Australian Government
Department of Industry, Science and Resources

National Measurement Institute

NATA
WORLD RECOGNISED ACCREDITATION

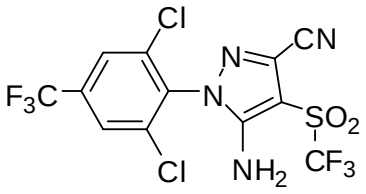
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1731: Fipronil sulfone

Report ID: P1731.2023.01 (Bottled 110201)

Chemical Formula: $C_{12}H_4Cl_2F_6N_4O_2S$

Molecular Weight: 453.2 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
01-AV-08	**120068-36-2**	**99.5 ± 0.4%**

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

IUPAC name: 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfonyl]-1H-pyrazole-3-carbonitrile

Expiration of certification: The property values are valid till 17 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 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 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%.

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 GC-FID 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.
26 July 2023

This report supersedes any issued prior to 26 July 2023.

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

Characterisation Report:

The identity was confirmed by a range of spectroscopic techniques, NMR, IR and MS. The certified purity value was obtained by mass balance from a combination of traditional analytical techniques, including 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

Supporting evidence is provided by elemental microanalysis.

GC-FID:	Instrument:	Agilent 6890N
	Column:	HP-1, 30 m × 0.32 mm I.D. × 0.25 μm
	Program:	160 °C (1 min), 10 °C/min to 300 °C (4 min)
	Injector:	230 °C
	Detector Temp:	320 °C
	Carrier:	Helium
	Split ratio:	20/1
	Relative mass fraction of the main component:	
	Initial analysis:	Mean = 99.5%, s = 0.02% (10 sub samples in duplicate, March 2002)
	Re-analysis:	Mean = 99.5%, s = 0.01% (5 sub samples in duplicate, September 2008)
	Re-analysis:	Mean = 99.4%, s = 0.02% (5 sub samples in duplicate, August 2011)
	Re-analysis:	Mean = 99.5%, s = 0.02% (5 sub samples in duplicate, July 2016)
	Re-analysis:	Mean = 99.5%, s = 0.03% (5 sub samples in duplicate, May 2019)
	Re-analysis:	Mean = 99.5%, s = 0.01% (5 sub samples in duplicate, July 2023)
HPLC:	Column:	Phenomnex C-18, 5 μm (2.1 mm × 150 mm)
	Mobile Phase:	Acetonitrile/MilliQ water (50:50) The aqueous phase was buffered at pH 4.2 using 25 mM NH_4OAc and AcOH
	Flow rate:	0.3 mL/min
	Detector:	PDA operating at 272 nm ELSD
	Relative peak area of main component:	
	Initial analysis:	Mean = 99.5% PDA, s = 0.01% (10 sub samples in duplicate, November 2001) Mean = 99.9% ELSD, s = 0.04% (10 sub samples in duplicate, November 2001)
Thermogravimetric analysis:		Volatile content < 0.1% and non volatile residue < 0.2% mass fraction (October 2005)
Karl Fischer analysis:		Moisture content 0.2% mass fraction (September 2008) Moisture content 0.1% mass fraction (August 2011) Moisture content 0.4% mass fraction (July 2016) Moisture content < 0.1% mass fraction (April 2019 and July 2023)

Spectroscopic and other characterisation data

GC-MS:	Instrument:	HP 6890/5973
	Columns:	ZB-5, 30 m × 0.25 mm I.D. × 0.25 μm
	Program:	150 °C (1 min), 10 °C/min to 300 °C (3 min)
	Injector:	230 °C
	Transfer line temp:	280 °C
	Carrier:	Helium
	Split ratio:	20/1
	The retention time of the parent compound is reported along with the major peaks for the $^{35}Cl_2$ isomer in the mass spectrum. Ions are reported as mass/charge ratios and (in brackets) as a percentage relative to the base peak.	
	Parent (12.2 min):	452 (31), 383 (100), 335 (17), 255 (50), 241(24), 213 (28), 77 (22) *m/z*
ESI-MS:	Instrument:	Finnigan MAT TSQ 700 with electrospray interface
	Operation:	Negative ion mode and positive ion mode, direct infusion at 3 μL/min
	Solvent:	Ammonium acetate buffer (7.5 mM, pH 7.5) / Methanol, 1:1
	Ionisation:	ESI spray voltage at 3.5 kV for negative ion and 4.5 kV for positive ion mode.
	Peaks:	584, 514, 451 ($M\text{-}H^-$, 100), 415 ($M\text{-}H^-\text{-}HCl$) *m/z* (negative ion mode) 493 ($M+K^+$), 475 ($M+Na^+$), 470 ($M+NH_4^+$, 100) *m/z* (positive ion mode)
IR:	Instrument:	FT-IR, Biorad Merlin
	Range:	4000-400 cm^{-1}, as film
	Peaks:	3460, 3364, 2253, 1635, 1368, 1322, 1293, 1098, 886, 820 cm^{-1}
^{1}H NMR:	Instrument:	Bruker ARX-500
	Field strength:	500 MHz
	Solvent:	DMSO-d_6 (2.5 ppm)
	Key spectral data:	δ 8.01 (1H, br s), 8.31 (1H, d) ppm
^{13}C NMR:	Instrument:	Bruker ARX-500
	Field strength:	126 MHz
	Solvent:	DMSO-d_6 (39.5 ppm)
	Spectral data:	δ 88.6, 110.1, 119.8 (q, J = 325 Hz), 122.2 (q, J = 274 Hz), 126.4, 126.9, 126.94 (q, J = 4.0 Hz), 133.8, 133.82 (q, J = 33.8 Hz), 135.9, 152.5 ppm Signal of trifluoromethyl and other nearby carbons split by F-C coupling.
Melting point:		196-200 °C (phase changes), 224 °C (melt)
Microanalysis:	Found:	C = 32.1%; H = 0.9%; N = 12.3% (May 2019)
	Calculated:	C = 31.8%; H = 0.9%; N = 12.4% (Calculated for $C_{12}H_4Cl_2F_6N_4O_2S$)