Why is the hang-down thermogravimetric analysis (TGA) technology superior to the horizontal and top loading technologies ?

ABSTRACT

- Buoyancy is an effect that modifies the TGA signal and must be subtracted by a blank.
- In a hang down thermobalance, the use of fine suspensions instead of a measuring rod reduces the contribution of buoyancy to the signal.
- Subtracting a small value generates less measurement uncertainty.

INTRODUCTION

Hang-down thermobalances or thermogravimetric analyzers are said to be more stable than their counterparts based on top loading or horizontal thermobalances. In addition to being less sensitive to external vibrations in the case of the former, and to sample transformations in the case of the latter, suspended sample technology owes its measurement quality mainly to the fact that it minimizes the so-called «buoyancy effect».

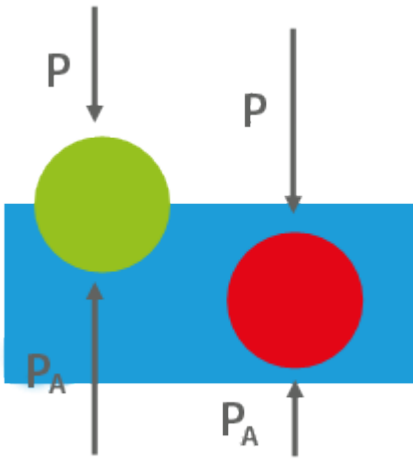
THE BUOYANCY EFFECT

Buoyancy is a force that opposes the weight of an object. It is a significant source of error in thermogravimetric analysis, particularly when the measured mass variations are small.
In TGA analysis, the buoyancy force measured is the one applied to the rod, crucibles and sample immersed in the gas flow. In this case, it is given by the relationship:

$$\text{Buoyancy} = \rho_{gas} \cdot V_{cce} \cdot g$$

With:

- ρ_{gas}: density of carrier gas
- V_{cce}: total volume of rod + crucible + sample
- g: 9.81 m/s^2



Buoyancy is temperature-dependent. As the density of a gas decreases with increasing temperature, buoyancy decreases with increasing temperature.

The phenomenon of buoyancy therefore varies with temperature, **resulting in a pseudo mass increase during heating.**

MINIMIZING BUOYANCY BY SELECTING A SUITABLE ATMOSPHERE

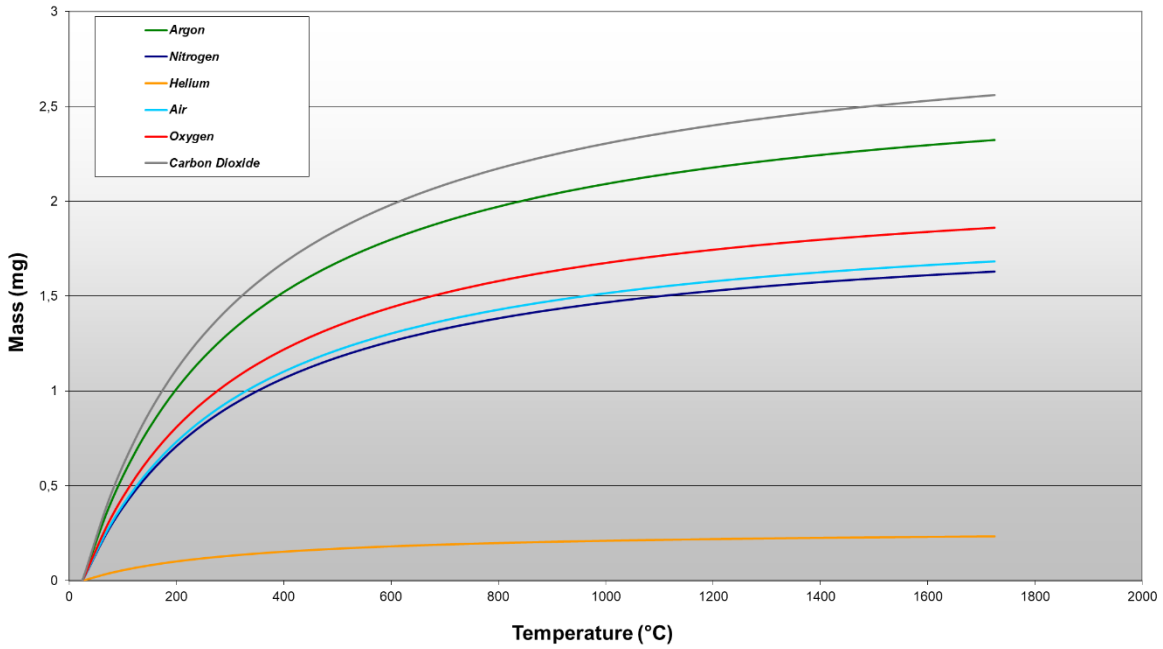


Figure 1 - Modeling of the effect on the TGA signal due to the buoyancy variation with temperature
Conditions: top-loading TGA; conventional TGA rod; small (130µl) platinum crucible; N2, Ar, He, air, O2 or CO2 flow at 20ml/min.

The choice of a l**ow-density gas such as helium** is a first solution to limit the effects of buoyancy variation. However, it is not suitable for all situations: firstly, it is inert, which is undesirable for certain measurements. Secondly, its thermal conductivity is very high, and can lead to disturbances in the temperature control system, particularly at low temperatures. Finally, helium cylinders can be very expensive.

MINIMIZING BUOYANCY BY USING SUSPENSIONS

To hold the sample crucible in the furnace, the hang-down thermogravimetric analyzer technology uses a series of thin and rigid pieces of wire less than a millimeter in diameter (see Figure 2). The wire pieces – also called suspensions - can be made of various metals or ceramics. The crucible can be hooked directly onto one of these suspensions by means of a simple handle, which is also thin. This avoids the use of massive measuring rods, whose stem and crucible support plate occupy a volume around ten times that of suspensions. This has a direct impact on the volume Vcce, and therefore on the buoyancy (see Figure 3).

Figure 2 - Examples of sample-holding systems and the volumes they occupy in the furnace

Themys One - Rod and crucible – top loading

V_{cce} = 1130 µl

Themys - Suspensions and crucible – hang-down

V_{cce} = 185 µl

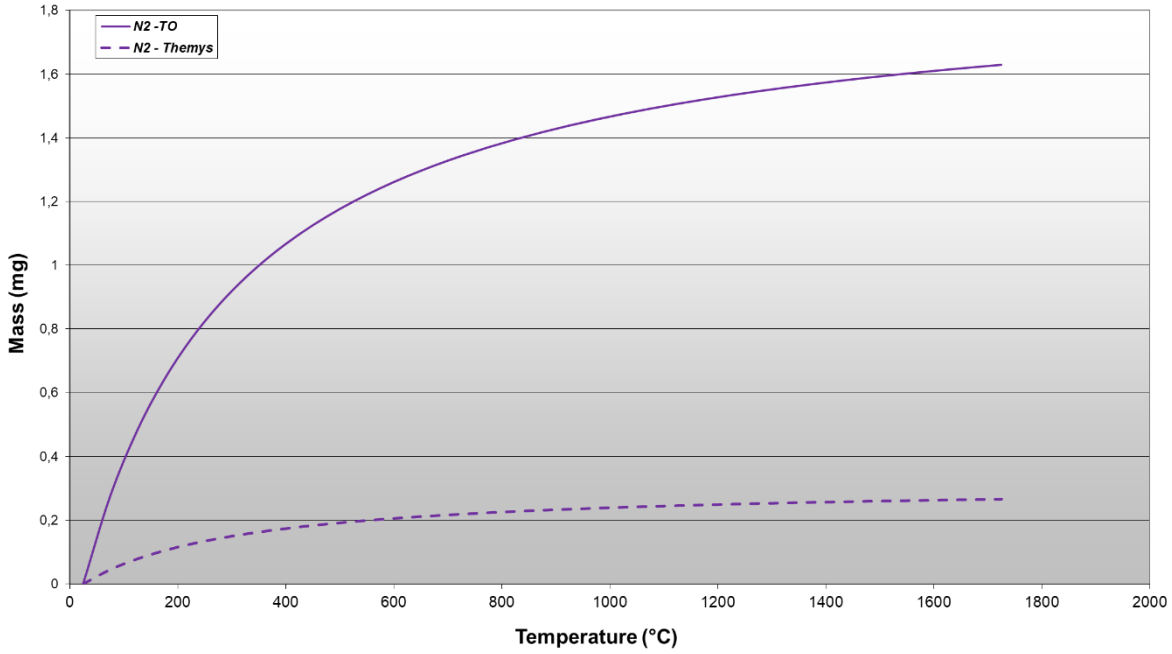


Figure 3 - Modeling of the effect on the TGA signal due to the buoyancy variations for a conventional TGA rod and for a set of suspensions, under a flow of nitrogen.

Conditions: Top loading TGA (TO) or hang-down TGA (Themys); small platinum crucible (130µl); N2 flow at 20ml/min.

BLANK SUBTRACTION AND UNCERTAINTY PROPAGATION

To accurately determine a mass change in thermogravimetric analysis, it is therefore necessary to subtract the contribution of the buoyancy effect. This is achieved by carrying out a «blank» measurement under identical experimental conditions to the initial measurement, but without the sample. The user thus obtains a signal that integrates the full contribution of buoyancy but without the variation in sample mass. The second signal is then subtracted from the first, using the processing software of the thermogravimetric analyzer.

Measurement 1 with sample	$\mathbf{\Delta m + A_1}$
Measurement 2 without sample	$\mathbf{A_2}$
Measurement 1 – Measurement 2	$\mathbf{\Delta m + A_1 - A_2 = \Delta m}$

With :

- Δm = true sample mass variation during measurement 1
- A_1 = apparent mass variation due to buoyancy during measurement 1
- A_2 = apparent mass variation due to buoyancy during measurement 2

However, when the mass variation value to be measured is low, it is necessary to take into account the measurement uncertainty, i.e. the deviations in results due to the repeatability and measurement accuracy of the instrument and method.

Measurement 1 – Measurement 2	$\mathbf{\Delta m + d\,(\Delta m) + A_1 + d(A_1) - [\,A_2 + d(A_2)\,]}$
Measurement 1 – Measurement 2	$\mathbf{\Delta m + d\,(\Delta m) + [\,A_1 - A_2\,] + [\,d(A_1) - d(A_2)\,]}$

With :

- $d\,(\Delta m)$ = uncertainty of the true sample mass variation measurement
- $d(A_1)$ = uncertainty of the apparent mass variation due to buoyancy during measurement 1
- $d(A_2)$ = uncertainty of the apparent mass variation due to buoyancy during measurement 2

Uncertainties $d(A_1)$, $d(A_2)$ and $d(\Delta m)$ include repeatability and accuracy errors. They are proportional to the measured value, which is why they are often expressed as a percentage of this value. So the higher the values of A_1, A_2 or Δm, the greater $d(A_1)$, $d(A_2)$ and $d(\Delta m)$ will be too.

This means that if the measurement conditions involve significant buoyancy effect, then $d(A_1)$ and $d(A_2)$ are large and can be very different from each other. Thus the subtraction $[\, d(A_1) - d(A_2) \,]$ may end up being of the same order of magnitude as Δm. As a result, a large uncertainty is introduced into the measurement of mass variation.

On the contrary, if measurement conditions are optimized to minimize buoyancy, then $d(A_1)$ and $d(A_2)$ are very small, and their subtraction $[\, d(A_1) - d(A_2) \,]$ will have little impact on measurement uncertainty.

This is how the use of a hang down thermobalance improves the results quality in thermogravimetric analysis.

CONCLUSION

In summary, buoyancy affects the thermogravimetric analysis (TGA) signal and must be subtracted using a blank to ensure accurate measurements. Buoyancy arises from the upward force exerted by the surrounding gas on the sample, which can distort the weight measurement. In a hang-down thermobalance, using thin suspensions instead of a solid measuring rod reduces the buoyancy contribution to the signal because fine suspensions cause less gas displacement. This reduction in displacement minimizes the buoyant force acting on the system.

Consequently, subtracting smaller buoyancy values decreases measurement uncertainty, leading to more precise and reliable TGA results.