



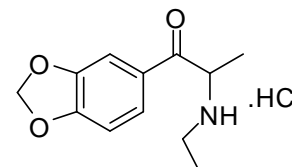
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA D959: (\pm)-N-Ethyl-3,4-methylenedioxyethanone hydrochloride

Report ID: D959.2019.03

Chemical Formula: $C_{12}H_{16}ClNO_3$

Molecular Weight: 257.7 g/mol (HCl)



Certified value

Batch No.	CAS No.	Purity (mass fraction)
10-D-12	1454266-19-3 (HCl)	99.3 \pm 0.9%

The uncertainty has been calculated according to ISO Guide 35 and is stated at the 95% confidence limit ($k = 2$).

IUPAC name: 1-(1,3-Benzodioxol-5-yl)-2-(ethylamino)-1-propanone hydrochloride (1:1)

Expiration of certification: The property values are valid till 15 August 2024, i.e. five years from the date of re-certification provided the **unopened** material is handled and stored in accordance with the recommendations below. The material as issued in the unopened container and stored as recommended below should be suitable for use beyond this date, subject to confirmation of batch stability from the issuing body. The expiry date/shelf life does not apply to sample bottles that have been opened. In such cases it is recommended that the end-user conduct their own in-house stability trials.

Description: White crystalline solid prepared by synthesis, and certified for identity and purity by NMIA. Packaged in amber glass bottles with a septum and crimped aluminium cap or screw top cap.

Intended use: This certified reference material is suitable for use as a primary calibrator.

Instructions for use: Equilibrate the bottled material to room temperature before opening.

Recommended storage: When not in use this material should be stored at or below 25 °C in a closed container in a dry, dark area.

Metrological traceability: The certified purity value is traceable to the SI unit for mass (kg) through Australian national standards via balance calibration. In the mass balance approach all impurities are quantified as a mass fraction and subtracted from 100%. Quantitative NMR provides an independent direct measure of the mass fraction of the analyte of interest, calibrated with an internal standard certified for purity (mass fraction).

Stability: This material has demonstrated stability over a minimum period of five years. The measurement uncertainty at the 95% confidence interval includes a stability component which has been estimated from annual stability trials. The long-term stability of the compound in solution has not been examined.

Homogeneity assessment: The homogeneity of the material was assessed using purity assay by HPLC with UV detection on ten randomly selected 1-2 mg sub samples of the material. The material was judged to be sufficiently homogeneous at this level of sampling as the variation in analysis results between samples was not significantly different at a 95% confidence level from that observed on repeat analysis of the same sample.

Safety: Treat as a hazardous substance. Use appropriate work practices when handling to avoid skin or eye contact, ingestion or inhalation of dust. Refer to the provided safety data sheet.

S. R. Davies

Dr Stephen R. Davies,
Team Leader,
Chemical Reference Materials, NMI.
20 September 2022

This report supersedes any issued prior to 20 September 2022.

NATA Accreditation No. 198 / Corporate Site No. 14214.

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

Characterisation Report:

The identity was confirmed by a range of spectroscopic techniques, NMR, IR and MS. The certified purity value was obtained from a combination of traditional analytical techniques and quantitative nuclear magnetic resonance (qNMR). The techniques used in the mass balance approach include GC-FID, thermogravimetric analysis, Karl Fischer analysis and ¹H NMR spectroscopy. The purity value is calculated as per Equation 1.

$$\text{Purity} = (100\% - I_{\text{ORG}}) \times (100\% - I_{\text{VOL}} - I_{\text{NVR}}) \quad \text{Equation 1}$$

I_{ORG} = Organic impurities of related structure, I_{VOL} = volatile impurities, I_{NVR} = non-volatile residue

Supporting evidence is provided by HPLC with UV detection, qualitative headspace GC-MS analysis of occluded solvents and elemental microanalysis.

GC-FID:	Instrument: Agilent 6890 Column: HP-1 or HP-5, 30 m × 0.32 mm I.D. × 0.25 μm Program: 120 °C (1 min), 10 °C/min to 200 °C, 30 °C/min to 300 °C (5 min) Injector: 250 °C Detector Temp: 320 °C Carrier: Helium Split ratio: 20/1 Relative mass fraction of the main component: Initial analysis: Mean = 99.8%, s = 0.04% (5 sub samples in duplicate, October 2013) Re-analysis: Mean = 99.8%, s = 0.01% (5 sub samples in duplicate, August 2016) Re-analysis: Mean = 99.8%, s = 0.004% (5 sub samples in duplicate, August 2019)
HPLC:	Instrument: Shimadzu Binary pump LC-20AB, SIL-20 A HT autosampler Column: Ascentis C-18, 2.7 μm (4.6 mm x 150 mm) Column oven: 40 °C Mobile Phase: Acetonitrile/MilliQ water (14:86 v/v) Both aqueous and organic phases contained 0.05 % trifluoroacetic acid (v/v) Flow rate: 1.0 mL/min Detector: Shimadzu SPD-M20A PDA operating at 282 nm Relative mass fraction of the main component: Initial analysis: Mean = 99.9%, s = 0.01% (10 sub samples in duplicate, November 2010) Re-analysis: Mean = 99.8%, s = 0.02% (5 sub samples in duplicate, October 2011) Re-analysis: Mean = 99.9%, s = 0.01% (5 sub samples in duplicate, November 2012)
Karl Fischer analysis:	Moisture content ≤ 0.3% mass fraction (November 2010, 2011, 2012, October 2013, August 2016 and July 2019)
Thermogravimetric analysis:	Non-volatile residue < 0.2% mass fraction (November 2010). The volatile content (e.g. organic solvents and/or water) could not be analysed accurately because of the inherent volatility of the material.
qNMR:	Instrument: Bruker Avance DMX-600 Field strength: 600 MHz Solvent: D ₂ O (4.71 ppm) Internal standard: Potassium hydrogen maleate (98.8% mass fraction) Initial analysis: Mean (5.05 ppm) = 99.3%, s = 0.64% (5 sub samples, November 2010)

Spectroscopic and other characterisation data

GC-MS:	Parent compound: Instrument: HP6890/5973 Column: TG-1MS 2, 30 m x 0.25 mm I.D. x 0.25 µm Program: 60 °C (1 min), 10 °C/min to 100 °C, 15 °C/min to 250 °C (5 min), 30 °C/min to 300 °C (2 min) Injector: 250 °C Split ratio: 20/1 Transfer line temp: 300 °C Carrier: Helium Scan range: 50-550 <i>m/z</i> <i>N</i> -Acetyl derivative: Instrument: Agilent 6890/5973 Column: TG-1MS, 30 m x 0.25 mm I.D. x 0.25 µm Program: 60 °C (1 min), 10 °C/min to 100 °C, 15 °C/min to 250 °C (5 min), 30 °C/min to 300 °C (2 min) Injector: 250 °C Transfer line temp: 300 °C Carrier: Helium, 1.0 mL/min Split ratio: 20/1 The retention times of the free base and <i>N</i> -acetyl derivative are reported along with the major peaks in the mass spectra. The latter are reported as mass/charge ratios and (in brackets) as a percentage relative to the base peak. Free base (12.8 min): 219 (2), 149 (11), 121 (7), 91 (4), 72 (100), 70 (21), 65 (7), 44 (18), 42 (17) <i>m/z</i> <i>N</i> -acetyl (15.0 min): 263 (1), 178 (3), 149 (13), 121 (6), 114 (49), 72 (100), 65 (7), 44 (33) <i>m/z</i>
HS-GC-MS:	Instrument: Agilent 6890/5973/G1888 Column: DB-624, 30 m x 0.25 mm I.D. x 1.4 µm Program: 50 °C (5 min), 7 °C/min to 120 °C, 15 °C/min to 220 °C (8.3 min) Injector: 150 °C Transfer line temp: 280 °C Carrier: Helium, 1.2 mL/min Split ratio: 50/1 Solvents detected: Ethanol and diethyl ether
TLC:	Conditions: Kieselgel 60F ₂₅₄ . Methanol/NH ₃ (100/1.5) Single spot observed, R _f = 0.7. Visualisation with UV at 254 nm
IR:	Instrument: Biorad FTS300MX FT-IR Range: 4000-400 cm ⁻¹ , KBr powder Peaks: 2970, 2793, 2458, 1675, 1605, 1555, 1453, 1258, 1120, 1089, 1039, 934, 871, 799, 753, 714, 520, 451 cm ⁻¹
¹ H NMR:	Instrument: Bruker Avance III-400 Field strength: 400 MHz Solvent: D ₂ O (4.79 ppm) Spectral data: δ 1.36 (3H, t, <i>J</i> = 7.3 Hz), 1.60 (3H, d, <i>J</i> = 7.2 Hz), 3.12 (1H, qd, <i>J</i> = 7.3, 12.5 Hz), 3.21 (1H, qd, <i>J</i> = 7.3, 12.5 Hz), 5.05 (1H, q, <i>J</i> = 7.2 Hz), 6.11 (1H, d, <i>J</i> = 2.6 Hz), 6.12 (1H, d, <i>J</i> = 2.6 Hz), 7.01 (1H, d, <i>J</i> = 8.3 Hz), 7.44 (1H, d, <i>J</i> = 1.8 Hz), 7.67 (1H, dd, <i>J</i> = 1.8, 8.3 Hz) ppm Ethanol estimated at 0.6% mass fraction was observed in the ¹ H NMR. Diethyl ether was not detected.
¹³ C NMR:	Instrument: Bruker Avance III-400 Field strength: 100 MHz Solvent: D ₂ O Spectral data: δ 10.7, 16.0, 41.4, 57.7, 102.6, 107.9, 108.7, 126.5, 126.7, 148.3, 153.5, 195.3 ppm
Melting point:	226-227 °C
Microanalysis:	Found: C = 55.9%; H = 6.4%; N = 5.4%; Cl = 13.7% (November, 2010) Calculated: C = 55.9%; H = 6.3%; N = 5.4%; Cl = 13.8% (Calculated for C ₁₂ H ₁₆ ClNO ₃)