→ White Paper

A Member of The Linde Group

Understanding measurement uncertainty in certified reference materials

The importance of measurement uncertainty.

This paper provides an overview of the importance of measurement uncertainty in the manufacturing and use of certified reference gases. It explains the difference between error and uncertainty, accuracy and precision.

No measurement can be made with 100 percent accuracy. There is always a degree of uncertainty, but for any important measurement, it's essential to identify every source of uncertainty and to quantify the uncertainty introduced by each source.

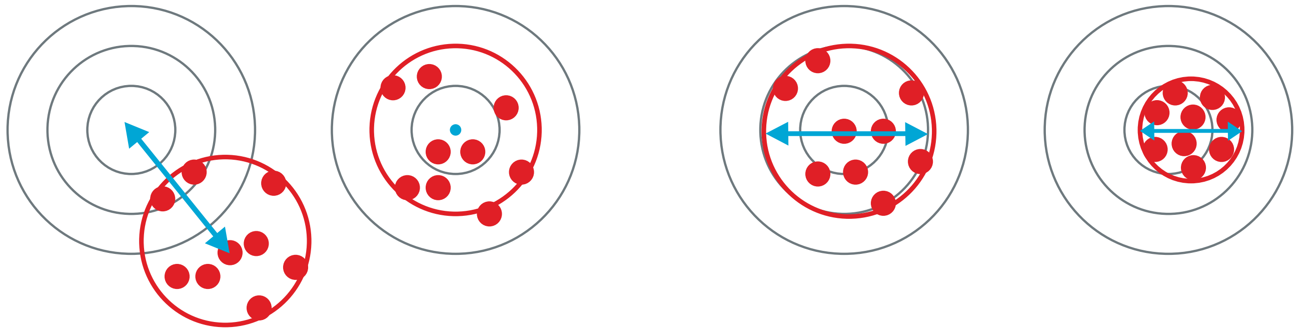
In every field of commerce and industry, buyers require certified measurements to give them assurances of the quality of goods supplied: the tensile strength of steel; the purity of a drug; the heating power of natural gas, for example.

Suppliers rely on test laboratories, either their own or third parties, to perform the analysis or measurement necessary to provide these assurances. Those laboratories in turn rely on the accuracy and precision of their test instruments, the composition of reference materials, and the rigour of their procedures, to deliver reliable and accurate measurements.

Every stage of the process, every measurement device used introduces some uncertainty. Identifying and quantifying each source of uncertainty in order to present a test result with a statement quantifying the uncertainty associated with the result can be challenging. But no measurement is complete unless it is accompanied by such a statement.

This white paper will provide an overview of sources of measurement uncertainty relating to the manufacture and use of certified reference gases. It will explain how uncertainty reported with a test result can be calculated and it will explain the important differences between uncertainty, accuracy and precision.

Measurement provides quantitative information about the properties of an object, substance or process.



Not Accurate	Accurate	Not Precise	Precise
Large deviation	Small deviation	High divergence	Low divergence
Far from correct	Close to correct	Dispersed results	Closely grouped

Figure 1

Some measurements are simple, referring to only one attribute such as size, mass, temperature, or speed. Others can be extremely complex such as determining the amount of each individual gas in a multi-component gas mixture.

However, all measurements have two things in common: they require some means of making the measurement and a unit of measurement.

Almost every country in the world today uses the same units of measurements: the SI system (abbreviated from the French Système international (d'unités)).

In the SI system there are seven fundamental units of measurement: length–metre; time–second; amount of substance–mole*; electric current–ampere; temperature–kelvin; luminous intensity–candela; mass–kilogram.

Today every one of the seven fundamental SI units has been restated in terms of fundamental properties of the universe. These are unchanging and can be measured with great accuracy.

The kilogram was the last to go. For over a century, until 2019, it was the mass of a single platinum iridium cylinder stored in a locked vault in the International Bureau of Weights and Measures in France known as the "Big K". In 2019 the kilogram was redefined as a fundamental property of matter, in terms of the Planck Constant. However that cylinder is still used as a practical reference standard and is calibrated against the fundamental standard.

Measurement uncertainty is critical to risk assessment and decision making. Organisations make decisions based on measurements. The more uncertain they are about the accuracy and precision of those measurements, the bigger the risks associated with those decisions.

Accuracy and precision are terms often interchanged, but they are not synonymous. There are uncertainties associated with both the accuracy and precision of measurements, so it is important to understand the distinction.

Accuracy is the closeness of a measurement to the true value of the property being measured.

Precision is a measure of how close repeated measurements are to each other, when there is no change in the property being measured.

It is perfectly possible to achieve very high precision with considerable inaccuracy: a large number of very similar measurements could be way off the mark if there were some aspect of each measurement introducing a similar level of inaccuracy, such as a wrongly calibrated instrument. See figure 1.

Only by identifying and quantifying all the uncertainties in a measurement – in its precision and its accuracy — can there be any estimate of the accuracy of a group of multiple measurements, no matter how close they are to each other.

* One mole of a substance is by definition 6.022×10^{23} particles of that substance. These could be molecules, atoms or electrons depending on the substance. One mole of water, for example contains 6.022×10^{23} molecules and has a mass of 18.015 grammes.

Measurement uncertainty is the doubt about the result of any measurement. For every measurement there is always an element of doubt.

Good measurement practice means identifying all possible uncertainties, determining their importance, estimating the degree of uncertainty, taking the steps necessary to reduce overall uncertainty to acceptable limits, and reporting the degree of uncertainty associated with a measurement.

Measurement **error** is not the same as uncertainty. When a device to be calibrated is compared against a reference standard, the difference is an error, but that error is meaningless unless the uncertainty associated with that measurement can be determined.

There are three components to estimating uncertainty:

- Identifying and quantifying the effect of any environmental factors that can affect the accuracy of measurement.
- Estimating the accuracy of the measuring equipment or material.
- Estimating the uncertainties in taking the measurement.

To take a simple example. If we attempt to measure the mass of an object using a balance, the weight of that mass (the gravitational force acting on it), and hence the balance reading, will be reduced by the buoyancy effect of the fluid surrounding it (the air). This effect will vary according to the temperature, pressure and humidity of the air.

No stage in this process is 100 percent accurate, but the overall uncertainty can be estimated and reported where important, for example in a contract to supply a precise quantity of some good.

Calculating uncertainty in practice.

Calculating uncertainty can be a complex and challenging task.

The composition of gases is measured by comparing the test gas with a reference gas whose composition is known with great precision. Each step in the production of a reference gas introduces uncertainties and reference gases are supplied with a certificate detailing the sources of those uncertainties and quantifying them.

Figure 2 represents all the sources of uncertainty in the production of a certified reference gas.

Table 1 shows an example of the values assigned to the Gravimetry portion of the uncertainty budget breakdown from figure 2.

Clearly the production of a certified reference gas with uncertainties correctly assessed and reported requires the identification and assessment of many contributions.

Strict international standards govern the manufacture and use of reference gases around the world, with compliance tightly controlled by accreditation bodies such as the National Association of Testing Authorities (NATA) in Australia.

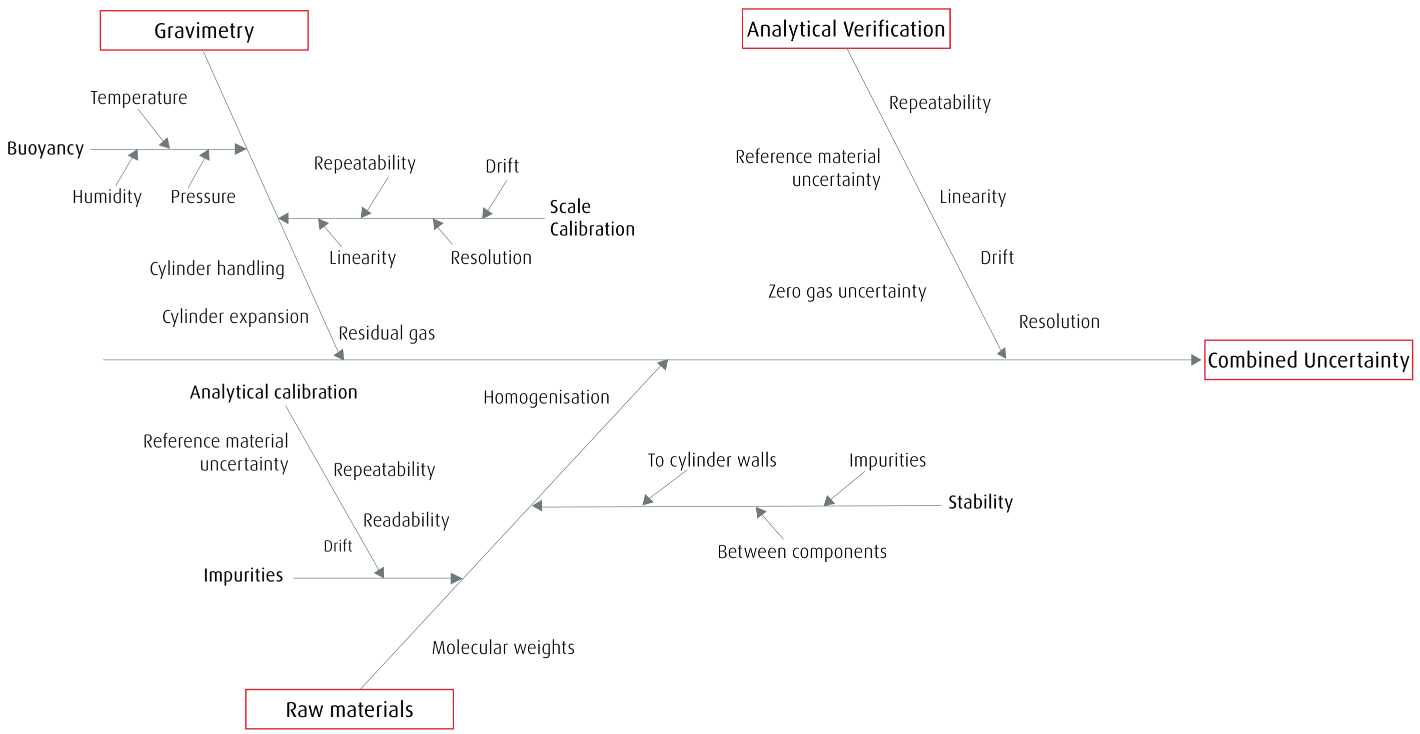


Figure 2

Symbol	Source of uncertainty	Value±	Probability distribution	Divisor	c_i	$u_1(C_x)$±g
t_1	Tare reading 1	0.0133	Normal	2.18	1	0.00610
m_1	Mass reading 1	0.0288	Normal	2	1	0.01442
t_2	Tare reading 2	0.0133	Normal	2.18	1	0.00610
m_2	Mass reading 2	0.0288	Normal	2	1	0.01442
BC	Buoyancy correction	0.0319	Rectangular	√3	1	0.018443
LE	Cylinder expansion due to pressure	0.0168	Rectangular	√3	1	0.0097
RG	Residual gas	0.0057	Rectangular	√3	1	0.0033
PH	Physical handling of cylinder	0.003	Normal	1	1	0.003
U(w)	Combined uncertainty		Normal			0.03073
U	Expanded uncertainty		Normal			0.0615

Table 1

Standards and accreditation are essential to give customers of test laboratories confidence as to the quality, accuracy and traceability of measurements and materials provided by those laboratories.

Why are standards important?

Standards fulfil two roles:

- They provide guidance to test and calibration laboratories on good practice in measurement, traceability, calibration and the identification and estimation of uncertainties.
- They give buyers confidence in the properties and specifications quoted by suppliers for the goods they supply, and importantly, values for the uncertainties associated with these properties and specifications.

There are two main international standards applicable to all test and calibration laboratories, and one specific to the gas industry.

ISO/IEC 17025 - *General requirements for the competence of testing and calibration laboratories.*

This is the main International Standards Organisation (ISO) standard used by testing and calibration laboratories. It enables laboratories to demonstrate they operate competently and generate valid results.

It also helps facilitate cooperation between laboratories and other bodies by generating wider acceptance of results between countries. Test reports and certificates from one country can be accepted by another without the need for further testing, facilitating international trade.

In most countries, most labs are required to hold ISO/IEC 17025 accreditation to be deemed technically competent. Most suppliers and regulatory authorities will not accept test or calibration results from a laboratory that is not ISO/IEC 17025 accredited.

ISO 17034:2016 - *General requirements for the competence of reference material producers.*

This standard covers the production of all reference materials used to make measurements, including certified reference materials. It specifies general requirements for the competence and consistent operation of reference material producers and specifies how reference materials are to be produced.

The International Bureau of Weights and Measures (BIPM) defines a reference material as "material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties."

ISO 6142-1:2015 *Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures.*

This standard specifies a gravimetric method for the preparation of reference gas mixtures for calibrating equipment used for measuring the composition of other gas mixtures. It describes a method for calculating the uncertainty associated with the concentration of each component in the mixture.

This uncertainty calculation requires the evaluation of the contributions from the weighing process, the purity of the components, the stability of the mixture, and the verification of the final mixture.

Guides to determining uncertainty.

In addition, the ISO produces a number of guides to the determination of uncertainty.

ISO/IEC Guide 98-1:2009 *Uncertainty Of Measurement — Part 1: Introduction To The Expression Of Uncertainty In Measurement.*

This guide addresses measurement science, considers various concepts used in measurement science, and covers the need to characterise the quality of a measurement through appropriate statements of measurement uncertainty.

ISO/IEC Guide 98-3:2008 *Uncertainty of Measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995).*

This guide establishes general rules for evaluating and expressing uncertainty in measurement that can be followed at various levels of accuracy and in many fields — from the shop floor to fundamental research. The principles it sets out are applicable to a broad spectrum of measurements:

- They provide guidance to test and calibration laboratories on good practice in measurement, traceability, calibration and the identification and estimation of uncertainties.
- They give buyers confidence in the properties and specifications quoted by suppliers for the goods they supply, and importantly, values for the uncertainties associated with these properties and specifications.

Assessment for standards conformance.

In Australia the National Association of Testing Authorities (NATA) is the body responsible for ensuring organisations are compliant with relevant international and Australian standards. In New Zealand this role is performed by International Accreditation New Zealand (IANZ).

Accreditation of a laboratory to ISO 17025 or ISO 17034 is recognised internationally. In recent years, mutual recognition between different accreditation bodies consistently includes ISO 17034 which is most common in Australia.

Australian laboratories are now typically audited every one and a half years. The process checks the laboratory has the correct practices and quality systems in place to undertake its contracted work in conformance with the applicable standards.

Failure to provide the right documentation and certificates can lead to loss of accreditation, putting a laboratory's whole business at risk.

The shelf life or storage life, of any substance is the time interval between manufacture and the date at which it is no longer fit for purpose.

Why is shelf life important?

Measurement of the composition of gases is generally by comparison to a sample of known composition, a certified reference material (CRM).

It is vital that the certification values of the CRM remain stable for the duration of the shelf life outlined on the certificate.

This is especially important when handling gas mixtures containing reactive components as they could form different compounds in the presence of contaminants.

These changes in a reference gas create uncertainties in the composition of any gas that is measured against them, and these uncertainties must be identified and quantified. So any CRM is supplied with specified shelf life – the length of time for which these uncertainties can be stated with confidence.

How is shelf life assessed?

The various standards detailed above all contain some specifications on the determination and reporting of shelf life.

ISO 17034 requires the stability of a reference material to be assessed, and any uncertainty due to instability to be added to the uncertainty budget.

ISO Guide 35:2017 is a guide to meeting these requirements. It provides guidance on:

— the assessment of homogeneity;
— the assessment of stability and the management of the risks associated with stability issues;
— the characterisation and value assignment of properties of a reference material;
— the evaluation of uncertainty for certified values;
— the establishment of the metrological traceability of certified property values.

ISO 17025 does not require any stability assessment. It gives no assurance on the long-term life of the product, only guaranteeing the value at the time of testing.

ISO 6142 also provides guidance on how to set up, run and evaluate a stability trial. It also outlines a method for incorporating the uncertainty due to stability into the total uncertainty.

Traceability.

Traceability is vital in ensuring measurements are accurate and that they meet required standards. Standards, accreditations and certificates are all important aspects of traceability.

For more information, please refer to BOC's white paper "Ensuring traceability in Australian laboratories."

Demonstrating competence.

The reliability and accuracy of gas testing in Australia is dependent on the quality of reference gases from suppliers — accredited to ISO 17304. That means they must provide, for every measurement used to produce that gas, information tracing back to a fundamental SI Unit and stating the uncertainty introduced at each step.

In addition to obtaining accreditation from regulatory bodies, manufacturers of certified reference material are able to demonstrate their capability by participating in a variety of proficiency tests that are designed to directly scrutinise the manufacturers' ability to analyse and or produce CRMs. These cover the full range of products offered by manufacturers but can also focus on specific end user applications which may be new or deemed critical.

For example, currently the increasing use of hydrogen in gases used for heating adds new challenges to gas testing, and the production of the necessary reference gases. To support producers, the National Measurement Institute staged a proficiency test to assess test laboratories' ability to manufacture gases with specified composition, and help them assess their measurement uncertainty estimates, as required by ISO 17034.

The participating laboratories, which included BOC, were asked to supply certified reference gases comprising specified percentages of nine different gases.

Each participant prepared a gas mixture with the specified composition and sent this to the NMI with a certificate detailing the method of manufacture, the composition of the mixture, and the uncertainties associated with composition percentages.

The NMI then analysed and certified these mixtures against its primary standard. It also detailed the procedures used to establish the traceability of its reference values, and the uncertainties associated with them.

For each sample submitted by participants the NMI calculated a 'z-score': a measure of the difference between the concentrations assigned by the participants and values determined by the NMI.

NMI combined its uncertainty figures with those provided by the laboratories to create an expanded figure for uncertainty, the 'En-score'.

NMI reported that BOC had achieved satisfactory Z-scores for all components and absolute EN scores ≤ 1 for every component. The accuracy of BOC's preparation of reference gas, and its assessment of uncertainties was independently verified and found to be very good.

Fiscal risk is the potential of revenue to deviate from a budgeted or forecast figure.

Why is measurement accuracy and uncertainty important in managing fiscal risk?

	Scenario A		Scenario B
LNG cargo capacity	175,000 m^3 ≈ 4,207,882 mmBtu	=	175,000 m^3 ≈ 4,207,882 mmBtu
Sell price	$6.94 AUD per mmBtu	=	$6.94 AUD per mmBtu
LNG cargo value	$29.2M	=	$29.2M
Calibration uncertainty	1%		0.5%
Value uncertainty	±$292K		±$146K

In this example, scenario B provides a significantly smaller uncertainty on the certification value of the cargo, reducing the fiscal risk in exporting the product.

Table 2

Why is measurement accuracy and uncertainty important in managing fiscal risk?

Deviations from budgeted or forecasted figures could be the result of expenditure in excess of the budgeted figure, or sales revenue being lower than forecast through either lower volumes or lower prices.

There can be no certainty in foretelling the future, but minimising and quantifying uncertainties in the present can limit fiscal risk. The supply of natural gas is a particularly telling example.

Pricing Australian LNG.

Huge quantities of liquid natural gas are exported from Australia, and while the gas is supplied by volume it is generally priced according to its ability to generate heat when burnt. Heat output is measured in millions of British thermal units (mmBtu).

The heating ability, and hence the money the supplier will receive for the shipment, is assessed prior to export. The degree of uncertainty in that measurement translates to a degree of uncertainty as to the value of the shipment (i.e. a fiscal risk).

Table 2 shows how reducing the stated uncertainty in the supplier's test result by just 0.5% can reduce fiscal risk by a significant sum.

Tracking Environmental emissions.

Plants around the world are strictly monitored against a maximum threshold for emitting pollutants into the environment. Emission limits have decreased over time and the regulatory bodies are more stringent in their enforcing of regulations.

Monitoring of pollutants needs to be performed in a manner that is traceable to accredited standards so that the results can be relied upon for audits or cases of legal action. When using calibration standards, the uncertainty of that calibration standard should be considered to ensure high confidence that emission thresholds are being adhered to.

For example, if emissions of a certain pollutant are limited to no more than 5ppm in concentration, a traceable reference material should be used to calibrate the analyser. If the reference material has a ±5% uncertainty at this concentration, the absolute range of uncertainty is ±0.25ppm. If the reference material has a ±2% uncertainty, the absolute range of uncertainty is ±0.1ppm. By using a reference material with lower absolute uncertainty, the emissions can be monitored more accurately, therefore ensuring stricter adherence to emissions limits.

Conclusion.

In this white paper we have:
- explained measurement uncertainty and its importance;
- distinguished between uncertainty, accuracy and precision;
- explained how individual components contribute to overall uncertainty of a measurement;
- explained how all measurement units are derived from seven fundamental units;
- explained how a practical measurement device can be calibrated by comparing it to a reference standard derived over multiple stages from the fundamental unit;
- identified the standards that testing laboratories must follow to identify, quantify and report uncertainties associated with their test results;
- explained traceability and its importance and demonstrated the challenges of tracing all steps and estimating all uncertainties in a complex measurement;
- shown how uncertainties contribute to fiscal risk.

Anyone who requires knowing properties of materials with accuracy needs to also know the uncertainties associated with those figures: to limit fiscal risk; to ensure safety; to ensure compliance to government legislation; to avoid waste.

Organisations supplying those materials must be able to assign the level of uncertainty to each measurement. They in turn rely on test laboratories, manufacturers of measuring equipment, suppliers of reference materials to assign an adequate level of uncertainty to their reference materials.

For all these parties the ability to identify every source of uncertainty and assign a value to it is important.

Utilising high accuracy and precision reference materials can help ensure values certified by laboratories have the lowest measurement uncertainty. For example, BOC's HiQ® Primary Gravimetric Standards deliver significantly higher precision and better analytical uncertainty than other gas mixture classes.

When it comes to measuring the composition of gases, BOC has a large team of scientific specialists who can advise on the correct reference gases to use, and are supported by a technical team.

A simple conversation today can save a painful corrective action later. BOC also has the capability to supply documentation online for ease of doing business.

For more information, please visit www.boc.com.au

Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages, and greater profitability.
Each concept is tailored specifically to meet our customers' requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimisation, and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

Linde – ideas become solutions.

For more information, please visit www.boc.com.au

BOC Limited
10 Julius Avenue, North Ryde NSW 2113, Australia
www.boc.com.au

970–988 Great South Road, Penrose, Auckland, New Zealand
www.boc.co.nz