Australian Government
Department of Industry, Science and Resources

National Measurement Institute

NATA
WORLD RECOGNISED ACCREDITATION

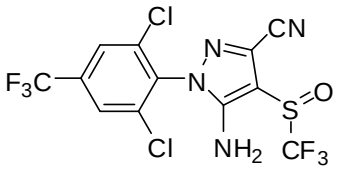
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1668: Fipronil

Report ID: P1668.2025.01

Chemical Formula: $C_{12}H_4Cl_2F_6N_4OS$

Molecular Weight: 437.2 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
00-AV-06	120068-37-3	97.1 ± 0.3%

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

Impurities: Contains fipronil sulfone (approx. 3% mass fraction)

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

Expiration of certification: The property values are valid till 10 April 2035, 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: Off-white crystals sourced from an external supplier and certified for identity and purity by NMI Australia. 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.

STABILITY WARNING: The material is a stable solid if stored as recommended. It is prone to oxidation and photodegradation when taken into solution. Standard solutions prepared from this material should be stored out of direct light at 4 ˚C and monitored regularly for oxidation to fipronil sulfone. This material has shown signs of degradation when injected onto a silanised glass liner at elevated temperatures.

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.

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.
25 April 2025

This report supersedes any issued prior to 25 April 2025.

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 qualitative headspace GC-MS analysis of occluded solvents and elemental microanalysis.

GC-FID:	Instrument:	Agilent 6890N or 8890	
	Column:	HP-1, 30 m × 0.32 mm I.D. × 0.25 μm	
	Program:	180 °C (15 min), 30 °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 = 97.2%, s = 0.01% (5 sub samples in duplicate, September 2010)	
	Re-analysis:	Mean = 97.2%, s = 0.03% (5 sub samples in duplicate, December 2015)	
	Re-analysis:	Mean = 97.1%, s = 0.05% (5 sub samples in duplicate, September 2021)	
	Re-analysis:	Mean = 97.1%, s = 0.05% (5 sub samples in duplicate, April 2025)	
GC-FID:	Instrument:	HP5890	
	Column:	ZB-1 Capillary, 30 m × 0.32 mm I.D. × 0.25 μm	
	Program:	130 °C (1 min), 12 °C/min to 260 °C	
	Injector:	230 °C	Detector Temp: 320 °C
	Carrier:	Helium	Split ratio: 20/1
	Relative mass fraction of the main component:		
	Initial analysis:	Mean = 97.2%, s = 0.03% (7 sub samples in duplicate, December 2000)	
	Re-analysis:	Mean = 96.9%, s = 0.01% (5 sub samples in duplicate, August 2005)	
	Fipronil sulfone at ~ 3% total peak area is seen by GC at longer retention time.		
Karl Fischer analysis:		Moisture content < 0.1 % mass fraction (August 2010) Moisture content < 0.1 % mass fraction (December 2015) Moisture content < 0.1 % mass fraction (September 2021) Moisture content < 0.1 % mass fraction (March 2025)	
Thermogravimetric analysis:		Volatiles content < 0.1% and non-volatile residue < 0.2% mass fraction. (September 2000 and February 2001)	

Spectroscopic and other characterisation data

GC-MS:	Instrument:	HP5890/5971
	Columns:	HP Ultra-1, 30 m × 0.25 mm I.D. × 0.25 μm
	Program:	170 °C (0.5 min), 12 °C/min to 300 °C (2 min)
	Injector:	250 °C
	Split ratio:	20/1
	Transfer line temp:	280 °C
	Carrier:	Helium, 1.0 mL/min
	The retention time is reported along with the peaks for the 35Cl2 isomer in the mass spectrum. The latter are reported in mass to charge ratios and (in brackets) as a percentage relative to the base peak.	
	7.7 min:	420 (4), 367 (100), 351 (11), 255 (11), 213 (29) *m/z*
HPLC:	Peak area percentage of total: Mean = 97.3 %, s = 0.03 (3 samples)	
	Column:	Phenomenex Luna C-18, 5 μm (2.0 mm × 150 mm)
	Mobile Phase:	65% Acetonitrile/water/conc. NH_4OH (65:35:0.3)
	Flow Rate:	0.3 mL/min
	Detector:	UV at 280 nm
IR:	Instrument:	Perkin-Elmer FT-IR
	Range:	4000-400 cm^{-1}, KBr disc
	Peaks:	3438, 3345, 2250, 1635, 1562, 1321, 1195, 1145, 1071, 888, 817 cm^{-1}
^{1}H NMR:	Instrument:	Bruker DMX-500
	Field strength:	500 MHz
	Solvent:	Acetone-d_6
	Spectral data:	δ 8.14 (2H, s), 6.86 (2H, bs)
	Signals ascribed to the presence of fipronil sulfone (est. 3% mass fraction) are also observed.	
^{13}C NMR:	Instrument:	Bruker DMX-500
	Field strength:	126 MHz
	Solvent:	Acetone-d_6
	Spectral data:	δ 94.5, 111.6, 123.1(q, $J_{C\text{-}F}$ = 273 Hz), 126.6, 126.7 (q, $J_{C\text{-}F}$ = 336 Hz), 127.5 (q, $J_{C\text{-}F}$ = 3.8Hz), 135.3 (q, $J_{C\text{-}F}$ = 35 Hz), 135.4, 137.3, 152.2 ppm
Melting point:		197-199 °C by DSC
Microanalysis:	Found:	C = 32.8%, H = 0.9%, N = 12.9%, F = 25.9%, Cl = 16.1%, S= 7.5%
	Calculated:	C = 33.0%, H = 0.9%, N = 12.8%, F = 26.1%, Cl = 16.2%, S= 7.3% (Calculated for $C_{12}H_4Cl_2F_6N_4OS$)