

MONTE CARLO METHOD APPLIED TO GRAVIMETRIC LEAK CALIBRATION

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Abstract:

The gravimetric method for standard leak calibration is already documented and has proven to be repeatable. However, neglecting the air buoyancy correction in some cases may lead to a significant increase of the uncertainty and a bias on the result. The aim of this work is to provide a method for atmospheric leaks calibration using simple mass comparisons and the Monte Carlo method in order to determine the associated uncertainty and check the validity of the GUM approach in specific cases. The main objectives are to provide a guideline on how to quickly and simply calibrate such equipment and take into account the air buoyancy correction despite the lack of knowledge about the standard leak density.

Keywords: standard leak; atmospheric leak; Monte Carlo; mass comparison

1. INTRODUCTION

The F-gas regulation 517/2014 intends to reduce the EU's F-gas emissions by two thirds by 2030 compared with 2014 levels. The regulation sets down, amongst other things, the obligation to carry out leak checks on installations containing greenhouse gases. The leak tightness of installations charged with more than 3 kg of refrigerants must be controlled periodically by leak detectors with a detection limit of 5 g·yr⁻¹ and qualified by means of traceable reference leaks. LNE developed in 2008 a national standard for calibrating refrigerant leaks, based on the measurement of the concentration of the gas emitted by the leak in a volume by means of a photo-acoustic spectrometer [1]. If this reference is suitable for calibrating reference leaks with adapted uncertainties, it requires an important investment in terms of cost and its implementation is time consuming. Because of these drawbacks, the gravimetric method might be a good alternative for standard leaks calibration.

Neglecting the air buoyancy correction during gravimetric leak calibration may lead to significant error if the standard leak density is far from the conventional 8 000 kg·m⁻³ or if important variations

of the ambient conditions occur during the measurements [2]. In this work the standard leak has a nominal value of 5 g·yr⁻¹ and weighs around 1 kg. Since hydrostatic weighing is impossible, accurately knowing its volume by weighing it in vacuum is at best rather complicated and time consuming. The main objective being to keep the measurement procedure as simple as possible, the leak density has been roughly estimated to be between 1 000 kg·m⁻³ and 5 000 kg·m⁻³ based on its geometry. Due to the importance of this uncertainty component, applying the Monte Carlo method might be a good way to estimate the expanded uncertainty on this measurement and assess the validity of the GUM uncertainty framework.

2. MEASUREMENT PRINCIPLE AND EXPERIMENTAL SETUP

The measurement in itself is rather simple. The leak value is simply given by the change in mass during a given time interval. At any given time, the mass M of the leak is given by equation (1).

$$M = E + \Delta X + \frac{a \times (q - r)}{q \times (r - a)} \times E, \quad (1)$$

where:

- E is the mass of the standards
- ΔX is the difference of mass indication given by the comparator
- a is the air density
- q is the density of the mass standards
- r is the density of the leak

This mass is measured twice (M_1 and M_2) at a few days interval (T_1 and T_2) and the leak value Q can be calculated from equations (2) and (3).

$$Q = \frac{M_2 - M_1}{T_2 - T_1}, \quad (2)$$

$$Q = \frac{(E_2 + \Delta X_2 + \frac{a_2 \times (q_2 - r)}{q_2 \times (r - a_2)} \times E_2) - (E_1 + \Delta X_1 + \frac{a_1 \times (q_1 - r)}{q_1 \times (r - a_1)} \times E_1)}{T_2 - T_1} \quad (3)$$

Depending on the leak's nominal value, the time interval must be adapted in order to allow the mass difference to be significantly greater than the

uncertainty contributions of the weighing process. The leak measured in this paper has a nominal value of $5 \text{ g}\cdot\text{yr}^{-1}$ therefore a 7-day interval has been chosen which represent a mass difference of about 100 mg.

The experimental setup simply consists of a Sartorius CC2000 balance shown in Figure 1. The balance is used as a mass comparator and the leak weigh is measured by double comparison with a set of mass standards. The odd shape of the standard leak may cause difficulties when positioning the leak on the weighing pan. Special care has been taken to make the measurement as repeatable as possible. The position effect of the leak on the weighing can cause significant bias. The creation of a special support for the leak would be a good way to reduce this effect. However, the purpose of this method is to be simple, quick and cost effective, therefore this solution was not implemented.

The balance used has a resolution of 0.1 mg and a typical repeatability of 0.3 mg. A reproducibility study has been done in order to take into account the positioning error of the leak on the weighing pan. The reproducibility of the mass measurement has been found to be about 1 mg. All measurements are performed in an environment-controlled lab in which the temperature is $(20 \pm 1.5)^\circ\text{C}$, the hygrometry is $(50 \pm 15)\% \text{RH}$ and the atmospheric pressure is $(1013 \pm 24) \text{ hPa}$.

Each ΔX is the result of an ABBA Borda double weighing scheme. The mass standards and the leak are placed on the weighing pan alternately following the order (standards – leak – leak – standards).

$$\Delta X = \frac{B_1 - A_1 + B_2 - A_2}{2}, \quad (4)$$

with:

- A_1 and A_2 the indications of the balance when the standards is on the weighing pan
- B_1 and B_2 the indications of the balance when the leak is on the pan

This weighing scheme is used in order to compensate for the balance error and for its drift over time.

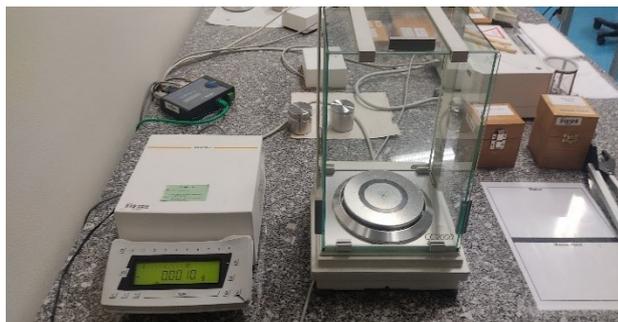


Figure 1: Balance used

Temperature, hygrometry and atmospheric pressure are carefully measured during each measurement. This data is useful to calculate the air density during each measurement and the air buoyancy correction. The air density is calculated using the OIML R111 formula.

3. MEASUREMENT RESULTS

3.1. Leak Value Determination

In order to check if the leak value is stable and if the measurement process is repeatable the mass of the leak has been measured six times over a period of one week.

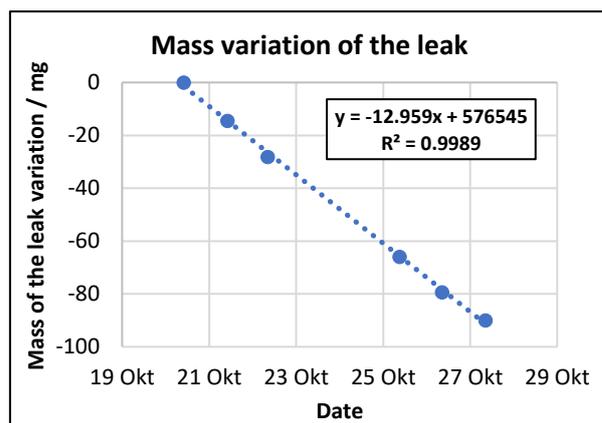


Figure 2: Variation of the mass of the leak

The slope of this curve gives us the value of the standard leak in $\text{mg}\cdot\text{d}^{-1}$. Figure 2 shows that the linearity is good and confirms the good stability of the leak value and of the mass measurement. Strictly speaking only two measurements are necessary but since the weighing process is quick and simple, additional measurements are easy to implement and allow to minimise error on the linear fit.

Since the mass of the leak is decreasing over time the different measurements have been performed using different standards. The mass of the standards should be as close as possible to the mass of the leak to reduce the bias due to the balance.

A simple linear regression between the first and last points is enough to determine the leak value. The leak value obtained is $12.97 \text{ mg}\cdot\text{d}^{-1}$ or $4.73 \text{ g}\cdot\text{yr}^{-1}$.

3.2. Uncertainty Calculation using the GUM Framework

The density of the leak is needed in order to determine the mass of the leak, more precisely to apply the air buoyancy correction. However, this density is unknown. Measuring the volume of the leak by hydrostatic weighing is not viable since this method is complicated and the leak needs to be submerged in water which can damage it. Using double weighing in air in an airtight mass comparator might also be an option but it is as complicated and require a lot of time as well as

extensive equipment. Therefore, the only value available is a rough geometric estimation of the leak volume and density. This density is estimated to be $(3\,000 \pm 2\,000) \text{ kg}\cdot\text{m}^{-3}$. This uncertainty might seem very large, it is a worst-case scenario in order to study its effect even if the leak volume has not been measured at all but only roughly estimated. Since the measurement is performed over an extended period of time, the ambient conditions may vary significantly. This, combined with the large uncertainty on the leak density, leads to a significant uncertainty on the air buoyancy correction and on the mass of the leak at any given time.

When applying the propagation of uncertainty to this measurement the expanded uncertainty obtained ($k = 2$) is $0.28 \text{ kg}\cdot\text{m}^{-3}$. The uncertainty on the leak density accounts for more than 60 % percent of the combined uncertainty as can be seen in Figure 3.

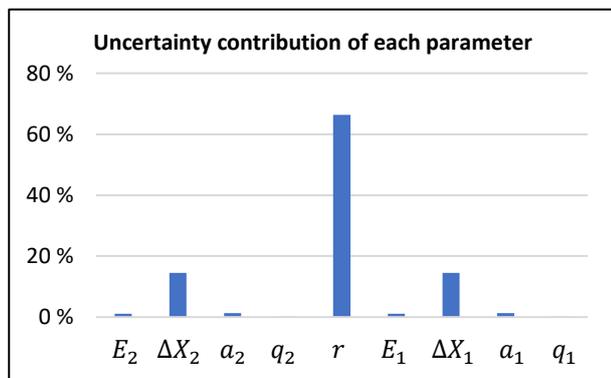


Figure 3: Uncertainty contribution of each parameter

4. LEAK VALUE DETERMINATION USING MONTE CARLO METHOD

4.1. General Principle

Another way to estimate the leak value and its uncertainty is applying the Monte Carlo method to the measurement process. First the mathematical model of the measurement needs to be known. As in a classical approach each parameter is associated with a standard uncertainty. Then a large number of random values (generally 10^6) of these parameters are generated. For each set of randomly generated parameters, a measurement result can be calculated. Finally, the dispersion of the results can be studied, the mean value giving the result and its dispersion giving its uncertainty.

4.2. Application to the Leak Value Determination

In order to apply Monte Carlo method to this standard leak calibration, equation (3) is used. The first step is to study each variable in this equation

and to associate it with a mean value and a distribution law:

- E_1 and E_2 , the masses of the standards follow a normal distribution with a standard deviation equals to the standard uncertainty of 0.28 mg. Since different stacks of standards are used at the beginning and at the end of the measurement process, the uncertainty on each stack has been calculated as the linear sum of the mass standards composing it.
- ΔX_1 and ΔX_2 the weighing results are considered to follow a normal distribution which standard deviation is the uncertainty on the weighing results. These uncertainties have been calculated taking into account repeatability and reproducibility of the balance, its resolution etc.
- a_1 and a_2 the air densities are measured continuously in the lab. Their value are calculated using OIML R111 formula and the recorded values of atmospheric temperature, pressure and hygrometry. The uncertainty on air densities is determined using classic propagation method. It is considered to follow a normal distribution.
- q_1 and q_2 the densities of the mass standards are considered to follow a normal distribution. As for the masses, the standard densities as well as their uncertainties have been calculated taking into account the different stacks of standards used.
- r finally, is the leak density, our parameter of interest. It is given a very broad estimation of its value between $1\,000 \text{ kg}\cdot\text{m}^{-3}$ and $5\,000 \text{ kg}\cdot\text{m}^{-3}$ following a uniform distribution.

Then for each parameter 10^6 random values are generated and for each set of values the leak value is calculated using equation (3). The random values are generated using LNE-MCM a free software developed at LNE.

4.3. Results and Discussion

10^6 leak values are obtained, and their distribution can be studied, it is represented in Figure 4.

The mean value obtained is $12.81 \text{ mg}\cdot\text{d}^{-1}$ with a standard deviation of $0.53 \text{ mg}\cdot\text{d}^{-1}$. The leak value can be expressed as $4.68 \text{ g}\cdot\text{yr}^{-1}$ with an expanded uncertainty ($k = 2$) of $0.38 \text{ g}\cdot\text{yr}^{-1}$. An interesting observation is the non-symmetrical distribution of the result which is in itself a good argument in favour of the Monte Carlo method.

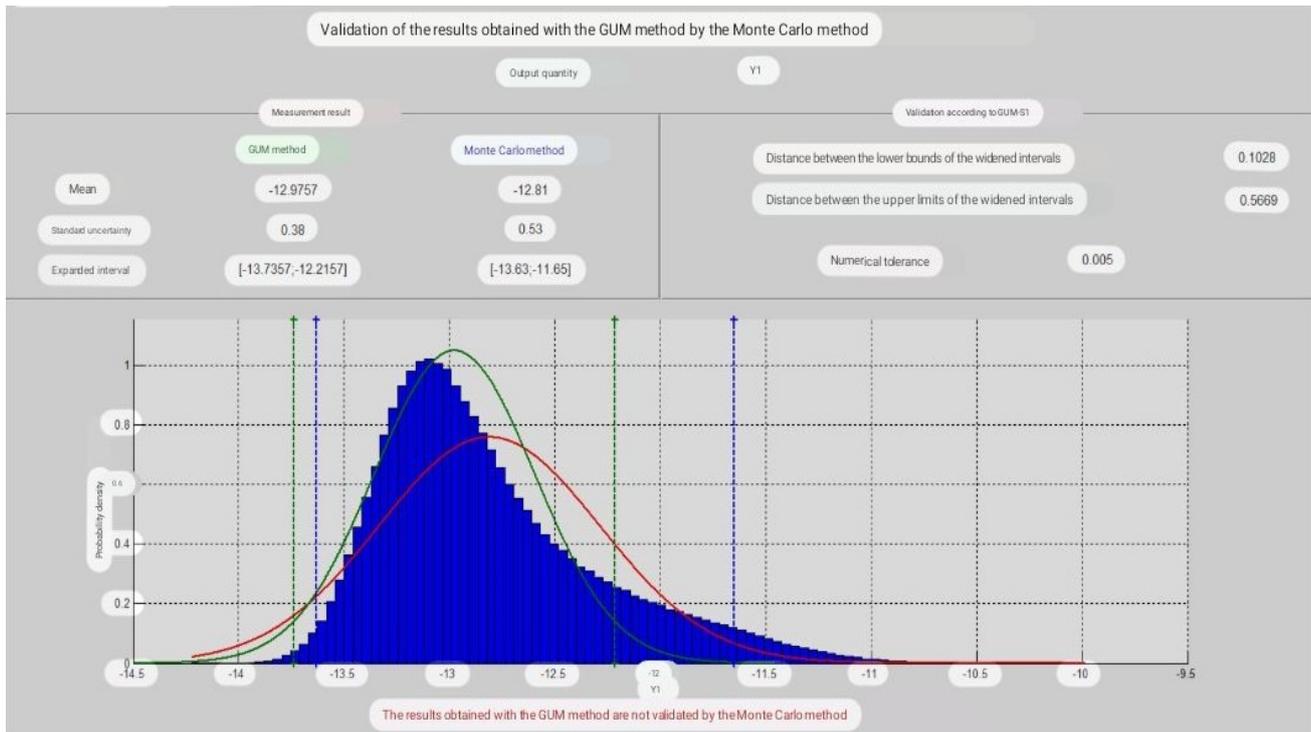


Figure 4: Distribution of leak values

With the leak value and its uncertainty determined by the two different methods, a validation procedure can be applied to check the validity of the GUM. For both methods the shortest 95 % coverage interval can be determined, and those intervals can be compared. The magnitudes of the endpoint differences d_{high} and d_{low} are compared to a numerical tolerance in order to determine whether the GUM framework approach is valid in this case.

The standard uncertainty obtained with the GUM framework is $0.14 \text{ g}\cdot\text{yr}^{-1}$, both digits are significant. Therefore, the numerical tolerance δ is 0.005.

Table 1: Validation of the GUM uncertainty calculation

Method	Q / $\text{g}\cdot\text{yr}^{-1}$	$u(Q)$ / $\text{g}\cdot\text{yr}^{-1}$	95 % coverage interval	d_{low}	d_{high}	GUM validated? ($\delta = 0.005$)
GUM	4.73	0.14	[4.41; 4.95]	0.16	0.02	NO
MCM	4.68	0.19	[4.25; 4.97]			

As seen in Table 1, both d_{high} and d_{low} are larger than the numerical tolerance and therefore the uncertainty calculation using the GUM framework is not validated.

This leak has already been calibrated by pressure department at LNE using the concentration variation method and its value is $(4.65 \pm 0.15) \text{ g}\cdot\text{yr}^{-1}$ ($k = 2$). The results obtained using Monte Carlo method can be compared to this reference value.

Table 2: Comparison of gravimetric and concentration variation method

Method	Leak value / $\text{g}\cdot\text{yr}^{-1}$	Expanded uncertainty / $\text{g}\cdot\text{yr}^{-1}$	Normalised error
Concentration variation	4.65	0.15	0.07
Gravimetric	4.68	0.38	

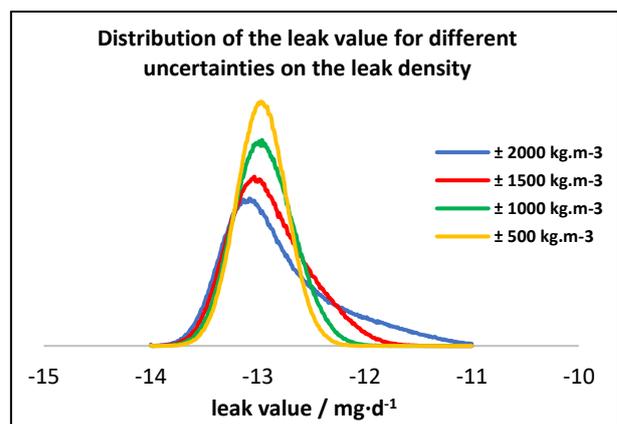


Figure 5: Distribution of leak values

As can be seen in Table 2, the concordance between the two calibrations is good which seems to confirm the pertinence of the gravimetric method using Monte Carlo estimation.

In this specific case the non-symmetrical distribution of the leak value explains why the GUM framework uncertainty evaluation cannot be validated. However, reducing the uncertainty on the leak density significantly improves this issue and in those cases the GUM method is valid. This can be

done by spending more time and being careful during the leak volume determination. In this work this uncertainty has been maximised in order to study the worst-case scenario. Reducing the uncertainty on the leak density drastically changes the distribution of the leak values as seen in Figure 5. In this case it can be observed that the distribution seems symmetrical for an uncertainty on the leak density of about $1\,000\text{ kg}\cdot\text{m}^{-3}$ and under. With such reduced uncertainties, the GUM uncertainty evaluation is validated and there is no need for a Monte Carlo study.

Finally, if the leak has a density close to $8\,000\text{ kg}\cdot\text{m}^{-3}$ [3] or if the measurements are performed in very stable conditions (in an airtight vessel for instance), the uncertainty due to the air buoyancy correction becomes negligible.

5. SUMMARY

The results obtained and the good concordance with the reference method show that applying the Monte Carlo method can be a good way to take into account the air buoyancy correction during standard leak calibration. The method presented allows the calibration of a standard leak with an expanded uncertainty less than 10 % of the nominal value. It is easy to implement and does not require sophisticated equipment. It is worth noting that the uncertainty could be further reduced by narrowing the interval of the leak density without a lot of effort. It should also be noted that applying the Monte Carlo method might not be absolutely necessary depending on the leak density, ambient conditions and their uncertainties. However, it

might be important to check the distribution of the leak values and the validation of the GUM method since it has been shown that these parameters might have a big influence on the result.

In conclusion, this method may be a good way to calibrate standard leaks which density is far from $8\,000\text{ kg}\cdot\text{m}^{-3}$ or have odd shapes making difficult the geometrical measurement of its volume. It may also be useful in cases where the measurements have to be performed over an extended period of time with large variations of ambient conditions. In this specific case, it was found that the classical GUM framework approach is validated only if the uncertainty on the leak density is lower than $1\,000\text{ kg}\cdot\text{m}^{-3}$.

6. REFERENCES

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