SIMPLE, LOW-COST FLOW CONTROLLERS FOR TIME AVERAGED ATMOSPHERIC SAMPLING AND OTHER APPLICATIONS.

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***Abstract*— In air sampling is often necessary to limit the air inflow into an initially void vessel in order to extend the filling time. This requires devices characterized by very low, known and stable conductance. Likewise devices may also be used to control the gas flow between two vessels, or the outflow from gas containers. Depending on the use, they are called flow controllers, controlled leaks or, as in our case, inflow regulators. In this work we describe simple and cheap inflow regulators designed to collect air samples in 0.5 L vessels with filling times of many days. These inflow regulators may be adjusted within a wide impedance range and proved to be very stable under laboratory conditions and reasonably stable even under much harder operating conditions in field experiments.**

***Keywords*— Flow controllers, Atmospheric trace gas, Time-averaged sampling**

I. INTRODUCTION

Low hydraulic conductance gas flow regulators, also named controlled leaks, are used in many laboratory and industrial applications. Some examples are leaks detection in complex system (Calcatelli *et al*, 2007), leaks quantification (Hidalgo and de Segovia, 2008), measurements of large, irregularly shaped volumes (ENEA, 2004), pressure regulation in plasma generators under continuous flow condition (Torven and Babic, 1972) and time-averaged air samples collection (Ki-Hyun *et al*., 2004; Trabue *et al.*, 2008; Hoshi *et al*., 2008). Usually, conductance C is expressed in terms of the rate of increment of the pressure in a previously evacuated vessel and is of the order of 10^{-9}- 10^{-7} mbar.L/s for a pressure difference of 1 bar. In this work we focus on the latter application, and we shall call *Inflow Regulators* (*IR*) the developed devices.

There are basically two kinds of low conductance *IR*: porous plugs or membranes, and geometric leaks. Porous plugs rely chiefly on material permeability, which must be in the range 0.1 to 1 mdarcy to achieve the desired conductance. These values are easily accessible by using baked clays. But permeability is sensible to temperature changes (ca. 3% for ºC). Besides, in the above range porous plugs are selective with respect to trace gases in air because pores diameters are of the order or smaller than molecular mean free paths (≈ 100 nm at NTP). This is a serious hindrance at least for atmospheric sampling applications.

On the contrary, the above effects are very small or absent in geometric leaks, currently constituted by segments of very thin capillary tubes (an inner diameter –ID– of 0.1 mm is the smallest commercially available) wherein a Poiseuille flow develops. Therefore, this solution has been adopted to collect air samples when time-averaging are mandatory, as, for instance, in applications of the Johnson SF_6 tracer technique, designed to measure the discontinuous CH_4 emission by grazing ruminants (Johnson *et al*., 1994; Johnson *et al*., 2007). Clearly, during the filling of initially void vessels through *IR*, the inflow rate decreases as the pressure difference decreases. Therefore, the time variation of the pressure p in the vessel is given by:

$$\frac{dp}{dt} = -\frac{C}{V}.(p - p_0)\,. \tag{1}$$

Here V is the vessel volume, p_0 the atmospheric pressure and C the conductance of the *IR*. Integrating:

$$\frac{p_{(t)}}{p_0} = 1 - e^{-C.t/V}\,. \tag{2}$$

Strictly speaking, filling is linear on time only if $t << C/V$. However, in the concern of air samples collection, it is usual to extend the filling until a time T for which $p \approx 0{,}5$ bar. This is a reasonable compromise between the need to collect enough air for analysis and to avoid excessive departures from linearity. Therefore, a good choice for C is:

$$C = -\ln(0.5)\frac{V}{T}\,. \tag{3}$$

Normally, T and V are fixed "a priori" when planning a field experiment. Therefore, the optimal C for the *IR* to be used should be close to that given by the above expression. According to Poiseuille law and Eq. 3 for a 1 m long capillary tube of 0.1 mm ID , and T = 8,64 10^4 s, V should be 1.5 L. We conclude that *IR* based on capillary tubes are reasonably suitable only for T of the order of 1 day or less.

On the other hand, both in applications of the aforementioned Johnson technique and in other field measurements, it is convenient to extend T up to many days. There are many reasons to use longer T: the smoothing out of local, fast fluctuations of scarce significance; the collection in places of difficult access; the determination of time-averaged concentration of trace gases through a small number of analyzed samples, which means important cost reductions and logistic simplifications. In these cases, the use of capillar-based *IR* becomes unpractical and expensive because very long tubes and large collecting vessels should be used.

During a field experiment designed to measure CH_4 emission by grazing steers (Bárbaro *et al.*, 2008) we carried out a first attempt to develop non-capillary geometric *IR* suitable for T = 24 h and V = 0.5 L. These values would imply capillary tubes some meters long, so we used *IR* based on a different low cost concept briefly described in the quoted work. These *IR* work reasonably well; however they are affected by a marked instability. Their conductance remains constant only during periods of the order of 1 day, but varies by significant factors (of the order of 2 or more) over longer time intervals.

We also study in laboratory *IR* made by porous plugs (prepared with baked white and red clay). They are stable, but, as said above, affected by a considerable selectivity with respect to different trace gases. In particular, the CH_4 mixing ratio in samples collected through the porous plugs we used were systematically some percent higher than in samples collected through geometric *IR*.

On the basis of these experiences we develop quite different geometric *IR* by assembling cheap commercially available components. Without change of the components they may be adjusted within a wide conductance interval. In particular we test two versions, respectively for 5-days and 15-days collections. With respect to the uncertainty of conductance values two points will be addressed: a) the spread of C between different *IR* nominally adjusted in the same range; b) the stability of a given *IR*, a relevant aspect especially for field work, where severe environmental conditions should be faced.

II. METHODS

A. Elements used

As shown in Fig. 1, we build up the *IR* by pressing with a screw top a bearing steel spherical ball (diameter 8 mm) against the border of the cylindrical central hole of a standard tubery union. The impedance of the thread is negligible in this arrangement. Both the union and the plug are brass made and all elements are commercially available at a total cost of about 6 US$ (the union and the screw top were provided by Casucci S.A).

B. Assembling and calibration

A moderate torque (≈ 1 Nm) on the hexagonal heads of the screw top is enough to reduce the conductance down to the desiderate range. Then, the *IR* is inserted as a leak toward atmosphere in a small vacuum system with a known volume (≈ 30 mL) evacuated with a mechanical pump. A Pirani gauge gives the pressure. After a first

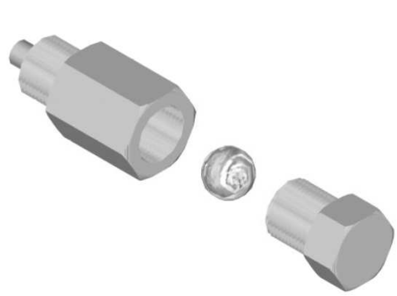


Figure 1: Schematic view of an Inflow Regulator.

online adjustment based on the minimum pressure attainable during pumping, pumping is stopped by closing an inserted valve and the inflow rate is determined typically by measuring the pressure rise-time from 0.3 to 0.5 mbar, of the order or less than 20 s. This fast determination of the conductance allows further adjustments when necessary. The procedure was used to assemble two sets of *IR*, adjusted to fill 0,5 L vessels up to 0.5 ± 0.1 bar (i.e. 0.30 ± 0.06 g of air at NTP) in T=*5* days (IR_5) and T=*15* days (IR_{15}) respectively. As differences in the conductance are not very relevant for air sampling applications, we do not pay special care in reducing the spread of conductance for an *IR* set below 10% -20%. This spread might be considerably reduced simply by a carefully fine adjustment; however**,** there remain some more deep causes affecting the calibration. First, especially at the beginning of the operation the pressure rise due to degassing is not negligible with respect to the rise due to air inflow through the *IR*, and this effect becomes progressively less important as time advances. Second, we use a simple needle vacuometer and a manual chronometer. In principle these effects could be considerably reduced by spending more time in the adjustment operation and by using more precise (and expensive) instruments, so that spread of C we have among a set of *IR* nominally adjusted for a given T is nor indicative of the precision in principle attainable by means of the above described procedure.

C. Leak geometry

A direct observation of the contact region between the steel ball and the brass border is, of course, impossible. However, some geometric feature of this region may be easily inferred. According to Poiseuille law, the conductance of a circular section tube of diameter d and length l is given by:

$$C = k.\frac{d^4}{l}. \qquad (4)$$

In our case (air), with d and l in cm, C in mbar.L/s /bar, $k \approx 1.33\ 10^8$. Therefore, if we assume that the leak is attributable to ***n*** identical microchannel, their common diameter should be:

$$d = 0.96\ 10^{-2}\ (Cl/n)^{1/4}\ cm.$$

On the other hand, for the IR_{15} set, $C \approx 3.\ 10^{-4}$, and due to the strong dependence of the conductance on d, only one or two main micro channels may contribute to C. In the extreme (but not improbable) case $n = 1$, with $l \approx 0.1$ cm, the micro channel diameter should be 7 μm. Different assumptions on n or l do not change very much this value. Therefore, we can conclude that the conductance of our *IR* is due to few micro channels with typical diameters of some microns.

D. Air filtering before *IR*

Medium or large size aerosols dragged by the air inflow easily obstruct such micrometric channels. Besides, water may produce oxidation and deposits. Of course, these problems are magnified in long-time field recollections. Therefore, we protect the *IR* with a double filter: an inner layer of hypoallergenic tape and an external layer of permeable hydrophobic tissue. Immersion in water for about 15 min does not produce appreciable change in the inflow rate. However, as we shall see, long expositions in wet condition are likely one of the major causes of recollection failures in field experiments.

E. Collection vessels

Long collection times require good quality vessels. Our previous experiments showed that PVC vessels are not reliable, both due to fragility (the detachment of fragments inhibes the use of the very practical and fast weighing method described below) and degassing of PVC and glues. Therefore, we use especially manufactured stainless steel 0.5 L cylinder weighing about 600 g, closed by a sphere valve. The cost of these cylinders (about 25 U$S) is more than twice the cost of likewise PVC vessels. However, their behavior is far better. With the valve closed, the air accumulation rate in the cylinders is of the order or less than 0.2 mbar/d, and they may be used many times without appreciable change of their void weigh.

F. Measurements of air accumulation in the collecting vessels.

The use of high quality vessels allows direct measurements of the accumulated air simply by weighing them in a precision balance (0.01 g). This very practical and fast method has the additional advantage that there is no need to remove the *IR*. Hence, it is possible to follow without interferences the filling process of a collector vessel in the laboratory through a weighing sequence. An IR_{15} gives a typical air mass accumulation of 0.02 g/d, so a regression of a sequence of weighing separated by 3days intervals gives an accurate value of the *IR* conductance.

III. RESULTS

A. Test of the *IR* in laboratory collections. Long time calibration.

We perform many laboratory collections to test the reliability of the technique and as a final pass to validate *IR* for field experiments. Even if we were not interested in the analysis of the collected samples, these recollections produce useful results in the concern of the *IR* behavior. They may be considered also as long-time calibrations, i.e. a more precise though time-expensive way to measure *IR* conductance. To be brief, we report in these subsection results concerning the IR_{15} only.

While collecting, the cylinders were weighed many times beyond a total 15 days period. A convenient way to represent the filling process takes profit from Eq. 2, which implies ($V = 0.5$ L) that

$$-0.5\ln\left(1 - m_{(t)}/m_0\right) = F_{(t)} = C.t \qquad (5)$$

Figure 2 represents $F_{(t)}$ for 9 *IR* of the IR_{15} set (the remaining *IR* show the same behavior). The slope of the linear regression of $F_{(t)}$ for each *IR* gives *C*, i.e the corresponding conductance, which are reported for the same *IR* in Table 1. The stability of the *IR*, as inferred from the high R^2 values given in this Table, is quite satisfactory. Note that this stability has nothing to do with the spread of *C* values for a same nominal value, which, as said above, is related to the adjustment.

We validate for field experiments the IR_5 with *C* giving pressure rise rates within 51.1 - 91.6 ml/d in 0.5 L vessels and the IR_{15} with corresponding rates between 17 - 30.5 ml/d. The lower limit ensures that samples contain enough air for a high-resolution chromatographic analysis. On the other hand, the higher limit is an approximate condition to consider samples as time-averaged over *T*. Such a progressive decrease of the inflow rate is usually accepted in long-time sampling, for instance when applying the aforementioned SF_6 tracer technique (Johnson *et al*., 2007; Lassey, 2007). Note again that the relatively large tolerance interval accepted is related to the adjustment methodology. If necessary it would be possible to reduce considerably the conductance spreading among an *IR*.

B. Use of the Inflow Regulators in field experiments.

The above described *IR* have been employed both to sample air near the mouth of grazing animals and in atmospheric air field sampling.

Many *IR* of the set IR_5 were applied to 6 five-day collections on 10 mature bovine females. To our knowledge, it was the first time in the world where many-days collection was used on grazing animals. However, here, we are interested in the *IR* performance only.

A set of two independent samplers formed each one by a stainless cylinder and an *IR*, were charged on the heads of the animals supported by especially designed halters. Including the base-line samples, we collected during this experiment 121 5-days samples.

Table 1: Laboratory conductances for the same IR as in Fig. 2 and correlation coefficients of the corresponding linear regressions.

Regulator	A (ml/día)	R^2
R513	31,95	0,9938
R516	36,27	0,9917
R512	36,45	0,9927
R511	30,73	0,9947
R515	35,69	0,9910
R30	24,52	0,9958
R510	24,42	0,9522
R10	40,26	0,9984
R38	30,44	0,9851

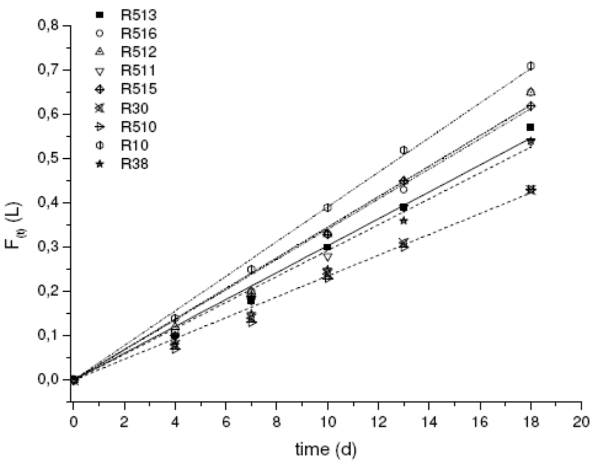


Figure 2: Laboratory filling F(t) function for 9 *IR* of IR_{15} set. Dots correspond to successive collected air masses and the lines are linear regressions.

Besides, by using IR_{15} we collected more than 50 15-days atmospheric samples in some location of interest: urban places, grassland, lagoons, steppe and at the border of the southern Patagonic ice-field.

Figure 3 reproduces histograms (number of samples per interval of accumulated air mass) for both kinds of experiments we observe very similar performances (an ANOVA test denied significant differences with a 95% reliability).

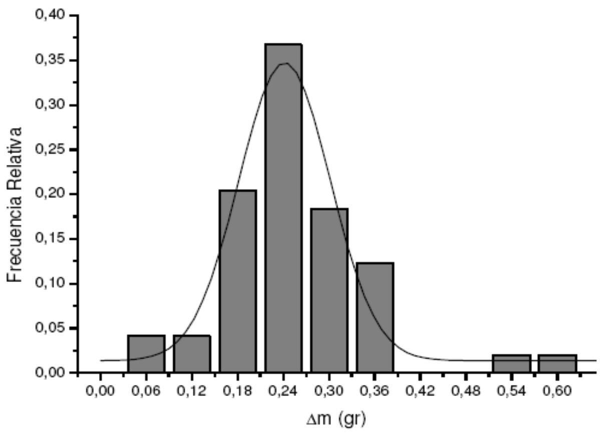
According to a gaussian fitting of the results (Table 2) a 78% of the air masses collected with IR_5 and a 67% of those collected with IR_{15} were within the correct ranges (see Subsection F of the preceding Section). These results reflect that duplication of sample collection practically ensures (> 90%) at least one correct collection. On the other hand, thank to the low cost and easy assembling of the *IR*, duplication is not a problem.
The stability of the *IR* in field experiments was satisfactory; however the collected air masses were systematically a bit lower than air laboratory recollections. This effect is clearly apparent in Figure 4, where we represent accumulated sample mass in field recollection vs. accumulated mass in laboratory recollections for a considerable number of IR_{15}.

A 10 % of the *IR* (5 of 49) was affected by strong anomalies in both sense, i.e., pronounced obstructions (circles in the lower sector of the figure) or strong conductance rise (circles in the upper part). In fact, even in these extreme cases, the conductance -measured *a posteriori* by using the "fast" method described in the Subsection B of the Section II- varied by a factor of the order of 2 only. Direct inspection revealed that obstructions are closely related to water filtrations. In contrast, we have no explanation for the conductance rises. None of these effects were observed in laboratory tests.

The conductance of the remaining 90% of the *IR* was in field recollection very near 0.8 times the laboratory conductance. The decrease of the conductance is very likely related to the high amplitude thermal excursions occurring along many days under field conditions. Clearly, thermal excursions are much more pronounced and fast in field than in laboratory. They produced successive dilatations and contractions in the metal pressed pieces, which may result in a net slight closure of the micrometric channels which determine the conductance.

Table 2: Parameters of best fitting Gaussian curves for the histogram reported in Figure 3.

Fit results				
IR_5				
Parameter	**Value**	**Error**	**LCL**	**UCL**
y_0	0.02017	0.0118	-0.00703	0.04737
xc	0.3315	0.0049	0.32011	0.34290
w	0.09805	0.01214	0.07006	0.12605
A	0.04548	0.00521	0.03346	0.05750
R^2	0.94741			
SSR = 0,00832229				
DOF = 8				
ChiSqr/DOF = 0.00104029				
IR_{15}				
Parameter	**Value**	**Error**	**LCL**	**UCL**
y_0	0.01375	0.01174	-0.01332	0.04081
xc	0.24169	0.0058	0.22828	0.25510
w	0.11991	0.01294	0.09006	0.14976
A	0.0501	0.0056	0.03716	0.06304
R^2	0.94941			
SSR = 0,00739389				
DOF = 8				
ChiSqr/DO. = 0,000924236				
F-Value=1.26279		**P=0.325139**		



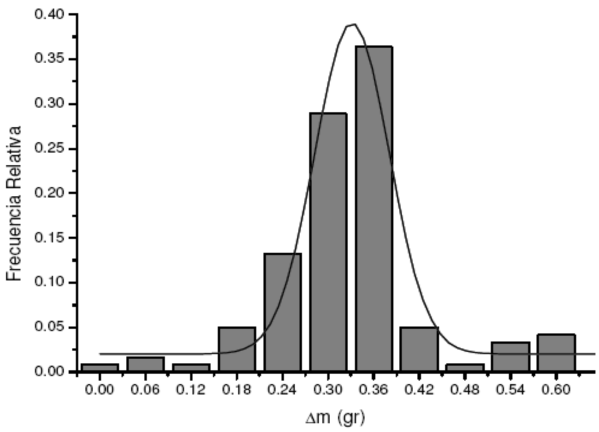


Figure 3: Histograms of the amount of air collected in the two field collections. The first (left), corresponding to sampling with IR_5 and the second (right) with IR_{15}.

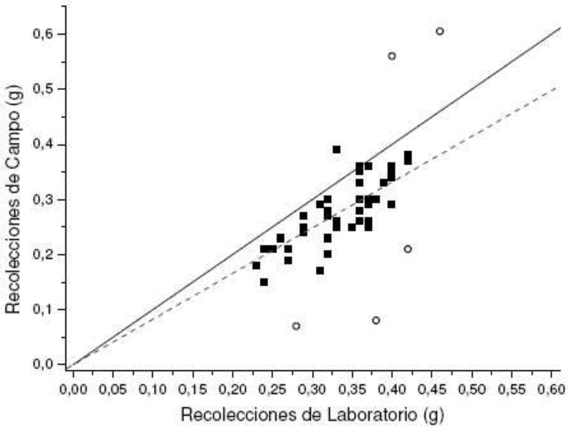


Figure 4: Field recollections vs. laboratory recollections. We represent also the line of slop one (continuous line) and the best-fit linear regression.

IV. CONCLUSION

We studied with some detail the range of attainable conductance and the stability of a kind of geometric controlled leaks based on a steel ball pressed against the contour of a hole in a brass piece. The conductance is due to few micrometric channels which remain open between the two components. The leak conception is extremely simple; the elements involved are commercially available at very low cost, and their assemblage is remarkably easy. Nevertheless, to our knowledge, likewise devices have not been studied insofar as adjustable, low hydraulic conductance flow controllers. Our interest is mainly centered on the determination of the CH_4 mixing ratio in time-averaged samples, where collector vessels are slowly filled along a time fixed by the controlled leaks, which are used as inflow regulators.

Time-averaged sampling is mandatory in some cases. For instance, methane emission by ruminants occurs through discontinuous exhalations, and the CH_4 concentration near the animal's mouth is strongly variable. But time-averaging is also useful when the sampling must be performed in places where access is difficult. Moreover, time-averaging smoothes fast local fluctuations which are not truly significant.

Thanks to the *IR* developed here, we were able to use sampling procedures based on 0.5 L stainless cylindrical vessels which are filled to 0.5 bars in times as long as 15 days. This requires a considerable stability of the inflow conductance even under field conditions, where thermal excursions are far larger than in laboratory, and the sampling set is exposed to rain. In addition, when mounted on animals, the sampling sets should also suffer considerable mechanical stresses.

Even if we develop flow controllers having in mind applications to air sampling, they may be certainly used in many other cases when low, regulated flow is required.

V. AKNOWLEGMENTS

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