



# Gas reference materials and measurements

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Details of the traceable, high-accuracy gas reference materials and measurement solutions provided by the **National Physical Laboratory**



## About the National Physical Laboratory

The National Physical Laboratory (NPL) is the UK's National Metrology Institute and the birthplace of Alan Turing's ACE computer, the first universal computer of its kind; packet switching, the basis of the internet; and atomic time, the backbone of GPS and global communications.

Our measurement expertise has underpinned prosperity and quality of life in the UK for more than a century. Our role is highly diverse and finds us working on world-leading science and engineering that impacts healthcare, environmental monitoring, advanced manufacturing and the development of next-generation technologies and techniques, with the potential to further transform our lives; from new antibiotics to tackle resistance and more effective cancer treatments, to unhackable quantum communications and superfast 5G.





# Contents

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## General information ..... 4-5

NPL gas reference materials .....	4
Accreditation, international comparability and certificates .....	5

## Energy gases ..... 6-14

Natural gas and hydrogen enriched natural gas .....	6
Odorants .....	7
Refinery gas .....	8
Hydrogen gaseous reference materials .....	9
Hydrogen purity .....	10
Biogas and biomethane .....	11-12
Carbon capture, utilisation and storage .....	13
Gas reference materials for nuclear .....	14

## Environmental gases ..... 15-24

Volatile organic compounds (VOCs) .....	15-16
Oxygenated-VOCs .....	17
Chemical ionisation mass spectrometry standards .....	18-19
Climate .....	20
Isotopic reference materials .....	21-22
Air quality .....	23
Industrial and vehicle emissions .....	24

## Industrial and emission gases ..... 25-26

Breath alcohol and interfering substances .....	25
Water vapour .....	26

## High purity gases ..... 27

High purity gases .....	27
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## Other products and services ..... 28-31

Pressurised (hyperbaric) environments .....	28-29
Gas metrology software .....	30
'On-demand' proficiency testing schemes .....	31

# NPL gas reference materials



NPL provides the following classes of gas reference materials:

## **NPL Primary Reference Materials (NPL PRMs)**

NPL PRMs (previously PRGMs) are prepared gravimetrically in accordance with ISO 6142-1 and are validated against NPL in-house PRMs. The certificate provided with an NPL PRM reports the gravimetric amount fraction value with an uncertainty that represents the best achievable analytical uncertainty. It also provides an expiry date for the mixture, which is assigned from data obtained from stability studies of similar mixtures.

These mixtures sit at the top of the traceability chain with the smallest uncertainties. It is only by comparison of these primary realisations of the mole with other National Metrology Institutes (NMIs) and Designated Institutes (DIs) around the world, using the measurement redundancy that this provides, that the full uncertainty of the realisation can be achieved. This takes place as part of Key Comparisons performed under the International Committee for Weights and Measures (CIPM) Mutual Recognition Arrangement (MRA) and results in Calibration and Measurement Capabilities (CMCs) claimed by the NMIs/DIs which are peer-reviewed and, when agreed, stored on the CIPM MRA database. This process provides the uncertainty with which these standards can be realised and disseminated.

**NPL PRMs provide the primary realisation of the mole in gas mixtures at a national level which is only available from NMIs/DIs.**

## **NPL Certified Reference Materials (NPL CRMs)**

NPL CRMs (previously SGSs) contain reactive and unstable components. These mixtures are prepared in the same way as NPL PRMs but due to initial changes in amount-of-substance fraction after filling, they are provided with a certificate that reports the value obtained from the analytical certification process by comparison to NPL in-house PRMs. The certificate may also contain an expiry date for the mixture, which is assigned from data obtained from stability studies of similar mixtures.

## **NPL Calibrated Gas Mixtures (NPL CGMs)**

NPL CGMs are mixtures that have been supplied by commercial organisations and individually certified against NPL in-house PRMs. The certificate provided with an NPL CGM reports the certified value determined by the analytical method used, and an analytical uncertainty (which is typically larger than that provided for an NPL PRM). A guarantee of stability is not normally provided for an NPL CGM due to a lack of knowledge of the history of the cylinder and the gas mixture.

# Accreditation, international comparability and certificates



## ISO 17034 and ISO 17025 accreditation

NPL has an extensive scope of accreditation to ISO 17034 (Reference Materials) and ISO 17025 (Calibration) awarded by UKAS (the United Kingdom Accreditation Service).

## International comparisons

NPL frequently participates in international comparison exercises with other National Metrology Institutes (NMIs) and Designated Institutes (DIs). These comparisons, which are organised by the Consultative Committee for Amount of Substance (CCQM) of the International Committee for Weights and Measures (CIPM), provide a robust framework to demonstrate the global comparability of gas standard mixtures and measurements.

## Calibration and Measurement Capabilities

Results of the comparisons operated by the CIPM CCQM are used to compile internationally-recognised Calibration and Measurement Capabilities (CMCs).

Further information regarding international comparisons and CMCs can be found from the BIPM Key Comparison Database: <http://kcdb.bipm.org>.

## CIPM Mutual Recognition Arrangement

Certificates for gas mixtures covered by NPL's CMCs display the logo of the Mutual Recognition Arrangement (MRA) of the CIPM. Certificates containing this logo are mutually recognised by all NMIs who are signatories to the MRA.



## Units

The composition of gases on NPL certificates are stated in units of amount-of-substance fraction (mol/mol) or decimal submultiples thereof. If requested by the customer, the certificates may be issued with other units.

The most common decimal submultiples of mol/mol used on NPL certificates are:

- mmol/mol (equivalent to  $10^{-3}$  mol/mol)
- $\mu$ mol/mol (equivalent to  $10^{-6}$  mol/mol, often called parts-per-million or ppm)
- nmol/mol (equivalent to  $10^{-9}$  mol/mol, often called parts-per-billion or ppb)

# Natural gas and hydrogen enriched natural gas



NPL's natural gas reference materials are typically used to calibrate gas analysers such as process gas chromatographs. This enables the composition of real natural gases to be determined, thus allowing accurate calculation of the calorific value and other physical properties of the gas.

In addition to the components usually found in synthetic natural gas reference materials ( $C_1$  to  $C_5$  alkanes, *n*-hexane, nitrogen and carbon dioxide), NPL's standards can also contain  $C_6$  to  $C_{10}$  hydrocarbon components and BTEX. Accurate measurement of these components is particularly useful when hydrocarbon dew point is to be calculated, reassuring the gas transporter that condensation of the mixture will not take place in the gas pipeline.

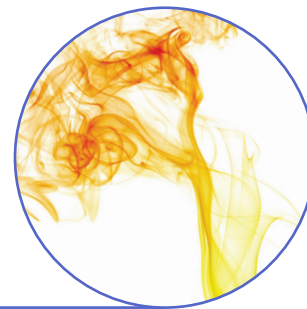
The range of natural gas reference materials covered by NPL's UKAS accreditation is shown in the table below. Hydrogen-enriched natural gas mixtures with hydrogen amount fractions of from 0.5-30 cmol/mol, and mixtures containing other components (including other  $C_6$  and  $C_7$  isomers) may be prepared on request.

All NPL's natural gas mixtures come with a 5-year stability period and minimum storage temperature recommendation to guarantee homogeneity.

Component	Amount fraction range (cmol/mol) *
Methane	55.0 to 99.9
Nitrogen	0.02 to 25.2
Carbon dioxide	0.04 to 25.0
Ethane	0.008 to 18
Propane	0.008 to 8.0
<i>iso</i> -butane	0.004 to 1.7
<i>n</i> -butane	0.004 to 1.7
<i>neo</i> -pentane	0.0005 to 0.5
<i>iso</i> -pentane	0.0025 to 0.6
<i>n</i> -pentane	0.0025 to 0.6
<i>n</i> -hexane	0.0008 to 0.5
Helium	0.001 to 0.5
Hydrogen	0.5 to 30
Oxygen	0.05 to 1.0

Component	Amount fraction range (μmol/mol)
Benzene	5 to 500
Toluene	5 to 250
Cyclohexane	10 to 400
Methylcyclohexane	10 to 400
<i>n</i> -heptane	10 to 500
<i>n</i> -octane	5 to 200
<i>n</i> -nonane	1 to 120
<i>n</i> -decane	1 to 20

\*1 cmol/mol is equal to 0.01 mol/mol and is equivalent to the 'unit' % mol/mol often used by the natural gas industry.



# Odorants

## Sulphur odorants

Sulphur-containing compounds are added to natural gas to provide a distinctive odour, allowing potentially hazardous leaks to be quickly detected. The odour thresholds of these compounds enable detection by the human nose at very low concentrations.

NPL's sulphur odorant standards are available as binary or multi-component mixtures, in a matrix of methane or nitrogen. The range of standards covered by NPL's UKAS scope of accreditation is shown in the table below.

Component	Amount fraction range ( $\mu\text{mol/mol}$ )	Component	Amount fraction range ( $\mu\text{mol/mol}$ )
Hydrogen sulphide	0.4 to 5000	Methanethiol	0.4 to 200
Carbonyl sulphide	0.4 to 5000	Ethanethiol	0.4 to 200
Carbon disulphide	0.4 to 200	2-propanethiol	0.4 to 200
Dimethyl sulphide	0.4 to 200	1-propanethiol	0.4 to 200
Ethyl methyl sulphide	0.4 to 200	2-methyl-2-propanethiol	0.4 to 200
Diethyl sulphide	0.4 to 200	Tetrahydrothiophene	0.4 to 200

Odorant gas reference materials can be provided in alternative matrices such as hydrogen or biogas.

## Non-sulphur odorant standards

NPL also supplies a range of non-sulphur odorant mixtures to provide traceability for the measurement of components which are being increasingly used to odourise natural gas across Europe. Please contact us for more details.

# Refinery gas, synthesis gas, and coke oven gas



NPL provides high-accuracy gas reference materials for the analysis of a range of refinery gases. These gases, which include syngas, coke oven gas, reformer gas and blast furnace gas, are produced and emitted during the production and refining of petroleum products and solid fuels.

NPL's refinery gas reference materials are typically used to calibrate gas chromatographs, enabling the composition of real refinery gases to be determined. This allows the user to calculate the carbon content and other physical parameters of the gas, thus ensuring compliance with carbon trading legislation.

The range of refinery gas reference materials covered by NPL's UKAS accreditation is shown in the table below. Mixtures containing other components may be prepared on request.

Component	Amount fraction range (cmol/mol) *
Nitrogen	0.1 to 95
Carbon monoxide	0.1 to 11
Carbon dioxide	0.3 to 8
Oxygen	0.2 to 2.5
Hydrogen	1 to 70
Helium	1 to 70
Methane	1 to 85
Ethane	0.3 to 35
Ethene	0.1 to 20
Ethyne	0.025 to 2
Propane	0.1 to 18

Component	Amount fraction range (cmol/mol) *
Propene	0.04 to 10
<i>iso</i> -butane	0.1 to 4
<i>n</i> -butane	0.1 to 6
1-butene	0.015 to 1.55
<i>iso</i> -butene	0.018 to 1.2
<i>trans</i> -2-butene	0.015 to 0.85
<i>cis</i> -2-butene	0.015 to 0.35
1,3-butadiene	0.01 to 3
<i>iso</i> -pentane	0.05 to 0.8
<i>n</i> -pentane	0.05 to 0.8

\* 1 cmol/mol is equal to 0.01 mol/mol and is equivalent to the 'unit' % mol/mol often used by the refinery gas industry.





# Hydrogen gaseous reference materials

The recent growth of hydrogen economy lead to an increase in measurements. Calibration and reference gas are essential to provide the reliability and traceability to the hydrogen sector to optimise or verify the hydrogen gas quality. Based on years of experience, stability studies and a curated selection of cylinders, NPL achieved to offer all hydrogen reference materials requires to cover all measurements required by ISO 14687 standards. To reduce gas calibration cylinders (for safety or inventory reasons), NPL developed a set of multi-components and binary mixtures to minimise the number of hydrogen reference materials present at analytical laboratories.

Example of Hydrogen reference materials available from NPL:

Analyte	Amount fraction ( $\mu\text{mol/mol}$ )	Expanded relative uncertainty (%)
Argon	300	2 – 5 %
Helium	300	2 – 5 %
Nitrogen	300	2 – 5 %
Methane	100	2 – 5 %
Water	5	5 – 10 %
Carbon dioxide	2	2 – 5 %
Ethane	1	2 – 5 %
Carbon monoxide	0.2	3 – 6 %
Ammonia	0.2	5 – 10 %
Dichloromethane	0.025	5 – 15 %
Dimethyl sulphide	0.004	2 – 7%
Hydrogen	Matrix	-

An exhaustive list can be provided on request including formaldehyde (0.3 – 10  $\mu\text{mol/mol}$ ), formic acid (0.3 – 100  $\mu\text{mol/mol}$ ), ammonia (0.3 – 100  $\mu\text{mol/mol}$ ) or sulphur compounds as dimethyl sulphide, carbonyl sulphide, hydrogen sulphide (0.004 – 10  $\mu\text{mol/mol}$ ), carbon disulphide ( $\text{CS}_2$ ).

## Proficiency testing

Proficiency testing is essential to demonstrate analytical laboratory competence to measure hydrogen gas quality. NPL has developed proficiency testing scheme suitable for hydrogen fuel quality according to ISO 14687. NPL has already managed several proficiency testing exercises (e.g. MetroHyVe 1 & 2, HyQuality Europe) with more than 30 laboratories. New PT schemes are available each year, please contact us for more information for registration and timelines.



# Hydrogen purity

Hydrogen fuel cell electric vehicles require high purity hydrogen for operation as even the presence of trace level impurities such as 4 nmol/mol of sulphur compounds can lead to the degradation of fuel cell catalysts. NPL has developed a comprehensive set of analytical methods, sampling techniques and calibration gases (primary and certified) to support the analytical community in delivering these challenging measurements.

Using a selection of state-of-the-art analytical methods, NPL can measure the concentrations of impurities in hydrogen as specified in the recent international standard ISO 14687 standard (Hydrogen fuel — Product specification). NPL operates various sampling system allowing representative sampling of hydrogen gas from a few bar up to 700 bar. These services are available for external parties and under our UKAS accreditation scope for hydrogen purity analysis.

Component	ISO 14687 threshold amount fraction ( $\mu\text{mol/mol}$ )
Water	5
Total hydrocarbons	2
Methane	100
Oxygen	5
Helium	300
Nitrogen	300
Argon	300

Component	Amount fraction ( $\mu\text{mol/mol}$ )
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.2
Formic acid	0.2
Ammonia	0.02
Halogenated compounds (including HCl)	0.016

Hydrogen samples are analysed against specially prepared traceable calibration gas reference materials, which can also be provided to customers. The laboratory provides additional services including validation of purity analysers, purity analysis of hydrogen production processes and consultation on the sampling process at hydrogen refuelling stations.



# Biogas and biomethane

NPL provides traceable gas mixtures for biogas and biomethane analysis, and also carries out composition measurements of real samples to support gas quality requirements, for example, as specified in EN 16723-1 and EN 16723-2.

NPL provides traceable gas mixtures for biogas and biomethane analysis, and also carries out measurements of real samples to support the quality requirements specified in European standard EN 16723.

## Biogas composition

UKAS accredited multi-component gas reference materials are available including, but not limited to, the components in the table below.

Component	Amount fraction range (cmol/mol)	Uncertainty ( $k=2$ ) (% rel.)
Methane	40 – 99.9	$\leq 0.2$
Carbon dioxide	0.04 – 55	$\leq 0.2$
Nitrogen	0.02 – 25	$\leq 0.3$
Hydrogen	0.05 – 10	$\leq 1.0$
Oxygen	0.05 – 1.5	$\leq 1.0$
Ethane	0.002 – 0.500	$\leq 1.0$
Propane	0.002 – 0.500	$\leq 1.0$

# Biogas and biomethane

## Trace-level impurities

Biogas and biomethane can contain a diverse range of impurities which vary in amount fraction depending on the source feedstock. Traceable gas reference materials containing any of the following components are available for instrument calibration needs:

## Siloxanes and total silicon

Standard NPL calibration gas sets are available to cover total silicon ranges of 0.1 – 1.5 mg/m<sup>3</sup> to meet EN 16723-1 and EN 16723-2 calibration requirements. The below components can also be ordered for individual calibration needs on request:

Component	Amount fraction range (μmol/mol)	Relative Uncertainty (%)	Matrix
<b>L2</b> ( <i>Hexamethyldisiloxane</i> )	0.004 – 3000	2 – 10	Biogas, Methane or Nitrogen
<b>L3</b> ( <i>Octamethyltrisiloxane</i> )	0.004 – 300	2 – 10	
<b>D3</b> ( <i>Hexamethylcyclotrisiloxane</i> )	0.004 – 700	2 – 10	
<b>D4</b> ( <i>Octamethylcyclotetrasiloxane</i> )	0.004 – 100	2 – 10	
<b>D5</b> ( <i>Decamethylcyclopentasiloxane</i> )	0.004 – 10	5 – 10	

- Sulphur species
- Terpenes
- BTEX
- Carbon monoxide
- Ammonia

Standards for other components found in biogas and biomethane may be available on request.

## Biogas and biomethane testing

NPL offers purity testing services against our traceable primary reference materials. See our website or contact us for more information.



# Carbon capture, utilisation and storage

Carbon capture, utilisation and storage (CCUS) technology deployment has been identified as critical in supporting reduction in global greenhouse gas emissions by 50 – 80 % by 2050, to avoid dramatic consequences of climate change. The presence of impurities in the carbon dioxide can have significant impacts on process control and safety, storage site integrity, flow assurance, and fiscal metering. Therefore, monitoring of impurities in the carbon dioxide is integral to ensuring safe, efficient, and cost-effective CCUS.

NPL can provide Primary Reference Materials (PRMs), analytical methods, representative sampling methodologies and support with quality control risk assessments to support with carbon dioxide quality assurance for use in CCUS processes.

Component	Upper limit [ $\mu\text{mol mol}^{-1}$ ]	
	Min	Max
H <sub>2</sub> O	20	50
H <sub>2</sub> S	5	20
O <sub>2</sub>	10	20
CH <sub>4</sub>	10000	40000
N <sub>2</sub>	10000	40000
Ar	10000	40000
H <sub>2</sub>	50	20000
C <sub>2</sub> H <sub>6</sub>	10000	40000
C <sub>3</sub> +	1500	20000
CO	100	2000
SO <sub>x</sub>	10	100
NO <sub>x</sub>	10	100

Key impurities for CCUS

Component	Upper limit [ $\mu\text{mol mol}^{-1}$ ]	
	Min	Max
NH <sub>3</sub>	10	1500
Particulates	1	1
HCl	10	70
HF	10	70
HCN	10	70
Glycol	0.025	0.05
MEA	0.08	1
Amine	10	10
Formaldehyde	20	60
Acetaldehyde	20	60
Cadmium	0.01	0.03
Selexol	0.6	0.6

# Gas reference materials for nuclear

NPL provides standards to support the nuclear industry, including standards for monitoring spent stored fuel and the fusion fuel cycle.

Component	Amount fraction range	Uncertainty ( $k=2$ ) (% rel.)
Helium	1-100 cmol/mol	$\leq 1$
Nitrogen	1-100 cmol/mol	$\leq 1$
Krypton	1-100 cmol/mol	$\leq 1$
Methane	5 $\mu$ mol/mol	$\leq 5$
Carbon dioxide	5 $\mu$ mol/mol	$\leq 5$
Carbon monoxide	5 $\mu$ mol/mol	$\leq 5$
Hydrogen	5 $\mu$ mol/mol	$\leq 5$



# Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) play a key role in the chemical reactions that lead to the photochemical production of ozone and particulate matter and influence the oxidation capacity of the troposphere. VOCs such as non-methane hydrocarbons are major precursors to boundary layer and tropospheric ozone with implications for human and ecosystem health. The need to minimise these effects is reflected by the regulation of the 30 most important ozone precursor species (listed in the table below) as part of the European Directive on ambient air quality and cleaner air for Europe (2024/2881/EU). To ensure legislative compliance there is a requirement for stable and accurate gas mixtures to facilitate the traceable calibration of analytical instrumentation.

NPL provides a 30-component ozone precursor ( $O_3P$ ) standards that contain all the hydrocarbon compounds listed in the European Directive (2024/2881/EU) with typical amount fractions of 4 nmol/mol, but other amount fractions from 1 to 200 nmol/mol are also available.

Ethane	1,3-butadiene	2,2,4-trimethylpentane
Ethene	Pentane	Benzene
Ethyne	2-methylbutane	Toluene
Propane	1-pentene	Ethylbenzene
Propene	<i>trans</i> -2-pentene	<i>m</i> -xylene
Butane	2-methyl-1,3-butadiene (isoprene)	<i>p</i> -xylene
2-methylpropane	Hexane	<i>o</i> -xylene
1-butene	2-methylpentane	1,2,3-trimethylbenzene
<i>trans</i> -2-butene	Heptane	1,2,4-trimethylbenzene
<i>cis</i> -2-butene	Octane	1,3,5-trimethylbenzene

NPL's ozone precursor mixtures are recognised by the World Meteorological Organisation Global Atmospheric Watch (WMO-GAW) programme as their primary standard for all ten components (ethane, propane, isobutane, *n*-butane, acetylene, isopentane, *n*-pentane, isoprene, benzene and toluene) identified as of key importance for global monitoring of atmospheric composition in GAW Report 171 <https://library.wmo.int/idurl/4/47478>. They are used for the assessment of global ambient levels providing the technical basis for the assessment of changes in the chemical composition of the atmosphere on a global scale.

# Volatile organic compounds (VOCs)

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## **BTEX mixtures**

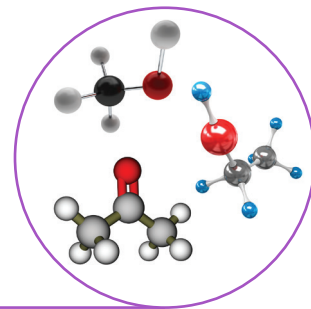
Benzene, toluene, ethylbenzene and xylenes are volatile mono-aromatic hydrocarbons that are key pollutants resulting from combustion processes. BTEX compounds are regularly monitored in surveys of indoor air quality as they are common constituents of products such as paints and adhesives. In an industrial environment, regulation of exposure to BTEX compounds is controlled through the application of occupational exposure limits and COSHH regulations.

NPL provides a range of stable and accurate BTEX gas reference materials, which contain benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene at amount fractions in the nmol/mol and  $\mu\text{mol/mol}$  range. Mixtures containing these compounds and 1,3-butadiene or dichloromethane are also available.

## **Bespoke VOC and halogenated hydrocarbon mixtures**

NPL can also prepare bespoke gas reference materials containing  $\text{C}_2$  to  $\text{C}_{10}$  hydrocarbons at a wide range of amount fractions. Contact us for more details.





# Oxygenated-VOCs

## Oxygenated VOCs

Oxygenated VOCs (oxy-VOCs) are a group of compounds which includes alcohols, ketones and aldehydes. Many of these compounds are emitted from both anthropogenic and biogenic sources. For example, methanol is the second most abundant organic compound in the Earth's atmosphere, is emitted in large amounts from vegetation and is a common industrial solvent. Oxy-VOCs are also found in biomass burning plumes and their emissions are closely monitored due to their influence on the HOx cycle and their influence on tropospheric ozone formation, which affects air quality.

NPL offers a range of traceable gas reference materials containing oxy-VOCs at an amount fraction of 1  $\mu\text{mol/mol}$ . One typical multi-component mixture contains the components shown in the list below; mixtures containing other oxy-VOCs (including acetaldehyde) are available on request.

Methanol	Ethanol	Acetone
2-Butanone (MEK)	Acetaldehyde	3-Buten-2-one (MVK)

# Chemical ionisation mass spectrometry standards

## Gas reference materials for calibrating PTR-MS instruments

NPL provides a 20-component gas mixture standard for calibrating the transmission function of Proton Transfer Reaction – Mass Spectrometry (PTR-MS) instruments - a state-of-the-art approach that allow for rapid and highly sensitive detection of trace volatile organic compounds (VOCs) in real-time. Their applications spread across several established disciplines from medicine and food science to cleanroom monitoring and environmental research. The composition of the gas standard includes the following compounds at nominally 1  $\mu\text{mol/mol}$  within a nitrogen balance gas. The uncertainties for each compound are in the range of 3-10 %.

Acetaldehyde	1,2,4-trifluorobenzene
Methanol	Toluene
Ethanol	Hexamethylcyclotrisiloxane
Isoprene	<i>m</i> -xylene
Acetone	Octamethylcyclotetrasiloxane
Dimethyl sulfide	1,2,4-trimethylbenzene
Acetonitrile	+3-carene
Perfluorotributylamine	Decamethylcyclopentasiloxane
3-buten-2-one	1,2,4-trichlorobenzene
Butan-2-one	Nitrogen balance
Benzene	

# Chemical ionisation mass spectrometry standards

## Gas reference materials for calibrating SIFT-MS instruments

Selected ion flow tube mass spectrometry (SIFT-MS) is a portable chemical ionisation technology designed to measure gases with high temporal resolution, detecting concentrations as low as  $\text{pmol mol}^{-1}$ . In SIFT-MS analyses,  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$  are used as reagent ions, avoiding interference from major air components and eliminating the need for sample pretreatment. The reagent ions are rapidly preselected using a quadrupole mass filter between the ion source and reaction chamber. SIFT-MS is also compatible with both positive and negative ion modes, as well as with flammable gases.

Regular calibration with traceable primary reference materials (PRMs) is crucial for reliable and reproducible SIFT-MS measurements (Langford et al., 2023, doi:10.1021/jasms.3c00312). However, a lack of high-quality, traceable calibration gas mixtures on the market currently poses challenges for cross-comparability in studies and monitoring projects, highlighting the need for consistent, stable gas reference materials for SIFT-MS.

NPL is the highest point of traceability and addresses this gap by offering a unique selection of PRMs specifically designed for SIFT-MS applications, including an eight-component gas reference material with an impressive five-year stability. These cost-effective standards support accurate, long-term performance across a wide range of sectors, from environmental monitoring to occupational health and safety, establishing global benchmarks and instilling confidence in your SIFT-MS calibration and results. The composition of this standard includes the following compounds at nominally  $2 \mu\text{mol mol}^{-1}$  within a nitrogen balance gas. The uncertainties for each compound are in the range of 3-5 per cent.

1,2,3,4-tetrafluorobenzene	benzene	isobutane
Octafluorotoluene	<i>p</i> -xylene	Hexafluorobenzene
Ethane	toluene	

# Climate



Terpenes are a diverse family of components that play a significant role in atmospheric chemistry due to their large anthropogenic and biogenic sources. The photochemical reactions of terpenes emitted by vegetation can lead to the production of tropospheric ozone, which is highly toxic to humans, and the formation of organic aerosols and particles that influence the climate.

Moreover, due to their known potential to create toxic ozone locally the influence of terpene emissions from household products upon indoor air quality is a new area of great importance. The measurement of atmospheric terpene concentrations are highly dependent upon the availability of traceable reference gas reference materials.

## Bespoke terpene mixtures

Mixtures containing the following monoterpenes, hemiterpenes and terpenoids at amount fractions of 2.5 to 100 nmol/mol are available for purchase:

1,8-cineole (eucalyptol)	3-carene
isoprene	limonene

Other components may be included on request such as *n*-octane, toluene or *n*-hexane.





# Isotopic reference materials

## Amount fraction

The National Physical Laboratory (NPL) provides SI traceable gas reference materials for amount fraction. Our gas reference materials are supplied in a synthetic air matrix comprising argon, oxygen and nitrogen at ambient amount fractions. These reference materials are suitable for calibrating a range of atmospheric gas analysers.

Component	Amount fraction range [ $\mu\text{mol mol}^{-1}$ ]	Typical amount fraction uncertainty ( $k=2$ ) [%]	Matrix
CO <sub>2</sub>	380 - 800 Other amount fractions may be available on request	0.2	Synthetic air N <sub>2</sub> is available on request
CH <sub>4</sub>	1.8 - 2.5 Other amount fractions are available on request	0.2	Synthetic air N <sub>2</sub> is available on request
N <sub>2</sub> O	0.32 – 0.35 Other amount fractions are available on request	1	Synthetic air N <sub>2</sub> is available on request
CO	Available on request		

## Isotope ratio

Information on the isotope ratio of the gases used to prepare these reference materials can be provided and we can offer certification of isotope ratio for some gas reference materials in-house. These measurements are traceable to VPDB, VSMOW/SLAP and Air/N<sub>2</sub>. These reference materials are suitable for calibration of isotopic analysers and are often used for source apportionment of greenhouse gases.

Component	Amount fraction range [μmol mol <sup>-1</sup> ]	Typical amount fraction uncertainty (k=2) [%]	Matrix	Isotopic values available [‰]			Isotope ratio traceability
CO <sub>2</sub>	400 – 420, 800	0.2	Synthetic air	δ <sup>13</sup> C: +2 -42 -20 -9	δ <sup>18</sup> O: -8 -36 -22 -15		VPDB
CH <sub>4</sub>	1.8 – 2.5	0.2	Synthetic air	δ <sup>13</sup> C: -39	δ <sup>2</sup> H: -195		VPDB, VSMOW/ SLAP
N <sub>2</sub> O	0.32 – 0.35	1	Synthetic air	δ <sup>15</sup> NSP: 1 -4 -0.7 20	δ <sup>15</sup> N: 0.2 53 16 33	δ <sup>18</sup> O: 39 103 55 40	Air N <sub>2</sub> , VSMOW/ SLAP

Multi component reference materials are available on request.

Reference materials are typically provided in a 10 L cylinder with BS314 no 14 valves at 100 bar.

## Zero air standard

Zero air reference materials with oxygen, nitrogen and argon closely matched to ambient composition are also available with accurate quantification of carbon dioxide, methane, nitrous oxide and carbon monoxide to low parts per billion levels.

Impurity	Matrix gas	Approximate quantification
Methane	Air (or N <sub>2</sub> )	< 15 nmol/mol
Carbon dioxide	Air (or N <sub>2</sub> )	< 200 nmol/mol
Carbon monoxide	Air (or N <sub>2</sub> )	< 15 nmol/mol
Nitrous oxide	Air (or N <sub>2</sub> )	< 10 nmol/mol



# Air quality

Routine measurements of air pollutants such as sulphur dioxide, oxides of nitrogen, carbon monoxide and benzene must be performed to fulfil the requirements of the EC Directive on ambient air quality and cleaner air for Europe (Directive 2024/2881/EU).

NPL provides gas reference materials for calibrating air quality monitors. Mixtures that meet the uncertainty requirements of Directive 2008/50/EC are shown in the table below; other mixtures are available upon request.

Component	Matrix gas	Amount fraction range	
		From	To
Sulphur dioxide	Nitrogen or air	100 nmol/mol	10 mmol/mol
Nitrogen monoxide	Nitrogen	100 nmol/mol	2 mmol/mol
Nitrogen dioxide	Nitrogen	1 $\mu$ mol/mol	1 mmol/mol
Carbon monoxide	Nitrogen or air	1 $\mu$ mol/mol	500 $\mu$ mol/mol

Standards of benzene and other hydrocarbon compounds are also available.

# Industrial emissions monitoring and vehicle emission



Monitoring of industrial and vehicle emissions is required to demonstrate conformity to legislation, such as the European Directive on industrial emissions (Directive 2024/1785). To achieve this it is necessary to utilise accurate and traceable gas reference materials.

NPL provides gas reference materials for calibrating a wide variety of analysers for measuring stack and vehicle emissions and other industrial emissions gases. Binary and multi-component gas mixtures can be prepared to the requirements of the customer. The table below provides an indication of the available mixtures; other mixtures are available upon request.

Component	Matrix gas	Amount fraction range	
		From	To
Carbon monoxide	Nitrogen	10 µmol/mol	100 mmol/mol
Carbon dioxide		10 µmol/mol	500 mmol/mol
Propane		10 µmol/mol	10 mmol/mol
Oxygen		10 µmol/mol	210 mmol/mol
Carbon monoxide	Nitrogen or air	1 µmol/mol	500 mmol/mol
Carbon dioxide	Nitrogen or air	1 µmol/mol	500 mmol/mol
Propane	Nitrogen or air*	1 µmol/mol	50 mmol/mol
Oxygen	Nitrogen	1 µmol/mol	500 mmol/mol
<i>n</i> -hexane	Nitrogen	1 µmol/mol	1 mmol/mol
Nitrogen monoxide	Nitrogen	1 µmol/mol	2 mmol/mol
Nitrogen dioxide	Nitrogen	1 µmol/mol	1 mmol/mol
Ammonia	Nitrogen	10 µmol/mol	2 mmol/mol
Hydrogen Chloride	Nitrogen	5 µmol/mol	90 µmol/mol

\*propane standards can only be prepared in an air matrix below 4 mmol/mol





# Breath alcohol and interfering substances

Traceable measurements of breath alcohol and interfering substances are required to underpin drink driving, airline and other workplace legislation. Gas reference materials containing these compounds can be used, for example, to calibrate evidential breath analysers as specified by the OIML (International Organization of Legal Metrology) International Recommendation OIML R 126 (Evidential breath analyzers).

Gas reference materials containing ethanol and interfering substances can be prepared to the requirements of the customer. Examples of the most common components in these mixtures are given below; other interfering substances (such as those listed in OIML R 126) may be available on request.

Component	Matrix gas	Amount fraction range	
		From	To
Ethanol	Nitrogen or air	20 $\mu\text{mol/mol}$	1 $\text{mmol/mol}$
Methanol	Nitrogen or air	10 $\mu\text{mol/mol}$	100 $\mu\text{mol/mol}$
Acetone	Nitrogen or air	10 $\mu\text{mol/mol}$	500 $\mu\text{mol/mol}$
Toluene	Nitrogen or air	10 $\mu\text{mol/mol}$	100 $\mu\text{mol/mol}$
Methyl ethyl ketone	Nitrogen or air	10 $\mu\text{mol/mol}$	500 $\mu\text{mol/mol}$
Carbon dioxide	Nitrogen or air	10 $\text{mmol/mol}$	100 $\text{mmol/mol}$



# Water vapour

Water vapour is one of the most difficult impurities to remove from gases, and it affects a number of manufacturing processes even at trace amount fractions. Instrumentation dedicated to measuring trace levels of water is therefore of paramount importance. The accuracy of these instruments can only be maintained through regular calibration to traceable reference standards.

Standards of water vapour provide an accurate method for calibrating instrumentation. Static reference standards of water (at amount fractions greater than 5  $\mu\text{mol/mol}$ ) in nitrogen are prepared in cylinders. Calibrations are also available at lower amount fractions using NPL's unique trace water vapour facility.

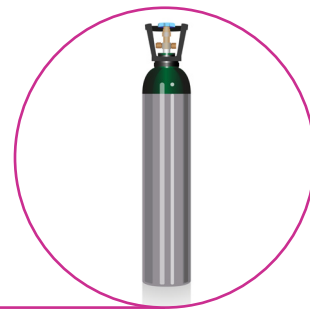
## Static standards

NPL provides gas mixtures containing water vapour in a matrix of nitrogen. These mixtures are available with the following amount fractions:

Component	Matrix gas	Amount fraction range	
		From	To
Water	Nitrogen	5 $\mu\text{mol/mol}$	100 $\mu\text{mol/mol}$

## Trace water vapour facility

The NPL trace water vapour facility is capable of generating an adjustable amount fraction of trace water (between 2 and 2000  $\text{nmol/mol}$ ) by using continuous accurate measurements of mass loss from a permeation device coupled with a dilution system based on an array of critical flow orifices. This is achieved with a relative expanded uncertainty of less than 3%.



# High purity gases

A wide range of regulations and industrial requirements depend on the accurate and robust analysis of trace and ultra-trace concentrations of a wide range of components in 'pure' gases. Examples of the areas where these analyses are highly important are atmospheric monitoring, ambient air measurement and indoor air measurements. They are also essential for process gases used in, for example, the health, micro-manufacturing, fuel cell and energy industries.

The NPL trace gas analysis facility provides traceable measurements of key contaminants found in high-purity gases. Measurement traceability is achieved through instrument calibrations using in-house traceable gas reference materials.

NPL's routine purity analysis of synthetic air or nitrogen 'pure' gases are summarised in the table below but quantification of additional impurities can be included on request.

Component	Approximate limit of detection (nmol/mol)
Nitrogen monoxide	< 1
Nitrogen oxides	< 1
Carbon monoxide	< 15
Carbon dioxide	< 200
Sulphur dioxide	< 1

Component	Approximate limit of detection (nmol/mol)
Methane	< 15
Other hydrocarbons	< 1
Water	< 200
Hydrogen sulphide	< 5

The NPL trace gas analysis facility is also available for instrument calibration and performance assessment work.

# Pressurised (hyperbaric) environments

NPL can analyse a wide variety of volatile compounds (hydrocarbons, oxygenated hydrocarbons, halocarbons, siloxanes and terpenes) in air sampled from both hyperbaric marine, diving environments and off-gassing from pressurised marine equipment, such as umbilicals. There is a real danger of contaminants in the atmosphere of these hyperbaric environments from paint, thinners and cleaning fluids used during routine maintenance and periodic refurbishment work and the toxicity of these contaminants is greatly enhanced under pressure. It is therefore essential that these compounds can be detected and measured.

NPL has more than 15 years' experience in rapid analysis and reporting the results to check compliance with occupational workplace exposure limits (HSE EH40/2020), occupational exposure limits for hyperbaric conditions (HSE EH75/2) and associated ISO guidelines. NPL has developed methods to identify a wide range of compounds and can perform any or all parts of the full analysis of hyperbaric gas samples:

## GC-FID analysis (Gas Chromatography – Flame Ionisation Detection)

All these compounds are quantified using GC-FID analysis and NPL reference materials, prepared in house gravimetrically and traceable to national standards. Compounds with an amount fraction greater than 1 nmol/mol will be reported. Typical uncertainties are 2 - 5 % ( $k = 2$ ).

Class of Compound	Compounds
Hydrocarbons	ethane, ethene, propane, propene, l-butane, n-butane, acetylene, trans-2-butene, 1-butene, cis-2-butene, 2-methyl-butane, n-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2/3-methylpentane, n-hexane, isoprene, n-heptane, benzene, 2,2,4-trimethylpentane, toluene, n-octane, ethylbenzene, m-&p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene

# Pressurised (hyperbaric) environments

## TD-GC-FID-MS analysis (thermal desorption - gas chromatography - flame ionisation detection - mass spectrometry)

All the compounds can be quantified using TD-GC-FID-MS. Samples are transferred to suitable sorbent tubes for this analysis. Calibration is achieved using a multi-point standard calibration derived from gravimetric liquid standards prepared by NPL. Typical uncertainties are 10 - 25 % ( $k = 2$ ). Unknown compounds will also be reported and identified if possible.

Class of Compound	Compounds
<b>Hydrocarbons</b>	propyl benzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1-ethyl-2-methylbenzene, 2-methyl-1-hexene, acetonitrile (other), THF
<b>Oxygenated Hydrocarbons</b>	acetone, ethanol, 2-methyl-2-propanol, acetaldehyde, methyl acetate, 2-propenal (acrolein), 2-butenal, 2,3-butanediol, vinyl acetate, ethyl acetate, isopropyl acetate, 1-butanol, butan-2-one, isopropyl alcohol, methyl isobutyl ketone, 2-butoxyethanol, methyl nonafluorobutyl ether
<b>Halocarbons</b>	dichloromethane, chloroform
<b>Siloxanes</b>	Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane

# Gas metrology software



## GravCalc2

GravCalc2 is Windows-based software that calculates the amount fraction and uncertainty of all components in gravimetrically prepared gas mixtures using the method described in ISO 6142. The program can be used for any gas mixture.

Further details about GravCalc2 are available from the NPL website.

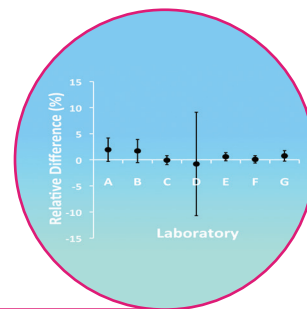
## XLGENLINE

XLGENLINE is Excel-based software that allows the user to perform generalised least squares regression analysis that is fully compliant with ISO 6143. XLGENLINE calculates the amount fractions and estimated uncertainties of 'unknown' samples, displays a plot of the fitted regression function, and outputs the parameters of the fit (gradient, intercept, covariance, etc.).

The software, which can also be used for ordinary least squares regression analysis, is available as a free download from the NPL website.



# 'On-demand' proficiency testing schemes



NPL organises bilateral 'on-demand' proficiency testing (PT) schemes to enable calibration and testing laboratories to achieve greater confidence in their analyses of the composition of these gases.

These are available for any gas mixture, and their scope and timing are arranged at the convenience of the participating laboratory.

The procedure for an 'on-demand' PT scheme is as follows:

1. NPL prepare and validate a NPL Primary Reference Material (NPL PRM).
2. The PRM is sent (without the certificate) to the participating laboratory.
3. The external laboratory measures the composition of the PRM and reports their results to NPL.
4. NPL provides the external laboratory with a comparison of their results against the gravimetric composition of the mixture, and a certificate showing the composition of the PRM.
5. The external laboratory retains the PRM for future use.

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