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INTEGRITY OF VOA-VIAL SEALS

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Abstract

Preservation of soil samples for the analysis of volatile organic compounds (VOCs) requires both the inhibition of VOC degradation and the restriction of vapor movement in or out of the sample container. The control of VOC vapor movement is generally assured through the use of screw caps with polytetrafluoroethylene (PTFE) faced silicone septa that can be tightened to form a vapor lock within the volatile organic analysis (VOA) vial. The U.S. Environmental Protection Agency's (EPA) Region 7 laboratory expressed concern that visual imperfections in the glass lips and threads of VOA vials might allow VOCs to escape during storage. The objectives of this study were to determine if these imperfections lead to VOC losses and to identify an inexpensive screening test that could be used to distinguish between "defective" and competent vials.

Clear, 40-mL glass VOA vials manufactured by the four major U.S. glass manufacturers were tested for seal integrity. The vials were purchased precleaned, with the manufacturer's or distributor's choice of PTFE faced silicone septa. All 216 vials from each manufacturer (864 vials, total) were visually inspected and then vacuum-tested for seal integrity by evacuating the vials, glass lips down against a polished aluminum plate.

Visual inspection revealed a variety of imperfections ranging from small indentations, bumps, and scratches on vial threads or lips, through obvious defects, such as large indentations or grooves in the vial lips and chipped or broken glass. Imperfections were found on the lips or threads of 4% to 15% of the vials depending upon manufacturer.

The aluminum plate vacuum test proved to be unreliable in identifying potentially leaky vials. No vials formed a complete seal regardless of the presence of visual imperfections. However, from each set of manufacturer's vials, the ten vials with the highest vacuum readings and the ten vials with the lowest vacuum readings (80 vials, total) while the pump was running were selected for two more tests, a septa-sealed vacuum test and a VOC-loss test.

The septa-seal vacuum test was conducted twice on the 80 selected vials. No clear conclusion could be drawn about whether the flexibility of the silicone septa is sufficient enough to form a complete seal against VOC losses. For one manufacturer, the test was capable of identifying vials that would leak while for the other manufacturers, the test failed. The septa-seal vacuum test appears to be subject to a noticeable rate of false positives.

Mean VOC concentrations after 14 days storage generally were within ± 20% of the known concentration with a majority of the concentrations within ± 15% of their known values. There were no statistically significant differences in VOC concentrations between vials in the potentially leaky and control group for any of the manufacturers. Only 1 vial lost VOCs and that was due to a large chip in the vial's lip and neck. These findings indicate that the silicone septa are flexible enough to overcome most vial imperfections and form a complete seal against VOC loss. A careful inspection of the VOA vials prior to use to remove any vials with large and obvious imperfections should be sufficient to screen out vials that are subject to VOC losses.

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Acronyms

EPA	United States Environmental Protection Agency
HP	Hewlett Packard
PTFE	polytetrafluoroethylene
RSD	relative standard deviation
VOA	volatile organic analysis
VOC	volatile organic compound

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Introduction

Preservation of soil samples for the analysis of volatile organic compounds (VOCs) requires both the inhibition of VOC degradation and the restriction of vapor movement in or out of the sample container. VOC degradation is generally controlled by chilling the sample to 4° C (or in special cases, -20° C) and/or adding a preservative to the sample. For soils with VOC concentrations expected to be between 0.5 and 200 µg/kg, the addition of sodium bisulfate to reduce the sample's pH to ≤ 2 is required (EPA, 1996). However, the sampler is cautioned that for soils containing carbonate minerals, the addition of sodium bisulfate is inappropriate due to sample effervescence effectively purging the sample prior to analysis. In contrast, for soils with high VOC concentrations (VOC concentrations > 200 µg/kg), the addition of methanol is required.

Where the use of preservatives in the field is impractical or undesirable, a soil sample may be collected and temporarily stored in hermetically sealed samplers, such as the EnCore™ or SoilCore™ discrete samplers. Once the soil is sealed in the sampler, the sampler is chilled to at least 4° C for transport to the analytical laboratory. The collected soil sample is then transferred to a volatile organic analysis (VOA) vial and preserved (as appropriate) as soon as possible or, at least, analyzed within 48 hours of collection.

The control of VOC vapor movement is generally assured through the use of polypropylene screw caps with polytetrafluoroethylene (PTFE) faced silicone septa that can be tightened sufficiently enough to form a vapor lock within the VOA vial. Leaky VOA vial seals allow volatile contaminants to either escape or enter a sample; thereby, resulting in erroneous data. Sample integrity can be compromised by vapor losses or cross contamination that can occur during sample collection, transport, and storage. The current EPA method for the preparation of VOC samples, SW 846 Method 5035 (EPA, 1996), requires that VOA vials remain hermetically sealed until analysis by a purge-and-trap instrument capable of purging the sample by puncturing the septa of the open-top 40-mL VOA vial. If the samples remain hermetically sealed, the potential routes of sample vapor loss or contamination are limited to leaky seals or diffusion of VOCs through the septa.

Poor vial sealing can occur due to: (a) the presence of sand grains (or other particles) on the lip or threads of the VOA vials; (b) septa expansion and contraction during temperature fluctuations associated with sample cooling/freezing or sample warming and cooling cycles during shipment from the field to the laboratory; or (c) puncturing the septa. The single-most important factor in sealing soil samples for VOC analysis is to insure that the lip and threads of the vial are clean before sealing. Traces of soil or grit on the glass lip will compromise the seals. Hewitt et al. (1995) intentionally left soil on the lip of three 135-mL (4 oz) bottles and thoroughly cleaned three others. Water (125 mL), spiked with a methanol solution containing four VOCs, was added to each of the six bottles and analyzed after 5 days storage at 4° C. Samples stored with dirty closures had an average of 41% to 46% lower VOC concentrations than the samples stored in the bottles where the threads and lips were cleaned prior to sealing.

Another potential cause of poor vial sealing is suspected to be slight aberrations in the lip and threads of the glass VOA vials. Quick preliminary visual examination of numerous VOA vials revealed that imperfections (e.g., indentations, grooves, and bumps) in the vial lips exist and may be large enough to provide a pathway for VOC loss. However, it is unclear whether the flexibility of the septa is sufficient enough to control the losses potentially associated with the imperfections in the VOA vials. Therefore, the study objectives were to: (1) identify the type and extent of imperfections in the lips or threads of VOA vials made by different glass manufacturers, (2) determine whether the imperfections lead to a loss of VOCs or if the septa creates a vapor tight VOA vial seal, and (3) determine if an inexpensive screening test could be used to distinguish between "defective" and competent vials.

Materials and Methods

Vial Selection

Multiple VOA vial distributors (e.g. Fisher Scientific, Cole Parmer, I-Chem, Qorpak, Wheaton, etc.) were contacted to determine if they manufactured their vials or if they assembled the pieces purchased from different manufacturers. Most distributors indicated that they perform the following before marketing their products: (1) select a vial manufacturer and screen the glass vials to meet minimum quality control specifications, (2) select septa from any of a large number of laminators, (3) select a screw cap for the vial, and (4) perform precleaning steps, as necessary. As a result of the calls, it appears that four glass manufacturers supply nearly all the U.S. distributors with the 40-mL glass VOA vials. These manufacturers are: Chase Scientific Glass (Rockwood, TN), Comar Glass (Baltimore, MD), Kimble Glass Inc (Vineland, NJ), and Wheaton (Millville, NJ).

The study was originally designed to include vials obtained directly from the major glass manufacturers. However, only one manufacturer offered precleaned vials. Therefore, the remaining three manufacturer's glass vials were ordered precleaned from distributors (i.e., Eagle-Pitcher, I-Chem, and Qorpak). A total of 864 vials (216 vials from each of the four major glass manufacturers) were examined. All vials were clear borosilicate glass and came with the manufacturer's or distributor's selection of open-top screw caps, and 3.05 mm silicone, 0.127 mm PTFE faced septa.

Analytical Instrumentation

VOCs were introduced by closed-system purge-and-trap (SW-846 Method 5035) into a gas chromatograph with mass spectrometer detector (MSD) following SW-846 Method 8260A except calibration was only for the analytes of interest (EPA, 1996). The Varian Archon™ purge-and-trap autosampler in conjunction with a Tekmar 3000 sample concentrator and a Vocarb 3000 trap was used to extract the samples. All samples were analyzed on a Hewlett-Packard (HP) Model 5890 Series II gas chromatograph with a HP Model 5970 mass spectrometer and a 60-m, 0.25-mm i.d. RTX Volatilization/RTX 5022 fused silica capillary column. The

MSD was scanned from 35 to 300 m/z at 70 eV in the EI mode. The spectroscopic signal was analyzed using HP Chemstation software.

Procedures

Three types of tests, visual inspection, vacuum tests, and VOC measurements were used to assess the integrity of the vial seals. If a correlation between the visual or vacuum tests and the VOC measurements was observed, then one of the simple visual or vacuum tests may be offered as a screening method for *a priori* insurance that the vials to be used will seal properly.

Visual Inspection

All 216 vials from each manufacturer were uncapped and the glass lip and threads inspected for any defects. Slight imperfections consisted of: indentations or, conversely, bumps on the lip or threads; variability in the smoothness of the lip or threads; or variations in the glass thickness near the lip or threads. Obvious defects included chipped or broken glass, or clearly noticeable imperfections of the types described above. Vials were tracked by the serial number affixed to the vials, or numbered 1 through 216 if the vials did not have manufacturer assigned serial numbers (i.e., bar codes).

Plate Vacuum Test

A flat plate vacuum test was conducted on all 216 vials from each of the manufacturers to determine if the vial lip imperfections prevented the formation of a vacuum tight seal. Vials were placed such that the vial lip was in direct contact with a polished aluminum plate (Fig. 1). In the center of the plate, a small hole was drilled and brass swagelok fittings were used to connect the open hole to a 0.25 horse-power vacuum/pressure pump (Gast Manufacturing Corporation, Benton Harbor, MI). The swagelok nut on the top had the hex points ground nearly smooth to allow the 40-mL VOA vial (21.74 mm neck id) to fit directly over the nut. A grade AA accuracy vacuum gauge (Marsh PG-73, KW Instruments, Ontario CA) was connected between the vial and a valve used to isolate the gauge and vial from the pump. No grease or other sealant was used in this test.

Vials were placed on the plate one at a time. The vacuum pump was turned on and a maximum vacuum reading was obtained in 30 seconds. While the vacuum pump was turned on, the readings remained stable. If the vial was isolated from the pump, the vacuum dissipated within 1 to 5 seconds indicating an incomplete seal between the aluminum plate and VOA vial. Therefore, the vacuum attained for each vial after 30 seconds was recorded for the test result.

After conducting this test, data were ranked (lowest to highest vacuum obtained) for each set of vials. The 10 vials with the lowest vacuum readings from the plate vacuum test and 10 vials with the highest vacuum readings were selected as “potentially leaky” and control vials, respectively, for each manufacturer. These vials were designated by manufacturer (A through D)

Figure 1. Aluminum plate vacuum test apparatus.

and numbered 1 through 10 for the vials with the lowest vacuum readings and 20 through 29 for the vials with the highest vacuum readings.

Septa-Sealed Vacuum Test

In the second vacuum test, vials were evacuated with the septa and open-top screw caps fastened in place. The screw caps were hand tightened until a dimple formed in the center of the septum. Two needles were inserted into the septum, the first needle was connected to the vacuum gauge and the second needle was clamped to a hose connected to the vacuum pump. Sturdy 18-gauge needles were used in this test. Smaller gauge needles tended to core the septa and bend too easily, causing more problems than the heavy gauge needles. The silicone appeared to seal after puncturing, leaving a visible puncture mark in the PTFE only.

The needles were inserted approximately 2 mm from and on opposite sides of the center point. Vials were evacuated to the capacity of the vacuum pump (i.e., 18620 ± 380 mm Hg). The evacuation needle was then removed leaving the vacuum gauge needle in place. The vacuum was noted and the needle was removed. After 3 days and 7 days, the vacuum remaining in each of the vials was measured. Puncture points for subsequent vacuum measurements were located approximately 2 mm off the center point and 90° from the prior insertion points.

VOC Loss Test

To monitor VOC losses from the sealed vials, VOC-spiked water was added to each of the 80 test vials. A bulk aqueous solution containing 50 ng/mL of each of the following analytes was prepared: acetone, benzene, chlorobenzene, 1,1-dichloroethene, methylene chloride, toluene, and trichloroethene. The spiked water was acidified with sulfuric acid to a pH $\leq$ 2 and transferred to a Tedlar bag. Approximately 5 mL of VOC-spiked water was added to each of the test vials by gravity flow through PTFE tubing. Each vial was weighed before and after the addition of the spiked water to calculate the spike addition to individual vials.

Vials were sealed, stored upright at 4° C, and VOC concentrations were measured after 14 days. Vials from the four manufacturers were prepared on four separate days to allow adequate time for the analysis. Duplicate samples were prepared by washing the vials after the first test was completed (water rinse, methanol rinse, and 105° C oven dry for 4 hours) and repeating the same spiking/storage/analysis procedure using a new septum for each vial. Internal standards (pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4) and system monitoring compounds (1,2-dichloroethane-d_4, toluene-d_8, and bromofluorobenzene) were added by the Archon™ purge-and-trap autosampler just prior to analysis.

VOC Gain Test

To monitor VOC gains from external contamination sources through the septa of sealed vials, 5 mL of deionized water were added to each of the 80 test VOA vials. The vials were capped with new, unpierced septa and placed in a 1 gallon paint can. An open vial containing 5 mL of methylene chloride was placed in the center of the paint can prior to closure. Samples were stored at room temperature for 14 days and then analyzed following SW-846 Methods 5035 and 8260A.

Results

Visual Inspection

Imperfections were observed in 15 out of 216 vials from manufacturer A, 8 out of 216 vials from manufacturer B, 32 out of 216 from manufacturer C, and 13 out of 216 vials from manufacturer D (Appendix A). The imperfections noted for manufacturer A vials were minor indentations along the lip, which could not be felt while running one's finger around the lip, but could be seen when the vials were held up to the light and rotated. Two of the eight imperfect vials from manufacturer B were observed to have somewhat larger indentations on the lip and one vial had a chip in the glass threads. The remaining five vials from manufacturer B had minor indentations along the lip. Imperfections in the manufacturer C vials included: seven vials with dips (i.e., large indentations or grooves) in the glass or uneven lips (i.e., where one side of the lip was obviously lower than the other side); one vial with a chipped thread; one vial with a small bump on the lip; and the remainder of the vials had indentations that could be seen when held up to the light. One vial from manufacturer D had a major defect, a chip in the lip that extended down the side of the neck. One vial had a crack in its neck while minor chips in the neck were observed on six other manufacturer D vials. The remaining five vials had chips on their lips.

Plate Vacuum Test

The vacuum system was capable obtaining a vacuum of 18620 ± 380 mm of Hg. Vacuum readings obtained in the vials after 30 seconds with the pump running ranged from 3800 to 19000 mm Hg (Appendix A). However, when the valve to the vacuum pump was turned off, the vacuum dissipated within 5 seconds. None of the vials sealed completely against the aluminum plate. Generally, the larger the visual imperfections, the worse the vial performed on the plate vacuum test. Very small or minor imperfections tended not to effect the results of the plate vacuum test.

Vacuum readings for the "potentially leaky" vials ranged from 3800 to 13680 mm Hg (Table 1). In contrast, in the control vials, vacuum readings were consistently greater than 16720 mm Hg and were as high as a full vacuum reading of 18620 mm Hg. Interestingly, while no visible imperfections were identified for any of the control vials, both imperfect and visually

Table 1. Results of Plate Vacuum Test for Selected Vials.

Vial ID	Serial No.	Visual defects	Plate Vacuum (mm Hg)
A1	5979	Y	5624
A2	6031	Y	6840
A3	4523	Y	7068
A4	5971	Y	7220
A5	4530	Y	7448
A6	6060	Y	8208
A7	5929	Y	8740
A8	6047	N	8740
A9	4564	N	9576
A10	6013	Y	10336
A20	5988	N	18620
A21	6025	N	18620
A22	4515	N	18468
A23	4567	N	18468
A24	6057	N	18392
A25	4471	N	18316
A26	4536	N	18316
A27	6061	N	18316
A28	4563	N	18316
A29	4568	N	18240

Table 1. Results of Plate Vacuum Test for Selected Vials (cont.).

Vial ID	Serial No.	Visual defects	Plate Vacuum (mm Hg)
B1	29200	Y	5168
B2	29214	Y	7144
B3	30547	N	10260
B4	29232	N	10640
B5	29163	N	10640
B6	29205	Y	10868
B7	29228	N	11400
B8	29223	N	11476
B9	29189	N	11476
B10	30584	N	11628
B20	29166	N	18468
B21	30530	N	18468
B22	30568	N	18392
B23	29220	N	18240
B24	30630	N	18164
B25	29196	N	18164
B26	30586	N	17860
B27	29235	N	17860
B28	30525	N	17860
B29	30508	N	17860

Table 1. Results of Plate Vacuum Test for Selected Vials (cont.).

Vial ID	Serial No.	Visual defects	Plate Vacuum (mm Hg)
C1	3291	Y	3800
C2	5016	Y	5320
C3	3982	Y	5320
C4	4071	Y	5548
C5	4351	Y	5700
C6	4254	Y	5776
C7	4399	Y	6688
C8	3893	Y	8208
C9	4583	Y	9576
C10	3337	N	8576
C20	5025	N	17708
C21	4570	N	17480
C22	4143	N	17480
C23	4777	N	17480
C24	4360	N	17328
C25	3365	N	17328
C26	4490	N	17328
C27	3541	N	17328
C28	4623	N	17328
C29	4266	N	17328

Table 1. Results of Plate Vacuum Test for Selected Vials (cont.).

Vial ID	Serial No.	Visual defects	Plate Vacuum (mm Hg)
D1	80	Y	5928
D2	117	Y	9728
D3	5	Y	12388
D4	183	N	12388
D5	213	N	12920
D6	38	N	13148
D7	161	N	13148
D8	16	N	13680
D9	48	N	13680
D10	202	N	13680
D20	212	N	17860
D21	156	N	17708
D22	159	N	17708
D23	165	N	17480
D24	167	N	17480
D25	67	N	17480
D26	17	N	17480
D27	7	N	17480
D28	14	N	17328
D29	32	N	17328

imperfection-free vials were found in the potentially leaky vials. In general, the imperfection-free vials in the potentially leaky group held the greater vacuum during the test.

Septa-Sealed Vacuum Test

The septa-sealed vacuum test was conducted twice to confirm the results. A loss of 3800 to 4560 mm Hg occurred each time the vacuum gauge was inserted into a vial caused by the dead air space in the vacuum gauge and needle. Vacuum readings that dropped by more than 4560 mm Hg by day 3 or more than 9120 mm Hg by day 7 were considered to be leaky. Vials that had readings of $\leq$ 7600 mm Hg were considered to have catastrophically failed to seal. Vials that successfully held their vacuum after 3 and 7 days in at least one test were considered to be capable of forming a complete seal (i.e., the silicone septa was flexible enough to fill any potential leaks caused by the vial imperfections).

Two vials from both the potentially leaky (vial numbers 1 - 10) and control groups (vial numbers 20 - 29) from manufacturer A were leaky after day 3 during the first test (Table 2). Three of those vials catastrophically failed to seal (i.e., vials A9, A21, and A24). After 7 days, 2 other vials, A5 and A28 had catastrophic seal failures. Upon retesting the vials, vial A24 again catastrophically failed and vials A21 and A28 successfully maintained its seal after 3 days but failed to hold a vacuum after 7 days.

All the potentially leaky vials and 6 control vials made by manufacturer B were leaky, with one catastrophic leak in vial B3, during the first septa-sealed vacuum test (Table 2). Upon retesting, all of the potentially leaky vials and 3 of the originally identified leaky vials in the control group (i.e., vials B20, B21, and B28) remained leaky.

Similar to the vials from manufacturer B, vials from manufacturer C gave very poor results on the first septa-sealed vacuum test with only one vial not being classified as leaky or having catastrophically failed after 3 or 7 days. It was noticed that the septa on these vials were more flexible than the septa on other vials. These septa would flex during puncturing by the needle gauge, causing leakage if the puncture was near the center. In the second test, all septa were punctured approximately 2-mm off the center point. During the retest, only 5 vials were deemed leaky and all those vials were from the potentially leaky group.

The three vials from manufacturer D that had visual defects were leaky or failed catastrophically during the first septa-sealed vacuum test. During retesting, all three vials again either failed catastrophically (i.e., vials D1 and D3) or were leaky (i.e., vial D2) after 3 days and catastrophically failed after 7 days. Vial D1 had a major chip in the lip and was expected to leak. The glass lip of vial D3 was slightly raised on one side, but this vial had maintained a partial vacuum during the plate vacuum test, reaching a maximum vacuum of 12388 mm Hg (Table 1). Only one of the control group vials failed catastrophically during the first test; however, the same vial (i.e., D26) maintained its vacuum seal during the second septa-sealed vacuum test.

Table 2. Septa-sealed vacuum test results*.

	Vacuum (mm Hg)					
Vial ID	Initial	Day 3	Day 7	Initial-D	Day 3-D	Day 7-D
A1	18430	14250	11590	18620	14440	≤1520
A2	18430	14250	11438	18620	14440	3230
A3	18430	14250	11400	18620	14630	11400
A4	18430	14250	11590	18620	12540	≤1520
A5	18468	14250	1900	18620	14440	11020
A6	18468	13680	10260	18620	14630	11020
A7	18468	13680	10070	18620	14820	11400
A8	18620	11856	7790	18620	14440	11590
A9	18620	5016	≤1520	18620	14630	9880
A10	18620	14250	11210	18620	14440	11020
A20	18620	14592	11590	18620	14820	≤1520
A21	18620	6460	4560	18620	14630	≤1520
A22	18620	14653	11590	18620	15010	≤1520
A23	18620	14630	11590	18240	15010	11590
A24	18620	≤1520	≤1520	18810	≤1520	≤1520
A25	18544	14630	11590	18810	14630	10830
A26	18620	14630	11590	18810	14820	≤1520
A27	18620	14440	11400	18810	14440	11020
A28	18620	14136	≤1520	19000	14440	9310
A29	18620	14630	11590	19000	6080	≤1520
B1	18620	12730	8930	19000	11590	7030
B2	18620	12730	8930	19000	11970	7790
B3	18620	4750	≤1520	19000	12730	8550
B4	18620	12350	8550	19076	2280	≤1520
B5	18620	11590	7258	19076	5320	1710
B6	18620	13718	10450	19152	14440	10830
B7	18620	10260	5700	19152	11970	7410
B8	18620	11438	7220	19190	11020	6460
B9	18620	13110	9500	19190	13490	9500
B10	18620	11552	7410	19190	13300	9120
B20	18620	13300	9880	19190	13490	9690
B21	18620	13110	9462	19190	8740	3800
B22	18620	14250	11020	18810	12350	9310
B23	18620	14136	11248	18810	8740	5510
B24	18620	14098	10868	18810	13300	9500
B25	18620	14098	11020	19000	13870	10450
B26	18620	13870	10488	19000	14440	11210
B27	18620	10602	5168	19000	14630	11780
B28	18620	8360	4180	19000	12350	7600
B29	18620	13718	10450	19000	14820	9120

Table 2. Septa-sealed vacuum test results* (cont.).

	Vacuum (mm Hg)					
Vial ID	Initial	Day 3	Day 7	Initial-D	Day 3-D	Day 7-D
C1	18620	≤1520	≤1520	19190	14630	10830
C2	18620	≤1520	≤1520	19000	13110	8930
C3	18620	12540	≤1520	19000	8170	3420
C4	18620	≤1520	≤1520	18620	15010	11780
C5	18620	12008	9690	19190	15010	11780
C6	18620	≤1520	≤1520	19190	14820	11400
C7	18620	≤1520	≤1520	19190	12160	7600
C8	18620	14440	4940	19190	14630	10450
C9	18620	1710	≤1520	19190	13490	9500
C10	18620	≤1520	≤1520	19190	11400	6650
C20	18620	≤1520	≤1520	19190	14630	11020
C21	18620	9880	≤1520	19190	14820	11590
C22	18620	11210	8550	19190	15010	11780
C23	18620	2280	≤1520	19190	15010	11780
C24	18620	10450	8056	19190	15010	11780
C25	18620	≤1520	≤1520	19190	15010	11780
C26	18620	14250	6080	19190	15010	11780
C27	18620	9348	4370	19228	15010	11590
C28	18620	14592	11590	19228	15010	11780
C29	18620	≤1520	≤1520	19228	15010	11780
D1	17480	≤1520	≤1520	18620	≤1520	≤1520
D2	18620	12388	8550	19380	11780	7220
D3	18620	≤1520	≤1520	19380	≤1520	≤1520
D4	18620	14250	11210	19380	14630	11210
D5	18620	14250	11210	19380	14630	11210
D6	18620	14212	11020	19380	14630	11210
D7	18620	14250	11020	19380	14630	11210
D8	18620	14250	11058	19380	≤1520	≤1520
D9	18620	14250	11172	19380	14630	11210
D10	18620	14060	10830	19380	14820	11210
D20	18620	14288	11362	19380	14630	11210
D21	18620	14250	11020	19380	14630	11210
D22	18620	14250	11020	19380	14630	11210
D23	18620	14250	11210	19380	≤1520	≤1520
D24	18620	14212	11020	19380	14820	11020
D25	18620	14288	11248	19380	14630	11400
D26	18620	≤1520	≤1520	19380	14630	11210
D27	18620	14250	11172	19380	14630	11210
D28	18620	14288	11210	19190	14630	11020
D29	18620	14288	11210	19190	14630	11400

* - Second run for all vials labeled "-D".

VOC Loss Test

Nearly all mean VOC concentrations after 14 days were within ± 20% of the initial VOC concentrations indicating little to no loss of VOCs during storage except for acetone in vials from manufacturer C (Table 3). The first analytical runs were performed on vials from manufacturer C. Acetone appeared to require a number of samples be run before the trap was properly "conditioned." Therefore, the "noise" in the acetone recoveries is unlikely to be related to the condition of the vial seals.

The somewhat consistently lower VOC recoveries observed for vials from manufacturer C can be attributed to instrument instability (Table 3). Vials from each manufacturer were run as a batch, alternating the potentially leaky and control vials in sequence to even out instrument drift that tends to occur over the 14 hour batch runs (Appendices B and D). VOC concentrations in manufacturer C vials tended to be lower near the end of the analytical run, but recovered to the initial values before the run ended (Appendix B - Tables B2-5 and B2-6, Appendix D). The influence of this instrument fluctuation on VOC concentrations is difficult to assess; however, the lower concentrations are more likely due to an artifact of the analytical system rather than caused by leaky vial seals.

Precision among the vials was acceptable with RSDs of ≤ 20% with one exception (Table 3). A RSD of 26% was found for 1,1-dichloroethene in the control vials from manufacturer C.

Upon examination of individual sample data, only vial D1 was clearly leaky (Appendix B). The chip in the side of the lip was so large that the vial would not seal. No data are reported for this vial because the recoveries of internal standards, added just prior to purging, were well below the QC criteria (Appendix D).

No statistically significant differences were identified between VOC concentrations in the potentially leaky and control group vials from the same manufacturer (Table 3). The maximum absolute concentration difference between the two vial groups was 2 µg/mL.

VOC Gain Test

Only 3 vials from this test were analyzed due to overwhelming concentrations of methylene chloride found in each of the tested vials. The resultant chromatographic peaks were so broad and the concentrations so far above the calibration range that no further analytical testing was performed. The results of this test indicate that the septa could not prevent sample cross contamination by methylene chloride. Whether the cross contamination was due to poor seals or diffusion through the septa is not be positively known although the later explanation is most probable.

Table 3. Summary of VOC-Loss Test Results.

	VOC Concentration, (ng/mL)							
	A1-A10		B1-B10		C1-C10**		D1-D10†	
	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Acetone	36	8	37	11	28	7	39	10
1,1-Dichloroethene	40	5	40	8	35	17	37	11
Methylene Chloride	57	2	61	5	53	6	56	5
Benzene	44	5	41	7	40	10	41	7
Trichloroethene	38	5	38	8	33	9	33	9
Toluene	40	5	37	8	35	9	36	8
Chlorobenzene	38	5	37	8	34	9	34	9
	A20-A29		B20-B29		C20-C29		D20-D29†	
	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Acetone	37	5	37	11	27	7	37	8
1,1-Dichloroethene	40	5	41	7	34	26	38	5
Methylene Chloride	57	4	61	3	53	9	57	7
Benzene	44	5	42	5	39	15	42	5
Trichloroethene	38	5	38	8	32	19	34	3
Toluene	39	5	37	8	34	14	37	3
Chlorobenzene	37	5	37	8	33	9	35	6

* - Mean and relative standard deviations (RSD) of ten potentially leaky vials (1 through 10) and ten control vials (20 through 29) for manufacturers A through D.

** - data are mean and RSDs of 8 vials (n=8).

† - data are mean and RSDs of 9 vials (n=9).

Summary and Conclusions

Visual inspection of numerous VOA vials from the four major manufacturers in the United States found minor imperfections ranging from small indentations, bumps, scratches on vial threads or lips, through obvious defects, such as large indentations or grooves in the vial lips and chipped or broken glass. A less obvious imperfection that could affect the ability of a vial to

seal completely was uneven rims in which one side of the vial's neck was clearly longer than the other side. Observed imperfections rates were 7, 4, 15, and 6% for manufacturer A, B, C, and D, respectively. Vials from manufacturer C had over twice as many imperfections (i.e., 32 out of 216) as vials from the other manufacturers.

An aluminum plate vacuum test was developed as a means to perform a quick and simple test to determine if a vial will form a complete vacuum seal. Unfortunately, no matter how smooth the plate's surface was, none of the vials sealed completely against the plate. With the vacuum pump on, some vials were capable of reaching the pump's maximum pressure; however, when the pump was turned off, the vacuum quickly dissipated. These results make the value of the aluminum plate vacuum test in selecting whether or not a vial will obtain a complete seal against VOC loss highly questionable.

A septa-sealed vacuum test was conducted to determine if the septa were flexible enough to form a complete seal even in the presence of vial imperfections. The results of this test were relatively inconsistent with the prior two tests. The vials from manufacturer A with visual imperfections did not lose their vacuum seal. In stark contrast, the only vials that failed to hold a vacuum were free from visual defects or were in the vial control group. All vials, with or without visual imperfections, in the potentially leaky group and 3 vials from the control group of manufacturer B were leaky. The aluminum plate vacuum test appeared to be a viable screening option for manufacturer B's vials although some false positives (i.e., vials falsely declared leaky) did occur. Vials made by manufacturer C had half of the vials in the potentially leaky group fail to hold their vacuum and the presence of a visual imperfection could not be used to clearly identify which ones. However, due to greater flexibility in the septa, the analyst had to be sure that the needle punctured the septa within 2 mm of the center or else the potential for seal leakage markedly increased. For manufacturer D, the presence of visual imperfections clearly indicated which vials would fail to hold their vacuum. All 3 vials with imperfections catastrophically failed to hold a vacuum while the remaining 7 vials identified as potentially leaky remained sealed after 7 days. No clear conclusion can be drawn based on the septa-sealed vacuum test about whether the flexibility of the silicone septa is sufficient enough to form a complete seal against VOC losses during storage. This test was subject to a noticeable rate of false positives.

Mean VOC concentrations after 14 days storage generally were within ± 20% of the known concentration with a majority of the concentrations within ± 15% of their known values. There were no statistically significant differences in VOC concentrations between vials in the potentially leaky and control groups for any of the manufacturers. Only 1 vial lost VOCs and that was due to a large chip in the vial's lip and neck. These findings indicate that the silicone septa are flexible enough to overcome most vial imperfections and form a complete seal against VOC loss. Further, the use of the other tests (excluding visual inspection) performed in this study are unnecessary to screen for potentially leaky vials. A careful inspection of the VOA vials upon receipt (or at least, prior to use) to remove any vials with large and obvious imperfections

should be sufficient to screen out vials that are subject to VOC losses through inadequate septum sealing.

It should be noted that when puncturing the septa, the point of entry of the sparging needle on the purge-and-trap unit should be in the center (or within a few mm) of the septa. If it is not in or near the center, differences in septa flexibilities may result in a loss of the vial's vapor tight seal. A study to evaluate the properties of septa that influence their flexibilities and thus, their sealing potential, may be warranted.

References

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Hewitt, A.D., T.F. Jenkins, and C.L. Grant. 1995. Collection, handling, and storage: Keys to improved data quality for volatile organic compounds in soil. Am. Environ. Lab. 2:25-28.

APPENDIX A[1]

Visual Inspection Log and Plate Vacuum Test Results by Vial

[1] NOTE: Vacuum readings presented in the following tables are directly from the vacuum gauge and have the units of inches Hg. To convert from inches Hg to mm Hg: 760 mm Hg = 1 inch Hg.

APPENDIX B

Individual VOA Vial Analytical Results by Manufacturer

Table B2-1. Analytical Results for potentially leaky vials from manufacturer A*.

	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A5D
	VOC Concentration, (ng/mL)										
Acetone	40	35	36	38	38[D]	34	31	37	34	33	26
1,1-Dichloroethene	40	38	38	36	39	41	41	41	41	42	36
Methylene Chloride	56	55	56	55	57[D]	57	57	58	57	59	41
Benzene	45	42	42	41	43	46	44	45	44	46	39
Trichloroethene	39	36	35	35	38	42	39	39	40	41	32
Toluene	40	37	37	36	39	42	40	41	41	42	33
Chlorobenzene	39	36	35	34	37	41	38	39	40	41	38
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichlorethane-d_4	88	88	90	89	87	88	89	91	85	85	76
Toluene-d_8	91	92	93	93	91	92	92	93	91	90	73[R]
Bromofluorobenzene	84	84	83	83	83	83	82	83	83	83	83

* - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-2. Analytical Results for control vials from manufacturer A*.

	A20	A21	A22	A23	A24	A25	A26	A27	A28	A29	A25D
	VOC Concentration, (ng/mL)										
Acetone	37	35	40	42	35	38	35	39	35	38	29
1,1-Dichloroethene	36	37	40	39	39	43	41	41	40	42	36
Methylene Chloride	53	55	56	56	56	58[D]	57	59	57	59	38
Benzene	40	41	44	43	42	47	45	44	44	45	38
Trichloroethene	35	35	37	36	36	42[D]	38	40	39	40	30
Toluene	36	37	38	37	37	42	40	41	40	41	32
Chlorobenzene	34	35	35	35	35	40	38	39	38	40	34
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichloroethane-d_4	89	91	90	89	89	95	89	91	89	91	78
Toluene-d_8	93	93	94	93	93	97	93	93	92	92	74[R]
Bromofluorobenzene	85	84	84	83	85	87	83	84	82	81	83

* - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-3. Analytical Results for potentially leaky vials from manufacturer B[*].

	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B5D
	VOC Concentration, (ng/mL)										
Acetone	39[C]	39[C]	37[C]	37[C]	40[C]	39[C]	35[C]	27[C]	41[C]	37[C]	31[C]
1,1-Dichloroethene	43	37	33	38	40	40	42	39	42	45	50
Methylene Chloride	61	58	57	60	62	60	61	61	63	66	58
Benzene	44	40	36	40	41	42	43	40	41	45	46
Trichloroethene	41	37	31	37	37	39	39	35	38	42	37
Toluene	40	37	31	36	36	37	38	34	37	41	39
Chlorobenzene	40	37	31	36	36	37	38	34	38	40	36
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichlorethane-d_4	89	87	89	89	88	88	88	87	88	89	94
Toluene-d_8	89	90	90	91	90	91	91	90	90	91	89
Bromofluorobenzene	87	85	84	84	85	83	84	84	84	85	82

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-4. Analytical Results for control vials from manufacturer B[*].

	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B25D
	VOC Concentration, (ng/mL)										
Acetone	34[C]	38[C]	39[C]	38[C]	39[C]	43[C]	37[C]	32[C]	31[C]	36[C]	38[C]
1,1-Dichloroethene	41	40	36	42	41	40[D]	44	38	43	45	51
Methylene Chloride	59	61	59	63	62	59	64	60	63	64	59
Benzene	42	42	37	43	41	41	44	40	44	45	47
Trichloroethene	39	38	32	40	38	37	40	35	41	42	37
Toluene	38	38	31	38	37	36	39	34	39	41	40
Chlorobenzene	38	38	30	38	37	36	39	33	40	41	36
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichlorethane-d_4	87	88	87	84	88	88	89	87	87	86	97
Toluene-d_8	89	89	89	90	90	90	91	90	90	91	90
Bromofluorobenzene	88	87	85	83	85	84	86	84	89	85	84

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-5. Analytical Results for potentially leaky vials from manufacturer C[*,].**

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C5D	C7D	C8D
	VOC Concentration, (ng/mL)												
Acetone	29[C]	26[C]	30[C]	25[C]	27[C]	27[C]	24[C]	nr[T]	32[C]	26[C]	27	32[C]	32[C]
1,1-Dichloroethene	40	33	38	34	28	40	6[D]	nr[T]	27	42	46	50	48
Methylene Chloride	53	52	56	52	49	54	30[D]	nr[T]	50	58	56	58	57
Benzene	43	38	41	38	34	43	17[D]	nr[T]	35	44	40	46	44
Trichloroethene	37	32	34	30	28	36	13[D]	nr[T]	29	36	32	37	33
Toluene	39	34	36	33	31	38	17[D]	nr[T]	32	38	34	39	37
Chlorobenzene	38	33	34	31	31	36	20[D]	nr[T]	32	436	30	35	33
	System Monitoring Compound (SMC), % Recovery												
1,2-Dichlorethane-d_4	90	91	89	88	89	87	87	nr[T]	93	90	88	90	89
Toluene-d_8	89	89	88	89	89	89	90	nr[T]	90	89	94	95	98
Bromofluorobenzene	80	81	81	83	81	80	79	nr[T]	82	79	91	86	88

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.
[**] - nr = not reported (see text for discussion).

Table B2-6. Analytical Results for control vials from manufacturer C[*].

	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C25D
	VOC Concentration, (ng/mL)										
Acetone	27[C]	29[C]	29[C]	25[C]	26[C]	29[C]	27[C]	25[C]	30[C]	26[C]	32[C]
1,1-Dichloroethene	39	33	39	38	42	43	21	23	22	42	49
Methylene Chloride	55	53	56	55	58	56	43	47	47	58	58
Benzene	43	37	40	41	44	44	30	32	32	44	43
Trichloroethene	36	30	33	34	38	38	24	26	25	38	34
Toluene	38	33	35	36	38	39	27	28	29	39	37
Chlorobenzene	36	32	33	34	37	37	28	29	29	36	33
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichlorethane-d_4	91	89	90	89	87	90	86	87	91	89	90
Toluene-d_8	89	89	89	90	88	91	89	89	90	89	93
Bromofluorobenzene	89	82	82	83	79	82	80	82	80	80	88

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-7. Analytical Results for potentially leaky vials from manufacturer D[*].

	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D5D
	VOC Concentration, (ng/mL)										
Acetone	nr	37	46	38	35[D]	40	37	40	41	33	21[C]
1,1-Dichloroethene	nr	32	29	37	38	38	39	39	40	41	38
Methylene Chloride	nr	51	52	56	57	57	58	59	59	59	50
Benzene	nr	36	36	41	43	41	43	43	43	44	41
Trichloroethene	nr	26	29	33	33	33	34	35	35	35	29
Toluene	nr	29	33	36	36	36	38	38	37	38	34
Chlorobenzene	nr	26	32	35	34	35	36	36	35	36	31
	System Monitoring Compound (SMC), % Recovery										
1,2-Dichlorethane-d_4	nd	90	92	88	89	88	87	86	88	90	87
Toluene-d_8	nd	93	91	91	91	90	90	90	90	90	85
Bromofluorobenzene	nd	84	84	85	84	84	85	83	85	83	84

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.

Table B2-8. Analytical Results for control vials from manufacturer D[*].

	D20	D21	D22	D23	D24	D25	D26	D27	D28	D29	D25D	D25D
	VOC Concentration, (ng/mL)											
Acetone	35	39	36	44[**]	33	40[D]	41	38	35	38	23[C]	27[CR]
1,1-Dichloroethene	34	36	38	nr[**]	38	38	38	40	41	42	38	39[R]
Methylene Chloride	50	54	56	4[**]	56	58	57	59	60	62	49	49[R]
Benzene	39	41	42	nr[**]	42	43	42	44	44	45	40	41[R]
Trichloroethene	31	33	34	nr[**]	33	34	34	35	35	35	27	28[R]
Toluene	34	36	38	2[**]	37	38	37	38	38	39	33	34[R]
Chlorobenzene	32	34	35	3[**]	34	36	35	36	37	37	29	30[R]
	System Monitoring Compound (SMC), % Recovery											
1,2-Dichlorethane-d_4	90	89	90	92	88	85	89	91	87	87	89	92
Toluene-d_8	92	91	92	85	91	90	91	91	90	89	84	86
Bromofluorobenzene	83	84	83	84	83	84	85	84	85	84	82	83

[*] - data superscripts indicate flagged data. Flag definitions are presented in Appendix D.
[**] - septum in vial PTFE-side up. Analytical results for information only. nr = not reported.

APPENDIX C

Quality Assurance/Quality Control Report for the Vacuum Studies

The frequency and types of quality control samples for the vacuum studies followed or exceeded the specifications in the QAPP, "Integrity of VOA Vial Seals," January 7, 1998, Draft 1.2. The same vacuum pump and Grade AA vacuum gauge were used throughout the study.

The maximum vacuum attained by the system was recorded each day before analyzing samples. Data for this calibration step are shown in Table A3-1.

Table A3-1. Check for vacuum system integrity on days that vacuum readings were made.

Date	Vacuum (mm Hg)
12/10/97	18620
12/15/97	18620
12/21/97	18620
12/22/97	18620
12/23/97	17860
3/31/98	18088
4/3/98	18468
4/6/98	18620
4/7/98	18620
4/10/98	18620
4/13/98	19380

Duplicate vacuum readings were performed every 10 samples for the plate-vacuum study and for all samples in the septa-seal vacuum study. Data for the duplicate samples are given in Tables B2-1 through B2-8. A summary of the percent difference (%D) for the plate-vacuum study duplicates is given in Table A3-2. The reproducibility of the test was less than anticipated with RPD values ranging from zero to 13.5%. The mean RPD was 3.8%.

Table A3-2. Relative percent differences for duplicate vacuum plate samples. Data presented are for 22 duplicate samples out of 216 vials from each manufacturer.

Manufacturer A	Manufacturer B	Manufacturer C	Manufacturer D
6.3	3.6	10.9	12.1
12.5	0.7	0	2.7
6.5	6.7	8.7	0
3.6	3.8	0	1.3
5.7	3.6	4.8	2.5
1.6	5.4	13.5	0
3.1	10.4	0.9	1.2
5.1	11.5	9.5	1.2
3.1	9.1	6.1	1.2
1.8	6.2	7.9	1.2
3.0	0.9	1.3	1.2
6.2	4.3	0	0
1.1	3.4	2.5	1.1
1.8	7.7	8.2	8.4
5.5	0	11.5	0.5
1.1	8.2	0.5	1.1
4.5	6.3	6.3	1.8
1.1	3.4	2.3	3.5
1.1	4.5	2.8	0
0.8	8.7	1.1	7.0
0.6	2.6	1.1	0
1.0	1.1	1.1	2.2

APPENDIX D

Quality Assurance/Quality Control Report for the VOC Loss Test

The types of quality control samples, acceptance criteria, and qualifiers given in Table A4-1 reflect those listed in Table 1 of the QAPP "Integrity of VOA Vial Seals," January 7, 1998, Draft 1.2. These qualifiers appear in Tables B2-1 through B2-8, where appropriate.

TABLE A4-1. VOC QC SAMPLES and ACCEPTANCE CRITERIA

QC Sample	Acceptance Criteria	Qualifiers
Duplicates	% D ≤ 25% for all target analytes	flag "D"
Continuing calibration	% D ≤ 25% for all target analytes	flag "C"
Internal standards	Area counts 50-200% of 50 µg/mL std.	flag "T"
SMC recovery	% R = 100 ± 25% for all target analytes	flag "R"
IDL (7 replicates)	% R = 100 ± 25% for SMCs	--

Duplicate Samples

One duplicate sample for each set of ten "potentially leaky" or "control" vials was reported. Additional duplicate data are given for samples C7, C8, and D23 because the initial data were questionable (either the internal standard or the system monitoring compound recovery was poor).

Instrument Detection Limits

The instrument detection limits (IDLs) were determined as 3.143 times the standard deviation obtained from the analysis of 7 replicates of the calibration standard at a nominal concentration of 5 ng/mL. The system monitoring compound (SMC) recoveries for all compounds were within the ± 25% as specified. By this method, the detection limits, in ng/mL, for the compounds were: acetone = 3.5, 1,1-dichloroethene = 0.8, methylene chloride = 1.0, benzene = 0.3, trichloroethane = 0.3, toluene = 0.7, and chlorobenzene = 0.5 ng/mL. These detection limits are approximately 2 orders of magnitude lower than the 50 ng/mL working VOC concentrations required for this work.

Instrument Blanks

Instrument blanks were run prior to the analysis of an initial 10 ng/mL standard used in a 5 point initial calibration curve. Blanks were not run following the CCVs (continuing calibration verification) prior to sample analysis. During preliminary analysis of VOC samples, it became evident that the first sample of a batch run immediately following a blank yielded low concentrations for the target analytes relative to the remainder of the batch. This was attributed to the blank which conditioned the trap differently than a sample. Because the CCV closely matches the nominal 50 ng/mL concentration of the sample target analytes, analysis of the CCV

conditions the trap in the purge and as if it were a sample. Since the objective of this project was to determine differences in VOC concentrations as a consequence of vial seal integrity, not trap dependency of previously run samples, analysis of blanks following a CCV was eliminated.

Continuing Calibration

Continuing calibration data are shown in Tables D2-1 through D2-4. Analytes in the CCVs that did not meet the 25% D window are flagged. Samples that were run immediately prior to the CCV that did not meet the 25% D window are also flagged.

The polar nature of acetone yielded widely variable recoveries for this analyte. Acetone failed the CCV most often while the remaining analytes easily met criteria. It was deemed impractical to run new calibration curve solely for acetone. This forced some portions of an analytical batch to be run with acetone failing the midpoint CCV. These samples are flagged.

SMC Recovery

The system monitoring compounds, 1,2-dichloroethane-d_4, toluene-d_8, bromofluorobenzene were added to every sample and CCV. SMC recoveries of samples are reported with the sample data (Tables B2-1 through B2-8). Those samples not meeting the ± 25% R criteria are flagged.

Samples

Analytical data for target analytes are presented in Tables B2-1 through B2-8. Each batch of 20 samples from one vendor were run in the sequence of CCV1 X1, X20, X2, X21, X3, X22, X4, X23, X5, X24, CCV2, X6, X25, X7, X26, X8, X27, X9, X28, X10, X29, and CCV3 where X represents the vendor letter identification.

Tables B2-1 and B2-2 contain VOC test results from Manufacturer A vials. For vial A5, acetone and methylene chloride did not meet %D criteria in the sample duplicate and were flagged. Variability in duplicates was not unexpected. The duplicate samples came from 2 different analytical runs using two different spiking solutions that were quantified from two different initial calibration curves. The polar nature of acetone introduces further variations in recoveries depending on the conditioning of the trap as has been discussed previously. In the sample duplicate A5D, recovery of the SMC, toluene-d8, was 2% low and was flagged. The remaining 2 SMCs were low, but passed.

For vial A25 in Table B2-2 methylene chloride and trichloroethene did not meet %D criteria in the sample duplicate and were flagged. In the sample duplicate A25D, recovery of the SMC, toluene-d_8, was low and was flagged. The remaining 2 SMCs were low but passed.

Tables B2-3 and B2-4 contain VOC test results from Manufacturer B vials. The target analyte acetone failed high in CCV2. Because this was a mid batch CCV, the samples preceding the CCV which include, B1, B20, B2, B21, B3, B22, B4, B23, B5, and B24 and the samples following the CCV which include B6, B25, B7, B26, B8, B27, B9, B28, B10, and B29 were flagged for acetone. The target analyte acetone failed high in CCV2D. Because this was a mid batch CCV, the sample B5D preceding the CCV and the sample B25D following the CCV were flagged for acetone.

For vial B25 in Table B2-4, 1,1-dichloroethene did not meet %D criteria in the sample duplicate and was flagged.

Tables B2-5 and B2-6 contain VOC test results from Manufacturer C vials. The target analyte acetone failed low in CCV2 and CCV3. Consequently samples C1, C20, C2, C21, C3, C22, C4, C23, C5, C24, C6, C25, C7, C26, C8, C27, C9, C28, C10, and C29 were flagged for acetone. The target analyte acetone also failed low in CCV3D. Because this was a closing CCV, the sample duplicates C7D and C8D preceding this CCV were flagged.

Vial C7 in Table B2-5 did not meet the %D criteria for all analytes and was flagged although the SMCs met their QC criteria. Visual inspection of the vial did not reveal observable defects. It is suggested the low recoveries of the analytes are a consequence of a loose cap due to incomplete tightening rather than defects in the sealing lip of the vial.

Vial C8 in Table B2-5 did not meet the %D criteria for all analytes and the recoveries for the SMCs were all significantly below 50% so this sample was flagged. Visual inspection of the vial did not reveal observable defects. It is suggested as for vial C7, the loss of analytes and SMCs are a consequence of a loose cap causing VOCs to be lost during the purge cycle rather than defects in the sealing lip of the vial.

Tables B2-7 and B2-8 contain VOC test results from Manufacturer D vials. The target analyte acetone failed low in CCV2D. Consequently samples D5D, D23D, and D25D were flagged for acetone.

The CCV and the sample D25D following the CCV were flagged for acetone. The recovery for the SMC 1,2-dichloroethane-d4 was low in CV3D and all analytes in sample D25D were “R” flagged.

Analytical results for sample D1 in Table B2-7 was not reported. The glass lip of the vial was so badly chipped, that a seal could not be obtained between it and the septum cap. Any remaining VOCs as well as SMCs added immediately prior to the purge were lost. Sample D5 did not meet %D criteria for acetone and was flagged. The septum cap in vial D23 had the Teflon-septum facing exterior to the vial which allowed permeation of VOCs through the septum. Interestingly, the polar VOC acetone, showed no loss by permeation into/through the silicone septum. All SMCs in the sample meet criteria indicative of a valid purge. Analytical

data for sample D23 are for information only as the vial cap was improperly configured. Sample D25 did not meet %D criteria for acetone and was flagged.

Table D2-1. Continuing calibration results for samples and duplicate samples from manufacturer A.

	CV1	CV2	CV3	CV1D	CV2D	CV3D
	VOC Concentration, (ng/mL)					
Acetone	46	50	57	57	48	40
1,1-Dichloroethene	52	48	49	43	41	40
Methylene Chloride	58	57	55	41	43	42
Benzene	52	48	47	45	44	45
Trichloroethene	52	50	49	42	42	42
Toluene	51	49	48	43	44	44
Chlorobenzene	52	50	50	50	51	50
	System Monitoring Compound (SMC), % Recovery					
1,2-Dichlorethane-d4	97	98	95	86	90	188
Toluene-d8	103	99	96	82	83	83
Bromofluorobenzene	104	100	98	98	102	98

Table D2-2. Continuing calibration results for samples and duplicate samples from manufacturer A*.

	CV1	CV2	CV3	CV1D	CV2D	CV3D
	VOC Concentration, (ng/mL)					
Acetone	59	64[c]	40	45	71[c]	43
1,1-Dichloroethene	50	51	46	54	57	53
Methylene Chloride	52	54	50	52	60	57
Benzene	48	49	46	51	53	53
Trichloroethene	51	52	49	48	52	48
Toluene	48	50	47	50	53	50
Chlorobenzene	51	51	49	48	51	48
	System Monitoring Compound (SMC), % Recovery					
1,2-Dichlorethane-d4	95	99	93	101	113	110
Toluene-d8	98	102	97	100	106	101
Bromofluorobenzene	106	105	102	97	105	100

* - data superscripts indicate flagged data. Flag definitions are presented in Table A4-1.

Table D2-3. Continuing calibration results for samples and duplicate samples from manufacturer C*.

	CV1	CV2	CV3	CV1D	CV2D	CV3D
	VOC Concentration, (ng/mL)					
Acetone	43	36[C]	31[C]	50	40	37[C]
1,1-Dichloroethene	51	48	48	56	54	57
Methylene Chloride	51	50	50	57	56	60
Benzene	52	49	50	53	51	54
Trichloroethene	51	49	49	53	51	51
Toluene	51	49	50	55	47	54
Chlorobenzene	52	50	50	53	50	49
	System Monitoring Compound (SMC), % Recovery					
1,2-Dichlorethane-d4	104	98	99	105	99	111
Toluene-d8	101	99	101	109	102	112
Bromofluorobenzene	103	101	102	110	105	102

* - data superscripts indicate flagged data. Flag definitions are presented in Table A4-1.

Table D2-4. Continuing calibration results for samples and duplicate samples from manufacturer D*.

	CV1	CV2	CV3	CV1D	CV2D	CV3D
	VOC Concentration, (ng/mL)					
Acetone	50	47	52	50	35[C]	44
1,1-Dichloroethene	48	49	48	53	44	49
Methylene Chloride	52	53	53	52	51	45
Benzene	49	57	48	52	47	42
Trichloroethene	51	51	51	52	46	41
Toluene	50	49	49	52	47	41
Chlorobenzene	51	51	52	51	47	39
	System Monitoring Compound (SMC), % Recovery					
1,2-Dichlorethane-d4	99	96	98	107	97	56[R]
Toluene-d8	100	100	101	104	95	81
Bromofluorobenzene	104	104	114	102	99	79

* - data superscripts indicate flagged data. Flag definitions are presented in Table A4-1.