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Gas adsorption and desorption effects on cylinders and their importance for long-term gas records

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Abstract

It is well known that gases adsorb on many surfaces, in particular metal surfaces. There are two main forms responsible for these effects (i) physisorption and (ii) chemisorption. Physisorption is associated with lower binding energies in the order of 1–

- ⁵ 10 kJ mol⁻¹ compared to chemisorption ranging from 100 to 1000 kJ mol⁻¹. Furthermore, chemisorption forms only monolayers, contrasting physisorption that can form multilayer adsorption. The reverse process is called desorption and follows similar mathematical laws, however, it can be influenced by hysteresis effects. In the present experiment we investigated the adsorption/desorption phenomena on three steel and
- ¹⁰ three aluminium cylinders containing compressed air in our laboratory and under controlled conditions in a climate chamber, respectively. We proved the pressure effect on physisorption for CO_2 , CH_4 and H_2O by decanting one steel and two aluminium cylinders completely. The CO_2 results for both cylinders are in excellent agreement with the pressure dependence of a monolayer adsorption model. However, adsorp-
- ¹⁵ tion on aluminium (< 0.05 and 0 ppm for CO₂ and H₂O) was about 10 times less than on steel (< 0.41 ppm and about < 2.5 ppm, respectively). The CO₂ amounts adsorbed (5.8×10^{19} CO₂ molecules) corresponds to about the five-fold monolayer adsorption indicating that the effective surface exposed for adsorption is significantly larger than the geometric surface area. Adsorption/desorption effects were minimal for CH₄ and for
- ²⁰ CO. However, the latter dependence requires further attention since it was only studied on one aluminium cylinder with a very low mole fraction. In the climate chamber the cylinders were exposed to temperatures between -10 and +50 °C to determine the corresponding temperature coefficients of adsorption. Again, we found distinctly different values for CO₂ ranging from 0.0014 to 0.0184 ppm °C⁻¹ for steel cylinders and
- $_{25}$ -0.0002 to -0.0003 ppm °C⁻¹ for aluminium cylinders. The reversed temperature dependence for aluminium cylinders point to significantly lower desorption energies than for steel cylinders and might at least partly be due to temperature and gas consumption induced pressure changes. Temperature coefficients for CH₄, CO and H₂O adsorption



were, within their error bands, insignificant. These results do indicate the need for careful selection and usage of gas cylinders for high precision calibration purposes such as requested in trace gas applications.

1 Introduction

- ⁵ Precision and accuracy of trace gas mole fractions of ambient air composition depend among other factors on the stability of primary and secondary standards. Several studies in the past have documented instabilities of gas composition in high pressure cylinders. These instabilities can either be viewed as temporal drifts of gas composition or as pressure dependent composition changes along the life-time of the cylinder
- gas. These drifts have been addressed to numerous diffusional fractionation processes such as ordinary diffusion (depending on molecular mass and molecular size), thermal diffusion or effusion (Bender et al., 1994; Keeling et al., 1998, 2007; Langenfelds et al., 2005) or were related to surface interaction alterations (Yokohata et al., 1985). These latter processes, i.e. adsorption and desorption, were investigated in more detail and
- play an important role regarding gas composition stability, in particular for trace gas species. Besides the choice of the metal, also surface condition, surface coating or finish as well as the humidity are critical for the gas composition (Matsumoto et al., 2005). The presented work was motivated by the fact that adsorption/desorption effects have been observed to play an important role not only in the laboratory, but also in the field
 during different experimental setups (Berhanu et al., 2015; Schibig et al., 2014).
 - In the sorption theory one distinguishes several terms such as absorption, adsorption, sorption, desorption, physisorption and chemisorption. Adsorption is a surface adhesion process of atoms, ions, or molecules from a gas, liquid or dissolved solid (adsorbate) resulting in a layer on the adsorbent surface (main material). In contrast, absorption is a volume process in which permeation or dissolution of the absorbate in
- a liquid or solid material (absorbent) takes place. Sorption summarizes both processes while desorption is the reverse process.



Surface atoms of the bulk material, being specified by the fact that they are not fully surrounded by other adsorbent atoms, can therefore attract adsorbates. Adsorption itself splits into physisorption and chemisorption. The former being a general phenomenon forming mono- or multilayers whereas the latter depends on the chemical feature of both the adsorbate and adsorbent and forms only monolayers. Similar to

surface tension, adsorption is a consequence of surface energy.

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Physical adsorption, also known as physisorption, is a process governed by low electrostatic interactions between the electron configuration of the adsorbate and the adsorbent, in particular van der Waals forces. The involved energy is weak (10–100 meV

¹⁰ corresponding to 1–10 kJ mol⁻¹) and therefore barely influences the electron structure of the substances involved and mainly appears under low temperature conditions (room energy). The upper energy limit involves the interaction with permanent electric dipoles of polar surfaces (salts) or with the image charges as present in electrically conductible surfaces such as metals. For these processes the energies can reach those of chemisorption.

Chemisorption in contrast involves much higher energies in the range of 1-10 eV (100–1000 kJ mol⁻¹) and often requires an activation energy finally resulting in a structure that is similar to a chemical bond of either ionic or covalent type. Sorption and desorption can differ, in this case we deal with hysteresis, i.e. the quantity adsorbed differs from the corresponding quantity desorbed.

The definition of adsorption given by the International Union of Pure and Applied Chemistry (IUPAC) reads as follows: an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase (McNaught et al., 1997).

Several mathematical models have been presented for adsorption. Equation (1) expresses the pressure dependence by adjusting the empirical constants k and n. x denotes the quantity adsorbed, m the mass of absorbent and P the pressure (Freundlich,



1906).

$$\frac{x}{m} = kP^{1/n}$$

Irving Langmuir (Langmuir, 1916, 1918) was the first to derive a scientifically based adsorption isotherm. It is based on four assumptions: (i) all of the adsorption sites
 are equivalent and each site can only accommodate one molecule; (ii) the surface is energetically homogeneous and adsorbed molecules do not interact; (iii) there are no phase transitions; (iv) at the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates. His final result expresses the fraction of the adsorption sites occupied, Θ, as given in
 Eq. (2):

$$\Theta = \frac{KP}{1+KP},$$

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where *K* is the ratio of the direct (adsorption) and reverse rate (desorption) constants (k, k_{-1}) and *P* is the pressure. For low pressures Θ corresponds to *KP* and for high pressure it approaches unity.

The four assumptions listed by Langmuir are often not fulfilled, in particular assumption (iv). This fact led to the BET model derived jointly by Brunauer, Emmett and Teller in (Brunauer et al., 1938) which relates to multilayer adsorption. Further extensions were made by Kisliuk (Kisliuk, 1957) by taking into account interactions of gas molecules in the adsorbed and gaseous phase. Since we neither refer to the BET nor the Kisliuk model in this publication, we omit corresponding equations.

Besides the pressure or gas (particle) density dependence there is also a temperature dependence of adsorption/desorption processes. According to the Polanyi–Wigner equation given in Eq. (3), the desorption rate (k_{-1}) is dependent on time, t, on a frequency term, $\upsilon(\Theta)$, a coverage order term, Θ^n , and an Arrhenius factor containing the activation energy, $E = E(\Theta)$, for desorption.

$$k_{-1}(\Theta, T(t)) = -\frac{\mathrm{d}\Theta}{\mathrm{d}t} = \upsilon(\Theta) \cdot \Theta^n \cdot \mathrm{e}^{-\left(\frac{E(\Theta)}{R \cdot T(t)}\right)}$$

(1)

(2)

(3)

A similar equation can be written for adsorption, however the adsorption energy is significantly lower such that the equilibrium condition are characterised by the desorption energy. Following the van't Hoff equation different equilibrium conditions, K(T) and $K(T_0)$, can be represented by

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$$K(T) = \frac{k(T)}{k_{-1}(T)} = K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}.$$

In this work we mainly investigate the adsorption and its reverse process. In particular we present results for the pressure and temperature dependent adsorption process of trace gases (CO_2 , CO, CH_4) as well as H_2O on two metal surfaces, namely steel and aluminium, using the cylinders tabulated in Table 1.

10 2 Methods

We ran two experiments in order to determine the pressure and temperature dependencies of gas adsorption on two different metal cylinder surfaces (steel and aluminium). In the first experiment we decanted 5 Lmin^{-1} from either a steel (50 L steel cylinder from Carbagas, Switzerland) or aluminium (30 L Scott-Marrin Luxfer aluminium 15 cylinder) cylinder, both without any additional pre-treatment of the inner surfaces, and monitored the mole fractions of CO₂, CH₄ and H₂O by a Picarro G2311f and G2401, in which case CO was measured in addition. Attached to the vertically standing cylinders were pressure regulators from Tescom (type: 64-3441KA412 dual stage). The starting pressures were about 110 and 95 bar for the steel and aluminium cylinder, respectively. Due to the large gas flow which was maintained by the detector itself in the

spectively. Due to the large gas flow which was maintained by the detector itself in the case of G2311f and by an external flow controller for the G2401, it took only about 14 (steel) and 8 (aluminium) hours, respectively to empty the cylinders. The mole fractions were monitored on a 0.1 s level with the G2311f instrument whereas on a 5 s level with the G2401. In parallel we recorded the pressure continuously. This experiment was per-



(4)

formed at the University of Bern under normal laboratory conditions (room temperature at 22 °C, room pressure about 950 mbar).

The second experiment was performed in the Climate Chamber at the Swiss Federal Institute of Metrology (METAS). The purpose of this experiment was to determine the temperature dependence of the adsorption/desorption process. Therefore, a temperature range from -10 to +50 °C was operated as documented in Fig. 1. The temperature was set to a fixed temperature for 2 h at each level. Within every two hours sequence we switched between the six horizontally on a wooden tray placed cylinders (Table 1) and an additional reference cylinder (CA03901) outside the climate chamber using

- ¹⁰ a 10-port VICI AG valve (type: EMT2CSD12MWE). Unfortunately, the electronics of the Vici valve was malfunctioning after the first night and therefore we had to replace it. Hence the experiment was extended in order to have two full temperature cycles for data evaluation. The temperature in the climate chamber was recorded directly from the cylinders using sensors of the type 80PK-1, -40...+260 °C and recorded by
- a GMH3250 temperature sensor from Greisinger. The pressure transducers used were PTU-S-AC160-31AC for high pressures and PTU-S-AC6-31AC for low pressures from Swagelok. Measurements were displayed by a homemade LCD device and logged by a Labjack U12 from the Meilhaus Electronic GmbH.

Both instruments were frequently calibrated with known standard gas admissions, i.e.in the case of experiment 1 before and after the experiment and in the case of experiment 2 during the complete experiment. Calibration corresponds to $CO_{2,calib.} = 1.0068 \times CO_{2,meas} - 0.666 \text{ ppm}$ for the Picarro 2401 and to $CO_{2,calib.} = 1.0039 \times CO_{2,meas} - 0.069 \text{ ppm}$ for the Picarro 2311f instrument.

3 Results

Figure 2 displays the CO₂ mole fraction change for experiment 1 (emptying gas cylinders) for a steel cylinder. A significant CO₂ and H₂O (Fig. 3) mole fraction increase of 6 ppm (30 ppm for H₂O) is observed towards lower cylinder pressure in contrast to CH₄



which does not exhibit any change (not shown). One could argue as detailed in (Langenfelds et al., 2005) that ordinary diffusion is at play. Diffusion coefficient for CO₂ in air are known since long (Kestin et al., 1984; Marrero and Mason, 1972, 1973). However, if one calculates the diffusion length, i.e. twice the square root of the product of the diffusion coefficient ($\approx 0.16 \text{ cm}^2 \text{ s}^{-1}$ for 20 °C and 1 bar, Massman, 1998) and time (60 s), of CO₂ diffusion in air in a cylinder at high pressure (100 bar) corresponding to 6 mm and compare it to the radius of the gas volume at high pressure (5 L min⁻¹) that is decanted from the cylinder during our experiment 1, i.e. 27.7 mm, ordinary diffusion has

- strongly to be questioned to be responsible for the observed CO₂ increase. It is worth-¹⁰ while mentioning that a comparison of the diffusion length with the radius of cylinders (100 mm) used for our experiments requires a diffusion time of 4–5 h, i.e. correspondent observation time is needed. Similar arguments can be used to exclude ordinary diffusion on the low pressure side, though with slightly lower confidence since the diffusion length is only half of the decanting volume. Furthermore, the diffusion fractionation
- should decrease with increasing gas flow just opposite to what has been observed in (Langenfelds et al., 2005). Only for the low flow decanting experiment, thermal diffusion induced by the Joule–Thomson cooling effect might play a role as shown below. Therefore, we follow the adsorption theory. According to Eq. (2), the initial CO₂ mole fraction (CO_{2, initial}) can be calculated from the measured mole fraction (CO_{2, meas}) through the following formula (see Appendix):

$$CO_{2,meas} = CO_{2,ad} \cdot \left(\frac{K \cdot (P - P_0)}{1 + K \cdot P} + (1 + K \cdot P_0) \cdot \ln\left(\frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)}\right) - 1\right) + CO_{2, initial},$$
(5)

where $CO_{2, ad}$ corresponds to the adsorbed CO_2 molecules on the wall, expressed as CO_2 mole fraction times the occupied adsorption sites. $CO_{2, ad}$ and *K* can be determined experimentally to fit the measured CO_2 mole fraction. Note that *K* is temperature dependent of the form as given in Eq. (5). For $P = P_0$ the measured CO_2 mole fraction corresponds to the initial CO_2 mole fraction minus the adsorbed CO_2 amount. In our experiment this results in an adsorbed $CO_{2, ad}$ mole fraction of 0.41 ppm corresponding to



about 2.15 mL STP ($P_0 = 105$ bar) or 96 micromole of CO₂ or $5.8 \cdot 10^{19}$ CO₂ molecules and 0.0436 bar⁻¹ for *K* by minimisation of the squared differences of Eq. (5) to the measured values. These values can be compared with a monomolecular layer of CO₂ molecules on the inner cylinder wall area. Our steel cylinders have an outer diameter of 0.24 m, an inner diameter of 0.2 m and a length of 1.5 m. Therefore, the inner area corresponds roughly to 1 m², which is about 5 times lower than a monolayer of the adsorbed CO₂ molecules corresponding to 5.25 m² when assuming a molecule diameter of 3.4 Å. It is interesting to note that the adsorbed water amount is about five times stronger (< 2.5 ppm) as shown by an equal pressure behaviour of desorption

- (Fig. 3) than for CO₂ (0.41 ppm). By taking into account the smaller molecule size, this corresponds to an even higher ratio to a mono-molecular layer. The observed pressure dependence of both mole fractions show only slightly increasing values in the range of 100–50 bar contrasting the nature of a multiple layer adsorption isotherm (Brunauer et al., 1938). Hence, it seems plausible to question the validity of our assumption that
- the exposed adsorption surface corresponds to the geometric surface. Due to surface roughness the adsorption surface might be significantly larger than the geometric measure. This is known in literature as rugosity. Values may range from 1 to more than 10 in the case of a sponge. For metals surface roughness is more often expressed as Ra, i.e. the arithmetic mean of the surface height changes. Our experimental results suggest
 that the rugosity value to be at least significantly above unity for steel cylinders.

Similar considerations can be made for the aluminium cylinder which results in empirically derived values of 0.047 ppm for $CO_{2, ad}$ and 0.001 bar⁻¹ for *K* (Fig. 4). The effect of adsorption is significantly less on aluminium than on steel surface, only about 35% of the adsorption sites are occupied. This further supports our approach to use the Langmuir model for a monomolecular layer in contrast to a multi-layer coverage.

It was also tested whether the decanting rate has an influence by performing tests with 5 and $0.25 \,L\,min^{-1}$, respectively. The results are displayed in Fig. 4 and show similar increases towards lower pressures but there are obvious trends superimposed that cannot be explained by the adsorption theory. In particular the slightly decreasing mole

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fractions in the low flow (0.25 L min⁻¹, Fig. 4, lower panel) decanting experiment on the aluminium is most probably a result of the Joule–Thomson effect. It leads to a significant temperature decrease of the gas and its surrounding at the regulator where the pressure decreases suddenly from high to ambient pressure (60–1 bar). The temper-

- ⁵ ature decrease can be estimated by using the Joule–Thomson coefficient for air, i.e. +0.27 Kbar⁻¹. For 100 bar pressure change a temperature decrease of 27 K is estimated. The gas exposed to this temperature gradient suffers from thermal diffusion as the heavier gas constituents tends to move to the colder end and hence are enriched in the gas measured by the detector. However, the regulator temperature decrease by the
- gas cooling effect is partly compensated by the heat exchange with the surrounding. We used a symmetrically built two stage Tescom regulator and therefore have a two step cooling induced. Yet, only the first cooling stage is important because this connects to the large gas volume in the cylinder whereas from thereon any fractionation cannot develop under quantitative transport of the gas into the analyser. It is difficult to
- determine the temperature distribution at the location where thermal fractionation due to the Joule–Thomson effect occurs. What we observe is exactly opposite to expectation, i.e. a CO₂ decrease pointing to a warmer temperature at the inter-stage compared to the high pressure side. This requires further dedicated experiments.

Unlike the steel cylinder, aluminium cylinder did not show any desorption effect for H_2O and CO and a hardly visible effect for CH_4 as displayed in Fig. 5. However, it has

 $_{20}$ H₂O and CO and a hardly visible effect for CH₄ as displayed in Fig. 5. However, it has to be stressed that the H₂O and CO mole fraction were very low and further experiment should be done in particular for CO including steel and aluminium cylinders.

The second experiment conducted in a climate chamber followed expectations in that the temperature dependence of CO_2 adsorption is considerable for steel sur-

faces but again significantly smaller on aluminium (Fig. 6). For the latter case it even changed sign to a slightly negative correlation with temperature, though statistically less robust than for steel. The temperature dependencies vary between 0.0014 and $0.0184 \text{ ppm}^{\circ}\text{C}^{-1}$ for steel and -0.0002 to $-0.0003 \text{ ppm}^{\circ}\text{C}^{-1}$ for aluminium cylinders. The pressure drop for gas consumption throughout this experiment was in the order



of 14 and 24 bar with initial pressures around 150 and 120 bar for the steel and aluminium cylinders, respectively (Table 1). The induced desorption changes are moderate and amount to about 0.01 ppm for both steel and aluminium cylinders according to Eq. (6). Also, the temperature induced pressure changes amounting to about 30 bar $(150 \text{ bar} \cdot \Delta T/T)$ are only twice as large. Hence no influence on the temperature dependencies is expected for steel cylinders. For the aluminium cylinders, though, these two influences are most probably the reason for the observed reversed temperature behaviour. All other measured gas species, i.e. CO, CH₄ and H₂O showed no temperature dependence as documented in Table 2, except for H₂O of the steel cylinder LK548528.

After Eq. (3), the coverage of the adsorption sites is temperature dependent. The desorption and adsorption rates depend on whether we increase or decrease the temperature from a mean value. During the temperature increase (decrease) the adsorption rate will be lower (higher) than the desorption rate and therefore the coverage of adsorption sites decreases (increases) and go along with an increase (decrease) of the gas mole fraction. A derivation of this temperature dependence is given in the Appendix that leads to Eq. (6).

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$$R \cdot \ln\left(1 - \frac{\operatorname{CO}_{2}(T_{0}, T) - \operatorname{CO}_{2}(T_{0})}{\operatorname{CO}_{2, \mathrm{ad}}}\right) = E \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right) - R \cdot \ln\left(\frac{\frac{T_{0}}{T} + P_{0} \cdot K(T_{0}) \cdot \mathrm{e}^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}{1 + P_{0} \cdot K(T_{0})}\right)$$

$$(6)$$

Hence, during a temperature increase or decrease we will determine the desorption energy, $E = E(\Theta)$ of the process when plotting the logarithm of 1 minus the temperature scaled relative CO₂ mole fraction changes (CO₂ (*T*) – CO₂ (*T*₀) to the adsorbed CO₂ vs. the difference of inverse temperatures. For steel cylinder 1 the values are plotted in Fig. 7. From this graph or through Eq. (6) we now can estimate CO_{2,ad}, *K*(*T*₀) and *E* by minimising the squared differences of using Eq. (6) with initial values obtained from experiment 1 for steel and aluminium cylinders, respectively. The slopes

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corresponding to the desorption energies for positive and negative temperature gradients do only slightly differ and vary between 14 741 and 15 095 J mol⁻¹ with an average value of 14 882 J mol⁻¹ for all measurements using a value of 1.2 ppm for $CO_{2, ad}$ and 0.0168 bar⁻¹ for K_0 . For the aluminium cylinders it looks very different with very low and even reversed temperature dependencies which indicates lower desorption based on the dependence given in Eq. (6). This equation shows a sign change for desorption energies around 2430 J mol⁻¹ when setting T_0 to 20 °C. This sign change moves towards zero when T_0 approaches absolute zero (see Appendix, Eq. A25–A27). Indeed, the optimised desorption energy (1577 J mol⁻¹) for aluminium cylinder 2 is below this threshold of 2430 J mol⁻¹ using a value of 0.45 ppm for $CO_{2, ad}$ and 0.001 bar⁻¹ for K_0 . However, the correlation is much worse than for the steel cylinder (Fig. 7) which might point to a small contribution of thermal diffusion on measured CO_2 mole fraction (Keeling et al., 2007) as discussed above. Therefore the determination of the desorption energy for aluminium cylinders is difficult due to the very small, hardly measureable CO_2 change. Hence, those lower values than for steel cylinders should be taken with

¹⁵ CO₂ change. Hence, those lower values than for steel cylinders should be taken with care.

4 Conclusions

The experiments performed clearly demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO₂, CO, CH₄ and H₂O than steel cylinders. The CO₂ desorption rate behaviour follows nicely a pressure driven monomolecular layer desorption as described by the Langmuir equation and is about 10 times larger for steel than for aluminium surfaces. Also, the adsorbed amount is about 10 times higher for steel (0.41 ppm) than for aluminium (0.028 and 0.047 ppm). The mole fractions towards atmospheric pressure are strongly influenced and reach values of about 100 times larger than the WMO target value of 0.1 ppm for steel and still significantly above it for aluminium. Therefore, special attention has to be given to which end pressure the cylinders should be used for calibration purposes.



The community is generally aware of this influence but it has not yet been quantified properly. It is noteworthy that desorption starts already close to 100 bar (1450 psig). At 30 bar it can already reach 0.5 ppm for steel cylinders. The WMO target value of 0.1 ppm might already be reached at 60 bar compared to the value at 100 bar.

- ⁵ The temperature dependence that was observed for three steel and aluminium cylinders ranged from 0.0014 to 0.0184 ppm°C⁻¹ and from –0.0002 to –0.0003 ppm°C⁻¹, respectively. This might have an influence on the precision when facing large temperature fluctuations in the laboratories or when measuring in the field with large ambient temperature variations, but only for steel and not for aluminium cylinders. A robust es-
- timate of the desorption energy was possible only for steel (14882Jmol⁻¹) but not for aluminium due to the low temperature dependence and temperature range investigated. The determined energy value underpins that the observed adsorption mechanism is physisorption only.

The two experiments are qualitatively in agreement in the present study, however, ¹⁵ made on different cylinders. Similar experiments are required using exactly the same cylinders, i.e. first determining the temperature dependence following by the decanting experiment. This would allow to check the consistency of the estimated parameters $CO_{2,ad}$, K_0 and E.

The recommendation for high precision greenhouse gas determination is to use alu-²⁰ minium cylinders and to minimize temperature fluctuations in order to limit desorption and thermal diffusion effects and that the usage should be restricted to pressure above 30 bar to remain within the WMO target.

Appendix A: Derivation of Eq. (4)

During experiment 1 gas is decanted from a cylinder with a fixed volume, *V*, and at a constant temperature, *T* after air with an initial CO₂ mole fraction, CO_{2, initial}, i.e. $n_{CO_2,initial}/n_{air}$, is compressed into a cylinder to a pressure P_0 . After reaching adsorption equilibrium, the CO₂ mole fraction in the cylinder is reduced by CO_{2, ad}. The CO₂



amount, n_{CO_2} , in the gas phase of the cylinder at any pressure, *P*, is expressed using the ideal gas law by

$$n_{\rm CO_2} = n_{\rm air} \cdot \rm CO_2 = \frac{P \cdot V}{R \cdot T} \cdot \rm CO_2, \tag{A1}$$

where *R* corresponds to the ideal gas constant and CO_2 to the mole fraction of CO_2 . Assuming that the CO_2 adsorption/desorption follows Eqs. (2) and (3), the Langmuir's adsorption isotherm, the change in the adsorbed amount, n_{ad} , is expressed according to

$$n_{\rm ad}(P) = a \cdot \frac{KP}{1 + KP},\tag{A2}$$

$$n_{\rm ad}(P_0) = a \cdot \frac{\kappa P_0}{1 + \kappa P_0} = \frac{P_0 \cdot v}{R \cdot T} \cdot CO_{2,\rm ad},\tag{A3}$$

10 this results in

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$$a = \frac{P_0 \cdot V}{R \cdot T} \cdot CO_{2,ad} \cdot \frac{1 + KP_0}{KP_0} = \frac{1 + KP_0}{K} \cdot \frac{V}{R \cdot T} \cdot CO_{2,ad},$$
(A4)

which results to

$$n_{\rm ad}(P) = (1 + KP_0) \cdot \frac{V}{R \cdot T} \cdot CO_{2,\,\rm ad} \cdot \frac{P}{1 + KP},\tag{A5}$$

where *K* represents the equilibrium constant at constant temperature *T* ($K = k/k_{-1}$). In the case of experiment 2, the temperature dependence of *K* needs to be taken into account.

Thus the change in the CO_2 amount in the gas phase of the cylinder according to pressure change is expressed by the following differential equation:

$$\frac{\mathrm{d}n_{\mathrm{CO}_2}}{\mathrm{d}P} = \frac{n_{\mathrm{CO}_2}}{P} - \frac{\mathrm{d}n_{\mathrm{ad}}}{\mathrm{d}P}.$$



(A6)

The first term on the right hand side corresponds to the change in the CO_2 amount due to the gas pressure change during gas decanting. The second term describes the effect of the CO_2 desorption from the inner cylinder walls that can be derived from the derivative of Eq. (A5).

$$\int \frac{dn_{CO_2}}{dP} = \frac{n_{CO_2}}{P} - \frac{(1 + KP_0) \cdot \frac{V}{RT} \cdot CO_{2, ad}}{(1 + KP)^2}$$
(A7)

Solving the differential Eq. (A7) yields

$$n_{\text{CO}_2} = c \cdot P - (1 + KP_0) \cdot \frac{V}{R \cdot T} \cdot \text{CO}_{2, \text{ad}} \cdot P \cdot \left(\frac{1}{1 + KP} + \ln(KP) - \ln(1 + KP)\right), \quad (A8)$$

with

$$n_{\rm CO_2}(P_0) = P_0 \cdot \frac{V}{R \cdot T} \cdot \left(\rm CO_{2,initial} - \rm CO_{2,ad} \right),$$

10 it follows

$$c = \frac{V}{R \cdot T} \cdot CO_{2,\text{initial}} + (1 + KP_0) \cdot \frac{V}{R \cdot T} \cdot CO_{2,\text{ ad}} \cdot \ln\left(\frac{KP_0}{1 + KP_0}\right),$$

and therefore

$$n_{\rm CO_2} = \frac{P \cdot V}{R \cdot T} \left\{ \rm CO_{2, \, ad} \cdot \left(\frac{K(P - P_0)}{1 + KP} + (1 + KP_0) \cdot \ln \left(\frac{P_0 \cdot (1 + KP)}{P \cdot (1 + KP_0)} \right) - 1 \right) + \rm CO_{2, initial} \right\}.$$
(A9)

Therefore, the measured CO_2 mole fraction of the cylinder according to Eq. (A1), ¹⁵ can be expressed as:

$$CO_{2, \text{meas}} = CO_{2, \text{ad}} \cdot \left(\frac{K(P - P_0)}{1 + KP} + (1 + KP_0) \cdot \ln\left(\frac{P_0 \cdot (1 + KP)}{P \cdot (1 + KP_0)}\right) - 1\right) + CO_{2, \text{initial}}, \quad (A10)$$
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which corresponds to Eq. (5) in the main text.

During experiment 2 cylinders are exposed to temperature changes and only a small amount of gas is decanted from a cylinder for analysis. Therefore, we assume that the changes in CO₂ mole fraction in the gas phase are only due to adsorption changes associated with direct temperature and through it induced pressure changes.

$$\frac{\mathrm{d}n_{\mathrm{CO}_2}}{\mathrm{d}T} = -\frac{\mathrm{d}n_{\mathrm{ad}}}{\mathrm{d}T} \tag{A11}$$

$$n_{\rm CO_2}(T) = C - n_{\rm ad}(T)$$
 (A12)

$$n_{\rm CO_2}(T_0) = C - n_{\rm ad}(T_0) = n_{\rm initial} - n_{\rm ad}(T_0)$$
(A13)
$$n_{\rm CO_2}(T) - n_{\rm CO_2}(T_0) = n_{\rm ad}(T_0) n_{\rm ad}(T)$$
(A14)

¹⁰ According to Eq. (4) in the main text the temperature dependence of K can be written as:

$$K(T) = \frac{k}{k_{-1}} = K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}.$$
(A15)

We can generalize Eqs. (A2) with (A15) to

$$n_{\rm ad}(P,T) = a \cdot \frac{P \cdot K(T_0) e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}{1 + P \cdot K(T_0) \cdot e^{-\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}},$$

$$n_{\rm ad}(P_0,T_0) = a \cdot \frac{1 + P_0 \cdot K(T_0)}{P_0 \cdot K(T_0)} = \frac{P_0 \cdot V}{R \cdot T_0} \cdot CO_{2,\rm ad},$$
(A16)

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this results in

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$$a = \frac{P_0 \cdot V}{R \cdot T_0} \cdot \operatorname{CO}_{2, \operatorname{ad}} \cdot \frac{1 + P_0 \cdot K(T_0)}{P_0 \cdot K(T_0)},$$

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(A18)

which results to

$$n_{\mathrm{ad}}(P,T) = \frac{P_0 \cdot V}{R \cdot T_0} \cdot \mathrm{CO}_{2,\mathrm{ad}} \cdot \frac{1 + P_0 \cdot K(T_0)}{P_0 \cdot K(T_0)} \cdot \frac{P \cdot K(T_0) \cdot \mathrm{e}^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}{1 + P \cdot K(T_0) \cdot \mathrm{e}^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}},$$

$$CO_{2,ad}(P,T) = \frac{H \cdot T}{P \cdot V} \cdot n_{ad}(P,T),$$

$$CO_{2,ad}(P,T) = \frac{R \cdot T}{P \cdot V} \cdot \frac{P_0 \cdot V}{R \cdot T_0} \cdot CO_{2,ad} \cdot \frac{1 + P_0 \cdot K(T_0)}{P_0 \cdot K(T_0)} \cdot \frac{P \cdot K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}{1 + P \cdot K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}.$$

5 Since the amount of air does not change during experiment 2, it follows

$$\frac{R \cdot T}{P \cdot V} \cdot \frac{P_0 \cdot V}{R \cdot T_0} = \frac{P_0}{P} \cdot \frac{T}{T_0} = 1,$$
(A22)
$$CO_{2,ad}(P,T) = CO_{2,ad} \cdot \frac{1 + P_0 \cdot K(T_0)}{P_0 \cdot K(T_0)} \cdot \frac{P \cdot K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}{1 + P \cdot K(T_0) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)}}.$$
(A23)

With Eq. (A14)

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$$CO_{2}(T_{0},T) - CO_{2}(T_{0}) = CO_{2,ad} - CO_{2,ad} \cdot \frac{1 + P_{0} \cdot K(T_{0})}{P_{0} \cdot K(T_{0})} \cdot \frac{P \cdot K(T_{0}) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}{1 + P \cdot K(T_{0}) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}, \quad (A24)$$

$$CO_{2}(T_{0},T) - CO_{2}(T_{0}) = CO_{2,ad} \cdot \left(1 - \frac{1 + P_{0} \cdot K(T_{0})}{P_{0} \cdot K(T_{0})} \cdot \frac{P \cdot K(T_{0}) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}{1 + P \cdot K(T_{0}) \cdot e^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}\right). \quad (A25)$$

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(A19)

(A20)

(A21)

It is noteworthy that Eq. (A25) has a root at energies around $2430 \,\text{Jmol}^{-1}$ for T_0 at 293.15 °C, a general dependence of E_0 (T, T_0) corresponds to

$$E_0(T,T_0) = \frac{R}{\left(\frac{1}{T} - \frac{1}{T_0}\right)} \cdot \ln\left(\frac{T_0}{T}\right) = \frac{R \cdot T \cdot T_0}{(T_0 - T)} \cdot \ln\left(\frac{T_0}{T}\right),$$
(A26)

above which Eq. (A25) is increasing and below decreasing. E_0 approaches zero when T_0 is close to the absolute zero temperature. This is important for the different adsorption/desorption behaviour on steel and aluminium cylinders (see main text).

$$R \cdot \ln\left(1 - \frac{\operatorname{CO}_{2}(T_{0}, T) - \operatorname{CO}_{2}(T_{0})}{\operatorname{CO}_{2, \mathrm{ad}}}\right) = E \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right) - R \cdot \ln\left(\frac{\frac{T_{0}}{T} + P_{0} \cdot K(T_{0}) \cdot \mathrm{e}^{\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{0}}\right)}}{1 + P_{0} \cdot K(T_{0})}\right)$$
(A27)

This equation allows us to estimate $CO_{2,ad}$, $K(T_0)$ and E by minimising the squared differences of using Eq. (A27) with initial values obtained from experiment 1 for steel and aluminium cylinders, respectively. This yields a $CO_{2,ad}$ of 1.2 ppm, $K(T_0)$ of 0.0168 bar⁻¹ and a desorption energy of 14882 ± 176 J mol⁻¹ for cylinder 1 (steel, robust estimate). Estimate for aluminium cylinders are significantly less robust due to much smaller adsorption/desorption effects.

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Table 1. Cylinders used for the two experiments with their identification and trace gas mole fractions. Note that the absolute values of both CO and H_2O are of lower quality due to values close to the lower end of the measurement range. Note that no pretreatment of cylinders has been applied, i.e. no steam cleaning, surface conditioning or finishing. Values displayed in Figures are non-calibrated values.

| Cylinder | Initial pressure [bar] | Final pressure [bar] | CO ₂ [ppm] | CO [ppb] | CH ₄ [ppb] | H ₂ O [ppm] | Calibration laboratory |
|--------------|---------------------------|-------------------------|--------------------------|-------------|--------------------------|---------------------------|---------------------------|
| Experiment 1 | | | | | | | |
| LK542039 | 106 | 1 | 412.26 | NA | 2095.55 | 4.5 | Bern |
| CB09790 | 97 | 1 | 406.44 | 9.5 | 1976.75 | 15 | Bern |
| CB09880 | 58 | 1 | 393.42 | NA | 1938.86 | 8.9 | Bern |
| Experiment 2 | | | | | | | |
| 1: LK502291 | 153.2 | 138.74 | 440.64 | 10.40 | 2058.0 | 0.88 | Bern |
| 2: CB09790 | 121.3 | 97.2 | 405.88 | 5.40 | 1977.04 | 2.4 | Bern |
| 3: LK548602 | 155.0 | 140.54 | 421.42 | 9.40 | 1967.04 | 0 | Bern |
| 4: CB09877 | 131.0 | 106.9 | 400.30 | 193.40 | 2080.04 | 28.4 | Empa |
| 5: LK548528 | 153.6 | 139.14 | 440.00 | 13.40 | 2058.04 | 2.9 | Bern |
| 5*: LK535353 | > 170 | 135.54 | 392.22 | 74.40 | 1995.04 | 17.7 | Bern |
| 6: CB09786 | 120.5 | 96.4 | 406.42 | 11.40 | 1977.04 | 4.9 | Bern |
| 7: CA03901 | 76 | 75 | 363.62 | 102.4 | 1796.04 | 1.2 | NOAA |
| | | | | | | | |

Due to a leak cylinder LK548528 had to be exchanged with cylinder LK535353 during the experiment.

| . Temperature o D, CH ₄ and H ₂ O | lependenci applying a | es of gas ac temperature | Isorption on range from - | steel and alu -10 to +50°C | uminium surface . NA when <i>r² <</i> |
|--|--------------------------|------------------------------|---|-------------------------------|--|
| Cylinder | CO ₂ | CO [ppb°C ⁻¹] | CH ₄ [ppb°C ⁻¹] | H₂O [ppm°C ^{−1}] | surface type |
| 1: LK502291 | 0.0061 | NA | NA | NA | steel |
| 2: CB09790 | -0.0003 | NA | NA | NA | aluminium |
| 3: LK548602 | 0.0141 | NA | NA | NA | steel |
| 4: CB09877 | -0.0003 | NA | NA | NA | aluminium |
| 5: LK548528 | 0.0184 | NA | NA | 0.113 | steel |
| 5*: LK535353 | 0.0014 | NA | NA | 0.00003 | steel |
| 6: CB09786 | -0.0003 | NA | NA | NA | aluminium |

Due to a leak cylinder LK548528 had to be exchanged with cylinder LK535353 during the experiment.

Table 2 for .02. CO_2, CO_2

Figure 1. Temperature exposed to the cylinders in the climate chamber. Every two hours the temperature changed by 10 °C. The actual temperature (red) is in good agreement with the set temperature (light blue) but delayed by 2.75 h (bold blue).

Figure 2. Emptying experiment within 14 h: CO_2 mole fraction of a steel cylinder vs. its pressure in red (only every 100 point of 0.1 s resolution data is shown). Langmuir monomolecular layer desorption model in blue ($CO_{2, ad} = 0.41 \text{ ppm}$, $K = 0.0436 \text{ bar}^{-1}$).

Figure 3. Emptying experiment within 14 h: H_2O even shows a five times stronger desorption effect documented by the linear correlation with the CO_2 mole fraction.

Figure 4. Emptying experiment within 8 h: CO_2 mole fraction of an aluminium cylinder vs. its pressure in red (5 s resolution). Langmuir mono-molecular layer desorption model in blue $(CO_{2,ad} = 0.047 \text{ ppm}, K = 0.001 \text{ bar}^{-1})$ for a decanting rate of 5 Lmin^{-1} upper panel and for 0.25 Lmin^{-1} in the lower panel $(CO_{2,ad} = 0.028 \text{ ppm}, K = 0.001 \text{ bar}^{-1})$. Temperature evolution corresponding to the pressure evolution is displayed for the aluminium cylinder (green line) and for the pressure regulator (in violet). Note that the decreasing trend can be explained by the Joule–Thompson cooling effect and has nothing to do with the adsorption theory and that the desorption energies cannot determined with confidence during these decanting experiments.

Figure 5. Emptying experiment within 8 h: H_2O and CO show no and CH_4 an extremely small desorption effect on this aluminium cylinder compared to the CO_2 mole fraction.

Figure 6. Temperature dependence for the CO₂ mole fraction deviations from their corresponding value at 20 °C (T_0) for the steel cylinders 1, 3, 5, 5^{*}, increasing values (left *y* axis) as well as for aluminium cylinders 2, 4, 6, decreasing values (right *y* axis). The *y* axes are different by a factor of 40. For clarity reasons measurements are only given for cylinder 1 together with its linear correlation line, whereas for the other cylinders linear correlation lines are given only. The temperature dependencies vary between 0.0014 and 0.0184 ppm °C⁻¹ for steel and -0.0002 to -0.0003 ppm °C⁻¹ for aluminium cylinders

Figure 7. Dependence of scaled CO_2 mole fraction difference plus offset *b* on the difference of inverse temperature for the steel cylinder 1 according to Eq. (6). Open red symbols correspond to negative and filled red symbols to positive temperature gradients in Fig. 1. The slopes corresponding to the negative desorption energy (Eq. 6) as we have changed the *x* axis with a minus sign due to visibility reasons. The desorption energies do slightly differ from 14741 to $15\,095\,Jmol^{-1}$ for positive and negative temperature gradients, respectively with a mean of $14\,882\,Jmol^{-1}$ for the overall correlation using a $CO_{2,ad}$ value of 1.2 ppm and 0.0168 bar⁻¹ for K_0 . Open and filled blue symbols correspond to the CO_2 mole fractions vs. temperature whereas the blue line corresponds to the estimated CO_2 mole fractions according to Eq. (A25).

Figure 8. Dependence of scaled CO_2 mole fraction difference plus offset *b* on the difference of inverse temperature for the aluminium cylinder 2 according to Eq. (6). Open red symbols correspond to negative and filled red symbols to positive temperature gradients in Fig. 1 together with their corresponding correlation lines (dotted red lines). The red line corresponds to all values. The slopes corresponding to the negative desorption energy (Eq. 6) as we have changed the *x* axis as in Fig. 7. The correlation is rather bad ($r^2 = 0.6$), therefore part of the variability might be due to temperature induced effects that are independent of adsorption/desorption phenomena. Hence desorption energies have to be taken with care. Open and filled blue symbols correspond to the CO_2 mole fractions vs. temperature whereas the blue line corresponds to the estimated CO_2 mole fractions according to Eq. (A25).

