

# **O<sub>2</sub>/N<sub>2</sub> Storage Aspects and Open Split Mass Spectrometric Determination**

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## ***Abstract***

A measurement system for high precision determination of O<sub>2</sub>/N<sub>2</sub> ratios in air samples using an open split inlet system and mass spectrometric detection is described. A major advantage of the system is the low consumption of sample gas (about 2 ml STP per minute). The open split system is made from fused silica capillaries moving alternately within a glass tube thereby providing the function of a Changeover Valve commonly used in stable isotope ratio mass spectrometry for high precision comparison of the isotopic composition of two clean gases. Long term precision of the measurements, comparing ½ hour averages are close to 2 per meg.

Storage of air samples in glass flasks has been improved considerably by replacing the soft polymer O-ring with a lathe machined PCTFE seal. In one liter flasks air samples kept at 2 Bar (abs.) do not alter their O<sub>2</sub>/N<sub>2</sub> ratio by more than 7 per meg in 100 days.

An effort to calibrate O<sub>2</sub>/N<sub>2</sub> ratio measurements across laboratories has been made using high pressure tanks. The original values of the tanks (measured by R. Keeling, SIO) were reproduced within an error of 1% of the assigned difference.

## ***Introduction***

The routine measurement of O<sub>2</sub>/N<sub>2</sub> ratios in air sampled in containers has been plagued by the stability of the gas mixture over time. This has proven to be the case for high quality stainless steel containers<sup>1</sup> as well as for glass flasks<sup>2</sup>. Some of the instability over time can be attributed to oxidizable, mostly organic material on the surfaces or within the O-ring material.<sup>3</sup> One of

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the major reasons for changes observed over time is permeation through O-ring seals which depend on the strongly temperature dependent permeability of the polymer as well as the pressure gradient between the air inside the flask and ambient.<sup>2</sup> Using published permeation coefficients we estimate that a typical 1 liter glass flask with two valves sealed with Viton O-rings can loose roughly 0.2 ml (STP) of air through diffusion over the period of one year when the pressure difference is one atmosphere. Owing to the differences in permeability these 0.2 ml of 'air', however, comprize about 55 % O<sub>2</sub> and only 45 % N<sub>2</sub>. Hence, the remaining air in the flask has been altered by about 200 per meg<sup>a</sup> in the O<sub>2</sub>/N<sub>2</sub> mixing ratio. Due to these storage effects, most air samples have been collected by filling the flasks to ambient pressure. On the other hand, sampling for trace gas concentration measurements often requires pressures above ambient for subsequent gas chromatographic quantification. Samples at higher pressure require proportionally less space. This is a logistical advantage especially when sampling in remote areas where routine shipment of flasks is a permanent challenge.

### ***Experimental setup***

In Jena, we have established routine precision quantification of trace gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, H<sub>2</sub>, CO and SF<sub>6</sub>) in air as well as high precision isotopic analysis of CO<sub>2</sub>. Trace gas quantification in general requires above ambient pressure, while the isotopic measurements can be made at sub-ambient pressures without special treatment. All measurements are made from the same flasks with a volume of 1 liter and a collection pressure of 2 bar. In order to analyse the collected air samples for O<sub>2</sub>/N<sub>2</sub> as well we have devised a low flow open split inlet system ('BG-AirFlo') already briefly mentioned in Werner et al.<sup>4</sup> at a priliminary stage. The system in the current version is depicted schematically in *Figure 1*.

Air samples are attached to a 16 port multiport valve (VICI-Valco, [www.vici.com](http://www.vici.com)) using ½" Ultratorr (Swagelock, [www.swagelock.com](http://www.swagelock.com)) connectors. The selected port is connected to a 6-port 2-position valve (VICI-Valco) which has a pressure gauge mounted between two ports and a membrane pump for initial evacuation and vacuum control of the connecting joint. In addition, the flask pressure can be determined this way. In the connecting line between the two valves a small stainless steel tube filled with Mg(ClO<sub>4</sub>)<sub>2</sub> serves as a guard trap against residual water (we exclusively sample dry air). From the 6-port valve a fused silica capillary restricts the flow to an open split which is made from a small glass tube closed at one end. For

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<sup>a</sup> 1000 per meg equals 1 per mill in the delta notation. Due to the nominal O<sub>2</sub> content in air of 20.95%, 4.8 per meg are equivalent to 1 ppm.

a pressure difference of 1 bar the flow amounts to about 2 ml per minute. The fused silica capillary enters the open split down to the tip where a transfer capillary to the mass spectrometer is taking gas into the ion source of the mass spectrometer (Delta+XL, Finnigan MAT, with small modifications in the ion source region). The capillary from the 6-port Valco valve is mounted on a piston so that it can be switched in and out of the open split assembly. A second fused silica capillary providing a continuous flow of reference air from a high pressure tank is alternately switched into the open split.

## BGC -AirFlo for O<sub>2</sub>/N<sub>2</sub> ratio determination

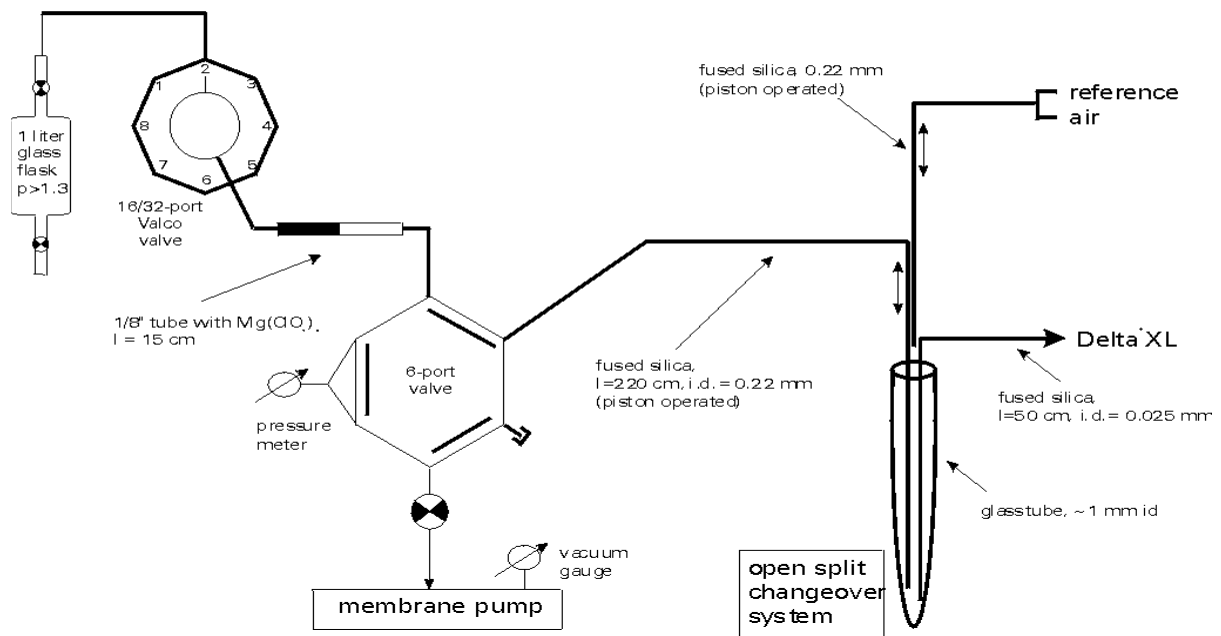


Figure 1; Schematic layout of the air inlet system including a multiport valve (VICI-Valco) and the glass tube with fused silica capillaries acting together as a Changeover Valve.

The arrangement serves the function of a changeover valve as is common in isotope ratio mass spectrometry. The major advantage of the open split setup is that the mass spectrometer does not record any change in pressure during switching. Pressure surges have a negative influence on the attainable precision due to the fact that sensitive equilibria between material and oxygen in the ion source are temporarily altered and require time for reestablishment: freshly bombarded surfaces are a pressure dependent sink for oxygen, the hot tungsten filament has a pressure dependent oxidation state, etc.. A second advantage relates to the common observation that the measured O<sub>2</sub>/N<sub>2</sub> ratio usually is very sensitive to pressure differences and great emphasis must be laid upon high precision flow balancing of sample and

reference gas. By using the open split principle the pressure between sample and reference gas remains precisely balanced with no further action required. Longer term pressure changes due to changing weather conditions do not interfere because they happen on a different time scale. An open split setup similar to ours with the additional capability to work against a constant sub-ambient pressure has been described by Leuenberger et al.<sup>5</sup>.

## Results and Discussion

### Alteration of sample air in glass flasks during storage

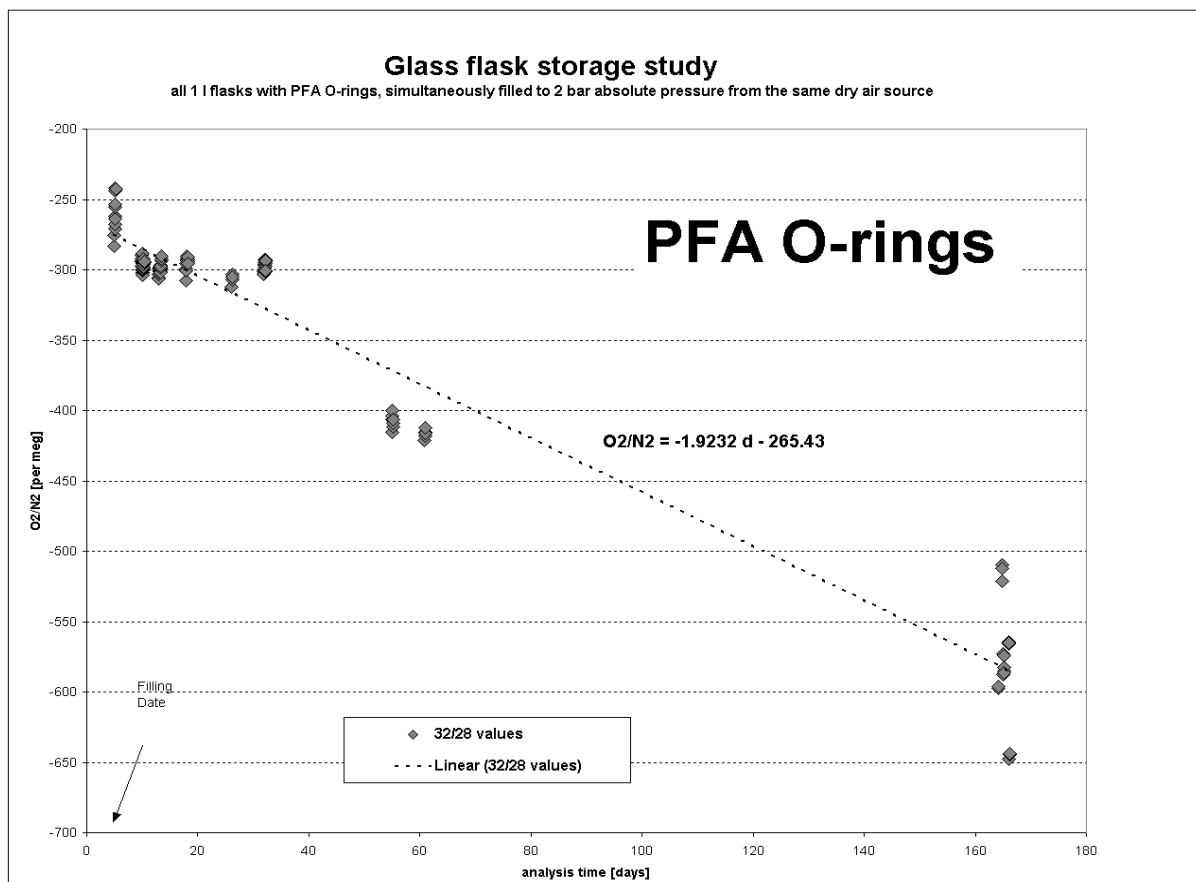


Figure 2; Air sample storage tests for  $O_2/N_2$  using PFA O-ring seals

In order to study the effects of sample gas alteration or aging inside our routine operation glass flasks we have observed the  $O_2/N_2$  ratio in a series of flasks over a period of 160 days. A total of 7 flasks sealed with **PFA O-rings** were involved in this study. All flasks were filled with dry air in a 'sausage' (connected in series with Cajon Ultratorr adapters) at a constant filling pressure of 2 bar (abs.). The flow through the system was 3 l per minute for 30 minutes. The analysis results are presented in Figure 2.

The flasks were measured repeatedly, with the first analysis varying over time. Within the limits of precision we did not detect any change of gas composition as a function of pressure drop. Two features are evident from *Figure 2*: there is a clear highly correlated ( $R^2 = 0.95$ ) drop of the measured  $O_2/N_2$  ratio with time and the scatter of the data increases over time as well. The drop in ratio amounts to an average of -310 per meg in 166 days. The scatter at the beginning was  $\pm 12$  per meg and increased to  $\pm 50$  per meg over the same observation period. The latter may be understood in terms of the details of the diffusion characteristics: The diffusion length and diffusion area control the diffusion rate in a linear fashion<sup>2</sup>. Both are a function of the O-ring geometry in its compressed form. We did not select the O-rings for maximum comparability in size nor did we use a torque wrench for controlling the force onto the O-rings.

In order to reduce the aging effects we devised two possible pathways: The preferred solution was to get rid of the permeation effect entirely (within measurement precision) by searching for a better polymer sealing material. In case this would prove unsuccessful, the effect should at least be minimized. Commonly used solutions to the problem (filling to ambient pressure and using large volumes of gas) are of this second type. We tried a third solution by adding a buffer volume in between two O-rings. The buffer volume is initially filled with sample air at the sample pressure. This gas acts as a shield towards alteration of the sample gas itself over time. The results of this study have been published elsewhere<sup>2</sup> and will not be considered further here.

The search for an alternative material quickly revealed that **PCTFE (Kel-f<sup>®</sup>)** would be a good alternative (see table in reference 2) primarily owing to its low permeability constants compared to all other materials. However, the material is much harder than usual O-rings suitable for sealing on glass. It is in common use in high quality vacuum valves or in high quality pressure regulators where force is not critical due to the use of metal as the counter-seal material. In an early attempt, our routine flasks were equipped with O-rings made from PCTFE. In spite of the difficulties in achieving a good seal, storage tests were conducted over an extended period of time<sup>6</sup> revealing that the storage problems could be overcome using this material provided the seal could be made in a reliable fashion with a torque size compatible with glass valves. By reducing the contact area and using a machined seal with tight size specifications instead of a simple O-ring we succeeded in generating a valve seat that can be used on the valve stems already in use in our glass flasks<sup>7</sup>. Storage tests for  $O_2/N_2$  are shown in *Figure 3*.

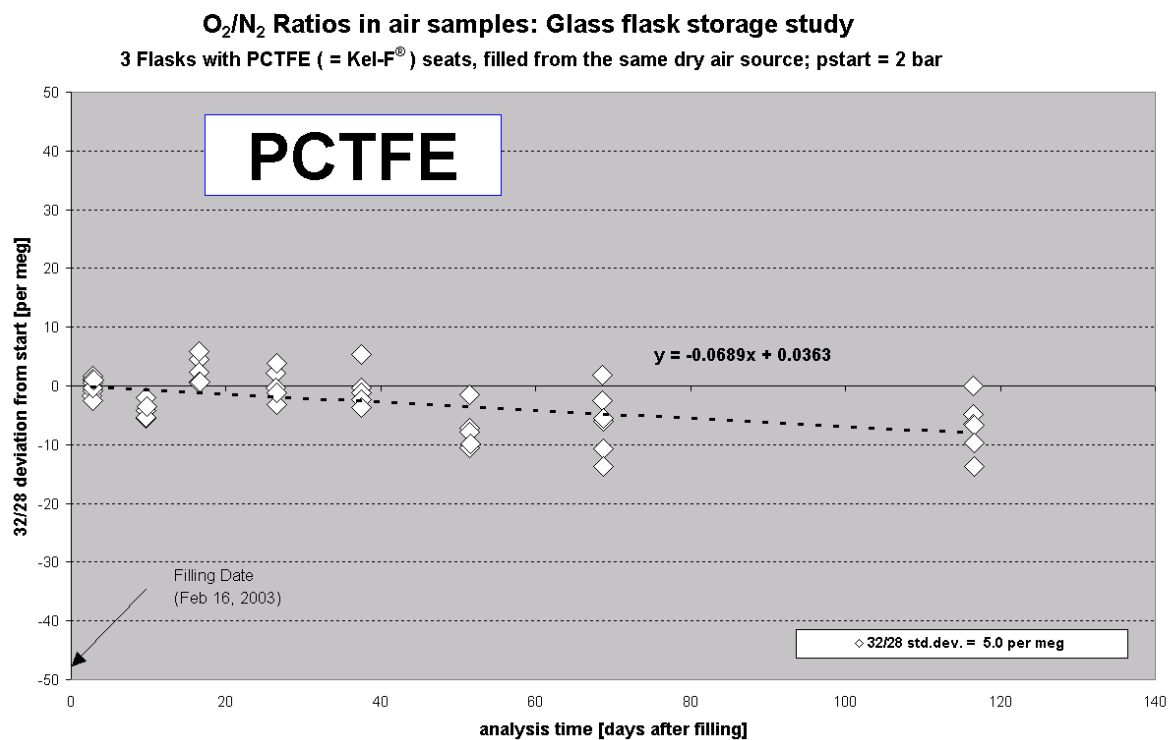


Figure 3; 32/28 stability in glass flasks sealed with PCTFE

The conditions and flask filling was identical to the earlier experiment. The data suggest that the effect of preferential oxygen loss from sample flasks has been reduced considerably. A residual loss corresponding to a concentration change of about 7 per meg in 100 days is observed which must be taken into account when analysing and reporting the flask results. Even without correcting for this drift, the total precision in the data, expressed as standard deviation is  $\pm 5$  per meg, exhibiting a considerable improvement over the previous data set obtained with PFA seats.

### O<sub>2</sub>/N<sub>2</sub> scale calibration

The improvements in storage stability described above offer new opportunities for calibrating O<sub>2</sub>/N<sub>2</sub> measurements over longer periods of time and in between laboratories. Provided the elevated pressure in the flasks does not impose new artifacts on analytical setups that are used to measure O<sub>2</sub>/N<sub>2</sub> in air samples interlab-precision could be brought to the  $\pm 5$  per meg level by filling a number of flasks and sending them to participating laboratories for intercomparison. In our lab (as in most others doing these kinds of analysis) high pressure tanks are used for maintaining the local scale. Differences between tanks are routinely

monitored and kept in a record file. Tanks are kept horizontally in order to minimize effects of diurnal temperature cycling and the regulators are carefully selected for inertness towards changes in the measured oxygen concentration.

We have obtained a pair of air tanks filled and calibrated for our institute by R. Keeling at Scripps Institution of Oceanography (SIO). We have used these tanks to establish a firm  $O_2/N_2$  value for a third tank serving as a continuous flow working reference on the BGC

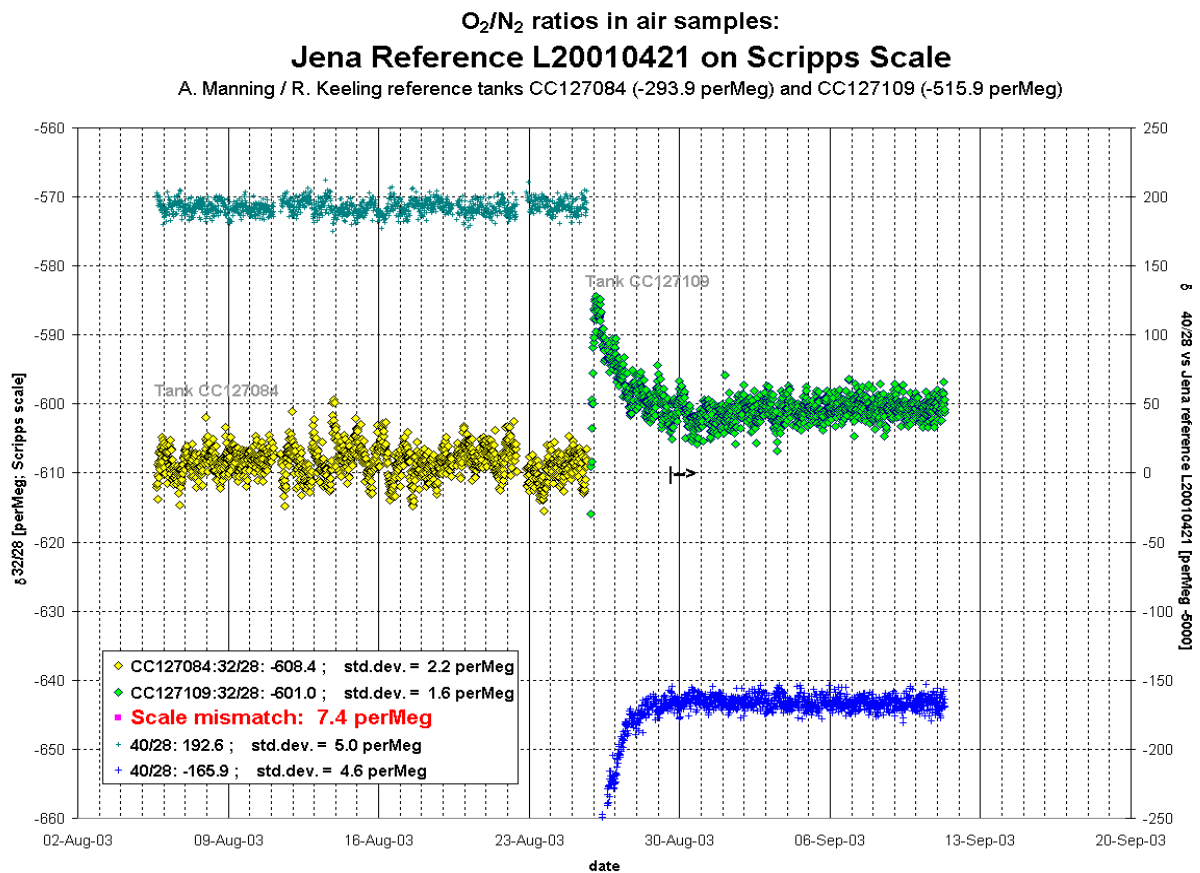


Figure 4; Determination of a Jena working reference tank using two tanks with different  $O_2/N_2$  ratios calibrated by R. Keeling, SIO

AirFlo system depicted in *Figure 1*. The SIO tanks were connected to one of the flask ports and the differences between the respective tank and the working reference were monitored over considerable periods of time. *Figure 4* exhibits the results obtained for the working reference assuming that the respective SIO tank assignment is correct. Each data point corresponds to a  $\frac{1}{2}$  hour average in the observed 32/28 ratio. On average over the whole measurement period we find a residual offset of +2.0 permeg between the measurements, i.e. our measurements indicate a slightly larger difference between the SIO tanks (224 per meg)

than assigned (222 per meg). For arriving at the correct O<sub>2</sub>/N<sub>2</sub> ratio for the tanks the raw data in *Figure 4* have been corrected for the difference in CO<sub>2</sub> concentration (421 ppm and 379.6 ppm): CO<sup>+</sup> (m/z 28, isobaric with N<sub>2</sub><sup>+</sup>) is formed from excited CO<sub>2</sub><sup>+</sup> ions in the ion source and comprises about 10% of the total ion current formed by electron impact ionization of CO<sub>2</sub> gas. This contribution to the m/z 28 ion current (a per meg correction of 0.13 times the CO<sub>2</sub> concentration difference) has been removed resulting in a reduction of the observed scale difference from 7.4 per meg to 2.0 per meg.

Taking the complexity of the analysis into account as well as the fact that the analysis principles in both laboratories are entirely different we consider this error of about 1% an excellent result which provides further confidence that O<sub>2</sub>/N<sub>2</sub> measurements can also be reliably calibrated using selected high pressure aluminium tanks.

### **Conclusions**

Precise determination of O<sub>2</sub>/N<sub>2</sub> ratios in air samples is possible using an open split changeover system and a low sample flow of less than 2 ml/min. For two ½ hour determinations a sample consumption of less than 120 ml is possible. Together with improvements in gas stability over time when PCTFE is used as a sealing material in glass containers, this offers the possibility to measure the major trace gas concentrations (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO, H<sub>2</sub>, SF<sub>6</sub>), O<sub>2</sub>/N<sub>2</sub> ratios as well as CO<sub>2</sub> isotope ratios from a single 1 liter glass flask filled to a pressure of 2 bar (abs.)

### **Acknowledgments**

Flask conditioning and filling has been made by Michael Rothe. The communication of preliminary results on storage tests using PCTFE by Ray Langenfelds is highly appreciated. These results triggered and encouraged the work presented in this contribution. Ralph Keeling and Andrew Manning generously provided the tanks for the calibration exercise.



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- <sup>4</sup> Roland A. Werner and Willi A. Brand, Referencing Strategies and Techniques in Stable Isotope Ratio Analysis, Rapid Comm. Mass Spectrom. 15 (2001) 501-519
- <sup>5</sup> Leuenberger M, Nyfeler P, Moret HP, Sturm P, Huber C, RAP. COMM. MASS SPECTROM. 14 (16): 1543-1551 2000
- <sup>6</sup> Ray Langenfelts, private communication
- <sup>7</sup> The valves are from Glass Expansion, GE, Australia. In a close collaboration with QVF (Ilmenau, Germany) we have been successful in developing a new glass valve for this purpose using Kel-F seats. These are available commercially now ([www.glasapparate.de](http://www.glasapparate.de)).