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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

Reference number
ISO 14965:2000(E)

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Foreword

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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.

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.*

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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.

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.

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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 shortcoming 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

6.1 Sample collection system (Figure 1)

6.1.1 Sample canisters.

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.

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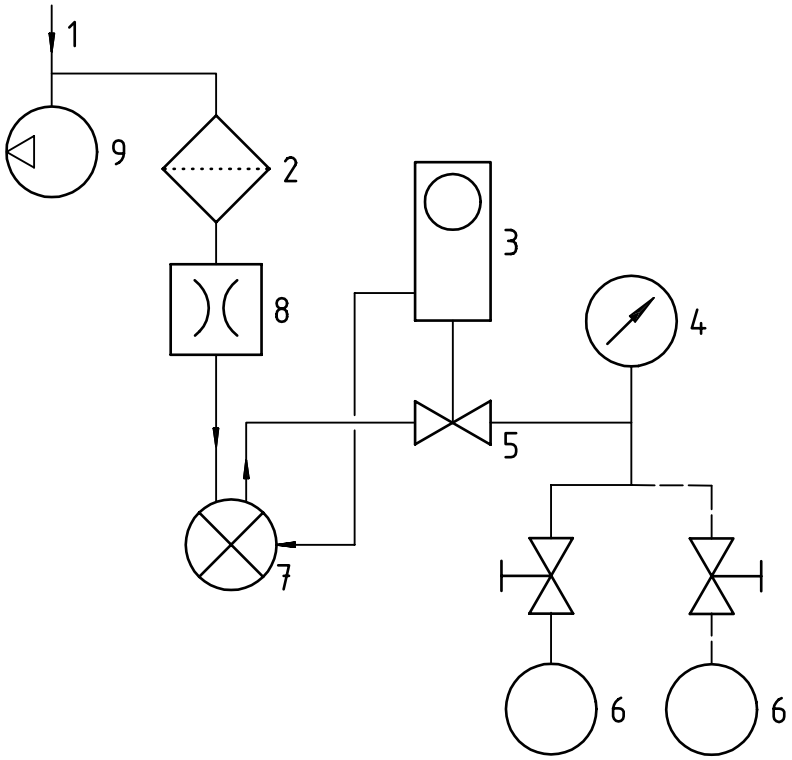

Key

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

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 $\leqslant$ 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).

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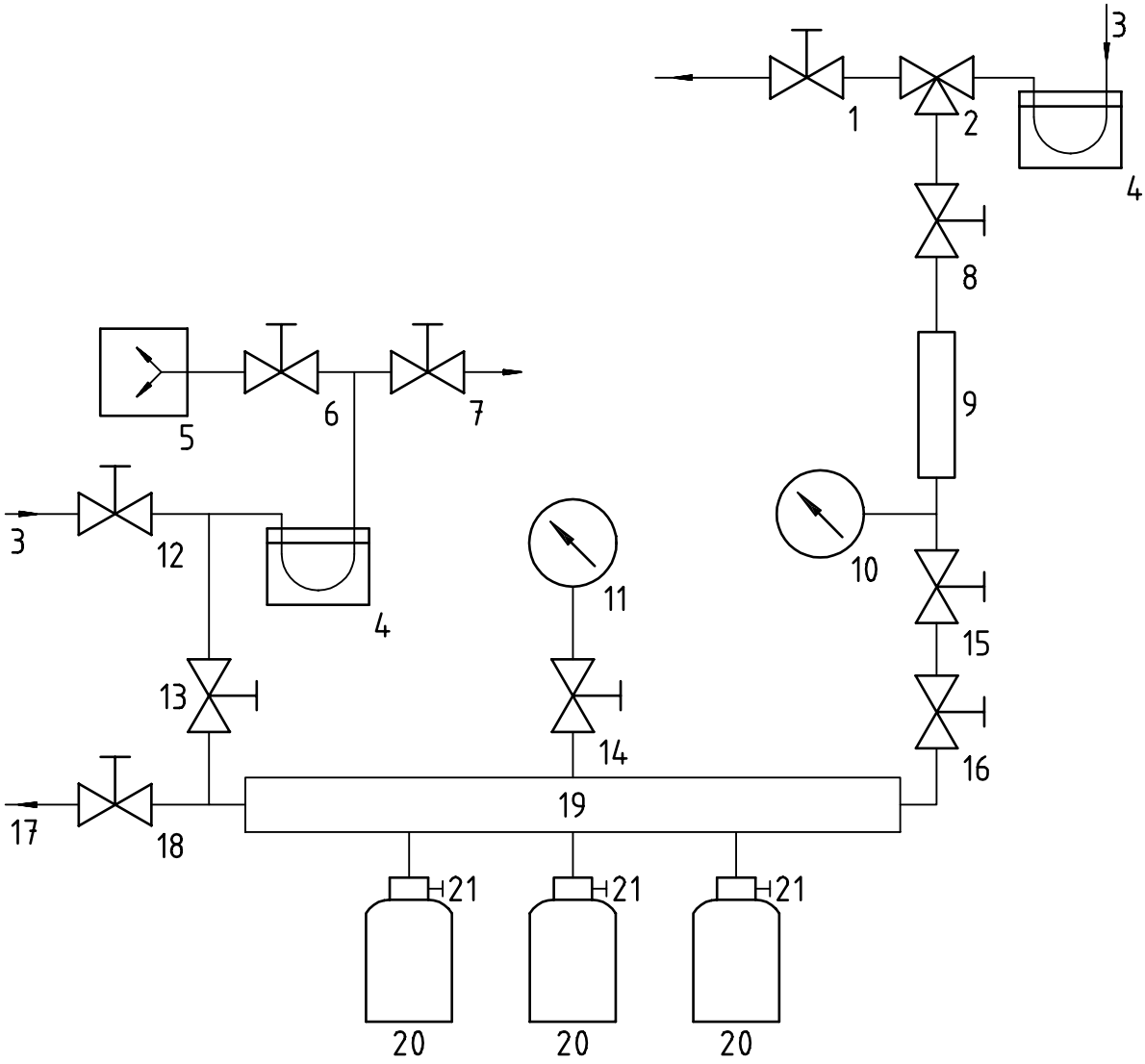

Key

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

Figure 2 — Canister cleaning system

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6.3 Analytical system (Figure 3)

6.3.1 FID system, including flowrate controls for the FID fuel and combustion air, temperature control for the FID, and signal processing electronics.

FID combustion air, hydrogen, and helium carrier gas flowrates shall be set as defined by the manufacturer's instructions to obtain an adequate FID response while maintaining a stable flame throughout all phases of the analytical cycle.

6.3.2 Data-reduction device, such as a computer, equipped with data-acquisition hardware and software and a laser printer, or an electronic integrator with chart recorder, capable of integrating the area of one or more FID response peaks and calculating peak area corrected for baseline drift.

If a separate integrator and chart recorder are used, exercise care to ensure that these components do not interfere with each other electrically or electronically. Range selector controls on both the integrator and the FID analyser may not provide accurate range ratios, so prepare individual calibration curves for each range. The integrator shall be capable of marking the beginning and ending of peaks, constructing the appropriate baseline between the start and end of the integration period, and calculating the peak area.

6.3.3 Cryogenic trap, constructed from a single piece of chromatographic-grade stainless steel tubing of 3 mm outside diameter, 2 mm inside diameter (see Figure 4).

Pack the central portion of the trap (70 mm to 100 mm) with silanized glass beads (diameter 180 μm to 250 μm), using small silanized glass wool plugs to retain the beads. The arms of the trap shall be of such length to permit the beaded portion of the trap to be submerged below the level of cryogen in the Dewar flask. Connect the trap directly to the six-port valve to minimize the line length between the trap and the FID. Mount the trap to allow clearance so the Dewar flask may be applied and withdrawn to facilitate cooling and heating the trap.

6.3.4 Six-port valve.

Locate the six-port valve and as much of the interconnecting tubing as practical inside an oven, or otherwise heat it to 353 K to 363 K, to minimize wall losses or adsorption/desorption in the connecting tubing. All lines shall be as short as practical.

6.3.5 Multistage pressure regulators (three).

Standard two-stage, stainless steel diaphragm regulators with pressure gauges for use with helium, air and hydrogen cylinders.

6.3.6 Auxiliary flowrate or pressure regulators (two), to maintain constant flowrates, within ± 1 ml/min, for the helium carrier and the hydrogen.

6.3.7 Fine needle valves (two).

One valve is used to adjust the sample flowrate through the trap, the other to adjust the sample flowrate from the canister.

6.3.8 Dewar flask, to hold cryogen used to cool the trap, sized to contain the submerged portion of the trap.

6.3.9 Absolute pressure gauge, covering the range 0 kPa to 60 kPa, with scale divisions of 0,25 kPa, to monitor repeatable volumes of sample air through the cryogenic trap.

6.3.10 Vacuum reservoir, of 1 l to 2 l capacity, typically 1 l.

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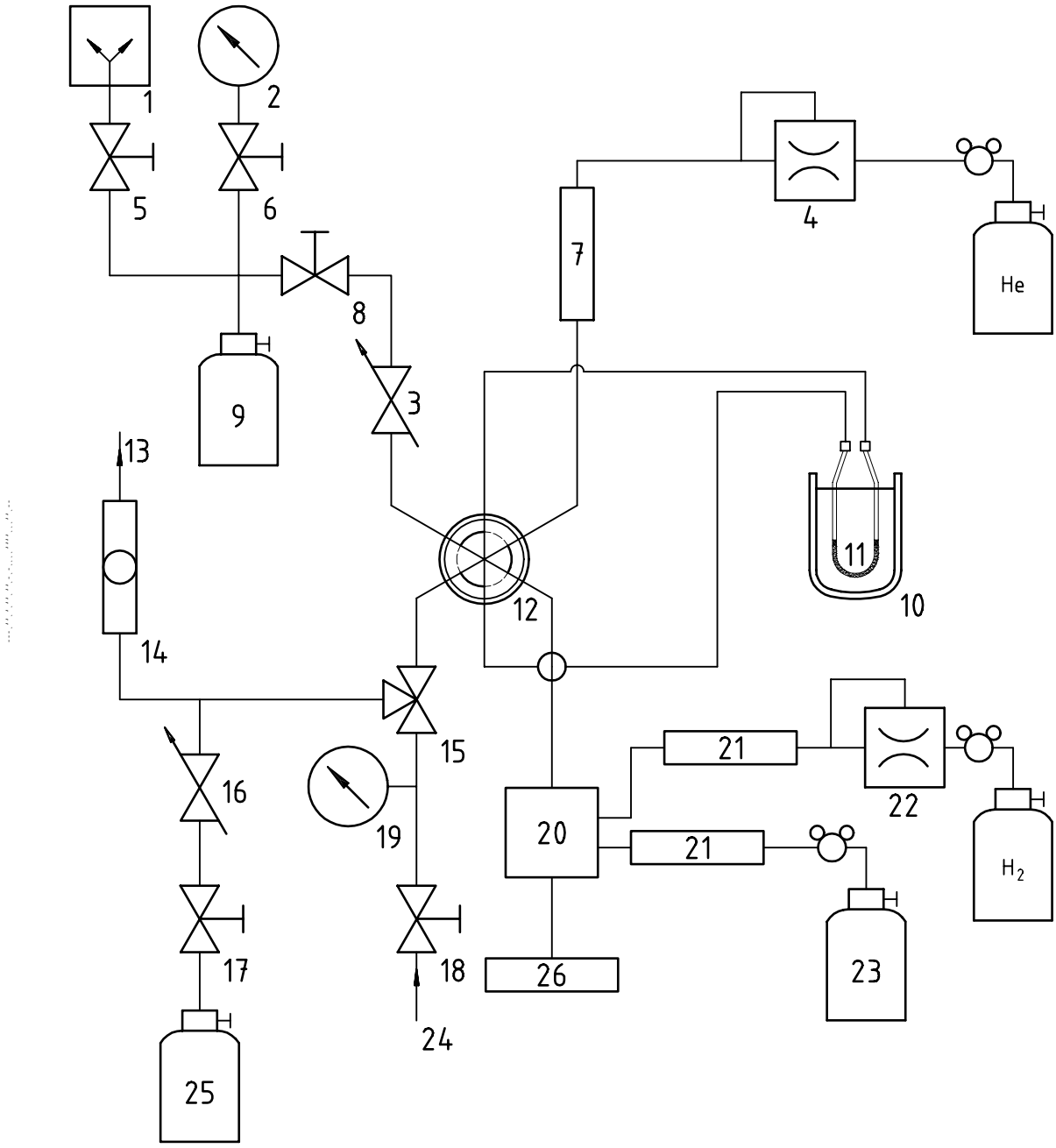

Key

1 Vacuum pump
2 Absolute pressure gauge
3 Fine needle valve (sample flow adjustment)
4 Flow or pressure regulator
5 Vacuum shut-off valve
6 Gauge shut-off valve
7 Gas purifier
8 Sample shut-off valve
9 Vacuum reservoir
10 Dewar flask
11 Cryogenic trap
12 Six-port valve
——— : Trapping position
- - - - - - : Inject position
13 Vent (excess)
14 Rotameter
15 Three-way valve
16 Fine needle valve
17 Canister valve
18 Zero air shut-off valve
19 Pressure gauge
20 FID system
21 Gas purifier
22 Flow or pressure regulator
23 Air
24 Zero-air
25 Pressurized canister sample
26 Data-reduction device

Figure 3 — Analytical system for NMVOC

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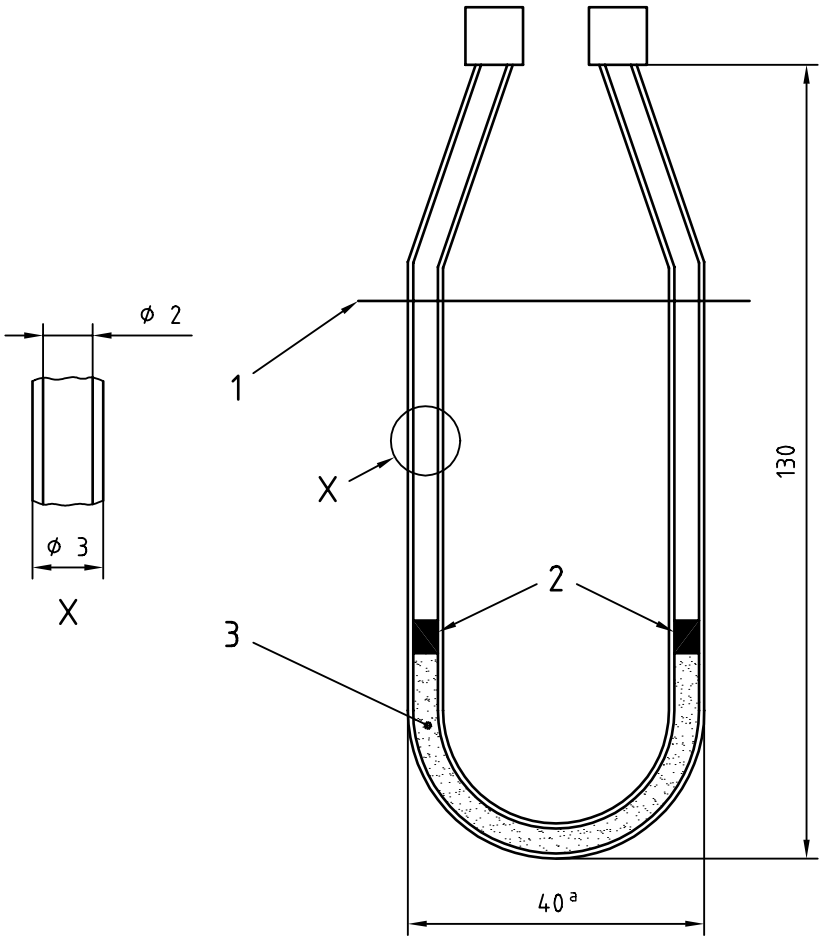
Dimensions in millimetres



Key

1 Liquid argon level
2 Glass wool
3 Glass beads of diameter 180 µm to 250 µm

[a] To fit Dewar.

Figure 4 — Cryogenic sample trap

6.3.11 Gas purifiers (three), containing anhydrous sodium sulfite or silica gel and 5A molecular sieve, to remove moisture and organic impurities from the helium, air and hydrogen gas flows.

Check the purity of the gas purifiers prior to use by passing zero-air through them and analysing the gas according to 10.3. The gas purifiers are clean if the concentration of NMVOC of the emitted gas is below the detection limit of the method.

6.3.12 Trap heating system, comprising a chromatographic oven, hot tap water, or other means to heat the trap to 353 K to 363 K.

A simple means of heating the trap is a beaker or Dewar flask filled with tap water maintained at 353 K to 363 K as required for the duration of the test. Heat sources with better repeatability are recommended, including a temperature-programmed chromatographic oven, electrical heating of the trap itself, or any type of heater that raises the temperature of the trap to 353 K to 363 K in 1 min to 2 min (not shown in Figure 3).

6.3.13 Toggle shut-off valves (four), leak-free, two positioned on each side of the vacuum reservoir, one at the absolute pressure gauge and one at the zero-air cylinder used for the analytical system leak test.

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6.3.14 Vacuum pump, general purpose laboratory oil-less diaphragm pump, capable of evacuating the vacuum reservoir to allow the desired sample volume to be drawn through the trap.

6.3.15 Vent, to keep the trap at atmospheric pressure during trapping.

6.3.16 Rotameter, to verify the vent flow.

6.3.17 Three-way valve.

6.3.18 Chromatographic-grade stainless steel tubing and fittings for interconnections.

All such materials in contact with the sample, analyte or support gases prior to analysis shall be of stainless steel or other inert metal. Do not use plastics or polytetrafluoroethylene tubing or fittings.

6.3.19 Pressure gauge, capable of reading up to 500 kPa.

7 Reagents and materials

7.1 Gas cylinders containing helium and hydrogen, of ultrahigh purity grade.

7.2 Cylinder of combustion air containing less than 0,02 ppm hydrocarbons, or equivalent air source.

7.3 Propane calibration standard.

Cylinder containing 1 ppm to 100 ppm propane (3 ppmC to 300 ppmC) in air, traceable to a national reference standard in accordance with the relevant part of ISO 6145 and ISO 6141. This standard gas may be volumetrically diluted with zero-air (see 7.4) to provide suitable concentration standards in the intended measurement range.

7.4 Zero-air.

Cylinder containing hydrocarbons in no greater concentration than the detection limit of the test method. Obtain zero-air from a cylinder of zero-grade compressed air scrubbed with anhydrous sodium sulfite or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air.

Pass the zero-air used for canister cleaning through the cryogenic cold trap for final cleanup, then through a hydrocarbon-free water bubbler (or other device) for humidification.

7.4 Cryogen (boiling point, 87 K).

Liquid argon is recommended.

If liquid argon cannot maintain the trap temperature at 87 K due to the location of the laboratory at high altitudes (where the normal atmospheric pressure is less than 101,3 kPa), a mechanical refrigeration system may be used (see 12.5). Cryogens with lower boiling points, such as liquid nitrogen, shall not be used because of possible trapping of oxygen from the sample air, which might lead to the possibility of explosion or fire. In addition, methane may be trapped.

8 Canister cleanup and preparation

Leak-test and clean the canisters of contaminants before sample collection.

Leak-test the canisters by pressurizing them to approximately 200 kPa above atmospheric pressure with zero-air using the canister cleaning system (see Figure 2).

Record the final pressure and close the canister valve, then check the pressure after 24 h. If leak-tight, the pressure will not have dropped by more than 15 kPa over the 24-h period at constant temperature.

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Record the leak-check result on the Sampling Data Sheet, (annex A).

Assemble the canister cleaning system, as illustrated in Figure 2.

Close all the valves. Add cryogen to both the vacuum pump and zero-air supply traps. Connect the canister(s) to the manifold.

Open the vent shut-off valve (18) and the canister valve(s) to release any remaining pressure in the canister(s). Now close the vent shut-off valve (18) and open the vacuum shut-off valve (14).

Start the vacuum pump, open the vacuum shut-off valves (13) and (6), and evacuate the canister(s) to $\leqslant$ 2 Pa for 4 h to 5 h, heating them to no more than 375 K in the isothermal oven.

On a daily basis or more often if necessary, blow out the cryogenic traps with zero-air, using valves (1) and (7), to remove trapped water from previous canister cleaning cycles.

Close the vacuum and vacuum-gauge shut-off valves (6) and (14) respectively, and open the zero-air shut-off valves (8) and (15) to pressurize the canister(s) with moist zero-air to approximately 200 kPa over atmospheric pressure. If a zero-gas generator system is used, limit the flowrate to maintain the zero-air quality.

Close the zero-air shut-off valve (15) and allow the canister(s) to vent down to atmospheric pressure through the vent shut-off valve (18). Close the vent shut-off valve (18).

As a ″blank check″ of the canister(s) and cleanup procedure, initially analyse the zero-air content of each canister until the cleanup system and canisters are proven reliable. The number of canisters checked may then be reduced.

Repeat the last three steps one or more times, until the blank is less than the detection limit of the procedure.

Do not use any canister that does not test clean.

Re-evacuate the canisters to $\leqslant$ 2 Pa, using the canister cleaning system. Close the canister valve(s), remove the canister(s) from the canister cleaning system and cap the canister connections with stainless steel fittings.

The canisters are now ready for collection of air samples. Attach identification tags to the neck of each canister for field notes and chain-of-custody purposes. Record the canister pressure as ″initial″ on the Sampling Data Sheet (see annex A).

Leak-test the sample system and the outlet side of the sample pump prior to field use by attaching the vacuum gauge to the canister inlet via connecting tubing with a tee fitting, capping the pump inlet, and evacuating to approximately 15 Pa. If the pressure remains at $\pm$ 0,4 Pa for 15 min, with the pump energized, the pump and connecting lines are leak-tight.

9 Sampling

9.1 General

General sampling strategy shall be in accordance with ISO/TR 4227.

Choose the flowrate control device to provide a constant flowrate such that the canister is pressurized to approximately 200 kPa (one atmosphere above ambient pressure), during the desired sampling period (see 9.2).

Use a second canister when a duplicate sample is desired for quality assurance (QA) purposes (see 11.2).

Exercise care in selecting, cleaning and handling the sample canisters and sampling apparatus to avoid losses or contamination of the samples.

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9.2 Sample collection

Assemble the sampling apparatus as shown in Figure 1, with the connecting lines between the sample pump and the canisters as short as possible to minimize their volume. Purge the sample inlet line at a flowrate of several litres per minute, using the small auxiliary vacuum pump to minimize sample residence time.

Determine the flowrate required to pressurize the canisters to approximately 200 kPa (1 atm above ambient pressure or 2 atm absolute pressure) during the desired sample period, utilizing the following equation:

$$q_V = \frac{p \cdot V \cdot n}{t}$$

where

q_V is the flowrate, in millilitres per minute;

p is the canister final absolute pressure ratio, $(p_a + p_g)/p_a$;

V is the volume of the canister, in millilitres;

n is the number of canisters connected together (for simultaneous sample collection);

t is the sample period, in minutes;

p_g is the pressure in the canister, in kilopascals, above atmospheric pressure; and

p_a is standard atmospheric pressure, 101,3 kPa.

As an example, if one 6 l canister is to be filled to approximately 100 kPa above atmospheric pressure in 3 h, the flowrate is calculated as follows:

$$p = \frac{100 + 101{,}3}{101{,}3} = 1{,}987$$

$$q_V = \frac{1{,}987 \times 6\,000 \times 1}{180} = 66 \text{ ml/min}$$

Adjust the flow-control device to maintain an essentially constant flow at the calculated flowrate into the canister over the desired sample period. This will maintain an approximately constant flowrate up to a canister pressure of about 200 kPa, after which the flowrate drops with increasing pressure. At 101,3 kPa above atmospheric pressure, the flowrate will be about 10 % below the initial flowrate, depending upon pump performance.

Place the particulate matter filter in front of the flow-control device. Check the sampling system for contamination by filling two evacuated, cleaned canisters (see clause 8) with humidified zero-air through the sampling system. Analyse the canisters according to 10.4. The sampling system is free of contamination if the canisters contain carbon in concentrations less than the detection limit of the system.

Observe the flowrate into the sampling system during the system contamination-check procedure to ensure that sample flowrate remains relatively constant (± 10 %) up to about 100 kPa above atmospheric pressure.

NOTE 1 A drop in the flowrate may occur near the end of the sampling period as the canister pressure approaches its final pressure, depending upon pump performance.

Reassemble the sampling system. Verify that the timer, pumps and solenoid valve are connected and operating properly.

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Verify that the timer is correctly set for the desired sample period, and that the solenoid valve is closed. Connect the cleaned, evacuated canister(s) to the non-contaminated sampling system, by way of the solenoid valve, for sample collection.

Verify that the solenoid valve is closed. Open the canister valve(s). Temporarily connect a small rotameter to the sample inlet to verify that there is no flow.

NOTE 2 Detection of flow would indicate a leaking (or open) solenoid valve or an untightened fitting connection.

Remove the rotameter after the leak detection procedure. Record the necessary information on the Sampling Data Sheet (see annex A). Program the automatic timer to activate and stop the pump or pumps and to open and close the solenoid valve at the appropriate time for the selected sample period. Sampling will automatically commence at the programmed time.

At the end of the sample period, record the final canister pressure on the Sampling Data Sheet (see annex A). Then close the canister valve(s) and disconnect the canister(s) from the sampling system. Note that the canister pressure ought to be approximately 100 kPa above atmospheric pressure.

If the canister pressure is not approximately 100 kPa above atmospheric pressure, attempt to determine and correct the cause before obtaining the next sample. Re-cap the canister valve.

Complete the required information on the identification tag on the sample canister(s) and on the Field Data Sheet. Note on the Sampling Data Sheet any atmospheric conditions or special activities in the area (such as rain, smoke, construction, plowing, etc.) that may affect the sample contents.

Return the canister(s) to the laboratory for sample analysis.

10 Sample analysis

10.1 Assembly

Assemble the analytical system (see Figure 3)

10.2 Analytical system leak check

Check the analytical system for leaks during the system checkout, before a series of analysis, or if leaks are suspected. Include this step in the user-prepared Standard Operating Procedure (SOP) manual (see 11.2). Leak-check the analytical system by placing the six-port valve (12) in the trapping position, closing the absolute pressure gauge toggle shut-off valve (6), and placing the three-way valve (15) in the zero-air position. Open the zero-air toggle shut-off valve (18), pressurize the system to about 350 kPa above atmospheric pressure, and close the valve. Read the pressure with the pressure gauge (19).

Recheck the pressure after approximately 3 h. If it has not dropped by more than 15 kPa, the system is considered leak-tight. If the system is leak-free, depressurize the system, close the zero-air toggle shut-off (18), open the absolute pressure gauge toggle shut-off valve (6), and put the three-way valve (15) in the sampling position.

10.3 Sample volume determination

Meter a precisely repeatable volume of sample air through the cryogenically-cooled trap, using the vacuum reservoir (9) and absolute pressure gauge (2), as follows.

Close the sample toggle shut-off valve (8), open the vacuum toggle shut-off valve (5), and evacuate the vacuum reservoir (9) with the vacuum pump to a predetermined initial vacuum (e.g. 15 kPa). Then close the vacuum toggle shut-off valve (5) and open the sample toggle shut-off valve (8) to allow sample air to be drawn through the cryogenic trap (11) and into the evacuated vacuum reservoir (9) until a predetermined reservoir pressure is reached (e.g. 40 kPa).

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Determine the (fixed) volume of air thus sampled by the pressure rise in the vacuum reservoir (difference between the predetermined pressures) as measured by the absolute pressure gauge.

Allow the vacuum reservoir to come to thermal equilibrium before recording the pressure.

Determine the approximate sample volume using the following equation:

$$V_s = \frac{\Delta p \cdot V_r \cdot T_s}{p_s \cdot T_a}$$

where

V_s is the volume of air sampled, in millilitres, at standard conditions of 273 K and 101,3 kPa;

Δp is the pressure difference measured by gauge, in kilopascals;

V_r is the volume of the vacuum reservoir, (typically 1 000 ml);

p_s is standard pressure, 101,3 kPa;

T_a is the ambient temperature, in kelvin; and

T_s is standard temperature, 273 K.

For example, with a vacuum reservoir of 1 000 ml, an ambient temperature of temperature of 298 K, and a pressure change of 25 kPa, the volume sampled is approximately 226 ml at standard conditions.

NOTE Typical sample volume using this procedure is between 200 ml and 300 ml.

The sample volume determination need only be performed once during the system check-out and is a part of the user-prepared SOP Manual (see 11.2)

10.4 Analytical system dynamic calibration

Perform initially a complete dynamic calibration of the analytical system before sample analysis, at five or more concentrations on each range to define the calibration curve. Thereafter periodically perform this procedure at least once during every series of analysis. Include this in the user-prepared SOP Manual (see 11.2). Verify the calibration with two- or three-point calibration checks (including zero) each day the analytical system is used to analyse samples. Use calibration standards of propane to calibrate the analytical system.

Sample the calibration standards directly from a vented manifold or tee.

NOTE 1 Remember that carbon concentration in propane expressed as ppmC is three times the volumetric concentration expressed as ppm.

Select one or more combinations of the following parameters to provide the desired range or ranges:

— FID attenuator setting,

— output voltage setting,

— data-reduction device resolution (if applicable), and

— sample volume.

Calibrate each individual range separately and prepare a separate calibration curve for each range.

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NOTE 2 Modern GC integrators provide automatic ranging such that several decades of concentration may be programmed through a single range. Include variations applicable to the specific system design in the user-prepared SOP manual (see 12.1).

Analyse each calibration standard three times according to the procedure in 10.3. Ensure that flowrates, pressure gauge start and stop readings, initial cryogen level in the Dewar flask, timing, heating, data-reduction device settings, and other variables are the same as those that will be used during analysis of ambient samples. Typical flowrates for the gases are:

— hydrogen, 30 ml/min,

— helium carrier, 30 ml/min, and

— combustion air, 400 ml/min.

Average the three analyses for each concentration standard and plot the calibration curves as average integrated peak area reading versus concentration expressed as ppmC. The relative standard deviation for the three analyses should be less than 3 % (except for zero concentration).

If the curve is not linear, repeat points that appear to deviate abnormally. Response has been shown to be linear over a wide range (0 ppmC to 10 000 ppmC). If nonlinearity is still observed, attempt to identify and correct the problem.

If the problem cannot be resolved, determine additional points in the nonlinear region to define the calibration curve adequately.

10.5 Analysis procedure (see Figure 3)

Ensure that the analytical system has been assembled properly, leak-checked, and properly calibrated through a dynamic standard calibration. Activate the FID (20) and allow it to stabilize. Check and adjust (4) the helium carrier pressure to provide the correct carrier flowrate for the system. Helium is used to purge residual air and methane from the trap at the end of the sampling phase and to carry the revolatilized NMVOC from the trap into the FID. A flowrate or pressure regulator between the cylinder and the FID is recommended to regulate the helium pressure or flowrate better than the multistage cylinder regulator. When an auxiliary pressure regulator is used, the secondary stage of the two-stage regulator shall be set at a pressure higher than the pressure setting of the single-stage regulator. Also check the FID hydrogen and combustion air flowrates (see 10.4).

Close the sample toggle shut-off valve (8), and open the vacuum toggle shut-off valve (5) to evacuate the vacuum reservoir (9) to a specific predetermined value, e.g. 15 kPa. With the trap at room temperature, place the six-port valve (12) in the inject position. Open the sample toggle shut-off valve (8) and adjust the sample flowrate fine needle valve (3) for an appropriate trap flowrate of 50 ml/min to 100 ml/min.

NOTE 1 The flowrate will be lower later, when the trap is cold.

Check the sample canister pressure before attaching it to the analytical system and record it on Sampling Data Sheet (see annex A). Connect the sample canister to the six-port valve, as shown in Figure 3. Either the canister valve or the fine needle valve installed between the canister and the vent is used to adjust the canister flowrate to a value slightly higher than the trap flowrate set by the sample flowrate needle valve. The excess exhausts through the vent, which assures that the sample air that flows through the trap is at atmospheric pressure. Connect the vent to a flowrate indicator such as a rotameter as an indication of vent flow to assist in adjusting the flowrate control fine needle valve.

Open the canister valve (17) and adjust the canister (16) or the sample flowrate fine needle valve to obtain a moderate vent flowrate as indicated by the rotameter (14). Close the sample toggle shut-off valve (8) and open the vacuum toggle shut-off valve (5) (if not already open) to evacuate the vacuum reservoir. With the six-port valve (12) in the inject position and the vacuum toggle shut-off valve (5) open, open the sample toggle shut-off valve (8) for 2 min to 3 min, to flush and condition the inlet lines. Close the sample toggle shut-off valve (8) and evacuate the vacuum reservoir to the predetermined sample starting pressure (typically 15 kPa) as indicated by the absolute pressure gauge (2).

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Switch the six-port valve (12) to the trapping position. Submerge the trap (11) in the cryogen. Allow a few minutes for the trap to cool completely (indicated when the cryogen stops boiling).

Add cryogen as necessary to maintain the initial level used during system dynamic calibration. Maintain the liquid level of the cryogen constant with respect to the trap. Ensure that the glass-beaded portion of the trap is immersed in the cryogen, but not the fitting that connects the trap to the valve.

Open the sample toggle shut-off valve (8) and observe the increasing pressure on the absolute pressure gauge (2). When it reaches the specific predetermined pressure (typically 40 kPa) representative of the desired sample volume, close the sample toggle shut-off valve (8). Add a little cryogen or elevate the Dewar flask (10) to raise the liquid level to a point 3 mm to 15 mm higher than the initial level at the beginning of the trapping.

NOTE 2 This ensures that organic compounds do not bleed from the trap and are counted as part of the NMVOC peaks.

Switch the six-port valve (12) to the inject position, keeping the Dewar flask on the cryogenic trap until the methane and upset peaks have diminished (10 s to 20 s). Now close the canister valve (17) to conserve the remaining sample in the canister. Energize the data-reduction device (26) and remove the Dewar flask (10) from the trap (11).

Close the GC oven door and allow the GC oven (or alternative trap-heating system) to heat the trap at a predetermined rate (typically 30 K/min) to 365 K. Rapidly heating the trap volatilizes the concentrated NMVOC as a uniform plug that enters the FID. A uniform rate of trap temperature rise helps to reduce variability and facilitates more accurate correction for the moisture-shifted baseline. When using a chromatographic oven to heat the trap, the following parameters have been found to be acceptable:

— initial temperature: 300 K;

— initial start time: 0,20 min (following the start of the data-reduction device);

— rate of temperature rise: 30 K/min;

— final temperature: 365 K.

Use the same heating process and temperatures for both calibration and sample analysis. Heating the trap too quickly may cause an intital negative response that could hamper accurate integration. Heating it too slowly broadens the peak, making integration of the peak are less repeatable. Some initial experimentation may be necessary to determine the optimal heating procedure for each system.

Once established, include the procedure established for each analysis in the user-prepared SOP Manual (see 11.2).

Continue the integration (generally, in the range of 1 min to 2 min is adequate) only long enough to include all of the organic compound peaks and to establish the endpoint FID baseline, as illustrated in Figure 5. The data-reduction device should be capable of marking the beginning and ending of peaks, constructing the appropriate operational baseline between the start and end of the integration period, and calculating the resulting corrected peak area. This ability is necessary because the moisture in the sample, which is also concentrated in the trap, will cause a slight positive baseline shift. This baseline shift starts as the trap warms and continues until all of the moisture is swept from the trap, at which time the baseline returns to its normal level. The shift always continues longer than the ambient organic peak(s).

Program the data-reduction device to correct for this shifted baseline by ending the integration at a point after the last NMVOC peak and prior to the return of the shifted baseline to normal (see Figure 5) so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic data-reduction devices either do this automatically or may be programmed to make this correction.

Alternatively, perform analysis of humidified zero-air prior to sample analysis to determine the water envelope and the proper blank value for correcting the ambient air NMVOC concentration measurements accordingly. Continue heating and flushing the trap after the integration period has ended to ensure that all the water has been removed, to prevent buildup of water in the trap. Therefore, be sure that the six-port valve remains in the inject position until all moisture has purged from the trap (3 min or longer).

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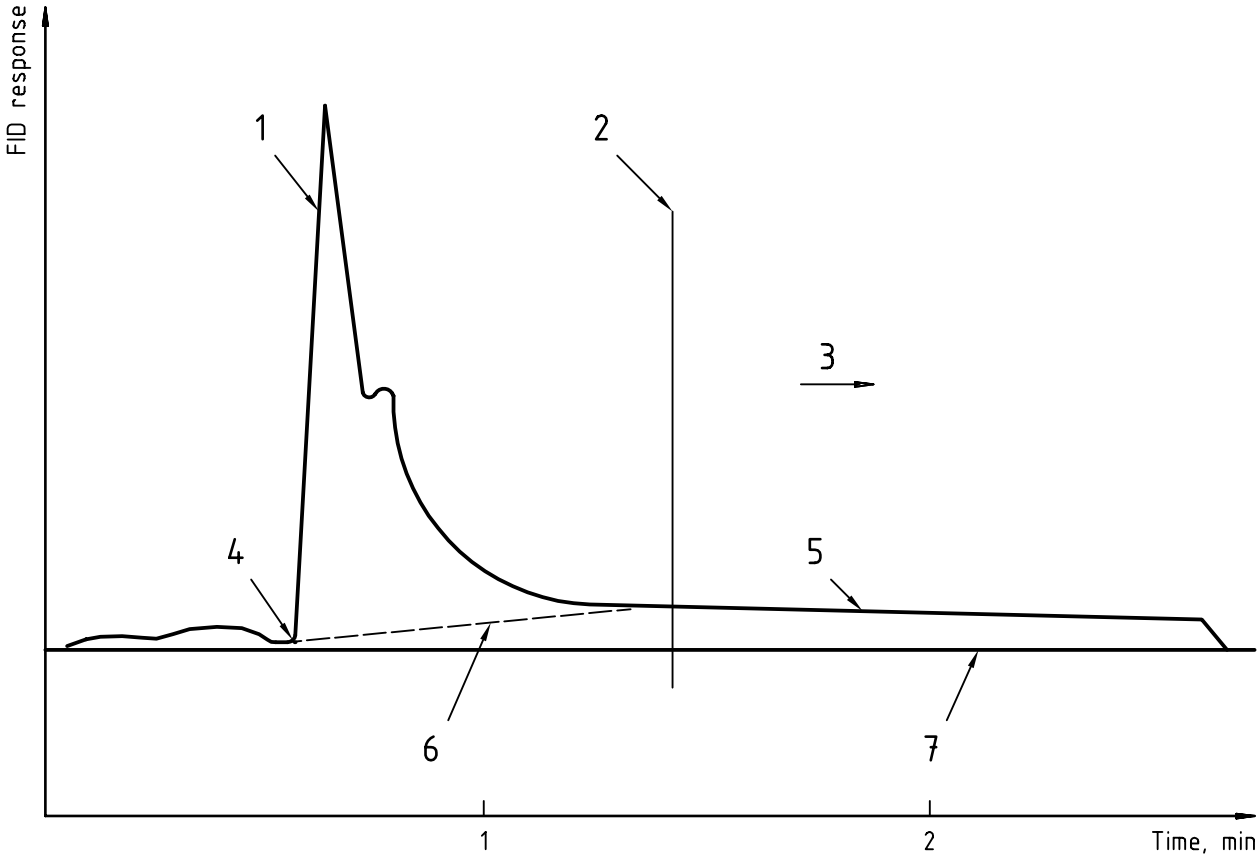

Key

1 NMOC peak
2 End integration
3 Continued heating of trap
4 Start integration
5 Moisture-shifted baseline
6 Operational baseline constructed by integrator to corrected area
7 Normal baseline

Figure 5 — Construction of operational baseline and corresponding correction of peak area

Use the dynamic calibration curve (see 10.4) to convert the integrated peak-area reading into concentration units (ppmC). Analyse each canister sample as least twice and report the average NMVOC concentration. The NMVOC peak shape may not be precisely reproducible due to variations in heating the trap, but the total NMVOC peak area should be reproducible. Problems during an analysis occasionally will cause erratic or inconsistent results.

If the first two analyses do not agree within ± 10 %, perform additional analyses to identify the source of the problem and produce a more precise measurement (see also 10.3).

11 Performance criteria and Quality Assurance

11.1 General

This clause summarizes the required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

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11.2 Standard operating procedure (SOP)

Describe and document in the SOPs the following activities:

a) assembly, calibration, leak-check and operation of the specific sampling system and equipment used;

b) preparation, storage, shipment and handling of samples;

c) assembly, leak-check, calibration and operation of the analytical system, addressing the specific equipment used;

d) canister storage and cleaning; and

e) all aspects of data recording and processing, including lists of computer hardware and software used.

Include in the SOPs specific stepwise instructions. Verify by audits that the SOPs are readily available to, and understood by, the laboratory personnel conducting the work.

11.3 Method sensitivity, accuracy and precision

The sensitivity and precision of the method described in this International Standard is proportional to the sample volume. However, ice formation in the trap may reduce or stop the sample flow during trapping if the sample volume exceeds 500 ml. Sample volumes below about 100 ml to 150 ml may cause increased measurement variability due to dead volume in lines and valves. For most typical ambient NMVOC concentrations, sample volumes in the range of 200 ml to 300 ml appear to be appropriate. If a response peak obtained with a 300 ml sample is off-scale or exceeds the calibration range, perform a second analysis with a smaller volume. The actual sample volume analysed need not be accurately known if exactly the same volume is used for both the calibration and sample analyses. Similarly, the actual volume of the vacuum reservoir need not be accurately known. Match the reservoir volume to the pressure range and resolution of the absolute gauge, so that the measurement of pressure change, and hence the sample volume, is repeatable within 1 %. A 1 000 ml vacuum reservoir and a pressure change of 30 kPa, measured with the specified pressure gauge, have provided a sampling precision of $\pm$ 1,31 ml. Use a smaller volume vacuum reservoir with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

Some FID systems associated with laboratory chromatographs may have autoranging capabilities. Others may provide attenuator control and internal full-scale output voltage selectors. Choose an appropriate combination so that an adequate output level for accurate integration is obtained down to the detection limit; however, the data-reduction device shall not be driven into saturation at the upper end of the calibration. Saturation of the electrometer may be indicated by flattening of the calibration curve at high concentrations. Additional adjustments of range and sensitivity may be provided by adjusting the sample volume used, as discussed in 12.4.

NOTE Some organic compounds contained in ambient air may be difficult to recover because of retention in the canister or trap and may require repeated analyses before they fully appear in the FID output. Also, some adjustment may be required in the data-reduction device off-time setting to accommodate compounds that reach the FID late in the analysis cycle. Similarly, such compounds from ambient samples or from contaminated propane standards may temporarily contaminate the analytical system and may affect subsequent analyses. Such temporary contamination can usually be removed by repeated analyses of humidified zero-air.

Simultaneous collection of duplicate samples decreases the possibility of lost measurement data from samples lost due to leakage or contamination in any of the canisters. Two (or more) canisters may be filled simultaneously by connecting them in parallel (see Figure 1) and selecting an appropriate flowrate to accommodate the number of canisters. Duplicate (or replicate) samples also allow assessment of measurement precision based on the differences between the measured concentrations of duplicate samples (or the standard deviations among replicate samples).

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12 Method modification

12.1 Sample metering system

Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques can prove effective. A constant sample flowrate may be established with a mass flow meter, or a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period. A gas volume meter, such as a wet test meter, may also be used to measure the total volume of sample air drawn through the trap. Test and evaluate these alternative techniques as part of a user-prepared SOP manual (see 11.2).

12.2 Canister cleaning

The canisters may be cleaned without heating to 375 K if the evacuation/pressurization cycles are repeated a minimum of four times.

12.3 FID system

A variety of FID systems are adaptable to the method. Evaluate the specific flowrates and necessary modifications for the helium carrier for any alternative FID instrument prior to use, as part of the user-prepared SOP manual (see 11.2).

12.4 Range

It may be possible to improve the sensitivity of the method described in this International Standard by increasing the sample volume. However, limitations may arise, such as plugging of the trap by ice. Evaluate attempts to increase sensitivity as part of the user-prepared SOP manual (see 11.2).

12.5 Alternative cryogenic trapping and heating systems

Other automatic cryogenic trapping systems that are coupled with alternative heating methods may be used in place of the immersion trap, Dewar flask and oven.

12.6 Sub-atmospheric pressure canister sampling

Collection and analysis of canister air samples collected at sub-atmospheric pressure is also possible with minor modifications to the sampling and analytical procedures. The Bibliography describes sub-atmospheric pressure canister sampling. Document any procedure developed in the user-prepared SOP manual (see 11.2).

12.7 Alternative sampling system

An alternative sampling system, described in the Bibliography, may be used in place of that shown in Figure 1. It utilizes a stainless steel pump with an inert plastics diaphragm, a proportional pressure-relief valve (set to ~ 200 kPa), a mass flow meter and a magnetic latch valve. In this configuration, the pump is purged with a large sample flow, eliminating the need to flush the sample inlet. The mass flow meter will maintain constant flowrate up to a canister pressure up to 150 kPa.

It may be possible to use other canisters with inert interiors. Evaluate their characteristics prior to use.

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13 Precision and accuracy

13.1 Precision

Precision for this International Standard was established by acquiring duplicate samples and analysing each sample twice. A total of 37 duplicate samples was taken for United States Environmental Protection Agency's (USEPA) NMVOC Program in 1990. The values ranged from 0,16 ppmC to 2,41 ppmC.

The average precision measured was 0,70 ppmC with an average absolute relative percent difference of 12,7.

13.2 Accuracy

Accuracy for this International Standard was established by analysing four audit cylinders acquired from the USEPA Quality Assurance Branch. The cylinders were prepared by diluting a reference cylinder of propane, which was traceable to the U.S. National Institute of Standards and Technology. Each audit cylinder was sampled and analysed four times.

The average bias determined was 0,04 ppmC, with an average absolute percent bias of 3,74.

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Annex A
(informative)

Example of pressurized canister Sampling Data Sheet

GENERAL INFORMATION

Project: ..... Operator: .....

Site: ..... Orifice No.: .....

Location: ..... Flowrate: .....

Monitor station No.: ..... Calibrated by: .....

Pump serial No.: ..... Leak check ❑ **PASS** ❑ **FAIL**

Table A.1 — Field data

Date	Canister No.	Sample No.	Sampling time		Average atmospheric conditions			Canister pressure			Comments
			Start	Stop	Temperature	Pressure	RH	Initial	Final	Laboratory	
					K	kPa	%	kPa	kPa	kPa	

Date..... Signature..... Title .....

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