Sample Canister Evaluation and Inertness Certification

Application Note:

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Authors
Doug Markle
Dan Cardin
Entech Instruments, Inc.
Simi Valley, CA 93065

Introduction

Stainless steel canisters offer a tremendous advantage over other air sampling media, namely Tedlar® bags and adsorbent traps. When canisters were first introduced, the “SUMMA” passivated canister was the only option available. Today, with the availability of electropolished, silica lined (Silonite™ and others), and glass (Bottle-Vac) canisters, as well as multiple valves and gauges to choose from, air monitoring personnel must be further educated on how to properly choose, clean, evaluate and certify a canister for TO14 and TO15 analysis. This document gives a background overview of different types of canisters as well as the procedure for properly certifying them for use.

Background

For chemicals to remain in the gas phase, the internal canister surface must be inert to minimize adsorption. Research efforts to create this level of inertness have led to SUMMA, electropolished, silica ceramic coated, and deactivated glass canisters. For more detail into the difference of each type of canister and properties, please refer to Entech Application Note Document 501, Understanding Sampling Canister Technology.

Due to the range of canister types and the wide variability of samples and conditions that each canister sees, it is a long established fact that not every canister will perform up to the original manufacturer's specifications. For this reason, canisters must be evaluated individually to ensure that all target compounds can be recovered after a reasonable holding time. Entech recommends that canisters go through the evaluation and certification process described in this document once every two years or whenever a canister is suspected of having a problem.

Figure 1 - Canister on the left is silica coated, whereas the rusty canister on the right is uncoated stainless steel, which is more subject to corrosion without the protective ceramic layer.

Concerns

A wide number of problems can cause a canister to perform poorly over time. Exposure to ozone, sand, grit, corrosive samples, pressurized high humidity samples,

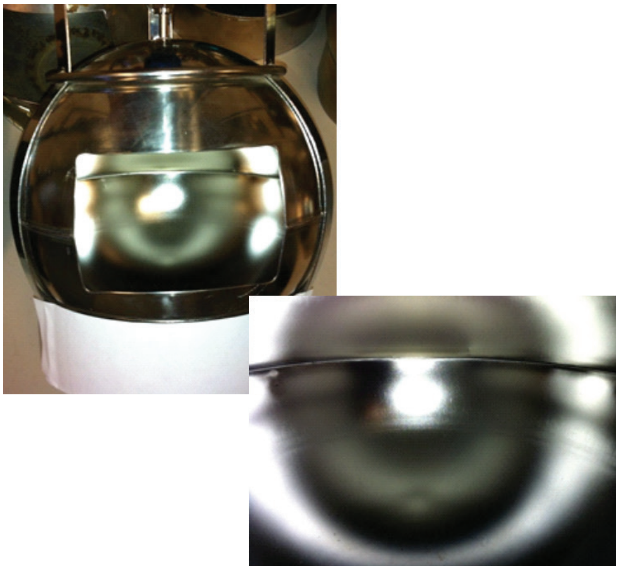

Figure 2 - This electropolished canister looked good both on the inside and outside but had virtually 0% recovery of Carbon Tetrachloride, indicating that there is exposed, catalytic iron on the surface.

Figure 3 - This rusty canister was still in use by a laboratory until it developed a leak.

Figure 4 - A canister which looks good on the outside can have rust and weld scars on the inside that will affect the stability of TO15 compounds.

or excessive moisture can all affect the canister. Other factors are the canister's surface coating or material, physical handling of the canister, valve type and sampling techniques.

Without proper testing, there is no way for a laboratory to know the quality of the data they will obtain from a canister. Photos of cut open canisters are shown here where rust and weld scars were preventing the recovery of several TO15 compounds. These canisters were probably never tested for inertness, even by the manufacturer.

Biannual Canister Certification

SUMMA and Silonite™ canisters have a virtually unlimited lifetime unless severely abused. Electropolished canisters have a considerably shorter lifespan due to the much thinner barrier between the sample and the surface Iron present in the stainless steel (70% iron in 304 stainless). Occasional testing of canister performance should be done to verify that the inside of the canister has not been compromised. Particles and/or heavy organics may build up enough in the canister to affect the recovery of compounds with lower vapor pressures, and can also result in carryover to later sampling events as these surfaces slowly outgas their impurities. The quality of the canister should be re- evaluated once every two years by filling the canister with a recovery standard. It is more challenging for a canister to maintain stable TO15 compound concentrations at low pressure and humidity. Low humidity conditions occur regularly in the winter when the outside temperature is lower than the ambient laboratory temperature. As the temperature increases for the canister containing a sample, the percent relative humidity (%RH) decreases. To show the canister will preform at all potential conditions, it should be evaluated under worst-case conditions. Each canister should be pressurized to within 1 psi of atmospheric pressure with a standard that is <15 %RH. The standard should be no more than 5 times the MDL for each compound. After filling the canister with the check standard, allow each canister to equilibrate for one week before analysis.

Below is an example of how this can be done easily in a laboratory.

1) Make an intermediate stock standard in a 6L canister

containing all of the reported analytes at 20 PPBv between 30-50 PSI Absolute (PSIA), depending on the volume needs of the laboratory for the month. Note: This standard can be used for up to one month for routine instrument calibration or until it reaches atmospheric pressure.

2) Verify the intermediate stock standard concentration by analyzing it under normal conditions at a volume that allows the analyte concentration to fall within the instrument's calibration curve. Note: The intermediate stock standard concentration should be re-verified any time during that month if an entire set of canisters fail the stability check.

3) Clean and fully evacuate the canister to be tested. Add 12ul of VOC free DI water to the top of the valve to provide a final humidity of about 10% at 20-22 deg C.

4) Using the Entech DDS (Digitial Diltuion System) add 0.75 psid (add 0.75 psi to whatever the initial vacuum reading is when the evacuated canister is attached and opened on the DDS) of the intermediate stock standard to the canisters to be tested.

5) Pressurize each canister prepared in Step 3 with dry Nitrogen to 15 psia (this will result in a 1 PPBv standard in the canister).

6) Close and disconnect the canister from the DDS.

Note: The 4700 can be used to automate both the initial creation of the 20PPBv stock canister, and its dilution into individual 6L canisters at 1PPBv. This is highly recommended when testing any more than 4-5 canisters per week.

7) Allow the canister to sit for one week before being analyzed for stability verification. Verify a minimum recovery of 0.75PPBv for every TO15 compound.

For canisters not meeting the required recovery (100%+-25%), a more involved cleanup may be possible. The manufacturer of each canister type should be consulted for an exact procedure to accomplish the more extensive cleanup. Contact Entech to learn more about the new "Silonite XR (Xtended Range) treatment of older Silonite canisters that can actually make them perform better than new. Very little can be done to fix electropolished canisters that have undergone corrosion or oxidation due to excessive exposure to ozone, water, or corrosive media (stack samples), as there is no easy way to cover up the catalytic iron that has become exposed on the internal surface.

Throughput and Logistics Concerns

Entech recognizes that this protocol will require the allocation of resources for the laboratory but would contend that this investment is critical for the canister method to remain the "gold standard" for air testing. To illustrate that it will not be too large of an investment of time and resources or be too time-consuming for the laboratory, below are practical examples of how this would look in different size labs.

Small-Medium Laboratories

A small-medium laboratory might have 100 canisters and one analytical system. This would correspond to one canister per week being analyzed for analytical standard recovery. This translates to just one canister of their 100 being out of service for any given week and one extra analytical run during that week. Within 2 years, all 100 canisters will be certified, assuming 2 weeks of down time every year.

Large Laboratories

A large laboratory might have 1500 canisters that are being serviced by four to eight analytical systems. If a laboratory had 1500 canisters, then approximately 15 canisters a week would be set aside for testing. If one system was used for one day to analyze these 15 canisters, then this would result in about 3.3% of that labs resources if they had 6 analytical systems running 5 days a week. In general, most labs do not run to 97% of full capacity, so the inclusion of the QA samples would not affect sample throughput. When very large projects are received, QA operations can be put off, with the potential for slightly higher QA efforts during slower periods.

Data

The following page contains data obtained by analyzing different coated and uncoated canisters both for stability and carry over potential. A higher than recommended concentration was used (10 PPBv instead of 1 PPBv), but the pressure was also set to 4.7

psi below atmospheric pressure (10 PSIA) to simulate a time integrated canister where sampling was stopped well below atmospheric pressure. Again, the lower the pressure, the greater the potential rate of analyte loss, as the resulting higher net diffusion rates allow faster interaction with the walls of the canister. From the data, it will be obvious that not only were some of the tested canisters unable to meet TO15 requirements, but these same canisters were harder to clean. Since the canisters with "active" surfaces are shown to retain a lot more contamination after cleaning, only inertness tested canisters should be considered for batch testing for cleanliness, where only 1 canister is tested to certify the entire batch. It is easy to see from the final two tables that inert and non-inert canisters do not clean up at the same rate.

6 Liter Canister 7 day Recovery Test - 10% RH Filled to 10 PSIA at 10 PPBv

	Silonite® Cans		**Summa® Cans**				**Uncoated Cans**			
Compound	SN:3662	SN:3661	SN:54106	SN:15275	SN:22094	SN:54102	SN:00405	SN:00490	SN:00548	SN:00408
Propene	9.58	9.73	8.87	7.49	8.89	6.88	8.8	9.04	9.01	9.05
Dichlorodifluoroethane	8.67	8.28	8.05	7.48	7.66	4.55	7.64	7.49	5.46	8.14
Chloromethane	8.5	8.53	7.91	5.94	7.79	5.98	7.82	7.92	7.4	7.89
Dichlorotetrafluorethane	7.94	7.99	7.46	5.52	7.28	5.24	7.27	7.38	6.3	7.43
Vinyl Chloride	8.38	8.39	7.69	5.82	7.7	5.84	7.65	7.79	7.54	7.83
1,3-Butadiene	8.53	8.46	7.84	6.05	7.93	6.03	7.8	8	7.82	8.08
Bromomethane	8.04	8.04	7.6	5.68	7.34	5.71	7.34	7.42	7.42	7.59
Chloroethane	8.43	8.53	7.94	6.02	7.79	6.06	7.66	7.83	7.88	7.99
Bromoethene	8.35	8.46	7.81	5.85	7.69	5.93	7.59	7.66	7.77	7.95
Trichlorofluoromethane	8.15	8.31	7.69	5.81	7.5	5.9	7.43	7.56	7.56	7.71
Acetone	9.28	11.59	10.02	13.07	8.84	9.68	10.4	11.7	10.08	10.79
Isopropyl Alcohol	8.75	8.86	8.13	10.92	8.26	6.63	6.68	6.97	9.25	5.78
1,1-Dichloroethene	9.03	8.96	8.35	6.13	8.32	6.17	8.26	8.41	8	8.47
Trichlorotrifluoroethane	9.04	9.08	8.4	6.33	8.31	6.42	8.28	8.39	8.42	8.48
Allyl Chloride	9.31	9.4	5.46	6.53	8.41	3.07 *	8.13	8.48	8.76	8.08
Methylene Chloride	9.3	9.31	8.55	6.59	8.48	6.57	8.52	8.63	8.71	8.68
Carbon Disulfide	9.03	9.16	8.37	6.34	8.32	6.36	8.52	8.58	8.49	8.55
trans-1,2-Dichloroethene	9.29	9.38	8.6	3.49	8.55	6.58	8.51	8.63	8.78	8.71
Methyl tert-Butyl Ether	9.29	9.35	8.35	6.51	8.63	6.48	8.46	8.56	8.81	8.51
Vinyl Acetate	9.33	9.34	**0.09 ***	3.74	8.1	**0.03 ***	**1.5 ***	**0.2 ***	8.87	**0.03 ***
1,1-Dichloroethane	9.19	9.28	8.39	6.42	8.47	6.44	8.33	8.42	8.67	8.45
2-Butanone	9.62	9.77	8.34	6.23	8.64	6.27	8.31	8.37	8.9	8.21
n-Hexane	9.7	9.62	8.86	6.77	8.76	6.73	8.68	8.9	8.97	9.04
cis-1,2-Dichloroethene	9.38	9.41	8.72	6.54	8.66	6.54	8.57	8.73	8.9	8.8
Ethyl Acetate	9.51	9.73	6.7	6.58	8.83	4.94	7.92	7.5	9.09	5.83
Chloroform	9.15	9.25	8.46	6.41	8.4	6.46	8.34	8.49	8.51	8.64
Tetrahydrofuran	9.57	9.82	8.63	6.87	8.94	6.53	8.52	8.71	9.16	8.5
1,1,1-Trichloroethane	9.36	9.45	8.62	6.5	8.61	6.44	8.47	8.67	8.77	8.69
1,2-Dichloroethane	9.29	9.4	8.61	6.52	8.49	6.54	8.49	8.64	8.73	8.74
Benzene	9.56	9.57	8.86	6.78	8.81	6.72	8.72	8.93	8.94	8.95
Carbon Tetrachloride	9.33	9.47	**2.27 ***	6.4	6.91	**0.04 ***	**1.71 ***	4.22	8.59	**0.96 ***
Cyclohexane	9.52	9.62	10.32	6.76	9.31	8.68	11.96	9.75	9.02	11.94

	6 Liter Canister 7 day Recovery Test - 10% RH Filled to 10 PSIA at 10 PPBv									
	Silonite® Cans		**Summa® Cans**				**Uncoated Cans**			
Compound	SN:3662	SN:3661	SN:54106	SN:15275	SN:22094	SN:54102	SN:00405	SN:00490	SN:00548	SN:00408
2,2,4-Trimethylpentane	13.42	10.97	10.17	7.43	11.14	9.45	11.61	11.61	12.45	11.34
n-Heptane	13.49	10.95	10.18	7.41	11.03	9.35	11.67	11.51	12.46	11.21
Trichloroethene	12.76	10.53	9.92	6.98	10.67	9.17	11.28	11.22	12.09	11.04
1,2-Dichloropropane	13.11	10.81	9.98	7.18	10.92	9.17	11.44	11.27	12.16	11.06
1,4-Dioxane	11.13	8.05	5.99	6.16	8.67	7.76	9.93	8.62	12.51	7.21
Bromodichloromethane	12.8	10.6	9.41	6.98	10.57	6.86	10.54	10.76	11.87	9.42
cis-1,3-Dichloropropene	13.01	10.75	9.36	6.99	10.78	8.08	11.2	11.27	12.16	10.81
4-Methyl-2-pentanone	13.35	10.79	5.8	7.27	11.23	6.37	8.41	8.08	12.57	6.49
trans-1,3-Dichloropropene	12.92	10.72	7.81	6.8	10.61	5.98	10.76	11	12.18	10.31
Toluene	13.34	10.86	10.05	7.5	11.08	9.28	11.57	11.52	12.36	11.3
1,1,2-Trichloroethane	13.3	10.82	10	7.29	11.14	9.06	11.47	11.52	12.35	11.24
2-Hexanone	12.82	10.33	4.54	6.93	10.61	5.07	6.76	6.23	12.56	4.39
Dibromochloromethane	13.18	10.9	9.19	7.11	10.74	4.62	10.05	10.76	12.15	7.78
Tetrachloroethene	13.35	10.85	10.18	7.24	11.16	9.17	11.6	11.51	12.42	11.14
1,2-Dibromoethane	12.84	10.53	9.63	6.93	10.73	8.56	11.2	11.07	12	10.86
Chlorobenzene	13.03	12.72	12.19	8.6	14.07	9.31	13.07	15.87	13.58	13.8
Ethylbenzene	13.27	12.72	12.14	8.77	14.29	9.69	13.21	15.88	14.11	13.66
m-Xylene	12.94	12.13	11.53	8.52	14	10	12.78	15.27	14.27	13.05
p-Xylene	12.21	11.99	11.12	8.17	13.5	8.98	12.43	14.75	13.15	12.65
Styrene	13	12.61	10.26	8.12	13.43	7.65	10.71	13.43	13	10.92
o-Xylene	13.14	12.59	11.84	8.7	14.25	9.85	13.01	15.62	14	13.49
Bromoform	12.88	12.71	10.49	8.41	13.24	**2.67 ***	10.27	14	13.14	6.99 *
1,1,2,2-Tetrachloroethane	12.78	12.47	10.99	8.39	13.47	8.2	12.5	15.12	12.97	13.05
4-Ethyltoluene	13.07	12.72	11.24	8.7	14.11	8.61	12.73	15.36	13.52	12.71
1,3,5-Trimethylbenzene	12.94	12.71	10.59	8.42	13.95	8.34	12.18	14.51	13.41	12.15
1,2,4-Trimethylbenzene	12.84	12.65	10.18	8.44	13.77	8.07	12.1	14.45	13.31	11.96
1,3-Dichlorobenzene	12.67	12.44	11.15	8.09	13.57	8.19	12.79	15.5	13.2	13.36
Benzyl Chloride	12.97	13.03	**0.09 ***	6.55	11.84	**0.10 ***	6.49 *	7.14	12.77	**2.62 ***
1,4-Dichlorobenzene	12.51	12.19	10.76	7.85	13.46	7.86	12.77	15.34	13.21	13.32
1,2-Dichlorobenzene	12.56	12.28	10.62	8.06	13.3	7.99	12.51	15.1	13.09	13.18
1,2,4-Trichlorobenzene	9.65	8.86	6.51	5.69	10.5	4.84	10.29	11.89	11.09	10.13
Hexachlorobutadiene	12.13	10.82	8.02	7.38	12.74	6.36	11.65	13.83	12.43	11.87

	6 Liter Canister Carryover Test 1ppm exposure for one day followed by 3 cycle cleaning, then evacuation to 50 mtorr. Oven at 80 deg. C									
	Silonite® Cans		Summa® Cans				Uncoated Cans			
Compound	SN:3662	SN:3661	SN:54106	SN:15275	SN:22094	SN:54102	SN:00405	SN:00490	SN:00548	SN:00408
Propene		0.09	0.07	0.1	0.11	0.07	0.05	0.06		0.11
Dichlorodifluoroethane										
Chloromethane										
Dichlorotetrafluorethane										
Vinyl Chloride										
1,3-Butadiene										
Bromomethane			0.06							
Chloroethane										
Bromoethene										
Trichlorofluoromethane										
Acetone			3.97	2.48	1.94	3.05	1.52	2.06	1.87	1.75
Isopropyl Alcohol			10.6	2.63	1.25	7.64	2.29	1.26	4.98	0.64
1,1-Dichloroethene										
Trichlorotrifluoroethane										
Allyl Chloride										
Methylene Chloride										
Carbon Disulfide										
trans-1,2-Dichloroethene										
Methyl tert-Butyl Ether										
Vinyl Acetate										
1,1-Dichloroethane										
2-Butanone			3.85	0.32	0.29	2.08	0.26	0.13	0.86	0.3
n-Hexane										
cis-1,2-Dichloroethene										
Ethyl Acetate			0.2		0.08	0.14				
Chloroform										
Tetrahydrofuran			6.77	1.81	0.08	3.9	0.81	0.2	2.66	
1,1,1-Trichloroethane										
1,2-Dichloroethane										
Benzene										
Carbon Tetrachloride										
Cyclohexane										

	6 Liter Can Carryover Test 1ppm exposure for one day followed by three cycle cleaning, then evacuation to 50 mtorr. Oven at 80 deg. C									
	Silonite™ Cans		Summa® Cans				Uncoated Cans			
Compound	SN:3662	SN:3661	SN:54106	SN:15275	SN:22094	SN:54102	SN:00405	SN:00490	SN:00548	SN:00408
2,2,4-Trimethylpentane										
n-Heptane										
Trichloroethene										
1,2-Dichloropropane										
1,4-Dioxane			13.54	3.4	0.84	8.89	0.98	0.27	3.3	0.05
Bromodichloromethane										
cis-1,3-Dichloropropene										
4-Methyl-2-pentanone			18.1	4.05	0.15	14.05	6.12	1.21	10.88	0.07
trans-1,3-Dichloropropene										
Toluene				0.05						
1,1,2-Trichloroethane										
2-Hexanone	0.13		22.89	3.22	0.58	17.96	8.05	0.95	11.88	0.13
Dibromochloromethane										
Tetrachloroethene										
1,2-Dibromoethane										
Chlorobenzene										
Ethylbenzene										
m-Xylene										
p-Xylene										
Styrene			0.16			0.11				
o-Xylene										
Bromoform										
1,1,2,2-Tetrachloroethane										
4-Ethyltoluene										
1,3,5-Trimethylbenzene										
1,2,4-Trimethylbenzene			0.08			0.06				
1,3-Dichlorobenzene										
Benzyl Chloride										
1,4-Dichlorobenzene						0.07				
1,2-Dichlorobenzene						0.06				
1,2,4-Trichlorobenzene	0.11	0.09	0.33	0.36	0.28	0.34	0.16	0.12	0.1	0.08
Hexachlorobutadiene			0.13		0.05	0.12				

Conclusion

There are canisters currently in use that are not producing TO15 acceptable analyses. Regular certification of canisters for their ability to recover the target compounds being reported by air laboratories is critical in getting both the correct analytical results, and preventing false positives due to failure in completely eliminating compounds collected from the previous sampling event. Certification every 2 to 3 years is a good compromise between maintaining good certainty in the results, without placing unnecessary burden on the TO15 laboratory.

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