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REVIEW

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Determination of complex mixtures of volatile organic compounds in ambient air: canister methodology

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Abstract Canister methodology is applicable to 150 polar and nonpolar VOCs found in ambient air from parts-per-billion by volume (ppbv) to parts-per-million (ppmv) levels, and has been validated at parts-per-trillion (pptv) levels for a subset of these analytes. This article is a detailed review of techniques related to the collection of volatile organic compounds (VOCs) in evacuated Summa and fused-silica-lined canisters, and their analysis by gas chromatography/mass spectrometry (GC/MS). Emphasis is placed on canister cleaning, VOC stability in canisters, sample dilution, water management, and VOC cryogenic and sorbent preconcentration methods. A wide range of VOC preconcentration and water management methods are identified from the literature, and their relative merits and disadvantages are discussed. Examples of difficulties that commonly arise when processing canister samples are illustrated, and solutions to these problems are provided.

Keywords Air analysis · TO-14, TO-14A, TO-15 · Volatile organic compound · VOC · Environmental monitoring · Industrial hygiene · Canister · Summa · Fused-silica-lined · Sorbent · Water management · GC/MS

Introduction

Volatile organic compounds (VOCs) are an important class of substances having environmental and toxicological effects. The most common methods used to measure their concentration in air are adsorbents and evacuated canister sampling. Although environmental monitoring and industrial hygiene methods target many of the same chemicals in air, the sampling and analytical techniques have developed largely independently. Overlap between the two fields has increased in recent years. Environmental scientists have increasingly been concerned with personal exposure measurements, and industrial hygienists have moved toward improved techniques applicable to a wider range of VOCs and having greater sensitivity and reliability. Practitioners from both fields have taken an increased interest in indoor air quality (IAQ) issues [1, 2]. Sorbent enrichment of VOCs from ambient air has been extensively reviewed in the scientific literature [3–13], but canister methodology has not. The latter method has been in use for 25 years, particularly in the field of environmental monitoring, and it continues to evolve. Evacuated canisters are increasingly used for personal monitoring of individuals exposed to VOCs in the workplace. The development of VOC sampling and gas chromatographic (GC) analysis was reviewed in a companion article to this one [14]. The present article is a review of evacuated canister methods that have been used and reported in the scientific literature.

During the 1980s the U.S. Environmental Protection Agency (EPA) adopted an evacuated canister method (TO-14 and TO-14A) targeting 40 nonpolar VOCs [15, 16]. It overcame many of the drawbacks of sorbent methods and was well suited to the monitoring of very low levels of a wide range of compounds. The method was further refined in 1999 and published as the TO-15 method, targeting a total of 97 VOCs, including polar compounds [17, 18]. The most important differences between the TO-14A and TO-15 methods were: (1) the TO-14A method required the use of a Nafion dryer to remove moisture from the air sample whereas the TO-15 method was performance-based and permitted any method that achieved the performance criteria: and, (2) the TO-14A method permitted the use of a flame ionization detector (FID), while the TO-15 method mandated the use of mass spectral detection only. The Canadian National Air Pollution Surveillance Program (NAPS) began using canisters in1987 to monitor outdoor ambient levels of 85 C_2–C_{12} nonpolar VOCs in urban and

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rural areas [19, 20]. That target list has since expanded to include 150 VOCs found to be stable in Summa canisters.

Air samples containing VOCs are not stable in untreated stainless steel canisters. Canisters used for air sampling are manufactured using Grade 304 or Grade 316 stainless steel, the latter having a higher chromium content. The canisters are then passivated by one of two processes. Summa passivation, originally developed by R.A. Rasmussen in the 1970s, is a process that coats the stainless steel surface of the canister with a pure chrome-nickel oxide layer to reduce its reactivity and the number of adsorption sites [21]. A more recent method involves chemically bonding a thin fused-silica layer to the stainless steel surface. As will be discussed below, each type of canister has its advantages and disadvantages.

Air samples collected into evacuated canisters are analyzed in the laboratory by GC/MS. Pressurized sampling can be used to increase the volume of air collected into a canister, but it does not concentrate the sample collected. An air sample taken from an urban environment typically contains 100–150 detectable VOCs in the C_2 through C_{12} carbon range, and the typical concentration range of these compounds is 0.1–50 ppbv (parts per billion by volume) [22, 23]. VOC preconcentration is, therefore, a necessary intermediate step that must be performed prior to analysis. Either sorbent or cryogenic trapping can be used to do this. The biggest challenge facing the analyst, however, is removal of water from the sample prior to injection on a GC column.

New canisters

Summa canisters are currently manufactured by BRC/Rasmussen (Portland, Oregon), Meriter (San Jose, CA), Restek Corporation (Bellefonte, PA), and Scientific Instrument Specialists (Moscow, ID). Fused-silica-lined (FSL) canisters are currently manufactured by Entech Instruments (Silonite canisters; Simi Valley, CA), and Restek Corporation (SilcoCan, SilcoSteel). There can be considerable variability between manufacturers in the quality of the passivation process, the cleanliness of the canisters that are shipped out, the quality and cleanliness of the valves that are used, and the quality of the welded seam. Poor quality welding can be one of the causes of memory effects in cleaned Summa canisters that were previously used to collect highly contaminated samples.

Canisters are assumed to be leak free if, after pressurizing to 200 kPa [30 psig (pounds per square inch gauge)], the pressure does not drop more than 15 kPa (2 psig) in 24 h. They are generally considered to be clean when the residual VOC content is <0.2 ppbv for each target compound when analyzing a total air volume of 500 mL [16, 18]. This criterion has more to do with the capability of the Agilent 5970MS used by the EPA during development of the TO-14A and TO-15 methods than with the limits of canister background contamination and cleaning effectiveness. The acceptability criteria for clean canisters should be approximately an order of magnitude lower (i.e., <0.02 ppbv) when using the more sensitive GC/MS instruments available today.

Canister cleaning

The canister cleaning process can be performed manually, or an automated system can be built in-house (Fig. 1) or purchased commercially from RM Environmental Systems or Entech Instruments. Canisters are cleaned, together with the valve, by three 1-h cycles of pressurization to 200 kPa (30 psig) with humid zero air at 100 °C and evacuation to −102 kPa (−30 in. Hg). A liquid-nitrogen-cooled trap

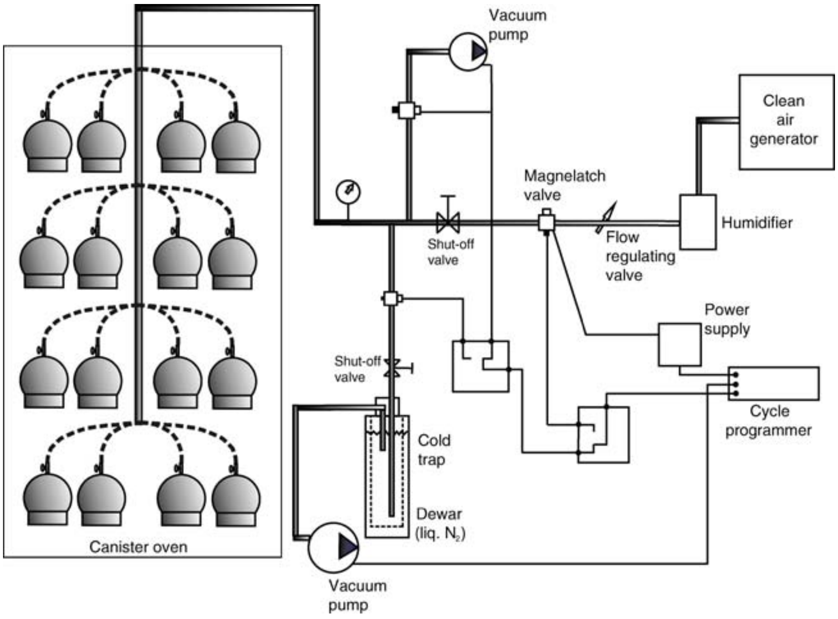


Fig. 1 Home-built automated canister cleaning system (Environment Canada)

must be placed inline between the canister and the oil vacuum pump to prevent oil vapours from contaminating the canisters and to prevent excessive air from entering the pump and causing a fire. The trap should be cleaned daily. Humidity enhances the passivation of the internal surface of Summa canisters, apparently by occupying active adsorptive sites [24].

More aggressive cleaning procedures are necessary in many cases. Summa canisters that are not effectively cleaned by the usual means must be steam-cleaned by adding 50 mL of water, pressurizing the canister to 70 kPa (10 psig) and baking it at 150–175 °C for 24 h [25]. The valve can remain on the canister provided that the valve itself is not subjected to temperatures higher than ~100 °C. FSL canisters should not be steam-cleaned since the process may compromise adhesion to the fused-silica lining. Canisters in which aldehydes and ketones had been stored for 16 days, and which remained contaminated after the usual cleaning procedures, were successfully cleaned by adding 5 mL of neat pentane to the canister before subjecting it to three cleaning cycles [26]. New canisters contaminated with C_6 hydrocarbons and chlorinated solvents have been successfully cleaned by adding methanol, acetone and water prior to heating and evacuation [92]. Following cleaning, canisters are filled with purified, humid air or humid zero-grade nitrogen, allowed to equilibrate for at least 24 h, and analyzed for contamination. They are then evacuated and stored at −102 kPa (−30 in. Hg) until ready to be used for either passive or active sampling.

Canister sampling

In the case of grab sampling, the valve of the evacuated canister is simply opened and allowed to fill to atmospheric pressure in less than 30 sec. There are a number of devices available that allow for passive, time-integrated sampling. A mechanical flow controller using a large pressure-regulating diaphragm and a sapphire orifice restrictor, available from Entech Instruments, has been successfully used to sample ambient air into Silonite canisters over a period of 1 week [27]. A good alternative to this is the Veriflo series of fixed and adjustable mechanical flow controllers (0.5–1,000 mL/min.; constant upstream pressure) available from Parker Hannifin (Richmond, CA). A capillary flow device (0.05–1 mL/min) has also been developed to collect samples over a period of 40 h [28–32]. In all cases, a stainless steel or glass micro filter should be fitted upstream of the canister prior to sampling to prevent the entry of particulates. Canisters that are filled to atmospheric or sub-atmospheric pressures should be pressurized with humid zero air in the laboratory as soon as possible after sampling to improve sample stability.

Pressurized sampling is used when it is necessary to collect a volume of air greater than the volume of the canister itself, or when it is desired to acquire a time-integrated sample over a longer period of time than can be achieved with a mechanical flow controller, or both. Flow diagrams can be found in the TO-15 method [18]. The canister is pressurized to a maximum of 200 kPa (30 psig) using a stainless steel pump and mass flow controller (300–400 mL/min) [33]. In one such system, an evacuated canister is fitted with a 2 μm Nupro stainless steel filter and filled with air through a stainless steel tube connected to a Xontech canister sampling system (Xontech, USA, Model 910A) [34]. A stainless steel diaphragm pump draws the air from a glass manifold attached to a blower motor assembly. The air stream to the canister is split by a mass flow controller (10 mL/min), the bulk of the air being vented to the outside to minimize contamination of the sampler. A built-in digital timer can be programmed to collect time-integrated samples at designated times. The XonTech VOC canister sampling system has been sold to RM Environmental Systems (Camarillo, CA) and is currently available from them. When sampling very humid air, condensation of water can block the air flow both in mechanical flow controllers and in mass flow controllers. In the case of passive sampling, this problem can be avoided by simply arranging the sampler inlet downward such that the air flows up and any condensation drips away. In the case of pressurized sampling, the entire mechanism downstream from the pump, including the valve and mass flow controller, can be heated to 40 °C. Water vapour remaining in the collected air sample will need to be removed in the laboratory prior to GC/MS analysis (discussed below under Water Management).

Sample stability and interferences

Summa and FSL canisters

Stability of VOCs in canisters depends on a number of variables, including the type of canister (Summa or fused-silica lining), canister quality, prior cleaning effectiveness, matrix effects (reactivity), and storage conditions (temperature, pressure, humidity). Consequently, sample stability and recovery of target VOCs should be experimentally determined for any particular application (e.g., ambient air, indoor air, landfill gas, smoke, breath, etc.).

It is thought that decreases in VOC levels during storage are due to their adsorption onto active sites on the walls of Summa canisters. Losses can be severe if canisters are not cleaned with humid air, particularly in the case of C_5 hydrocarbons and higher. Humidity has been shown to increase the stability of VOCs in Summa canisters, presumably by competitive inhibition [21, 35–41], although some polar compounds appear to be less sensitive than nonpolar compounds to drier canisters [42]. The water molecules occupy active sites that may still remain after the electropolishing process or that arise in older canisters. This peculiarity of Summa canisters is an obvious advantage in environmental and occupational sampling where the humidity in the air might interfere with some other sampling methods. When collecting dry air, stability of the sample can be improved by adding approximately 10 μL water per litre of air to the evacuated canister prior to sampling to obtain a relative humidity of approximately 50–70% in the final sample. The addition of too much water, however, could lead to losses of target analytes—particularly polar compounds.

In general, polar and nonpolar C_2–C_{10} VOCs store well in both Summa and FSL canisters at ppbv levels [24, 35, 41–50]. Compounds tested include alcohols, alkanes, alkenes, aromatics, ethers, halocarbons, ketones, and terpenes, and samples containing the reactive species NO, NO_2, and HCl. The exceptions are benzyl chloride and most of the bromomethanes. Also, thiols store well in FSL canisters whereas they are highly unstable in Summa canisters. Good recoveries of VOCs (including acrylonitrile, alkanes, benzene and its derivatives, 1,3-butadiene, Freons, halocarbons, isoprene, styrene, toluene, and xylenes) from both Summa and FSL canisters have also been achieved at parts-per-trillion levels, although there are indications that it may be necessary to conduct the analysis within 14 days of sample collection [27, 51–53]. FSL canisters are a relatively new development and as such have not yet been subjected to the accumulated experience and test of time that Summa canisters have undergone. The principal advantage of FSL canisters appears to be the stability of sulphur compounds, which undergo severe losses in Summa canisters. However, thiols may be adsorbed onto active sites created by residual silanols in FSL canisters, and it is recommended that they be chemically deactivated with a silanizing reagent prior to sampling [54, 55]. Losses due to low humidity levels may also be less of a factor in FSL canisters than in Summa canisters.

The experience of some laboratories with respect to the stability of VOCs in Summa canisters has been mixed, particularly with respect to alcohols, aldehydes, oxygenated hydrocarbons, and terpenes [55–57]. This is a difficult issue because, in addition to sample stability, there are many other factors in the sample conditioning and analytical systems that can potentially affect the results. Unfortunately, none of the stability studies control for these other factors. When there is agreement between laboratories that a particular compound has been observed to be stable or unstable, this is less of an issue. However, contradictory observations leave open the possibility that apparent losses may be due to some other factor, such as, for example, the quality of the canisters, the cleaning process, humidity levels, condensation, or the drying and preconcentration techniques used.

Other issues

Condensation

Water present in samples collected at relatively high humidity and temperature levels (e.g., stacks, engine exhaust, and human breath) may condense in canisters at normal laboratory temperatures. For example, the amount of condensed water from human breath at body temperature (37 °C) collected into a 6-L canister at 24 °C is calculated to be 0.12 mL [58]. Pressurization of canister samples may also cause water condensation when the relative humidity is higher than 70% [59, 60]. There is a theory that increases in VOC levels during storage may be due to volatilization from condensed water. However, in one study, the addition of 0.2 mL of water to canisters did not affect recoveries of VOC test mixtures (containing halogenated hydrocarbons, aromatic hydrocarbons, 1,3-butadiene, oxygenated hydrocarbons, volatile sulphur compounds) except for alcohol in both Summa and FSL canisters and all thiols in Summa canisters [58]. The loss of thiols in the Summa canisters was undoubtedly due to wall losses, not to the presence of water in the canister.

Interference from ozone and nitrogen oxides

The reaction of VOCs having a vinyl group (e.g., 1,3-butadiene, chloroethene, styrene) with ozone (O_3) and nitrogen oxides such as NO_2 is problematic when using sampling methods that rely on cryogenic, sorbent or derivatization techniques. Analytical biases from ozone interferences and ozone-removal techniques have been reviewed previously [61]. Chemical reactants that have been used for removal of O_3 in the analysis of atmospheric VOCs include aluminum oxide, copper oxide, cotton, ferrous sulphate, indigo-carmine, magnesium sulphate, manganese dioxide, nitrogen oxide, palladium/platinum, phenoxazine, polyethylene, potassium carbonate, potassium hydroxide, potassium iodide, rubber, sodium carbonate, sodium hydroxide, sodium sulphite, sodium thiosulphate, N,N,N′,N′-tetramethyl-1,4-phenylenediamine dihydrochloride, and triethanolamine. The most frequently used agents are sodium carbonate, sodium sulphite, sodium thiosulphate, and potassium iodide [61]. These techniques are seldom necessary when sampling with Summa canisters since metal surfaces (gold, iron, mercury, nickel, platinum, and silver) favor the catalytic destruction of ozone.

Carbon dioxide interference

High levels of carbon dioxide (CO_2) in a canister sample can cause two problems further down the line: (1) too much carbon dioxide can block cryogen traps used to concentrate the VOCs prior to transfer to the GC and (2) a large, broad peak can saturate the MS thereby suppressing the response of early eluting compounds (Fig. 2). However, samples high in CO_2 may not cause any problems at all if the concentration of target compounds is high enough that small sample aliquots, of the order of 1–10 mL, are withdrawn from the canister for analysis. If necessary CO_2 can be selectively removed from the air stream by passing it through a lithium hydroxide (LiOH) trap located upstream from the water management system. High CO_2 levels are never a problem in the EnTech system, discussed below, because it traps the VOCs in a Tenax trap at −60 °C, allowing the CO_2 to be vented to the outside before the sample is transferred to a cryofocus trap.

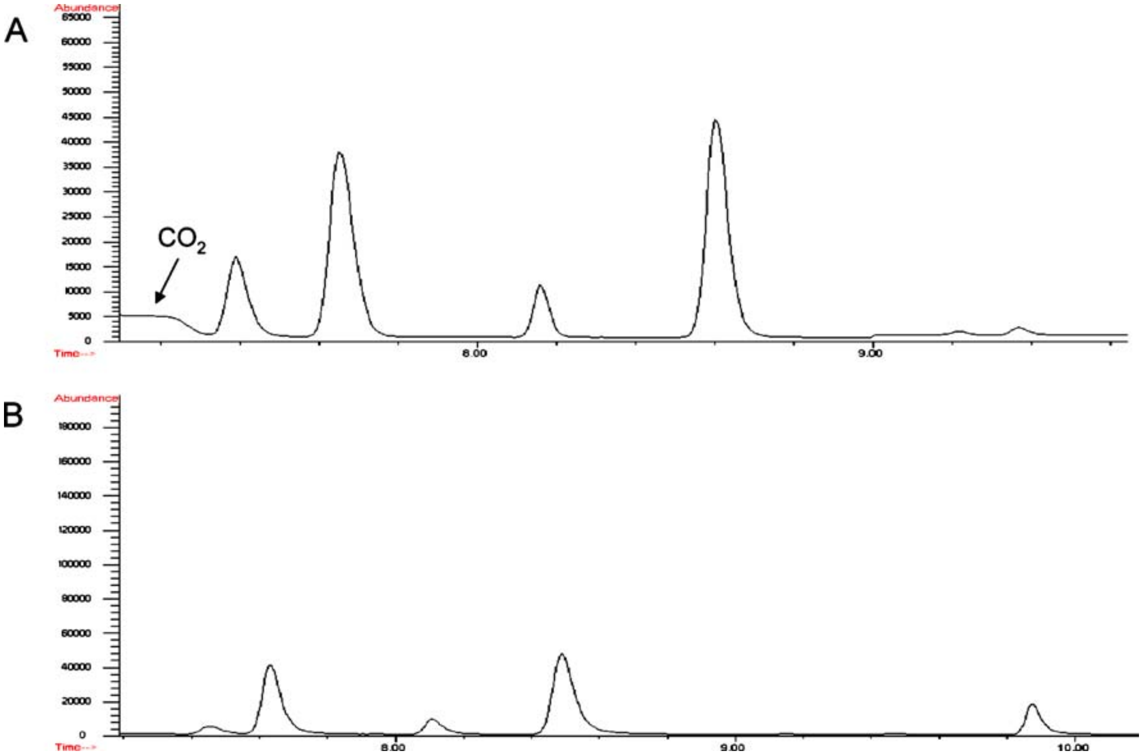


Fig. 2 Carbon dioxide interference is seen when analyzing an ambient air sample using a NuTech preconcentrator and an Agilent 6890GC/5973MSD (**a**). There is no CO_2 interference seen when a similar sample is analyzed using an EnTech preconcentrator and an Agilent 6890GC/5973MSD (**b**)

Sample preparation

Preparation and conditioning of aliquots of air withdrawn from canisters for analysis by GC is a complex task. The sample may be too dilute, too concentrated, too complex, or too humid, or may contain interfering substances. In addition to the usual factors that must be taken into consideration during air sampling, particular attention must be paid to the possibility that both losses and gains may occur as a result of adsorption and desorption of vapours onto particles trapped by pre-filters and as a result of wall effects in sampling and analytical apparatus. All surfaces coming into contact with the sampled air must be made of "inert" materials. Thus, transfer lines must be made of grade 316 stainless steel, or preferably pure nickel, and cleaned regularly to prevent carry-over from one sample to the next. Ideally, fused-silica-lined stainless steel tubing should be used for all sample transfer lines to eliminate adsorption/desorption problems [41]. Copper lines cannot be used due to their reactivity with VOCs.

Sample dilution

Canister samples of ambient air are normally processed by transferring 250–1,000 mL aliquots (50–100 mL/min) to the preconcentrator for subsequent analysis by GC/MS. In cases where this would result in transfer of target compounds exceeding the upper limit of the instrument's linear calibration curve, it is necessary to either process smaller sample volumes or dilute the sample prior to preconcentration, or both, such that the amounts of target compounds injected into the GC fall within the calibration range of the instrument. Mass flow controllers take 10–15 s to recover from the pressure surge at the beginning of sample preconcentration, causing a small error in the total sample volume. In practice, the volume of air withdrawn from a canister when using a mass flow controller should not be less than approximately 100 mL. Smaller aliquots may be withdrawn from the canister using either a sample loop (1–50 mL) or a gas-tight syringe. For more concentrated samples, the sample may first be diluted with humidified zero air or humidified ultra-pure nitrogen by pressurizing the canister in which the sample was collected [to a maximum of 200 kPa (30 psig)]. In the case of very concentrated samples, sequential dilutions can be performed by withdrawing an aliquot of air from the sample canister and transferring it to a second clean, evacuated canister which is then pressurized. Some authors inject pure water into the canister with a gas-tight syringe and then pressurize with dry gas [26]. This procedure introduces an unnecessary risk of additional error resulting from septum leakage and contamination. There is no reason why the dilution gas cannot be simply humidified in line with the sample canister by bubbling zero air or dry gas through pure water prior to pressurization (Fig. 3). Dilution factors, at STP, are calculated based on the initial sample pressure and the final dilution pressure of the canisters. The relationship between canister pressure and volume is determined by filling an evacuated canister with purified

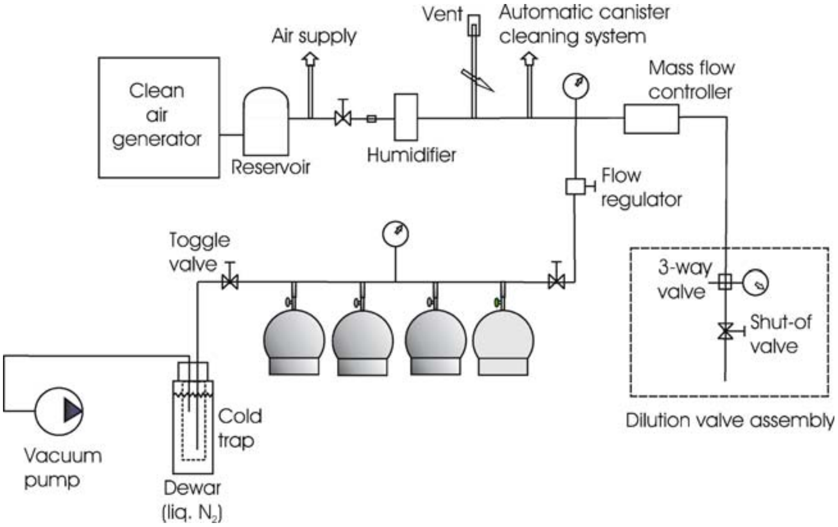


Fig. 3 Home-built manual canister-cleaning and sample-dilution system (Environment Canada)

humid air at a known flow rate (e.g., 200 mL/min, STP) controlled by a mass flow controller. Time and pressure are recorded at regular intervals. The time is used to calculate the volume of air delivered for different canister pressures. The relationship between canister pressure and volume is found by linear regression. Correlation coefficients should be greater than or equal to 0.999. A dilution factor at STP is calculated based on the volume of dilution air added to the canisters, cross-checked with the respective pressure readings. Where there are large differences in the relative concentrations of target compounds, it may be necessary to run the analysis two or more times using different volumes of sample aliquots or different dilution factors.

Water management

Ambient air contains approximately 1–3% water vapour. For example, 1 L of ambient air with a relative humidity of 50% at 25 °C contains approximately 10 mg (10 μL) of water. The presence of water in an air sample interferes with subsequent analytical techniques such as GC, MS, and Fourier-transform infrared (FTIR).

While humid air can adversely affect sorbent sampling methods, it is an advantage in the case of Summa canisters where it enhances the stability of collected VOCs. However, this sampling advantage can quickly become a problem during sample preconcentration and GC analysis. Potential effects resulting from humid air streams include: (1) loss of target compounds in condensed water; (2) co-adsorption of water on sorbents; (3) blockage of cryogenic traps through condensation and the formation of ice; (4) ice blockage of carrier gas flow through a GC column (although the use of 0.32 to 0.53 mm i.d. columns allows a higher loading of analytes, including water vapour); (5) increased variability in GC retention time by overloading the stationary phase of the GC column; (6) shifted elution times as a result of changes in stationary phase polarity; (7) damage to the GC column; (8) detector baseline shifts; (9) attenuation detector response for target compounds co-eluting with the water; (10) deterioration of a mass spectrometer ion source due to ionization of H_2O; and, (11) extinguishment of the flame in FID detectors [62].

Basic techniques for removal of water vapour from gas streams have been previously reviewed [63] and include adsorbtion, desiccation, permeation drying, cryo-condensation and cold trap dehydration. Adsorbents are frequently used in the preparation of “zero” air used. The most commonly used substances for this purpose include silica gel impregnated with cobalt salts as an indicator (blue=dry, pink=saturated with water), aluminum oxide, and zeolites (synthetic sodium or calcium silicates). Adsorbents are not used to remove humidity from air samples prior to VOC analysis because they cause severe losses of polar or heavy compounds. Substances commonly used as desiccants have also been reviewed [63]. They include Anhydron (anhydrous magnesium perchlorate), Aquasorb (P_2O_5 on a vermiculate base), Ascarite (sodium hydroxide on a silicate base), anhydrous calcium chloride, Chromosorb WAW (supported lithium chloride), Drierite (anhydrous calcium sulphate), magnesium carbonate, potassium carbonate, Sicapent (phosphorous pentoxide), and sodium carbonate. Moisture has successfully been removed by passing the sample air stream through a short drying tube containing $Mg(ClO_4)_2$, K_2CO_3, or $MgCO_3$ upstream from the preconcentrator [12, 64, 65]. $Mg(ClO_4)_2$ tubes were found to be the most effective (50–200 mL/min) [65]. However, early attempts to use these techniques to dry ambient air prior to VOC analysis were abandoned for the following reasons [63]: (1) loss of C_1- to C_3-substituted benzenes and long-chained olefins on magnesium perchlorate [66, 67]; (2) loss of heavier aromatics on potassium carbonate in addition to caking and creating excessive back pressure; (3) calcium chloride requires frequent conditioning; (4) calcium sulphate has low capacity (low breakthrough volume); (5) increased flow resistance with prolonged use, generally; and, (6) the need to filter the dried gas. In the early days of canister sampling and analysis, the most common method used to remove humidity from air samples was permeation drying. Most methods used today have replaced permeation drying with cryocondensation or cold trap dehydration techniques. A method has also been developed to derive a correction factor, converting wet mole fraction to dry mole fraction, for cases where an air sample is analyzed without prior removal of the water vapour [68]. Failure to apply a correction factor in such cases would result in measured VOC concentrations being less than the dry air mole fraction.

Permeation drying

Nafion (a copolymer of tetrafluoroethylene and perfluoropoly[trifluoromethyl(oxapropylo)]-sulphonic acid, manufactured by DuPont) is a hygroscopic semipermeable ion-exchange membrane. The sulphonic groups being rapidly hydrated, diffusion of water molecules across the membrane depends upon the concentration of water vapour on either side of the wall [69]. A Perma-Pure Nafion dryer (Perma-Pure Product, Farmingdale, NJ) may be purchased or it can be made in-house.

An efficient dryer can be easily constructed in-house by inserting a 3.0 m length of Nafion tubing (1.6 mm o.d.) through either a Teflon or polypropylene tube (3.2 mm o.d.) and coiling it to fit into a 100-cm-diameter metal cylinder around which is wrapped heating tape connected to a thermocouple. New dryers may exhibit a large peak (principal ions 81, 47, 96) eluting just after chloromethane at approximately 8.9 min and another large peak (principal ions 155, 156, 157, 125) eluting at approximately 19.7 min, just before hexane. A small constellation of contaminants may also be found in the vicinity of 25 min near the elution time of toluene. These contaminants can be eliminated by passing humidified zero air through the Nafion tube and a counter flow of dry zero air through the outer tube and baking it out repeatedly at 100 °C over a few days. The dryer must also be baked out and purged for 24 h following 40–100 h of operation. During normal operation, it should be heated to 100 °C and purged with humid zero air at 100 mL/min for 20 min following each sample injection, maintaining the line pressure at 55 kPa (8 psig). In practice, the ability of the Nafion dryer to remove water efficiently from the air stream is limited to approximately 1.5 L of ambient air. If it is found that the dryer allows an excessive amount of water to pass through to the GC for 1.5 L or less of air, the following possible causes should be investigated: (1) the fittings were too tight on the tubing surrounding the Nafion tube, thereby restricting the flow of the counter-current purge air, (2) the Nafion tube collapsed because it had been placed under vacuum while hot, or (3) an excessive amount of water flowing through the Nafion tube caused it to swell, thereby restricting the flow of the counter-current purge air in the surrounding tubing. Permeation drying is the technique used in the NuTech (Graseby, Smyrna, GA) system described below.

Use of a Nafion dryer results in excellent analytical results for nonpolar compounds, but there can be significant losses of water soluble (polar) compounds such as acids, alcohols, amines, and ketones, the latter being converted into alcohols [21, 70, 71]. The Nafion membrane is also reactive toward some compounds, particularly alkenes and terpenes that undergo rearrangement reactions resulting in losses of these sensitive substances [72, 73]. In the case of alkenes, this latter problem is resolved by continually purging the Nafion dryer with humidified zero air between analyses [34]. The terpenes, however, completely disappear and cannot be recovered.

Cryocondensation

The advantage of cryocondensation over permeation drying is that it does not lead to the loss of polar compounds. Essentially, VOCs and water are collected in a cryogenic trap after which the trap is slowly heated to ~20 °C and held there during a slow helium purge (e.g., 10 mL/min for 12 min), transferring the VOCs and CO_2 to the next stage (e.g., a Tenax trap) while leaving most of the water behind (~18 μL). Analysts should experiment to find the optimal heating temperature. For example, if the trap is held at 10 °C, rather than 20 °C, more water will stay behind in the trap while still allowing the VOCs to pass through.

The Tekmar 6000 (Tekmar Dohrman, Cincinnati, OH) uses cryocondensation in its moisture control system (MCS). It consists of a 1/16-in-diameter silo coated stainless steel loop. The idea is that hot pressure injection from the cryogenic trap to the MCS will result in water condensing on the walls of the loop while the volatiles pass through. The problem with this unit is that the MCS is the final stage before injection to the GC. As a result, some VOCs are lost by condensing in the water in the MCS.

Cold trap dehydration

Cold trap dehydration results in fewer VOC losses than seen with the cryocondensation technique described previously. Water vapour is first removed by passing the air stream through an “empty” FSL 1/8″ stainless steel trap usually held at −20 °C. The author has found that holding the temperature at −26 °C results in removal of more water without affecting VOC recovery. The VOCs pass through to a second Tenax trap which is held at −80 °C to retain the CO_2. Its temperature is then raised to −50 °C to remove the CO_2 after which the VOCs are thermally desorbed and transferred to a cryofocus trap before injection to the GC. Cold trap dehydration is used in the EnTech system described below.

VOC preconcentration

VOC levels in ambient air are of the order of 2–50 ppbv. GC sensitivity is typically ~0.05 ng. Consequently, 500–1,000 mL of air must be concentrated in a trap prior to injection. A fixed volume of an internal standard (i.s.) spiking mixture (bromochloromethane, chlorobenzene-d_5, 1,4-difluorobenzene, and 1-bromo-4-fluorobenzene) is also added to the air stream via a sample loop during preconcentration so that target compounds can be quantified using the internal standard method, and to monitor system performance during acquisition. The integrated peak areas of the internal standards should be approximately equivalent to those of the calibration standard mixture.

There are two techniques available for the preconcentration of VOCs withdrawn from a canister: cryogenic and sorbent trapping. Cryogenic concentration of ambient VOCs in nickel (Ni) capillary traps has been used for more than 30 years and presents two major advantages over the newer sorbent techniques [74–76]: there are no thermal desorption artefacts created with cryogenic trapping, and it is possible to analyze sulphur compounds that are neither well retained by nor easily desorbed from sorbents [77, 78].

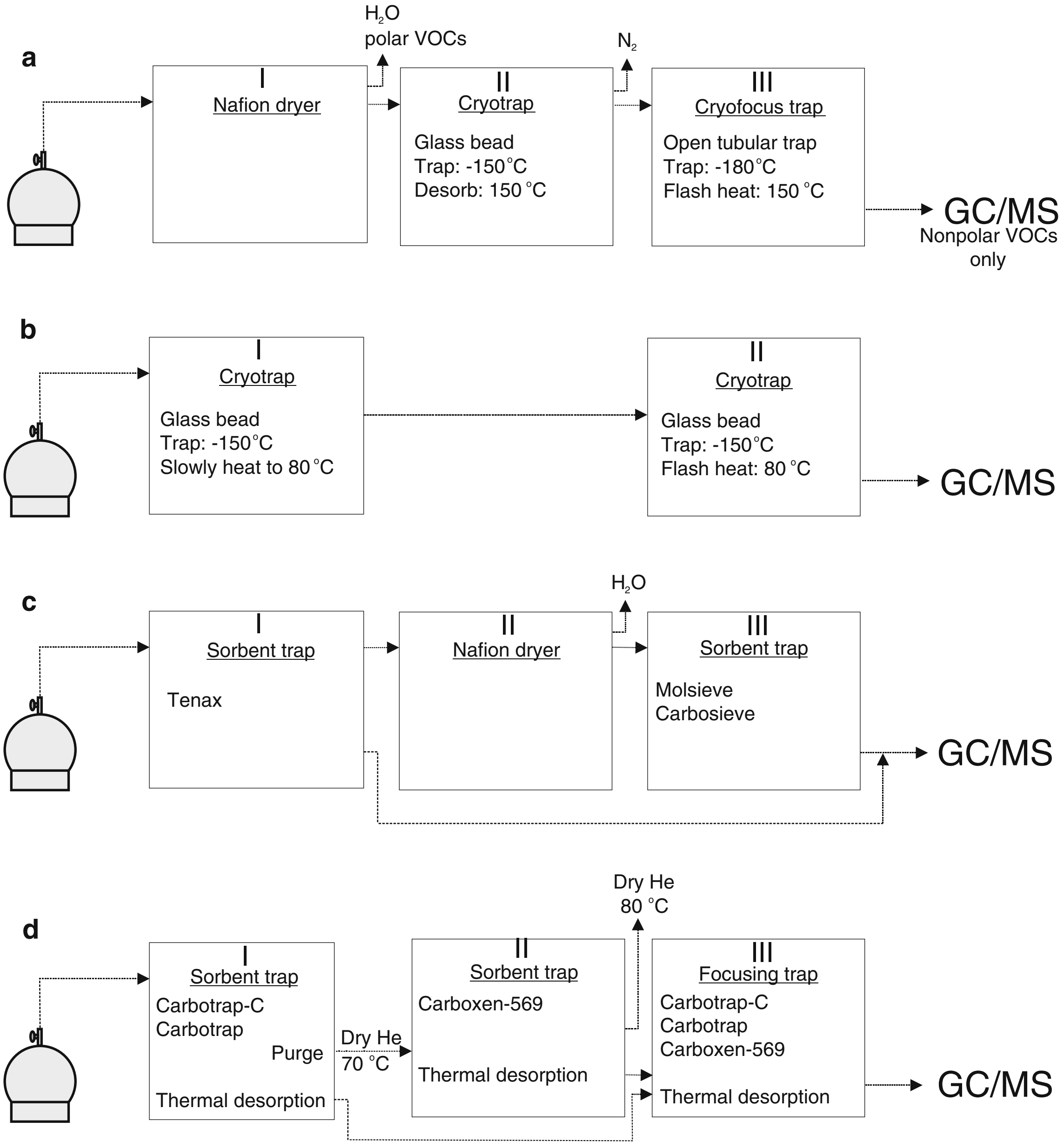
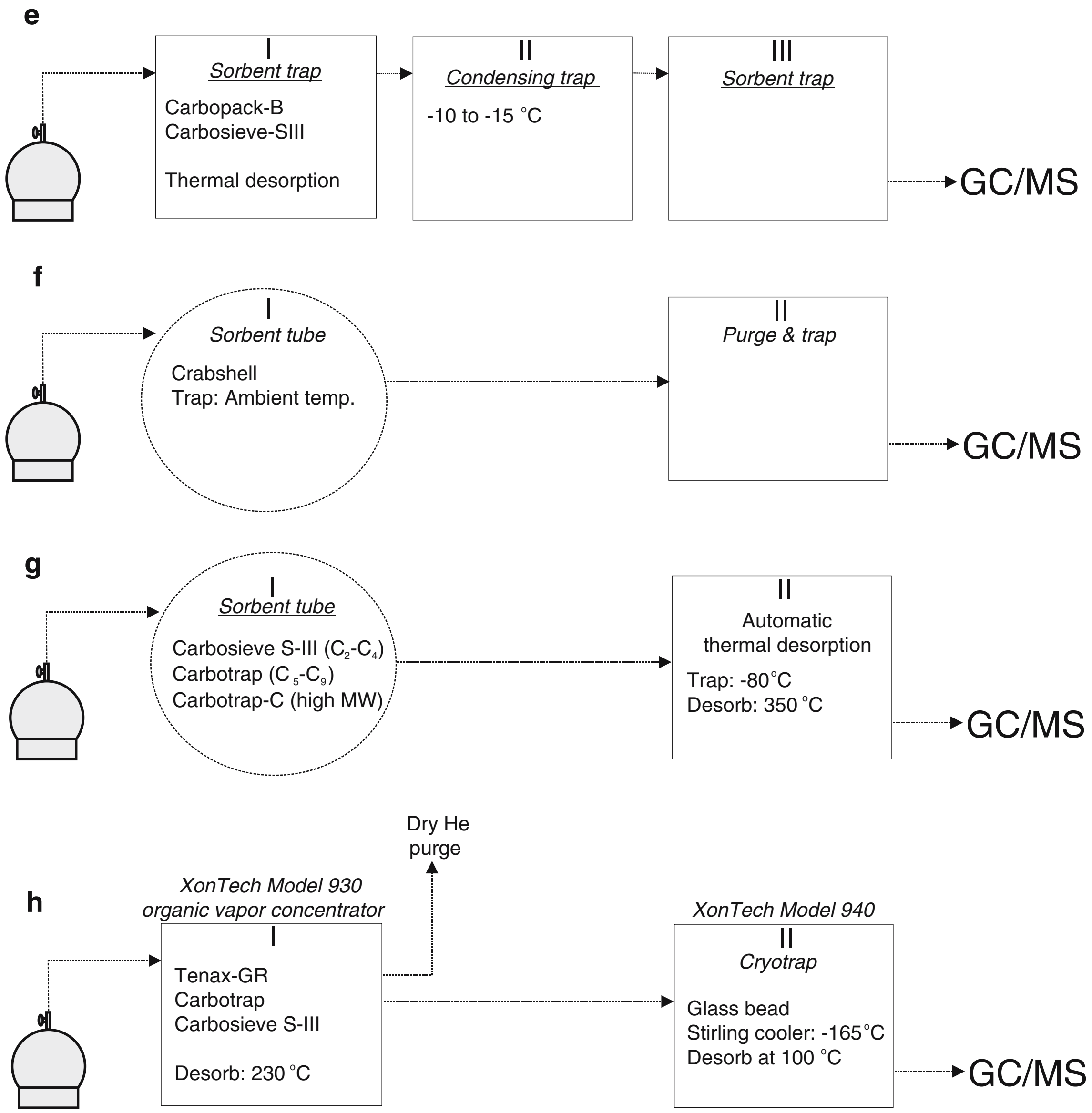


Fig. 4 Examples of different configurations used in various home-built and commercially available systems for cryogenic and/or adsorbent trapping for water removal and preconcentration of volatile organic compounds found in ambient air collected in evacuated canisters. A variety of possible configurations are shown, including those developed by NuTech (**a**), Greenberg et al., 1994 [81, 82] (**b**), Haunold et al., 1997 [84] (**c**), Knobloch et al., 1997 [85] (**d**), Dewulf et al., 1996, 1998 [86, 87] (**e**), Park et al., 1998 [88] (**f**), Tolnai et al., 2000 [53] (**g**), Oliver et al., [106] (**h**), EnTech (**i**), Chrompack (**j**), and Varian (**k**)

Fig. 4 (continued)

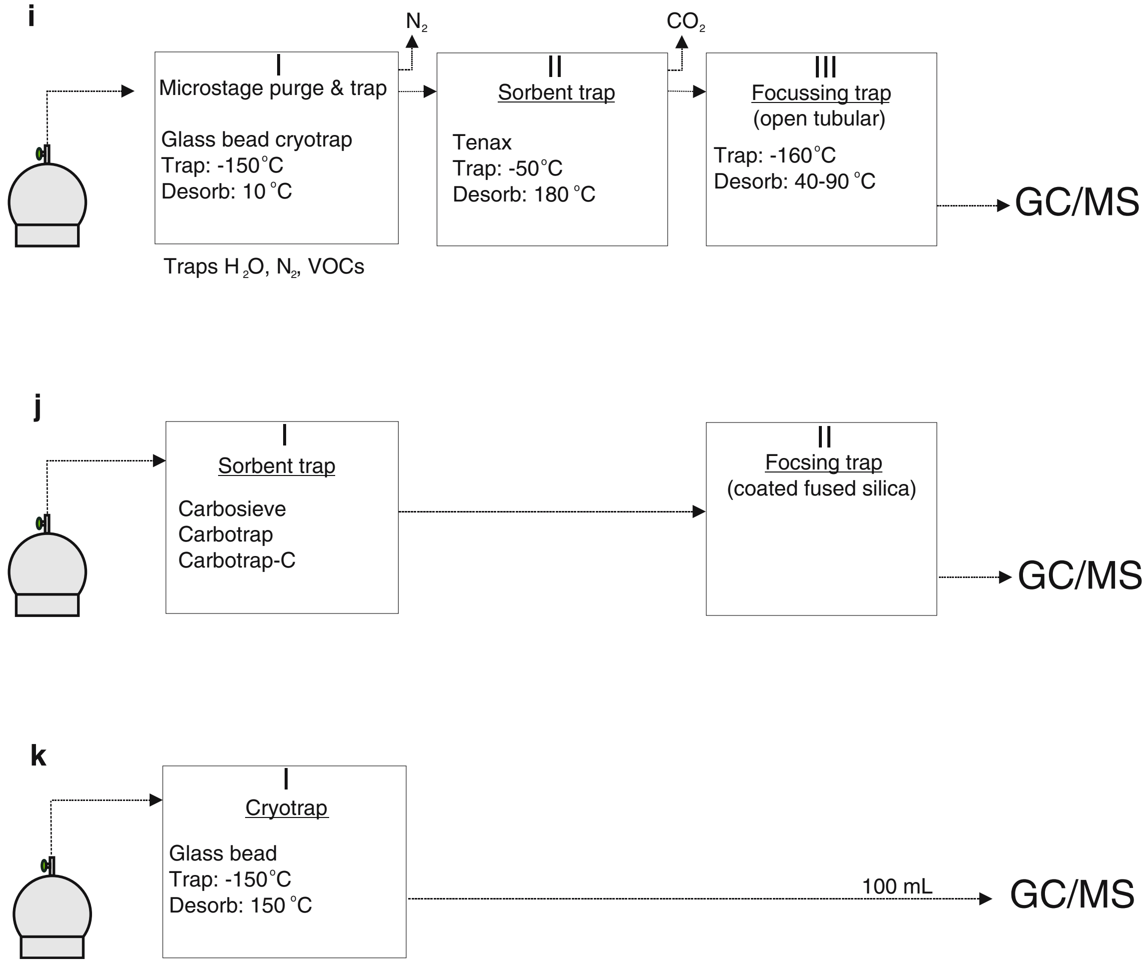


There are, however, other difficulties that can arise with cryogenic trapping: (1) artefact formation due to reactions of VOCs with ozone during sampling [61], (2) poor trapping efficiency, (3) plugging of the trap with ice in the case of highly humid air streams; and, (4) decomposition and/or elimination reactions during trapping in the Ni capillary trap or during subsequent flash heating. Sophisticated, and expensive, equipment is commercially available for water removal and VOC preconcentration of air samples collected in canister samples. It should be emphasized, however, that it is not absolutely necessary to invest in this type of equipment in order to be able to analyze canister samples. Although it may be difficult to eliminate dead spaces and cold spots, home-built systems can perform as well or better than the commercially available units. However, they are very labour intensive and lack the advantage of unattended operation—a necessity when processing a large number of canisters. The principal advantage of commercial systems lies in their ability to interface with computer-controlled GCs and to process a series of canisters automatically. A wide variety of configurations have been used for removal of water and trapping of VOCs from air prior to GC analysis. Some of these are illustrated in Fig. 4 and discussed below.

Cryogenic trapping

The TO-14A method calls for use of a cryogenic trap. Condensation and freezing of water vapour in the cryogenic trap are avoided by passing the air stream through a Nafion dryer upstream from the trap, thereby selectively removing the water vapour from the air stream. Sample flow is set at 15–60 mL/min. Counter flow of dry zero air is set at 200 mL/min. Target VOCs are transferred to the GC following flash heating of the trap at 40–70 °C.

Fig. 4 (continued)



There is little risk of thermal degradation occurring in this temperature range.

The trap can be a U-shaped borosilicate glass tube containing quartz wool, or a U-shaped stainless steel tube packed with 180~250 μm glass beads held in place by glass wool at either end. Nickel capillary traps have also been found to be inert when tested with tert-butyl alcohol, 2-bromopentane, and cyclohexyl iodide (prone to dehydration or dehydrohalogenation forming the corresponding olefin), and with bis(chloromethyl) ether (BCME), which is prone to hydrolysis [74, 76, 79]. If the U-tube is positioned too high in the cryogen, some of the VOCs will pass straight through. A 0.5–1.0 m, 0.625 mm o.d., 0.020 mm i.d. transaxial trap (the tubing parallel to the entrance and exit of the exiting purge gas stream) approximately 50% submerged in liquid nitrogen results in 100% trapping efficiency [76]. Submerging the transaxial trap too deeply can reduce the efficiency by 3–13%. The latter situation may result in splitting of the chromatographic peaks of the early-eluting analytes such as propane, Freon22, Freon12, chloromethane, isobutene, and vinyl chloride (Fig. 5). If this does occur, the integrated areas of the split peaks can be added together for calculation of the corrected amount of analyte present in the sample. A coaxial trap (the tubing wound around the axis of the exiting purge gas stream) is not recommended since its efficiency is only 89% on average (range 75–100%). The problem of icing and plugging that occurs when processing highly humid air streams (90% relative humidity) through 0.508 mm i.d. transaxial traps is resolved by using 1.016 mm i.d. Ni capillary traps with a flow rate of 10–30 mL/min [76]. Trapping efficiency depends upon the length and configuration of the tubing.

Liquid argon, liquid nitrogen, and liquid oxygen have been used as the cryogen. Liquid argon is ideal because it allows the oxygen to pass through, but it is very expensive so it is seldom used for this purpose. If the trap is cooled to the temperature of liquid nitrogen (b.p. −196 °C), oxygen (b.p. −183 °C) will be trapped along with the VOCs. If this oxygen is then cryofocused on the GC column, its rapid expansion during heating will change the pressure in the column resulting in peak splitting and changes in retention time. When liquid oxygen is used, carbon dioxide will be retained on the trap, but the use of liquid oxygen presents a fire hazard.

The NuTech Model 3550A (Graseby, Smyrna, GA) concentrator automates the unattended processing of up to 16 canister samples (Fig. 4a). This unit, sold during the

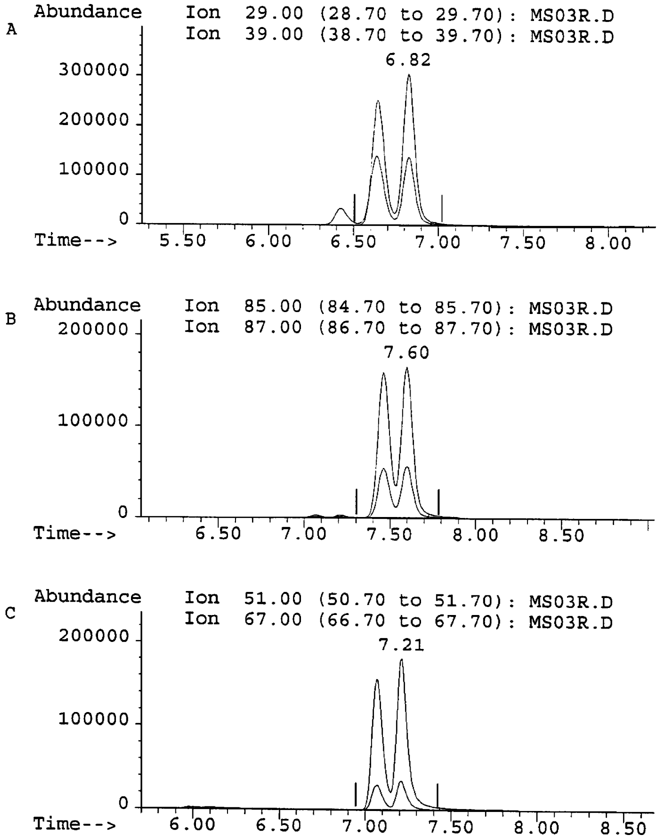
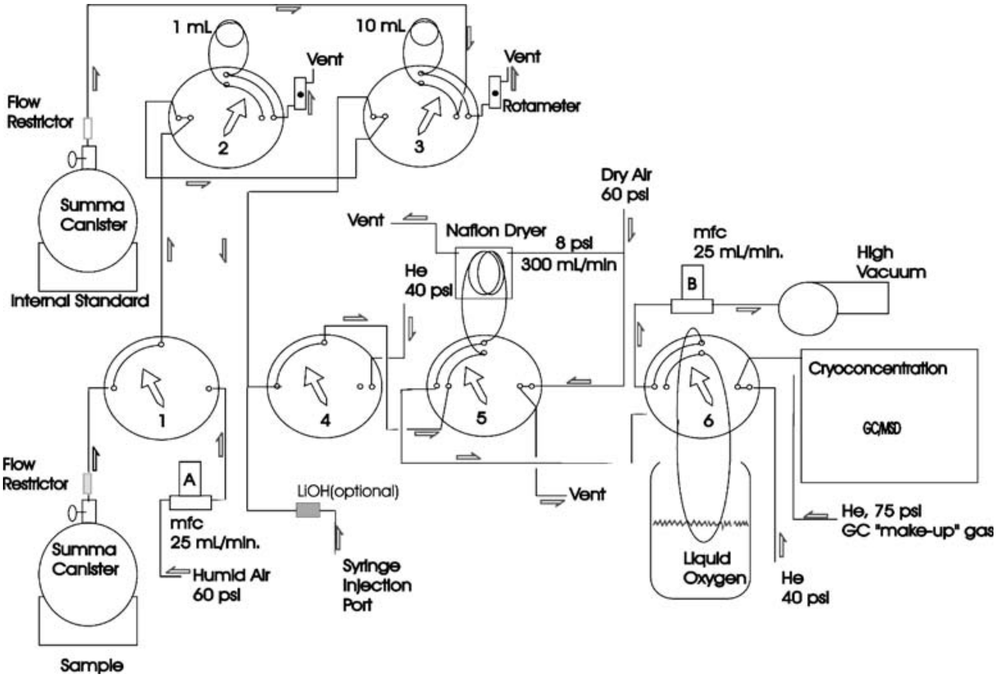


Fig. 5 Split peaks [propane (**a**), Freon22 (**b**), Freon12 (**c**)] arising from an artefact due to the immersion of the U-tube too deeply into the cryogen during sample trapping. The integrated areas of both peaks must be added together manually

1990s but no longer commercially available or supported, is still successfully used in a number of laboratories for the analysis of nonpolar VOCs. However, its 1-m-length Nafion dryer should be replaced with a 2-m length dryer to prevent the cryogenic trap from plugging up with ice and to achieve good analytical results. An aliquot of air is withdrawn from the canister at 50 mL/min and cryogenically preconcentrated at −150 °C in a trap consisting of 0.32 cm o.d. and high purity nickel tubing and packed with glass beads over a 5-cm length to increase trap surface-to-volume ratio [24, 69]. The major constituents of the air are vented to the outside. The organic components are revolatilized by flash heating (to 120 °C in 60 s) and transferred to a high-resolution GC equipped for sub-ambient-temperature programming. Samples containing very high levels of the heavier VOCs should probably not be run on this system, however, because clean-up is difficult. The lines can be evacuated but there is no mechanism to purge them with zero air continuously. The home-built system shown in Fig. 6 does not suffer from this limitation, but it must be manually operated (Fig. 7).

It is possible to analyze polar compounds, including alcohols and ketones, by removing the Nafion dryer and introducing a smaller load volume to the cryogenic preconcentrator. This results in a method detection limit (MDL) two to three times higher than would be otherwise obtained but which is satisfactory for more highly contaminated samples where it is not necessary to concentrate more than 200 mL of air prior to injection [80]. It has been found, however, that there can be sufficient water vapour and CO_2 in a 50 mL air sample to interfere with GC/MS analysis, causing peak splitting, retention time shifts or saturation of the MS signal [27]. One solution is to pass the air stream through two cryogenic traps in series [81, 82]. The first is heated slowly, leaving most of the water behind, and the second is

Fig. 6 Schematic diagram of a home-built ambient air conditioning unit in “collection mode” showing the movement of air sample from the Summa canister through Nafion dryer and the cryogenic preconcentrator to the gas-liquid chromatograph (GC) and mass selective detector (MSD) (Environment Canada)



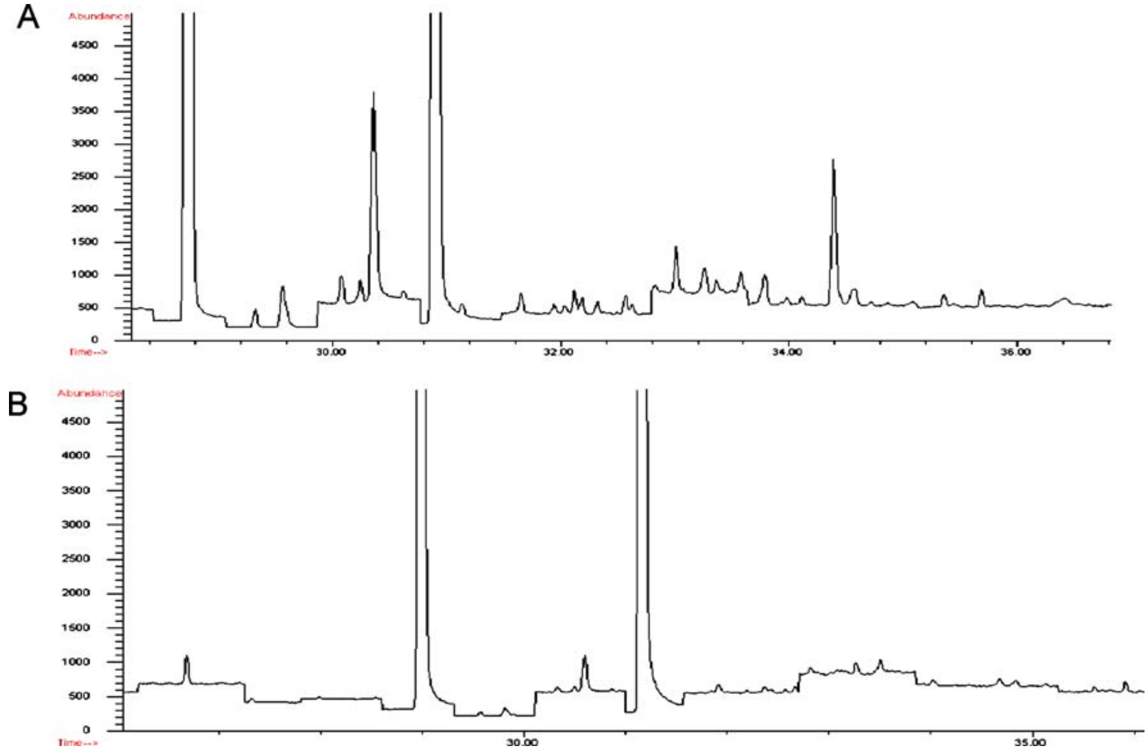


Fig. 7 The second air blank following an instrument calibration standard mixture run on a NuTech Model 3550A cryogenic VOC preconcentrator shows significant carry over of heavy VOCs between C_{10} and C_{12} (**a**). Only trace amounts of heavy VOCs are carried over in the case of the EnTech system (**b**)

flash-heated to transfer the target compounds to the GC (Fig. 4b).

Sorbent trapping

In the 1999 EPA TO-15 method, sorbents are used for water management rather than a Nafion dryer, thus eliminating the need for cryogenic trapping [18]. The air sample is preconcentrated on a solid sorbent trap while nitrogen, carbon dioxide, and most of the water vapour are vented to the outside. The method is applicable to both polar and nonpolar C_2–C_{12} VOCs. Method detection limits are lower than with cryogenic trapping because larger volumes (500–2,000 mL) of air can be preconcentrated in the trap. Although sorbent traps have largely replaced permeation drying methods, sorbent trapping still presents many of the same problems as sorbent sampling, namely, breakthrough and the formation of artefacts, particularly in the presence of high humidity and oxidants such as ozone [83].

One solution to the water management problem is to place the Nafion dryer between two sorbent traps, the first to collect the polar compounds and the second to collect the nonpolar compounds [84], the VOCs on both traps then being thermally desorbed and transferred to the GC (Fig. 4c). VOCs could also be collected and thermally desorbed from two different types of sorbent traps in series, both of which are dried with a slow helium purge prior to thermal desorption [85] (Fig. 4d). Alternatively, both the VOCs and trapped water could be thermally desorbed from a first sorbent trap, the air stream then passing through a condensing trap to a second sorbent trap [86, 87] (Fig. 4e). VOCs from 800 mL of sample air have also been trapped in a stainless steel tube filled with crab-shell adsorbent powder that was thermally desorbed and transferred to a purge-and-trap concentrator [88] (Fig. 4f). Finally, cryogenic preconcentration has been successfully combined with a multilayer sorbent tube to analyze pptv levels of 52 C_3–C_{10} VOCs contained in a 200 mL aliquot of ambient air from a Summa canister [53]. Quartz tubes were packed with Carbosieve S-III (for C_2–C_4 hydrocarbons), Carbotrap (for C_5–C_9 compounds), and Carbotrap-C (for higher molecular weight compounds) (Fig. 4g). The tubes were desorbed using an automatic thermal desorption unit coupled to a GC. Similarly, Oliver et al. (1996) have used two commercially available units in series to trap VOCs from canisters [106] (Fig. 4h). Other configurations are also possible.

The currently available Entech 7100A automated system uses a three-stage preconcentrator that removes excess water and carbon dioxide without loss of polar VOCs using a method analogous to purge and trap commonly used in water analysis, but on a much smaller scale (Fig. 4i). The method has been described previously [27, 41, 52, 58]. VOCs from a 100-mL air sample (or 40–1,000 mL of calibration mixture) and 100 mL of internal standard gas are initially collected in a glass bead cryogenic trap held at −150 °C. The temperature of the trap can then be raised to 20 °C and held there during a slow helium purge (10 mL/min for 12 min) that transfers the VOCs and CO_2 to a

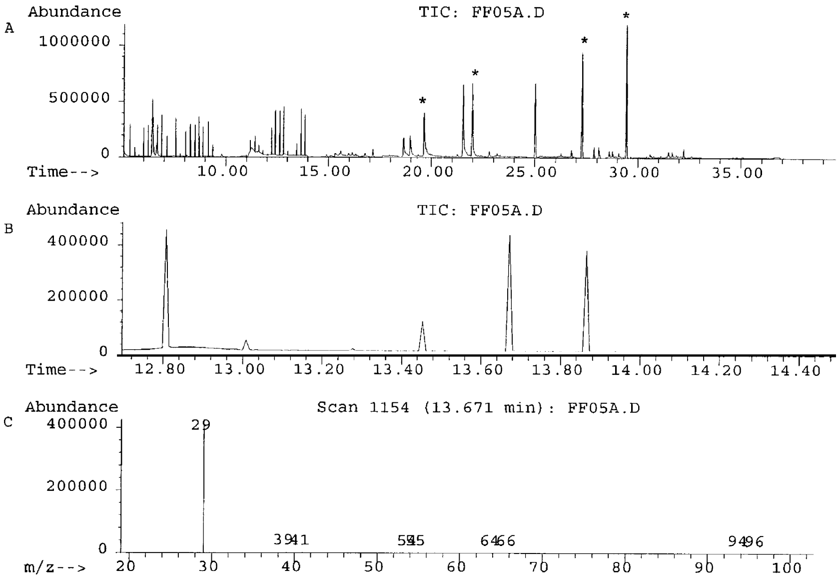


Fig. 8 Chromatogram from a system blank where air has leaked into the system causing the appearance of numerous sharp spikes (**a**). The region from 12–15 min retention time has been magnified (**b**) to show the characteristic triangular shape of these extraneous spikes that appear when the 29^+ ion fragment is monitored (**c**). *Asterisks* indicate the internal standards normally added to samples prior to analysis

Tenax trap while leaving most of the water behind (~18 μL). The CO_2 is vented to the outside while the VOCs remain on the Tenax trap. This works with a system such as the Agilent Model 5970, which is less sensitive to the water. When using the newer Agilent MSD Model 5973, which is more sensitive to water, the temperature of the cryogenic trap should be raised to a maximum of 10 °C. It is necessary that the purge volume be high enough to desorb the most volatile VOCs (40 mL) but not so high that too much water is transferred to the Tenax trap (maximum 150 mL) or that the very volatile components (Freon 12, Freon 114) break through the Tenax trap. Breakthrough of the more volatile components is prevented by holding the Tenax trap at −50 °C during the slow helium purge of the first cryogenic trap. This is still warm enough to allow the CO_2 to pass through without freezing. A Tenax trap temperature of −30 °C, used in some laboratories, is not cool enough to prevent losses of some of the lighter hydrocarbons. Finally, the VOCs on the second trap are flash-heated to 180 °C and back-flushed for 3.5 min onto a capillary-focusing trap prior to injection onto the GC. There is very little carryover of the heavier VOCs compared to the NuTech system described previously.

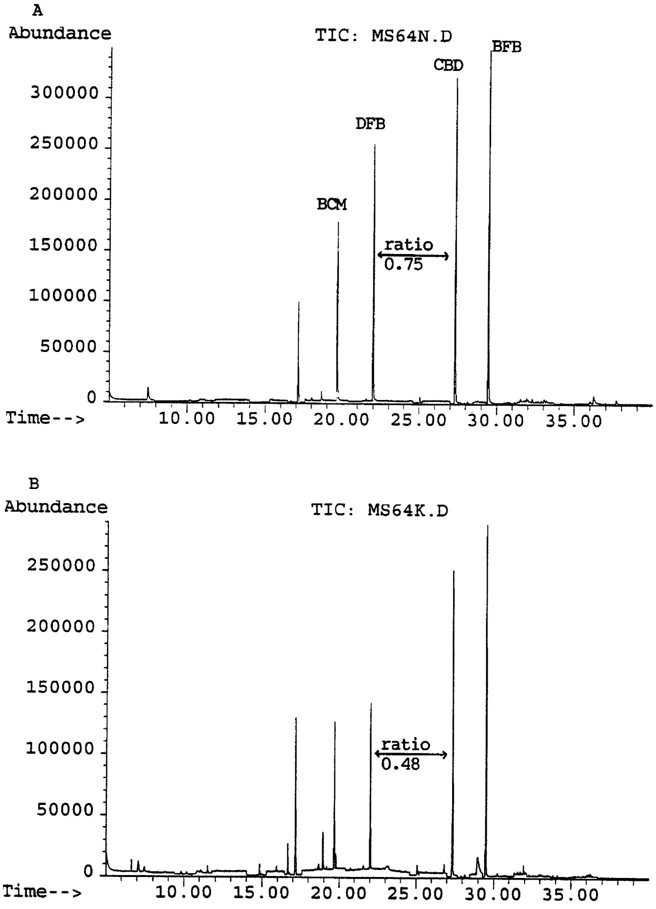


Fig. 9 Chromatograms of "air blanks" containing internal standards bromochloromethane (*BCM*), 1,4-difluorobenzene (*DFB*), chlorobenzene-d5 (*CBD*) and 1-bromo-4-fluorobenzene (*BFB*) showing **a** the normal pattern and **b** that when water is not efficiently removed from the air stream the elevation of the baseline leads to the suppression of peaks

Other commercially available systems

A commercially available automated preconcentrator to be used as part of the analytical system for C_2–C_5 hydrocarbons collected in Summa canisters is described in the *Manual for Sampling and Analysis* published by the United Nations Economic Commission for Europe Co-operative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) [89–92]. This instrument was initially built by Chrompack (Middelburg, The Netherlands) and later modified in cooperation with H. Bloemen (RIVM, Bilthoven, The Netherlands) (Fig. 4j). It has two traps and can be used with or without a Nafion dryer. The first trap is a 1/4-in glass tube packed with Carbosieve, Carbotrap and Carbotrap-C. The refocusing trap is a 10-cm piece of coated fused silica

(Poraplot-U). A drying-tube (10 cm of 1/4-in Teflon tube filled with 4 cm NaOH in the middle and 3 cm of K_2CO_3 on either end and capped with 20 μm steel sinters) with a back flush and heating option can be added. The EMEP manual notes that the Chrompack instrument, as it comes from the factory, has to be modified to some extent to obtain results as good as some of the various in-house devices that are also in use.

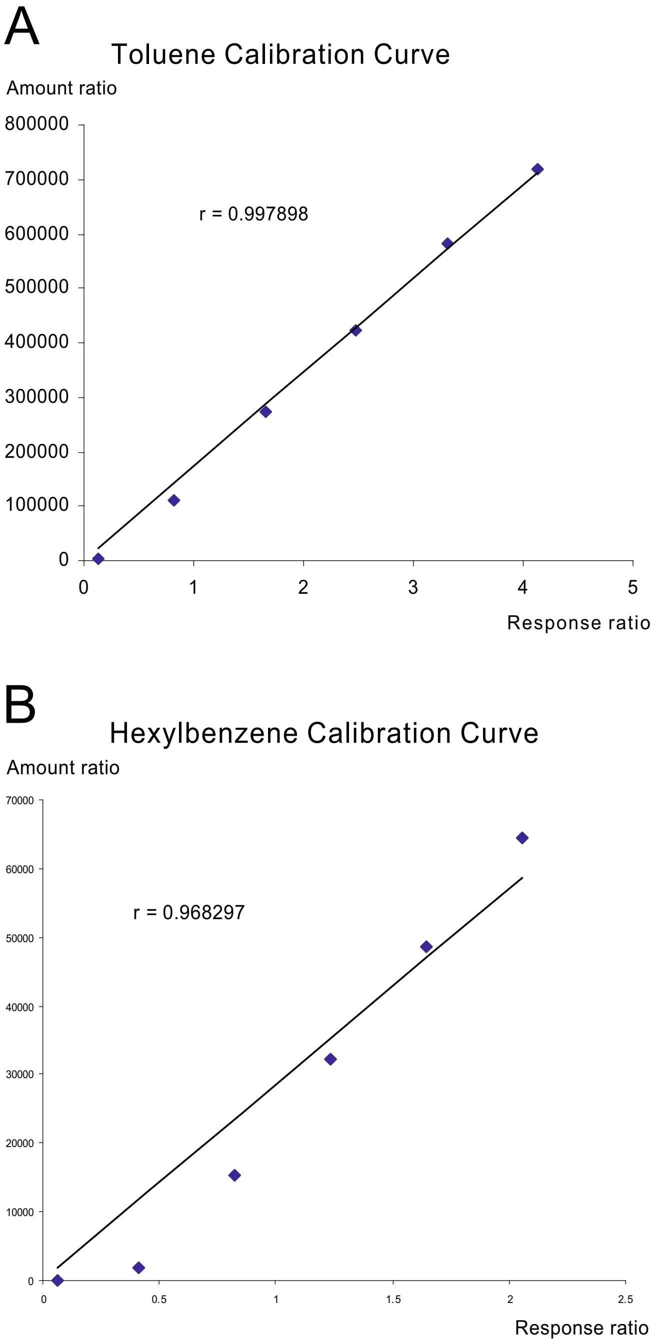


Fig. 10 Examples of the best and the worst six-point calibration curves spanning 0.1–10 ppb obtained from a 150-component instrument standard calibration mixture analyzed on an Agilent 6890GC/5973MSD operated in selected ion monitoring (SIM) mode. Both curves are statistically significant at the 99% confidence level, the critical value for the Pearson correlation coefficient being 0.917 (n=6). However, it is more difficult to obtain reliable results for some of the heavier C_{12} compounds, such as hexylbenzene, which are closer to the semivolatile (SVOC) class of compounds

The Varian (Varian Chromatography System, Walnut Creek, CA) instrument has no water management system but can be used by trapping and injecting a small volume of air (maximum 100 mL) such that there is not enough water to affect the mass spectrometer (Fig. 4k). However, CO_2 at the front end creates interferences with the analysis of C_2 and C_3 VOCs. The presence of the water does not harm the response too much, but the detection limits are too high for this small volume to be useful for outdoor ambient air. The system can be used, however, for high-level ppmv industrial hygiene samples.

Mass chromatographic analysis

Given the low level (ng) working range of the analytical method, leakage and contamination of the system can easily become a major problem. System contamination is monitored by running 500 mL samples of three different types of blanks: (1) system air blanks will detect contamination in the Nafion dryer (if present), preconcentrator, valves, transfer lines, and GC/MS; (2) helium blanks will detect contamination in the GC/MS only; and (3) clean canister blanks will detect contamination in the interface between the canister and the sample conditioning system. Leakage of air into the GC/MS system results in the appearance of numerous sharp spikes, recognizable by their triangular shape and characteristic molecular ion fragment of 29 amu (Fig. 8). This problem is avoided by periodic replacement of O-rings in the GC/MS and by the use of Grade 316 stainless steel Swagelok two-ferrule tube fittings between transfer lines. Care must be taken not to tighten the fittings too much as this will crush the ferrules and result in leakage also, sometimes first evidenced by losses of the lighter VOCs. The nuts should be tightened 3/4 of a turn for 2, 3, and 4 mm fittings, and 1 1/4 turn for 5–25 mm fittings. A Swagelok gap-inspection gauge can be used to check that the fittings are sufficiently tightened. These fittings do need to be replaced periodically, particularly if they are frequently reconnected. The gap connector gauge is not used with reassembled fittings. Optimum performance of the MS is maintained by adjusting (tuning) the instrument weekly for maximum sensitivity over the full scan range using, for example, the ions with mass-to-ion ratios (m/z) of 69, 219, and 502 present in the spectrum of the calibration gas perfluorotributylamine (PFTBA). Since the volume of the calibration gas injected varies significantly with ambient temperature, it is important that the instrument be tuned at the same ambient temperature as that used to run samples.

Following preconditioning, liquid nitrogen is used to cryofocus the VOCs in a narrow band at the head of the GC's capillary column at −60 °C, thereby minimizing the injection volume. This results in narrower GC peaks and improved compound separation. Temperature program-

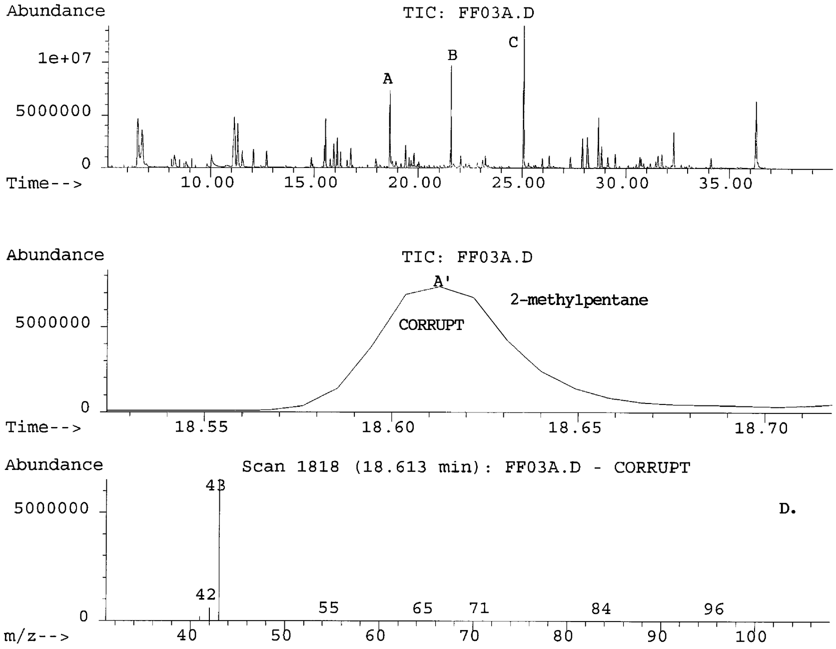


Fig. 11 A chromatogram showing the saturation of the mass selective detector by the ion fragments from 2-methylpentane (**a**), benzene (**b**) and toluene (**c**) when the concentrations of these exceeds approximately 6,000,000 abundance counts. Such corrupted peaks can be found only by checking each suspect peak manually (*A′* and *D*)

ming is then used to gradually raise the temperature of the column during chromatographic separation (e.g., 7 °C/min to 250 °C, then 20 °C/min to 280 °C) lasting approximately 60 min. Data analysis is based on the internal standard method of quantitation, which compensates for run-to-run system variations, thereby improving the precision. The presence of the i.s. also allows monitoring of system performance during data acquisition, providing the opportunity for the analyst to implement immediate corrective action. In cases where it has been observed that the response of the i.s. has been suppressed by the presence of water, for example, the affected data can be corrected by the same factor as the error in the i.s. (Fig. 9), or the analyst can choose to quantify that data using the external standard method.

The TO-15 method requires that the GC/MS be calibrated at five concentrations spanning the monitoring range of interest [18]. Given the lower limits of detection of the instruments available today, it would be advisable to add a sixth point at the lower end of the calibration curve when performing analysis of low-level outdoor ambient air samples. Linear regression is performed, forcing the curve through the origin (Fig. 10). Some laboratories prepare different standard calibration mixtures for each of the required concentrations. A more straightforward, less error-prone method, is to prepare a single standard calibration mixture from which 100, 200, 300, 400, and 500 mL are withdrawn using a temperature- and pressure-independent mass flow controller to prepare a five-point curve (2–10 ppbv). The lower limit of the calibration curve is determined by the point at which there is a deviation from linearity due to inaccurate sample volume. The accuracy of the additional sixth point at the low end of the curve can be improved by preparing a second low-level standard (20× less concentrated than the lowest point on the five-point curve) from which 100 mL is withdrawn. A mid-range concentration of the standard calibration mixture should be run daily to monitor system performance and calibration. Continuous calibration curves should be prepared daily by updating one of the six calibration levels. New six-point curves are prepared when the continuing calibration curves no longer meet the acceptance criteria, or following system modifications such as cleaning the MS detector, replacing the dryer, etc. High-level samples are best handled by the injection of a sufficiently small volume of appropriately diluted sample such that the target compounds fall within the range of their respective calibration curves. This approach allows for the analysis of both low- and high-level samples on the same instrument while minimizing the potential for system contamination. Laboratories that simply use higher level standards to prepare calibration curves that bracket the expected high-level concentrations can expect disappointing results due to contamination of the system by the high-level standards leading to high blank levels, carryover from one sample to the next, and ultimately, poor accuracy and precision.

The upper limit of the calibration curves is determined by the MS. Linearity of the MS response may fall off at high concentrations due to detector saturation. Figure 11, for example, shows corruption of the 2-methylpentane, benzene and toluene peaks from a 125-mL aliquot of a smoke sample when their concentration exceeded approximately 6,000,000 mass abundance counts.

In practice, the linearity of calibration curves may fall off due to suppression of the signal by water. As larger aliquots are introduced to the GC, the amount of water that finds its way through the water management system increases. Eventually there is enough water present to suppress the GC signal, generally in the region roughly between hexane and benzene, and target compounds in this region of the chromatogram cannot be quantified. In addition to the water problem introduced by excessively long preconcen-

Table 1 VOCs monitored by Environment Canada using GC/MSD analysis of outdoor ambient air collected in Summa canisters

Target compound[a]	MDL[b] (ppbv)	MDL (mg/m^3)	Quantitation ion	Confirmation ion	Secondary confirmation ion
Benzene	0.01	0.03	78	77	51
Benzyl chloride (alpha-chlorotoluene)	0.002	0.01	91	126	
Bromodichloromethane	0.005	0.03	83	85	
Bromoform	0.003	0.01	173	171	175
Bromomethane	0.01	0.05	94	96	
Bromotrichloromethane	0.003	0.02	117	119	
1,3-Butadiene	0.006	0.01	39	54	53
Butane	0.02	0.05	43	41	29
iso-Butane (2-methylpropane)	0.02	0.04	43	42	41
1-Butene/2-methylpropene	0.03	0.07	41	56	39
c-2-Butene	0.01	0.03	41	56	55
t-2-Butene	0.005	0.01	41	56	55
iso-Butylbenzene	0.004	0.02	91	92	134
n-Butylbenzene	0.003	0.02	92	91	
sec-Butylbenzene	0.003	0.01	105	134	91
tert-Butylbenzene	0.003	0.02	134		
1-Butyne (ethylacetylene)	0.01	0.02	54	39	53
Camphene	0.01	0.06	93	121	79
Carbontetrachloride	0.004	0.02	117	119	121
Chlorobenzene	0.003	0.02	112	77	114
Chloroethane	0.009	0.02	64	66	29
Chloroform	0.008	0.02	83	85	47
Cyclohexane	0.003	0.009	84	41	56
Cyclohexene	0.007	0.02	82	67	
Chloromethane	0.01	0.02	50	52	
Cyclopentane	0.003	0.01	42	55	70
Cyclopentene	0.006	0.02	67	68	
p-Cymene (1-methyl-4-isopropylbenzene)	0.003	0.02	134		
Decane	0.002	0.01	57	43	71
1-Decene	0.006	0.03	55	56	
Dibromochloromethane	0.002	0.02	129	127	
1,2-Dibromoethane (EDB)	0.003	0.03	107	109	
Dibromomethane	0.004	0.03	174	93	176
1,2-Dichlorobenzene	0.004	0.02	146	148	111
1,3-Dichlorobenzene	0.004	0.02	146	148	111
1,4-Dichlorobenzene	0.002	0.01	146	148	111
1,4-Dichlorobutane	0.007	0.03	55	90	
1,1-Dichloroethane	0.006	0.02	63	65	27
1,2-Dichloroethane	0.004	0.01	62	64	27
1,1-Dichloroethene (1,1-dichloroethylene)	0.009	0.04	61	96	63
c-1,2-Dichloroethene (c-1,2-dichloroethylene)	0.005	0.02	61	96	98
t-1,2-Dichloroethene (t-1,2-dichloroethylene)	0.006	0.02	61	96	98
Dichloromethane	0.006	0.02	49	84	86
1,2-Dichloropropane	0.006	0.03	63	62	27
c-1,3-Dichloropropene	0.001	0.005	75	77	110
t-1,3-Dichloropropene	0.003	0.01	75	77	110
1,2-Diethylbenzene	0.003	0.02	105	119	134
1,3-Diethylbenzene	0.003	0.01	110	134	105
1,4-Diethylbenzene	0.006	0.03	105	119	
2,2-Dimethylbutane	0.01	0.04	57	71	43
2,3-Dimethylbutane	0.002	0.008	42	43	71
c-1,2-Dimethylcyclohexane	0.004	0.02	97	112	55

Table 1 (continued)

Target compound[a]	MDL[b] (ppbv)	MDL (mg/m^3)	Quantitation ion	Confirmation ion	Secondary confirmation ion
c-1,3-Dimethylcyclohexane	0.002	0.008	97	55	112
c-1,4/t-1,3-Dimethylcyclohexane	0.001	0.005	97	112	55
t-1,2-Dimethylcyclohexane	0.003	0.01	97	112	55
t-1,4-Dimethylcyclohexane	0.001	0.004	97	55	112
2,2-Dimethylhexane	0.003	0.01	57	41	56
2,5-Dimethylhexane	0.002	0.01	57	43	71
2,4-Dimethylhexane	0.004	0.02	85	57	43
3,6-Dimethyloctane	0.004	0.02	57	71	43
2,2-Dimethylpentane	0.003	0.01	57	43	85
2,3-Dimethylpentane	0.003	0.01	56	71	57
2,4-Dimethylpentane	0.003	0.01	43	57	85
2,2-Dimethylpropane	0.007	0.02	57	41	29
Dodecane	0.006	0.03	57	43	71
Ethylbenzene	0.003	0.02	91	106	
Ethylbromide	0.003	0.01	108	110	
2-Ethyl-1-butene	0.004	0.01	69	84	
2-Ethyltoluene	0.003	0.01	105	120	
3-Ethyltoluene	0.003	0.01	105	120	
4-Ethyltoluene	0.005	0.03	120	105	
Freon 11 (trichlorofluoromethane)	0.002	0.01	101	103	
Freon 113 (1,1,2-trichlorotrifluoroetha	0.002	0.01	151	101	103
Freon 114 (1,2-dichlorotetrafluoroethan	0.005	0.03	85	135	87
Freon 12 (dichlorodifluoromethane)	0.007	0.04	85	87	
Freon 22 (chlorodifluoromethane)	0.008	0.03	51	67	
Heptane	0.01	0.04	71	57	43
1-Heptene	0.003	0.01	41	56	70
c-2-Heptene	0.003	0.01	56	55	41
c-3-Heptene	0.004	0.01	69	98	
t-2-Heptene	0.001	0.006	55	56	41
t-3-Heptene	0.004	0.02	69	98	56
Hexachlorobutadiene	0.002	0.02	225	223	227
Hexane	0.009	0.03	57	41	43
c-2-Hexene	0.004	0.01	55	42	84
t-2-Hexene	0.004	0.02	55	42	84
1-Hexene/2-methyl-1-pentene	0.01	0.04	56	55	41
Hexylbenzene	0.004	0.04	91	162	
Indane (2,3-dihydroindene)	0.004	0.02	117	118	
Isoprene (2-methyl-1,3-butadiene)	0.005	0.01	67	68	53
Limonene	0.01	0.05	68	93	136
2-Methylbutane	0.01	0.04	57	42	41
2-Methyl-1-butene	0.003	0.01	55	70	42
2-Methyl-2-butene	0.003	0.009	55	41	70
3-Methyl-1-butene	0.003	0.009	55	70	42
Methyl-t-butyl ether (MTBE)	0.01	0.03	73	57	
Methylcyclohexane	0.002	0.007	83	98	69
1-Methylcyclohexene	0.007	0.03	81	96	
Methylcyclopentane	0.003	0.01	56	41	69
1-Methylcyclopentene	0.007	0.02	67	82	
2-Methylheptane	0.008	0.04	57	43	
3-Methylheptane	0.001	0.006	57	43	85
4-Methylheptane	0.002	0.009	70	71	43
2-Methylhexane	0.004	0.02	85	57	43
3-Methylhexane	0.003	0.01	70	43	57
2-Methylpentane	0.009	0.03	71	42	43

Table 1 (continued)

Target compound[a]	MDL[b] (ppbv)	MDL (mg/m^3)	Quantitation ion	Confirmation ion	Secondary confirmation ion
3-Methylpentane	0.01	0.04	56	57	41
3-Methyl-1-pentene	0.003	0.009	55	69	41
4-Methyl-1-pentene	0.007	0.02	43	41	
c-3-Methyl-2-pentene	0.004	0.01	41	69	55
c-4-Methyl-2-pentene	0.006	0.02	69	84	
t-3-Methyl-2-pentene	0.003	0.009	41	69	84
t-4-Methyl-2-pentene	0.005	0.02	69	84	
Naphthalene	0.003	0.02	128	127	
Nonane	0.003	0.02	57	43	85
1-Nonene	0.005	0.02	55	43	70
Octane	0.005	0.02	57	85	43
1-Octene	0.003	0.01	41	55	70
t-2-Octene	0.006	0.03	41	55	70
Pentane	0.03	0.09	41	27	43
1-Pentene	0.01	0.04	55	42	70
c-2-Pentene	0.004	0.01	55	42	70
t-2-Pentene	0.004	0.01	55	42	70
α-Pinene	0.006	0.03	93	77	
β-Pinene	0.007	0.04	93	69	
Propane	0.02	0.03	29	43	
Propene (propylene)	0.02	0.03	41	39	42
iso-Propylbenzene	0.002	0.01	105	120	
n-Propylbenzene	0.003	0.02	91	120	
Propyne	0.01	0.02	39	40	
Styrene	0.003	0.02	104	78	103
1,1,2,2-Tetrachloroethane	0.003	0.01	83	85	
Tetrachloroethene (tetrachloroethylene)	0.002	0.01	130	132	95
Toluene	0.009	0.03	91	92	
1,2,4-Trichlorobenzene	0.005	0.03	180	182	
1,1,1-Trichloroethane	0.004	0.02	97	61	99
1,1,2-Trichloroethane	0.003	0.02	97	83	61
Trichloroethene (trichloroethylene)	0.006	0.03	166	164	
1,2,3-Trimethylbenzene	0.003	0.01	105	120	
1,2,4-Trimethylbenzene	0.006	0.03	105	120	
1,3,5-Trimethylbenzene	0.003	0.02	105	120	
2,2,3-Trimethylbutane	0.003	0.01	57	56	85
2,2,5-Trimethylhexane	0.001	0.005	57	71	41
2,2,4-Trimethylpentane	0.004	0.02	57	41	
2,3,4-Trimethylpentane	0.003	0.01	43	71	
Undecane	0.004	0.02	57	43	71
1-Undecene	0.007	0.04	41	55	70
Vinylchloride (chloroethene)	0.004	0.01	62	64	
m/p-Xylene	0.007	0.03	106	91	
o-Xylene	0.003	0.02	91	106	

[a] Standard calibration mixture analyzed using an EnTech 7100 preconcentrator and an Agilent 6890GC equipped with a J&W DB-1, 60-m fused silica column (0.32 i.d. and 1 μm thickness) and an Agilent 5973MSD. The oven temperature was initially held at −60 °C for 3 min, then raised to 240 °C at a rate of 7 °C/min

[b] Method detection limit equal to 3.14 times the standard deviation of seven replicate determinations near the expected MDL (100 mL of a low level standard calibration mixture)

tration times, some of the more unstable compounds can be lost in the preconcentrator.

Lower method detection limits are achieved using selected ion monitoring (SIM), and chromatographic peaks are identified by retention time and qualifier ion ratios. The ratio of the integrated peak area of each target ion to the integrated peak area of the nearest internal standard is computed for each analyte. Target compounds are quantified by comparing each of these ratios to their previously determined calibration curves. The MDL for each target compound is determined from the analysis of seven replicate measurements at a concentration near the expected detection limit (within a factor of five), multiplying the resulting standard deviation by 3.14 (Student's *t* value at the 99% confidence level) [18]. The TO-15 method requires that the MDL be less than or equal to 0.5 ppbv. Given the sensitivity of GC/MS instruments available today, this criterion should be approximately 10 times lower. MDLs ranging from 0.004–0.09 ppbv are achieved in the author's laboratory for 150 target compounds analyzed by GC/MS in selected ion monitoring (SIM) mode (Table 1).

Accuracy and precision are also considerably improved if the analyst does not rely upon automated peak integration for quantitative analysis, which can introduce errors of 25–70%. Figure 12 shows examples of automated computer integration of the ion chromatographic peaks for 4-ethyltoluene, benzene and styrene using Agilent's HPChem software, peak areas being underestimated by approximately 25–70%. Peak areas for the 150 target compounds were underestimated by 38%, on average, using optimal software parameters and automated peak integration only. Consequently, all peak areas must be manually determined using computer-assisted integration—a very labour intensive process. Also, automated computer identification of chromatographic peaks is not reliable in the case of all co-eluting compounds.

Applications

Evacuated canisters have most often been used for the sampling and analysis of VOCs in outdoor and indoor ambient air, and at landfill sites using the EPA TO-14, TO-14A, or TO-15 methods. However, other interesting applications have also been reported in the literature. Smoke from fires has been collected in Summa canisters via passive sampling and analyzed using an in-house sample conditioning and preconcentrator unit interfaced with an Agilent GC-MSD [93–95]. Breath samples collected in Summa canisters have been analyzed using an early model Nutech 320-01 cryoconcentrator and a

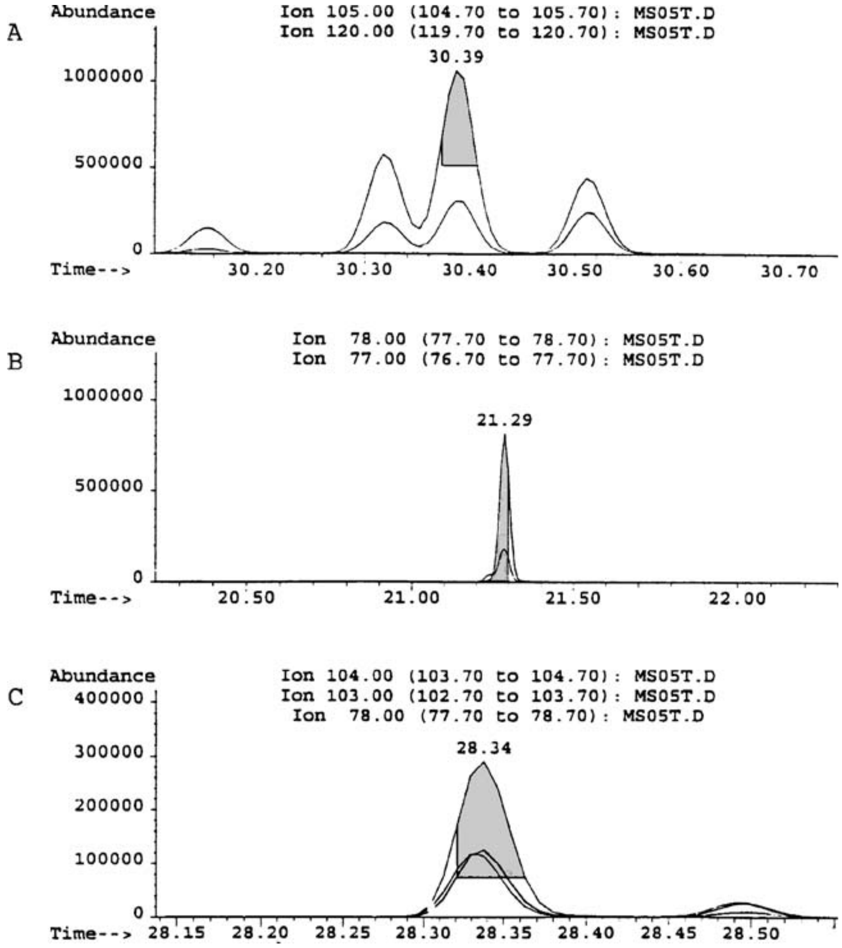


Fig. 12 A chromatogram of detector response (abundance) vs. retention times (min) showing the results of automated computer integration (*shaded area*) using HPChem software for 4-ethyltoluene (**a**), benzene (**b**) and styrene (**c**). The concentrations of these target compounds were underestimated by approximately 25–70%, illustrating the importance of manual peak integration

prototype "valveless concentrator" (Graseby-Nutech, Smyrna, GA) interfaced to Magnum ITS40 GC-MS ion trap instrument (Finnigan MAT, San Jose, CA) [96–100]. The volume of breath sample that could be processed was limited to 100 mL, however, due to the high levels of carbon dioxide (3.8%) which interfered with the GC analysis. Larger breath sample volumes (up to 400 mL) can be processed using a three-stage cryogenic trapping preconcentration system such as the Entech 7100 described above [58]. With slight differences in temperatures and flow rates, this method has also been used for the analysis of ppt levels of VOCs in ambient air [27, 52].

The most unusual use of evacuated canisters reported in the literature was for the headspace collection of VOCs emanating from the temporal gland of a male Asian elephant, *Elephas maximus*, during musth [101–103]. An evacuated Summa canister was connected to an open-bottom stainless steel cup via ultra clean Nupro SS-4H4 bellow-stem valves. The open end of the device was held against the cheek and over the temporal gland of the restrained elephant for 30 s at which point the Nupro valve was opened to collect the headspace VOCs. In the same study, headspace samples were collected into Summa canisters from blood and urine samples.

Rasmussen has collected and stored historic air samples collected at Cape Meares, Oregon, from 1978–1997, at Point Barrow, Alaska, from 1995–1998, and at Palmer Station, Antarctica, from 1991–1997 [64, 104]. This extraordinary 20-year air archive consists of samples taken using in situ air liquefaction to compress approximately 1,000 L of air at STP into 35-L Summa stainless steel tanks filled to a final pressure of 3000 kPa (450 psig) [105]. Samples can be withdrawn from these tanks into 850 mL Summa canisters to a pressure of 200 kPa (30 psig).

Conclusion

The TO-14/TO14A and TO-15 methods were developed for monitoring parts-per-billion ambient levels of the particular VOCs of interest to the U.S. EPA. However, evacuated canister sampling and analysis is not restricted to the EPA's target list of 40 VOCs. Indeed, upwards of 180 polar and nonpolar VOCs are currently analyzed using canisters, and many of these have been validated for analysis at parts-per-trillion levels. Canister methods are well suited for the analysis of high-level VOC samples as well, provided that sample dilution, instrument calibration, and system clean-up are performed correctly. The most challenging aspect of canister analysis is the water management problem. Sorbent trapping has largely replaced the cryogenic trapping methods originally developed for canister analysis. The advantage of sorbent methods is that it is possible to analyze polar VOCs in addition to the nonpolar VOCs. In-house systems provide increased flexibility and control over the analytical process, particularly in the case of special applications, but are prone to difficulties arising from dead space and cold spots. Commercial systems are less susceptible to these difficulties and offer the added advantage of unattended automated canister processing.

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