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. In the present experiment we investigated the adsorption/desorption phenomena on three steel and three aluminium cylinders containing compressed air in our laboratory and under controlled conditions in a climate chamber, respectively. We proved the pressure effect on physical sorption for CO\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2}O by decanting a steel and an aluminium cylinder completely. The results are in excellent agreement with a monolayer adsorption model for both cylinders. However, adsorption on aluminium (<0.05 ppm and 0 ppm for CO\textsubscript{2} and H\textsubscript{2}O) was about 10 times less visible than on steel (<0.5 ppm and <2.5 ppm, respectively) cylinders at 100 bar filling pressure. In the climate chamber the cylinders were exposed to temperatures between -10 to +50 °C to determine the corresponding temperature coefficients of adsorption. Again, we found distinctly different values for CO\textsubscript{2} ranging from 0.0014 to 0.0184 ppm°C for steel cylinders and -0.0002 to -0.0003 ppm°C for aluminium cylinders. The reversed temperature dependence for aluminium cylinders is most probably due to temperature and gas consumption induced pressure changes. After correction, aluminium cylinders showed no temperature independence. Temperature coefficients for CH\textsubscript{4}, CO and H\textsubscript{2}O 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.

Pressure experiment: We decanted 5 liter per minute from either a steel (50 liter steel cylinder from Carbagas, Switzerland) or aluminium (30 liter Scott-Marrin Luxfer steel cylinder, USA cylinder) without any additional pre-treatment of the inner surfaces and monitored the mole fractions of CO\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}O by a Picarro G2311f and G2401, in which case CO\textsubscript{2} was measured in addition. Attached to the cylinders were pressure regulators from Tescom (type: 64-3441KA412 dual stage). The starting pressures were about 110 bar for the steel and 95 bar for the aluminium cylinders, respectively. Due to the large gas flow which was maintained by the detector itself in the case of G2311f and by an external flow meter 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 second level with the G2311f instrument whereas on a 5 second level with the G2401. In parallel we recorded the pressure continuously. In an additional experiment we decanted another aluminium cylinder (starting pressure 60 bars) with a 20 times reduced flow rate, i.e. 0.25 liter per minute.

Temperature experiment: In a second experiment performed in the Climate Chamber at the Swiss Federal Institute of Metrology (METAS), we determined the temperature dependence of the adsorption process. Therefore, a temperature range from -10 °C to +50 °C was operated as documented in Figure 2. The temperature was set to a fixed temperature for 2 hours at each level. Within every two hours sequence we switched between six cylinders and an additional reference cylinder outside the climate chamber using 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-, 40,...+260°C and recorded by a GMH250 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.

CONCLUSIONS
The experiments performed clearly demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO\textsubscript{2} (shown), CO, CH\textsubscript{4} and H\textsubscript{2}O (not shown) than steel cylinders. The desorption rate behaviour follows nicely a monolayer model as described by the Langmuir equation [1,2]. CO\textsubscript{2}ads corresponds to the adsorbed CO\textsubscript{2} amount and CO\textsubscript{2}init is the known CO\textsubscript{2} concentration filled into the cylinder. K is the ratio of the adsorption and desorption rates, P\textsubscript{0} the starting an P the present pressure. Adsorbed CO\textsubscript{2} amounts to about 0.5 ppm for steel and 10 times less for aluminium cylinders at 100 bar filling pressure.

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CO_{2\text{meas}} = K \cdot \left( \frac{P - P_0}{1 + K - P_0} \right) \cdot \ln \left( \frac{P_0}{1 + K - P_0} \right)
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Figure 1: CO\textsubscript{2} concentration dependence on pressure
The measured concentration (CO\textsubscript{2meas}) for steel and aluminium cylinders nicely follows a monolayer layer desorption described by the Langmuir equation [1,2]. CO\textsubscript{2} ads corresponds to the adsorbed CO\textsubscript{2} amount and CO\textsubscript{2} init is the known CO\textsubscript{2} concentration filled into the cylinder. K is the ratio of the adsorption and desorption rates, P\textsubscript{0} the starting an P the present pressure. Adsorbed CO\textsubscript{2} amounts to about 0.5 ppm for steel and 10 times less for aluminium cylinders at 100 bar filling pressure.

Figure 2: CO\textsubscript{2} concentration dependence on temperature
The temperature dependence of the CO\textsubscript{2} observed for three steel and aluminium cylinders is 0.0014 to 0.0184 ppm°C and -0.0002 to -0.0003 ppm°C, respectively. This might have an influence on the precision when facing large temperature fluctuations in the laboratory or when measuring in the field with large ambient temperature variations, but only for steel and not for aluminium cylinders. From these measurements, a robust estimate of the desorption energy was possible only for steel (14 882 J mol\textsuperscript{-1}) but not for aluminium cylinders due to the low temperature dependence and temperature range investigated. The determined energy value underpins that the observed adsorption mechanism is physisorption only.

References

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