Australian Government
Department of Industry, Science and Resources

National Measurement Institute

NATA
WORLD RECOGNISED ACCREDITATION

CERTIFIED REFERENCE MATERIAL
CERTIFICATE OF ANALYSIS

NMIA MX015: Hydrocarbon-contaminated Soil

Certified values

	F2 (ECN > C10-C16)	F3 (ECN > C16-C34)	F4 (ECN > C34-C40)	TRH-silica (> C10-C40)
w (g kg^{-1})	**0.90**	**7.2**	**1.1**	**9.2**
U (g kg^{-1})	**0.15**	**1.1**	**0.20**	**1.4**

The measurand is the mass fraction (w) for silica-treated total recoverable hydrocarbons (TRH-silica). Certified mass fractions for TRH-silica in three equivalent carbon number (ECN) ranges are also provided. These were obtained by Soxhlet extraction into n-hexane:acetone (1:1 v/v) followed by clean-up with activated silica gel and gas chromatographic analysis with flame ionisation detection. The reported uncertainty is expanded to provide a level of confidence of 95%.

Expiry: 08 August 2027. **Batch No.:** 2013.01

The certified values are valid for sealed bottles of the material, provided that the bottles are handled and stored in accordance with the instructions given on this certificate.

Description: This reference material consists of a screw-cap amber glass bottle containing weathered petroleum hydrocarbon-contaminated soil diluted with clean river sand.

Intended use: The reference material is intended to be used in validation of analytical methods for the measurement of total recoverable hydrocarbons according to the National Environment Protection (Assessment of Site Contamination) Measure (NEPM), as amended 2013 [1]. It may also be used to calibrate secondary reference materials of similar composition or as a matrix calibration standard.

Instructions for use: The recommended minimum sample size is 5 g. The material must be thoroughly mixed before sampling. The certified property values apply to the sample without correction for moisture content. The water content at the time of certification was determined by drying in a desiccator for six weeks to be 0.99 ± 0.05 g/100g.

Production: The material was prepared in 2012 using highly contaminated soil (TRH > 80 g kg^{-1}) from a refinery in Sydney, Australia. The soil was air dried and broken up before mixing with oven-dried river sand in a ratio of 1 part to 7. The mixture was ground, blended with repeated sub-division and bottled to produce 703 units of NMIA MX015.

Analytical method: Total recoverable hydrocarbon is a procedure-dependent measurand. The property values provided for NMIA MX015 represent the TRH-silica mass fractions expected when the material is analysed using measurement procedures equivalent to the analytical method used for certification. The extraction method used for certification of NMIA MX015 is based on the reference method for the Canada-wide standard for petroleum hydrocarbons in soil [2]. It was modified to meet NEPM requirements for calibration and reporting of ECN fractions [1]. Soil was extracted with n-hexane:acetone (1:1 v/v) in a Soxhlet apparatus, the extract was solvent-exchanged to n-hexane:dichloromethane (1:1 v/v) and then activated silica (100 °C, min 24 h, 3 g per 5 g sample) was used to remove any more polar compounds. The solvent was exchanged to toluene for gas chromatography with flame ionisation detection (GC-FID).

Equivalent carbon number fractions are defined by the elution times of specified linear hydrocarbons. The certified mass fractions specifically apply under the particular GC conditions used. A multimode injector fitted with a top hole drilled

Uniliner® was operated in splitless mode. At 0.1 minute after injection (1 µL) the injector temperature was ramped from 90 to 350 °C. A 100% polydimethylsiloxane capillary GC column (DB-1ht 30 m × 320 µm, 0.1 µm film) was used with

hydrogen as the carrier gas at a constant flow of 6 mL/min. The oven temperature program was: equilibrate 1 min, 40 °C hold 2.5 min, heat @15 °C/min to 340 °C and hold for 10 min.

Calibration against external standards of mixed hydrocarbons was performed according to the NEPM [1] by calculating response factors for representative hydrocarbons from each fraction (C_{14}, C_{24} and C_{34}) and integrating fractions in the sample between the retention times corresponding to the ends of the marker peaks (C_{10}, C_{16}, C_{34} and C_{40}).

The Soxhlet extracts of the candidate material were tested for naphthalene using an accredited in-house GC-mass spectrometric method and the mass fraction (<0.0004 g kg^{-1}) determined to be insignificant in comparison to the mass fraction of hydrocarbons reported for the >C_{10}-C_{16} fraction.

Full details of analytical procedures are provided in the MX015 certification report [3].

Homogeneity: Assessment of the homogeneity of CRM NMIA MX015 was conducted in accordance with ISO Guide 35 [4] and involved analysis of 27 bottles of the CRM selected at random from the batch. Duplicate sub-samples were analysed from 16 of these bottles and single subsamples were analysed from the remaining 11 bottles. Homogeneity testing was carried out using the analytical procedures described in Section (vii) and the results used to calculate the within-bottle and between-bottle variances. The uncertainties in the certified values incorporate these variances.

Storage stability: The material should be stored at -20 °C out of direct light in the closed container as issued. The stability of the material for six months, when stored under these conditions, was demonstrated by an isochronous stability trial. Stability under conditions likely to be encountered during transportation was also demonstrated by an isochronous accelerated stability study conducted at 40 °C for up to two weeks. The long term stability of the certified value was re-assessed in August 2019.

The uncertainties in the property values incorporate a long-term storage stability component extrapolated to cover a period of certification of 12 months, and a transport stability component extrapolated to cover a period of 7 days at 40 °C [4].

Measurement uncertainty: Measurement uncertainties were estimated according to international standards [4,5] and National Measurement Institute standard operating procedures. All factors that could reasonably be expected to affect the measurement result were identified and the standard uncertainty of each evaluated. The standard uncertainties of the various components were combined as described in the Guide to the Expression of Uncertainty in Measurement [5]. The combined standard uncertainties were expanded to a level of confidence of 95% using coverage factors calculated from the effective degrees of freedom obtained from the Welch-Satterthwaite equation (see Table 1).

Table 1: Coverage factors (k) and effective degrees of freedom (v_{eff}) associated with the measurement uncertainties in the certified values for CRM NMIA MX015.

	F2 (ECN >C10 – C16)	F3 (ECN >C16 – C34)	F4 (ECN >C34 – C40)	TRH-silica (>C10 – C40)
k	2.1	2.1	2.0	2.1
v_{eff}	15	25	33	26

The major contributing factors to the measurement uncertainties were the heterogeneity of the samples and the stability component extrapolated to cover the period of certification.

The certified values and their associated expanded uncertainties apply to any correctly stored and un-opened bottle of NMIA MX015 until the expiration date specified on this certificate. The corresponding expanded uncertainties represent the 95% confidence limits for the property values certified until the date of expiry. The validity of the certification of the material may be extended by the National Measurement Institute as additional information about the long-term storage stability of the material becomes available.

Metrological traceability: Mass fractions of the total recoverable hydrocarbon (TRH-silica) and ECN fractions are procedurally defined measurands. The certified property values for TRH extracted using the above specified analytical method are traceable to the SI unit of mass (kg) through the Australian standard for mass. Sample and calibration solutions were prepared using appropriately calibrated balances. Certified reference materials used for instrument calibration were traceable to the SI unit for mass, the kilogram (kg).

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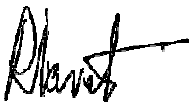

Raluca Iavetz
Manager Chemical Reference Values
4 August 2022

Accreditation No. 198

References:

1. National Environment Protection Council (2013) National Environment Protection (Assessment of Site Contamination) Measure 1999. http://www.scew.gov.au/nepms/assessment-site-contamination#Key_documents.
2. Canadian Council of Ministers of the Environment (CCME) (2001) Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 method.
3. National Measurement Institute (2014) Production and certification of certified reference material NMIA MX015 (hydrocarbon contaminated soil), Australia.
4. ISO (2017) Guide 35 (fourth edition): Reference materials – Guidance for characterization and assessment of homogeneity and stability
5. JCGM100 (2008) Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM:1995 with minor corrections), 1st edition (corrected 2010), BIPM/IEC/IFCC/ILAC/ISO/IUPAC/OIML (published by JCGM).

This Certificate for NMIA MX015 supersedes any issued prior to 4 August 2022.

Legal notice: Terms and Conditions associated with the provision of this reference material can be found on the NMIA website**.**

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