Australian Government
Department of Industry, Science and Resources
National Measurement Institute
CIPM MRA
NATA
WORLD RECOGNISED ACCREDITATION

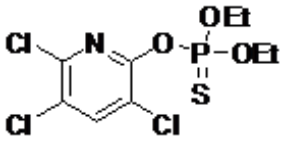
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1666A: Chlorpyrifos

Report ID: P1666A.2020.03

Chemical Formula: $C_9H_{11}Cl_3NO_3PS$

Molecular Weight: 350.6 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
00-AV-09	2921-88-2	99.3 ± 0.3%

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

IUPAC name: O,O-Diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate.

Expiration of certification: The property values are valid till 11 March 2030, i.e. ten 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: Colourlesscrystals prepared by sourced from an external supplier, 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 4 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 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 three 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 GC-FID on five 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.
6 September 2022

This report supersedes any issued prior to 6 September 2022.

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

CIPM MRA notice: This certificate is consistent with the capabilities that are included in Appendix C of the CIPM MRA drawn up by the CIPM. Under the CIPM MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C. The "CIPM MRA Logo" and this statement attest only to the measurement(s) applied for determining the certified values on the certificate (for details see http://www.bipm.org).

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, 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 certified purity value by qNMR was obtained using a combination of the six-proton multiplet at 1.11 ppm and the four-proton multiplet at 4.30 ppm measured against a certified internal standard of dimethyl sulfone.

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

GC-FID:	Instrument:	HP5890 or Agilent 6890N
	Column:	HP-1 Capillary, 29.85 m × 0.32 mm I.D. × 0.25 µm
	Program:	130 °C (1 min), 10 °C/min to 300 °C (3 min)
	Injector:	230 °C
	Detector Temp:	320 °C
	Carrier:	Helium
	Split ratio:	20/1
	Relative mass fraction of the main component:	
	Initial analysis:	Mean = 99.7%, s = 0.03% (5 sub samples in duplicate, November 2000)
	Re-analysis:	Mean = 99.7%, s = 0.02% (5 sub samples in duplicate, February 2007)
	Re-analysis:	Mean = 99.7%, s = 0.01% (5 sub samples in duplicate, March 2010)
	Re-analysis:	Mean = 99.7%, s = 0.04% (5 sub samples in duplicate, March 2020)
HPLC:	Instrument:	Waters Model 1525 Binary pump, 717 plus autosampler
	Column:	Alltima C18, 5 µm (4.6 mm × 150 mm) Lot Number 3441
	Column temperature:	Ambient
	Mobile Phase:	82% Acetonitrile / 17.5% water / 0.05% TFA
	Flow rate:	1.0 mL/min
	Detector:	PDA 230nm
	Retention time:	4.68 min
	Relative mass fraction of the main component:	
	Initial analysis:	Mean > 99.9% (4 sub samples in duplicate, 2000)
	Re-analysis:	Mean = 99.5%, s = 0.02 (5 sub samples in duplicate, February 2007)
Karl Fischer analysis:		Moisture content < 0.2% mass fraction (March 2010 and January 2020)
QNMR:	Instrument:	Bruker Avance-III-500
	Field strength:	500 MHz
	Solvent:	benzene-d_6 (7.16 ppm)
	Internal standard:	Dimethyl sulfone (100.0% mass fraction)
	Initial analysis:	Mean (1.11 ppm) = 99.4%, s = 0.09% (5 sub samples, March 2020)
	Initial analysis:	Mean (4.30 ppm) = 99.3%, s = 0.09% (5 sub samples, March 2020)

Spectroscopic and other characterisation data

GC-MS:	Parent compound:	
	Instrument:	HP6890/5973
	Column:	ZB-5MS, 28 m x 0.25 mm I.D. x 0.25 µm
	Program:	170 °C (0.5 min), 12 °C/min to 300 °C, hold 2min
	Injector:	250 °C
	Split ratio:	20/1
	Transfer line temp:	280 °C
	Carrier:	Helium
	Scan range:	50-550 *m/z*
	The retention time of the parent compound is reported 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.	
	Parent (4.56 min):	314 (M^+, 20), 258 (16), 199 (58), 197 (61), 125 (27), 97 (100) *m/z*
IR:	Instrument:	Perkin-Elmer FT-IR
	Range:	4000-500 cm^{-1},KBr disc
	Peaks:	3959, 3053, 2986, 1848, 1549, 1412, 1340, 1275, 1239, 1170, 1023, 969, 851, 835, 747, 720, 676, 650, 633, 532 cm^{-1}
^{1}H NMR:	Instrument:	Bruker DMX-600
	Field strength:	600 MHz
	Solvent:	$CDCl_3$ (7.26 ppm)
	Spectral data:	δ 1.43 (6H, dt, *J* = 1.0, 7.0 Hz), 4.41 (4H, m), 7.85 (1H, d, *J* = 1.1 Hz) ppm
^{13}C NMR:	Instrument:	Bruker DMX-600
	Field strength:	150 MHz
	Solvent:	$CDCl_3$ (77.16 ppm)
	Spectral data:	δ 15.9, 66.0, 120.4, 126.8, 141.1, 144.0, 150.8
Melting point:		41.0-42.5 °C
Microanalysis:	Found:	C = 31.0%; H = 3.3%; N = 4.0%; Cl% = 30.4%, S = 9.2%, P = 9.1% (2000)
	Found:	C = 31.1%; H = 3.2%; N = 4.0% (November 2005)
	Found:	C = 31.0%; H = 3.1%; N = 4.0%; S = 9.3%, P = 8.9% (March 2007)
	Calculated:	C = 30.8%; H = 3.2%; N = 4.0%; Cl% = 30.3%, S = 9.2%, P = 8.8% (Calculated for $C_9H_{11}Cl_3NO_3PS$)