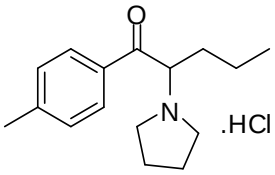
Australian Government
Department of Industry, Science and Resources

National Measurement Institute

NATA
WORLD RECOGNISED ACCREDITATION

CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA D985: Pyrovalerone hydrochloride



Report ID: D985.2023.01

Chemical Formula: $C_{16}H_{23}NO.HCl$

Molecular Weight: 281.8 g/mol (HCl) 245.4 g/mol (free base)

Certified value

Batch No.	CAS No.	Purity (mass fraction)
12-D-13	**1147-62-2**	**97.5 ± 1.2%**

The uncertainty is stated at the 95% confidence limit.

IUPAC: 1-(4-Methylphenyl)-2-(1-pyrrolidinyl)-1-pentanone hydrochloride (1:1)

Expiration of certification: The property values are valid till 13 July 2028, 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 solid sourced from an external supplier, 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 ºC 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 all the 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% coverage interval includes a stability component which has been estimated from long term 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 GC-FID on seven 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.

Caution: 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.
18 July 2023

This report supersedes any issued prior to 18 July 2023.

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 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 ^{1}H NMR spectroscopy. The purity value is calculated as per Equation 1.

Purity = (100 % - I_{ORG}) x (100 % - I_{VOL} – I_{NVR}) Equation 1

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

The purity estimate by QNMR was obtained using a combination of the one-proton quartet at 5.5 ppm, the two two-proton doublets at 7.8 ppm against a certified internal standard of maleic acid.

Supporting evidence is provided by headspace GC-MS analysis of occluded solvents and elemental microanalysis.

GC-FID:	Instrument:	Agilent 6890 or 7890
Free base	Column:	HP-1MS or HP-5, 30 m × 0.32 mm I.D. × 0.25 µm
	Program:	100 °C (1 min), 10 °C/min to 170 °C, 20 °C/min to 300 °C (3 min)
	Injector:	250 °C
	Detector Temp:	320 °C
	Carrier:	Helium
	Split ratio:	20/1
	Relative mass fraction of the main component:	
	Initial analysis:	Mean = 99.6%, s = 0.02% (7 sub samples in duplicate, September 2012) [HP-1]
	Initial analysis:	Mean = 99.6%, s = 0.05% (7 sub samples in duplicate, September 2012) [HP-5]
	Re-analysis:	Mean = 99.4%, s = 0.02% (5 sub samples in duplicate, August 2013)
	Re-analysis:	Mean = 99.8%, s = 0.01% (5 sub-samples in duplicate, July 2014)
	Re-analysis:	Mean = 99.8%, s = 0.007% (5 sub-samples in duplicate, July 2015)
	Re-analysis:	Mean = 99.6%, s = 0.06% (5 sub-samples in duplicate, June 2019)
	Re-analysis:	Mean = 99.6%, s = 0.01% (5 sub-samples in duplicate, July 2023)
QNMR:	Instrument:	Bruker Avance-III-400
	Field strength:	400 MHz
	Solvent:	d_6-DMSO (2.50 ppm)
	Internal standard:	Maleic acid (98.7% mass fraction)
	Initial analysis:	Mean (5.5 ppm) = 97.1%, s = 0.4% (3 sub samples, October 2012)
	Initial analysis:	Mean (7.8 ppm) = 97.4%, s = 0.1% (3 sub samples, October 2012)
Thermogravimetric analysis:		Non volatile residue < 0.2% mass fraction (September 2012). The volatile content (e.g. organic solvents and/or water) could not be determined because of the inherent volatility of the material.
Karl Fischer analysis:		Moisture content 1.8 % mass fraction (September 2012) Moisture content 2.1 % mass fraction (August 2013) Moisture content 2.0% mass fraction (July 2014 and July 2023) Moisture content 2.3% mass fraction (June 2015) Moisture content 2.4% mass fraction (May 2019)

Spectroscopic and other characterisation data

GC-MS:	Instrument:	Agilent 6890/5973
	Column:	TG-1MS, 30 m x 0.25 mm I.D. x 0.25 μm
	Program:	150 °C (1 min), 10 °C/min to 250°C (5 min), 15°C/min to 300°C (3 min)
	Injector:	250 °C
	Transfer line temp:	280 °C
	Carrier:	Helium
	Split ratio:	20/1
	The retention time of the free base is reported along with the major peaks in the mass spectrum. The latter are reported as mass/charge ratios and (in brackets) as a percentage relative to the base peak.	
	Free base (7.8 min):	243 (M^+, 7), 126 (100), 124 (24), 91 (10), 70 (12) *m/z*
ESI -MS:	Instrument:	Micromass Quatro LC Micro
	Operation:	Positive ion mode, direct infusion at 20 μL/min
	Ionisation:	ESI spray voltage at 3 kV positive ion
	EM voltage:	650 V
	Cone voltage:	20 V
	Peak:	246.1 ($M+H^+$) *m/z*
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, diethyl ether and butanal
TLC:	Conditions:	Kieselgel 60F_{254}. DCM/ Methanol (90/10) Single spot observed, R_f = 0.6. Visualisation with UV at 254 nm
IR:	Instrument:	Biorad FTS3000MX FT-IR
	Range:	4000-400 cm^{-1}, KBr powder
	Peaks:	3447, 2960, 2928, 2612, 2473, 1680, 1605, 1442, 1375, 1338, 1288, 1238, 1187, 1137, 1038, 1008, 867, 842, 813, 772, 731, 576, 540, 469 cm^{-1}
^{1}H NMR:	Instrument:	Bruker Avance III-400
	Field strength:	400 MHz
	Solvent:	D_2O (4.79 ppm)
	Spectral data:	δ 0.59 (3H, t, *J* = 7.2 Hz), 0.84-1.08 (2H, m), 1.77-1.95 (5H, m), 1.97-2.06 (1H,m), 2.22 (3H, s), 2.83 (1H, m), 3.14 (1H, m), 3.47 (1H, m), 3.55 (1H, m), 5.05 (1H, t, *J* = 5.3 Hz), 7.22 (2H, *J* = 8.0 Hz), 7.72 (2H, *J* = 8.3 Hz) ppm
^{13}C NMR:	Instrument:	Bruker Avance III-400
	Field strength:	100 MHz
	Solvent:	D_2O
	Spectral data:	δ 12.9, 16.8, 20.9, 22.6, 22.7, 31.9, 51.9, 55.0, 69.0, 128.9, 129.9, 130.9, 147.6, 197.1 ppm
Melting point:		167-172 °C
Microanalysis:	Found:	C = 66.7%; H = 8.4%; N = 4.8%; Cl = 12.2% (September 2012)
	Calculated:	C = 68.2%; H = 8.6%; N = 5.0%; Cl = 12.6% (Calculated for $C_{16}H_{23}NO.HCl$)