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Accepted author version posted online: 25 Sep 2017.
Published online: 13 Oct 2017.

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Critical Periods of Storage of the Greenhouse Gases in Polypropylene Syringe

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ABSTRACT

It is convenient to store gas samples containing e.g. carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), in polypropylene syringes before chromatographic analysis. However, there is no study of the integrity of these samples or of what storage condition may be critical. To investigate we filled polypropylene syringes with two standard mixtures of CO_2, CH_4, and N_2O, and stored them at ~2 °C and ~25 °C, and analyzed the contents using gas chromatography. Our results suggest that the storage of gases on the syringe at room temperature is not viable due the CO_2 storage integrity when in low concentration. However, the quantitative integrity of samples is maintained when the syringe is kept refrigerated up to 19 h, period limited by CO_2 and CH_4, taking into account the three gases CO_2, CH_4, and N_2O.

Introduction

The current scientific interest in climate change has provided focus on the emission and measurement of greenhouse gases in the fields of agricultural and environmental science mainly by carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Among the most used methods for quantification of greenhouse gases flow, detaches the sampling through static chambers under different incubation periods, combined with quantification by chromatography (Bowden et al. 1990). This technique allows detection of small magnitude flow in addition to the spatial variability of the emission (Baggs et al. 2002). However, this method involves appropriate procedures during both sampling and storage to preserve sample integrity (Hutchinson and Livingston 2002).

The ideal container for the storage of gaseous samples should have a seal which minimises the diffusion of gas to/from the atmosphere, as well as adsorptive loss on to the body. Plastic syringes are usually used to collect and, consequently, to store gas samples until analysis (Khalil, Mary, and Renault 2004; Rachid et al. 2012; Sainju, Caesar-TonThat, and Caesar 2012), with the inference of a small time but undefined integrity (Rochette and Bertrand 2007). Thus storage periods are usually less than 24 h in polypropylene (Choudhary, Akramkhanov, and Saggar 2002; Fernandes et al. 2002; Rochette and Bertrand 2003) and polystyrene (Costa et al. 2008). Samples can also be stored in gas-tight syringes (Ferrón et al. 2007), or gas bags (Wang et al. 2009). However, storage for up to 48 h has been reported (Parkin and Venterea 2010). In contrast, Rochette and Bertrand (2003) state that polypropylene syringes do not preserve the integrity of gas samples for even short periods of time. Septum-capped vials and vaccum and exetainers® provide secure storage for extended periods of time (Glatzel and Well 2008).

Storage temperature is a major factor, as it has an influence on the volume/pressure of gases (Flaconnèche, Martin, and Klopffer 2001). This can alter the flux of the samples to the atmosphere,

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as well as the contamination inside of the samples. The use polyethylene boxes under cooling at the field sampling until lab determination has been an alternative to reduce that.

We investigated the effect of storage temperature on the integrity of mixtures of CO_2, CH_4 and, N_2O in polypropylene syringes.

Materials and methods

Characterization of gaseous mixtures

Two certified gas samples of different composition were purchased (White Martins®, Ltd., Brazil) which we designate as *high* and *low* (Table 1).

We filled 20 mL polypropylene syringes (BD® Luer-Lok™, U.S.) with the standard gas mixtures using 3-way valves. Samples were stored for 5 periods (6, 18, 24, 48 and 72 h) in either a refrigerator (2 °C) or on the bench at room temperature (25 °C). For each treatment, there were eight replicates.

The gas chromatograph was equipped with two detectors: by electron capture (ECD) that quantifies the nitrous oxide and the flame detector (FID), which quantifies the methane and carbon dioxide indirectly (Shimadzu® GC-2014, Japan). The chromatographic conditions employed were: column packed at 80 °C, FID at 250 °C and EDC detector at 325 °C, with carrier gas N 5.0 and P5 gas (95% argon and 5% methane) for improved efficiency of EDC. To reduces the analytical errors, due to the determinations being on different days, it was established a minimum peak area for each type of gas and standard, to be complemented during daily calibration curves and subsequent determination of the samples.

Experimental design and analysis

It was used a completely randomized design in a factorial design with five storage periods and two storage temperature and eight repetitions. Regression analysis (t-test) to fit the results of the gas concentration as a function of storage period in each gas mixture and temperature was done.

The variation from the certified gas mixtures (supplied by the manufacturer), were used as amplitude of the upper and lower values of each gas mixtures and considered for the limits tolerable in the regression curve (Table 1), and the confidence bands were used to the fitted curve.

Results

CO_2 storage

It was decreased the CO_2 content over the storage period for the *high* concentration mixture, independent of the storage temperature (Figure 1A and 1B). However, the intensity of this decrease was significant different between temperatures of storage. Based on the standard 1 or *high* mixture (1896 ± 39,41 µmol mol^{-1}) and using the mean concentration values for each timing, the period that gives integrity to the sample when kept at room temperature is around 19 h, whereas under refrigeration the CO_2 concentration within the syringes remained stables until the maximum storage period tested (72 hours). Concerning the standard 2, *low* concentration mixture, the results were inverted, in other words, there was an increase of the concentration mixtures with the growth of the storage period,

Table 1. Certified composition of the high and low concentration gas mixtures.

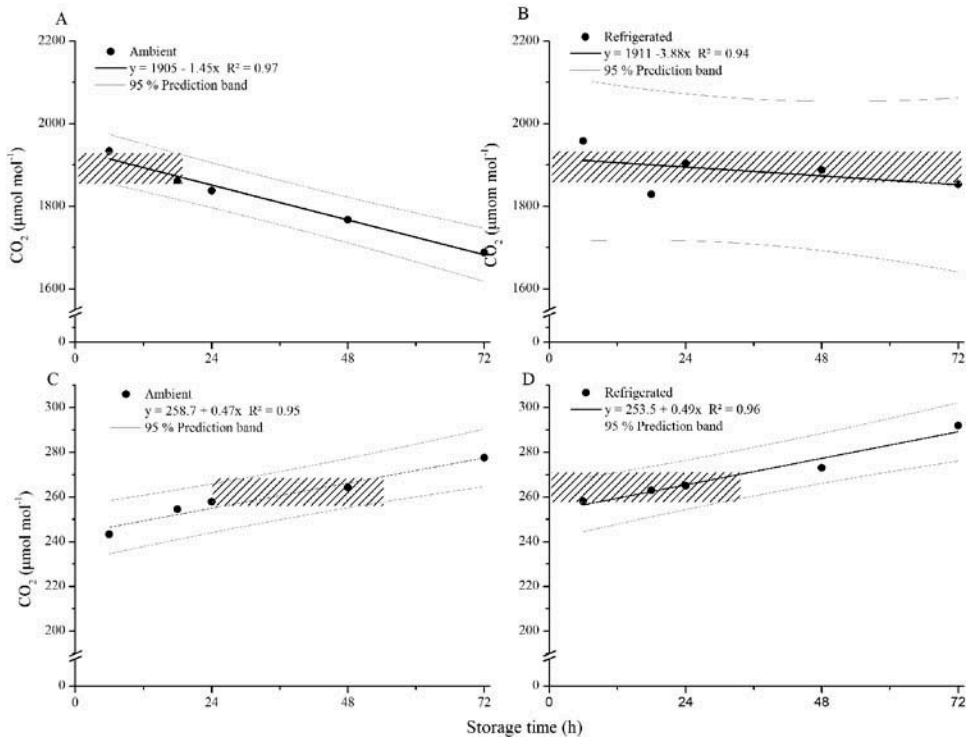|	CO_2 (µmol mol^{-1})	CH_4 (µmol mol^{-1})	N_2O (ηmol mol^{-1})
high	1896 ± 39.41	3.06 ± 0.025	1035 ± 43.98
	± 2.08%	± 2.98%	± 4.25%
low	264 ± 4.83	0.65 ± 0.04	310 ± 12.71
	± 1.83%	± 4.52%	± 3.82%

Figure 1. CO2 contents2 in the syringes storage periods solutions with high concentrations (A, C, E) and low (B, D, F).

with practically the same magnitude between storage temperatures (Figure 1C and 1D). Under the ambient condition, the CO_2 concentration after 6 hours of storage was very low (243 μmol mol^{-1}) and out of the lower limits of tolerance (259.1 μmol mol^{-1}). However, it was observed that over time the values returned to acceptable limits.

N₂O storage

The N_2O behavior was similar of CO_2, with decrease and increase under high and low concentration gas mixtures, respectively. However, under this gas, we found higher limits of storage periods. The critical periods of N_2O storage with *high* concentration mixture were 36 and 71 h in the room temperature and under refrigeration, respectively, representing increase almost double, reaching the upper limit 1078.98 ηmol mol^{-1}. While with the *low* concentration mixture, other than what occurred with the CO_2, the N_2O sample was not compromised in the room temperature, at least by a period less than 31 h, occurring an increase of 7 hours when the sample was kept refrigerated, allowing storage up to 38 h (Figure 2), consisting an slight increase up 22% on period, reaching the lower limit 322.7 ηmol mol^{-1}. The *low* concentration mixtures used had N_2O concentration closer to the atmospheric air when compared to the CO_2, so the gas diffusion was milder than CO_2.

CH₄ storage

In general, the acceptable CH_4 storage periods were lower than those of the other gases. Different from CO_2 and N_2O, the CH_4 gas concentration increased in both standards, except
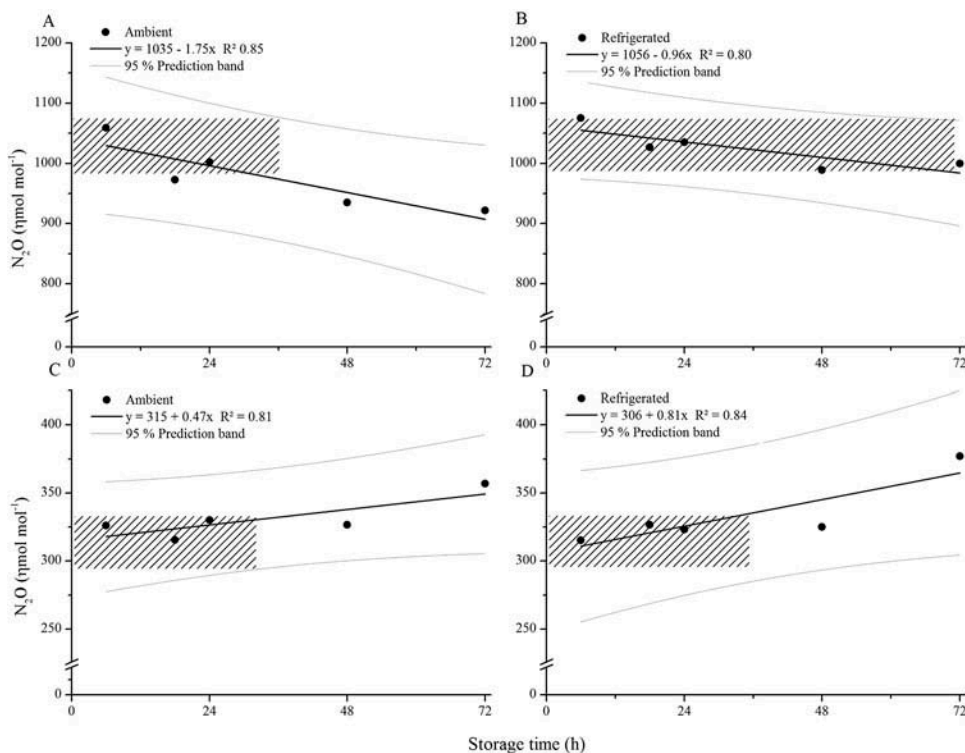
Figure 2. N2O contents in the syringes storage periods solutions with high concentrations (A, C, E) and low (B, D, F).

for *high* concentration mixture under refrigerated, which did not reach the critical limit of this standard until 72 h storage. Under *high* concentration gas mixture, the concentration limit (3.09 μmol mol^{-1}) was reached after 26 h (Figure 3A). For the *low* concentration mixture, as well as the observed on the CO_2 and N_2O, the storage period of CH_4 was lower, as the samples remained to integrate until the periods of 19 and 21 h, for the refrigerated sample condition and storage room temperature, respectively (Figure 3C, D).

Discussion

CO_2 storage

This different behavior between standards occurred because the *high* concentration gas mixture had a huge difference of CO_2 concentration in relation to atmospheric air (1896 μmol mol^{-1} and 400 μmol mol^{-1}), while when we used the sample with *low* CO_2 concentration this difference was smaller (264 μmol mol^{-1} and 400 μmol mol^{-1}). These CO_2 different concentrations were purposely chosen to analyze the reliability of storage period until its determination. Therefore, any small effusion reflects in the significant change of the determination, observed by the high slopes of the curves of CO_2 and the fast change of the concentration according to the storage periods. Thus, it may be inferred that there was gas exchange with the atmosphere, indicating that the seal was not perfect. This process is explained by the gas law, where the effusion rate is inversely proportional to the square root of its density or of its molar mass (Graham 1966). The reduction of values in the *high* concentration mixture occurred due to the diffusion process and consequent standard sample dilution by the entrance of atmospheric gases (Figure 1A, B). The difference between the periods of storage (19 and 72 h), clearly indicates the influence of the storage temperatures in the gas
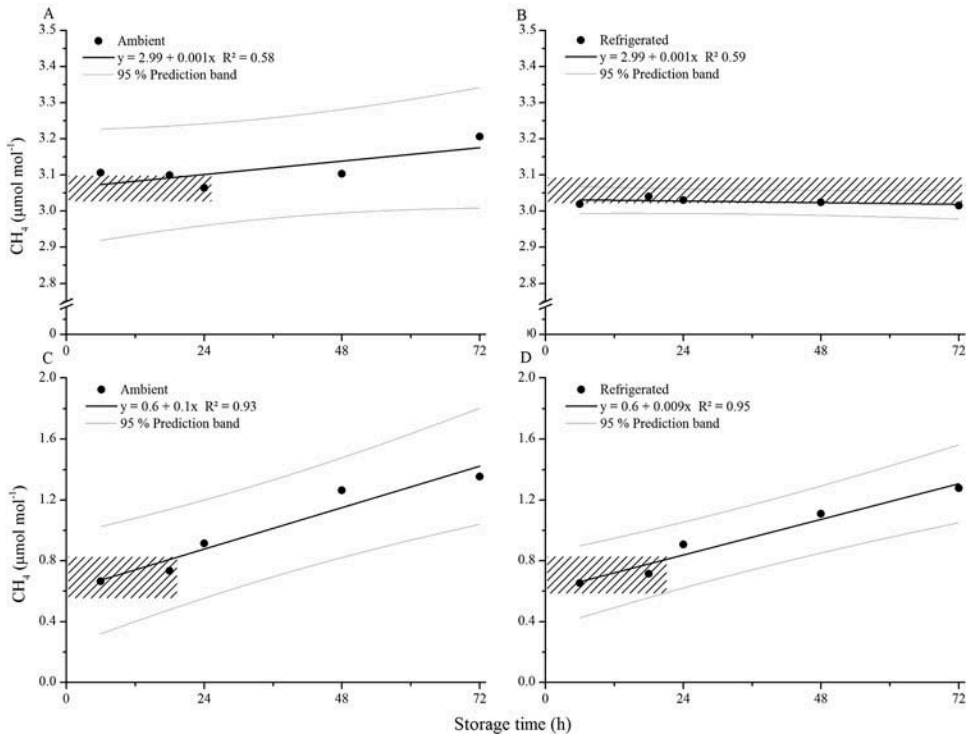
Figure 3. CH4 contents4 in the syringes storage periods solutions with high concentrations (A, C, E) and low (B, D, F).

diffusion either by gas permeability and/or pressure. Whereas in the *low* concentration mixture the result was opposite, precisely because of the entry of atmospheric air into the syringe, which causes the internal concentration of gases tends to match the external concentration. Although this reversed behavior, the difference between storage temperature the periods was lower. These effects also could explain the lower value on the *low* concentration gas mixture kept at 25 °C, evincing that low temperatures are required to keep a viable sample during stored. Thus, the storage of sample non-refrigerated after gas collection limits the CO_2 reliability under low concentration.

N$_2$O storage

It was expected the same behavior between the N_2O and CO_2, due the similar characteristics about the effusive flow of these gases. The less intense process of gas dilution on N_2O compared to CO_2 through the inlet of the atmospheric air was due the closer concentration difference between atmospheric air and the mixtures. Besides, may also have occurred partial N_2O adsorption-desorption of the sample on the walls of the syringes, and/or chemical reactions of N_2O with syringe and piston gasket materials (Rochette and Eriksen 2008). This loss of N_2O smaller than occurred with CO_2 was already reported in study using glass vials to storage gas samples (Lange, Allaire, and Van Bochove 2008). According other studies the loss of N_2O in glass vials is different because the gas exchange is through punctures on the septa and/or through the contact surface between rubber and vial, however, the temperature had no significant effect on the sample (Glatzel and Well 2008).

Despite the distinctions, our data with low critical periods resemble another study with N_2O in polypropylene syringe stored samples (Rochette and Bertrand 2003). This makes infeasible the gas storage in polypropylene syringes under periods up two days (Parkin and Venterea 2010).

CH₄ storage

The lower storage periods of CH_4 can be explained by the law of gases, since the pressure of CH_4 is 2.75 times higher compared to CO_2 and N_2O due to their different densities and critical pressures as effusion rate (Bird, Stewart, and Lightfoot 1960; Fujita 1961) and hence the output or input of CH_4 is facilitated. It may be deducted that it was, firstly, a fast effusion of CH_4 and CO_2 and N_2O to a lesser degree and at the same time an initial dilution of the sample with the entrance of atmospheric gas, which reaches in the smaller critical periods of CH_4 storage. Such principle of flow between the gases is even used for analytical separation columns in gas chromatography due to different retention times. Concerning the higher storage period under low temperature can be explained by the reduction of the gas pressure. Was observed a significant increase of permeability of CO_2 and N_2O under high temperature and pressure in a study of diffusion of gas between the polyethylene polymers (Flaconnèche, Martin, and Klopffer 2001). According to the authors, the Arrhenius law describes the temperature influence over the gas transport coefficients in these polymers. The influences of ambient temperature and pressure were also observed in another study in which it was found that the glass syringes promote less influence on gas pressure compared to those of polypropylene (Deane et al. 2004), however, the large number of samples typically generated in studies evaluating emission of greenhouse gases and the high cost of glass syringes limit its use.

Although many researches on greenhouse gases stipulate the use of polypropylene syringes for sample collection and report that they are determined within 24 hours of the collection (Bayer et al. 2012; Maljanen et al. 2006; Siljanen et al. 2011; Zhang et al. 2012), or transferred within this period for pre-evacuated vials and stored for long periods (Silvennoinen et al. 2008).

Our results suggest that the storage of gases on the syringe at room temperature is not viable due the CO_2 storage integrity when in low concentration. However, when the syringe is kept refrigerated, the sample storage can be done up to 19 h, considering the overall integrity of the three gases CO_2, CH_4, and N_2O. Thus, it is important to emphasize that both the period and the storage temperature interfere with the conservation and integrity of the samples of greenhouse gases inside the polypropylene syringes, independent of its initial concentration, and that despite that the cooling reduces losses of gas, the temperature reduction does not guarantee the quantitative integrity of the samples for a long period.

Acknowledgment

Disclosure Statement

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

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