Designation: D 5953M – 96
METRIC

An American National Standard

Standard Test Method for Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection Method (Metric)[1]

This standard is issued under the fixed designation D 5953M; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method[2] covers a procedure for sampling and determining concentrations of non-methane organic compounds (NMOC) in ambient, indoor, or workplace atmospheres.

1.2 The test method describes the collection of cumulative samples in passivated stainless steel canisters and subsequent laboratory analysis.

1.2.1 This test method describes a procedure for sampling in canisters at final pressures above atmospheric pressure (referred to as pressurized sampling).

1.3 This test method employs a cryogenic trapping procedure for concentration of the NMOC prior to analysis.

1.4 This test method describes the determination of the NMOC by the simple flame ionization detector (FID), without the gas chromatographic columns and complex procedures necessary for species separation.

1.5 The range of this test method is from 20 to 10 000 ppbC **(1, 2)**.[3] See 13.4 for procedures for lowering the range.

1.6 The test method may yield less accurate results for some halogenated or oxygenated hydrocarbons emitted from nearby sources of industrial air pollutants. This is especially true if there are high concentrations of chlorocarbons or chlorofluorocarbons present.

1.7 The values stated in SI units are regarded as the standard.

1.8 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[4]
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]
D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[5]
D 5466 Test Method for the Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)[5]

3. Terminology

3.1 *Definitions*— For definitions of terms used in this test method, refer to Terminology D 1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *cryogen*—a refrigerant used to obtain very low temperatures in the cryogenic traps of the analytical system.

3.2.1.1 *Discussion*—Liquid argon (bp − 185.7°C at standard pressure) is recommended for this test method. Cryogens with lower boiling points, such as liquid nitrogen, should not be used because of possible trapping of oxygen from the sample air, which might lead to the possibility of an explosion or fire. In addition, methane would be trapped.

3.2.2 *dynamic calibration*—calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system, such as by quantitative, flow-rate dilution of a high-concentration gas standard with zero gas.

3.2.3 *NMOC*—non-methane organic compounds.

3.2.3.1 *Discussion*—Total non-methane organic compounds are those compounds measured by a flame ionization detector, excluding methane and compounds with vapor pressure above 10^{-2} kPa, recovered from the canister.

3.2.4 *ppm C and ppb C*—concentration units of parts per million and parts per billion of organic carbon as detected by the FID.

3.2.4.1 *Discussion*—During calibration with propane, for example, they are equivalent to parts per million by volume (ppm (v)) or parts per billion by volume (ppb (v)), respectively, multiplied by the number of carbon atoms in propane.

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[1] This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved May 10, 1996. Published July 1996.

[2] This test method is based on EPA Method TO-12: "Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Pre-Concentration and Direct Flame Ionization Detection (PDFID)", *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* , EPA 600 4-89-017, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1990.

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 11.03.

4. Summary of Test Method (2-6)

4.1 An air sample is extracted directly from the ambient air, collected in a precleaned sample canister and transported to a laboratory.

4.2 A fixed-volume portion of the sample air is drawn from the canister at a low flow rate through a glass-bead filled trap that is cooled to approximately −186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC using condensation, while allowing the nitrogen, oxygen, methane, and other compounds with boiling points below −186°C to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.

4.3 After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to 80 to 90°C.

4.4 The organic compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units using a previously obtained calibration curve relating integrated peak areas with known concentrations of propane.

4.5 The cryogenic trap simultaneously concentrates the NMOC while separating and removing the methane from air samples. The technique is thus direct reading using FID for NMOC and, because of the concentration step, it is more sensitive than conventional continuous NMOC analyzers.

4.6 The sample is injected into the hydrogen-rich flame of the FID, where the organic vapors burn, producing ionized molecular fragments. The resulting ion fragments are then collected and detected. Because this test method employs a helium carrier gas, the detector response is nearly identical for many hydrocarbon compounds of interest. Thus, the historical short-coming of varying FID response to aromatic, olefinic, and paraffinic hydrocarbons is minimized. The FID is much less sensitive to most organic compounds containing functional groups such as carbonyls, alcohols, halocarbons, etc.

5. Significance and Use

5.1 Many industrial processes require determination of NMOC in the atmosphere.

5.2 Accurate measurements of ambient concentrations of NMOC are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants **(7, 8)**.

5.2.1 The NMOC concentrations typically found at urban sites may range up to 1 to 3 ppm C or higher. In order to determine transport of precursors into an area, measurement of NMOC upwind of the area may be necessary. Rural NMOC concentrations originating from areas free from NMOC sources are likely to be less than a few tenths of 1 ppm C.

5.3 Conventional test methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain when speciated measurements are not needed. The test method described here involves a simple, cryogenic preconcentration procedure with subsequent direct detection with the FID. The test method is sensitive and provides accurate measurements of ambient total NMOC concentrations where speciated data are not required.

5.4 An application of the test method is the monitoring of the cleanliness of canisters.

5.5 Another use of the test method is the screening of canister samples prior to analysis.

5.6 Collection of ambient air samples in pressurized canisters provides the following advantages:

5.6.1 Convenient integration of ambient samples over a specific time period,

5.6.2 Capability of remote sampling with subsequent central laboratory analysis,

5.6.3 Ability to ship and store samples, if necessary,

5.6.4 Unattended sample collection,

5.6.5 Analysis of samples from multiple sites with one analytical system,

5.6.6 Collection of replicate samples for assessment of measurement precision, and

5.6.7 Specific hydrocarbon analysis can be performed with the same sample system.

6. Interferences

6.1 In laboratory evaluations, moisture in the sample has been found to cause a positive shift in the FID baseline. The effect of this shift is minimized by carefully selecting the integration termination point and adjusting the baseline used for calculating the area of the NMOC peaks.

6.2 With helium as a carrier gas, FID response is quite uniform for most hydrocarbon compounds, but the response can vary considerably for other types of organic compounds.

7. Apparatus

7.1 *Sample Collection System*, (Fig. 1).

7.1.1 *Sample Canister(s)*, stainless steel, Summa[6]-polished vessel(s) of 4 to 6 L capacity, used for automatic collection of integrated field air samples.

7.1.1.1 Mark each canister with a unique identification number stamped on its frame.

7.1.2 *Sample Pump*, stainless steel, metal bellows type.

7.1.2.1 Ensure that the pump is free of leaks, and uncontaminated by oil or organic compounds.

7.1.2.2 Shock mount the pump to minimize vibration.

7.1.3 *Pressure Gage*, 0 to 210 kPa (0 to 30 psig).

7.1.4 *Solenoid Valve*, controls the sample flow to the canister with negligible temperature rise.

7.1.5 *Flow Control Device*, mass flowmeter, critical orifice, or short capillary to maintain the sample flow over the sampling period.

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[6] The Summa process is a trademark of Molectrics, Inc., 4000 E. 89th St., Cleveland, OH 44105.