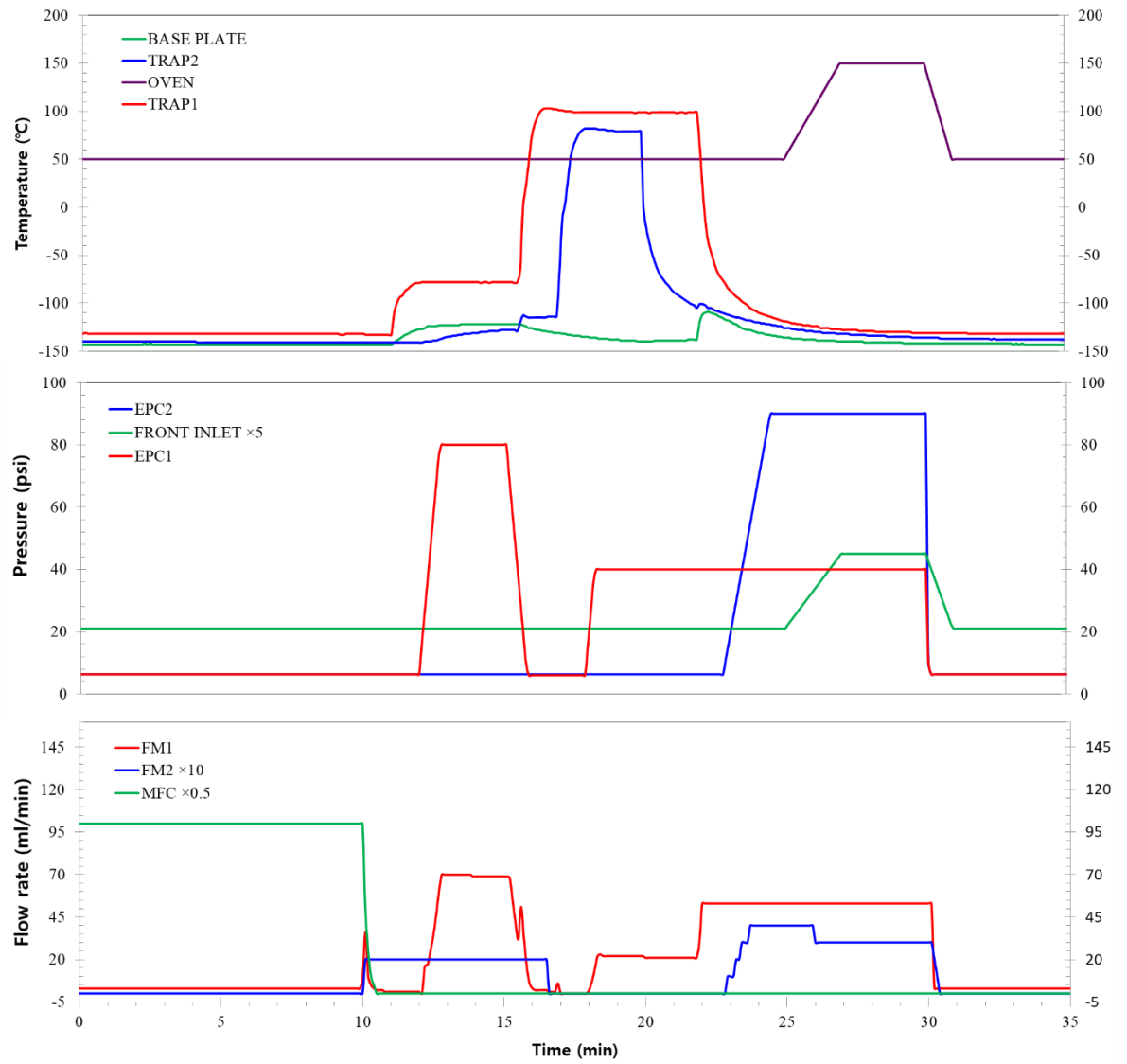

Figure S2. Strip chart of the NF_3 measurement procedure. The temperature and flow rate are the measured values. The pressure was controlled by the electric pressure controllers (EPC1, EPC2) and the software at the front inlet. The temperature of the trap and baseplate are displayed by the thermocouple installed at the corresponding locations, and the flow rate is determined using FM1 and FM2 located at each vent position. Though the temperature of T2 in the initial stage of sample collecting at T1 (~12 min), no disturbance in analyte transfer to T2 was expected because of helium-flushed T2 in previous measurement. Impulsive temperature incensement of T2 and the baseplate was caused by reattachment of T1 to be cooled down was observed at 22 min. But, this is trivial to the measurement precision due to no gas flow between T2 and GC-MS. T2 was flushed by high purity helium for the preparation of next measurement.

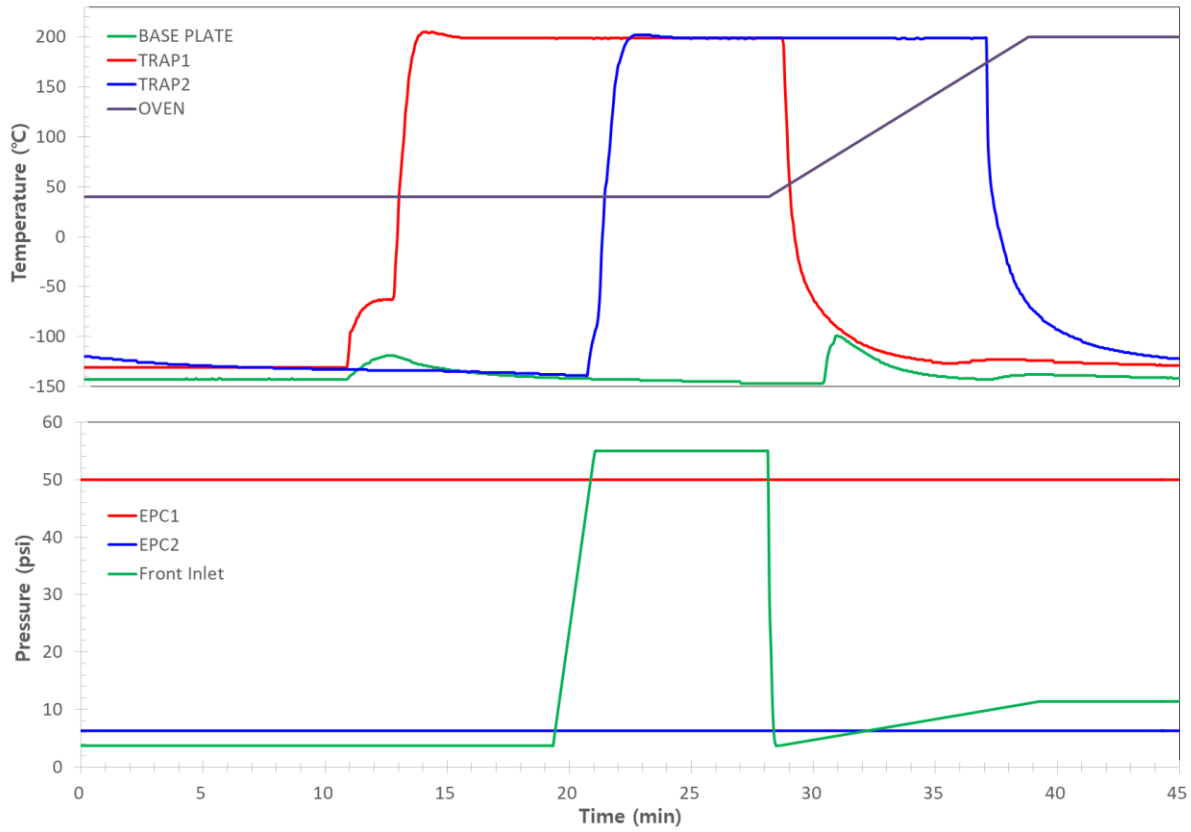

Figure S3. Strip chart of HFCs measurement procedure. Compared with NF_3 analysis, the retaining time in Step 8, which is the preparation step for injection, is longer.

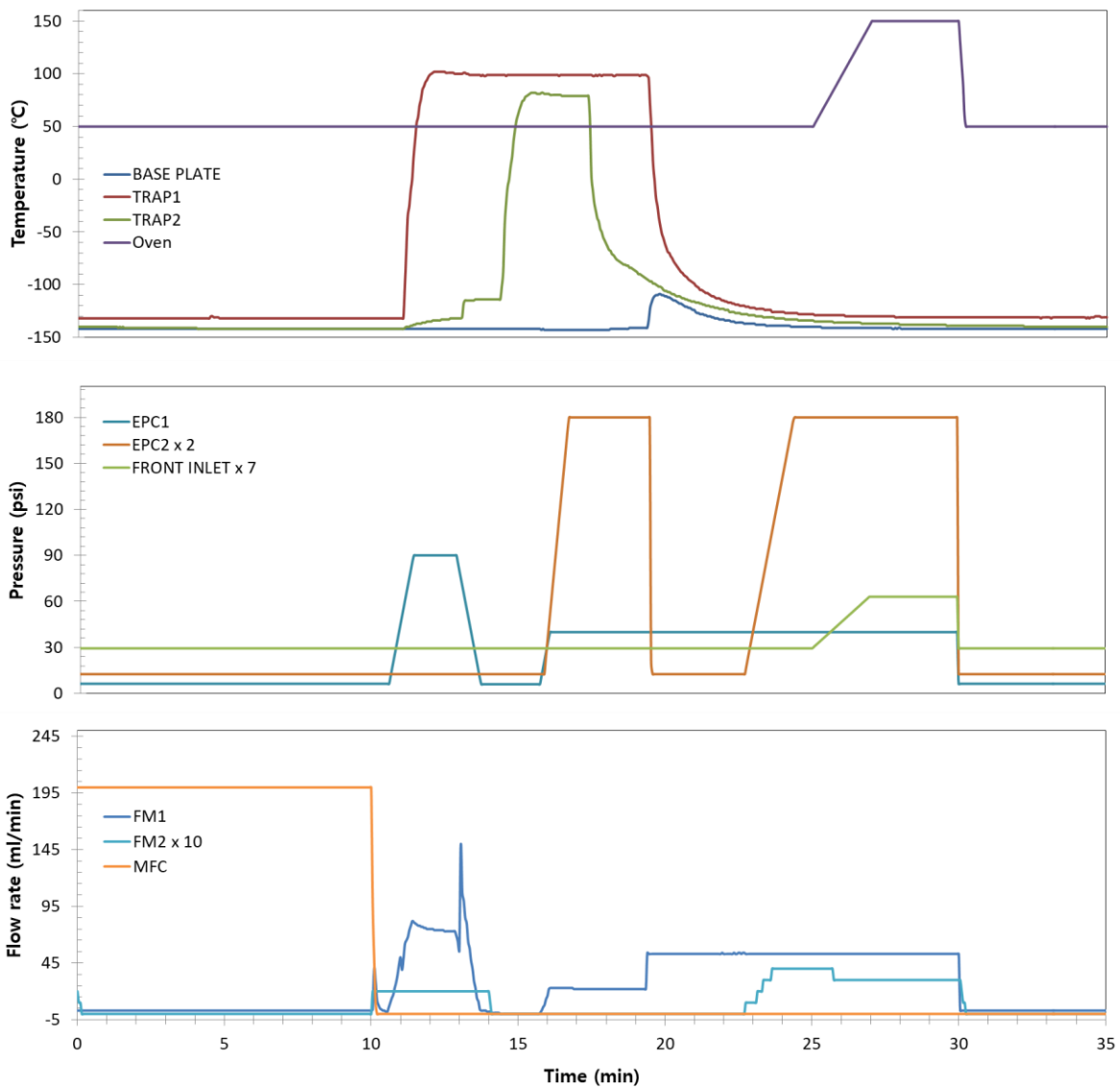

Figure S4. Strip chart of NF_3 in CO_2 free synthetic air measurement procedure. When the balance gas is pure nitrogen, it is not necessary to consider CO_2, so the temperature is raised to 100℃ when transferring from T1 to T2. Applying this condition reduces the transfer time, and the time to cool down to a temperature where it is again possible to concentrate is shortened, allowing measurement in a shorter time per cycle.

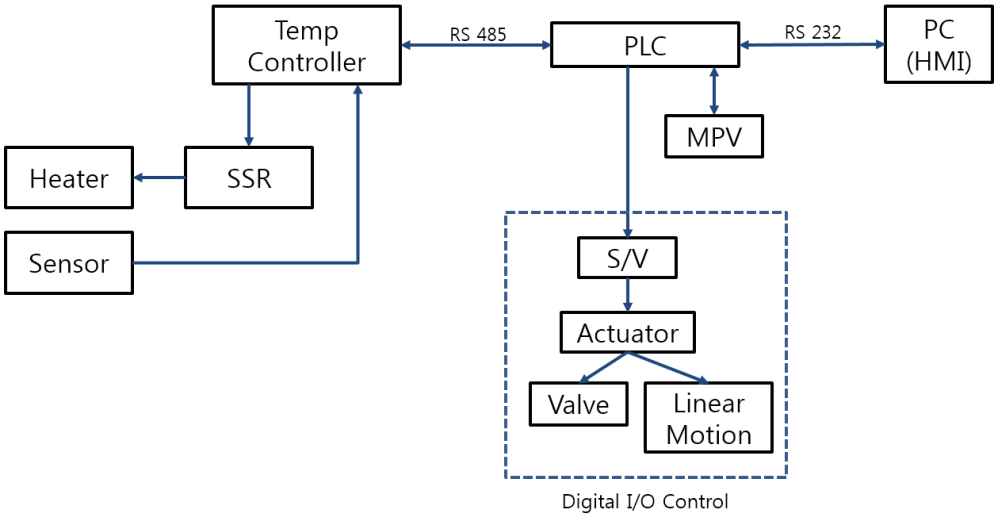

Figure S5. Schematic illustration of the electronic control unit.

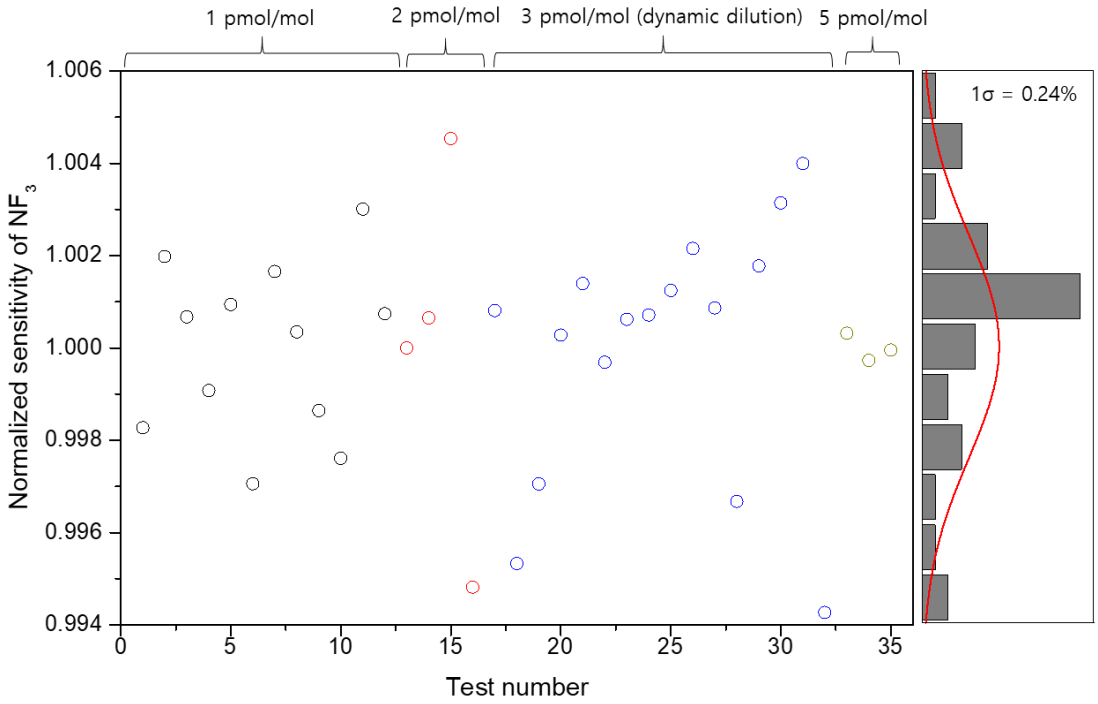

Figure S6. Precision test of NF_3 measurement. Gravimetric gas mixtures of 1 pmol/mol, 2 pmol/mol, and 5 pmol/mol NF_3 in synthetic air were measured. Results at 3 pmol/mol were given by dynamic dilution of 5 pmol/mol NF_3/air gas mixture by high purity N_2 (> 99.999%) by adjusting ratio of flow rates, implying that measurement uncertainty includes uncertainty of flow rates. Overall precision was evaluated to be less than 0.35% (1σ)

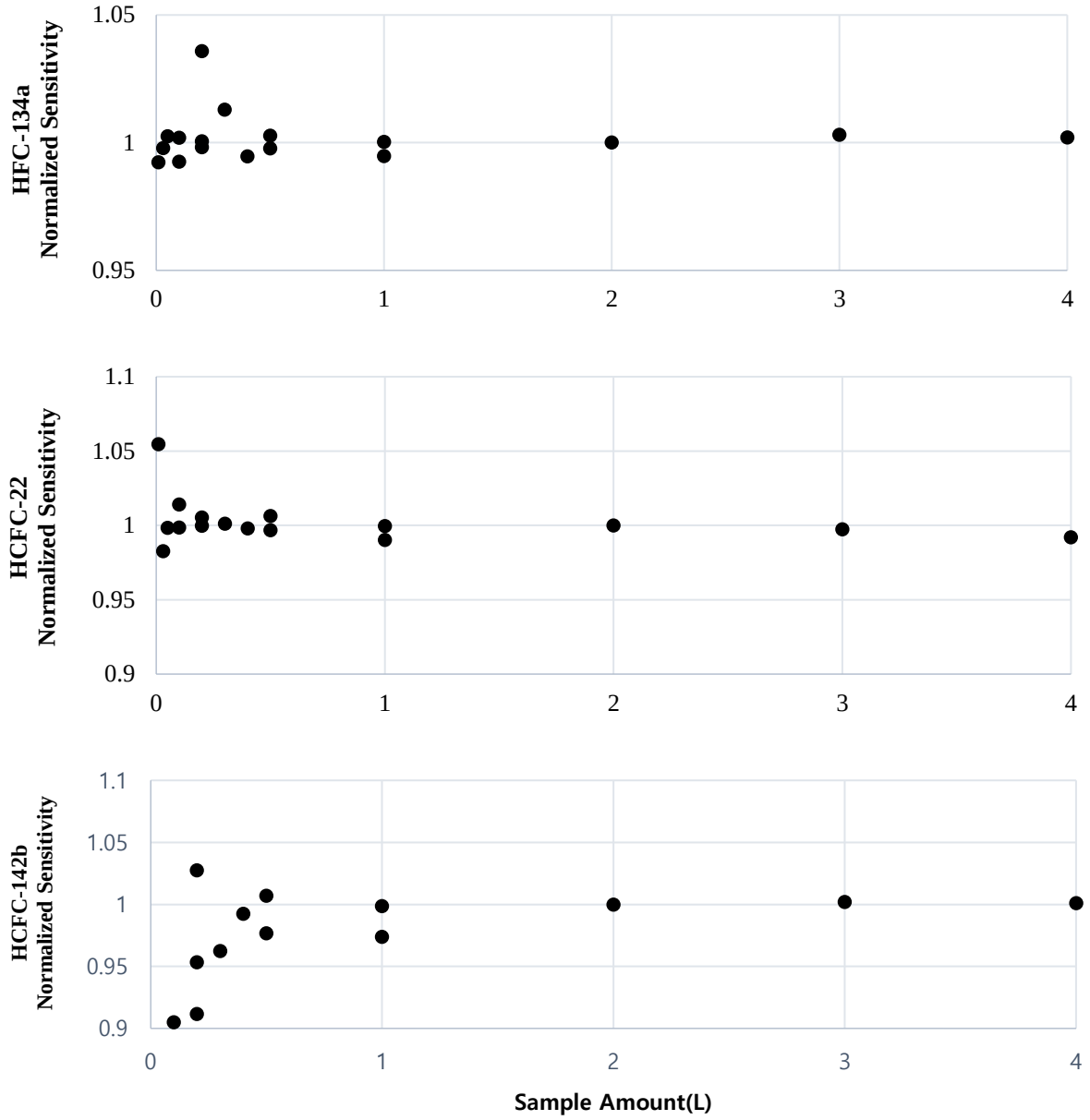

Figure S7. Response linearities of HFCs. The result obtained by dividing the value obtained from the response by the sample volume is sensitivity, and each value was divided based on the sensitivity of 2L and normalized. Sampling time was adjusted with sampling flow of 200ml/min when measuring 0.5L or more, while sampling time was adjusted with sampling flow of 60ml/min when measuring less than 0.5L.

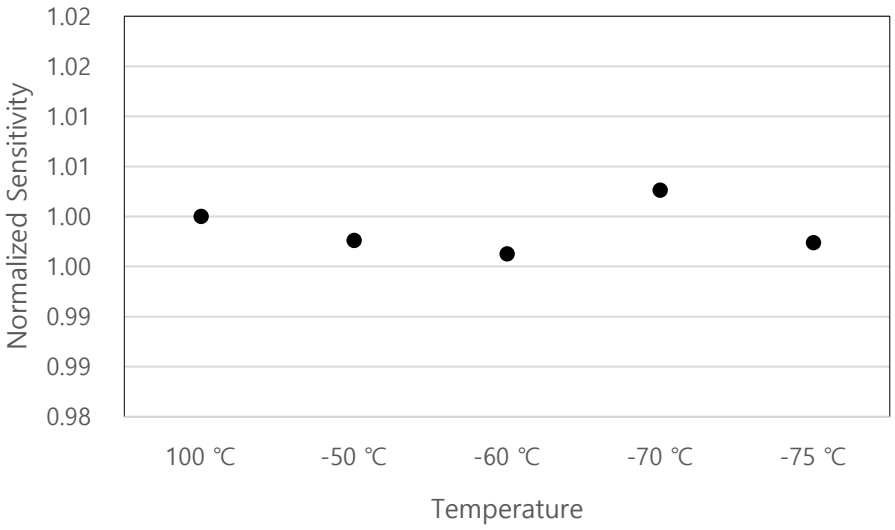

Figure S8. Comparison of NF_3 transfer efficiency as a function of T1 temperature.

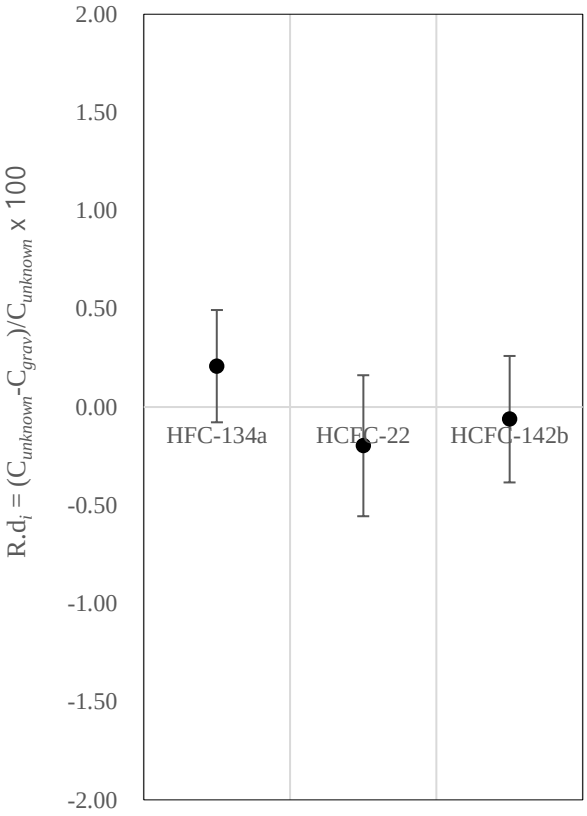

Figure S9. Difference between the calibrated concentration ($C_{unknown}$) and the gravimetrically assigned concentration (C_{grav}). $C_{unknown}$ is calculated as 66.81, 218.65 and 21.90 pmol/mol for HFC-134a, HCFC-22 and HCFC-142b, respectively. New result shows better verification uncertainty compared to that of CCQM-K84 of which part were conducted by KRISS.

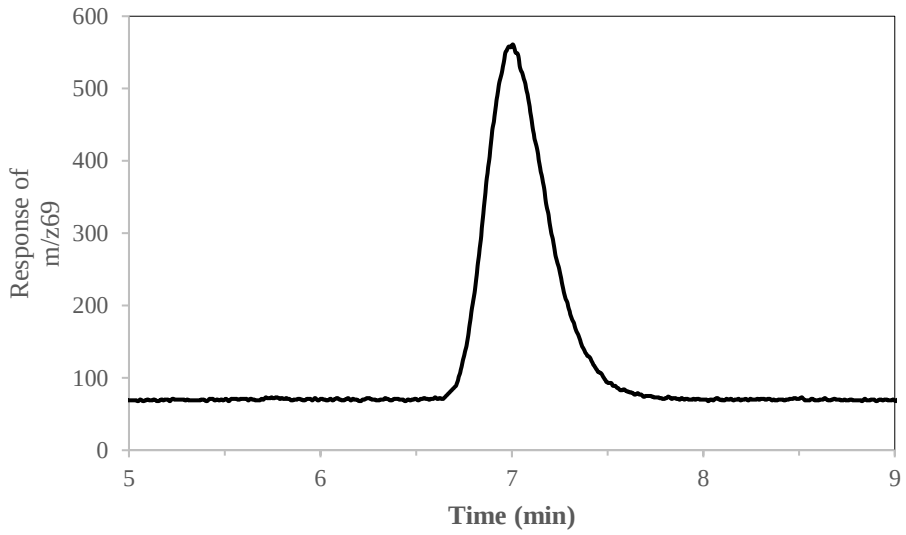

Figure S10. Chromatogram of CF_4. The retention time and peak shape are different from those under the conditions described in the main section due to non-identical analytical condition described in the main text. Only separation condition was changed.

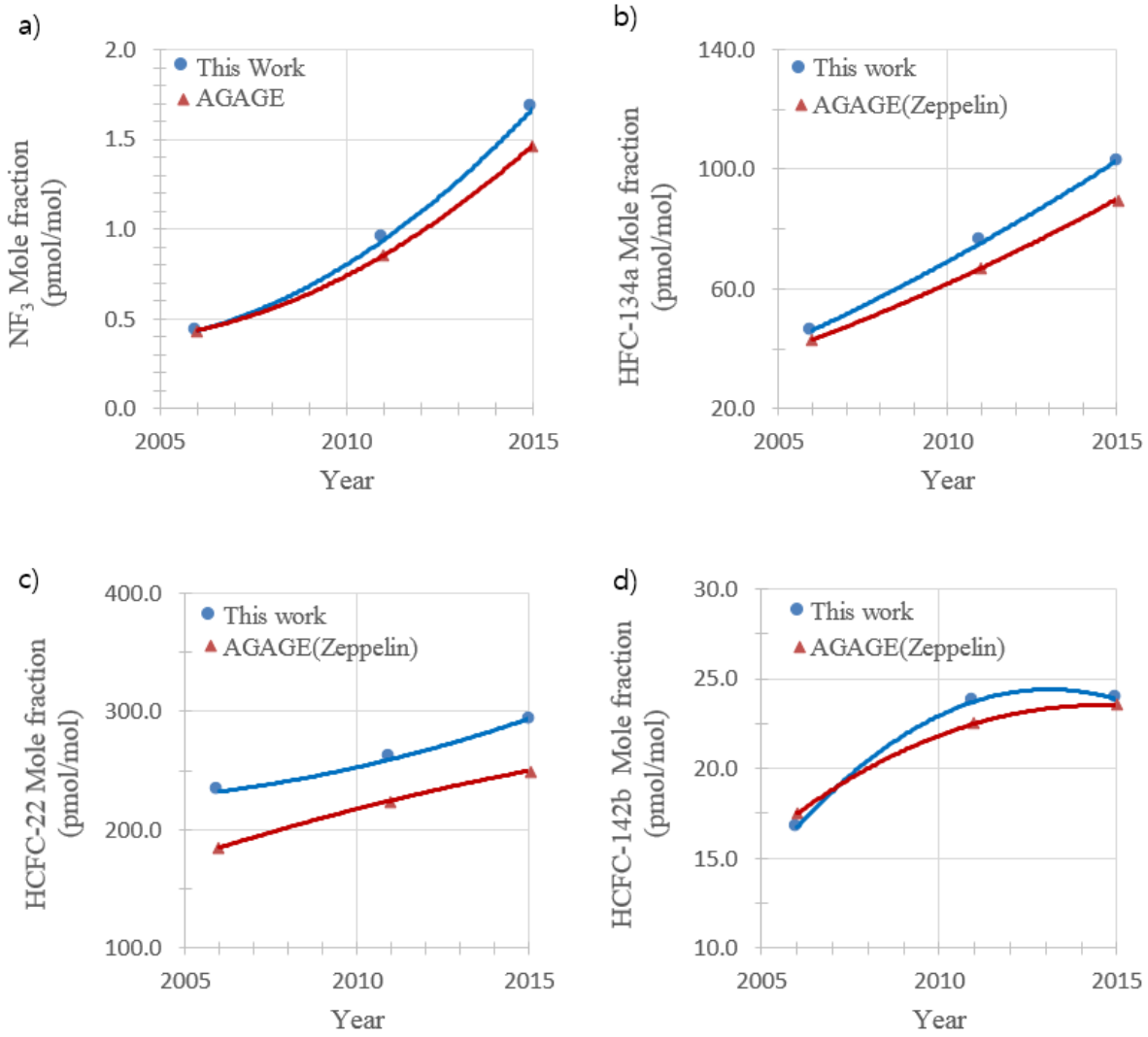

Figure S11. a) Comparison of ambient NF_3 concentration between the data reported by AGAGE and this work. The blue circle (●) is the result of measuring the air sample stored with this instrument, and the red triangle (▲) is the value reported by AGAGE. The concentration of NF_3 in the cylinder, which was collected in the Gosan area of Jeju Island, was measured in this study and corrected to 3 pmol/mol NF_3 in N_2 developed by the gravimetric method. The red triangles (▲) are the values reported at AGAGE Trinidad Head site.[13] b) The results of HFC-134a, c) The results of HCFC-22, and d) The results of HCFC-142b. The blue circle (●) in b–d) was calibrated using a cylinder, D015147 for 65.8 pmol/mol HFC-134a, 222.10 pmol/mol HCFC-22, and 22.75 pmol/mol HCFC-142b in air, which was produced by KC-83. The AGAGE value was measured at Zeppelin and is published on the website.[13] The AGAGE value was calibrated to SIO-05.

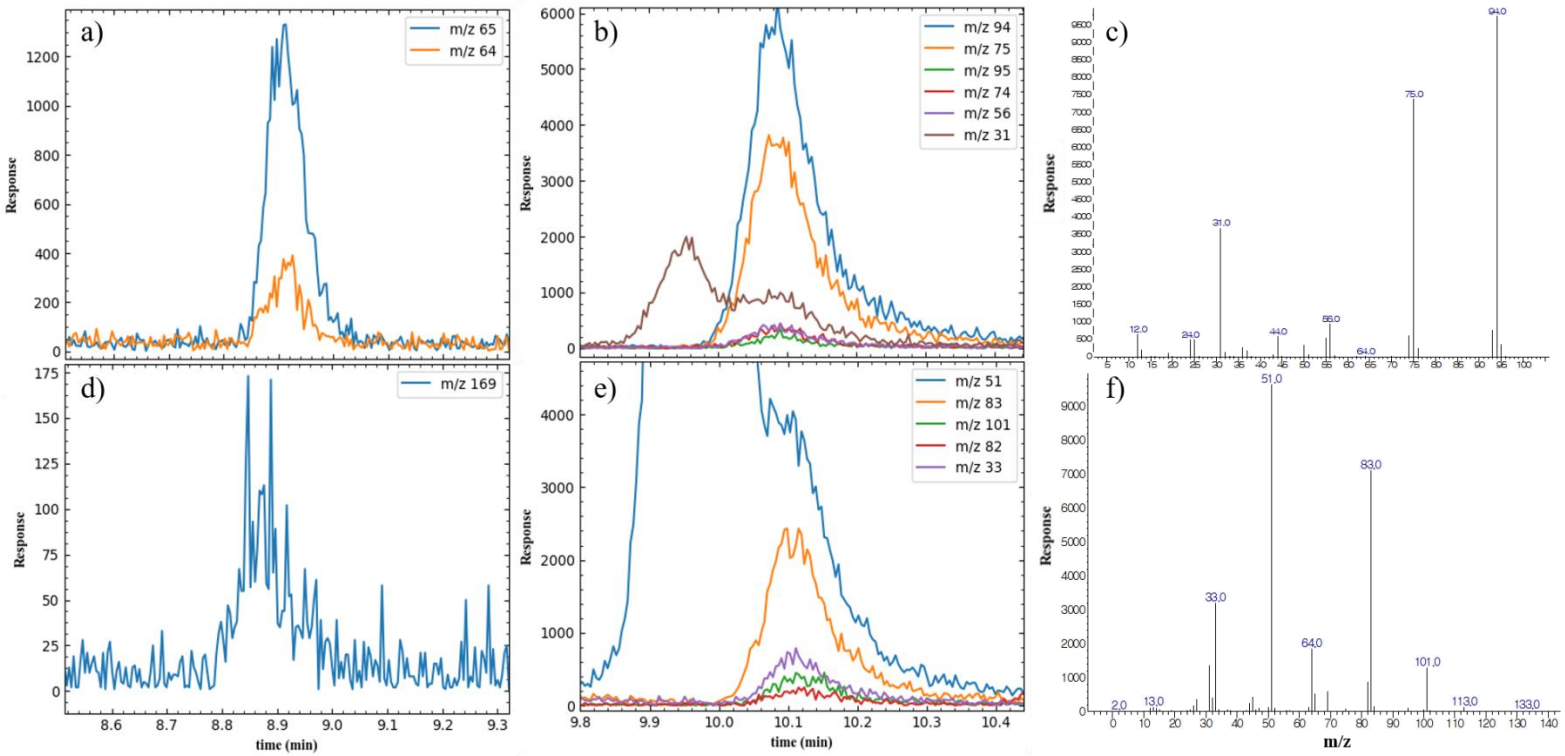

Figure S12. a) Chromatograms of target m/z = 65 and qualifier m/z = 64 for HFC-143a (CH_3CF_3), b) Combined chromatogram of m/z = 94, 75, 95, 74, 56, and 31 for 3,3,3-trifluoropropyne (CF_3C_2H), c) Mass spectrum of 3,3,3-trifluoropropyne (CF_3C_2H) provided by the NIST Mass library, d) target = m/z 169 of PFC-218 (CF_2CFCF_2), e) Combined chromatogram of m/z = 51, 83, 101, 82, and 33 of HFC-245ca ($CH_2FCF_2CHF_2$). m/z = 64, which could lead to confusion in the shape of the chromatogram due to interference of other substances, was excluded. a) and d) were qualitatively determined using the target and qualifier ions reported in ref 10. b) and e) were assigned the most potent results, c) and f) in contrast to the NIST mass library results, to the corresponding substance.

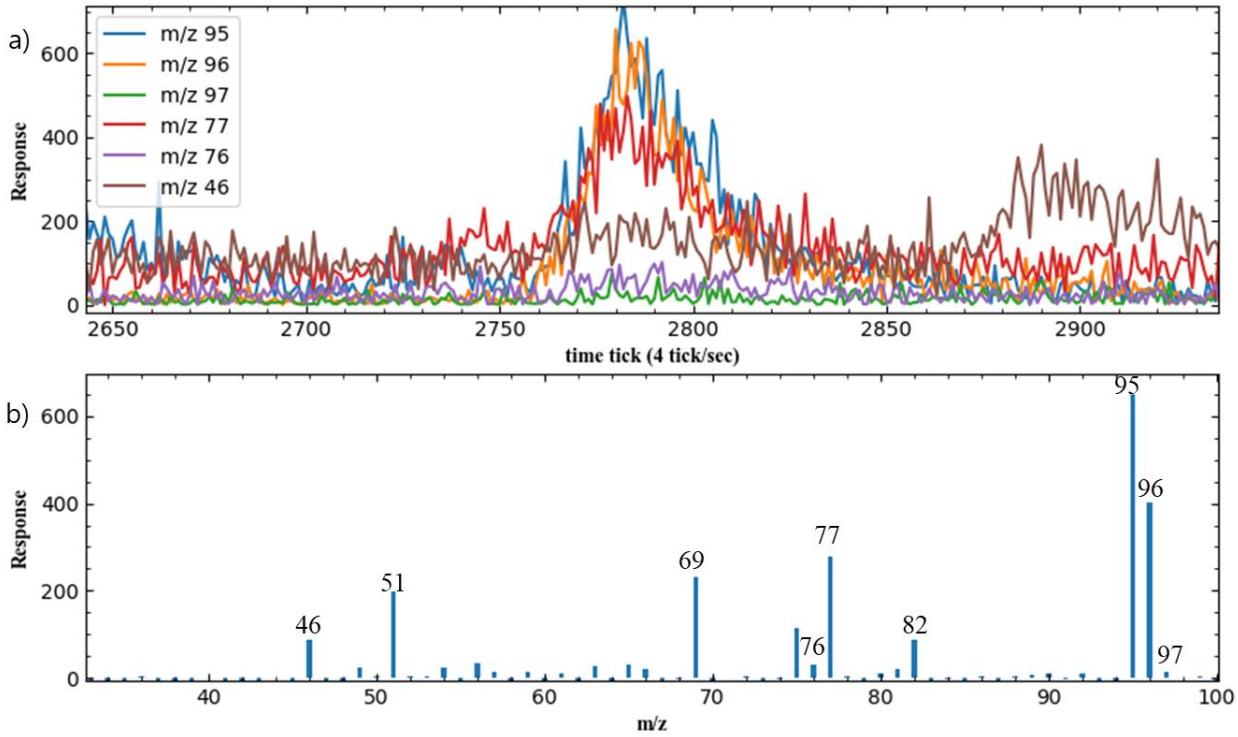

Figure S13. a) Combined chromatogram of HFO-1234zf at various m/z levels denoted in the legend, b) mass spectrum obtained at the peak around 2600 time ticks, which shows over 90% Q factor with the NIST mass spectroscopy library.