Sampling with MiniCans and Bottle-Vacs

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Introduction
Canisters offer a simple and highly effective means of measuring volatile chemicals in air ranging from PPM to sub-PPB levels. The "GC grade" internal surfaces of canisters allow for a much wider range of recovery relative to most adsorbent-based samplers, without the inaccuracies inherent with adsorbent- based methods such as volume measurement errors during sampling, inconsistent recoveries, breakthrough, and reverse adsorption, to name a few. Over the years, smaller canisters have become more popular due to their ease of use relative to the heavier 6L canisters, as well as to the reduced need for very large sample sizes as laboratory analyzers become more sensitive. Along with the reduction in size has come the development of different surface treatments and types of canisters, including fused silica lined stainless steel (eg.Silonite MiniCans) and deactivated glass (Bottle-Vac) canisters. These canisters actually extend the range of compounds that can be successfully collected, stored, and analyzed by GC and GCMS relative to the older SUMMA technology, as their internal surfaces are much more like that of a GC column. Looking at this another way, if a volatile or light semivolatile compound is GC compatible, it will likely be compatible with these newer sampling canisters. A complete overview of the different types of canisters in use today can be found in the Entech Document 501, "Understanding Sampling Canister Technology".

Bottle-Vac Samplers are deactivated amber glass canisters that have been demonstrated to provide 30 day stability of sampled chemical, at a fraction of the cost, size, and weight of the older 6L SUMMA cans. These sampling containers are available in sizes ranging from 32 oz all the way down to 40mL. Like most of the MiniCan technology, these Bottle-Vac samplers use a small valve called a Micro-QT valve that virtually eliminates the introduction of unwanted air when connecting the sampler up to a field sampling inlet, or to an analyzer in the laboratory. It's the small volume connections of the Micro-QT valve that have made it possible to shrink the sampling canister down to as little as 40mL. Even the 40mL Bottle-Vac is capable of 1PPB detection limits or lower, again based on today's more sensitive analyzers.

Choosing Between the MiniCan and Bottle-Vac

Both the MiniCan and Bottle-Vac have shown excellent recoveries of most GC compatible compounds. Currently, the MiniCan is the only one of the two that is mentioned specifically in OSHA PV2120. But like EPA Methods TO-14A and TO-15, the actual construction of the container is not as important as the demonstrated ability of the container to sample, store, and recover target compounds. Like many other of the newer methods being developed, these methods are "Performance-Based" as opposed to "Design-Based", leaving an

opening for superior technology to be developed and incorporated more easily into existing methods. Selection of the actual container is more a matter of choice, although the one exception to date is formaldehyde, which has demonstrated better recovery out of Silonite coated MiniCans.

SelectingAppropriate Sampler Size

In selecting the appropriate sample container size, the following three questions must be answered:

1. What detection limits are required?
2. Are duplicates being taken?
3. Is it a grab, short, or long-term sample integration?

1.4L and 0.6L MiniCans™ are Silonite coated to provide superior recovery for all EPA and OSHA Canister Method Analytes. (PN-29-MC1400QT & PN-29-MC600QT2, respectively).

Silonite™ coated (fused silica) canisters create a "GC-like" environment for sample storage, providing the most inert sampling solution available.

The 16 and 32 oz Bottle-Vac glass canister samplers demonstrate vastly superior performance over Tedlar bags, and are fully reusable like other canisters.

Safety netting provided for 8, 16, and 32oz Bottle-Vac samplers.

			Approx. Full Scan GCMS Detection Limits			Max. Integration Times(Hrs)	
Type	Part Number	Volume	(PPM)	with Preconcentration		Vacuum Samp	Helium Diffusion
			Loop-Inj. (0.5-1cc)	1-shot	2-3 Analyses/ Sampler		
Bottle-Vac	29-BV040A	40mL	0.1	2 PPB	40 PPB	0.05	8
Bottle-Vac	29-BV060A	60mL	0.1	1 PPB	30 PPB	0.1	12
Bottle-Vac	29-BV240A	8oz	0.1	0.2 PPB	2 PPB	0.3	48
Bottle-Vac	29-BV460A	16oz	0.1	0.1 PPB	0.5 PPB	10	4 days
Bottle-Vac	29-BV920A	32oz	0.1	0.05 PPB	0.1 PPB	24	1 week
MiniCan	29-MC200Q	200mL	0.1	0.2 PPB	2 PPB	0.3	-
MiniCan	29-MC450QT	450mL	0.1	0.1 PPB	0.5 PPB	10	-
MiniCan	29-MC600QT	600mL	0.1	0.1 PPB	0.5 PPB	12	-
MiniCan	29-MC1000QT	1000mL	0.1	0.05 PPB	0.1 PPB	24	-
MiniCan	29-MC1400QT	1400mL	0.1	0.03 PPB	0.1 PPB	24	-

Table 1 is a guide to answer these questions Historically, canisters were always selected to be large enough so that a laboratory would be able to try two or even three times to get a good analysis, to avoid having to resample. Since re-collecting the sample in the field is sometimes not feasible, this is a very important consideration. However, with MiniCans and Bottle-Vacs becoming much cheaper than 6L canisters, the option for taking duplicate samples also becomes a possibility.Taking duplicates in the field means that all of the sample can now be used in a single analysis, and the detection limits indicated in the table assume that 100% of the canister's contents are preconcentrated and injected into a GCMS. Note that when using a fixed sample loop to achieve 0.1PPM detection limits, the sample container size does not make much of a difference to sensitivity.

Sample integration time also determines the required size of a canister. Virtually all vapor sampling being done today utilizes vacuum as the driving force that pulls the air sample into the canister. Due to the 1-2cc internal volume of flow controllers used for time integrated sampling, these flow controllers are generally reserved for canisters of 400mL and greater. Therefore, maximum integration times for smaller canisters (40mL, 60mL, 8 oz) are determined by fill times using Critical Orifice Samplers, which are discussed later in this document.

Helium Diffusion Sampling (HDS) is a new technique developed by Entech for reducing the sample collection rate by another factor of 10-20 times slower than is possible with vacuum sampling using flow controllers. This technology is now being developed for 0.2 to 8 hour sampling into 40mL canisters for Personal Monitoring of chemicals in the workplace. Actual detection limits utilizing HDS are a factor of two times higher, as only about half of the container is filled with air during sampling, the remaining volume being the original helium. More information about how this technique works can be obtained by contacting Entech Instruments.

Quick "Grab" Sampling

Grab sampling is a means of quickly filling a MiniCan or Bottle-Vac by opening the isolation valve and allowing the container to fill to atmospheric pressure within 1 to 10 seconds. Grab sampling into MiniCans is generally performed using Silonite coated stainless steel filters to prevent dust and particulates from compounds with vapor pressures greater than that of C13 and heavier hydrocarbons at 25°C to pass unimpeded through the filter. Filters should be cleaned or replaced every few sampling events to insure a clean sample pathway.

Sampling can be performed without a filter under certain circumstances. Some laboratories utilizing more current analytical technology have the ability to recover many semivolatile compounds from MiniCans by preheating the MiniCan before analysis. In this case, the presence of a small abundance of particulates inside the canister will have less of an effect on recovery, as heating will still drive compounds into the gas phase. In these cases, a liquid washing procedure is available from Entech that should be performed about every 5-10 sampling events to keep particulate levels at a minimum.

Finally, grab sampling with Bottle-Vac samplers never requires filters. The low cost of Bottle-Vac containers allows these to be thown away every 3-5 samplings, with just the valve retained to be placed on a new deactivated bottle. Keep in mind that integrated sampling with Bottle-Vacs (to be described later) will still need to use filters, but this is more to keep the flow controllers and small restrictive orifices clean.

Step-by-Step Procedure for Grab Sampling

1. Remove any cap or seal on the canister valve.
2. Use a vacuum gauge to verify the canister is still under vacuum (PN 29-70010QT).

3. Open canister using one of the techniques shown.

4. Wait for sound of hissing to stop (1-10 seconds), then close valve.
5. Verify canister pressure with gauge.

6. Replace cap, if any.
7. Fill out canister tag and documentation.
8. Place in shipping box and send to lab.

Short Term Integrated Sampling (1-30min.)

MiniCans and Bottle-Vacs can be filled over an extended period to obtain an average concentration over the sampling period. The more concentrations are “expected” to change over the monitoring period, the more this becomes necessary for risk assessment. Short term, time integrated sampling can be performed using simple critical orifice inlets that achieve a constant flow from about 15 to 600 cc/min, depending on the orifice used. This flow rate remains constant until the canister has filled half way to atmospheric pressure, after which the flow will start to drop off. Although sampling can be stopped at ½ atmosphere, followed by pressurization in the laboratory to assist in recovery of the collected air sample, it is generally accepted to continue the sampling to / or ¾atm, as the flow rate will still be about 70% at about ¾atm.Table 2 shows several MiniCan and Bottle-Vac samplers, with restricted orifice samplers and their corresponding flow rates and fill times to 50% and 80% full.

The smaller the orifice, the more important a particulate filter is to keep this orifice from becoming obstructed. Although the larger diameter, faster flowing orifice samplers may operate acceptably without a filter, using a Silonite coated stainless steel filter will insure that a proper sample is collected. As with grab sampling, this filter should be changed or at least reverse purged every couple of sampling events, or every event when sampling in a high concentration or dusty environment.

Step-by-Step Short Term Integrated Sampling

Before going out to the field, select a MiniCan or Bottle-Vac, and the appropriate critical orifice restricted sampler inlet from Table 2 based on the sampling times required.

In the field:

1. Remove any cap or seal on the canister valve.
2. Use a vacuum gauge to verify the Container is still under vacuum (PN 29-70010QT). If using a 40/60mL Bottle-Vac, pre-evacuate the gauge using a separate evacuated canister to first bring it to vacuum so its internal 1cc volume will not be flushed into the canister. For larger canisters, this 1cc volume is generally negligible.
3. Connect the Restricted Sampler to the canister for the period indicated in Table 2 for sampling to 80%.

4. Disconnect the Restricted Sampler.

5. Verify canister pressure with gauge.
6. Replace cap, if any.
7. Fill out canister tag and documentation.
8. Place in shipping box and send to lab.

Table 2 Canister Fill Time in Minutes

		PN:01-39-RS-6		PN:01-39-RS-5		PN:01-39-RS-4		PN:01-39-RS-3		PN:01-39-RS-2		PN:01-39-RS-1	
Bottle/Vial	Part Number	13ccm		19ccm		38ccm		63ccm		150ccm		600ccm	
		50%	80%	50%	80%	50%	80%	50%	80%	50%	80%	50%	80%
40ml	29-BV040A	1.5	3	1	2	0.5	1	0.3	0.6	0.1	0.3	*	*
60ml	29-BV060A	2.3	4.3	1.5	3	0.8	1.5	0.5	1	0.2	0.4	*	*
8oz	29-BV230A	9	17	6	12	3	6	2	3.5	0.8	1.5	0.2	0.4
16oz	29-BV460A	18	34	13	23	6	12	4	7	1.7	3	0.4	0.7
32oz	29-BV920A	36	68	25	46	12	23	7.5	14	3	6	0.8	1.5

* Use PN: 01-39-RS-0 for fill rates less than .1 min

		PN:01-39-RS-6		PN:01-39-RS-5		PN:01-39-RS-4		PN:01-39-RS-3		PN:01-39-RS-2		PN:01-39-RS-1	
MiniCan	Part Number	13ccm		19ccm		38ccm		63ccm		150ccm		600ccm	
		50%	80%	50%	80%	50%	80%	50%	80%	50%	80%	50%	80%
200ml	29-MC200QT	8	14	5	10	2.5	8.5	1.5	3	0.7	1.3	0.2	0.3
450ml	29-MC450QT	17	32	12	22	6	11	3.5	7	1.6	3	0.4	0.7
600ml	29-MC600QT	23	43	16	29	8	15	5	9	2	4	0.5	0.9
1000ml	29-MC1000QT	39	76	27	49	13	25	8	15	3.5	6.5	0.9	1.5
1400ml	29-MC1400QT	54	100	37	69	18	34	11	21	5	9	1.2	2.2

Long Term Time Integrated Sampling
(0.5 to 24 hour)

Long Term vacuum sampling requires the use of a more sophisticated flow control system that can achieve flow rates down to 0.3 cc/min in order to fill a 450mL canister over 8 hours, or a 1.4L canister over 24 hours. Entech has done years of testing to develop the CS1200E flow controller that provides a lower stable flow rate than any other mechanical flow controller, while minimizing the internal volume and maximizing the inertness of the flow path. Several studies have been conducted to determine how best to perform accurate sampling while minimizing contamination. The result is the current CS1200 flow controller, which is available in both an Environmental version (CS1200Ex) and a personal sampling version (CS1200Px) as shown . The diaphragm of the CS1200 has been specifically designed to allow a constant flow from 30" down to just 2"Hgvacuum in the canister.

The CS1200 can be tailored for a particular flow range by selecting from the inlet restrictors shown in Table 3. The CS1200 also has a flow adjustment built into it for fine-tuning the flowrate, but this only provides a dynamic range of about 3-4x. In order to change from a 3 hour sampler to an 8 or 24 hour sampler, you must change out the flow restrictor element, then reset the flow rate. Setting the flow rate is done most rapidly using a digital flow meter as shown.

Since a little variation over time may occur, the flow is never set to exactly fill the canister to 100%. Instead, a target of about 90% is chosen, so even a +-10% variation after shipping will still result in a sampling event where flow remained constant through the entire sampling period. Refer to Table 4 for flow rate settings to achieve 90% filling of the respective canisters. The CS1200 comes with a document showing how a simple field test can also be performed without a flow meter by using a straightforward vacuum decay test to verify that the flow rate is correct. By simply attaching the CS1200 to the canister momentarily and then removing it, the gauge on the CS1200 can be monitored to see how long it takes for the pressure to drop from 20"Hg to 10" Hg. The internal volume on each CS1200E and CS1200P is virtually identical, so time can be converted to flow rate by referring to a table, which is provided with each CS1200E and P. This will help to verify that the sampling will occur properly.

CS1200E

CS1200P

Table 3

Part No.	Restrictor		Canister Fill Times					Replacement Restrictor
	Code	Flow Range	16oz Bottle	0.6L	1.0L	1.4L	6.0L	
39-CS1200E1 39-CS1200ES1*	1	40cc/min to 160cc/min	2 min to 12 min	3 min to 15 min	6 min to 25 min	8 min to 35 min	35 min to 2.5 hrs	39-23010 39-23015*
39-CS1200E2 39-CS1200ES2*	2	13.5cc/min to 54cc/min	8 min to 30 min	10 min to 35 min	20 min to 74 min	25 min to 100 min	2 hrs to 8 hrs	39-23030 39-23035*
39-CS1200E3 39-CS1200ES3*	3	5cc/min to 20cc/min	25 min to 90 min	30 min to 120 min	50 min to 3 hrs	70 min to 5 hrs	5 hrs to 20 hrs	39-23080 39-23085*
39-CS1200E4 39-CS1200ES4*	4	1.2cc/min to 6.8cc/min	1.2 hrs to 4 hrs	1.5 hrs to 5 hrs	2.5 hrs to 10 hrs	3 hrs to 12 hrs	12 hrs to 2 days	39-23240 39-23245*
39-CS1200E5 39-CS1200ES5*	5	0.4cc/min to 1.2cc/min	4 hrs to 12 hrs	5 hrs to 15 hrs	8 hrs to 24 hrs	20 hrs to 36 hrs	2 days to 7 days	39-24010 39-24015*

**Silonite® Coated*

Table 4

Bottle/Vial	Part Number	30 Min	1 Hour	3 Hours	8 Hours	24 Hours
16oz	29-BV460A	14ccm	7ccm	2.3ccm	9ccm	n/a
32oz	29-BV920A	28ccm	14ccm	5ccm	1.8ccm	.6ccm

MiniCan	Part Number	30 Min	1 Hour	3 Hours	8 Hours	24 Hours
450ml	29-MC450QT	14ccm	7ccm	2.3ccm	.9ccm	n/a
600ml	29-MC600QT	19ccm	10ccm	3.3ccm	1.3ccm	n/a
1000ml	29-MC1000QT	30ccm	15ccm	5ccm	1.9ccm	.6ccm
1400ml	29-MC1400QT	42ccm	21ccm	7ccm	2.6ccm	.9ccm

Again, the use of Silonite coated filters is not an option with Long Term Integration, as the same type of critical orifice is being used on the inlet to the CS1200 as the flow element. In this case, the sapphire orifice is not acting as a critical orifice, just as an inert, low surface area restrictor. The CS1200E and P have been designed to incorporate the filter at the very inlet in order to keep particulates out of the entire flow path. The CS1200Pis worn on a sampling belt, with an inlet line coming up to the breathing zone, where the filter is also located. The CS1200E has a short, candy-cane inlet with the filter contained on the inlet, under a stainless steel enclosure that keeps dust and volatile contaminants out of the flow controller and off the filter during shipping. This cover also acts to keep rain off of the filter, which might otherwise greatly impede flow through the filter.

Step-by-Step Long Term Sample Integration with the CS1200E

Before going out to the field, select a MiniCan or Bottle-Vac, and the appropriate CS1200E or P restrictor from Table 3 based on the sampling times required.
In the field:

1. Remove any cap or seal on the canister valve
2. Use a vacuum gauge to verify the Container is still under vacuum (PN 29-70010QT).
3. Connect the CS1200 sampler to the canister. The vacuum reading on the CS1200 should agree with step 2.

4. If verifying the flow rate in the field, perform one of the following, depending on what kind of canister valve is being used:
   a. For Nupro or Diaphragm valves: Turn off the valve and watch for the time needed for the CS1200 vacuum gauge to climb from 20"Hg to 10"Hg.

   b. For Micro QT valves: Totally remove the CS1200 from the canister. The Micro valve on the CS1200 will automatically seal, allowing flow only from the CS1200 inlet. Watch for the time needed for the CS1200 vacuum gauge to climb from 20"Hg to 10"Hg.
5. Re-attach the CS1200E to the sampler, or turn on the valve to start the flow.
6. Record the pressure on the CS1200 after the sampling period. If performing personal monitoring, the pressure should be recorded multiple times to validate constant sampling rate.
7. Close the valve (Nupro valve only) and remove the CS1200E from the canister.
8. Replace cap, if any.
9. Fill out canister tag and documentation.
10. Place in shipping box and send to lab.

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