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**Air quality — Determination of total non-methane organic compounds — Cryogenic preconcentration and direct flame ionization detection method**

*Qualité de l'air — Dosage des composés organiques non méthaniques totaux — Méthode par préconcentration cryogénique et ionisation sélective directe dans la flamme*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 14965 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

Annex A of this International Standard is for information only.

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## Introduction

Accurate measurements of ambient concentrations of total non-methane volatile organic compounds (NMVOC) are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants.

The NMVOC concentrations typically found at urban sites may range up to 1 ppmC to 3 ppmC (see definition 3.4) or higher. In order to determine transport of precursors into an area, measurement of NMVOC upwind of the area may be necessary. Rural NMVOC concentrations originating from areas free from NMVOC sources are likely to measure less than a few tenths of 1 ppmC.

Conventional methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain. The method described in this International Standard involves a simple, cryogenic preconcentration procedure with subsequent direct detection with the flame ionization detector (FID). The method is sensitive and provides accurate measurements of ambient total NMVOC concentrations where species data are not required.

This International Standard is intended for analysis of air samples from sampling canisters and has not been designed for continuous ambient air monitoring.

Another application of this International Standard is the monitoring of the cleanliness of canisters and screening of canister samples prior to analysis.

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

- convenient integration of ambient samples over a specific time period;
- capability of remote sampling with subsequent central laboratory analysis;
- ability to ship and store samples, if necessary;
- analysis of samples from multiple sites with one analytical system;
- collection of replicate samples for assessment of measurement precision;
- specific hydrocarbon analysis may be performed with the same sample system.

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# Air quality — Determination of total non-methane organic compounds — Cryogenic preconcentration and direct flame ionization detection method

## 1 Scope

This International Standard describes a procedure for sampling and determining concentrations of total non-methane volatile organic compounds (NMVOC) in the ambient atmosphere.

This International Standard describes the collection of cumulative samples in passivated stainless steel canisters and subsequent laboratory analysis. It describes a procedure for sampling in canisters at final pressures above atmospheric pressure (referred to as pressurized sampling). It employs a cryogenic trapping procedure for concentration of the NMVOC prior to analysis.

This International Standard describes the determination of the NMVOC by simple flame ionization detection (FID), without the gas chromatographic columns and complex procedures necessary for species separation.

This International Standard is applicable to carbon concentrations in the range from 20 ppbC to 10 000 ppbC. See 12.4 for procedures for lowering the range.

Several variations to the method described in this International Standard are also possible; see clause 12.

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## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO/TR 4227:1989, *Planning of ambient air quality monitoring*.

ISO 6141:2000, *Gas analysis — Requirements for certificates for gases and gas mixtures*.

ISO 6145-1:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration*.

ISO 6145-3:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 3: Periodic injections into a flowing gas stream*.

ISO 6145-4:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 4: Continuous injection methods*.

ISO 6145-6:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 6: Sonic orifices*.

### 3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

#### 3.1

##### **cryogen**

refrigerant used to obtain very low temperatures in the cryogenic traps of the analytical system

NOTE Liquid argon (boiling point, 87 K, at standard atmospheric pressure) is recommended for the method described in this International Standard.

#### 3.2

##### **dynamic calibration**

calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system

NOTE An example of such a system is the quantitative, flowrate dilution of a high-concentration gas standard with zero gas.

#### 3.3

##### **total non-methane volatile organic compounds:**

those compounds measured by a flame ionization detector, excluding methane, and compounds with vapour pressure above  $10^{-2}$  kPa, recovered from the canister

#### 3.4

##### **parts per million [billion] of organic carbon**

##### **ppmC [ppbC]**

concentration unit, as detected by the FID, equivalent to parts per million [billion] by volume multiplied by the number of carbon atoms in the calibration gas molecule

NOTE During calibration with propane, for example, it is equivalent to parts per million by volume (ppm) or [parts per billion by volume (ppb)], multiplied by three.

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### 4 Description of the method

#### 4.1 Sampling

An air sample is extracted directly from the ambient air, collected into a precleaned sample canister, and transported to a laboratory for analysis.

#### 4.2 Analysis

A fixed-volume portion of the sample air is drawn from the canister at a low flowrate through a glass-bead-filled trap that is cooled to approximately 87 K with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMVOC, while allowing the nitrogen, oxygen, methane and other compounds 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 shall be precisely repeatable between the calibration and the analytical phases.

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 353 K to 363 K.

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 via a previously obtained calibration curve relating integrated peak areas with known concentrations of propane.



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

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 method employs a helium carrier gas, the detector response is nearly unity for all hydrocarbon compounds. 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.

This International Standard may yield less accurate results for some halogenated or oxygenated hydrocarbons emitted from nearby sources of industrial air pollutants.

## 5 Interferences

In laboratory evaluations, moisture 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 NMVOC peaks.

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

## 6 Apparatus

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### 6.1 Sample collection system (Figure 1)

#### 6.1.1 Sample canisters.

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Stainless steel electropolished vessels of 4 l to 6 l capacity, used for automatic collection of integrated field air sample. Each canister shall be stamped on its frame with a unique identification number.

#### 6.1.2 Sample pump.

Stainless steel, metal bellows type, capable of at least 200 kPa maximum pressure. Ensure that pump is free of leaks, and uncontaminated by oil or organic compounds. Shock-mount the pump to minimize vibration.

#### 6.1.3 Vacuum/pressure gauge, covering the range 0 kPa to 210 kPa.

#### 6.1.4 Solenoid valve, to control the sample flow to the canister with negligible temperature rise.

#### 6.1.5 Flowrate control device, e.g. mass flowmeter, of critical orifice or short capillary, to maintain the sample flowrate over the sample period.

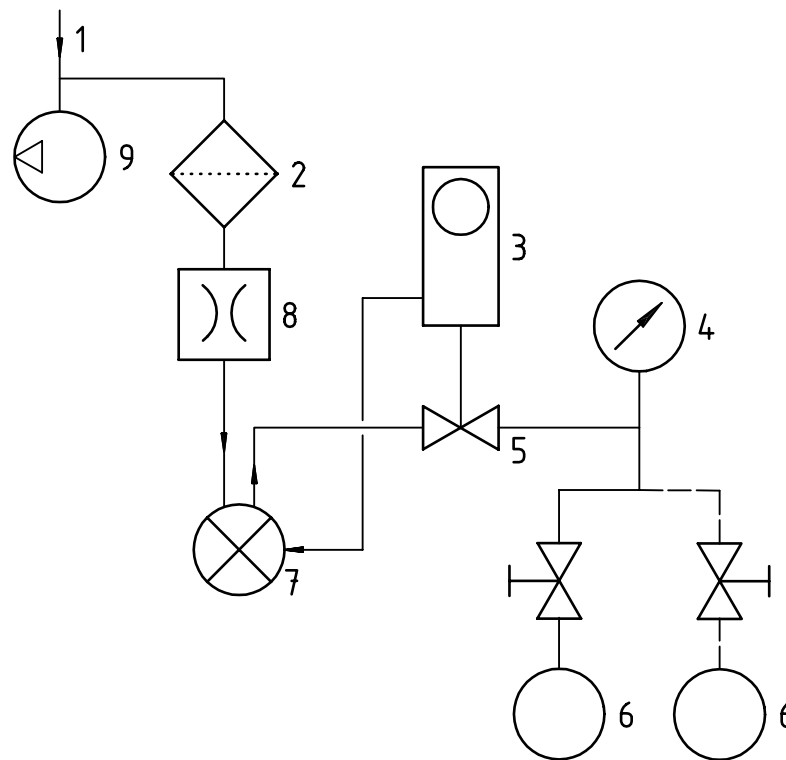
#### 6.1.6 Particulate matter filter.

Inert in-line filter, of pore size 2 µm or less, or other suitable filter, used to filter the air sample.

#### 6.1.7 Auxiliary vacuum pump or blower, capable of drawing sample air through the sample inlet line to reduce inlet residence time to no greater than 10 s.

#### 6.1.8 Timer, programmable and electrically connected to the solenoid valve and pumps, capable of controlling the pumps and the solenoid valve.

#### 6.1.9 Sample inlet line, consisting of stainless steel tubing components, to transport the sample air into the sample system.



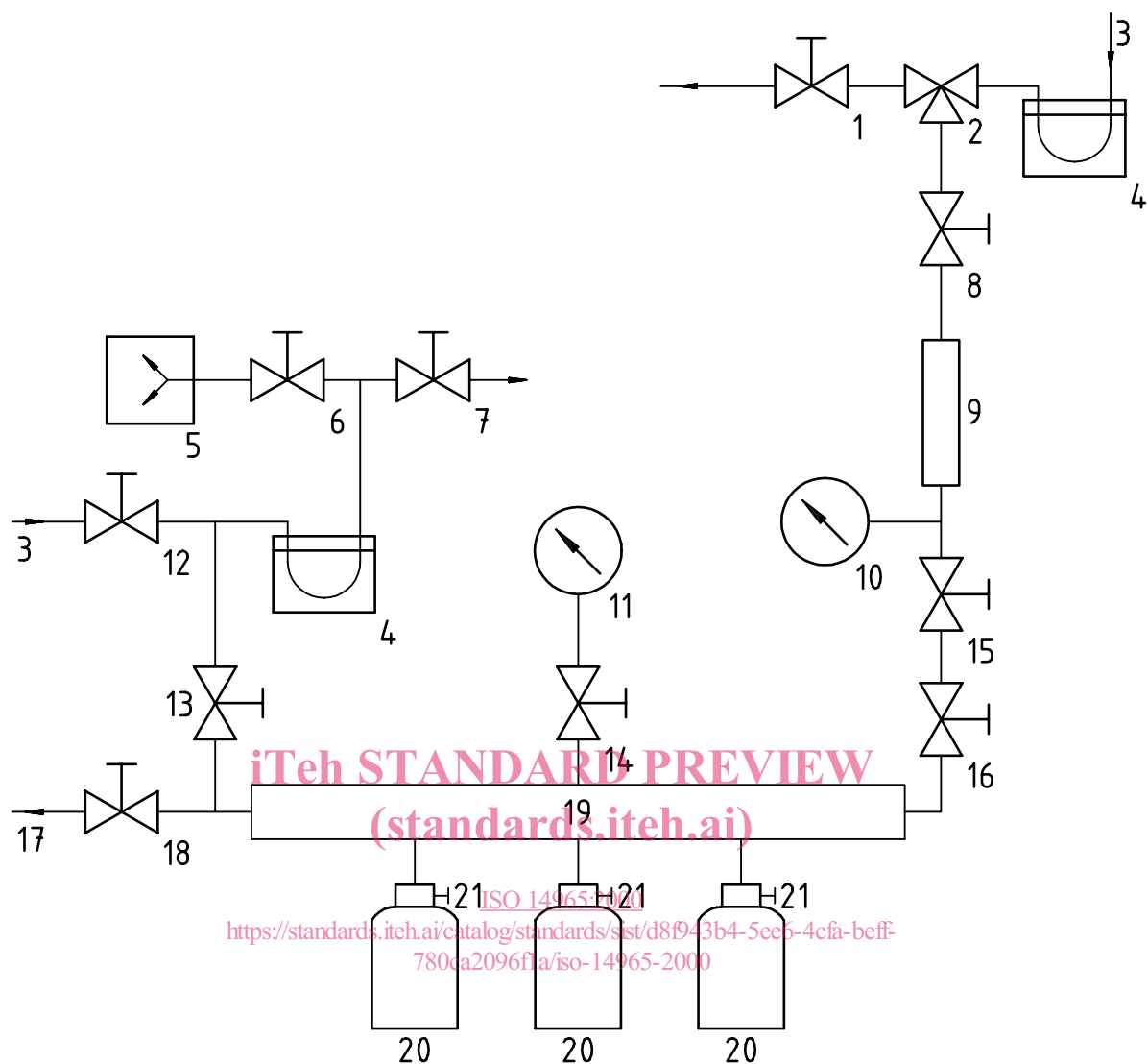
#### Key

- |                             |                         |
|-----------------------------|-------------------------|
| 1 Sample inlet line         | 6 Sample canister(s)    |
| 2 Particulate matter filter | 7 Sample pump           |
| 3 Timer                     | 8 Flow control device   |
| 4 Pressure gauge            | 9 Auxiliary vacuum pump |
| 5 Solenoid valve            |                         |

Figure 1 — Sample system for automatic collection of integrated air samples

## 6.2 Sample-canister cleaning system (Figure 2)

- 6.2.1 Vacuum pump**, capable of evacuating sample canister(s) to an absolute pressure of  $\leq 2$  Pa.
- 6.2.2 Manifold**, of stainless steel, with connections for simultaneously cleaning several canisters.
- 6.2.3 Shut-off valves** (nine).
- 6.2.4 Pressure gauge**, covering the range 0 kPa to 350 kPa, to monitor zero-air pressure.
- 6.2.5 Cryogenic traps** (two), consisting of U-shaped open tubular traps cooled with liquid argon, to prevent contamination from back-diffusion of oil from the vacuum pump and to provide clean, zero-air to the sample canisters.
- 6.2.6 Vacuum gauge**, capable of measuring vacuum in the manifold to an absolute pressure of 15 Pa or less, with scale divisions of 0,1 Pa.
- 6.2.7 Flowrate control valve**, to regulate flowrate of zero-air into the canisters.
- 6.2.8 Humidifier**, e.g. water bubbler or other system, capable of providing moisture to the zero-air supply.
- 6.2.9 Isothermal oven**, for heating canisters to 375 K (not shown in Figure 2).

**Key**

- |                              |                                |
|------------------------------|--------------------------------|
| 1 Vent valve                 | 12 Vent shut-off valve         |
| 2 3-port gas valve           | 13 Vacuum shut-off valve       |
| 3 Zero-air supply            | 14 Vacuum gauge shut-off valve |
| 4 Cryogenic trap             | 15 Zero-air shut-off valve     |
| 5 Vacuum pump                | 16 Flow control valve          |
| 6 Vacuum pump shut-off valve | 17 Vent                        |
| 7 Vent valve                 | 18 Vent shut-off valve         |
| 8 Shut-off valve             | 19 Manifold                    |
| 9 Humidifier                 | 20 Sample canisters            |
| 10 Pressure gauge            | 21 Canister valves             |
| 11 Vacuum gauge              |                                |

**Figure 2 — Canister cleaning system**