



Certificate of Calibration

CENTRE FOR OPTICAL AND ENVIRONMENTAL METROLOGY

CERTIFIED REFERENCE GAS MIXTURE

FOR:

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DESCRIPTION:

Certified Reference Gas Mixture

Mixture of 30 hydrocarbons at trace concentrations in nitrogen
(see Table 1 of concentrations)

MIXTURE PREPARATION:

Mixture gravimetrically diluted from primary gravimetric parent mixture in August 1998

IDENTIFICATION:

Cylinder no: 2851B

UNCERTAINTIES:

The reported uncertainty of the hydrocarbon concentrations is based on a standard uncertainty multiplied by a coverage factor which provides a level of confidence of approximately 95%.

Reference: Q9E1/98/026

Date of issue: August 1998

Checked by: HDS

Signed:

Name: Dr R H Partridge

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(Authorised Signatory)

for Managing Director

This certificate provides traceability of measurement to recognised national standards, and to the units of measurement realised at the NPL or other recognised national standards laboratories. This certificate may only be published in full, unless permission for the publication of an approved extract has been obtained in writing from the Managing Director. It does not of itself impute to the subject of calibration any attributes beyond those shown by the data contained herein.

MIXTURE PREPARATION

This multi-component hydrocarbon Certified Reference Gas Mixture (CRGM) was prepared by two successive dilutions from an original parent mixture produced at NPL.

The parent mixture was prepared gravimetrically by weighing the 30 hydrocarbons individually and then combining them with high purity nitrogen diluent gas, with further weighing. The starting materials, including the nitrogen diluent, were all analysed individually to determine any impurities, using gas chromatography. The concentrations of the individual hydrocarbons were derived as mole fractions from the mass of each hydrocarbon in the mixture and its relative molar mass, as compared to similar quantities for the nitrogen diluent gas, taking into account the purity analyses of the starting materials.

The parent mixture was diluted gravimetrically twice with high purity nitrogen to form the daughter CRGM.

The CRGM was checked by gas chromatography against a daughter mixture that had been prepared in a similar fashion and which is retained at NPL as a Primary Gas Standard.

The gas chromatograph that was used to perform the analyses employed cryogenic pre-concentration, in order to ensure sufficient detection sensitivity at the low hydrocarbon concentrations, and was equipped with a flame ionisation detector.

NATIONAL PHYSICAL LABORATORY

Continuation Sheet

HYDROCARBON CONCENTRATIONS

The parent mixture from which the certified reference mixture was diluted was contained in NPL cylinder number 0637A .

The CRGM has the concentrations and uncertainties shown in Table 1:

Table 1

	Concentration		Uncertainty	
	Mole fraction by ppb		Mole fraction by ppb	
ethane	7.54	±	0.02	
ethene	11.82	±	0.02	
ethyne	9.85	±	0.08	
propane	2.85	±	0.01	
propene	7.45	±	0.01	
propyne	3.21	±	0.01	
n-butane	2.88	±	0.01	
iso-butane	3.34	±	0.01	
iso-butene	3.16	±	0.01	
but-1-ene	3.70	±	0.01	
trans-2-butene	2.47	±	0.01	
cis-2-butene	2.64	±	0.01	
1,3-butadiene	5.91	±	0.02	
n-pentane	2.94	±	0.01	
i-pentane	1.32	±	0.01	
trans-2-pentene	4.49	±	0.01	
cis-2-pentene	1.71	±	0.01	
isoprene	2.05	±	0.01	
2-methylpentane	3.53	±	0.01	
3-methylpentane	4.04	±	0.01	
cyclo hexane	3.71	±	0.01	
n-hexane	1.96	±	0.01	
benzene	3.81	±	0.01	
n-heptane	3.08	±	0.01	
toluene	3.58	±	0.01	
ethylbenzene	1.97	±	0.01	
o-xylene	1.11	±	0.01	
m-xylene	1.56	±	0.01	
1,2,4-TMB	1.26	±	0.01	
1,3,5-TMB	1.03	±	0.01	

The concentration values quoted above are presented as mole fractions (ratio of the number of moles of component to the total number of moles in the gas mixture) - expressed in parts per billion (ppb) [1].

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UNCERTAINTIES

The hydrocarbon concentrations in this CRGM have been assigned the combined expanded uncertainties shown in Table 1, which represents 95% confidence limits (but see Guidance Notes on Stability).

The uncertainties were evaluated according to the Guide published by the International Organisation for Standardisation in association with the Comité International des Poids et Mesures (CIPM) [2]. The evaluation used CIPM classification type A uncertainties, evaluated by statistical methods, combined with CIPM classification type B uncertainties, evaluated by other means. The combined expanded uncertainty contains components arising from the following:

- Gravimetric preparation of the parent hydrocarbon mixture.
- The two-fold dilution of the parent mixture to produce the CRGM.
- Chromatographic analysis of the starting hydrocarbon components and diluent nitrogen gas used to create the parent mixture.
- The uncertainty in the relative molar masses used in the calculation of the mole fraction concentrations from the gravimetric data.

The CRGM concentrations were checked by gas chromatography against the similar Primary Standard held at NPL but the concentrations, and hence the uncertainties, quoted here are derived solely from the gravimetric values.

GUIDANCE NOTES**Stability**

This CRGM is contained in a passivated aluminium cylinder treated by a proprietary process that minimises the reaction of hydrocarbon species with the walls of the cylinder. The stability of similar gas mixtures in similar cylinders have been checked regularly over a period of two years and no evidence of a change of concentration in any of the hydrocarbons was observed. However, the performance of individual cylinders in this respect cannot be guaranteed.

The cylinder should be stored and used at normal room temperature, and should not at any time be allowed to cool below 0°C. It is recommended that the cylinder should not be used at pressures below 0.5 Mpa (5 bar). Contamination of the mixture by air or other gases must be avoided.

The certified concentration values quoted in Table 1 are the values existing at the time that the cylinder of hydrocarbon mixture was despatched from NPL. Although the hydrocarbon concentrations are expected to remain stable for a period of at least two years, provided that the cylinder is not mishandled in the ways indicated above, the performance of the passivated cylinder cannot be guaranteed. The hydrocarbons most likely to be unstable in the mixture are ethyne, isoprene, the trimethyl benzenes and 1,3 butadiene. The mixture should be measured by gas chromatography on receipt and periodically thereafter to check for any such instability.

Cylinder details

This Secondary Gas Standard is supplied in a cylinder with a water volume of 10 litres ($10 \times 10^{-3} \text{ m}^3$) and at a nominal pressure of 100 bar (10 MPa). The cylinder conforms to the following British and German Standard specifications.

- (i) Health & Safety Executive (BS 5045)
- (ii) DIN 1 outlet (DIN 477)
- (iii) Colour coding (BS 349)

Gas Handling

NPL recommends the use of a stainless steel low volume regulator for high purity gases in order to deliver the mixture from the cylinder at a safe pressure. The regulator should be purged several times, or evacuated, before use to avoid sample contamination. Heating of the gas transfer line to at least 50°C is desirable in order to avoid adsorption of the heaviest hydrocarbon species.

References

- [1] BS 5775 : 1993 (ISO 31-8 : 1992)
Specification for Quantities, Units and Symbols.
Part 8. Physical chemistry and molecular physics.
- [2] Guide to the Expression of Uncertainties in Measurement, 1993.
International Organisation for Standardisation, Geneva, Switzerland, ISBN 92-67-10188/9