The Evaluation of Techniques and Development of Guidelines for Cleaning Ambient Air Canisters

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Abstract

Ambient air sampling canisters, such as SUMMA or SilcoCan™ canisters, must be cleaned and certified clean prior to use. There are many cleaning techniques analysts can use for ambient air sampling canisters. Most involve pressure and evacuation steps; some include humidified air, others use dry gases; and some incorporate heat. This paper will evaluate the different techniques and develop proper guidelines for cleaning ambient air sampling canisters.

Practical Canister Cleaning Guide

I. Introduction

For many years there has been much discussion of proper cleaning procedures for air sampling canisters. Compendium Method TO-14 has provided guidance, and in the last 10 years many commercially available automated canister cleaning systems have evolved. The downfall is that these systems are quite expensive and some designs have limitations, therefore many laboratories design their own cleaning systems and methodologies for cleaning canisters. This paper describes a practical cleaning procedure to ensure the canisters are cleaned properly for ambient air sampling, whether using a commercially available cleaning system or a "homemade" cleaning system,

A Basic Canister Cleaning System

To begin, the design of the system is important. The system must be able to provide a humidified air stream by using bottled gases or an air or nitrogen generator. We recommend using an air generator because it provides very pure gas. When using either a generator or bottled gas, attach an activated charcoal or carbon trap on the outgoing line to collect VOC contaminates from the air source. The system should possess a good vacuum source and large vacuum lines. There should be a condensation trap on the vacuum pump to prevent pump oil vapor from contaminating the lines or canisters, and a cold trap to collect impurities during cleaning. As the contaminants are removed from the canister, they are cold-trapped, preventing them from contaminating the system. Using heat to help remove the contaminants is optional but also highly recommended. Heating speeds up the canister cleaning process; without heat, it can take twice as long to clean a canister. Highly contaminated canisters must have heat and humidified air to properly clean them. Accurate gauges that are calibrated to 0.25% accuracy full scale, to read vacuum and pressure in the canisters are recommended. Most systems are designed to clean four 6-liter canisters up to 24 canisters and can be automated by using a programmable computer.

II. How to Clean a Canister

Whether you are using a new canister or a used canister, it must be cleaned beforehand. However, there are small differences between cleaning SUMMATM and SilcoCan TM canisters. We will discuss these in this procedure.

Typical Methodology for Cleaning Canisters

STEP 1: Connect canisters to the cleaning system, the first step is release any pressure within the canister. Then the system is put under vacuum to evacuate the canister. TO-14 recommends evacuating to 50mtorr for 1 hour, but this is not necessary during general cleaning. 22-25in Hg is sufficient for general cleaning by providing adequate mass dilution of air within the canister. The high vacuum of 50mtorr is more important on the final vacuum for sampling.

STEP 2: Once the canisters have been under vacuum for approximately 1 hour, pressurize them with humidified air up to 30psig if not using heat and to 5psig if using heat. Allow the canisters to bake while filled with the humidified air for at least 1 hour. This will help dilute the impurities, and the moist air will help remove the impurities. It is theorized that there are active sites on the interior walls of the canister, and the water and impurities will compete for these sites. Using a saturated air stream, the water will occupy the active sites and the impurities will be removed during cleaning.

STEP 3: Heat is applied between 120-250oC to create steam, depending on which type of canister being cleaned. SUMMA™ canisters cannot exceed 155°C, but SilcoCan™ canisters are capable of temperatures up to 250°C. The limiting factor of the SUMMA™ canisters are the Nupro™ valves used with these canisters. These valves have lubricants that cannot be exposed to high temperatures. The SilcoCan™ canisters use a Parker diaphragm valve, which is capable of 250°C. This permits heating the canister and valve to 250°C to help remove volatile impurities. Many commercially available cleaning systems avoid this problem by ensuring the valves are not in the heated zone. The canisters below the valve are heated, but the valves only experience radiant heat. This will protect the Nupro™ valves from being overexposed to heat.

STEP 4: Re-evacuate the canisters to remove the impurities. Let the canister sit for 1 hour. Repeat steps 3 and 4 until the canister is cleaned. The number of cycles will be determined by how dirty the cans are and how easily they come clean. We recommend developing a procedure, and testing after each evacuation/pressurization cycle to determine number of cycles necessary for proper cleaning. If not using heat, the number of cycles may be higher.

STEP 5: The next step is to determine if the canisters are thoroughly cleaned. This is done by filling the canister to 30psig with humidified ultra-high-purity air and then analyzing by GC/MS or GC/FID/ECD. Compendium Method TO-14 specifies less than 0.2ppbv of target VOC compounds and TO-12 specifies 0.02ppmv of total carbon. Both methods recommend testing every canister until a reliable procedure is developed.

STEP 6: Once the canister is certified clean, it must be prepared for sample collection. To achieve this, the final step of the system is to evacuate the canisters to 50mtorr or below. This can be done using a roughing pump if your system is leak-tight, however many commercially available canister cleaning systems use additional high vacuum pumps such as a turbo molecular drag pump to reach final vacuum quickly.

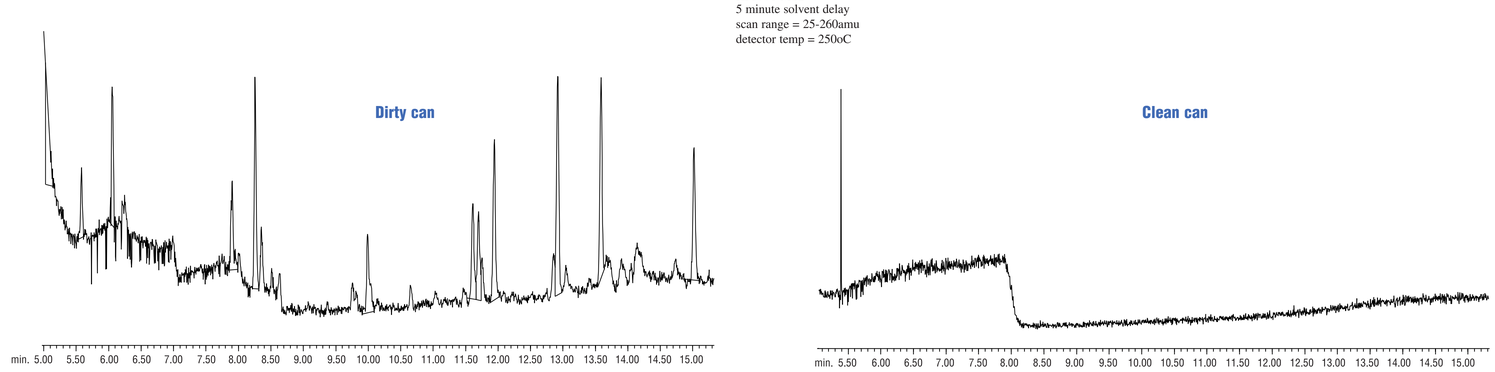
Application #1

A canister before cleaning and after cleaning with humidified air and heating to 200°C.

Rtx-1 60M x 0.32mm ID x 1.0um
50oC (1min) 8oC/min to 165oC then 15oC/min to 220 (5min)
flow rate = 1.4ml/min

Nutech 3550 Preconcentrator conditions
sample= 300cc from canister
cyrotrap = -160oC
desorb = 150oC
cyrofocuser = -190oC
desorb = 150oC

MSD conditions
HP5971 MSD
5 minute solvent delay
scan range = 25-260amu
detector temp = 250oC



III. Heat versus No-Heat

Many homemade designs of canister cleaning systems do not use heat. This typically is not a problem when cleaning canisters that are used in ambient air collection. For most ambient air samples, compounds collected are in the low ppbv range and can be removed from a canister by multiple cycles of pressurization with humidified air and evacuation. However, if there are contaminants in the canister at higher concentration, then heat may be required. Please note that when adding heat and humidified air or nitrogen, there is the potential to create a steam pressure vessel. Some commercially available cleaning systems incorporate a pressure release valve to ensure that the pressure rating of the canisters are not exceeded.

How to add heat to a homemade design

There are several ways to add heat to the canister cleaning system. They are by oven, heat band, insulated jacket, and infrared heat.

Oven

Some canister cleaning system designs are built within an oven. The lines for the humidified air stream and to the vacuum system are plumbed directly into the oven. This design will heat the entire canister, including the valve. This is a benefit to using the oven design. This will help remove the contaminants if the valve is dirty as well. However, as mentioned earlier, this may shorten the lifetime of the Nupro™ valve on SUMMA™ canisters. This high temperature will begin to affect the lubricants within the valve parts. Typically, when using heat it is recommended to create steam from the humidified air stream. To do this, at least 120°C is required for the oven temperature; however, it is not uncommon to go to higher temperatures. SilcoCan™ canisters are stable up to 250oC.

Another concern with oven-built systems is space. Most commercial ovens are not very large and this restricts the number of canisters that can be cleaned at one time. When using heat, total clean-up times are shorter than when not using heat, therefore more cleanings can be done in the same time.

Heat Bands

Heat bands are commonly used by placing an individual band heater around the equator of the canister. The band heaters are capable of heating a canister to approximately 120-130°C, but there may be a heat gradient and the valves only see radiant heat to approximately 60-70°C. This method still allows for sufficient removal of contaminates.

Insulated Heat Jackets

Insulated heat jackets are individual jackets made to surround and heat the entire canister. Designs are commercially available, however they don't cover the valve area. A customized version would have to be made to cover the valve. The jackets are made of silicone, or Teflon®-coated fiberglass fabric for the exterior and fiberglass insulation for the interior. Some have fixed temperature and others have variable temperature control up to 400-500oF.

Infrared Heat Rays

An infrared heating system would include an infrared heat source or panels and a reflective panel similar to the cylinder drying rack used on gas cylinder systems. The infrared heat panel is placed on one side of the canisters and the reflective panel is placed on the opposite side. The infrared rays heat the cans, and the rays that go past the canister hit the reflective panel and heat the other side of the canister.

IV. Air Versus Nitrogen

The two gases recommended for cleaning canisters are ultra-high-purity air or nitrogen. Air is used when oxidation of the interior surface walls is desired. The 21% oxygen in air is sufficient for oxidation-it is not necessary or recommended to use pure oxygen gas to achieve oxidation. When using heat along with humidified air, hydrolysis is accomplished with the moisture, and oxidation is accomplished with the oxygen. Nitrogen is also a good gas for cleaning ambient air canisters, however oxidation is not feasible. As mentioned earlier, generated air or nitrogen are recommended because of the generator's ability to produce very pure gas streams. It is always recommended to use purification traps on the gas lines to trap any impurities from the gas sources.

V. Certifying Canisters

After cleaning, every canister should be tested until a proven process is developed. To certify a canister clean, the canister is filled to 30psig with humid air or nitrogen. (The humid air or nitrogen stream also must be certified clean and should be done prior to the canister certification step.) The analytical system should be either a GC/FID or ECD or GC/MSD system. According to EPA Compendium Method TO-14, a canister must have less than 0.2ppbv of the target compounds detected, EPA Compendium Method TO-12 requires less than 0.02ppm C detected by GC/FID. If the canister does not meet either of these specifications, it must go through the cleaning process again and must be retested for certification. Figure 1 shows a canister before and after cleaning with two cycles of humidified air and heat to 200°C tested using a Agilent GC/MSD 5971.