Adsorption of CFC on Carboxen during sampling in the stratosphere

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Abstract

DESCARTES is a lightweight balloon-borne instrument for the measurement of long-lived trace gases in the stratosphere. The principle behind the instrument is to let a measured amount of air pass through sample tubes containing the adsorbent Carboxen. The trace gases will then be trapped inside the tubes. DESCARTES is, during a flight, capable of taking 15 samples over a range of altitudes. The samples are analysed after recovery of the instrument using a GC-ECD system. With the current setup DESCARTES is optimised for CFC-11.

The objective with this study was to investigate if quantitative adsorption of CFC-11 can be secured during sampling with DESCARTES in the stratosphere. In order to study the adsorption efficiency of the sample tubes, double trap experiments were performed to test for leakage of CFC-11 during sampling. The results indicate that CFC-11 exhibits an exponentially declining distribution inside the adsorbent tube, giving rise to an exponential increase in breakthrough when sampling continuously. The exponential distribution of CFC in the adsorbent tubes of DESCARTES differs from the common way of seeing the sample tube as a chromatographic column. Furthermore the breakthrough of CFC-11 seems to increase exponentially when the flow rate is increased.

During a normal flight with DESCARTES, samples are taken at pressure levels from 250 up to 20 hPa. Typical sample sizes are between 30 and 200 scc with flow rates varying from 5 to 200 sccm. If a breakthrough of 5 per cent is acceptable most samples taken with DESCARTES can be seen as safe samples when considering the mass flow. The reduced pressure in the stratosphere will however give rise to enlarged sample volumes, resulting in volume flows of 200 to 600 ml/min. Since the important flow parameter when considering breakthrough seems to be somewhere in-between mass flow and volume flow, breakthrough of CFC-11 exceeding 5 per cent may still be expected due to the high volume flow rates occurring at low pressure.

Table of contents

1 Introduction

The chlorofluorocarbons, CFC, are man-made compounds used in refrigerators, cooling systems, foam blowing, aerosol propellants and industrial solvents. When released in the atmosphere, the CFC may migrate to the stratosphere where photolysis releases the chlorine atoms, which in turn participate in reactions that lead to stratospheric ozone depletion (Brune et al., 1991). Until recently, large quantities of CFC were released into the atmosphere but the signing of the Montreal Protocol in 1987, an agreement to phase out the production and use of ozone depleting CFCs, has greatly reduced the emissions. Despite the reduction, CFC will, due to their chemical stability, stay in the atmosphere for decades up to centuries. The fact that the CFCs are long-lived makes them suitable as tracers of atmospheric motions. Regular measurement of long-lived tracers are important to be able to compare with atmospheric models used to understand the circulation of the middle atmosphere and to estimate the impact of anthropogenic trace gases on the climate of the Earth. Measurements of long-lived trace gases in the stratosphere in this way serve a double purpose both in ozone loss chemistry but also for climatic modelling (Andrews et al., 1987).

Measurements of CFCs have been made by instruments on balloons, aircraft and satellites (Danis et al., 2000). The balloon-borne instrument mainly used to be based on cryo-sampling techniques, where large volumes of air were pumped into sample canisters immersed in a low temperature bath of liquid neon or nitrogen. Cryo samplers allows a wide range of stable gases to be measured, even at low concentrations but the number of samples are limited which reduces the spatial resolution. In recent years, gas chromatographs flown on aircraft that makes in situ measurements of tracers have been modified to suit balloons. These instruments are sophisticated but require large balloons and the number of flight opportunities are often limited due to operational and financial reasons. (Robinson et al., 2000).

DESCARTES is a balloon-borne instrument for the measurement of long-lived trace gases in the stratosphere. DESCARTES was developed at the University of Cambridge with the main objectives to be met: to develop an instrument with good precision that is reliable and easy to use (Danis et al., 2000). The low weight of less than 20 kg and no need for telemetry make the instrument suitable of being launched both on small balloons and to fly piggyback on heavier pay-loads carried on large balloons. During a flight DESCARTES is capable of collecting 15 samples over a range of altitudes. Samples are taken by pumping a measured amount of air through sample tubes containing a Carboxen adsorbent. The instrument adsorbs CFC-11, CFC-113, CCl_4 and CH_3CCl_3 in measurable quantities but is, with the current setup, optimised for CFC-11. After the flight the samples are analysed by using a GC-ECD system. One copy of DESCARTES is operated by the Swedish Institute of Space Physics, IRF. With the DESCARTES instrument IRF has since 1997 participated in large stratospheric ozone campaigns like the ILAS validation campaign (Nilsson et al., 1997), the EU funded SAMMOA campaign (Orsolini et al., 2002) and the THESEO campaign (Arvelius et al., 1999), but also in the national Swedish SKERRIES balloon programme.

This study focuses on the uncertainty of the measurements made with DESCARTES due to the adsorption efficiency of the sample tubes. When sampling using adsorbent tubes, care must be taken to avoid loss of analyte during sample collection.

2 Objectives

The overall objective of the study was to investigate if quantitative adsorption of primary CFC-11 can be secured during sampling with DESCARTES in the stratosphere.

3 Breakthrough volume

The term breakthrough volume is defined as the volume of carrier gas that will purge an analyte through 1.0 gram of adsorbent resin in a desorption tube at a specific temperature (Scientific Instrument Services, Inc.[1], 2003). The breakthrough volume, also referred to as retention volume, is usually expressed as litre/gram.

A sample tube filled with an adsorbent may be seen as a chromatographic column (Ruud et al., 1994). When air is flowing through the tube, the adsorbed analyte will migrate through the adsorbent bed in the direction of the airflow. After a certain time the analyte will reach the end of the tube and start to elute from the tube giving rise to a chromatogram type peak when detected (Figure 1). The sample tube in this way resembles a packed GC column with the adsorbent acting like the stationary phase. As in a GC column the analyte will have a retention time based on resin bed volume, column flow rate and temperature (Scientific Instrument Services, Inc.[1], 2003). The top of this peak corresponds to the retention time, t_r (Figure 1). Multiplying the retention time by the constant flow rate gives the volume required to move the analyte through the adsorbent bed. If the gas volume is divided by the weight of the adsorbent, the breakthrough volume is received. By injecting a non retained analyte into the sample tube and then calculating the retention volume of the non retained analyte, a correction of the dead volume of the packed adsorbent and connecting lines can be made from the breakthrough volume according to

$$B_v = (t_r \text{ flow} - V_d) / w_a \qquad (1)$$

where V_d is the dead volume and w_a is the weight of the adsorbent (Scientific Instrument Services, Inc.[1], 2003).

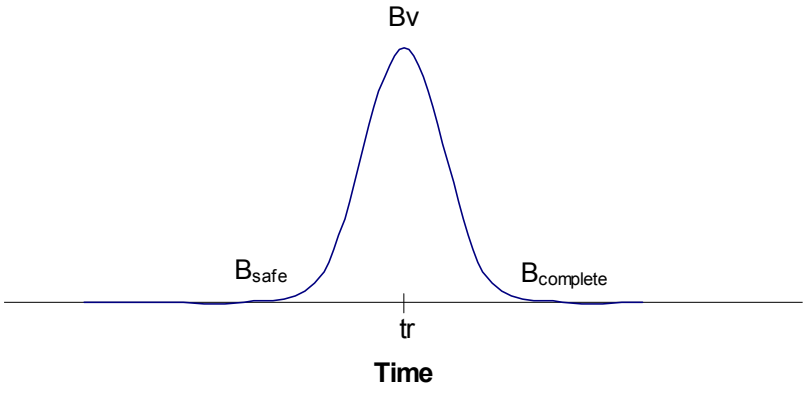

Figure 1. Breakthrough volume expressed as a chromatographic peak. The retention time, t_r, multiplied by the constant flow and divided by the weight of the adsorbent gives the breakthrough volume, B_v. The safe sample volume, B_{safe}, and complete sample elution volumes, $B_{complete}$, are received by multiplying B_v by a factor 0.5 and 2, respectively.

Source: Scientific Instrument Service, Inc.[1], 2003

Breakthrough volume data should be taken into account when collecting samples using adsorbent resin to assure that the analytes of interest are not purged of the adsorbent bed during sample collection. Due to the fact that the elution peak is gaussian in shape the retention time of the analyte will correspond to the volume required to elute half of the analyte (Figure 1). When using breakthrough volume data for a collecting process the safe sample volume should be used,

$$B_{safe} = 0.5\ B_v. \quad (2)$$

Breakthrough volume data are also important during desorption processes. To fully purge the analyte off the adsorbent, the breakthrough volume data should be multiplied by a factor two to receive the complete sample elution volume,

$$B_{complete} = 2\ B_v. \quad (3)$$

3.1 Distribution of analyte in a sample tube

When air is flowing through a sample tube the adsorbed analyte will migrate through the adsorbent bed if exchange between mobile phase and stationary phase occurs. If the kinetics of the adsorption and desorption processes are fast, the system will be close to equilibrium and the analyte will move through the column in a narrow band. The breakthrough pattern of such a sample tube would resemble a chromatographic column. In the beginning of the sampling no leakage of analyte can be observed but as the analyte migrates in the direction of the air stream and finally reaches the end of the sample tube a sudden increase in breakthrough occurs. Such a column can be considered a good chromatographic column. On the other hand if the mass transfer is to slow the analyte will not move through the tube in a narrow band instead band broadening is achieved, resulting in a broad peak when detected (McNair, 1997).

When using adsorbent tubes for sampling the goal is to trap all analyte and to avoid having already adsorbed analyte to desorb. The ideal case would be to have a sample tube with an adsorption coefficient approaching infinity and a desorption coefficient equal to zero at the actual sampling temperature. The analyte would in the ideal case be distributed according to a high concentration in the front of the sample tube. Since the ideal adsorbent tube has no desorption, no redistribution of analyte take place and no leakage of analyte occurs during sampling as long as saturation of the adsorbent bed is not reached. In practice, the non-ideal adsorbent tube will to different extents give rise to leakage of analyte due to limitations in the adsorption and desorption coefficients of the adsorbent, i.e. the adsorption coefficient is too small and the desorption can not be considered as negligible.

3.2 Factors influencing Breakthrough volume

The breakthrough volumes derived from GC retention volumes assume ideal conditions during sampling i.e. small sample sizes resulting in narrow peak width and that the analyte "likes" the adsorbent as a stationary phase. If samples are collected continuously over a period of time competition for the active sites of the adsorbent may occur causing the breakthrough volume to be less than determined. The analyte will thereby not be put onto the adsorbent in a small plug but rather as a broad band with the bandwidth depending on the affinity of the adsorbent for the analyte, giving rise to broad peaks when detected (Scientific Instrument Services, Inc.[1], 2003).

If ideal behaviour of the adsorbent is assumed, breakthrough volume is not a function of concentration of the analyte. High concentration may however cause non-ideal behaviour of the adsorbent e.g. condensation or formation of a second layer, which may be indicated by irregularities in the breakthrough curves (Ruud et al, 1994). A factor that may influence the breakthrough volume of a compound adsorbed on a sample tube is the presence of other compounds that may be alike or differ in their properties. Studies have shown that the breakthrough volume of a single substance in a mixture can be strongly reduced (Ruud et al, 1994).

The flow rate through the adsorbent may also influence the breakthrough volume. The maximum linear velocity through the adsorbent resin should not exceed 500 cm/min (Scientific Instrument Service, Inc.[1], 2003). A higher velocity may not allow the analyte to interact with the pores of the adsorbent resin and may thereby result in inefficient trapping. The maximum flow rates for the adsorbent resins can be calculated according to

$$Q_{max} = B_{max}\pi r^2 \qquad (4)$$

where r is the radius of the adsorption tube and B_{max} is the maximum linear velocity of the gas (Scientific Instrument Service, Inc.[1], 2003).

4 DESCARTES

The principle behind the instrument is to let a measured amount of air pass through sample tubes containing an adsorbent. Trace gases will then be trapped inside the sample tube while the rest passes through. 16 tubes filled with adsorbent are placed on a 16 position valve allowing only one tube at a time to be exposed to the air flow. 15 samples may be collected during a flight, the 16th sample tube is used as a waiting position before and after flight. The sample tubes are made out of stainless steel with an inner dimension of 1.27 mm. The instrument adsorbs CFC-11, CFC-113, CCl_4 and CH_3CCl_3 in measurable quantities but is, with the current setup, optimised for CFC-11.

An on-board computer controls DESCARTES during flight and allows housekeeping data to be stored during and after each flight. In addition to control the sampling sequence, the computer also reads and integrates the flow to determine the volume passed through the sample tubes, reads the on-board sensors for pressure and temperature, the level of the batteries, the state of the valves and the position of the 16-position valve. The external pressure is measured to determine when samples are taken but is not accurate enough to be used in data interpretation. Accurate external pressure is measured by other instruments on the payload. The pressure of the sampling line is measured, relative to the external pressure, both before and after the sampling box (Figure 2). The temperature of the instrument is, during flight, measured at a number of locations using thermistors. The power usage of the instrument is supplied by two 12 V batteries, one supplying the computer and the other supplying the pump.

After a flight, the flight data is downloaded from the onboard computer and the sample sizes of the different traps are determined. The sample box is connected to a gas chromatograph for quantification and the traps are thermally desorbed by direct resistive heating. In order to obtain good electrical contact, a gold plated circlip is attached to each sample tube and the wire conducting the current is welded onto the circlip. An electronic box, called the heater box manages the heating of the traps. The heater box also allows the traps to be manually controlled. The tracers are quantified by using calibration curves received by passing measured amounts of a standard sample through the sample box. The standard is then analysed by using the typical analysis sequence as for a flight with corrections for trap individuality.

4.1 Sampling

A schematic of DESCARTES is showed in Figure 2. Sampling usually takes place through an inlet tube placed at the top of the instrument while the balloon is ascending. Air is pumped into the instrument through a particle filter passing three-way solenoid valve B and C.

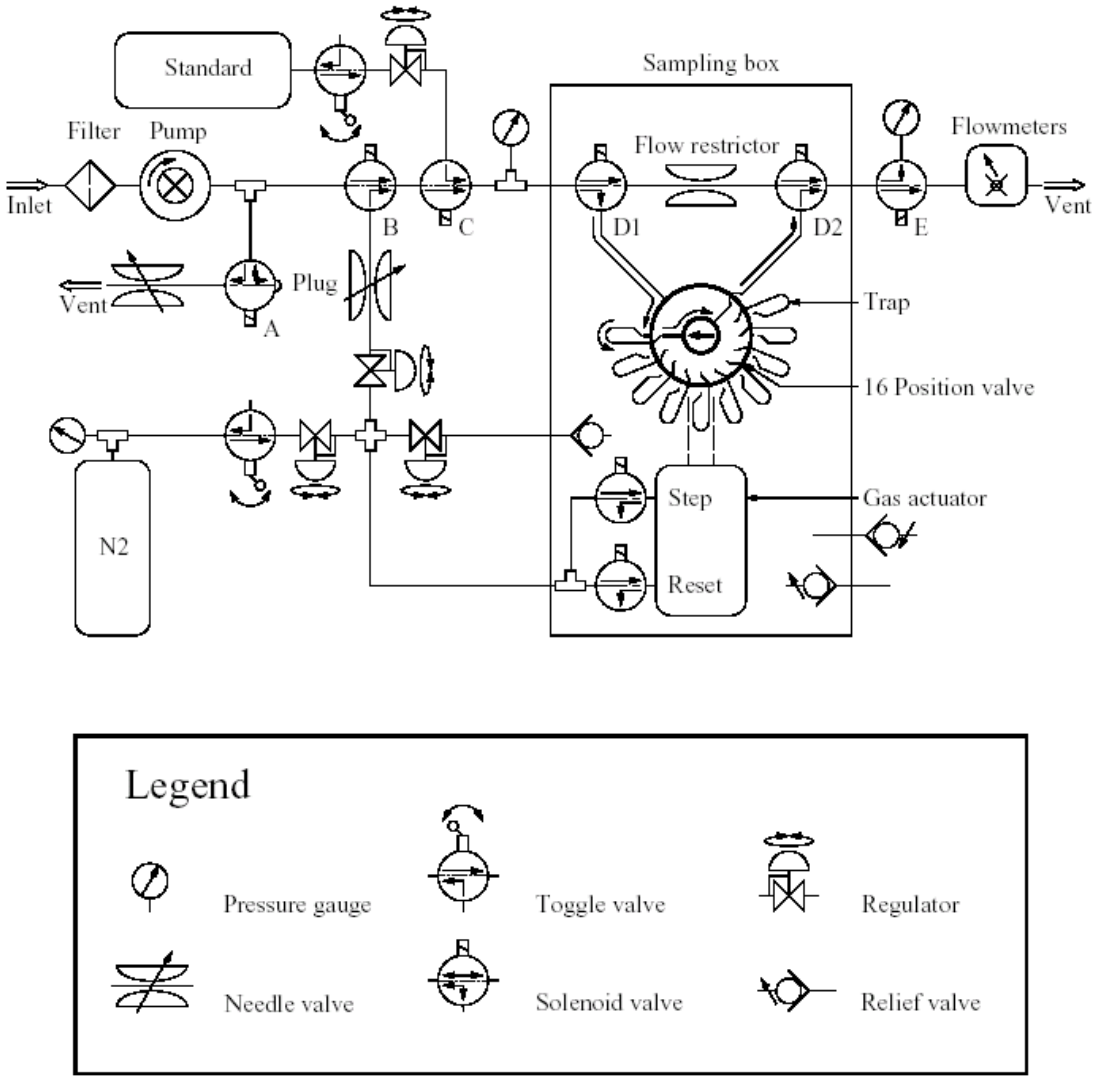

Figure 2. Schematic of DESCARTES

Source: Reprinted from Danis et. al., 2000

First the air stream bypasses the traps to flush through the system. When the first predefined atmospheric pressure level is reached air is redirected, by switching solenoid valve D_1, through one of the 16 sample tubes on the 16 position valve. After the sampling box the air passes the flowmeters before being vented into the atmosphere (Figure 2). The flow meters measure the flow in sccm, standard cubic centimetre per minute. Sccm is a mass flow unit corresponding to 1 cm^3/min of gas at 0 °C and 1 atm. Consequently the sample size is measured in scc, standard cubic centimetre. The flow meters cover two ranges, 0-200 and 0-1000 sccm, respectively. When the ambient pressure is high, the flow generated by the pump is large. In order to reduce the flow at high ambient pressure an overflow vent is opened by switching solenoid valve A (Figure 2) and part of the flow from the pump is diverted through a needle valve. The flow is thereby kept below 200 sccm. When the flow drops under 70 sccm at around 90 hPa the vent is closed and the flow will increase before dropping again as the ambient pressure decreases.

A second side channel of the sampling line, introduced into the sampling line by switching solenoid valve B, connects to a cylinder containing high pressure nitrogen which is used to flush the lines and to pressurise the sample tubes after a sample has been collected. The nitrogen is also used to step the 16 position valve (Figure 2).

Figure 3 shows an example of CFC-11 and CFC-113 profiles for a flight with DESCARTES in 1999-02-12. Samples are normally taken at pressure levels from 250 hPa up to 20 hPa, altitudes of approximately 10 to 27 km. Typical sample sizes during a flight are 30-200 scc, but samples may occasionally exceed 200 scc. The sample size is increased with decreasing pressure in the stratosphere due to the decrease in CFC concentration with altitude (Figure 3). Typical sampling times are 7-600 seconds and the flow rate normally varies between 5-200 sccm with the highest mass flows in the beginning of the sampling at 250 hPa and the lowest mass flows in the end of the sampling at 10-20 hPa. Flows exceeding 200 sccm have occasionally been observed during sampling near 250 hPa despite the overflow vent being in an open position.

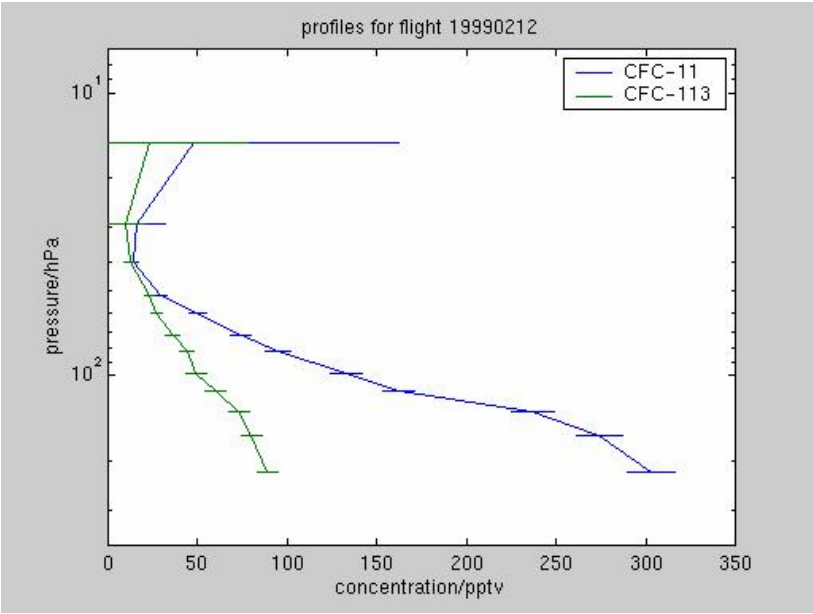

Figure 3. CFC-11 and CFC-113 profiles for a flight with DESCARTES 1999-02-12. CFC concentrations are expressed in pptv.

Source: Atmospheric Physics, IRF, 2003.

The pressure levels at which the samples are taken are chosen before each flight. An example of a sampling schedule is shown in Table 1. The sampling schedule starts at the set pressure level (*When hPa*, Table 1). The sample is taken at a pressure measured by DESCARTES (*Ambient pressure*, Table 1). *Required mass* (Table 1) is the predetermined sample size in scc, which is controlled by continual integrating of the mass flow but also by the pre-set maximum sample time (*Max sample secs*, Table 1). Either of the two conditions has to be fulfilled before sampling stops. The achieved sample size (*Mass*, Table 1) does normally not reach the *Required mass* at low pressure levels, due to the fact that the condition *Max sample secs* is reached before. The *Mass flow* (Table 1) is the mean flow during the whole sampling and the *Estimated volume* is an estimation of the sample size expressed in ml, calculated according to equation 10 in the Material and method section. *Estimated volume flow* is an estimation of the flow in ml/min based on the *Estimated volume* and *Duration* in seconds.

Table 1. Flight schedule parameters and flight data from flight with DESCARTES from Esrange 2000-12-11.

When hPa	Ambient pressure/hPa	Duration /secs	Required mass/scc	Max sample secs	Mass flow /sccm	Mass /scc	Estimated volume* /ml	Estimated volume flow * /ml min^{-1}
250	250.6	18.3	30	35	137.2	41.8	114	374
220	216.1	18.4	30	40	116.7	35.7	58	189
200	195.3	22.0	30	40	102.9	37.8	120	327
180	172.8	22.0	30	50	85.3	31.3	67	183
150	148.1	25.6	30	50	69.7	29.7	74	173
120	124.8	40.0	40	50	55.4	37.0	109	164
100	105.	50.9	40	90	44.2	37.5	131	154
80	87.8	29.2	50	100	117.6	57.2	246	505
70	77.7	32.8	50	120	99.8	54.6	271	494
60	68.5	47.3	60	180	79.6	62.7	352	447
50	57.3	97.9	100	250	58.7	95.7	640	392
40	46.9	126.8	100	250	42.7	90.1	749	354
30	3.4	300.3	200	300	25.2	125.9	1405	281
20	2.1	600.3	300	600	7.8	77.8	1268	127

*Estimation of sample volume according to equation 10 in the Material and method section.

4.2 The adsorbent Carboxen

The sample tubes contain the adsorbent Carboxen, a carbon molecular sieve for trapping of smaller organic analytes with a low affinity for water. Two different kinds of Carboxen are used. The adsorbent in the traps of sample box I and sample box II is Carboxen 1000 and Carboxen 569, respectively. Carboxen 1000 is considered to have stronger adsorbent strength towards volatile materials compared to Carboxen 569 (O`Doherty et al., 1993).

The minimum quantity of Carboxen required was determined experimentally in the laboratory at atmospheric pressure, during construction of DESCARTES, by passing mixtures of CFC-11 and CFC-12 through a known amount of Carboxen until they were no longer quantitatively trapped. The required amount of adsorbent was estimated to 4 mg but was increased to 15 mg to allow for the effect of reduced ambient pressure on trapping efficiency (Danis et al., 2000).

4.2.1 Breakthrough of CFC-11 on Carboxen

In Figure 4 the breakthrough volume of CFC-11 on Carboxen 569 is expressed as litre per gram adsorbent vs. temperature. The breakthrough volume of CFC-11 exhibits an exponential decrease when the temperature is increased and can be calculated according to

$$B_{cfc\text{-}11} = 5.0199e^{-0.024t/^{o}C} \text{ litre/gram.} \qquad (5)$$

According to equation 5, the breakthrough volume of CFC-11 on Carboxen is 5 litre per gram adsorbent at 0 ºC. The safe sample volume would in DESCARTES case, according to equation 2, therefore be

$$B_{safe} = 0.5 \cdot 5 \text{ ml/mg} \cdot 15 \text{ mg} \approx 40 \text{ ml.}$$

At 260 °C the breakthrough volume of CFC-11 on Carboxen 569 is, according to equation 5, 0.01 litre per gram adsorbent. Since a breakthrough volume of less then 0.010 litre is needed to assure complete desorption, 260 ºC can be considered a sufficient temperature for a thermal desorption process (Scientific Instrument Services, Inc.[2], 2002).

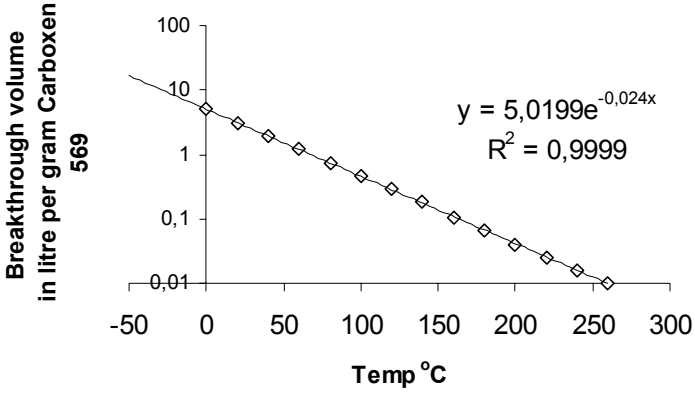

Figure 4. Breakthrough volume of CFC-11 on Carboxen 569. Breakthrough volume at temperatures between 0 – 260 °C are experimentally calculated breakthrough volumes from Scientific Instrument Services, Inc. Breakthrough volumes at temperatures below 0 °C are extrapolated values, assuming an exponential growth, to predict breakthrough volumes for temperatures not determined experimentally.

Source: Scientific Instrument Services, Inc.[2], 2003

5 Material and method

To study breakthrough during sampling with DESCARTES, laboratory tests were performed by connecting two sample boxes in series, box I and box II. Air volumes of different quantities were passed through the two boxes and the traps of the second box were manually shifted after predetermined time intervals by using the step-reset function of the heater box. The traps of box II were then analysed to detect when a breakthrough in the first box occurred. The compound studied during the breakthrough test was restricted to CFC-11. By quantifying each peak area of CFC-11 obtained when analysing the traps of sample box II and then taking the sum of the CFC-11 content, the actual total breakthrough at a specific sample size could be determined. The breakthrough of CFC-11 was expressed as percentage of a mixing ratio of 263 pptv when sampling compressed air (Appendix A) and 265 pptv when sampling air in the troposphere. The laboratory tests, performed at atmospheric pressure and room temperature, were divided into preparatory tests and flow rate tests. In addition the double trap experiment was modified to suit a technical flight and tests in vacuum tank.

The flow meters of DESCARTES measure the flow in sccm, which will result in sample sizes expressed in mass units. Since the low pressure in the stratosphere give rise to enlarged sample volumes there are reasons to believe that the leakage of CFC-11 may depend on the actual volume of the sample. By using the ideal gas law, an estimation of the sample volume can be obtained from the mass. In terms of mass the ideal gas law looks like

$$m = kVp / T \qquad (6)$$

where k is the proportionality constant,

$$k = 1 \text{ scc} \cdot 273.15 \text{ K} \cdot 1 \text{ cm}^{-3} \cdot 1 \text{ atm}^{-1},$$

V is the volume, p is the pressure and T is the temperature.

In order to calculate the volume of gas passing a trap during sampling the pressure inside the trap has to be estimated. Figure 5 shows the assumed pressure drop in the sampling system of DESCARTES. The pressure in the sampling line is measured, before and after the sample box (Figure 2), relative to the ambient pressure giving

$$p_0 = p_{amb}. \quad (7)$$

The measured pressure is lower after the sample box than before the box. Since the sampling lines are more or less symmetric around the trap, an assumption can be made that the pressure drop exhibit the same pattern both before and after the trap. If the pressure inside the whole trap is close to constant and the main pressure drop occur elsewhere in the sampling system, verified in *6.4 Test in vacuum tank*, the pressure inside the trap during normal sampling through one single trap may be estimated, according to

$$p_{trap} = ½\ p_b + ½\ p_{amb} \quad (8)$$

where p_{amb} is the measured ambient pressure and p_b is the measured pressure inside the sampling line before the trap (Figure 5).

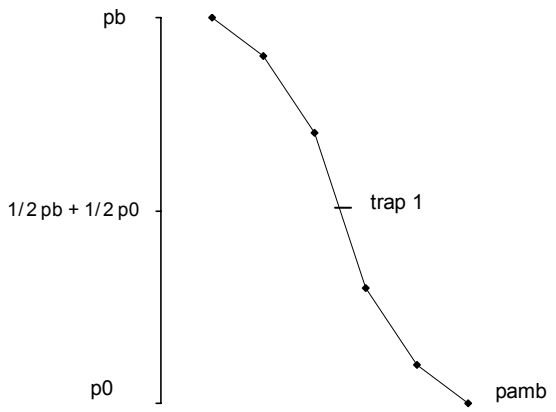

Figure 5. Pressure drop in the sampling system of DESCARTES with one trap connected. Due to symmetry of the sampling lines the pressure drop can be assumed to exhibit the same pattern before and after the trap. The pressure is measured relative to the ambient pressure and pressure inside the trap can be estimated to ½ pb + ½ pamb.

When two similar sample boxes are connected in series, the pressure drop can be assumed to occur according to Figure 6 and the pressure inside the first trap may be estimated as

$$p_{double\ trap} = ¾\ p_b + ¼\ p_{amb}. \quad (9)$$

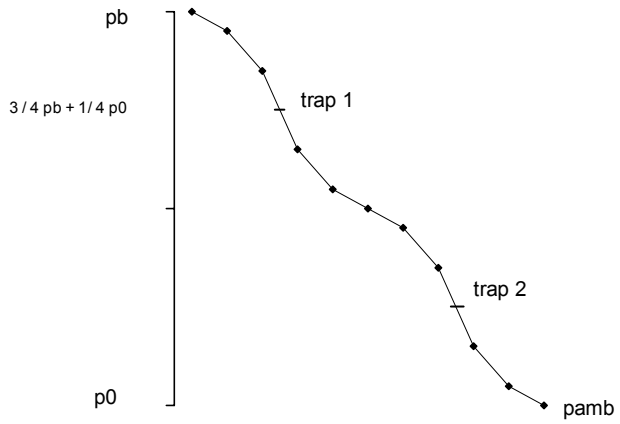

Figure 6. Pressure drop in the sampling system of DESCARTES with two sample boxes connected in series. Due to symmetry of the sampling lines the pressure drop can be assumed to exhibit the same pattern before and after the trap. The pressure is measured relative to the ambient pressure and the pressure inside the first trap can be estimated to ¾ p_b + ¼ p_{amb}.

The sample volume of the traps could then be estimated in accordance with the ideal gas law, equation 6, as

$$V_{trap} = m\ T_{trap} / (1\ scc \cdot 273.15\ K \cdot 1\ cm^{-3} \cdot 1\ atm^{-1} \cdot p_{trap}) \quad (10)$$

where p_{trap} is the estimated pressure inside the trap during sampling, equation 8 and equation 9, respectively and T_{trap} is the estimated temperature inside the trap during sampling. Since the temperature is measured in the flow before the sample box but not inside the trap during sampling an assumption was made that no rise in temperature occurs inside the trap during sampling giving

$$T_{trap} = T_{flow}. \quad (11)$$

The compressed air standard used in the laboratory test was a dried air sample from Niwot Ridge, Colorado. The standard is analysed for N_2O, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3, CCl_4 and Halon-1211 (Appendix A). The flow of the standard was during tests regulated by the regulator of the compressed air standard tube and measured by the flow meters of Descartes.

5.1 Preparatory test before technical flight

Preliminary tests were made in the laboratory to study at which volumes the sample tubes exhibit breakthrough for CFC-11. Compressed air standard at a constant flow was running through one trap in box I while the traps of box II were shifted at predetermined time intervals. The flow rate was held at approximately 118 sccm. The minimum quantities of Carboxen had during development of DESCARTES been determined to 4 mg and then been increased to 15 mg to compensate for reduced pressure in the stratosphere (Danis et al., 2000). The maximum required sample size taken with Descartes of 300 scc (Table 1) may according to this be increased by a factor 3.75 before a breakthrough occurs when sampling at atmospheric pressure. This assumption would imply a safe sample volume of approximately 1000 scc. On the other hand, according to Scientific Instrument Service, Inc.[1] the calculated safe sample volume for CFC-11 on the traps of DESCARTES at 0 ºC is only 40 ml, equation 2 and equation 5.

The fact that the CFC-11 concentration decreases with decreasing pressure in the stratosphere may lead to difficulties in detecting a breakthrough at low pressure levels. The concentration of CFC-11 at pressure levels around 30 hPa may be below 25 pptv (Figure 3). Taking a tropospheric air sample followed by the actual air samples at low pressure to "initiate" the trap may simplify detection of a breakthrough. This initiating was first tried in the laboratory. Compressed air standard with a flow of approximately 112 sccm was sampled for two minutes giving rise to a mass volume of about 220 scc. To simulate low concentrations of CFC-11, corresponding to pressures below 30 hPa, the compressed air was changed to CFC-free N_2. Repetitive two minutes sampling intervals followed by shifting of traps in box II was performed. The N_2 flow was regulated to approximately 112 sccm by a needle valve connected to the sampling line.

5.2 Technical flight

To be able to study breakthrough during normal sampling conditions, a double trap experiment was performed during flight. A sample box was modified by mounting a fixed trap after the three-way solenoid valve, D_1, upstream the 16 trap valve, with one end electrically insulated. To be able to clean the fixed trap before flight the gold plated circlip of trap number fifteen was moved to the fixed trap. The air was directed through the bypass when no samples were collected or through the fixed trap and further to the selected trap on the 16 position valve during sampling. The modified sample box was leak tested with helium. After the flight the fixed trap was removed and replaced by the origin stainless steel tube before the analysis took place. The pressure inside the fixed trap was estimated according to equation 9, with the assumption that the pressure drop occuring in the sampling system when two traps are connected in series resemble the pressure drop occuring when two boxes are connected in series.

The first sample in the technical flight was predetermined to take place at 400 hPa in order to initiate the fixed trap with a tropospheric air sample of higher CFC concentrations. The remaining samples were supposed to be taken at low ambient pressure with a total required mass of 2000 scc which would secure that a breakthrough of CFC-11 took place during the flight. The flight schedule parameters of the technical flight is shown in Table 2. The technical flight took place in 2002-11-25 from Esrange, Kiruna.

5.3 Flow rate test

During a typical flight with DESCARTES, sampling is performed using flow rates ranging from approximately 5 to 200 sccm. The largest mass flows occur in the beginning of the flight before the overflow vent is closed. The recommended maximum flow rate to permit efficient trapping of analyte on the adsorbent can, according to equation 4, be estimated to

$$Q_{max} = 500 \text{ cm/min} \cdot \pi \cdot (0.127 \text{ cm})^2 = 25 \text{ ml/min}.$$

Since DESCARTES uses much higher flow rates then the recommended maximum flow, a flow rate test was performed in order to study how the flow rate influences breakthrough of CFC-11 at atmospheric pressure. Compressed air standard at a constant flow was running through one trap in box I while the traps of box II were shifted at predetermined time intervals. Four different flow rates were tested: 20, 47, 114 and 200 sccm.

5.4 Test in vacuum tank

Double trap tests in vacuum tank were performed to study how low pressure influences breakthrough of CFC-11 during sampling with DESCARTES. By stabilising a low pressure in the tank, continuous sampling can be made at a constant low-pressure level. The tests in vacuum tank were compared with tests made in the laboratory at atmospheric pressure to be able to investigate how volume flow and mass flow, respectively, influence breakthrough.

The software of DESCARTES was modified to suit a double trap experiment in vacuum tank. Two boxes were connected in series. One trap of box I was held open during the flight by applying a 12 V voltage over the bypass valve. The pressure inside the vacuum tank was stabilised at approximately 50 hPa. The initial sample in the sampling sequence was taken at a slightly higher pressure to make sure that the sampling sequence started while the following samples were taken after the pressure of the vacuum tank had been stabilised. In addition a sampling sequence at atmospheric pressure in the laboratory was taken. To avoid contamination of the vacuum tank, DESCARTES was wrapped into aluminium foil during the experiment and the ordinary outer box made of polystyrene was not used.

5.5 Distribution of CFC-11 in the sample tube

In order to understand the distribution of CFC-11 inside the sample tube an attempt was made to evaluate a model, simulating adsorption and desorption of CFC during sampling with DESCARTES. In the simulation the model was adjusted to produce breakthrough patterns according to the results obtained in this study. Simulation of CFC-11 was performed in MATLAB.

6. Results and discussion

The figures in the result section express the total breakthrough of CFC-11 at every sample size, i.e. the sum of the CFC-11 content obtained when analysing the traps of the second sample box. Exceptions are Figure 9, which expresses the actual breakthrough of CFC-11 at every single pressure level and Figure 7, which expresses the sum of the analysed peak areas.

6.1 Preparatory test

Preliminary test in the laboratory at atmospheric pressure showed that breakthrough of CFC-11 occurs at sample sizes less than 500 scc when sampling air at a constant flow of 118 sccm (Figure 7). Also purging an air sample with N_2 at a flow of 112 sccm confirmed that sample sizes less than 500 scc exhibit breakthrough of CFC-11, although the breakthrough was lower for the last case (Figure 7). When sampling air continuously, the breakthrough of CFC-11 seems to exhibit an exponential growth while purging an air sample with N_2 shows a steady increase in breakthrough. The steady increase in breakthrough of CFC-11 in the case of purging the tube with CFC-free N_2 must originate from a desorption process that continuously redistributes CFC-11 inside the sample tube.

When analysing the traps of the compressed air-N_2 test, two large peaks appeared at a total sample volume of approximately 1350 and 2250 ml, respectively. The peaks reached an area of around 2400 and 5800 · 5Hz*s. If only one large peak had appeared, it could have been explained as being the air sample that had been purged to the end of the adsorbent bed and then eluted from the sample tube. This explanation would have been in agreement with the sample tube resembling a good chromatographic column. Since no explanation could be found for having two separate large peaks, the peaks were excluded from Figure 7 as being non-desorbed remains of CFC-11 from an earlier analysis. Abnormal peaks have occasionally appeared during earlier analysis, and could also then be explained by ineffective thermal desorption.

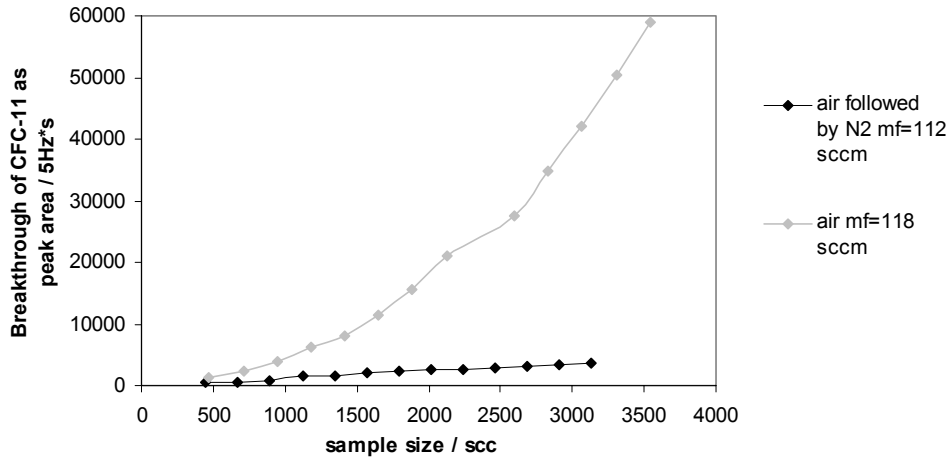

Figure 7. Total breakthrough of CFC-11 expressed as peak area vs. sample size in scc. Double trap experiment during constant flow and changing of trap in the second box every second minute. In the first test compressed air was sampled during the first 2 minutes at a flow rate of 112 sccm followed by N_2 during the rest of the two minutes intervals. In the second test compressed air was sampled in 2 minutes interval at a flow rate of 118 sccm.

6.2 Technical flight

The flight parameters and flight data are shown in Table 2. Due to battery failure only five samples were taken during the flight. In the tropospheric sample the required mass was predetermined to 200 scc but the integrated mass reached 310.9 scc with a mass flow of 214.3 sccm (Table 2). The volume of the first sample was estimated to 433 ml according to equation 10. Four stratospheric samples were taken at decreasing pressure, the first sample at 67 hPa and the last sample at 36 hPa. The required mass of 100 scc was almost reached in all four stratospheric samples but the estimated sample volume of the samples increased however due to decreasing pressure up in the stratosphere. The decreasing pressure in the sampling schedule also resulted in decreasing mass flow but when considering the estimated volume flow, it remains high through the different pressure levels during the flight (Table 2).

Table 2. Flight schedule parameters and flight data from double trap experiment during flight with DESCARTES from Esrange 2002-11-25.

Sample type and number	Ambient pressure /hPa	Required mass/scc	Duration /secs	Mass flow /sccm	Mass /scc	Estimated flow /ml min^{-1}	Estimated volume /ml	Temp flow /^{0}C
1 tropos	416	200	87.0	214.3	310.9	298.8	433.4	5
2 stratos	67	100	83.4	70.2	97.6	290.3	403.5	-2
3 stratos	54	100	112.4	50.3	94.3	261.8	490.3	-3
4 stratos	45	100	144.8	37.7	91.0	247.6	597.6	-4
5 stratos	36	100	246.1	22.1	90.6	180.6	740.8	-5

Figure 8 expresses the breakthrough of CFC-11 in percentage of the tropospheric sample. Already the first tropospheric sample of about 300 scc unexpectedly exhibited a large breakthrough of approximately 8 percent (Figure 8). An explanation of the large breakthrough may be that the high flow rate (Table 2) does not allow the CFC-11 to interact with the active sites of the Carboxen, resulting in inefficient trapping. The following four stratospheric samples showed a steady increase in leakage of CFC-11, despite the fact that the concentration of CFC-11 was decreasing up in the stratosphere.

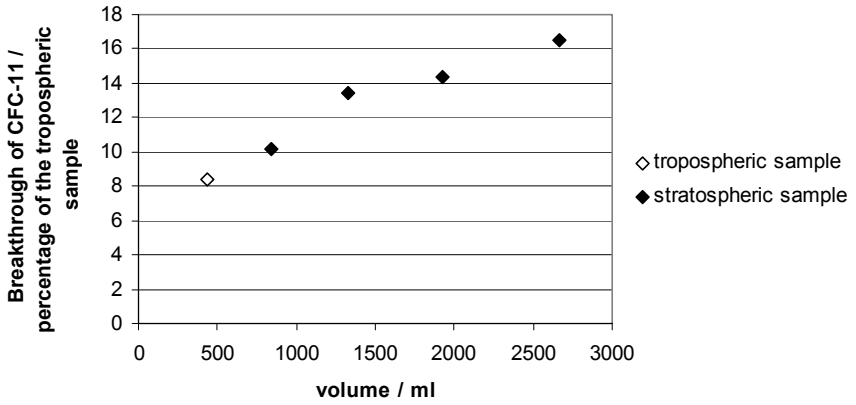

Figure 8. Total breakthrough of CFC-11 during a double trap experiment on a flight expressed as percentage of the tropospheric sample vs. total sample volume in ml. The first trap was initiated by a tropospheric sample and then four stratospheric samples were taken at decreasing pressure.

In Figure 9 the breakthrough is instead expressed as percentage of the assumed CFC-11 concentration at every pressure level. The CFC-11 concentrations were approximated according to measurements made during the SOLVE campaign in Kiruna, 1999-11-19, using the instrument LACE, Lightweight Airborne Chromatograph Experiment (LACE, 2003). The approximation was made from one balloon flight by calculating the mean from two measurements at each pressure level during ascent and descent. The concentrations can only be seen as rough approximations of the actual stratospheric CFC-11 concentrations during the double trap experiment, but since the measurements were made inside the polar vortex in both 2002-11-25 and 1999-11-19, the CFC-11 concentrations were assumed to be comparable.

Since Figure 9 shows abnormal breakthrough patterns, occasionally exceeding 100 per cent, the conclusion was made that a major part of the breakthrough of CFC-11 during sampling in the stratosphere must originate from the tropospheric sample. The steady increase in breakthrough in Figure 8, therefore indicates that adsorbed tropospheric CFC-11 is desorbed and redistributed inside the sample tube, i.e. the stratospheric samples purge the tropospheric sample off the resin.

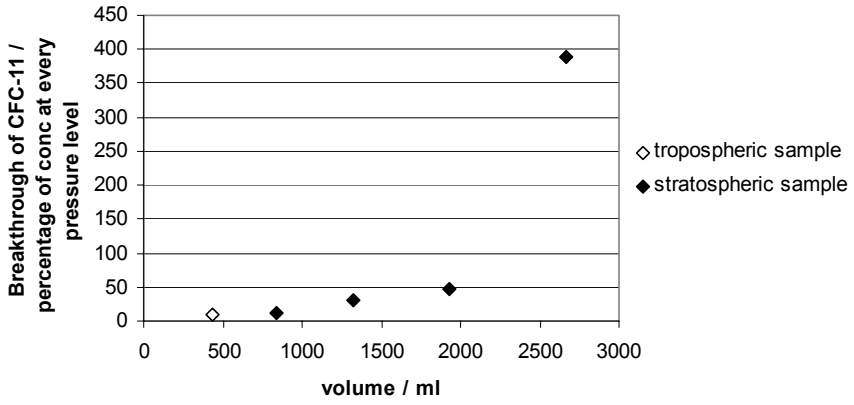

Figure 9. Breakthrough of CFC-11 during a double trap experiment on a flight expressed as percentage of estimated concentration at every pressure level vs. total sample volume in ml. The first trap was initiated by a tropospheric sample at 416 hPa and then four stratospheric samples were taken at 67, 54, 45 and 36 hPa, respectively. The CFC-11 concentrations at the different stratospheric pressure levels were approximated to 124.8, 91.9, 17.7 and 4.9 pptv according to measurements made with the instrument LACE in 1999-11-19.

Source, CFC-11 concentrations: SOLVE: LACE, NASA Earth Science Project Office, 2003

6.3 Flow rate test

Figure 10 shows how the mass flow rate during sampling influences breakthrough of CFC-11. A clear pattern can be observed as an increase in mass flow give rise to increasing breakthrough. The results from the flow rate test seem to agree quite well with the results from the technical flight. Sampling an air volume of approximately 430 ml with a mass flow around 200 sccm gave in the flow rate test rise to a breakthrough of around 7 per cent (Figure 10). A similar mass flow and sample volume during the flight showed a breakthrough of approximately 8 per cent (Figure 8). The flow rate test in this way strengthen the explanation that the high flow rate being the main factor to the large breakthrough of the tropospheric air sample during the flight.

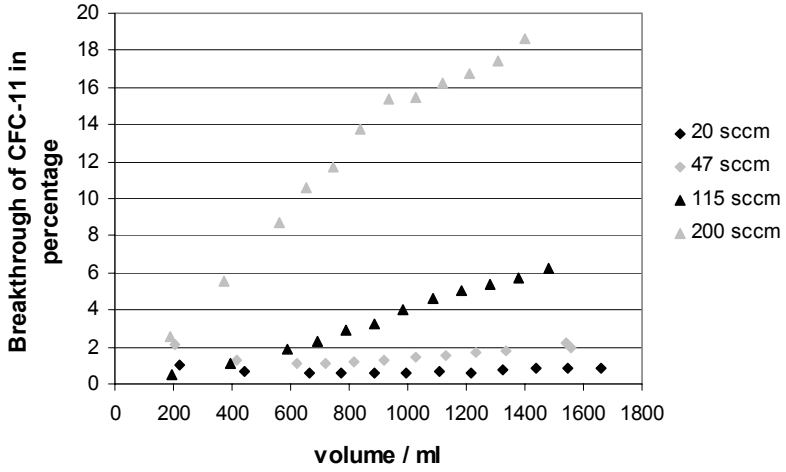

Figure 10. Total breakthrough of CFC-11 expressed as percentage vs. total sample volume in ml. Double trap experiment with flow rates varying between 20 to 200 sccm and changing of trap in the second box at predetermined time intervals in order to achieve desired sample sizes.

Figure 11 compares the total breakthrough of CFC-11 at a volume of approximately 1380 ml when sampling using flow rates between 20 to 200 sccm. The breakthrough increases linearly with mass flow when expressed on a logarithmic scale, which implies that the breakthrough of CFC-11 shows an exponential growth when the flow rate is increased.

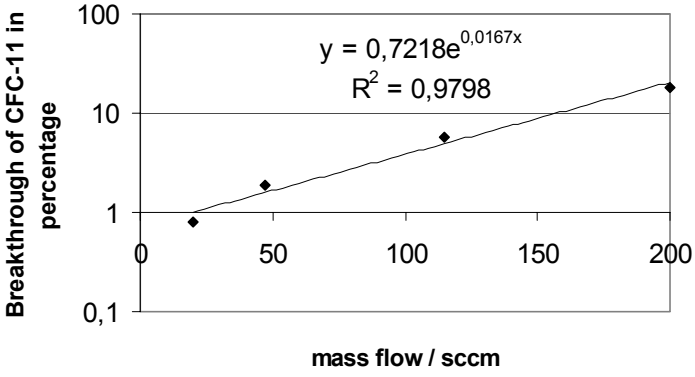

Figure 11. Total breakthrough of CFC-11 at a sample volume of approximately 1380 ml on a logarithmic scale vs. mass flow in sccm. The breakthrough exhibits an exponential growth when the flow rate is increased.

The highest mass flows used by DESCARTES, occasionally exceeding 200 sccm, normally occur at pressure levels around 250 hPa. The sample sizes taken at these pressure levels are usually around 30 to 60 scc but the reduced pressure will according to equation 10 give rise to sample volumes of approximately 100 to 250 ml. The expected CFC-11 leakage at sample sizes around 250 ml using mass flows of 200 sccm is approximately 4 per cent (Figure 10). The increase in volume due to decreasing pressure will at the same time give rise to higher volume flow rates. Due to the fact that the flow rate test took place at atmospheric pressure the estimated pressure inside the trap was close to ambient pressure, implying that during the flow rate test the mass flow was almost equal to the volume flow. During a flight on the other hand, estimated flow rates up to 600 ml/min are not unusual.

When sampling at pressure levels beneath 50 hPa, the mass flow usually stays within 50 sccm and even when sampling large volumes only a leakage of a few percent can be expected (Figure 10). But since the reduced pressure gives rise to large sample volumes the volume flow will also be quite large. The mass flow used at low pressure of a few sccm will in this way reach or sometimes even exceed 200 ml/min. Since the breakthrough pattern of CFC-11 shows an exponential growth when the mass flow rate increases (Figure 11), an increase in breakthrough due to increase in volume flow may also be expected. Larger breakthrough then in Figure 10 may therefore be expected due to high volume flow rates during a flight at low pressure.

6.4 Test in vacuum tank

In Figure 12, a comparison is made between the breakthrough patterns of CFC-11 of a test in vacuum tank at 50 hPa and of a test in the laboratory at atmospheric pressure. The test in vacuum tank took place at 50 hPa at a mass flow of around 25 sccm (Figure 12). A typical required mass during a normal flight at 50 hPa is around 100 scc (Table 1), which would imply a sample volume of approximately 600 up to 1500 ml when considering the reduced pressure, equation 10. A sample volume of 600 to 1500 ml would according to Figure 12 give rise to a breakthrough of approximately 1 to 3 percent. During normal sampling at 50 hPa using one sample box, a typical mass flow would however be around 50 sccm. According to the flow rate test, Figure 10, an increase in mass flow from 25 to 50 sccm would increase the breakthrough of CFC-11 by a factor 2, indicating that a larger leakage then 1 to 3 per cent probably can be expected when sampling at 50 hPa.

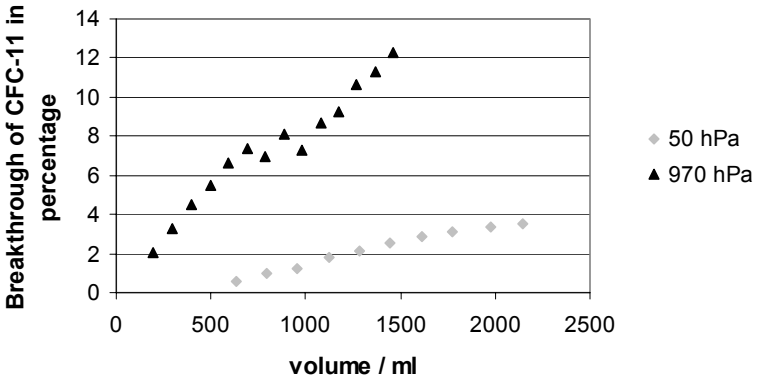

Figure 12. Total breakthrough of CFC-11 expressed in percentage vs. total sample volume in ml. Double trap experiment in vacuum tank at 50 hPa using a mass flow of 25 sccm and in the lab at atmospheric pressure using a mass flow of 390 sccm. The traps of the second box were changed at predetermined time intervals in order to achieve desired sample sizes.

The reduced flow rate when using the pump during a double trap experiment can be considered being a limitation in the double trap method and can probably be explained by the increased resistance in the sampling lines when two sample boxes are connected in series. During the technical flight on the other hand the double trap experiment was performed by connecting one fixed trap to the sampling line upstream the 16 position valve (Figure 2). This approach did not seem to affect the resistance of the sampling lines since no abnormal flow rates could be observed during the flight (Table 2). When estimating the pressure inside the trap, equation 8 and equation 9, an assumption is made that the pressure drop in the sampling system does not occur in the trap but elsewhere in the sampling lines. The pressure inside the trap can therefore be estimated as the pressure in one single spot assuming that the pressure remains close to constant through the trap during sampling. The observed differences in resistance between connecting a second box and connecting a fixed trap verify that the main pressure drop in the sampling system occur elsewhere than inside the trap. The estimation of the pressure inside the trap of DESCARTES can therefore be considered as good and as valid for the whole trap.

In Figure 13 a comparison is made between flows used in the vacuum tank test expressed as estimated volume flow in ml/min and mass flow in sccm. The low ambient pressure at 50 hPa will give reduced pressure inside the sample tube which in turn results in a higher volume flow, compared to the mass flow. At atmospheric pressure the opposite arise, the high ambient pressure will lead to increased pressure inside the sample tube and the mass flow will at high flows be larger then the volume flow (Figure 13). At 50 hPa the sampling was performed using a mass flow of approximately 25 sccm. When comparing the breakthrough pattern of the test made in vacuum tank at 50 hPa (Figure 12) with the flow rate test at a similar flow rate (Figure 10), the test in vacuum tank showed a larger breakthrough, indicating that the volume flow may be the important parameter. However when comparing the estimated volume flow of approximately 160 ml/min at 50 hPa with the flow rate test at a similar flow, the breakthrough at 50 hPa should have been larger for such a high flow. The results in this way indicate that when considering breakthrough the important flow parameter seems to be somewhere in-between mass flow and volume flow. Repetetive tests may explain if increased volume flow due to low pressure give rise to enlarged breakthrough of CFC-11.

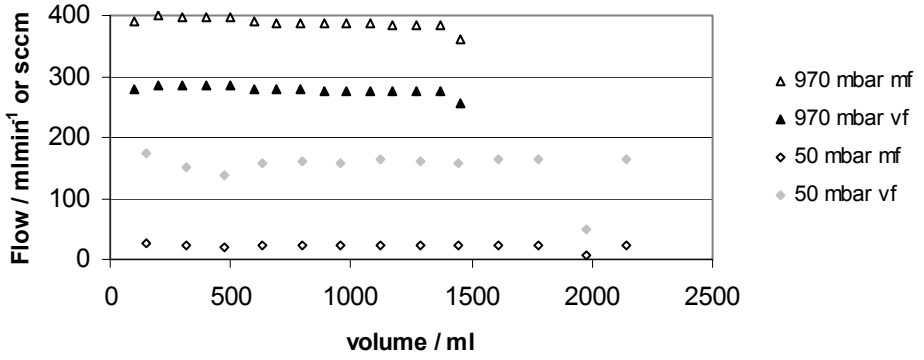

Figure 13. Comparison between mass flow, mf, and estimated volume flow, vf, during sampling at 50 hPa and 970 hPa.

6.5 Technical problems during sampling

Technical problems seem to arise when comparing the flow rate test made with compressed air (Figure 10) and the test made when sampling air with the pump of DESCARTES (Figure 12). The tests with the pump exhibit lower breakthrough of CFC-11 although the same flow meters are used to read the mass flow and approximately the same concentration of CFC-11 can be expected in both tests. A breakthrough of approximately 12 per cent may be expected when sampling a volume of 1500 ml with the pump at a flow of about 390 sccm or 280 ml/min (Figure 12 and Figure 13). The same sample volume of calibration gas at a flow of about 200 sccm shows a breakthrough of about 19 per cent (Figure 10). Repetitive tests, both in vacuum tank and at laboratory, may explain whether the differences in breakthrough between the two different methods can be explained by normal variation or arise from technical problems.

6.6 Distribution of CFC-11 in the sample tube

The results in this study indicate that when sampling continuously with DESCARTES the sample tubes do not resemble chromatographic columns. The fact that breakthrough does occur even at small sample sizes and that breakthrough is increasing exponentially when the sample size is increasing (Figure 7), rather indicate that CFC-11 exhibits an exponentially declining distribution inside the adsorbent tube during sampling (Figure 14). Two physical processes may explain the distribution, adsorption and desorption. Since the adsorbent bed can be considered as homogenous the chance for a particle to get adsorbed per time unit is equal, which will give rise to an exponentially declining distribution. At the same time a continuous desorption of already adsorbed CFC takes place. The desorbed CFC will then redistribute inside the sample tube according to the same exponentially declining distribution.

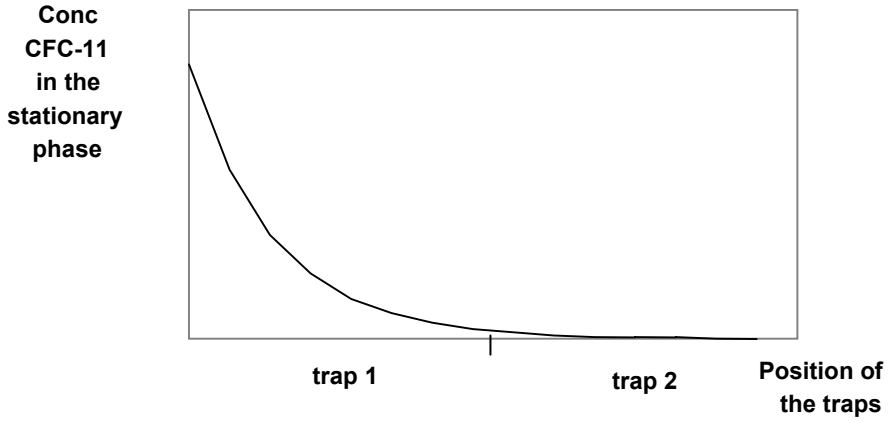

Figure 14. Principle sketch of the exponentially declining distribution of CFC-11 in an adsorbent tube of DESCARTES during a double trap experiment with two traps connected in series.

The exponentially declining distribution of CFC-11 may to some extent explain the observed individuality of the traps of DESCARTES, which is compensated for during analysis of the traps. If the Carboxen is packed tight inside the sample tube, more adsorption surfaces will be available in the front of the tube. If the Carboxen is loosely packed, less adsorption surfaces will be available in the front allowing the CFC to move to the end of the tube and thereby increasing the chance for breakthrough.

The ideal case when using adsorbent tubes for sample collection is to have a desorption coefficient approaching zero. The results in this study indicate that, in DESCARTES case, desorption can not be considered as negligible and has to be taken into account when studying distribution of CFC in the adsorbent tube during sampling (Figure 7 and Figure 8). The desorption must however be a much slower process then the adsorption.

The results further indicate that the kinetics of the adsorption can be considered as being too slow to secure quantitative adsorption of CFC-11 during particular sampling conditions. The time span between each adsorption occasion will, due to slow kinetics, allow the analyte to travel relatively long, seen on a microscopic scale, before being adsorbed again and thereby give rise to band broadening inside the sample tube and increased chance for leakage. This phenomenon will be obvious when the flow rate is increased. A higher flow rate will shorten the time it takes for the analyte to pass the adsorbent bed, increasing the distance between each interaction and thereby increasing the chance for breakthrough (Figure 10).

6.6.1 Model simulation

The model allowed changing of the parameters adsorption coefficient, desorption coefficient and mass flow. By changing the parameters the intention was to receive breakthrough patterns resembling the results in the study according to:

- Exponentially increasing breakthrough of CFC-11, expressed as peak area, with increasing sample size.
- Linearly increasing breakthrough of CFC-11, expressed as percentage of total sampled CFC-11, with increasing sample size.
- Exponentially increasing breakthrough of CFC-11, expressed as percentage of total sampled CFC-11, with increasing flow rate.
- Steady increase in breakthrough, expressed as peak area, when purging an air sample with CFC-free nitrogen.

The breakthrough pattern of the model showed exponentially increasing breakthrough with increasing sample size. Also linearly increasing breakthrough expressed in percentage was achieved when the sample size was increased. It was noticeable that the concentration of CFC in the trap seemed to be close to saturation when the above requirements were fulfilled. The proportions of the increase in breakthrough were however not in accordance with the results obtained in this study. Further work has to be done to improve the model.

7 Conclusions

The sample tubes of DESCARTES do not resemble chromatographic columns. The results in this study rather indicate that CFC-11 exhibits an exponentially declining distribution inside the adsorbent tube during sampling, resulting in an exponential increase in breakthrough of CFC-11 with increasing sample size. The breakthrough also increases exponentially with increasing flow rate.

The overall uncertainty associated with measurements of CFC-11 by DESCARTES is estimated to approximately 5 per cent and an error due to the adsorption efficiency of the sample tubes below the overall uncertainty can be considered as acceptable. The results of this study indicate that flow rates up to 50 sccm can be considered as safe flow rates even when sampling volumes in the two-litre range. The critical sampling volume when using a flow rate of approximately 100 sccm would be around 1200 ml. Sampling using mass flows of 100 sccm occurs around 100 hPa and just after the overflow vent has been closed at around 80 hPa. The sample volume taken by DESCARTES at these pressure levels usually reach between 200 to 400 ml and can therefore be considered as safe samples. Sampling at 200 sccm only allows sample volumes of 300 ml to avoid leakage of CFC-11 exceeding 5 per cent. Mass flows around 200 sccm occur in the beginning of the sampling around 250 hPa and typical sample volumes are around 100 to 250 ml, which normally can be considered as safe samples. In summary, when considering the mass flow most samples taken with DESCARTES can be seen as safe samples. However, the results in this study indicate that the important flow parameter when considering breakthrough is somewhere in-between mass flow and volume flow. The fact that the estimated volume flow during sampling due to low pressure often reaches 200 up to 600 ml/min is therefore a source of concern and implies that breakthrough of CFC-11 exceeding 5 per cent may occur when sampling at high volume flows. Real high volume flows, exceeding 200 ml/min, seem to occur at varying pressure levels and have to be estimated from sample to sample.

Breakthrough of analyte during sampling using adsorbent tubes may be considered as being a problem as long as the leakage is unpredictable. If the breakthrough patterns are repeatable and can be predicted under specific sampling conditions, the measured concentrations can be corrected for errors due to losses of analyte during sampling. During a flight with DESCARTES different parameters are varying simultaneously which make predicting of breakthrough difficult. By evaluating a model that simulates the distribution of CFC inside the sample tube during sampling with DESCARTES at different sampling conditions, the losses of analyte may be compensated for and even larger breakthrough than 5 per cent may be acceptable.

Acknowledgement

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SOLVE: LACE, NASA Earth Science Project Office. Internet, 2003-05-07: GC19991119.BAL.
http://espoarchive.nasa.gov/archive/arcs/solve/data/balloon/GC19991119.BAL

Appendix A

Compressed air standard from NOAA

A natural dried air sample from Niwot Ridge, Colorado analysed according to:

Species	Conc
CFC-11 (CCl_3F)	263.0 ± 2.6 ppt
CFC-113 (CCl_2F-$CClF_2$)	82.6 ± 0.8 ppt
CH_3CCl_3	44.1 ± 0.9 ppt
CCl_4	98.5 ± 2.0 ppt
Halon-1211 ($CBrClF_2$)	4.30 ± 0.2 ppt
N_2O	316.1 ± 0.7 ppb
SF_6	4.69 ± 0.2 ppt
CFC-12 (CCl_2F_2)	535.7 ± 1.6 ppt

(Cylinder ID: ALM-67702)