CFC-measurements with DESCARTES during the THESEO campaign in Kiruna spring 1999

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Abstract

DESCARTES is a lightweight instrument for in-situ measurements of long-lived stratospheric tracers from balloons. The instrument is designed to fly piggyback on other payloads; it weighs 16 kg and there is no need for telemetry. The instrument collects samples by letting a measured amount of air pass though a tube containing a carboxen adsorbent. The instrument can measure CFC-11, CFC-113, CCl_4 and CH_3CCl_3 quantitatively. Results from the four flights with DESCARTES during the THESEO-O_3-loss campaign in the spring of 1999 are presented.

1 Introduction

Regular measurements of long-lived anthropogenic trace gases in the stratosphere serve a double purpose. Firstly they are interesting because of their potential impact on the global climate, e.g. the role of halocarbons in stratospheric ozone depletion. Secondly, because they are long-lived they can be used as tracers of atmospheric motion. In both cases regular measurements are important for comparison with the atmospheric models used to understand the circulation of the middle atmosphere and to estimate the impact of anthropogenic trace species on the climate of the Earth.
For this season a new version of the instrument DESCARTES has been built, and is operated in northern Scandinavia by the Swedish Institute of Space Physics, IRF. The major modification is to the heating system which improves the precision of the measurements. Results from the ILAS validation campaign in 1997 with the former version of the instrument is presented in Nilsson et al. [4]. The original instrument is described in Danis et al. [3] and the improved version is described in Danis et al. [2].

2 Instrument description

The general principle for the instrument is to adsorb tracer gases from air samples during the flight. After the flight these adsorbed tracers are thermally desorbed and passed through a gas chromatograph where they are separated, and on to an electron capture detector (ECD) that measures the amounts of the different species.

Sampling. The samples are taken at predefined pressure levels during the flight by pumping air through small tubes containing the adsorbent carboxen 1000 which is a strong adsorbent of CFC. The instrument contains 16 similar such 'traps' mounted on a 16-position valve. One sample is taken in each trap and then the valve is stepped to the next position. 15 samples are taken on each flight. The 16th trap is in position during the preparation and after the flight while waiting for analysis and may therefore be contaminated.

Analysis. The adsorbed samples are thermally desorbed by running an electrical current through the material of the trap. Before and during this season the heating system was modified. The system, the modifications and the problems with it on the first flights are described in Arvelius et al. [1].
The response of the ECD is monitored by taking standard samples containing CFC-11, CFC-12, HCFC-22, CFC-113, CCl_4 and CH_3CCl_3 between the analysis of each sample tube.

3 Instrument performance

The instrument performance is dependent on several different factors: the adsorption of the tracers in the traps, the desorption in the analysis, the performance of the on-board flow meters and the response of the ECD. The idea in the calibration of the flow meter and the detector is rather to caracterize the instruments and use them the same way in the absolute calibration as during analysis to make systematic errors cancel each other out. Finally the way the chromatograms are integrated will affect the result.

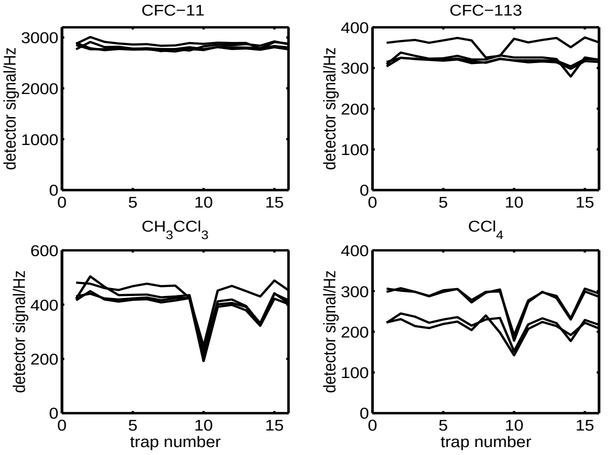

Figure 1: Raw output from detector from repeatability test.

Performance of the traps. DESCARTES was designed to provide optimal performance for CFC-11. In practice the adsorption during the sampling is thought to be good for all species except CFC-12 [2]. This is the reason we cannot measure this species.

Some differences between the individual traps are evident from the repeatability test (figure 1). The normalised deviation from mean for the filling is calculated for each trap. Averaged over all fillings of the traps this gives an individual coefficient for the traps. This coefficient is then multiplied to the detector response. There is some drift between different runs which is probably due to a temperature dependence of the current controlling diode in the heating circuit. This is compensated for by weighting the measurements with the standard analysis made during the flight analysis procedure.

ECD response. The response of the ECD was determined by a test where the traps were filled with different amounts of standard. The analysis was done both for peak area and peak height, both with the built-in automatic integration function of the program. After the individuality of the traps is taken into account, the result for peak areas of this response test is shown in figure 2.

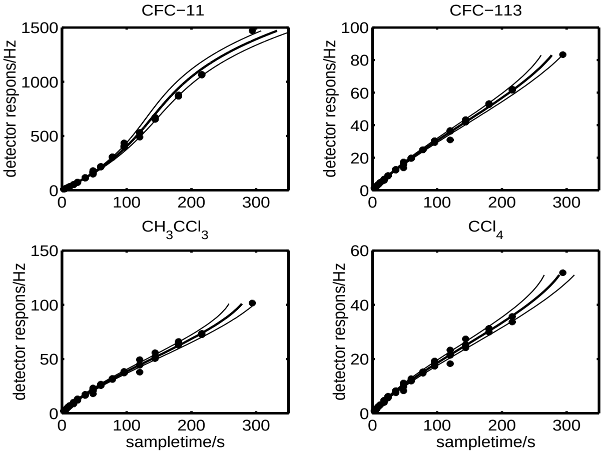

Figure 2: The detector response during the response test.

On-board flow meters. The on-board flow meters are calibrated by letting through a flow of air controlled by a well-calibrated flow controller (Aera FC2600 for the low flows and Tylan FC2900 for the high).

Absolute calibration After taking all of the different calibrations above into account we should have a linear relationship between the amount of the tracer trapped in the trap and the detector response. To learn the slope of this relationship an absolute calibration was performed. The test is set up the same way as the ECD response test. By controlling the flow and the sampling time the amounts of CFCs in the samples can be controlled by using the known mixing ratio in the standard air.

4 Error estimation

The expression for calculation of the mixing ratios of the CFCs is

$$\text{mixing ratio} = \frac{L(A)\ C\ r_f}{r_t\ F(f)\ t},$$

where: $F(f)$ is the inverse of a second degree polynomial for the flow estimation from the raw flow-meter readout f on the on-board flow-meter, according to flow-meter calibration, $L(A)$ is a third order

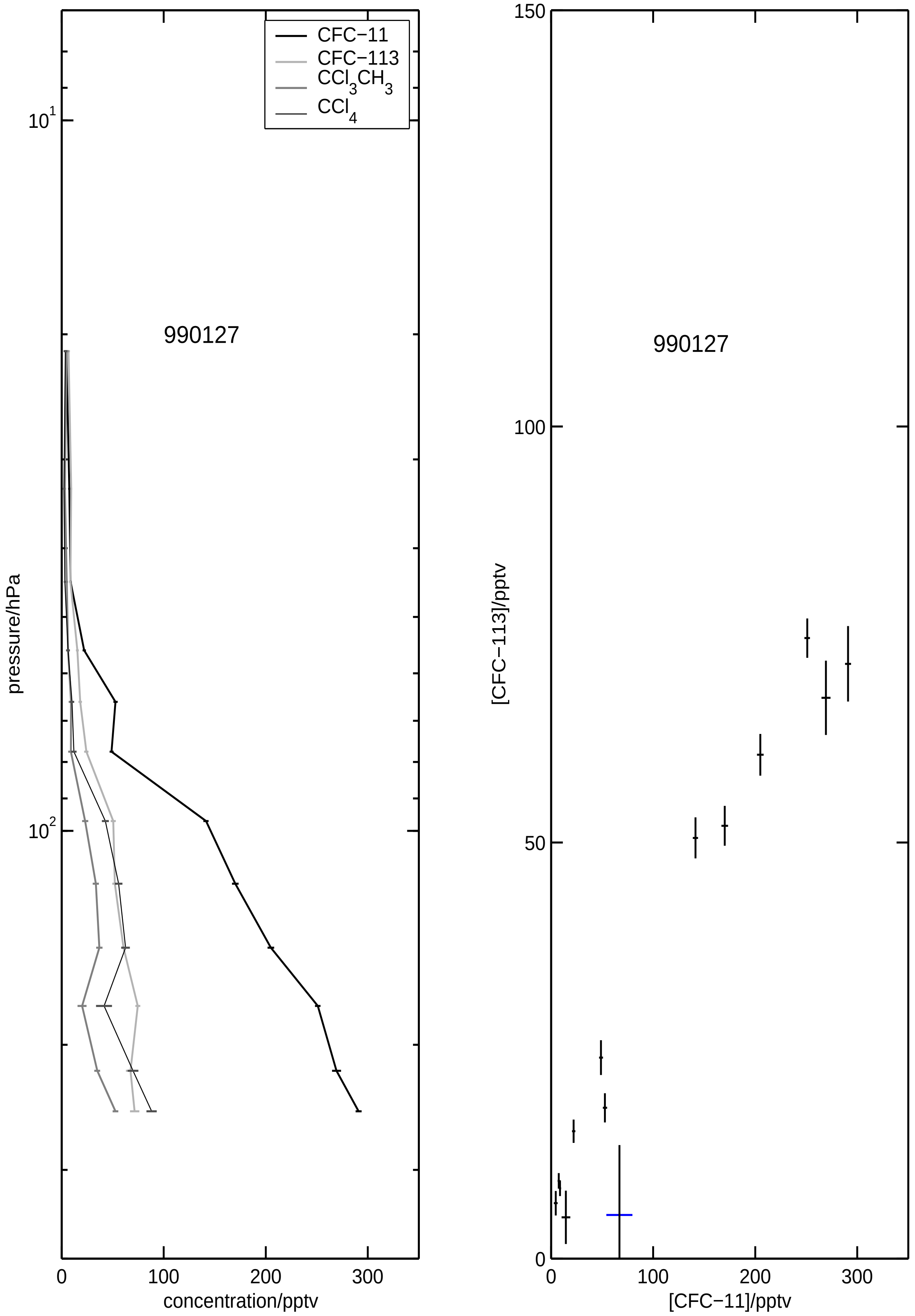

Figure 3: Profiles from flights 1999 of all the measured species as discussed in section 5 and plots of the concentration of CFC-113 vs CFC-11.

polynomial calibration function from the calibration of the detector response in raw counts from the detector A, r_f is the flight factor from the standard sample during flight analysis, r_t is the trap factor from the repeatability test, t is the sample time according to the on-board computer and C is the absolute calibration coefficient as described in section 3.

As the absolute calibration factor is determined in a procedure very much like the normal measuring procedure most systematic errors cancel and the remaining error is thought to be random error that can be estimated from statistics. For F the error is estimated as the standard deviation of the regression fit. The error in L is taken from the standard deviation in the function fitting and for the detector response A the standard deviation for three operators of the instrument integrating independently. For the traps the trap factor error is independently estimated as the standard deviation from the repeatability test. The error in the time reading is small so it is ignored. As C is determined with the same equipment as the result, the remaining error for inclusion of this is thought to be the statistical error from the finite number of calibration points, and is estimated from the standard deviation in calculation of this factor.

5 Results

Profiles for all the analysed species for all flights is seen in figure 3.

981117, flight with SAOZ from Andøya. Flight under good conditions but the heating was not working well and the analysis of these data is still under investigation.

981208, flight with Skerries from Esrange. Flight with the same heating system as above.

990127, flight with SAOZ/Br O from Esrange. The flight was done under very cold conditions, −40 °C during the release and even colder after landing. The instrument was left out for more than 24 hours as the recovery team did not work in the field due to the low temperature. This might have caused leaks in the traps. However the fact that no other peaks than usual are seen in the chromatograms from this flight indicates that there were no leaks.

990212, technical flight from Esrange. This flight had the slowest ascent during the campaign. The quality of these measurements seems better than the rest. With this in mind it might be best for future flights to have a slow ascent, but this might be at odds with achieving a high float. A slower ascent also makes the samples better defined in height.

990218, technical flight from Esrange. Preliminary results indicated extremely low values for this flight. Careful calibration and analysis yield a much more normal data than indicated in [1].

990420, technical flight from Esrange. Flight done after turnaround. Instrument performance appears nominal.

990826, flight with Skerries from Esrange. Flight done close to turnaround. The flight response test for CCl_4 is peculiar. This is being investigated further and this profile is left out for the time being.

6 Discussion and conclusions

The desorption of the traps works out very well for all species during laboratory tests as seen in the linearity test (figure 2). The real data samplings from flight do not seem as easy to desorb; there are always more leftovers after the first heating. The result using compressed air is much more similar to real samples than the Nitrogen-CFC gas mixture.

References

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