GASCATENA · TECHNICAL BACKGROUND

Measurement uncertainty explained

Which contributions GasCatena takes into account in the uncertainty of a prepared calibration gas, how they are evaluated and combined according to the GUM, and what is planned.

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A certified calibration gas mixture is only as useful as the uncertainty stated with it. This document explains, for analysts and quality managers in gas laboratories, which contributions GasCatena takes into account when it evaluates the uncertainty of a gravimetrically prepared mixture according to ISO 6142-1, how each contribution is evaluated, and how they are combined into the expanded uncertainty on the certificate. It also states plainly what is included in the certified result today, what the laboratory can switch on, what is recorded and monitored alongside it, and what is planned. GasCatena is in development; the release is expected in early 2027. The approach throughout is the same: conservative, traceable, transparent and in line with the GUM.

From weighing to mole fraction

In gravimetric preparation, the composition of a mixture follows from the masses of the gases added to a cylinder. Every addition is a difference weighing: the cylinder is weighed before and after the addition, and the added mass is the difference. GasCatena then follows each addition along a fixed chain of steps, and every step carries its own uncertainty.

```
Δm        = W_after − W_before              added mass, from two weighings
m_pure    = p · Δm                          mass of the component, corrected for purity p
n         = m_pure / M                      amount of substance, with molar mass M
n_final   = f · n_pre + n_post              after a dilution or blow-off step (factor f)
y_j       = n_final,j / Σ n_final,k         mole fraction, normalised to a sum of one
```

The uncertainty of the mole fraction y_j therefore depends on the weighings, the purity of the base gases, the molar masses, any dilution and the normalisation. Around the weighing itself sit the physical effects that can disturb a balance reading: the buoyancy of the air, the condition of the air at the balance, and the temperature of a cylinder that has just been filled. The following chapters treat each of these in turn.

All calculations in GasCatena use standard uncertainties (k = 1). Only when results are presented, on screen and on the certificate, are they expanded with a coverage factor k = 2.

The same calculation core also runs before the first weighing. For every recipe, GasCatena estimates the additions from the chosen cylinder, target pressure and balance, and shows the expected uncertainty of the composition

and of the gas properties. The estimate is clearly marked as such; after the actual preparation the result may differ.

One principle: the larger one counts

In two places GasCatena has two estimates of the same uncertainty: one **specified**, from a calibration certificate or a data sheet, and one **measured**, from the measurement itself. In both places it takes the larger of the two.

- **At the balance**: the repeatability stated on the calibration certificate of the balance, and the scatter of the readings of the weighing itself.
- **At the ambient sensor**: the specified accuracy of each sensor, and the scatter of its readings during the weighing.

This rule works in one direction only. A balance or sensor that happened to be quieter than its specification never leads to a smaller uncertainty than the calibration supports, so the laboratory never claims more than it can trace. A balance or sensor that was less quiet than usual, because of a draught, vibration or a reading taken too early, makes the budget honestly larger. The result is conservative where it should be, and still reflects what actually happened at the bench.

The weighing

A weighing is a series of readings

A weighing in GasCatena is not a single reading but a series of n readings taken in succession. From the series GasCatena determines the mean, which becomes the weighing value, and the scatter of the readings. The standard deviation of the readings is the **experimental repeatability**: the repeatability of the balance as it was during this weighing.

The calibration certificate of the balance also states a repeatability. Following the principle above, GasCatena uses the larger of the two as the random uncertainty per reading. Averaging over the n readings then reduces the random part with $\sqrt{n}$.

Random and systematic parts

The uncertainty of a weighing has two parts, both taken from the calibration certificate of the balance.

- The **random part**: reading noise, independent from one weighing to the next and reduced by averaging.
- The **systematic part**: the scale error of the balance, which depends on the load. Averaging does not reduce it.

The expanded uncertainty on the certificate of the balance is described as a straight line over the load, $U(W) \approx A + B \cdot W$, with an intercept A and a slope B. GasCatena divides both by two to convert the expanded values ($k = 2$) into standard uncertainties. A and B are entered per balance, together with the number of readings, the resolution and the stability margin.

Correlation between the weighings before and after

The two weighings of a difference weighing are made on the same balance, at nearly the same load, a short time apart. Their scale errors are therefore strongly correlated, and most of the systematic part cancels in the difference. GasCatena takes this into account with a correlation coefficient ρ between the systematic parts of the two weighings:

```
u_r0         = max( A/2 , s )                    random, per reading [mg]
u_r          = u_r0 / √n                         random, mean of n readings
u_sys,x      = (B/2) · W_x                       systematic, at load W_x

u²(Δm) = u_r,before² + u_r,after² + u_sys,before² + u_sys,after²
         − 2 · ρ · u_sys,before · u_sys,after
```

Here s is the measured standard deviation of the readings of that weighing, and A and B are the expanded values from the certificate of the balance.

The effect of the correlation is large. As an illustration, with assumed values: a cylinder of 5000 g receiving 300 g, A = 1.0 mg, B/2 = 0.0002 mg per gram of load, n = 10 and ρ = 0.99. The systematic parts are about 1.0 mg each, but their contribution to the difference is only about 0.16 mg; the random part adds about 0.22 mg. The combined u(Δm) is about 0.27 mg. Without the correlation it would be about 1.5 mg.

Checks at the balance

Two checks at the balance keep doubtful weighings out of the calculation altogether.

- **Stability**: the spread of the readings in a series (maximum minus minimum) must stay within the stability margin of the balance, by default its resolution. An unstable weighing is rejected, and the operator waits and reads again. Because of this check, the measured repeatability rarely exceeds the certificate value; when it does, the budget follows.
- **Direction**: after an addition the cylinder must be heavier, and only after a blow-off step may it be lighter. A weighing in the wrong direction would produce a negative added mass and is rejected on the spot.

Base gases and molar masses

Purity of the base gases

Each component is added from a base gas whose purity is stated on its certificate, usually as a grade such as 5.0 (99.999 %) or 3.5 (99.95 %). A grade gives a lower limit for the purity: the actual impurity lies somewhere between zero and the stated maximum. GasCatena treats the impurity as uniformly distributed over that interval, which gives:

```
p      = 1 − (10 − r) · 10^−(q+1)          grade "q.r": q nines followed by the digit r
u(p)   = (1 − p) / (2·√3)                  uniform distribution of the impurity

m_pure     = p · Δm
u(m_pure)  = √( p² · u²(Δm) + Δm² · u²(p) )
```

For grade 5.0 this gives p = 0.99999 and u(p) ≈ 2.9×10^{-6}; for grade 3.5, p = 0.9995 and u(p) ≈ 1.4×10^{-4}. The grade is taken per base gas from the register, and can be overridden per preparation when a cylinder comes with a different certificate.

The register of base gases also records the impurities that a supplier declares. Adding those impurities to the composition as separate components, each with its own uncertainty, is planned.

Molar masses

The amount of substance of each component follows from its pure mass and its molar mass. GasCatena calculates the molar masses from the atomic weights given in ISO 6976:2016, including their uncertainty:

```
M      = Σ n_e · M_e                      n_e atoms of element e with atomic weight M_e
u(M)   = √( Σ (n_e · u(M_e))² )

n      = m_pure / M
u(n)   = n · √( u²(m_pure)/m_pure² + u²(M)/M² )
```

For most components the contribution of the molar mass is small compared with that of the weighing, but it is always included.

Dilution and normalisation

Dilution and blow-off steps

Some mixtures are made in stages: a pre-mixture is prepared, part of it is blown off, and further components are added. The fraction of the pre-mixture that remains in the cylinder is the dilution factor f, which GasCatena determines from the weighings around the blow-off step and the weight of the evacuated cylinder:

```
f = ( W_after blow-off − W_empty ) / ( W_before blow-off − W_empty )

n_final,j   = f · n_pre,j + n_post,j
u²(n_final,j) = f² · u²(n_pre,j) + n_pre,j² · u²(f) + u²(n_post,j)
```

The uncertainty of the dilution factor follows from the uncertainties of those weighings, and it affects only the components that were present before the blow-off step.

Normalisation

The mole fractions of a mixture add up to exactly one. GasCatena normalises the amounts of substance to mole fractions according to ISO 14912. Because every mole fraction is divided by the same total, the normalised values are correlated: when one goes up, the others must go down. GasCatena propagates this through the Jacobian of the normalisation, which gives the uncertainty of every mole fraction and the covariance between every pair:

```
y_i = n_i / N              N = Σ n_k

u²(y_i)      = (1/N²) · [ (1 − 2·y_i) · u²(n_i) + y_i² · Σ u²(n_k) ]
cov(y_i,y_j) = (1/N²) · [ −y_j · u²(n_i) − y_i · u²(n_j) + y_i · y_j · Σ u²(n_k) ]
```

These covariances are passed on to the calculation of the gas properties, so that a property such as the calorific value receives a correct uncertainty, neither inflated nor understated by ignoring the constraint that the fractions add up to one.

A fuller covariance model, in which correlations between components that share a weighing or a base gas are propagated as well, is planned.

Air buoyancy and ambient conditions

The effect

A balance weighs in air. The air exerts an upward force on the cylinder equal to the weight of the air it displaces, so the reading is lower than the true mass by the air density ρ_air times the outer volume of the cylinder V_cyl. The air density depends on the pressure, the temperature and the humidity of the air. The companion document *Air buoyancy and ambient conditions* treats the physics in more detail.

In a difference weighing, the constant part of this effect cancels. Only the **change** in air density between the weighing before and the weighing after an addition remains:

```
reading     = m − ρ_air · V_cyl
Δm          = ΔW + V_cyl · ( ρ_after − ρ_before )
```

The effect is small but not negligible for the best uncertainties. For a cylinder with an outer volume of 5 L at 20 °C and 50 %RH, a change between the two weighings of 0.1 kPa in air pressure shifts the result by about 6 mg; a change of 1 K in temperature by about 22 mg; a change of 10 %RH by about 5 mg. Because the effect depends on the volume of the cylinder and not on the amount added, it is roughly constant in absolute mass, and its relative weight is largest for small additions.

Three levels of treatment

For buoyancy, as for every effect at the balance, there are three levels of treatment, each with a smaller remaining uncertainty than the one before:

- **Assume**: allow for the worst case with a conservative uncertainty term.
- **Measure and demonstrate**: measure the conditions and show that the effect stays within a smaller bound.
- **Measure and correct**: calculate the effect for every weighing and correct for it, leaving only a small residual uncertainty.

By default: a conservative fixed term in the certified result

By default, GasCatena does **not** correct the weighings for air buoyancy in the certified result. The certified composition is based on the balance readings as taken, and buoyancy is covered by a conservative fixed uncertainty term of about 0.003 % (relative, expanded), applied to every component. This term comes from a study of the weighing process and holds as long as the air pressure varies by no more than 1 kPa (10 mbar) and the temperature by no more than ±5 °C over a preparation. Within those limits the effect is not significant; the ambient readings at every weighing show whether the limits were respected.

The value of the term is a setting of the method and can be adapted by the laboratory to its own validation.

Calculated and shown: the per-step correction with the Aura1

The Aura1 ambient sensor module next to the balance measures temperature, relative humidity and barometric pressure, and GasCatena reads it at every weighing. From these readings GasCatena calculates the air density at each weighing, the buoyancy correction of each addition and the residual uncertainty of that correction. The results are shown during the preparation and reported on the certificate. With the default method they are clearly marked there as **informational**: the certified composition and its uncertainty remain those of the fixed term described above.

The residual uncertainty of the correction is small because a constant offset of a sensor cancels in the difference ρ_after − ρ_before. Only the short-term uncertainty of the readings counts, once for each of the two weighings:

```
u(Δm)_buoyancy = V_cyl · √( 2 · Σ_x ( ∂ρ/∂x · u_st,x )² )        x = p, T, RH
```

Without ambient readings at both weighings, GasCatena can estimate the per-step effect from typical drift rates of pressure, temperature and humidity and the actual time τ between the two weighings, capped at the permitted stability band. With typical drift rates this gives about 0.33 mg per litre of cylinder volume per minute; for a 5.25 L cylinder weighed 5 minutes apart, about 8.6 mg, or 0.0029 % of a 300 g addition. That is in line with the fixed term, and it makes explicit how the effect scales with the volume of the cylinder and the time between the weighings.

Air density and its uncertainty

GasCatena calculates the air density with an established approximation of the CIPM-2007 equation for the density of moist air, valid over the working range of a weighing room:

```
ρ = 0.001 · ( Kp·p − Khr·hr·exp(KT·T) ) / ( 273.15 + T )        [kg/m³]

    p in Pa, T in °C, hr in %RH;  Kp = 3.4848,  Khr = 9.024,  KT = 0.0612
```

The uncertainty of the air density has two sources, and GasCatena takes both into account:

- **The sensor**: the specified accuracy of the temperature, humidity and pressure sensors, from the data sheet or a calibration.
- **The measured scatter**: like the balance, the Aura1 reads every quantity as a series, and the standard deviation of the series is a Type A contribution.

Following the principle of this document, GasCatena uses the larger of the two for each quantity. Each sensor uncertainty is then propagated to the air density through its sensitivity coefficient $\partial\rho/\partial x$, strictly according to the law of propagation of uncertainty of the GUM:

$$u^2(\rho) = (\partial\rho/\partial p \cdot u(p))^2 + (\partial\rho/\partial T \cdot u(T))^2 + (\partial\rho/\partial hr \cdot u(hr))^2$$

For a single value of the air density, the uncertainty of the equation itself also counts: according to CIPM-2007 about 2.2×10^{-5} relative, or about 4.6×10^{-5} when the carbon dioxide content of the air is assumed rather than measured. GasCatena shows this for information. In a difference weighing the model uncertainty cancels, because both air densities are calculated with the same equation.

Monitoring the ambient conditions

Independently of the buoyancy, the ambient readings at every weighing are checked against the limits of the accreditation scope, or against stricter internal specifications of the laboratory. The certificate carries an ambient snapshot per weighing, with a flag for every reading inside or outside the limits. An auditor can see at a glance under which conditions each addition was made.

Applying the correction to the certified result

Applying the buoyancy correction to the certified result replaces the fixed term by the per-step correction and its residual uncertainty. GasCatena offers this as a method setting of the laboratory (*Settings → Buoyancy*, changed by an administrator): the certified mass and its uncertainty are then based on the measured ambient conditions, falling back on the fixed term when no readings are available. The setting is off by default, and the correction has not yet been validated for accredited use: a laboratory should switch only after it has validated the correction within its own accreditation. Until then, the laboratory loses nothing: the certified result rests on the established fixed term, and the correction is available alongside it as additional information. Part of such a validation is a comparison of the per-step evaluation with the fixed term over the range of additions the laboratory makes, from trace components to the balance gas. A validation of the correction for GasCatena itself is planned.

Large pressure steps

Heating and the cooling wait

Filling a cylinder with a large pressure step, typically the balance gas, warms the cylinder by a few degrees. A cylinder warmer than the surrounding air disturbs the weighing through convection and a local change of the air at the balance pan. Unlike buoyancy, this effect cannot be corrected from the readings of an ambient sensor,

because the sensor does not see the air layer around the warm cylinder. The remedy is to wait until the cylinder has cooled.

GasCatena compares the expected pressure increase of every addition with a configurable threshold, for example 25 bar. Above the threshold it requires a cooling wait before the cylinder is weighed: either a fixed time, for example 20 minutes, or a time per bar of pressure increase. The laboratory chooses whether the wait is enforced, with a countdown that blocks the weighing, or shown as a warning.

The residual term

Even after cooling, a small residual effect may remain. GasCatena covers it with an additional uncertainty term, applied to the component added with the large pressure step: the component with the largest amount of substance in the mixture. The term holds on the condition that the cooling wait has been observed. Its value is a setting of the method, set conservatively, and like every additional term it can be combined linearly or in quadrature (see the next chapter).

A model that quantifies this residual from the measured temperature difference between the cylinder and the air, rather than from the elapsed time, is planned. It would allow the weighing to be released as soon as the cylinder is in equilibrium, and the residual to be based on a measured quantity.

Cylinder deformation

A large pressure increase also expands the cylinder elastically. A larger outer volume displaces more air, so the cylinder appears lighter and the added mass is slightly too low:

```
ΔV/V        = ( Δp · D ) / ( 4 · t · E ) · ( 5 − 4ν )      thin-walled cylinder
Δm_apparent = ρ_air · ΔV
```

with D the inner diameter, t the wall thickness, E the modulus of elasticity and ν the Poisson ratio of the cylinder material. For a 5 L aluminium cylinder and a pressure increase of 90 bar this is of the order of 20 mg, or about 0.008 % of a 300 g addition. The effect is deterministic and falls on the main component, whose uncertainty propagates to the other mole fractions only weakly through the normalisation. Accounting for it, by a correction based on the expansion coefficient of each cylinder or by an equivalent uncertainty term, is planned.

Stability over the shelf life

A calibration gas mixture is used long after it has been prepared, and some components can drift during its shelf life. ISO 6142-1 (9.2) therefore adds a stability contribution to the uncertainty when a drift is expected. In GasCatena the scope of the laboratory carries, next to the shelf life, a **drift rate**: the expected relative change of a mole fraction per year, entered as a standard uncertainty, together with its basis (a stability study, the literature, or no drift observed). A component in the CMC table can have a drift rate of its own.

```
u_stab  = b · t_s          b: drift rate per year (relative, k = 1),  t_s: shelf life in years
U_stab  = 2 · u_stab       expanded, k = 2, combined in quadrature (see Additional terms)
```

The stability contribution enters everywhere the uncertainty of the composition is used: the gas properties, the scope check, the estimate for a recipe and the preparation itself. When it is used, the certificate states that the uncertainty includes a stability contribution, and a note gives its value and basis. By default the drift rate is zero: there is then no contribution, and the certificate says that stability is not included. A laboratory sets a drift rate once a stability study for the type of mixture, or another documented basis, supports it.

Combining the contributions

According to the GUM

Every contribution described above is expressed as a standard uncertainty and propagated through the measurement model of the first chapter, according to the GUM (JCGM 100). This gives, for every component, the combined standard uncertainty u(y) of its mole fraction, together with the covariances from the normalisation. The result is reported as an expanded uncertainty with a coverage factor k = 2, in line with EA-4/02, both in absolute terms and relative to the mole fraction:

```
U = k · u(y)        k = 2
```

Additional terms

The two terms from the study of the weighing process, the fixed buoyancy term and the residual term after a large pressure step, are given as expanded relative uncertainties. GasCatena adds them to the expanded relative uncertainty of each component at the end. For each term the laboratory chooses how: linearly, which is the conservative choice for a systematic effect and the default for both terms, or in quadrature:

```
U_rel,final = √( (U/y)² + Σ U_rel,quadratic² ) + Σ U_rel,linear
U_final     = U_rel,final · y
```

The stability contribution of the previous chapter always enters in quadrature, as one of the terms U_rel,quadratic. The same additional terms appear in the same way in the recipe estimate, during the preparation and on the certificate.

Gas properties according to ISO 6976

From the composition, GasCatena calculates the gas properties according to ISO 6976:2016: the gross and net calorific value on a molar, mass and volume basis, the density, the relative density, the gross and net Wobbe index and the compression factor. Each property comes with its uncertainty according to Annex B of the standard, calculated from the mole fractions, their uncertainties and the correlations from the normalisation. The reference conditions for combustion and metering are set once and used everywhere: in the recipe estimate, in the preparation and on the certificate.

Checked against the scope

The expanded relative uncertainty of each component is checked against the calibration and measurement capability (CMC) of the accreditation scope. Within the measuring range of a component, the CMC at the actual concentration c follows by linear interpolation between the values at the ends of the range:

```
CMC(c) = CMC_low + ( CMC_high − CMC_low ) · ( c − c_low ) / ( c_high − c_low )

within scope:  U_rel,final ≤ CMC(c)
```

A laboratory can hold more than one scope, and chooses per preparation which one applies. A component outside the measuring range of the scope is reported as not covered by it.

Verified by an independent analysis

A prepared mixture can be compared with an independent analysis of the same cylinder, judged with the E_n test of ISO 13528:

```
E_n = ( x_prep − x_analysis ) / √( U_prep² + U_analysis² )        |E_n| ≤ 1: consistent
```

The test uses the expanded uncertainties of both results, so it is only as meaningful as the uncertainty budget behind the preparation. NexChrom, the GC software from the same product line, can provide the independent analysis, with GUM uncertainty on every mole fraction. The companion document *Analytical verification of calibration gases* explains why the verification matters and how it relates to the certified value.

Included, recorded and planned

The table below gives the status of every contribution. **Included** means that the contribution is part of the certified composition and its expanded uncertainty. **Optional** means that the laboratory can switch it on; it is off by default. **Recorded** means that it is calculated, shown or checked, and kept on record or on the certificate, without changing the certified result. **Planned** means that it is not yet part of GasCatena.

Contribution	Status	How
Weighing, random part	Included	Larger of certificate repeatability and measured scatter, averaged over n readings
Weighing, systematic part	Included	Scale error from the balance certificate, with correlation between the weighings before and after
Stability and direction of every weighing	Recorded	Unstable weighings and weighings in the wrong direction are rejected
Purity of the base gases	Included	Purity from the grade, uniform distribution of the impurity
Declared impurities as separate components	Planned	Impurities are recorded in the register of base gases
Molar masses	Included	From the atomic weights of ISO 6976:2016, with their uncertainty
Dilution and blow-off steps	Included	Dilution factor from the weighings, applied to the components before the blow-off
Normalisation	Included	ISO 14912, with the covariance between all mole fractions
Fuller covariance model (shared weighings and base gases)	Planned	
Air buoyancy, fixed term	Included	Conservative relative term, about 0.003 %, for every component
Air buoyancy, per-step correction with the Aura1	Recorded	Calculated per addition and reported on the certificate, as informational with the default method
Air buoyancy correction in the certified result	Optional, not yet validated	A method setting of the laboratory, to be switched on only after validation in its own accreditation; a validation for GasCatena is planned
Uncertainty of the air density	Recorded	Sensor specification or measured scatter, whichever is larger; model uncertainty shown for information
Ambient conditions at every weighing	Recorded	Snapshot per weighing on the certificate, checked against the limits of the scope
Cooling wait after large pressure steps	Recorded	Configurable threshold and waiting time, enforced or as a warning

Contribution	Status	How
Residual term after a large pressure step	Included	Conservative term on the component added with the large pressure step
Thermal residual from the measured cylinder temperature	Planned	
Cylinder deformation at high pressure	Planned	
Stability over the shelf life	Included (when the scope sets a drift rate)	ISO 6142-1, 9.2: drift rate × shelf life, combined in quadrature; the drift rate is zero by default
Gas properties according to ISO 6976	Included	Calorific value, density, Wobbe index and compression factor, with Annex B uncertainty
Scope check (CMC)	Recorded	Every component checked against the CMC of the chosen scope
Verification by independent analysis	Recorded	E_n test according to ISO 13528

In one sentence: GasCatena takes into account the weighing (random and systematic, with correlation), the experimental repeatability, the purity of the base gases, the molar masses, the dilution, the normalisation, the effects of the air and of large pressure steps and, when the scope sets a drift rate, the stability over the shelf life; where it has to choose, it takes the larger and more conservative contribution; and it combines everything according to the GUM into an expanded uncertainty with k = 2, visible during the preparation and on the certificate.

Further information

The accreditation of a calibration gas mixture belongs to the laboratory that prepares it. GasCatena is built to give that laboratory a complete, documented and conservative uncertainty budget for every cylinder, and to keep every link of the traceability chain on record. This document describes the product as it is being developed; details may change before release.

The GasCatena product factsheet and the Aura1 quick start are available on the Downloads page. For questions about the uncertainty model, to register your interest or to request a preview of a preparation from recipe to certificate, contact us at info@qualimetric.nl · nexchrom.nl/gascatena