# Factors affecting air pycnometer performance for its use in the composting process

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This is a pre-print of an article published by Taylor & Francis in Compost science & utilization on 2009, available online: http://www.tandfonline.com/doi/abs/10.1080/1065657X.2009.10702433 [Article DOI 10.1080/1065657X.2009.10702433]."

**Abstract**

Air filled porosity (AFP) is a crucial factor in composting to guarantee aerobic conditions inside the composting matrix. Among the different methods proposed to measure AFP in composting processes, air pycnometry is defined as the most adequate. There is a lack of a standard methodology for air pycnometry utilization for AFP determination in heterogeneous samples as those from composting materials. Air pycnometers currently used for this purpose are custom made instruments operating under different conditions (sample volume, initial pressure, etc.). All factors affecting air pycnometry accuracy in the composting process are related to the proper maintenance and handling of the air pycnometer and the composting sample. In this study, AFP measurements have been performed in more than 50 samples of a wide range of composting materials using two different custom made pycnometers, one of them coupled to a composting reactor allowing in situ AFP measurement. While temperature variation during AFP measurement has been discarded as an error source, the determination of the sample volume of the sample has been found to be a significant factor affecting the air filled porosity calculation. Regarding the initial pressure to use, a compromise between accuracy and practicality has to be established for each pycnometer design as AFP values obtained with diverse initial pressures (from 200 to 500 kPa gauge pressure) were found to present no statistical differences. An initial pressure in the range of 300-500 kPa (gauge pressure) is recommended. In conclusion, there is a need for a standard methodology for AFP determination or prediction at industrial scale. A complete procedure for air filled porosity determination by air pycnometry is also presented in this work.

## Introduction

As it is widely known, the composting process consists of the aerobic decomposition of the biodegradable organic matter present in different types of organic wastes (Haug, 1993). Water and oxygen are necessary for the biological activity of the microorganisms involved in the composting process and their availability is directly related to the porosity and the air filled porosity (AFP) (Ruggieri et al., 2009a). Maintaining adequate AFP levels satisfies the oxygen content requirement to achieve the desired composting conditions and thus, enhancing the biological activity (Agnew et al., 2003). AFP is defined as the ratio of air volume to total volume of the sample (Haug, 1993). Moreover, Eftoda and McCartney (2004) proposed that the total volume of air in a composting matrix can be further divided into inter-particle and intra-particle air voids based on whether air is contained in interstitial voids between particles or in pore spaces within particles, respectively. They distinguished the first one as the readily available air for aerobic microorganisms and named it free air space (FAS), whereas the intra-particle voids represent what they called unavailable air space (UAS), since it is not accessible to microorganisms. According to these authors, the sum of both concepts FAS and UAS results in the total air space (TAS). However, it is difficult to differentiate between FAS and TAS in experimental measures, which causes that most of the authors avoid this difference in their works using the terms FAS and TAS as equivalent (Alburquerque et al., 2008).



Among the different methods used to measure AFP in composting materials such as the particle density method (Oppenheimer et al., 1997) or water pycnometry (Annan and White, 1998), air pycnometry is considered as the most adequate methodology by a wide number of researchers (Agnew and Leonard, 2003; Annan and White, 1998; Eftoda and McCartney, 2004; Oppenheimer et al., 1997; Su et al., 2006).

Air Pycnometry method is fast, typically less than twenty minutes are required for determination (Tamari, 2004), accurate and does not have some negative implications that other methods have. For instance, water pycnometry presents three main disadvantages: potential air entrapment (Blake and Hartge, 1986), the fact that some substance can react or interact with water (Tamari, 2004), and the destruction of the sample during the analysis. An extensive review on the comparison between the utilization of air pycnometry and other empirical and theoretical methods has been recently published (Ruggieri et al., 2009a).

However, there is still no any standard air pycnometry methodology to be applied to heterogeneous solid wastes and different authors present different pycnometer designs and operational conditions. In this framework, a standard procedure is required for AFP analysis in the waste management field.



All factors affecting air pycnometry accuracy in the composting process are related to the proper maintenance and handling of the air pycnometer and the composting sample. The system calibration and the potential deformation of the pycnometer components have been discarded as error sources (Tamari, 2004; Oppenheimer et al., 1997), as the calibration is assumed to be simple and accurate and the selected components of any air pycnometer must be resistant to the applied pressure. Initial pressure used in the pycnometer, filling percentage or volume determination of the sample chamber, repeatability of the measurement, temperature variation and handling of the sample are examples of potential error sources.

The objectives of this work are to study the potential error sources in AFP determination in composting samples by air pycnometry and to suggest the procedures to minimize the uncertainty of AFP obtained values.

# Methods

Air pycnometry principle

Air pycnometry consists of applying Ideal Gas's law (Equation 1) to indirectly measure the volume of the air voids within a solid matrix using air at a known pressure in a known-volume sealed system.

$$PV = n\,R\,T \qquad \text{(Equation 1)}$$

where: P is the system absolute pressure; V is the system volume; n is the total number of mols of gas present in the system; R is the Ideal Gas's constant and T is the system temperature.

Figure 1 represents a general scheme of an air pycnometer that consists of a gas reservoir chamber (air chamber, $V_{gc}$) containing air at a known pressure ($P_1$) and a sample chamber ($V_{sc}$) filled with a known volume sample of material ($V_s$). Both chambers are initially open to atmosphere, and both are connected by an air valve. After the system is completely sealed the connecting valve is opened and compressed air from the reservoir chamber is released to the sample chamber allowing the pressure to equilibrate. A pressure gauge in the reservoir chamber registers the pressure before and after opening the connecting valve. It is assumed that in a closed system with moderate pressures, as in a pycnometer, the temperature remains constant so the term nRT of the ideal gas law remains constant (Agnew and Leonard, 2002). This law can be used to derive the general equation for the pressure-volume relationship under these two pressure regimes by assuming that the relative pressure in the reservoir chamber is initially zero. Equation 2 reflects the above mentioned relationship:

$$P_1 V_{gc} = P_2 V_t \qquad \text{(Equation 2)}$$

where: $P_1$ and $V_{gc}$ are the initial pressure and the volume of the gas reservoir chamber respectively; $P_2$ is the final pressure once the system is equilibrated and $V_t$ is the total volume of the system as described by Equation 3.

$$V_t = V_{gc} + V_{sc} - V_s + V_g \qquad \text{(Equation 3)}$$

where: $V_{sc}$ is the sample chamber volume; $V_s$ is the sample volume in the sample chamber; and $V_g$ is the volume of gas in the sample. Pipes and fittings volumes are included in chambers volumes.

Equation 2 can be rearranged considering Equation 3 to directly obtain the volume of the air voids in the composting sample ($V_g$), resulting in Equation 4.

$$V_g = \frac{(P_1 - P_2)V_{gc}}{P_2} + (V_{sc} - V_s) \qquad \text{(Equation 4)}$$

However, to derive an expression for AFP defined as the ratio of the sample gas-filled volume ($V_g$) to total volume of sample ($V_s$), Equation 4 should be divided by $V_s$ obtaining Equation 5:



$$AFP = \frac{V_g}{V_t} = \frac{(P_1 - P_2)V_{gc}}{P_2 V_s} + \frac{V_{sc}}{V_s} - 1 \qquad \text{(Equation 5)}$$

On the other hand, an empirical relationship of AFP with $P_2$ for a given $P_1$ can be obtained and used for the calibration of the air pycnometer. A calibration curve can be generated by plotting the different $P_2$ readings obtained for different $V_s$ with a known AFP. The experimental data obtained will follow the expression of Equation 6 as well as the theoretical application of Equation 5.

$$AFP = a + \frac{b}{P_2} \qquad \text{(Equation 6)}$$

where: $P_2$ is the final pressure of the entire system and a and b, experimentally determined coefficients.

Equation 6 is then used to obtain the AFP of a sample from the final gauge pressure reading.

## Air pycnometers design and calibration

Two custom made constant volume pycnometers were used in this study. For both pycnometers a digital pressure transducer (model ISE-60, SMC, Vitoria, Spain) was used with a measuring range between 100-1000 kPa and an uncertainty of ±0.2% FS (full scale). The main characteristics of the constructed pycnometers are shown in Table 1.

The design of the first pycnometer (Pyc1) corresponds to a constant volume pycnometer, with a volume of 21 L (Agnew and Leonard, 2002) for both sample and gas chambers. Two temperature probes (R-205, Termo-Metal S.A., Barcelona, Spain) were inserted through the lid of each chamber for temperature monitoring during AFP determination. The use of a sample cup that perfectly fits in the sample chamber is recommended for a better handling of the material, a better maintenance of the pycnometer and a more precise sample volume determination. A 14.85 L sample cup was used in Pyc1 to place the sample for all AFP determinations. The second equipment used in this work (Pyc2) corresponds to a constant volume pycnometer coupled to a pilot composting reactor acting as sample chamber. A detailed description is presented elsewhere (Ruggieri et al., 2009b). In Pyc2, the gas chamber volume (21 L) is smaller than the sample chamber volume (60 L). Configuration of Pyc2 corresponds to one of the recommendations suggested by Tamari (2004), where the author stated that the air chamber volume should be approximately one-third to two-thirds of the sample chamber volume. Moreover, using this configuration, the overall AFP of a composting matrix can be determined in situ and thus the uncertainty caused by sample handling when using ex situ pycnometers is avoided. Figure 2 shows an image of Pyc2 with all its components.

Calibration of the pycnometers was necessary prior to their use. Calibration allows establishing an empirical relationship between AFP and the final pressure in the system ($P_2$) as presented in Equation 6 for a given initial pressure $P_1$. Both $P_1$ and $P_2$ are expressed as gauge pressure throughout the manuscript. Five calibration curves corresponding to five different $P_1$ were generated. Values selected for $P_1$ were 100, 200, 300, 400 and 500 kPa. Parameters a and b in Equation 6 were determined for each pycnometer and for each initial pressure ($P_1$). In order to undertake pycnometers calibration, a material with known AFP content was used. Water is the most widely used material as air dissolved in water can be considered negligible and it is costless (Ruggieri et al., 2009a). For each pycnometer, eleven water subsamples were successively added to the sample chamber filling its volume ($V_{sc}$) from 0 to 100% and measuring the resulting $P_2$ after each addition in order to generate the calibration curve for each initial $P_{1.}$ The exact volumes of all the pycnometers components were determined either by calculating the volume from exactly measured dimensions measured or by using water to fill the void volumes.



### Statistical analysis

For all statistical comparisons the software SPSS 15.0® (SPSS Inc., Chicago, USA) was used. All data were analyzed for the univariate general linear model. Data analysis was performed under a 95% confidence interval. To perform the model, individual subject contrasts were determined (where all possible combinations among all the subjects under study were calculated), then all individual contrasts were subjected to a conjunction analysis with a Bonferrini correction ($p<0.001$) that identified only those areas strictly activated (Draper and Smith, 1966; Freund et al., 1986; Verbeke and Molenberghs, 1997).

### Materials

A broad number of composting materials with different physical characteristics was used for statistical analysis. A brief characterization of the materials used in each specific analysis is explained in the corresponding section. All materials were obtained in Jorba composting plant (Barcelona) and Montcada mechanical-biological treatment plant (Barcelona).

## Results

## Measurement repeatability



The possible variability in pressure measurements with a single material sample was investigated. This part of the study was carried out with four different materials: woodchips, sewage sludge, sewage sludge and woodchips mixture (1:3 sludge:woodchips volumetric ratio) and mature compost. Pycnometer 1 was used for this analysis and initial pressures tested were 100, 200, 300, 400 and 500 kPa. Once the sample was placed in the chamber and the system was perfectly sealed, $P_2$ was determined three times for the same initial pressure, $P_1$, without opening or handling the pycnometer. No variation within the three final pressure ($P_2$) readings was detected considering the pressure transducer accuracy according to the manufacturers. Therefore, the repeatability of the AFP measurements was confirmed for the tested equipment.

## Initial pressure used

Initially, before running any air pycnometry measurement, a simple airtight sealing test must be done by pressurizing the entire system to the maximum $P_1$ used to ensure that $P_2$ remains constant for at least three minutes.

As pointed by Su et al. (2006), the robustness of the air pycnometer method with regard to the initial pressure should be investigated for standardization. However, there is an open discussion about the most adequate initial pressure to use. Agnew and Leonard (2002) established that an initial pressure of approximately 200 kPa provides a good compromise between accuracy and practicality. Likewise, it is believed that higher operating pressures result in more accurate readings - as the higher initial pressure gives values of $P_2$ with lower relative errors - but extreme pressures require impractical designs due to requirements on wall-thickness (Agnew et al., 2003).

Moreover, it is unclear whether the initial pressure used in air pycnometry can discriminate between the determinations of total air space (TAS) or the free air space (FAS) of a matrix. In relation to this last discussion, some authors (Agnew and Leonard, 2003; Eftoda and McCartney, 2004) stated that the initial “high” [200 kPa (abs)] pressures used in their custom made pycnometers may lead to TAS measurements if compared with values of AFP obtained by other methods. When comparing air pycnometry to the traditional solid method, Su et al. (2006) stated that this last one determines the TAS because its aggressiveness since the sample is boiled in the determination (Ruggieri et al., 2009a). On the contrary water pycnometry (The US Department of Agriculture and The US Compost Council, 2001) seems to measure only FAS. This phenomenon has been explained as a result of pressurized air ability to penetrate all voids, including micropores, which water does not reach because of its higher viscosity (Agnew and Leonard, 2003; Eftoda and McCartney, 2002). However, this comparison may lead to an erroneous determination as it has been proved that those traditional methods imply a significant intrinsic error (Ruggieri et al., 2009a). On the other hand, Su et al. (2006) compared different initial pressures for air pycnometry, but these authors used different pycnometers with different sample chamber volumes, from 0.15 L of the commercial pycnometer to 20 L of the custom-made one. Moreover, Su et al. (2006) stated that FAS could be only determined by the commercial air pycnometer used in their study that used a "low" pressure of 134 kPa, in contradiction with the conclusions obtained by Eftoda and McCartney (2004), who stated that the "high" pressure of 70 kPa used in their custom made pycnometer might have determined the TAS value. The need for further research in this subject has been recently highlighted by different researchers (Albuquerque et al., 2008; Ruggieri et al., 2009a).

For this reason a series of AFP measurements were performed in Pyc1 to finally select the working initial pressure. Initial pressures tested were 100, 200, 300, 400 and 500 kPa. The used materials were samples obtained from (i) three windrows processing organic fraction of municipal solid waste (OFMSW, including food and green wastes), sampled at different times during a three-months composting process; (ii) a windrow processing spent mushroom substrate, sampled at different times during a two-months composting process; (iii) different materials and ad hoc prepared mixtures at the laboratory using food waste, woodchips and sewage sludge. Forty-four different samples were used and the experimental data obtained is presented in Table 2.



Results obtained for all the materials at the different initial pressures selected were statistically analyzed in pairs using a univariate model. All possible combinations of $P_1$ values in pairs were considered. AFP values obtained using initial pressures of 200, 300, 400 and 500 kPa were found not to be statistically different, but AFP values obtained using an initial pressure of 100 kPa were found to be statically different from the rest. Table 3 shows the significance of the relationship for initial pressures of 100 and 500 kPa; the analysis was based on estimated marginal means, where the mean difference is significant at the 0.05 level.

AFP values obtained using an initial pressure of 100 kPa were statistically higher than values using the other initial pressures (no reasonable explanation was found for this fact). Considering data on Table 2 this phenomenon was observed in 21 samples and more frequently on samples with average AFP values over 47%. As mentioned before, AFP values obtained with initial pressures of 200, 300, 400 and 500 kPa were found not to be statistically different. However, a common trend of increasing AFP by increasing initial pressure used was observed in samples with average AFP values below 62% (Table 2). A lower AFP leads to higher final pressure readings that are less sensitive to intrinsic errors. For this reason it could be deduced that a higher initial pressure used may lead to AFP values closer to TAS, as pointed by other authors (Tamari, 2004). However, from the statistical analysis presented in this section, it is not possible to precisely establish the initial pressure required to determine TAS. Regarding the possibility stated by Su et al. (2006) by which low initial pressure values may lead to FAS measurements and high values to TAS measurements, it can be concluded that the pressure gauge intrinsic error at low pressure values does not make possible to establish reliable differences with measurements at high initial pressures. Therefore, although theoretically possible, the difference between FAS and TAS could not be practically determined.



In relation to the initial pressure that must be selected, the authors' opinion is in agreement with Agnew et al. (2003), who emphasized the importance of deciding a compromise value between accuracy and practical design. This compromise value specifically depends on some pycnometer characteristics such as the nominal burst pressure of its components and the pressure transducer accuracy. Both Pyc1 and Pyc2 have a maximum pressure design of 500 kPa. Moreover, the pressure transducer readings ranged between 100-1000 kPa (gauge pressure) with an uncertainty of ±0.2 PFS, expressed as a fraction of the highest pressure that the transducer is adjusted to measure. Regarding these two factors, it is expected that the higher $P_1$ selected the lower error associated to the pressure transducer would be, and in this case the maximum $P_1$ selected will be defined by the pycnometer components. For this reason, pressures between 300 and 500 kPa were found to be a good compromise for AFP determination with the used pycnometer.

## Filling percentage of the sample cup

Tamari (2004) studied the theoretical contribution of the sample chamber handling to the uncertainty of sample volume estimation, and concluded that the pycnometry accuracy is greatly improved when the sample chamber is completely filled.



Likewise, an experimental study about the influence of the sample chamber filling percentage on AFP measurement was conducted in Pyc1 using an initial pressure ($P_1$) of 400 kPa (Ruggieri et al., 2009a). Organic materials with a broad range of physical characteristics were selected for this sequence of experiments: sewage sludge, wood chips, chicken manure, sewage sludge and wood chips mixture (1:3 sludge:woodchips volumetric ratio), and mature compost obtained from OFMSW. Measurements on these five materials were undertaken in triplicate for each filling percentage. The sample cup volume filling percentages studied for all materials were 50%, 75%, 85% and 100%.

The statistical analysis showed that values obtained for a 50% filling percentage were statistically different from values obtained with the rest of filling percentages (Table 4). Likewise, values obtained with 75% filling percentage were found to be different from values corresponding to 100%. All other possible comparisons of filling percentages values were not statistically different. Simultaneously, in the analysis of the mean values obtained for each percentage filling factor, an increasing trend for AFP values when decreasing the filling percentage could be observed (Table 4). This could be due to the effect of compaction in the sample analyzed. Regarding this, it can be concluded that at higher filling percentages, the compaction effect will be more evident on AFP values, since it represents more accurately the real situation of the composting matrix in a composting reactor or windrow (Ahn et al., 2008; McCartney and Chen, 2001). Further discussion on the effect of the amount of sample and compaction in AFP measurement is presented later.



Moreover, it is important to highlight the difficulty of measuring the exact volume of the material placed in the sample cup when it is not completely filled. As this volume is needed for AFP determination, the error in sample volume measurement directly influences the final AFP value.

For the reasons stated before, and in agreement with Tamari's previous theoretical study (Tamari, 2004), it is recommended to fill completely the sample cup in order to obtain a representative and repeatable AFP measurement.

## Re-filling the sample chamber for measurement repetition

This section is related to the repeatability of the method that is intrinsically related to the homogeneity and/or representability of the sample under study. A re-filling test of the sample chamber for replicates in the measurement of AFP of several samples was run in order to study the influence of the entire measurement repetition with different sub-samples of the same material, for a maximum filling volume of the sample chamber. Pyc 1 was used in this test. The used materials were homogenized samples of sewage sludge and woodchips mixtures, woodchips and matured compost from OFMSW. These three materials were selected because they present a different particle size and porosity. Statistical analysis showed that results were not statistically different (p=0.348). Thus, re-filling the sample chamber is not necessary in order to obtain a representative AFP value of the studied materials, regardless the material particle size.

## Temperature variation

Another remarkable source of error is represented by the occurrence of non-isothermal conditions in the system. This error is associated with the operation of the pycnometer in a regime not covered by the calibration. Thermal equilibrium between initial and final states of the system (at each measurement point) is required to cancel temperature from the ideal gas law, and to calculate AFP according to Equation 4. Most researchers do not include this aspect and assume that temperature remains constant during AFP determination.

Firstly, it is important to avoid any influence of possible heat sources in the immediate vicinity that may cause the temperature to vary during AFP determination. During the test time (approximately 20 minutes), no significant heat losses through the chamber walls were observed in both pycnometers.

Secondly, during AFP determination, when the connecting valve is open the gas expansion causes the temperature in the system to decrease. In order to study the potential influence of temperature variation on AFP determination, three different approaches were tested and are presented below.

The first approach consists in performing three calibrations at three different temperatures of an inert material (water) in Pyc1. Selected temperatures were 22ºC (common room temperature), 25ºC and 37ºC (the last two temperatures were tested by placing the pycnometer in isothermal chambers). If AFP values obtained for the same initial pressure at the three tested temperatures are compared using a regression curve, a good regression coefficient is obtained as shown in Figure 3. This last observation shows the similarity between them and permits to state that the influence of the temperature in AFP determination is not significant in the covered temperature range. On the other hand, the statistical analysis corresponding to the comparison of the three regression curves shows that slopes of each curve were found not to have statistical differences among them.



The second approach tested the variation of the temperature in both pycnometer chambers during the pycnometry measure for different sub-samples (from 0 to 14.85 L) of water. The results obtained for the traditional theoretical AFP determination (Equation 5) were compared to the theoretical AFP results that take into account the temperature variation by including the temperature in the equation ($T_1$ and $T_2$) during calibration. Both AFP values obtained by these two methods were found to linearly correlate with an $R^2$ = 0.99.

The third test is another statistical approach, where the initial and final temperature values of both air and sample chamber are compared. Temperatures were recorded in both chambers before and after opening the connecting valve. Results showed that initial temperature (at initial pressure) of the air chamber is statistically higher than the other three temperatures tested due to air compression. The maximum difference, considering a confidence interval of 95%, represented 1.75ºC. Since temperature working conditions in pycnometry are usually near to 22ºC or over, this difference means that the maximum deviation in temperature would represent an 8%. This low difference should not affect the AFP measurement since, as previously explained, no significant differences were observed when working in a temperature range from 22 to 37ºC.

According to these considerations it can be concluded that error sources associated to a non-isothermal system can be neglected.

## Pycnometer components and sample handling

During pycnometry measurements, the most handled pycnometer components are the sample chamber and the air valves. The correct handling of the pycnometer components is necessary to maintain the system airtight; otherwise the air filled porosity might be overestimated. A protocol for the correct utilization of the pycnometers used in this study was proposed. The steps that must be followed in order to correctly measure the AFP of a composting material are listed below. Differences are highlighted between AFP ex-situ measurements with Pyc1 and AFP in-situ measurements with Pyc2.



A) AFP ex-situ determination

When determining AFP of a composting sample with a regular pycnometer such as Pyc1, the sample is withdrawn from the composting reactor, windrow or similar, and located in the sample chamber. This intrinsically involves an alteration of the physical structure of the material. For this reason and to obtain a representative measure of AFP, a careful sampling has to be done (Ruggieri et al., 2008). The protocol for a correct utilization of Pyc1 includes the steps that the pycnometer operators must follow and explains in detail how the sample must be handled when it is withdrawn from a composting matrix. These steps are:

1. Pressurize the entire system empty to the maximum pressure to be used and ensure that the pressure reading remains stable for 3 minutes.
2. The sample must be representative. Withdraw a sample volume 1/3 larger than the volume of the sample chamber cup ($V_{sc}$).
3. Place a first subsample of material in the sample cup of a volume equivalent to 1/4 the sample cup volume.
4. Drop the sample cup from a height of 10 cm twice.
5. Place the next two layers of material repeating the same procedure of points 3 and 4.
6. Place the fourth and final layer without compaction.
7. Smooth the top of the sample cup.
8. Place the sample cup in the sample chamber.
9. Close the sample chamber.
10. Pressurize the gas chamber to the corresponding initial pressure (recommended values within 300 and 500 kPa). Once the exact reservoir pressure is set, wait until the pressure reading remains stable for 2 minutes.
11. Open slowly the connecting valve.
12. Wait for at least 3 minutes until pressure equilibrates in all the system.
13. Record the final pressure reading.
14. Slowly release air in the system through the release valve.
15. Close the release and connecting valves and repeat steps 10 to 13. Initial pressure $P_1$ must be equal to the one first selected in step 10.

16. If the value recorded in step 15 is the same than that of step 13, the final pressure reading is considered correct and that unique value must be used for AFP calculation.

17. If the value recorded is not the same than that of step 15, repeat for a third time steps 10 to 13. The value considered correct for AFP calculation is the mean of the three pressure readings.

18. Undertake regularly a calibration following this same procedure. Use water or solids of exact known volume. A calibration curve must be determined for each initial pressure $P_1$ used in AFP measurements.

B) AFP Determination in-situ

As previously pointed, Pyc2 allows in-situ AFP determination of composting matrices, thereby avoiding the uncertainty caused by the sample handling when using a regular pycnometer as Pyc1.



Each time AFP was measured in situ during the composting process, the volume of the composting mass ($V_s$) was determined, as there is a decrease in composting material volume during the process caused by organic matter degradation and material settling. After determining the sample volume by measuring the height of the material in the reactor (previously smoothing the material surface), all pipes of the exhaust gases and inlet air and the temperature probe were disconnected and the reactor was perfectly sealed to resist the applied pressure. At this point, steps 10 to 17 of the ex-situ protocol were followed to operate Pyc2. When AFP determination was completed, the system was allowed to equilibrate to atmospheric pressure and finally all probes and pipes were reinserted and reconnected again. During AFP measurement a decrease in reactor temperature was detected due to pycnometry air entrance. However, temperature quickly recovered once the composting process restarted (data not shown). Berthe et al. (2007) coupled a respirometer to a pycnometer and found that in-situ air pycnometry measurements alter neither the physical properties nor the biological activity of the organic matrix.

## AFP determination in situ versus ex situ

The variation of AFP during the composting process is intrinsically related to the physical characteristics of the initial composting mixture and the biodegradation that occurs in the process, but with sample withdrawal, an additional alteration factor is added. A specific experiment was carried out to study the alteration caused by withdrawing the material from the composting matrix and the difference between AFP measured in-situ and AFP measured ex-situ. A mixture of raw wastewater sludge and woodchips was used. Woodchips were added to sludge to reach initial AFP values of 65%.



AFP measurements along the process were undertaken in five steps as follows: 1) AFP1 was determined in-situ (by Pyc2 configuration); 2) a sample was carefully withdrawn from Pyc2 sample chamber (composting reactor), without homogenization to minimize alterations in the physical structure, and placed in the sample chamber of Pyc1 without additional compaction, that is, ignoring step 4 in procedure; then AFP2 was determined in Pyc1 (ex-situ determination); 3) sample was gathered together with the material in the reactor and all the material was mixed in order to homogenize it; 4) another sample was withdrawn and AFP3 was determined again ex-situ (Pyc1); and 5) all the homogenized material was placed back in the reactor and AFP4 was measured again in-situ (Pyc2). Obtained results are presented in Table 5.

The statistical analysis for a univariate model revealed a significant difference between AFP values obtained in-situ and ex-situ. As can be observed in Table 5, ex-situ values were always higher than in-situ ones. This can be explained by the higher level of compaction of the material. The same phenomenon was observed when filling the sample cup to different levels ('Filling percentage of sample cup' section). This fact highlights the need for a standard methodology that permits the determination or prediction of AFP at industrial scale, where larger volumes of material are exposed to considerable compressive loading and thus ex-situ measurements can overestimate the available AFP (Ahn et al., 2008; McCartney and Chen, 2001).

The mean difference found in the statistical analysis between in-situ and ex-situ AFP values was 2.98%. The 95% confidence interval of this difference was in the range 1.98-3.97%. Thus, although a significant effect of compaction could be noticed when increasing sample chamber volume from 20 (ex-situ, Pyc1) to 60L (in-situ, Pyc2), AFP changed only in 4 units (4% as absolute value). Nevertheless, as pointed before, the air pycnometry method carries an intrinsic error that is related to the pressure gauge precision and the repeatability of the measurements. Therefore, both error sources, the air pycnometry intrinsic error and the error caused by the ex-situ determination, must be compared in order to determine if the ex-situ determination results in a higher uncertainty than that associated to the intrinsic uncertainty of the method.

By analyzing the uncertainty of the pressure gauge used in this work, which is ±0.1 kPa, it could be theoretically estimated that it would have resulted in a maximum absolute error of a ±3.5% in AFP measurement undertaken at the lowest $P_1$ pressure considered in this study (100 kPa). On the other hand, the absolute error associated to the repeatability of the measurement was in the range within 0 - 2.9%, as it was concluded from the statistical analysis of the experimental results presented in section "Measurement repeatability".

From the results previously shown, it can be concluded that regardless the error sources compared in this section, uncertainty values are always in a range between 0-4%, which is actually within the acceptable range considered for Air Pycnometry determination (Tamari, 2004; Su et al., 2006).

## Conclusions

Air filled porosity can be determined by air pycnometry with a maximum absolute error of 4% if the analysis is carried out following the protocols presented in this paper.

The determination of the sample volume was found to be a significant factor affecting the air pycnometry performance. For this reason the filling percentage of the sample chamber is of great importance, as an uncertainty in volume estimation will lead to a great uncertainty in AFP values. Therefore, the complete filling of the sample chamber is recommended.



It was demonstrated that higher initial pressures give higher AFP values, which could be an indication that TAS could be determined at high pressures. On the other hand, values obtained with diverse initial pressures were found to have no statistical differences among them, which could indicate that there are no significant differences between FAS and TAS when studying composting materials. On this sense, the term AFP is confirmed as the most adequate when referring to composting material air spaces, since the difference between FAS and TAS, although theoretically possible, is not clear from the experimental point of view.

For this reason, when selecting the initial pressure to use, a compromise value between accuracy and practical design has to be established for each custom made pycnometer. The most adequate $P_1$ found for the tested pycnometers ranges between 300 and 500 kPa.

The handling of the sample when AFP is determined ex-situ must be done carefully.

Finally, the error source associated to a non isothermal system can be neglected.

**Acknowledgements**

Financial support was provided by the Spanish Ministerio de Educación y Ciencia (Project CTM2006-00315/TECNO).



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**TABLE 1**

Main characteristics of the custom-made pycnometers used.

| Characteristics | Pycnometer<br>Pyc1 | PycnoComposter<br>Pyc2 |
|---|---|---|
| Pycnometer Material | Stainless steel | Stainless steel |
| Gas chamber Volume (L) | 21 | 21 |
| Sample chamber volume (L) | 21 | 60 |
| Sample cup volume (L ) | 14.85 | - |
| Initial pressure (kPa, gauge pressure ) | 100, 200, 300, 400, 500 | 300, 400, 500 |

**TABLE 2**

Air filled porosity experimental data for initial gauge pressure analysis.

| Sample* | AFP (%) | | | | |
|---|---|---|---|---|---|
| | $P_1$=100kPa | $P_1$=200kPa | $P_1$=300kPa | $P_1$=400kPa | $P_1$=500kPa |
| OFMSW | 79.6 | 63.7 | 70.6 | 68.3 | 67.1 |
| | 89.4 | 83.3 | 79.5 | 75.9 | 75.0 |
| | 94.6 | 90.6 | 79.5 | 78.2 | 79.7 |
| | 79.6 | 76.4 | 73.5 | 74.8 | 74.1 |
| | 84.4 | 76.4 | 74.9 | 78.2 | 74.1 |
| | 70.4 | 67.8 | 74.9 | 75.9 | 67.9 |
| | 79.6 | 76.4 | 77.9 | 79.3 | 83.5 |
| | 79.6 | 76.4 | 74.9 | 74.8 | 77.8 |
| | 74.9 | 69.9 | 70.6 | 67.2 | 67.9 |
| | 84.4 | 81.0 | 82.6 | 77.0 | 81.6 |
| | 79.6 | 76.4 | 74.9 | 73.7 | 74.1 |
| | 84.4 | 76.4 | 77.9 | 77.0 | 75.0 |
| | 66.1 | 72.0 | 76.4 | 68.3 | 73.2 |
| | 79.6 | 63.7 | 74.9 | 69.3 | 71.4 |
| | 79.6 | 74.2 | 74.9 | 77.0 | 75.9 |
| | 79.6 | 72.0 | 69.2 | 69.3 | 69.7 |
| | 89.4 | 72.0 | 76.4 | 75.9 | 75.0 |
| | 57.8 | 57.8 | 59.6 | 58.1 | 59.6 |
| | 70.4 | 69.9 | 69.2 | 69.3 | 69.7 |
| | 66.1 | 63.7 | 65.0 | 63.1 | - |
| | 57.8 | 57.8 | 62.3 | 65.1 | 64.5 |
| | 53.8 | 63.7 | 66.4 | 68.3 | 64.5 |
| | 79.6 | 81.0 | 77.9 | 78.2 | 77.8 |

| | | | | | |
|---|---|---|---|---|---|
| MS | 87.0 | 67.3 | 58.4 | 64.0 | 71.6 |
| | 68.1 | 62.8 | 68.9 | 71.2 | 65.1 |
| | 75.3 | 72.0 | 73.3 | 80.4 | 80.8 |
| | 65.4 | 46.3 | 50.6 | 54.6 | 56.0 |
| | 57.1 | 50.2 | 50.6 | 54.6 | 55.0 |
| | 50.8 | 42.4 | 45.1 | 47.1 | 50.2 |
| | 60.4 | 38.7 | 46.9 | 50.8 | 53.1 |
| WC | 74.5 | 76.4 | 74.9 | 76.0 | 75.1 |
| | 85.7 | 81.8 | 83.4 | 86.3 | 86.2 |
| FW | 42.3 | 46.0 | 45.1 | 43.9 | 45.5 |
| FW+WC | 39.5 | 41.7 | 39.5 | 41.8 | 39.9 |
| BS | 23.6 | 23.7 | 24.0 | 26.0 | 26.2 |
| | 34.0 | 35.0 | 36.7 | 36.3 | 35.0 |
| BS+WC | - | 44.5 | 44.1 | 45.4 | 46.1 |
| | 42.3 | 44.5 | 44.1 | 46.8 | 46.1 |
| | 45.2 | 47.4 | 48.0 | 49.0 | 49.0 |
| | 39.5 | 40.4 | 43.2 | 42.5 | 43.2 |
| | 36.7 | 37.6 | 40.4 | 39.7 | 39.9 |
| | 36.7 | 37.6 | 37.6 | 39.7 | 38.2 |
| | 42.3 | 43.1 | 42.2 | 43.9 | 43.2 |
| | 44.5 | 41.7 | 44.1 | 45.5 | 43.2 |

* OFMSW: samples from three different composting windrows treating source-selected organic fraction of municipal solid waste (including food and green wastes); MS: samples from spent mushroom substrate composting windrow; WC: wood chips; FW: food waste; BS: Biosolids; FW+WC: 2:1 volumetric ratio; BS+WC: several volumetric ratios.

**TABLE 3**

Pairwise comparisons for all tested initial gauge pressures ($P_1$).

| Initial pressure for AFP determination ($P_1$) | | Significance |
|---|---|---|
| Independent variable | Dependent variable | (p value) |
| 100 | 200 | <0.001 |
| | 300 | 0.002 |
| | 400 | 0.019 |
| | 500 | 0.030 |
| 500 | 100 | 0.030 |
| | 200 | 0.535 |
| | 300 | 1.000 |
| | 400 | 1.000 |

**TABLE 4**

Pairwise comparisons for tested filling percentage of sample cup and mean AFP values.

| Filling percentage | 50 | 75 | 85 | 100 |
|---|---|---|---|---|
| samples mean | 0.655 | 0.646 | 0.614 | 0.601 |
| | | p values | | |
| 50 | 1 | 1 | 0.071 | 0.007 |
| 75 | | 1 | 0.281 | 0.033 |
| 85 | | | 1 | 1 |
| 100 | | | | 1 |

**TABLE 5**

Variation of Air Filled Porosity measured in-situ and ex-situ. Procedure: 1) AFP1 was determined in-situ (by Pyc2 configuration); 2) a sample was carefully withdrawn from Pyc2 sample chamber (composting reactor), without homogenization to minimize alterations in the physical structure, and placed in the sample chamber of Pyc1 without additional compaction, that is, ignoring step 4 in procedure; then AFP2 was determined in Pyc1 (ex-situ determination); 3) sample was gathered together with the material in the reactor and all the material was mixed in order to homogenize it; 4) another sample was withdrawn and AFP3 was determined again ex-situ (Pyc1); and 5) all the homogenized material was placed back in the reactor and AFP4 was measured again in-situ (Pyc2).



| Day of process | AFP1 in-situ (%) | AFP2 ex-situ (%) | AFP3 ex-situ (%) | AFP4 in-situ (%) |
|---|---|---|---|---|
| 3 | 55.1 | 58.4 | 63.0 | 59.2 |
| 5 | 59.0 | 62.3 | 67.5 | 61.8 |
| 7 | 61.1 | 63.7 | 64.0 | 62.9 |
| 9 | 63.5 | 64.6 | | |

FIGURE 1

Scheme of a constant volume air pycnometer

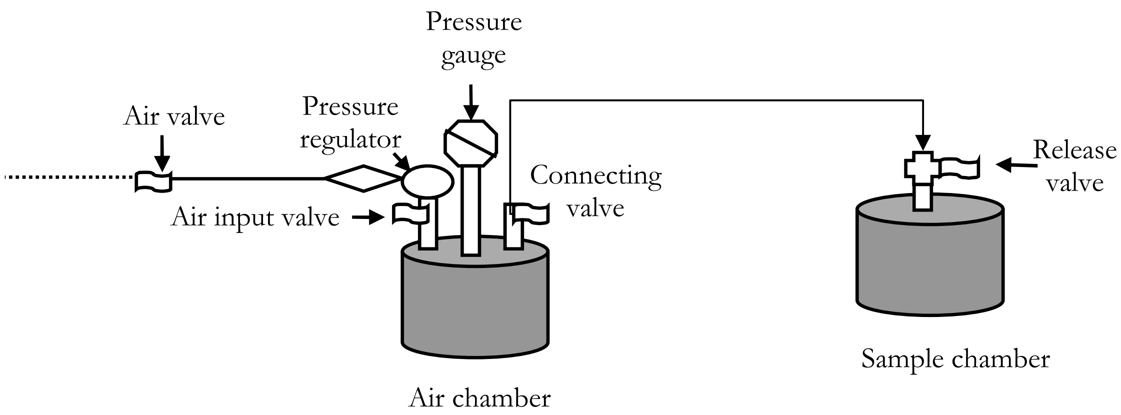

FIGURE 2

Experimental set up: air pycnometer coupled to a composting reactor (Pyc2).

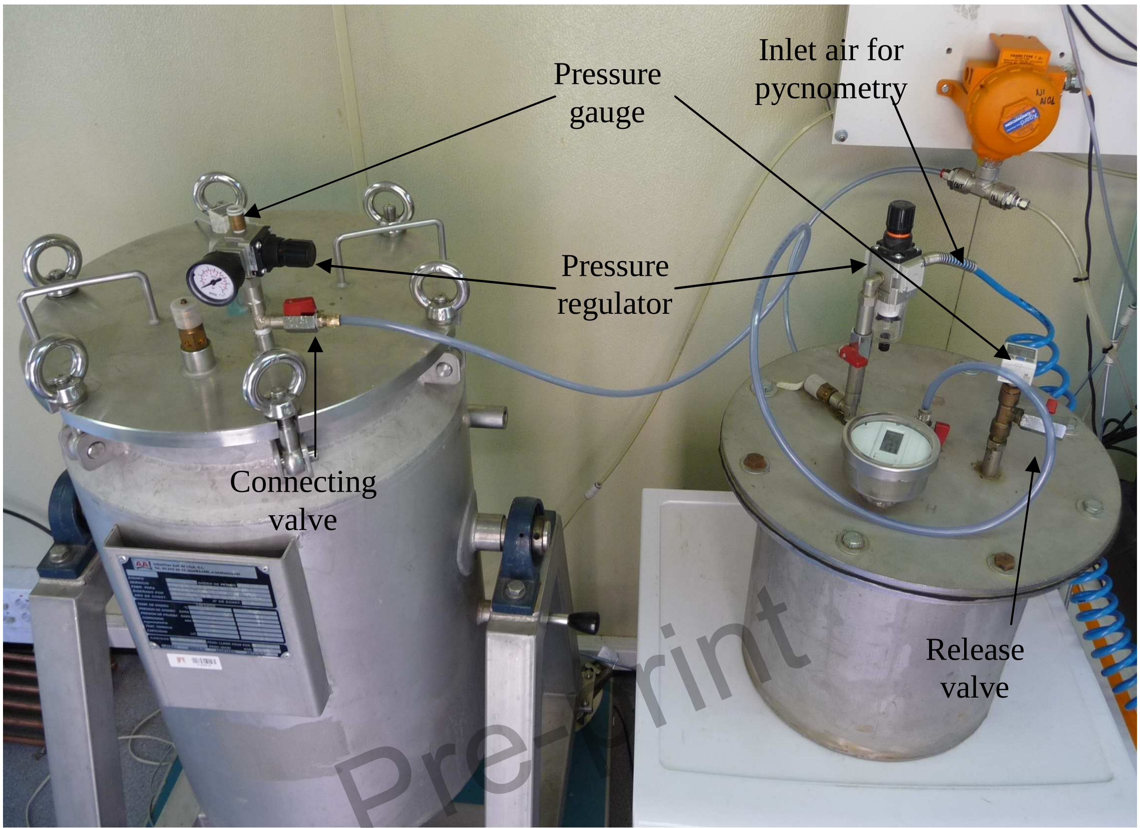

FIGURE 3

Air filled porosity regression curves obtained for two different initial pressures ($P_1$, 400 and 500 kPa) at three different temperatures: 22ºC, 25ºC and 37ºC. Filled symbols correspond to $P_1$ = 400 kPa and blank symbols correspond to $P_1$ = 500 kPa.