



A New Method for **WHOLE-AIR** SAMPLING

NIOSH Method 3900 for Sampling Volatile Organic Compounds Using Evacuated Canisters

BY RYAN F. LEBOUF, DRU A. BURNS, ANAND RANPARA, AND ALAN ROSSNER

Sorbent tubes are typically used for occupational exposure monitoring of volatile organic compounds in many different industrial environments. To choose an appropriate sorbent, the user must have some prior knowledge of the target analytes as well as environmental conditions (humidity and temperature) and approximate concentrations to effectively sample exposures. Whole-air sampling into evacuated canisters requires no prior knowledge of air concentrations since breakthrough (the loss of sample that occurs when chemicals are not effectively trapped by sampling media) is not an issue. Canisters can handle chemical air concentrations ranging from sub-part per billion to part per million, and the technique is amenable to a wide range of compounds, such as alcohols, ketones, alkanes, aromatics, and terpenes. EPA has been using evacuated canisters for decades to sample VOCs in ambient air via the agency's TO-15 method. Why not use canisters for occupational exposure monitoring?

One challenge is the size of the canisters. Traditional whole-air sampling uses 6L canisters, but who wants a volleyball-sized canister strapped to their back? Smaller canister sizes (400 or 450 mL) are now available. Analytical instruments are more sensitive and no longer need the large injection volumes to reach sub-ppb concentrations of VOCs. Using sample injection volumes of 250 mL, the canister method can easily achieve 0.2 ppb detection limits for most analytes using gas chromatography-mass spectrometry (GC-MS).

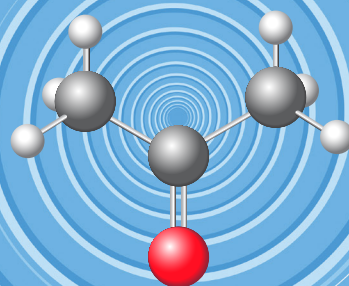
The second challenge is controlling the sampling flow

rate. Metal diaphragm flow controllers are heavy (approximately 1 lb.), but researchers at Clarkson University have addressed this issue through the use of capillary flow controllers. NIOSH continued this work with capillary flow controllers and applied a canister sampling method in a field survey to characterize healthcare workers' exposures to cleaning and disinfecting products. Canisters coupled with restrictive flow controllers make sampling easier for the field industrial hygienist because the flow controllers require no onsite pre- or post-sampling calibration.

The focus of NIOSH's canister method development was to evaluate an evacuated canister-based (passive) sampling approach followed by preconcentration of samples into a gas chromatograph/mass spectrometer. The agency recently added a new method for sampling and analysis of VOCs using personal evacuated canisters to the *NIOSH Manual of Analytical Methods*. In NIOSH method 3900, samples are analyzed using a pre-concentrator/gas chromatograph-mass spectrometer system. The NIOSH Respiratory Health Division Organic Laboratory in Morgantown, W. Va., evaluated this method for 17 VOCs: ethanol, acetone, 2-propanol, dichloromethane, hexane, trichloromethane, 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, benzene, methyl methacrylate, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, α -pinene, and *d*-limonene. This article describes the canister method.

APPLICATIONS

Industrial hygiene applications for canisters are numerous. Canisters can be used for sampling durations that range



from less than 30 seconds to more than 40 hours for occupational exposure monitoring or area sampling. We have found particular utility in the use of canisters for monitoring short-duration peak exposures and source emissions; these applications are described in two NIOSH Health Hazard Evaluations of coffee roasting facilities. Evacuated containers have also been paired with photoionization detectors to trigger peak sampling in the laboratory, as discussed in the June 2018 issue of the *Journal of Occupational and Environmental Hygiene*. The flexibility of the canister sample allows for applications in personal air sampling for VOCs where multiple solvents (both polar and non-polar) are often present—for example, in painting or solvent

cleaning operations where polar and non-polar VOCs are present typically in the ppm levels. This application would allow for an easier sampling approach than using multiple tubes and sampling pumps. In addition, canister sampling is useful for monitoring indoor air quality or vapor intrusion, which often require detection limits in the low- or sub-ppb concentrations.

SAMPLING

A fused-silica lined canister is evacuated prior to sampling using a system equipped with a rough pump and a high vacuum pump. Fused-silica lined canisters reduce analyte losses from interactions of the analyte with the canister

surface. This coating is important for sampling low-ppb concentration environments. Sampling can be performed with a fitting for instantaneous samples or a flow controller for time-integrated sampling into a canister for area or personal sampling. Selection of the appropriate flow controller and flow rate will depend upon the size of the canister and the sampling period necessary to characterize exposures. For diaphragm flow controllers, follow the manufacturer's procedures for calibration to an appropriate flow rate (for example, 10 mL/min for a 6L canister for an 8-hour work shift) prior to each day of sampling. The final canister pressure should be less than 0.9 atmosphere (that is, 90 percent full). For capillary flow controllers, the flow is a physical constant governed by the length and internal diameter of the capillary. The capillary flow controller should be designed to fill the canister volume to 0.3 atm (30 percent full) but no more than 0.5 atm (50 percent full) during the sampling period. Flow rate will become increasingly non-linear for sample pressures above 0.5 atm.

Calibration and Sample Preparation

Calibration and sample canisters require pressure dilutions with ultra-high purity (UHP) nitrogen or air. A 200-ppb calibration gas can be purchased from ISO Guide 34 suppliers and diluted to 20 ppb with UHP nitrogen. The calibration curve is developed by injecting varying volumes of the calibration standards. The lowest reproducible injection volume is 25 mL. The curve is generally valid (a change of less than ten percent in each analyte verified with an independently produced 20 ppb check standard) for one to two weeks depending on sample throughput.

Most laboratories do not pressurize canister samples when running TO-15 analysis. Typically, the canisters have a large volume (6L) and a diaphragm flow controller is used. They are received under a slight vacuum (less than 0.9 atm), which means the correct volume of sample was collected. In NIOSH method 3900, samples are pressurized because the canisters are generally 450 mL received at 30 percent full (for time-weighted average samples ranging from 15 minutes to hours) or 100 percent full (instantaneous). The extra volume is needed for a 250 mL injection. The positive pressure also ensures that any leaks from the canister push the diluted sample out instead of pulling dirty air in.

Accurate pressure dilutions are key to producing quality data. Like most measurement devices, pressure transducers are not reliable at the extremes of their measurement ranges. When we transfer a known amount of gas between canisters, the receiving canister should be partially filled (approximately 30 to 50 percent) with UHP nitrogen or air to reduce the vacuum in the canister prior to sample transfer. This allows for a less aggressive introduction of the sample or calibration standard and also moves the pressure measurement into the optimal range of the pressure transducer. In NIOSH method 3900, a portion of the sample, in terms of a pressure differential (for example, 0.3 to 8 pounds per square

inch absolute), is added to the receiving canister at a slow rate (0.03 to 0.3 psia per second depending on the desired pressure differential). Then, UHP nitrogen or air is added to the receiving canister at a slow rate until the final pressure is reached. The ratio of the final pressure to the sample pressure differential is equal to the dilution factor (for example, if the final pressure is 25 psia and the sample pressure differential is 2.5 psia, the dilution factor is 10). Final pressure should not exceed 30 psia to keep the pressure of the sample flow path (including sample transfer lines, fittings, traps, and loop if used) to similar pressures as those used to calibrate the system; otherwise, the volume transferred to the preconcentration system can be different than requested and require pressure correction factors. Final pressures of 21.5 psia for samples and 25 psia for calibration and quality control standards are recommended for routine analysis. Although pressure dilutions of up to 100x might be achievable, they are not as reproducible as multiple, lower dilutions (for example, two 10x dilutions for a 100x final dilution). Following NIOSH method 3900, allow the pressurized canisters to equilibrate for a minimum of six hours before analysis to allow time for mixing and stabilization.

Storage Stability

Most of the 17 analytes are stable (less than 10 percent bias) in canisters for 58 days at room temperature at low-ppb concentrations. The exceptions are ethanol, 2-propanol, and acetone, which are stable for 30 days, according to a study published in the *Journal of Environmental Monitoring* in 2012. The same study found that fourteen analytes at high-ppb concentrations were stable for 30 days, except α -pinene and *d*-limonene, which remained stable for 21 days. Other research published in *Environmental Science and Technology* and *Atmospheric Environment* suggests that the shorter acceptable storage time for α -pinene and *d*-limonene might be due to losses from chemical reactions with other components of canister contents, particularly oxidizing species such as ozone or hydroxyl and nitrate radicals naturally found in indoor air.

ANALYSIS

Sample analysis requires a whole-air preconcentration system to manage water content and reduce the transfer volume to the gas chromatograph. Some water content is added to canisters containing analytical standards to mimic humidity seen in field canister samples. Using MS scan mode allows unknown chemicals to be qualitatively identified and concentrations estimated based on the closest internal standard and an assumed response factor. Limits of detection could be improved by using SIM mode.

The current recommended strategy for higher concentration samples is pressure dilutions into the ppb-level calibration range, or loop injection with a dilution factor correction for volume injected onto the pre-concentrator compared to a nominal 250 mL injection volume.

An inter-laboratory study was conducted with nine

laboratories to assess repeatability and reproducibility of the test method prior to incorporation of the method in the NMAM. Precision estimates for repeatability ranged from 0.04 to 0.55 at ppb concentrations and from 0.10 to 0.47 for ppm concentrations over all analytes and nominal levels. Precision estimates for reproducibility ranged from 0.10 to 0.62 at ppb concentrations and from 0.19 to 0.58 at ppm concentrations, depending on analyte and nominal levels. Plots of *h* and *k* statistics, which measure the between- and within-laboratory consistency, indicated inconsistencies with reported results from three laboratories. All results were retained due to the low number of participating laboratories. Training on pressure dilution techniques and preconcentration systems as well as proficiency testing should be periodically conducted to ensure operating laboratories maintain optimal canister method performance.

Humidity Effects

Humidity (that is, water content) of field samples does not affect recovery of most compounds (for example, ketones, alkanes, aromatics, and terpenes) but can affect recovery of polar analytes such as ethanol and isopropyl alcohol. Polar, early-eluting compounds like ethanol are notoriously challenging to quantify in the presence of humidity. During the water management step of some pre-concentrators, water is removed on a cold trap and some polar analytes are lost. Pre-concentrator operating conditions need to be optimized to remove water while minimizing the removal of polar compounds. Reducing the cold trap temperature to reduce the amount of water removed can be an effective strategy to reduce the loss of polar compounds during the water management steps. Another strategy would be to separate the analyte of interest from the water peak by adjusting chromatographic and/or preconcentration conditions. It is recommended to work with the manufacturer on optimizing the operating conditions of the pre-concentrator for your analytes.

Influence of Particles

To preserve canister longevity, canisters should be protected against particles. Particles can be removed from the air stream using a 2- μ m, sintered, stainless steel particulate filter.

CANISTER SAMPLER INTEGRITY

Canisters should be leak tested periodically with a leak rate criterion of 0.1 psia over a 24-hour period. Canisters' cleanliness and ability to recover analytes should be periodically assessed. We certify each of our canisters prior to sending them into the field by checking carryover with humid UHP nitrogen (40 percent relative humidity at 22°C). Analyte carryover less than the limit of detection and system background are considered clean. A canister's ability to maintain analyte recoveries is checked on an annual basis. We dispose of canisters when recoveries of any analyte fall outside plus-or-minus 25 percent of the concentration tested, but canister suppliers might provide a service to repair the fused-silica lining.

FOR MORE INFORMATION

We hope this article is helpful and welcome your comments if you use canisters or are interested in NIOSH method 3900. Please send feedback or questions about the method to rlebouf@cdc.gov. ☎

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RESOURCES

Atmospheric Environment: "Gas-Phase Tropospheric Chemistry of Biogenic Volatile Organic Compounds: A Review" (2003).

Environmental Science & Technology: "Development of a Flow Controller for Long-Term Sampling of Gases and Vapors Using Evacuated Canisters" (November 2002).

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BY BOB LIECKFIELD, JR.

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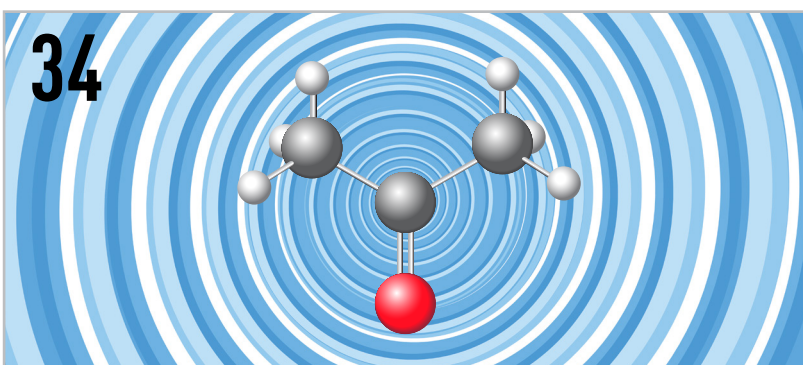
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