Supplemental information

The new dilution system almost exclusively consists of stainless steel parts (Figure S1). Low pressures (50 to 300 mbar, measured with a PX764-005GI Industrial Pressure Transmitter from Omega, UK) of pure gases can be trapped inside two sample loops (obtained from VICI AG International, Switzerland) which have calibrated volumes (used here: 2.00±0.1 ml). The loop is connected to a 1/16" six-port two-position Valco valve (with Valcon E rotor, also from VICI) which is used to isolate the sample loop after filling. The system is then filled with OFN to about 2 bars (measured with a Swagelok S Model Transducer) and evacuated to about 1 mbar (measured with a TPR-280 gauge from Pfeiffer Vacuum, Germany) using a XDS-10 scroll pump from Edwards, UK. This procedure is repeated 10 times to remove residual compound from the system. It is then again filled with OFN and the valve leading to an aluminium drum (filled with OFN at atmospheric pressure) with a volume of 99.7 litres is opened. When a constant flow (here: about 300 ml/min measured with a Tylan 260 Series MFC from Millipore, USA) into the drum has established the sample loop with the pure gas is switched into this flow and flushed for about 4 minutes. The drum is then closed and an inside fan turned on for 30 minutes to create a uniform gas mixture. As an evaluation of this dilution system we chose to add a gas with known mixing ratios (here: CF_2Cl_2 as obtained from Fluorochem Ltd., UK) as internal reference. All first steps of the dilution procedure were repeated for this purpose. After additional 30 minutes of mixing the drum is reconnected to a second similar system which contained similar parts i.e. a volume-calibrated sample loop (here: 10.00 ± 0.5 ml) connected to another six port Valco valve and a Pfeiffer APR-262 Pressure Gauge (range: 2000 mbar). The second dilution step is carried out in a similar manner by taking an aliquot out of the first dilution drum, cleaning the exposed gas lines with OFN (10 times) and flushing it into a second 99.7 litre aluminium drum. After another 30

minutes of mixing this drum was measured against a tertiary compressed air standard filled and calibrated in 2006 by the Global Monitoring Division (GMD) of the National Oceanic Atmospheric Administration - Earth System Research Laboratory (NOAA-ESRL, USA).

CF_2Cl_2 dilutions containing 136, 186 and 192 pptv were prepared. Both drums were flushed for at least 3 hours with OFN (flow of about 10 l/min) before reusing them. All mixing ratios agreed with those derived via the NOAA calibration value (2001 scale) within 1.4 %. It should be noted, that both the NOAA-scale and our mixing ratios are reported as dry air mole fractions. NOAA values are, however, derived gravimetrically whereas our values depend on a volume measurement and thus on the ideal gas law. Comparing these values includes the assumption, that intermolecular interactions are negligible. For the pressures and compounds used the systematic errors introduced by assuming ideal gas conditions are far smaller than the accuracy and precision of our determinations.

The three prepared dilutions contained CF_2Cl_2 and HFC-227ea (97%, obtained from Apollo Scientific, UK) with mixing ratios of 144, 194 and 222 pptv for the latter. The mixing ratio assigned to the NOAA standard via these dilutions was (0.3536 ± 0.0063) pptv. As we were bridging almost three orders of magnitude with this calibration we needed to make sure that the response behaviour of the whole analytical procedure including pre-concentration, separation, detection and retrieval was linear over that range. Thus, different amounts of the same NOAA standard (49, 102, 194, 199, 224 and 301 ml) were pre-concentrated and measured. The response behaviour was checked and found to be linear within the average 1 σ standard deviation of the standard not only for HFC-227ea but also for CF_2Cl_2 (534.1 ppt in standard), $CF_2ClCFCl_2$ (79.8 ppt, NOAA 2002 calibration scale), SF_6 (5.95 ppt, NOAA 2006), and CF_3Br (3.0 ppt, NOAA 2006). Therefore we conclude that the analytical system responds linearly within the given range. By propagating the average 1σ standard deviation

uncertainty of the dilutions, of the NOAA standard (about 2 %), the sample loop volume (5% for each of them), the drum volume (0.5 %) and the pressure gauge (less than 0.5 %) we estimate our total scale uncertainty to be about 15 %. However, taking into account the good agreement of the CFC-12 dilutions with the NOAA scale it is likely to be significantly lower.

The complete dilution system was evaluated for blank levels which were found to be consistently about 2.5 ppt for CFC-12 and 0.025 pptv for HFC-227ea. These were taken into account for the mixing ratio calculation but are negligible especially for HFC-227ea. Blank levels of the pre-concentration/GC-MS system were negligible for CFC-12 and about 0.001 pptv for HFC-227ea.

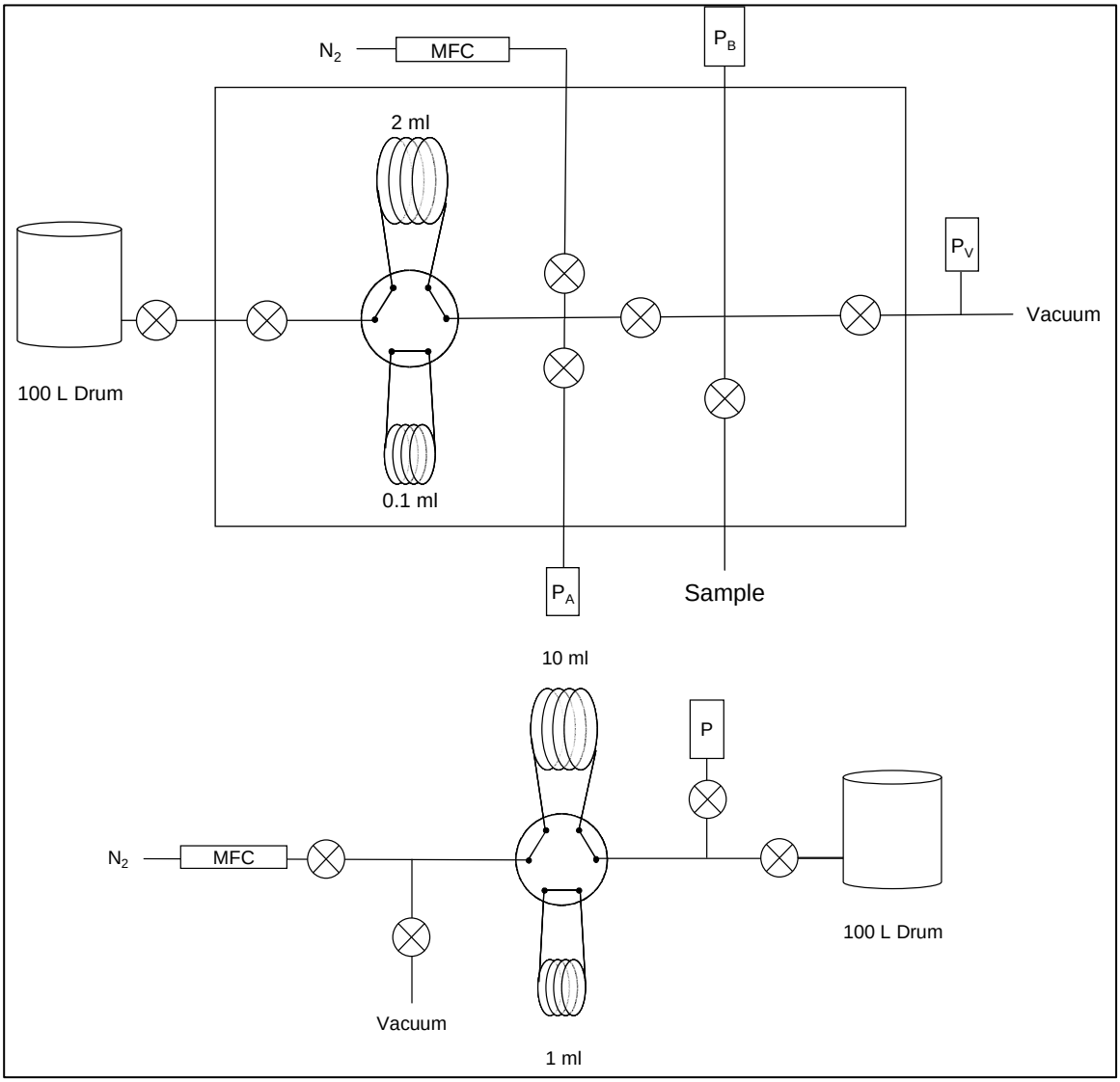

Figure S1. Layout of the dilution system used to calibrate HFC-227ea. At stage one (upper part) a sample loop is filled with the pure compound at low pressures which are monitored by a high accuracy pressure gauge P_A. Low accuracy pressure gauges are used to avoid over-pressurisation of the system during cleaning with N_2 (P_B) and to monitor the vacuum (P_V). After filling, the sample loop is isolated and the rest of the system cleaned. Then the contents of the sample loop are flushed into a 100 litre drum which is filled with N_2 at atmospheric pressure while maintaining the flow with a mass flow controller (MFC). Most of the system used for this dilution step is heated (box) to achieve quantitative transport into the drum. For

the second step an aliquot is taken out of the first drum and diluted into a second by carrying out a similar procedure (lower part).