GASCATENA · TECHNICAL BACKGROUND

Air buoyancy and ambient conditions

From pressure, temperature and humidity at the balance to air density, buoyancy and the uncertainty of a weighing, and the role of the Aura ambient sensors.

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A balance in a gas laboratory never weighs in a vacuum. The air around a cylinder pushes it upwards, and that push changes with the barometric pressure, the temperature and the humidity of the room. In gravimetric preparation according to ISO 6142-1, where a few grams of a component may be added to a cylinder of several kilograms, air buoyancy is one of the effects that decide how small the uncertainty of the composition can honestly be. This document follows the chain from the ambient conditions at the balance to the air density, from the air density to the balance reading, and from the reading to the mass of gas added and its uncertainty. It explains why a sensor next to the balance matters, what GasCatena does with the readings of the Aura1 today, and what is planned. GasCatena is in development; the release is expected in early 2027.

Why a balance does not read mass

Two forces on the pan

A cylinder on the pan of a balance is subject to two forces: gravity pulls it down, and the buoyancy of the air it displaces pushes it up. The balance does not measure the mass of the cylinder, but the net result of the two.

$$
\begin{aligned}
F_{grav} &= m \cdot g && \text{(gravity)} \\
F_{buoy} &= \rho_a \cdot g \cdot V && \text{(buoyancy of the displaced air)} \\
F_{reading} &= F_{grav} - F_{buoy} = (m - \rho_a \cdot V) \cdot g
\end{aligned}
$$

Here m is the mass of the complete cylinder with its valve, g the local acceleration of gravity, ρ_a the density of the air at the balance and V the **external** volume of the cylinder: the volume of air it displaces, including the wall and the valve. The balance converts the force into a mass through its calibration.

Note the minus sign. Denser air means more upward force and therefore a lower reading. A cylinder weighed on a dry, cold day with a high barometer reads lighter than the same cylinder on a warm, humid day with a low barometer.

The effect is not small. A typical 5 L aluminium cylinder has an external volume of about 5.25 L. At an air density of 1.2 kg/m³ it displaces about 6.3 g of air, so the balance reads some 6 g less than the true mass of the cylinder. Compared with an addition of a few grams of a minor component, that is large. Fortunately, most of it cancels in the way an addition is determined, as the next chapters show.

The weights behind the calibration

An electronic balance is calibrated with reference weights whose mass is expressed as *conventional mass* (OIML D 28), defined for weights of density 8000 kg/m³ in air of density 1.2 kg/m³. The buoyancy of the weights is thereby part of the balance calibration. What the calibration does not cover is the buoyancy of the object on the pan: a steel weight of 7 kg displaces less than 0.9 L of air, an aluminium cylinder of the same mass about six times more. The buoyancy of the cylinder, and above all its variation, is the subject of this document.

The external volume of the cylinder

Buoyancy is proportional to the volume of air the cylinder displaces, not to its nominal water capacity. GasCatena records it per cylinder as a value entered by the laboratory, rather than deriving it: the internal volume plus the empty mass divided by the density of aluminium overestimates it considerably (about 7.8 L for a 5 L cylinder of 7.5 kg), because the heavy valve and fittings add mass but displace little air. A measurement, or a small allowance of a few per cent on the internal volume, is more realistic.

From ambient conditions to air density

The equation

The density of moist air depends on three quantities that can be measured at the balance: the barometric pressure p, the temperature t and the relative humidity h. GasCatena uses a compact empirical form of the air density equation:

```
ρₐ = 0.001 · (K_p · p − K_h · h · exp(K_T · t)) / (273.15 + t)

K_p = 3.4848     K_h = 9.024     K_T = 0.0612

ρₐ in kg/m³, p in Pa, t in °C, h in %RH
valid for 90 kPa to 110 kPa, 10 °C to 30 °C, below 80 %RH
```

The authoritative reference for the density of moist air is the CIPM-2007 equation. The compact form agrees with it within the working range of a weighing room, and is well suited to buoyancy in a difference weighing, where what matters is the *change* in air density over a few minutes rather than its absolute value. Readings outside the validity window fall outside the range in which the model is used.

Sensitivities

Splitting the equation into a dry-air term and a humidity term makes the sensitivities easy to read. The humidity term is negative because water vapour (18 g/mol) is lighter than dry air (about 29 g/mol). At 101 325 Pa, 20 °C and 60 %RH:

```
ρ_dry = 0.001 · K_p · p / (273.15 + t)                 = +1.20449 kg/m³
ρ_hum = −0.001 · K_h · h · exp(K_T · t) / (273.15 + t)  = −0.00628 kg/m³
ρₐ    = ρ_dry + ρ_hum                                  =  1.19821 kg/m³

∂ρₐ/∂p = ρ_dry / p                       = +1.189 · 10⁻⁵ kg/m³ per Pa
∂ρₐ/∂t = K_T · ρ_hum − ρₐ / (273.15 + t)  = −4.472 · 10⁻³ kg/m³ per °C
∂ρₐ/∂h = ρ_hum / h                       = −1.047 · 10⁻⁴ kg/m³ per %RH
```

Change at the balance	Change in air density	Relative change
Pressure +1 hPa	+0.0012 kg/m³	+0.10 %
Temperature +1 °C	−0.0045 kg/m³	−0.37 %

Change at the balance	Change in air density	Relative change
Relative humidity +1 %RH	−0.0001 kg/m³	−0.009 %

A change of 1 °C has the same effect as almost 4 hPa in barometric pressure. Humidity matters least: even 10 %RH moves the air density by less than 0.1 %.

Difference weighing: what remains of buoyancy

Only the change counts

An addition is determined as a difference: the cylinder is weighed before and after a filling step, and the mass of gas added follows from the two readings. Writing W for a balance reading expressed in mass, the buoyancy relation of the previous chapter gives:

```
Δm = (W_after − W_before) + V · (ρ_after − ρ_before)
```

If the air density is the same at both weighings, the buoyancy term vanishes completely: the 6 g of displaced air is in both readings and cancels in the difference. What remains is the external volume multiplied by the **change** in air density between the two weighings. That residual is the buoyancy effect on an addition, and it is the subject of the uncertainty evaluation.

The external volume itself can also change between the two weighings, because a cylinder expands slightly under pressure. That is a separate, smaller effect, treated in the chapter on large pressure steps.

What drives the change

Around the mean conditions of the two weighings, the change in air density can be linearised. Written with the ideal-gas form of the density of air:

```
ρ_after − ρ_before ≈ (M / (R · T̄ · Z)) · Δp − (p̄ · M / (R · T̄² · Z)) · ΔT
```

with M the molar mass of air, R the molar gas constant, Z the compression factor of air, $\bar{T}$ the mean absolute temperature and $\bar{p}$ the mean pressure. Two observations follow, and both matter for the choice and use of sensors:

- The dominant term is the **pressure difference** Δp. Its prefactor needs the absolute temperature, but not the absolute pressure. A barometer that reads consistently 5 hPa too high has that error in both readings, and it cancels in Δp.
- The absolute pressure appears only in the prefactor of the temperature term, which is small when the room is well conditioned.

In short: for a buoyancy correction, temperature enters in absolute terms, pressure only as a difference.

Substitution weighing

When the cylinder is weighed against a reference cylinder of similar external volume, both see the same air, and the buoyancy term shrinks to the effect of the difference in their volumes. The physics is the same, the residual smaller. This document considers the general case of direct difference weighing.

How large is the effect

Over a whole preparation

Over a preparation of about an hour, the conditions in a weighing room can be shown to stay within about ± 10 hPa in pressure, ± 5 °C in temperature and ± 10 %RH in humidity around 101 325 Pa, 20 °C and 60 %RH. Combined in quadrature according to the GUM, that envelope corresponds to $u(\rho_a)$ = 0.0254 kg/m³, about 2.1 % of the air density. Temperature contributes about 78 % of the variance, pressure 22 %, humidity almost nothing.

Applied to a single addition, this envelope would mean about 133 mg for a 5.25 L cylinder, or 0.044 % of an addition of 300 g. That is far too pessimistic: between two weighings a few minutes apart, the conditions do not run through the whole band of an hour.

Per filling step

For a difference weighing, the relevant variation is the change between the two weighings of one filling step. With assumed per-step changes of 1 hPa, 0.5 °C and 5 %RH:

$$u(\Delta\rho) = \sqrt{\left[(1.189\cdot10^{-5} \cdot 100)^2 + (4.472\cdot10^{-3} \cdot 0.5)^2 + (1.047\cdot10^{-4} \cdot 5)^2 \right]} = 2.59 \cdot 10^{-3}\ \mathrm{kg/m^3}$$

$$u(\Delta m) = V \cdot u(\Delta\rho) = 0.00525\ \mathrm{m^3} \cdot 2.59 \cdot 10^{-3}\ \mathrm{kg/m^3} = 13.6\ \mathrm{mg}$$

Relative to the addition, that is 0.0045 % of 300 g, 0.014 % of 100 g and 0.040 % of 34 g. Temperature contributes about 75 % of the variance, pressure 21 % and humidity 4 %. Temperature is the most sensitive quantity, and its stability between the two weighings of a step should be demonstrated rather than assumed.

Drift multiplied by time

A band and a rate of change are different things. Over an hour, the pressure may lie anywhere within ± 10 hPa; between two weighings it only moves by its drift rate multiplied by the time τ between them. A refined conservative bound therefore takes the per-step change of each quantity x as drift × τ, capped at its stability band. Below the caps, the time moves outside the square root and the bound becomes one constant per room:

$$\Delta x = \min(\mathrm{drift}_x \cdot \tau\ ,\ \mathrm{band}_x)$$

$$u(\Delta m) = V \cdot \sqrt{\left[\Sigma\ (\partial\rho_a/\partial x \cdot \Delta x)^2 \right]} \approx k \cdot V \cdot \tau$$

$$k = \sqrt{\left[(\partial\rho_a/\partial p \cdot \mathrm{drift}_p)^2 + (\partial\rho_a/\partial t \cdot \mathrm{drift}_t)^2 + (\partial\rho_a/\partial h \cdot \mathrm{drift}_h)^2 \right]}$$

With drift rates of 20 Pa/min, 0.05 °C/min and 0.2 %RH/min, k is about $3.3\cdot10^{-4}$ kg/m³ per minute: 0.33 mg per litre of external volume per minute. For a 5.25 L cylinder and five minutes between the weighings, u(Δm) is about 8.6 mg, or 0.0029 % of an addition of 300 g; the caps only come into play after some 40 to 50 minutes. That reproduces a familiar figure: a flat additional term of 0.003 % for air buoyancy, found in an earlier study of the weighing process at additions of about 300 g. The flat percentage is the per-step bound evaluated at one working point.

Constant in mass, not in percentage

The buoyancy uncertainty of a step, V · u(Δρ), depends on the external volume and the change in air density, not on how much gas is added. In absolute mass it is roughly the same for every step; as a percentage it scales with one over the added mass. A flat percentage set at 300 g therefore fits the major components best; for small additions, a per-step evaluation gives a larger relative contribution. When a laboratory moves from a flat term to a per-step evaluation, the uncertainty of major components goes down and that of minor and trace components may go up. That is the point of the evaluation: the budget then follows the physics of each step.

Assume, measure, correct

Three levels

For air buoyancy, as for many uncertainty sources, there are three levels of treatment:

- **Assume.** A conservative term from a study of the weighing process: the flat 0.003 % or the drift-times-time bound.
- **Measure and demonstrate.** Record the conditions at every weighing and scale the bound to the variation that actually occurred. No correction, but the uncertainty rests on evidence.
- **Measure and correct.** Correct each addition for the actual change in buoyancy; only the measurement uncertainty of the correction remains.

The correction

With pressure, temperature and humidity measured at the weighing before and the weighing after a filling step, the air density at both moments follows from the equation, and the addition can be corrected:

```
Δm_corr = (W_after − W_before) + V · (ρ_after − ρ_before)
```

Why the residual uncertainty is so small

At first sight, the uncertainty of a correction is that of two air densities, each with the full calibration uncertainty of the sensors. It is not, because the two densities come from the same sensors: a systematic offset is present in both and cancels in the difference. Splitting each reading into a shared offset (u_sys) and independent short-term noise (u_rand), with sensitivity s:

```
u²(Δρ) = u²(ρ_before) + u²(ρ_after) − 2 · cov(ρ_before, ρ_after)
       = 2 · s² · (u_sys² + u_rand²) − 2 · s² · u_sys²  =  2 · s² · u_rand²

summed over the three quantities:
u²(Δρ) = 2 · [ (∂ρₐ/∂p · u_p)² + (∂ρₐ/∂t · u_t)² + (∂ρₐ/∂h · u_h)² ]
u(Δm)  = V · u(Δρ)
```

The inputs are therefore not the absolute accuracies of the sensors, but their short-term repeatability over the minutes between two weighings. That is exactly where modern MEMS sensors are strong. The table gives, as an example, the sensors currently fitted in the Aura1; another sensor can take their place, and its own data sheet values then apply:

Quantity	Example sensor (current Aura1)	From the data sheet	Short-term u used (1σ)
Pressure	Bosch BMP390	noise 0.9 – 2.0 Pa RMS; relative accuracy ± 3 Pa; absolute accuracy ± 50 Pa, which cancels	3 Pa
Temperature	Sensirion SHT45	repeatability 0.04 °C (3σ); accuracy ± 0.1 °C	0.013 °C
Relative humidity	Sensirion SHT45	repeatability 0.08 %RH (3σ); accuracy ± 1.0 %RH	0.027 %RH

GasCatena applies the same principle here as elsewhere in its budget: the larger one counts. For each quantity it uses the larger of the data sheet value and the standard deviation of the mean measured by the Aura1 at that weighing (SD/√n). A sensor that happens to be quieter than its data sheet never leads to a smaller uncertainty than the data sheet supports.

Worked example

At 101.3 kPa, 20 °C and 45 %RH, for a cylinder with an external volume of 5.25 L:

```
pressure:     1.19 · 10⁻⁵ · 3       = 3.6 · 10⁻⁵ kg/m³
temperature:  4.38 · 10⁻³ · 0.013   = 5.7 · 10⁻⁵ kg/m³
humidity:     1.05 · 10⁻⁴ · 0.027   = 0.3 · 10⁻⁵ kg/m³

u(Δρ) = √2 · √(3.6² + 5.7² + 0.3²) · 10⁻⁵ = 9.5 · 10⁻⁵ kg/m³
u(Δm) = 0.00525 m³ · 9.5 · 10⁻⁵ kg/m³ = 0.50 mg
```

That is less than 0.0002 % of an addition of 300 g, against 8.6 mg for the conservative bound and 13.6 mg for the assumed per-step variation: more than an order of magnitude smaller. Notably, the repeatability of the temperature sensor dominates the residual, not the noise of the barometer: a barometer without an individual calibration is amply sufficient, because its offset cancels and its short-term noise is small. The external volume enters multiplied by a small change in air density, so its own uncertainty has only a second-order effect; in this residual it is treated as exact.

Additional terms from process studies, such as the term for air buoyancy, are added linearly to the uncertainty of each component, not in quadrature: a change in air pressure acts as a systematic effect shared by the steps of a preparation, and linear addition treats it conservatively as fully correlated.

What a correction does not do

It does not correct the disturbance of a warm cylinder on the balance, nor the expansion of the cylinder under pressure; both are treated in the next chapter. Nor does it replace the calibration of the balance: the mass, and with it the traceability of the composition, rests on the balance and its calibration. The ambient sensors refine the weighing; they do not carry it.

Heat after a large pressure step

A second disturbance

Some recipes require a large amount of one component, typically the balance gas, which means a large and fast pressure increase, for example from about 10 bar to about 100 bar. Compression heats the gas and the cylinder wall: measurements with a thermal imaging camera showed a rise of 3 °C to 6 °C within 7 to 8 minutes, followed by a slower cooling phase, with the cylinder approximately back at its starting temperature after about 20 minutes. The pressure also expands the cylinder slightly.

A warm cylinder on the balance sets up convection in the surrounding air and a locally disturbed air density. The resulting weighing error cannot be calculated from ambient sensors, because the room air is not what changed. The only remedy is to wait until the cylinder is back in equilibrium with its surroundings.

Effect	Cause	Size	Correctable?
Convection around a warm cylinder	compression heating, 3 °C to 6 °C	a weighing error that cannot be modelled from the ambient conditions	No; wait until the cylinder has cooled
Pressure deformation	internal pressure of about 100 bar	about 20 cm³ (0.38 % of the volume), some 24 mg of buoyancy, about 0.008 % of an addition of 300 g	In principle, from a pressure-volume model; small
Thermal expansion	warming of about 3 °C	about 1 cm³	Negligible

The effect that could be corrected, thermal expansion, is negligible; the effect for which one waits, convection, cannot be corrected.

It is the pressure step, not the component

The disturbance depends on how far and how fast the pressure rises in a filling step, not on which gas is added. Methane is a common case because it is often the balance gas, but in a mixture of carbon dioxide in nitrogen with 80 % nitrogen, it is the nitrogen step that needs the cooling wait.

What GasCatena does

- A **cooling wait** after a filling step with a large pressure increase, before the cylinder is weighed. The trigger is the pressure increase of the step, regardless of the component; the threshold and the waiting time are configurable.
- An **additional uncertainty term** for the residual disturbance after cooling, placed on the pressurised balance component.
- A **stability check** on every weighing: unstable weighings, and weighings in the wrong direction, are rejected on the spot.

Planned: measuring instead of waiting by the clock

A fixed waiting time assumes equilibrium; a measurement can demonstrate it. The planned extension is a sensor for the temperature of the cylinder wall, contactless (infrared) or in contact: the weighing is released as soon as the difference between cylinder and ambient air is below a threshold, and the residual disturbance is quantified from that measured difference rather than from the time elapsed. For infrared, the surface matters: on bare, shiny aluminium (emissivity about 0.05 to 0.1) the reading is unreliable; on a painted or anodised surface (0.7 to 0.95) or a high-emissivity patch, it works.

The pressure deformation is deterministic, and could be corrected with a thin-wall model of the cylinder once the compliance of a cylinder type is known; given its size, this is rarely decisive.

Sensors at the balance: the Aura1 and the Aura2

Two channels, three roles

A weighing is disturbed through two physically different channels: **channel A**, a change in the air density of the room between the two weighings of a step, which can be corrected from measured pressure, temperature and humidity; and **channel B**, convection around a warm cylinder, which cannot be corrected and can only be allowed to die out. A sensor can serve a weighing in three ways, and the role determines what is required of it:

Role	What the sensor does	Channel	What counts in the sensor
Input to a correction	its readings enter the equation that corrects the result	A	absolute temperature; pressure only as a difference; humidity, small
Readiness gate	it decides *when* a weighing is valid, without entering the result	B	relative accuracy: a shared offset between cylinder and air sensor largely cancels
Adaptive bound	its logged readings scale a conservative term to the variation actually measured	A	stability and resolution

For a correction that enters a certified result, a laboratory will want its inputs calibrated in the measure in which they enter: the temperature in absolute terms, the pressure as a difference. The temperature and humidity sensor of the Aura1 is calibrated by its manufacturer, without an individual certificate; a calibration of the Aura1 with a

Qualimetric certificate for temperature, humidity and pressure is available on request. A periodic check of the barometer against a reference barometer is a straightforward way to demonstrate its relative stability.

The Aura1 at the balance

The Aura1 is the ambient sensor module of GasCatena: a digital sensor for temperature and relative humidity and a digital barometric pressure sensor, powered and read over USB. It is the recommended companion of every GasCatena installation.

- **Placement.** Close to the balance, at the height of the weighing pan and in the same air; away from heat sources and draughts. After connecting or moving it, allow 30 minutes to settle.
- **At every weighing.** GasCatena reads the Aura1 and records the mean, the standard deviation and the number of readings for each quantity with the weighing.
- **On record.** The ambient snapshot of every weighing appears on the certificate, flagged against the limits of the laboratory's scope or its stricter internal specifications.

Without the Aura1, GasCatena still works: the certified uncertainty uses the conservative term for air buoyancy, as it does by default. What is lost is the evidence: no record of the conditions at each weighing, no check against the limits, and no correction or measured residual to compare with the conservative term.

The Aura2 in the room

The Aura2 is a separate ambient sensor for temperature, relative humidity and barometric pressure, with Wi-Fi and USB, that logs around the clock without a computer; calibration is available on request. Where the Aura1 captures the conditions at the moment of each weighing, the Aura2 shows how the room behaves over hours, days and seasons: the stability band over a preparation, the drift per minute, the air-conditioning cycle and the day-night rhythm. Those are precisely the inputs of the conservative bound. The temperature band usually follows from the conditioning in the laboratory's scope; for pressure and humidity, the laboratory characterises its own room. A logging sensor turns assumed drift rates into documented ones, and shows that the conditions also stayed within the limits of the scope between preparations.

Air buoyancy in GasCatena

GasCatena treats air buoyancy in three layers: a conservative term in the certified result by default, a correction calculated and reported alongside it, and a method setting with which the laboratory moves from one to the other once it has validated the correction.

Function	Status
Aura1 snapshot at every weighing (mean, SD and n), recorded and shown on the certificate with limit flags	Built
Air density per weighing, consistent with CIPM-2007; external volume per cylinder	Built
Buoyancy correction per step with its residual uncertainty: calculated, shown during the preparation and reported on the certificate; with the default method as information, not applied	Built
Conservative fixed term for air buoyancy in the certified uncertainty	Built, the default
Room model settings (validity range, stability band, drift) with an indicative per-step estimate	Built
Certified result based on the corrected mass and its residual, as a method setting of the laboratory (Settings → Buoyancy, administrators), falling back on the fixed term without readings	Built, off by default; not yet validated
Validation of the correction against the fixed term, for use in accredited certificates	Planned

Function	Status
Cooling wait triggered by the pressure step; additional term on the pressurised balance component	Built
Drift-times-time bound in the certified uncertainty instead of the flat term	Planned
Bound scaled to the variation measured by the Aura1	Planned
Additional term per filling step, sized by pressure step and waiting time	Planned
Cylinder wall temperature: release at thermal equilibrium, measured residual	Planned
Pressure-volume model to correct the cylinder deformation	Planned
Correlation of the buoyancy effect between steps in a full covariance model	Planned

Switching follows a simple rule: *reproduce, then switch*. A laboratory first confirms that the new evaluation reproduces its existing certified values where it should, and judges the effect on its own mixtures, which is why the correction is already reported as information. Only then, within its own accreditation, does it change the basis of the certified result with the method setting in GasCatena, expecting the uncertainty of major components to fall and that of small additions to rise, and checking both against its calibration and measurement capabilities.

Further information

For questions about air buoyancy and ambient conditions in GasCatena, about the Aura1 and the Aura2, to register your interest or to request a preview, contact info@qualimetric.nl. More about GasCatena and the Aura sensors: nexchrom.nl/gascatena and nexchrom.nl/aura.

References: ISO 6142-1 (gravimetric preparation of calibration gas mixtures); A. Picard, R. S. Davis, M. Gläser and K. Fujii, *Revised formula for the density of moist air (CIPM-2007)*, Metrologia 45 (2008) 149–155; OIML D 28 (conventional value of the result of weighing in air); JCGM 100 (GUM).