Australian Government
Department of Industry, Science and Resources

National Measurement Institute

CIPM MRA

NATA
WORLD RECOGNISED ACCREDITATION

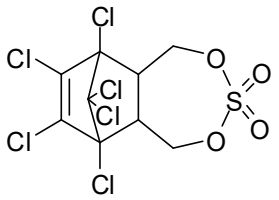
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1372: Endosulfan sulfate

Report ID: P1372.2021.02

Chemical Formula: $C_9H_6Cl_6O_4S$

Molecular Weight: 422.9 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
96-19416	1031-07-8	97.9 ± 3.0%

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

IUPAC name: (1R,2S,8R,9S)-1,9,10,11,12,12-Hexachloro-4,6-dioxa-5-thiatricyclo[7.2.1.$0^{2,8}$]dodec-10-ene 5,5-dioxide

Expiration of certification: The property values are valid till 10 September 2026, 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 powder 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. 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 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 22 August 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 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 value by qNMR was obtained using the one-proton doublet of doublets at 2.4 ppm measured against a certified internal standard of potassium hydrogen maleate. The purity value by qNMR was obtained using a

combination of the two proton singlet at 3.53 ppm the two proton doublet at 4.65 ppm, and the two proton doublet at 4.92 ppm against a certified internal standard of triphenylphosphine oxide.

Supporting evidence is provided by elemental microanalysis.

GC-FID:	Instrument:	Agilent 6890N or 8890
	Column:	HP-1, 30 m × 0.32 mm I.D. × 0.5 µm
	Program:	180 °C (2 min), rate rise 10 °C /min to 260 °C (2 min) or to 300 °C (3 min)
	Injector:	230 °C
	Detector Temp:	320 °C
	Carrier:	Helium
	Split ratio:	20/1
	Relative peak area of the main component:	
	Initial analysis:	Mean = 99.4%, s = 0.06% (3 sub samples in duplicate, 1997)
	Re-analysis:	Mean = 99.3%, s = 0.02% (5 sub samples in duplicate, January 2009)
	Re-analysis:	Mean = 99.3%, s = 0.01% (5 sub samples in duplicate, November 2016)
	Re-analysis:	Mean = 99.3%, s = 0.06% (5 sub samples in duplicate, September 2021)
HPLC:	Method:	Peak area percentage of total, mean of replicates = 99.3%, s = 0.1%
	Column:	Alltima C-18 5 µm (4.6 mm x 250 mm)
	Mobile Phase:	Acetonitrile/water (80/20)
	Flow Rate:	1.0 mL/min
	Detector:	Refractive Index detector
Karl Fischer analysis:		Moisture content ≤ 0.1% mass fraction (January 2009, September 2016 & August 2021)
Thermogravimetric analysis:		Volatile content < 0.1% and non-volatile residue < 0.2% mass fraction (November 2001)
QNMR:	Instrument:	Bruker Avance-III-500
	Field strength:	500 MHz Solvent: DMSO-d_6 (2.50 ppm)
	Internal standard:	Triphenylphosphine oxide (100% mass fraction)
	Initial analysis:	Mean (3.5 ppm) = 96.2%, s = 0.5% (5 sub samples in duplicate, Dec 2011)
		Mean (4.6 ppm) = 95.9%, s = 0.5% (5 sub samples in duplicate, Dec 2011)
		Mean (4.9 ppm) = 97.3%, s = 0.6% (5 sub samples in duplicate, Dec 2011)

Spectroscopic and other characterisation data

GC-MS:	Instrument:	HP5890/5989A. Ionisation: EI/70ev
	Column:	DB5MS, 24 m x 0.25 mm I.D x 0.11 µm
	Temp Program:	70 °C to 300 °C at 20 °C/min
	Injector Temp:	230 °C
	Split ratio:	10/1
	Transfer line temp:	280 °C
	Carrier gas:	Helium, 1.0 mL/min
	Scan Range:	40-500 *m/z*
	Matches the Wiley GCMS Library (computer database) reference spectrum of endosulfan sulfate. Peaks observed (in isomer sets) at 422, 387, 272, 229, 170, 121, 102 *m/z*	
TLC:	Conditions:	Kieselgel 60F_{254}. Cyclohexane/diisopropylether/diethylamine (52/40/8) Single spot observed, Rf = 0.72
IR:	Instrument:	FT-IR, BIORAD WIN FTS40
	Range:	4000-400 cm^{-1}, KBr pellet
	Peaks:	1606, 1411, 1383, 1200, 1017, 964, 903, 829, 785, 628, 518 cm^{-1} Matches literature reference spectrum for endosulfan sulfate
^{1}H NMR:	Instrument:	Bruker Avance-400
	Field strength:	400 MHz
	Solvent:	DMSO-d_6 (2.49 ppm)
	Spectral data:	δ 3.47 (2H, br s), 4.71 (2H, br s), 4.91 (2H, d, *J* = 14.4 Hz) ppm
^{13}C NMR:	Instrument:	Bruker Avance-400
	Field strength:	100 MHz
	Solvent:	DMSO-d_6 (39.5 ppm)
	Spectral data:	δ 49.4, 67.5, 80.3, 103.3, 130.9 ppm
Melting point:		178-181 °C
Microanalysis:	Found:	C = 25.6%; H = 1.4%; S = 7.3% (September 2001)
	Calculated:	C = 25.6%; H = 1.4%; S = 7.6% (Calculated for $C_9H_6Cl_6O_4S$)