



Designation: D 5303 – 92 (Reapproved 2002)^{e1}

An American National Standard

Standard Test Method for Trace Carbonyl Sulfide in Propylene by Gas Chromatography¹

This standard is issued under the fixed designation D 5303; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (e) indicates an editorial change since the last revision or reapproval.

^{e1} NOTE—Warning notes were editorially moved into the standard text in March 2003.

1. Scope

1.1 This test method covers the determination of traces of carbonyl sulfide (COS) in propylene. It is applicable to COS concentrations from 0.5 to 4.0 mg/kg (parts per million by mass). See Note 1.

NOTE 1—The lower limit of this test method is believed to be below 0.1 mg/kg, depending on sample size and sensitivity of the instrumentation being used. However, the cooperative testing program was conducted in the 0.5 to 4.0 range due to limitations in preparing commercial test mixtures.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 8.*

2. Referenced Documents

2.1 ASTM Standards:

D 3609 Practice for Calibration Techniques using Permeation Tubes²

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry³

E 840 Practice for Using Flame Photometric Detectors in Gas Chromatography⁴

3. Summary of Test Method

3.1 A procedure is given for removing a sample from the sample cylinder, separating COS from propylene, detecting

COS, calibrating the detector, quantitating COS content in the sample, and assaying the gas standard. General comments and recommended techniques are given.

3.2 A relatively large volume of sample is injected into a gas chromatograph having a single packed column, operated isothermally at 10 to 50°C, that separates COS from propylene. COS is detected with a flame photometric detector.

3.3 Calibration data, based on peak areas, are obtained using a known gas standard blend of COS in the range expected for the sample. The COS peak area in the sample is measured and the concentration of COS calculated.

3.4 The COS gas standard blend is assayed prior to use for calibration.

4. Significance and Use

4.1 In processes producing propylene, COS usually remains with the C₃ hydrocarbons and must be removed, since it affects product quality. COS acts as a poison to commercial polymerization catalysts, resulting in deactivation and costly process downtime.

4.2 Accurate gas chromatographic determination of trace COS in propylene involves unique analytical problems because of the chemical nature of COS and idiosyncracies of trace level analyses. These problems result from the reactive and absorptive nature of COS, the low concentration levels being measured, the type of detector needed, and the interferences from the propylene sample matrix. This test method addresses these analytical problems and ways to properly handle them to assure accurate and precise analyses.

4.3 This test method provides a basis for agreement between two laboratories when the determination of trace COS in propylene is important. The test method permits several calibration techniques. For best agreement between two labs, it is recommended that they use the same calibration technique.

5. Interferences

5.1 Hydrogen sulfide (H₂S) or sulfur dioxide (SO₂) can be present in the propylene and must be separated from COS. (See Note 2.)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.03 on Propylene.

Current edition approved Dec. 10, 2002. Published April 2003. Originally approved in 1992. Last previous edition approved in 1997 as D 5303 – 92 (1997).

² Annual Book of ASTM Standards, Vol 11.03.

³ Annual Book of ASTM Standards, Vol 05.06.

⁴ Annual Book of ASTM Standards, Vol 03.06.



NOTE 2—H₂S and SO₂ are separated from COS with the Carbowack BHT 100 columns or with the Chromosil 300 column.

6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph (GC) equipped with a flame photometric detector/electrometer system (FPD), as described in 6.2, may be used. A GC/FPD equipped with an output signal linearizer is also permitted.

6.2 *Detector System*, flame photometric detector, either single or dual burner design. Noise level must be no more than one recorder chart division (see 6.5). The signal for COS must be at least twice the noise level at the 0.1 mg/kg level. A discussion of this detector is presented in Practice E 840. The electrometer used with the detector must have a sensitivity of 10⁻¹² A full scale on a 1 mV recorder to achieve optimum detectability at lowest levels.

6.3 *Column*—Any column that will effect the complete separation of COS from propylene and other compounds normally present in propylene concentrates, and that is sufficiently inert to preclude the loss of COS, may be used. Columns that meet these criteria, and that were used in the cooperative study for this test method, are listed in Table 1.

6.4 *Sample Inlet System*—Any gas sampling valve or gas tight syringe that will permit introduction of up to 5.0 mL to the column, and that will not cause any loss of COS, is suitable.

6.5 *Recorder*—Any strip chart recorder with a full scale range of 1 mV, a maximum full scale balance time of 2 s, and a minimum chart speed of 0.5 cm/s, may be used.

6.6 *Data Handling System*—Any commercially available GC integrator or GC computer system capable of accurately integrating the area (uVs) of the COS peak is satisfactory. Data systems that will linearize the logarithmic output of the FPD are also satisfactory.

6.7 *Sample Cylinders*, 300 mL capacity or larger, fluorocarbon lined stainless steel, Type DOT 3E, 12409 kPa (1800 psi) working pressure.

7. Reagents and Materials

7.1 *Air*, zero grade.

TABLE 1 Suitable GC Columns and Temperatures^A

Column Number	Size, m × mm	Tubing ^B Type	Packing and Oven Temperature, °C
1	0.9 × 3.78	SS	Porapak R, 80/100 Mesh; 47
2	1.4 × 3.78	TFE ^C	Carbowack BHT 100, 40/60 Mesh; 25,40 ^D
3	1.8 × 3.78	TFE	Carbowack BHT 100; 25,30 ^D
4	1.8 × 3.78	TFE	Porapak Q, AW, 50/80 Mesh (Above in Series); 74
5	2.4 × 3.78	SS	Carbowack BHT 100; 47
6	2.8 × 3.78	TFE	Carbowack BHT 100, 40/60 Mesh; 50
7	3.6 × 3.78	TFE	Carbowack BHT 100, 40/60 Mesh; 50
8	4.3 × 3.78	TFE	Chromosil 300; 50 ^E
9	6.1 × 3.78	TFE	Hayes Sep Q, 80/100 Mesh; 65

^A These columns have been tested cooperatively and found suitable for use with this test method.

^B 316 SS Tubing for columns or connection of sample cylinder to sampling system can be TFE lined internally to improve on system stability. This tubing is commercially available from chromatography vendors.

^C TFE—Homopolymer of tetrafluoroethylene.

^D Identical columns used by different labs at different temperatures.

^E Propyne (methyl acetylene) can interfere with COS using this column.

7.2 *Carbonyl sulfide (COS)*, lecture bottle, 97.5 % min. (**Warning**—Toxic! See Section 8, Hazards.)

7.3 *Gas Calibration Blends*, 1 to 10 mg/kg COS in either nitrogen, argon, propylene or a propylene/argon mixture. They can be obtained from any commercial supplier or prepared as shown in Appendix X1 or Test Method D 4468.

7.4 *Gas Sampling Syringe*, 0.1, 1.0, and 5.0 mL.

7.5 *Gas Sampling Valve and Sample Loops*, fluorocarbon or 316 stainless steel. See Footnote B of Table 1.

7.6 *Glass Vials*, 125 cm.

7.7 *Hydrogen*, pure grade, 99.9 %.

7.8 *Isooctane* (2,2,4-trimethylpentane), sulfur free, minimum purity 99 mol %. (**Warning**—Flammable! Health Hazard.)

7.9 *Nitrogen or helium*, 99.999 % min.

7.10 *TFE-fluorocarbon septa and aluminum seals for vials*.

8. Hazards

8.1 Carbonyl sulfide is toxic and narcotic in high concentrations, and upon decomposition can liberate hydrogen sulfide. Exposure to dangerous concentrations of COS is most likely when handling the pure component for preparation of standard blends for assaying the COS calibration gas standards.

9. Sampling

9.1 Supply samples to the laboratory in high pressure cylinders coated internally with TFE-fluorocarbon, or otherwise specially treated to reduce or eliminate loss of COS due to reaction with the cylinder walls.

9.2 The sample cylinder and contents should be at room temperature prior to sampling to the chromatograph. Test samples as soon as possible after receipt.

NOTE 3—Cooperative studies indicate that the measured value for COS will decrease with time.

9.3 Place the sample cylinder in a vertical position and use either of the following two techniques to obtain a vaporized sample from the container for introduction into the GC.

9.3.1 Connect the sample cylinder to the sampling valve on the chromatograph, using a minimum length of 316 ss tubing, so that sample is withdrawn from the bottom of the cylinder. Adjust the flow rate from the sample cylinder so that complete vaporization of the liquid occurs at the cylinder valve. A flow rate of 5 to 10 bubbles/s through a water bubbler placed at the sample vent is sufficient (see Note 4). Turn the sampling valve to the “flush” position and flush for approximately 15 s. Shut off the cylinder valve and allow the pressure to drop to atmospheric.

NOTE 4—If the flow rate is too fast, warming of the valve can be required to avoid freezing and to ensure complete vaporization of the sample.

9.3.2 Alternatively, obtain a sample with a gas tight syringe. A convenient way to do this is to use flexible plastic tubing to connect the bottom of the sample cylinder to the water bubbler and then to pierce the tubing with the syringe needle after flow is established.

