Sulfur Compound Stability in Air Sampling Canisters:

How Fill Gas Choice Affects Method Accuracy

When it comes to validating a method or protocol, we all rely on samples of known concentrations, whether we buy them or make them ourselves. We also know that for many types of samples, the matrix can bias the results (positively or negatively), particularly for complex matrices like soil or food. A sample of known concentration in a pure solvent often will not adequately approximate the results for a real sample, so some applications require a representative blank matrix that can be fortified and processed according to the method to get an accurate approximation of "real world" conditions. Sulfur compound stability in air sampling canisters is a good example of an application where choice of fill gas (blank matrix) can have a considerable impact on the accuracy of the results you ultimately report.

One might think that because air seems like a relatively clean sample matrix, compared to something like wastewater sludge or human tissue samples, that it does not need to be closely approximated when making samples for method validation or quality control (QC) checks. Indeed, it is common to find air sampling/analysis studies performed using high-purity nitrogen as the surrogate matrix for method development, validation, and routine performance checks. Air is approximately 78% nitrogen, so the use of nitrogen appears to be appropriate, and with it being readily available from the cryogenic equipment commonly used in air analysis laboratories, it seems like a good candidate for making analytical standards.

However, although the majority of our atmosphere is nitrogen, it is not 100% nitrogen. And, the oxygen present in true air samples can dramatically affect sulfur compound stability in air sampling canisters, especially in the presence of water vapor. Figure 1 shows that when using humidified air as the fill gas for a standard, significant loss occurs quickly for hydrogen sulfide in both a Restek and a competitor's treated (i.e., coated) air canisters. A 50% relative humidity (RH) level was used in this demonstration, but even the driest regions of the most arid desert on Earth (the Atacama in Chile) still have average RH values of around 17%. Since water vapor exists in even the driest atmospheres, correlating results from dry nitrogen environments to actual air samples collected in the field may lead to error because it does not represent the impact of oxygen in the presence of water vapor. In a worst case scenario, if dry nitrogen is the fill gas for standards and QC samples, and you see passing QC recoveries along with undetected levels in your samples, you may report that no sulfur compounds were present in the samples when in fact they were there but had degraded prior to analysis.

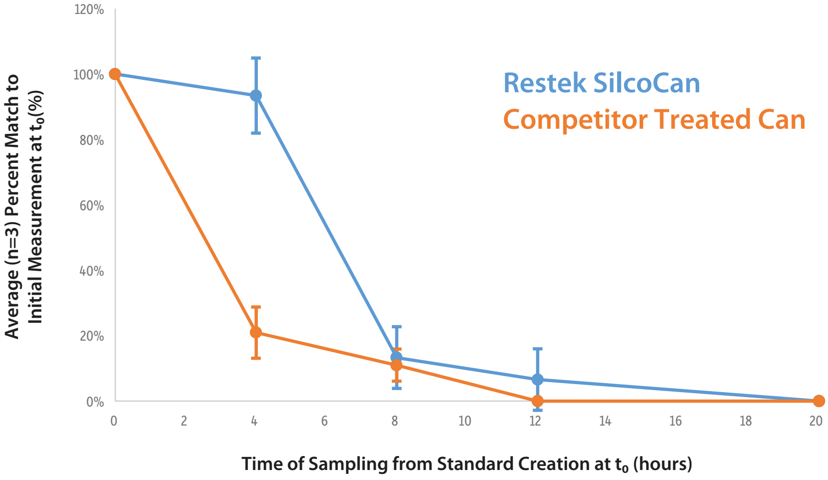
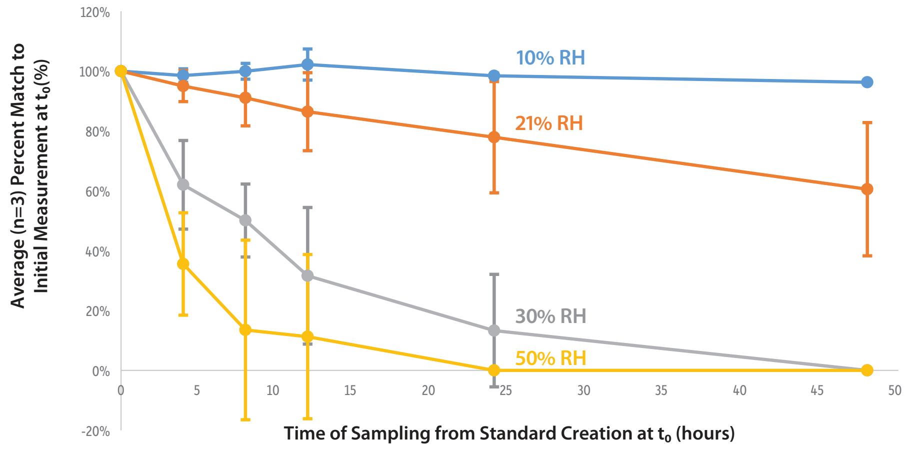


Figure 1: Stability of hydrogen sulfide over time under 50% relative humidity conditions in air (error bars = 1 standard deviation; MS detector).

Effects of Varying %RH in Air on Sulfur Compound Stability in Air Sampling Canisters

A relative humidity of 50% is not at all unusual to encounter in many parts of the world, but how is sulfur compound stability in air sampling canisters affected by different levels of relative humidity? From Figure 2, it is evident that severe degradation of hydrogen sulfide occurs in just a few hours at relative humidity levels above 10%. Considering most places being sampled for the presence of sulfur compounds will be well above 10% RH, this highlights the challenge of maintaining sample integrity when samples need to be shipped to a laboratory for analysis rather than being tested onsite.

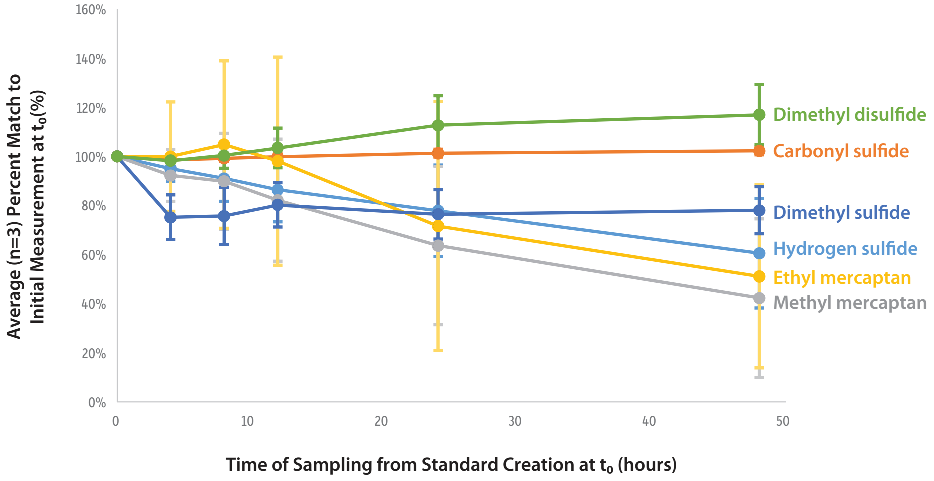
Figure 2: Stability of hydrogen sulfide over time under different relative humidity conditions in air using Restek SilcoCan air sampling canister (error bars = 1 standard deviation; flame photometric detector).



Effect of Humidity on Other Volatile Sulfur Compounds in Air

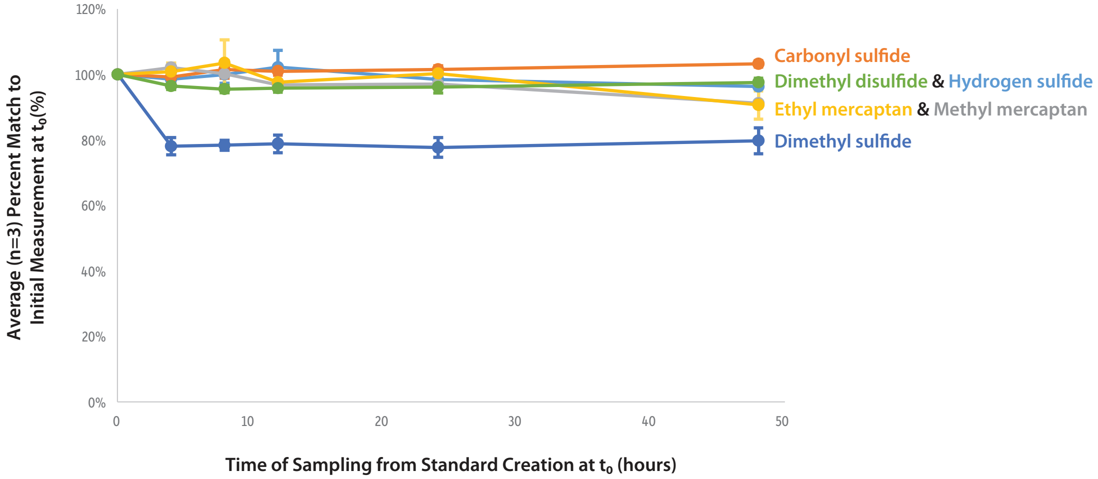
Hydrogen sulfide is just one of many different volatile sulfur compounds. Do others show the same dramatic decrease over time? Figure 3 illustrates the stability of various sulfur compounds at 21% RH, the first humidity level where substantial loss of sample is observed (performance gets worse at higher humidity levels). Many compounds exhibited a substantial loss of stability, except carbonyl sulfide. Dimethyl disulfide, on the other hand, actually increases in response over time, which is likely caused by its formation from the degradation of the other sulfur compounds in the mix. Polymerization of mercaptans is known to result in the formation of larger sulfur compounds [1].

Figure 3: Stability of various volatile sulfur compounds at 21% relative humidity in air. Note the performance of dimethyl disulfide in particular, which is discussed further in the text. Results for Restek SilcoCan air sampling canister only (error bars = 1 standard deviation; flame photometric detector).



These results paint a pretty bleak picture of expected sulfur compound stability in air sampling canisters at typical ambient humidity levels when held for more than a few hours, let alone days. The best practice in this scenario is to use humidified air as the fill gas for standards and QC samples and to analyze samples immediately using onsite or mobile equipment. However, if we plot the stability data for the same compounds under 10% relative humidity conditions in air (Figure 4), we see an interesting opportunity to mitigate this stability issue.

Figure 4: Stability of various volatile sulfur compounds at 10% relative humidity in air. Note that even though there was an observed drop in recovery for dimethyl sulfide initially, its performance does stabilize near 80% of the initial measurement. Results for Restek's SilcoCan air sampling canister only (error bars = 1 standard deviation; flame photometric detector).



Effect of Sample Drying on Sulfur Compound Stability in Air Sampling Canisters

While Figures 1-4 suggest that sampling done for these compounds under most ambient conditions will lead to rapid degradation of sulfur compounds over a relatively short time even in treated air cans, regardless of the vendor, Figure 5 reveals an opportunity to mitigate this effect by actively drying samples at the point of collection, as has been noted elsewhere in the literature [2,3].

To evaluate this approach, we filled an air canister with 50 ppb of sulfur mix and 50% relative humidity air. We analyzed that sample initially, and then immediately following analysis, we passed the sample from the first air can, through a length of treated ¼" stainless-steel tubing packed with calcium chloride as a drying agent, and into a second air canister where it was analyzed again. After the second analysis, the relative humidity in the second air can containing the dried (i.e., dehumidified) sample was measured. The amount of drying agent was varied by packing stainless-steel tubing of three different lengths. In all three setups studied, the relative humidity dropped from the initial 50% to 0%, as verified with a hygrometer. The results are presented in Table I.

Table I: Relative responses of sulfur compounds after passing through a drying apparatus.

Length of 1/4" Stainless-Steel Tubing Packed with Calcium Chloride drying agent (cm)	% Response Compared to Initial Direct Analysis at Time Zero and without Drying					
	Hydrogen Sulfide	Carbonyl Sulfide	Methyl Mercaptan	Ethyl Mercaptan	Dimethyl Sulfide	Dimethyl Disulfide
2.5	124	100	137	121	99	79
5	112	98	118	94	100	73
10	13	109	65	46	103	54

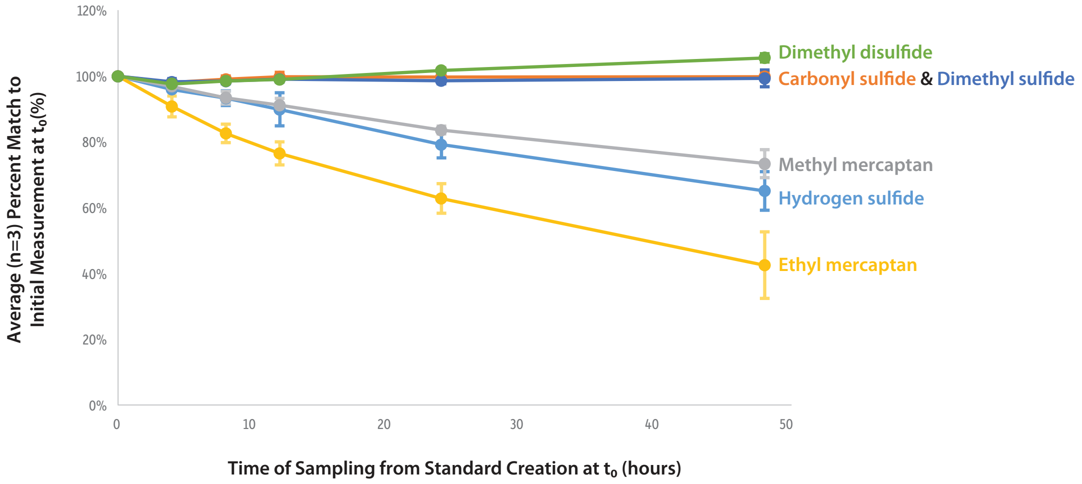
This experiment illustrated that a simple device filled with calcium chloride can effectively and dramatically reduce the relative humidity inside the air can, which translates into a much more stable sample compared to air cans that collect air at most ambient humidity levels. The values greater than 100% are believed to be the result of a loss of response in the initial measurement, because even though the sample was tested immediately after it was created, the high humidity air might still create opportunity for sample degradation to occur in the transfer and analysis hardware. This loss in the initial reference sample created an elevated relative response in the stable, dehumidified sample.

Also, the results suggest that too much desiccant in the 5 and 10 cm devices is counterproductive, resulting in analyte loss. A separate water vapor capacity experiment was conducted in which the 2.5 cm length of tubing was packed with 0.3244 g of calcium chloride. This amount of calcium chloride was able to dry 89.5% RH air down to 0% RH for 9.6 L of air (a 0.17 g water capacity), demonstrating that it would be more than sufficient to dry a 6 L air can's volume of humid air. Therefore, the larger amounts of calcium chloride that negatively impacted recoveries are not necessary. A commercially available hydrocarbon trap containing a calcium chloride drying bed was also tested and its results were poor for the same reasons (results not shown).

In sum, these experiments indicate that drying samples at the point of collection with an appropriate amount of calcium chloride may preserve sample integrity long enough to permit a quick shipment to an offsite laboratory for analysis. However, it is important to emphasize again that method accuracy will still depend in part on how well the blank matrix used for calibration standards and QC samples matches the actual sample matrix. So, if the actual samples will be dried at the point of collection, then calibration standards and QC samples should be treated the same way.

In light of these results, one may wonder if drying the air sample during collection is enough to create a sample that is stable for at least a few days and maybe getting a cheaper, uncoated electropolished stainless-steel air can will do the job. As shown in Figure 5, major loss occurs in an untreated canister, even when reducing humidity in the air canister to 10%. Thus, a coated (deactivated) air sampling can, such as Restek's SilcoCan air canister, is necessary to avoid losing active compounds like some of the sulfurs analyzed here.

Figure 5: Stability of various volatile sulfur compounds at 10% relative humidity in air. Results for Restek's electropolished TO-Can air sampling canister only (error bars = 1 standard deviation).



Conclusion

Even though nitrogen is a major component of the air being sampled, it is not sufficient as a fill gas, even if humidified, when used to represent sulfur compound stability in air sampling canisters for actual samples. The best way to validate the performance of a method or process is to approximate the test conditions as closely as possible. For air sampling, using humid air is a more accurate representation of real-world conditions, making it a better choice than nitrogen fill gas for method validation and quality control. However, because sulfur compound stability in air sampling canisters is often poor under humid conditions, steps should be taken to dry actual air samples or analyze them immediately. By removing humidity at the time of collection, sulfur compound stability can be increased, which can preserve sample integrity during transport, helping to ensure accurate results.

References

[1] H.W. Chin, R.C. Lindsay, Ascorbate and transition-metal mediation of methanethiol oxidation to dimethyl disulfide and dimethyl trisulfide, Food Chemistry 49 (4) (1994) 387-392. https://doi.org/10.1016/0308-8146(94)90009-4

[2] S. Trabue, K. Scoggin, F. Mitloehner, H. Li, R. Burns, H. Xin, Field sampling method for quantifying volatile sulfur compounds from animal feeding operations, Atmospheric Environment 42 (2008) 3332-3341. https://doi.org/10.1016/j.atmosenv.2007.03.016

[3] C. Merlen, M. Verriele, S. Crunaire, V. Ricard, P. Kaluzny, N. Locoge, A preconcentration method based on a new sorbent for the measurement of selected reduced sulfur compounds at ppb level in ambient air, Microchemical Journal 143 (2018) 47-54. https://doi.org/10.1016/j.microc.2018.07.020

SilcoCan Air Sampling Canisters with RAVE Valve

Siltek-treated canister with optional Siltek-treated valve offers unsurpassed inertness, even for sulfur-containing or brominated compounds.

Description	Modification	Volume	qty.	cat.#
SilcoCan Canister	2-Port RAVE Valve	1 L	ea.	27400
	2-Port Siltek-Treated RAVE Valve	1 L	ea.	27401
	3-Port RAVE Valve with Gauge*	1 L	ea.	27402
	3-Port Siltek-Treated RAVE Valve with Gauge*	1 L	ea.	27403
	without Valve	1 L	ea.	22090
	2-Port RAVE Valve	3 L	ea.	27404
	2-Port Siltek-Treated RAVE Valve	3 L	ea.	27405
	3-Port RAVE Valve with Gauge*	3 L	ea.	27406
	3-Port Siltek-Treated RAVE Valve with Gauge*	3 L	ea.	27407
	without Valve	3 L	ea.	22091
	2-Port RAVE Valve	6 L	ea.	27408
	2-Port Siltek-Treated RAVE Valve	6 L	ea.	27409
	3-Port RAVE Valve with Gauge*	6 L	ea.	27410
	3-Port Siltek-Treated RAVE Valve with Gauge*	6 L	ea.	27411
	without Valve	6 L	ea.	22092
	2-Port RAVE Valve	15 L	ea.	27412
	2-Port Siltek-Treated RAVE Valve	15 L	ea.	27413
	3-Port RAVE Valve with Gauge*	15 L	ea.	27414
	3-Port Siltek-Treated RAVE Valve with Gauge*	15 L	ea.	27415
	without Valve	15 L	ea.	22093

*Range of standard gauge is –30" Hg to 60 psi.
Do not exceed canister maximum pressure of 40 psig (2.75 bar).

27405

Canisters are the gold standard for ambient VOC monitoring.

RAVE Diaphragm Valves

For Restek air sampling canisters

Description	Material	Used with	qty.	cat.#
1/4" Diaphragm Valve, RAVE (2-port)	Stainless Steel	Restek air sampling canisters	ea.	26385
	Siltek Treated	Restek air sampling canisters	ea.	26386
1/4" Diaphragm Valve, RAVE (3-port)	Stainless Steel	Restek air sampling canisters	ea.	26387
	Siltek Treated	Restek air sampling canisters	ea.	26388

RAVE and RAVEn Diaphragm Rebuild Kit

Description	Includes	Material	qty.	cat.#
RAVE and RAVEn Diaphragm Rebuild Kit	a tube of grease; two screws; a bonnet (metal ring); a button assembly (small white circular piece); and a diaphragm stack (thin metal disks)	Stainless Steel	kit	26389
	a tube of grease; two screws; a bonnet (metal ring); a button assembly (small white circular piece); and a diaphragm stack (Siltek-treated thin metal disks)	Siltek Treated	kit	26390

26389

Sulfur 5-Component Mix

(5 components)

Stability is 12 months from date of manufacture: +/– 10% accuracy.

Note: Actual cylinder pressure may vary due to loss from quality testing procedure.

Airgas (formerly Scott/Air Liquide gas) 110 L Cylinders (PI-marked Cylinders for EU Regulations):
Aluminum construction
Size: 8.3 x 29.5 cm
Volume/Pressure: 110 liters of gas @ 1800 psig (124 bar)
Outlet Fitting: CGA-180
Weight: 2.2 lb/1 kg
U.S. DOT Specs: 3AL2216

Carbonyl sulfide
Dimethyl sulfide
Ethyl mercaptan

Hydrogen sulfide
Methyl mercaptan

Description	Concentration	Conc. in Solvent	Certification	Product Grade	Shelf Life	qty.	cat.#
Sulfur 5-Component Mix	1 ppm	1 ppm in nitrogen, 110 liters @ 1800 psig		Blend tolerance: ±10%; Analytical accuracy: ±10%	1 yr	ea.	34561
	1 ppm	1 ppm in nitrogen, 110 liters @ 1800 psig	TPED (Pi) compliant	Blend tolerance: ±10%; Analytical accuracy: ±10%	1 yr	ea.	34561-PI

ordering notes

Gas standards are subject to hazardous materials shipping fees by most freight carriers.

All calibration gas standards are nonreturnable due to DOT hazardous shipping requirements.

27367

Valve	Max Flow @ 29” Hg (mL/min)**	6 L Grab Sample Time (sec)
RAVEqc quick-connect air valve	2500	240
RAVEqc high-flow quick-connect air valve	3850	120
RAVE diaphragm valve	40,000	10

*** Flow rates calculated on a 1/4” platform.*

RAVEqc Quick-Connect Air Valves

Description	Material	qty.	Similar to Part #	cat.#
Female RAVEqc Valve to 1/16” Male Compression Fitting	Stainless Steel	ea.	Entech FQT-100	27341
	Siltek Treated	ea.	Entech FQT-100S	27342
Female RAVEqc Valve to 1/8” Male Compression Fitting	Stainless Steel	ea.	Entech FQT-200	27343
	Siltek Treated	ea.	Entech FQT-200S	27344
Female RAVEqc Valve to 1/4” Male Compression Fitting, High-Flow, Open-Position	Stainless Steel	ea.		27345
	Siltek Treated	ea.		27346
Female RAVEqc Valve to 1/4” Tube-End Fitting	Stainless Steel	ea.	Entech FQT-T400	27347
	Siltek Treated	ea.	Entech FQT-T400S	27348
Male RAVEqc 3-Port Valve to 1/4” Male Compression Fitting without Gauge	Stainless Steel	ea.	Entech MQT-400L-D	27349
	Siltek Treated	ea.	Entech MQT-400L-DS	27350
Male RAVEqc 3-Port Valve to 1/4” Male Compression Fitting with Gauge	Stainless Steel	ea.	Entech MQT-400L-G	27351
	Siltek Treated	ea.	Entech MQT-400L-GS	27352
Male RAVEqc Valve to 1/4” Male Compression Fitting	Stainless Steel	ea.	Entech MQT-400	27367
	Siltek Treated	ea.	Entech MQT-400S	27368
Female RAVEqc Valve to 1/4” Male Compression Fitting	Stainless Steel	ea.	Entech FQT-400	27369
	Siltek Treated	ea.	Entech FQT-400S	27370
Male RAVEqc Valve to 1/4” Tube End Fitting, Extended (1.58”)*	Stainless Steel	ea.	Entech MQT-T400	27371
	Siltek Treated	ea.	Entech MQT-T400S	27372
Male RAVEqc Valve to 1/4” Tube End Fitting, Short (1.23”)*	Stainless Steel	ea.	Entech MQT-ST400	27373
	Siltek Treated	ea.	Entech MQT-ST400S	27374
Female RAVEqc Valve to 1/4” NPT Fitting	Stainless Steel	ea.		27365
	Siltek Treated	ea.		27366

* Requires a 1/4” nut and ferrule set, sold separately in 5-pks. as cat.# 23161.

Passive Air Sampling Kits—Integrated (Stainless Steel & Siltek Treated)

Superior Performance—an Excellent Restek Value

- Provide accurate integrated sampling without a sampling pump.
- Siltek-treated components ensure accurate sampling of active components.
- Excellent for sampling times from 0.5 hour to 125 hours.

Description	Flow Capacity	Material	Orifice Size	qty.	cat.#
Passive Air Sampling Kit	0.5–2 mL/min	Siltek Treated	0.0008”	kit	24217
	0.5–2 mL/min	Stainless Steel	0.0008”	kit	24216
	2–4 mL/min	Siltek Treated	0.0012”	kit	24160
	2–4 mL/min	Stainless Steel	0.0012”	kit	24165
	4–8 mL/min	Siltek Treated	0.0016”	kit	24161
	4–8 mL/min	Stainless Steel	0.0016”	kit	24166
	8–15 mL/min	Siltek Treated	0.0020”	kit	24162
	8–15 mL/min	Stainless Steel	0.0020”	kit	24167
	15–30 mL/min	Siltek Treated	0.0030”	kit	24163
	15–30 mL/min	Stainless Steel	0.0030”	kit	24168
	30–80 mL/min	Siltek Treated	0.0060”	kit	24164
	30–80 mL/min	Stainless Steel	0.0060”	kit	24169
	80–340 mL/min	Siltek Treated	0.0090”	kit	22101
	80–340 mL/min	Stainless Steel	0.0090”	kit	22100

Vacuum/pressure gauge included in kit; air sampling canisters sold separately.

RESTEK

Pure Chromatography

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