GASCATENA · TECHNICAL BACKGROUND

Analytical verification of calibration gases

Why an independent analysis adds value to a gravimetric preparation, how it is judged with the E_n test, and how it relates to the certified value and its uncertainty.

Qualimetric · Nijmegen, The Netherlands · info@qualimetric.nl · nexchrom.nl · 6 November 2026

CONTENTS

1. Two methods, two questions
2. What the gravimetric budget cannot see
3. What ISO 6142-1 requires
4. The compatibility test: E_n
5. From verification to certificate uncertainty
6. Verification by GC: ISO 6143 and NexChrom
7. Verification in GasCatena
8. Key points
9. Further information

A gravimetrically prepared calibration gas mixture has a smaller uncertainty than any routine analysis of it. Why, then, should a laboratory verify each cylinder with an analysis that is less accurate than the preparation itself? This document explains why analytical verification is required by ISO 6142-1, what it adds that the gravimetric uncertainty budget cannot provide, how the agreement between preparation and analysis is judged with the E_n test, and how the verification will become part of the uncertainty on the certificate. It also describes how GasCatena and NexChrom, two products of the same line, work together in this step. GasCatena is in development; the release is expected in early 2027.

Two methods, two questions

Gravimetry is the primary method for calibration gas mixtures. The composition follows from the masses of the components weighed into the cylinder, their purity and their molar masses. For the main components, the gravimetric uncertainty is usually considerably smaller than that of a gas chromatographic analysis. That is the metrological hierarchy, not a coincidence: the preparation assigns the value, the analysis checks it.

If the purpose of verification were to improve the gravimetric value, the analysis would indeed need a smaller uncertainty than the preparation. That is not what verification does. The two methods answer different questions:

- **Gravimetry** answers: *what was put into the cylinder* at the time of preparation.
- **Analysis** answers: *what is in the cylinder now*.

As long as nothing unexpected happened, the two answers agree. Over time, or with components that adsorb on the cylinder wall or react, they can drift apart. Only an analysis can show the stability of a mixture; the gravimetric record, by definition, cannot.

The analysis also changes the certified value very little. If the gravimetric value and a much less precise analytical value were combined into one weighted result, that result would stay close to the gravimetric value, because the greater weight lies with the smaller uncertainty. The analysis adds little to the *value*, but a great deal to the *confidence* in it. The certified value therefore remains the gravimetric value.

A nuance for trace components

For a trace component, a small addition on a heavy cylinder, the *relative* weighing uncertainty becomes large. In that range a well-calibrated GC can be competitive with gravimetry or even better. The assumption that gravimetry is always the more accurate method holds for the main components, not automatically for minor and trace fractions.

What the gravimetric budget cannot see

A gravimetric uncertainty budget, evaluated according to the GUM, describes the spread of the result *if everything went as intended*. It does not contain the events that make a preparation go wrong:

- a cylinder that was not properly evacuated before filling;
- a component that **adsorbs** on the cylinder wall or reacts, such as water, hydrogen sulfide or other reactive species;
- incomplete mixing or stratification;
- a **leak** between preparation and use;
- a mix-up of cylinders, a **wrong base gas** or a pre-mixture with the wrong composition;
- a weighing or transcription mistake;
- **drift** of the composition over time.

None of these appears in the uncertainty budget, and none of them can be calculated away. An independent analysis tests exactly the assumption the budget is built on. A 2 % loss through adsorption, or a swapped cylinder, is detected without difficulty by a GC with an uncertainty of 0.5 %, even when the gravimetric uncertainty is 0.05 %.

GasCatena already prevents many errors at the balance: it gives the target pressure and the expected balance reading for every addition, rejects unstable weighings and weighings in the wrong direction, and keeps every weighing on record. But no software at the balance can see what happens inside the cylinder. That is the task of the verification.

The value of verification lies not in measuring more accurately, but in being independent. It demonstrates that nothing invisible went wrong, which the uncertainty budget by its nature cannot do.

What ISO 6142-1 requires

In ISO 6142-1:2015, verification is not an optional extra. The standard requires that the composition of a calibration gas mixture is verified experimentally, to demonstrate that it is consistent with the composition calculated from the gravimetric preparation. It adds that the composition can only be considered traceable to the SI once it has been verified.

The standard then specifies how the certificate uncertainty is calculated: the combined standard uncertainty brings together the preparation, the verification and the difference between the two (its Formula 9; see the chapter *From verification to certificate uncertainty*). The preparation uncertainty itself combines the gravimetric uncertainty with the contribution from the stability of the mixture.

The wider framework points the same way. ISO 6142-1 refers to comparison with other mixtures (ISO 6143) for checking the composition, and the standards for reference material producers (ISO 17034 and ISO Guide 35) require an assessment of homogeneity and stability, which is analytical work. A gravimetric value without independent verification does not count as a fully validated reference material.

The compatibility test: E_n

The right criterion for verification is not "smaller than", but **compatibility**: do the gravimetric and the analytical value agree within their combined uncertainty? This is the logic of the E_n number from proficiency testing (ISO 13528). The E_n number is the difference between the two values divided by the expanded uncertainty of that difference:

$$E_n = \frac{x_{grav} - x_{ver}}{\sqrt{U_{grav}^2 + U_{ver}^2}}$$

where x_grav is the gravimetric value, x_ver the value from the independent analysis, and U_grav and U_ver their expanded uncertainties (k = 2, about 95 % coverage). The denominator is the uncertainty of the *difference*: two independent contributions added in quadrature.

- **$|E_n| \leq 1$**: the difference lies within the combined 95 % uncertainty; the preparation is **confirmed**.
- **$|E_n| > 1$**: the difference is larger than both methods together can explain; the preparation must be **investigated**.

Both uncertainties count. The analysis does *not* need to be more accurate than the gravimetry for the test to be meaningful.

Worked example

A main component is prepared at 80.00 mol% with an expanded uncertainty U = 0.02 mol%. The independent analysis gives 80.12 mol% with U = 0.20 mol%.

$$\begin{aligned} &\text{difference} && 80.00 - 80.12 = -0.12 \text{ mol\%} \\ &\text{denominator} && \sqrt{0.02^2 + 0.20^2} = \sqrt{0.0404} \approx 0.20 \text{ mol\%} \\ &E_n && -0.12 / 0.20 \approx -0.6 \rightarrow |E_n| \approx 0.6 \leq 1 \end{aligned}$$

The result is consistent: the deviation lies well within what the less precise analysis allows. Only a difference larger than about 0.20 mol% would give $|E_n| > 1$.

How good must the analysis be?

There is a sound core in the intuition that a check must be accurate enough. The requirement, however, is relative to the **errors you want to detect**, not to the gravimetric uncertainty. A GC so imprecise that the combined uncertainty accepts almost any difference is a toothless test. The criterion is therefore:

$$U_{ver} \ll \text{size of the error to be detected} \qquad (\text{not: } U_{ver} \leq U_{grav})$$

These are different thresholds. In the example above, the analysis would reliably flag an adsorption loss, a leak or a wrong base gas that shifts the main component by a few tenths of a mol% or more.

From verification to certificate uncertainty

The E_n test is a pass or fail decision. ISO 6142-1 goes one step further: the verification result, *with its uncertainty*, becomes part of the uncertainty reported on the certificate.

Formula 9 in words

The certified *value* remains the gravimetric value. The reported *uncertainty* is a combination of three elements:

- the uncertainty of the preparation (gravimetry and stability);
- the uncertainty of the verification;
- the difference between the gravimetric and the verified value.

A large difference between preparation and analysis, even one that still passes the E_n test, therefore makes the certified uncertainty larger. A close agreement keeps it small.

The lower limit: half the verification uncertainty

The way Formula 9 combines these elements sets a floor. Even when the preparation uncertainty is negligible and the two values agree exactly, the combined uncertainty cannot be smaller than half the expanded uncertainty of the verification:

```
best achievable certificate uncertainty  =  ½ · U_ver
```

This has a direct consequence for the calibration and measurement capability (CMC) a laboratory claims for its preparations. A preparation CMC can only be supported by verified mixtures if the verification is good enough to reach it:

```
CMC_prep  ≥  ½ · U_ver        or, equivalently,        U_ver  ≤  2 × CMC_prep
```

If the verification is less precise than that, it dominates the certificate uncertainty, however good the weighing is.

Reported uncertainty and the CMC

Under accredited conditions (ISO/IEC 17025 and ILAC-P14), the reported expanded uncertainty is the real uncertainty of that particular preparation, and it is never smaller than the CMC in the scope of accreditation:

```
U_reported  =  max( U_calculated , CMC )
```

- If the calculated uncertainty is **larger** than the CMC, because of a modest agreement, a large difference or a non-routine preparation, the larger calculated value is reported. A weaker batch cannot hide behind the CMC.
- If the calculated uncertainty is **smaller** than the CMC, the CMC is reported. A laboratory does not claim better than its validated capability.

Example: what the verification must achieve

The table below shows how the rule U_ver ≤ 2 × CMC_prep works out for a laboratory with typical CMCs for natural gas components. All values are relative expanded uncertainties (k = 2). The figures are an illustration from practice, not a specification.

Component	Preparation CMC	Required U_ver	Typical analysis CMC	Improvement needed
Nitrogen	0.1 %	≤ 0.2 %	2 %	about 10×
Carbon dioxide	0.16 %	≤ 0.32 %	1 %	about 3×
Ethane	0.1 %	≤ 0.2 %	0.5 %	about 2.5×
Methane, propane, butanes				consistent

For nitrogen, carbon dioxide and ethane in this example, the verification would have to be substantially better than the laboratory's routine analysis capability; for nitrogen by about a factor of ten. For methane, propane and the butanes, the preparation CMC and the analytical capability are consistent.

This does not mean such preparation CMCs are impossible. A verification analysis can be better than a routine analysis of an unknown gas: the reference gases can be chosen close to the prepared composition, the nominal

value is known, and the measurement can be repeated. An analysis CMC is also often a single number for the whole range, driven by the low end; at higher concentrations the GC may perform better. But that is a claim to be demonstrated with verification data resolved by component and concentration, not an assumption. Combining preparation and verification in one calculation makes this visible for every component.

Verification by GC: ISO 6143 and NexChrom

The independent analysis is a gas chromatographic analysis. In conformity with ISO 6143, the GC is calibrated with a set of certified reference gases, typically around seven calibration points covering the composition of interest, and the prepared mixture is analysed against that calibration function.

ISO 6143 uses **errors-in-variables regression**: unlike ordinary least squares, it takes into account the uncertainty of both the reference gas compositions and the GC responses. The result is an analytical value with an uncertainty that reflects the reference gases, the response precision of the GC and the fit of the calibration function. Because the verification is a GC analysis and not a relative comparison in which systematic effects cancel, its uncertainty is fundamentally an analytical uncertainty, limited by the response precision of the GC.

For the verification to be independent, the reference gases used to calibrate the GC should not come from the same preparation process as the mixture being verified. A GC calibrated with the laboratory's own preparations would confirm the preparation with itself.

NexChrom, the GC software from the same product line, takes the analysis from the chromatography data system to a certified result. It performs the errors-in-variables calibration in conformity with ISO 6143 against certified reference gases and gives every mole fraction its uncertainty according to the GUM, together with quality control charts for the analytical system. This is exactly the input the verification step needs: a value x_ver with its expanded uncertainty U_ver.

Verification in GasCatena

Available today

- For every prepared mixture, the result of an independent analysis of the same cylinder is entered manually: the value and its expanded uncertainty per component.
- GasCatena compares it with the gravimetric value and its uncertainty, calculates E_n for each component and judges the result: confirmed ($|E_n| \leq 1$) or to be investigated ($|E_n| > 1$).
- The verification is recorded with the preparation, so that the comparison remains on record next to the weighings. A mixture can have more than one verification, for example a repeat or a later stability check; the most recent one determines its status: awaiting verification, verified, or verification failed.
- With every verification, the origin of the reference gases used to calibrate the GC is recorded, together with the confirmation that they were not prepared with GasCatena itself.
- Separately, every result is checked against the CMCs of one or more accreditation scopes.

The analysis itself is not part of GasCatena. GasCatena records and judges the analytical result that the laboratory supplies, whichever system produced it.

Planned

- **Certificate uncertainty according to ISO 6142-1, Formula 9.** The intended next step is to combine the preparation, the verification and their difference into the uncertainty on the certificate, with the rule U_reported = max(U_calculated, CMC). The certified value remains the gravimetric value.

- **Direct transfer from NexChrom.** The analytical result and its uncertainty are planned to come directly from NexChrom, without retyping, so that the link from the GC calibration to the certificate is as complete and documented as the link from the balance to the certificate.

Together, these steps are intended to close the chain: the gravimetric preparation documented weighing by weighing in GasCatena, the independent analysis calibrated in conformity with ISO 6143 in NexChrom, and one certificate that reflects both.

Key points

- Gravimetry is more accurate than a GC analysis for the main components; that intuition is correct.
- Verification earns its place not by being more accurate, but by being **independent**: it detects what the uncertainty budget cannot contain, such as leaks, adsorption, a wrong base gas, incomplete mixing, weighing mistakes and drift.
- The criterion is a **compatibility test** ($|E_n| \leq 1$) in which both uncertainties count. The analysis must be small relative to the errors to be detected, not relative to the gravimetric uncertainty.
- ISO 6142-1 requires verification, and its Formula 9 makes the verification uncertainty part of the certificate uncertainty. The certified value remains the gravimetric value.
- The best achievable certificate uncertainty is ½·U_ver, so a preparation CMC requires U_ver ≤ 2 × CMC_prep. The reported uncertainty is never smaller than the CMC.
- For trace components, the analysis can sometimes be more accurate than the gravimetry.
- In GasCatena today, the independent analysis is entered manually and judged with the E_n test; Formula 9 on the certificate and the direct transfer from NexChrom are the intended next steps.

Further information

For questions about verification in GasCatena, to register your interest or to request a preview, contact info@qualimetric.nl. More about GasCatena and NexChrom: nexchrom.nl/gascatena and nexchrom.nl.