

Avoiding Inaccurate Ethylene Oxide Analysis Caused by Undetected Air Canister Contamination

You could be doing everything by the book and still miss contaminants in air sampling canisters that can lead to positively biased results for ethylene oxide analysis.

Ethylene oxide is heavily used in chemical manufacturing, and its 2016 classification by the U.S. EPA as a carcinogen [1] has generated debate about safety and exposure levels. With the question of how tightly to regulate emissions being discussed by manufacturers and lawmakers alike, it's more important than ever to develop accurate and efficient methods for ethylene oxide analysis in ambient air. Applying industrial hygiene procedures is not an ideal approach because they target ethylene oxide alone. Monitoring ethylene oxide along with other volatiles would be much more efficient, and many labs are interested in adding it to standard methods for the collection and analysis of volatiles in ambient air, such as EPA Method TO-15A.

While researching the use of Method TO-15A for monitoring ethylene oxide, we noticed an issue that the EPA is also now investigating: the potential for positive bias due to ethylene oxide growth in air canisters. Seemingly clean air canisters can develop an ethylene oxide signal that, in worst-case scenarios, continues to increase. This situation is similar to the problematic growth of acrolein in air canisters over time. For ethylene oxide, we have seen an almost six-fold increases in signal after two weeks of storage, and observations like this can make analysts wonder what is happening. The air canisters passed a cleanliness evaluation, so it can't be that, right? As it turns out, it is easier than you might think to miss relevant air canister contamination given the targeted approach to cleanliness that is often used in standard volatiles methods.

For Air Canisters, How Clean Is "Clean?"

It is well understood that air canisters must be demonstrated to be free of background contamination, but this can be especially challenging with volatile compounds that are sometimes present in the testing environment itself. For volatiles methods, clean air canisters are usually tested specifically for target analytes present at background contamination levels that might lead to reporting inaccuracies. However, this careful, targeted approach using selected ion monitoring (SIM) can mask clues that an air canister actually may not be suitable for ethylene oxide sampling.

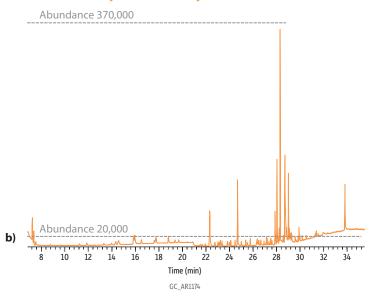
For example, when performing a routine targeted cleanliness check on an air canister, results like the chromatogram shown in Figure 1A are pretty typical. The background is fairly free of volatile contamination for the ions monitored, even when the fill gas used in the evaluation is humidified air (which is a much harder test than using dry air or a humidified or dry inert gas, such as nitrogen). So, the air canister in Figure 1A would likely pass cleanliness testing requirements and be qualified for ethylene oxide analysis projects. However, when we switch from a targeted cleanliness test that uses the narrow, but sensitive, field of view provided by SIM to a broader scanning method, we now see the presence of nontarget, unidentified contamination (Figure 1B).



Figure 1: Using full scan conditions reveals background contamination that could affect ethylene oxide analysis, which is not detected using a targeted SIM cleanliness evaluation.



Cleanliness by full scan analysis



Column Rxi-624Sil MS, 60 m, 0.25 mm ID, 1.4 µm (cat.# 13869) Sample Diluent: Air (50% RH) Injection Oven Oven Temp.: 0 °C (hold 5 min) to 60 °C at 3.5 °C/min to 260 °C at 24 °C/min (hold 5 min) Carrier Gas Flow Rate: He, constant flow 2 mL/min Detector Mode: Scan Program: Start Time Scan Range Scan Rate Group (min) 0 (amu) (scans/sec) 1 Transfer Line Temp.: 250 °C Analyzer Type: Quadrupole Source Type: Extractor Lens: Extractor 6 mm ID Source Temp.: Quad Temp.: 350 °C 200 °C Electron Energy: Solvent Delay Time: 0 min BFB Tune Type: Ionization Mode: Preconcentrator Trap 1 Settings Markes Unity 2 - CIA Advantage - Kori Type/Sorbent: Markes U-T3ATX-2S Cooling temp.: Desorb temp.: -30 °C 300 °C Desorb flow: 6 mL/min 180 sec Desorb time: Internal Standard Purge flow: 50 mL/min Purge time: 60 sec 50 mL Vol.: ISTD flow: 50 mL/min Standard 400 mL Size:



Agilent 7890B GC & 5977A MSD SIM ions monitored: 15, 29, 43, 44, and 56.

50 mL/min 60 sec

100 mL/min

Purge flow:

Purge time: Sample flow:

Instrument Notes If the nontarget contamination is severe enough, it might affect analyte stability in the sample, which often results in lower-than-expected recovery. But, is it possible that these contaminants could also lead to the formation and growth of ethylene oxide in "clean" canisters over time? This was the next question we investigated.

The Effect of Nontarget Contaminants on Ethylene Oxide Analysis

To explore whether ethylene oxide could potentially be formed from nontarget contaminants in air canisters, we monitored the change in ethylene oxide signal over time in canisters that showed different degrees of contamination in an initial full-scan cleanliness check. The qualitative difference in the full-scan background test is shown chromatographically in Figure 2.

For each canister, we then monitored ethylene oxide stability over time under the same conditions. As shown in Figure 3, after 14 days both canisters showed a net increase in the ethylene oxide signal, with the more contaminated canister exhibiting a greater increase in response. These canisters, which passed a targeted SIM cleanliness screening, developed detectable levels of ethylene oxide and would likely have produced positively biased results if they were used for sampling in the field and had even just a few days hold time before they were analyzed.

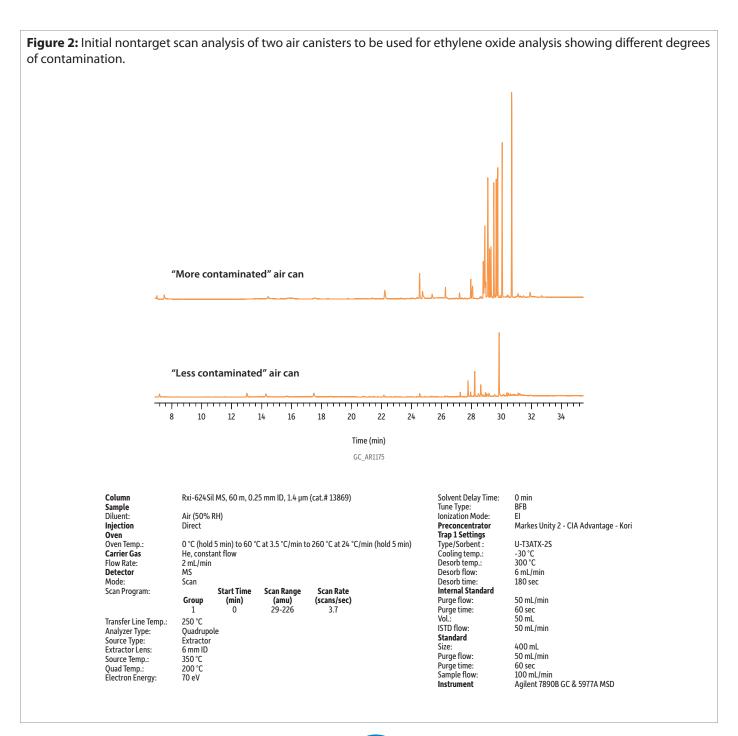
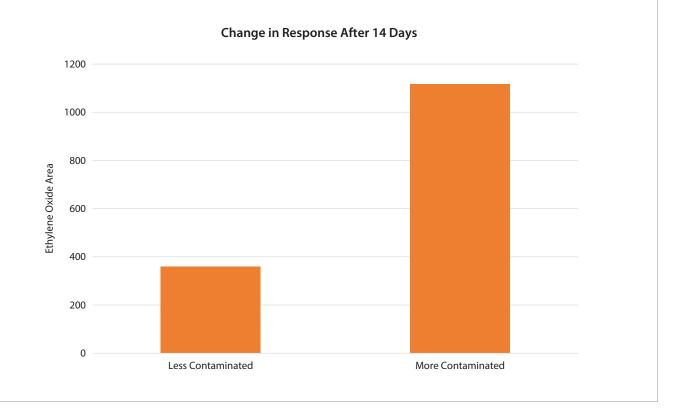




Figure 3: After 14 days of storage, the canisters shown in Figure 2 developed detectable levels of ethylene oxide. The net signal increase in the more contaminated canister was three times larger than the net increase in the less contaminated canister.



Using scan/SIM mode, instead of SIM alone, for cleanliness checks theoretically can reveal nontarget contaminants that may skew accuracy for ethylene oxide analysis. However, as we will discuss next, this can only be seen under real-world conditions that reflect those that samples experience in the field.

It Takes Real-World Conditions to See This Effect

One way that the potential for ethylene oxide growth can be missed is if cleanliness checks are performed using a fill gas other than humidified air. Use of nitrogen for cleanliness checks or method validation work may seem logical because air is mostly nitrogen and labs often already have a source of clean, cheap nitrogen available. However, nitrogen is an inert gas, so results obtained with it are not representative of what would occur in actual air samples that contain reactive oxygen and moisture. The changes found in Method TO-15A that call for the use of humidified air (40–50% RH) during method validation or canister suitability testing are clear acknowledgements of the importance of using conditions that simulate real-world conditions.

As an example, we conducted a small study comparing the evolution of ethylene oxide in canisters containing dry versus humidified fill gases. As shown in Table I, clean canisters filled with dry air or dry helium did not develop ethylene oxide, but the canister filled with humid air did. This indicates that although the canisters may test "clean" when filled with dry air, they could experience ethylene oxide growth if used to collect humid field samples.



Table I: Ethylene oxide analysis in SilcoCan air sampling canisters after seven days using humidified air (50% RH) versus other fill gases (n = 3).

Humid Lab Air (pptv)	Dry Lab Air (pptv)	Dry Helium (pptv)
132	Not detected	Not detected

Further evidence that ethylene oxide can develop in air canisters under real-world conditions was found in experiments we conducted while helping a customer troubleshoot their abnormally high ethylene oxide levels from samples collected in the field using what their tests showed were clean air canisters. We were able to get the problematic air canisters from the customer, and we were able to reproduce their results. The air canisters in question looked clean when we used nitrogen during the canister cleaning process and as a fill gas for the cleanliness evaluation. However, when we tested the air canisters with humid air, like they would experience in the field, we saw the same elevated background of ethylene oxide that the customer was seeing from their field samples.

Even though the use of nitrogen as a fill gas for cleaning and canister evaluation is common, it can hide the effects that lingering contamination can have under real-world conditions. In addition to the potential bias for ethylene oxide analysis explored here, problems have been reported for other sensitive compounds. It has been shown that the stability of certain sulfur-containing compounds is dramatically reduced in humid air, so using anything but humid air might overestimate a real sample's shelf life [2]. It is clear from both experimental evidence and the guidance in Method TO-15A that when evaluating method or canister performance, the use of humid air (e.g., 50% RH) is the best way to gauge actual robustness and stability.

Strategies for Preventing Ethylene Oxide Formation

If air canisters can pass standard cleanliness evaluations for tough protocols like Method TO-15A and still exhibit problems for ethylene oxide stability, how can you be sure that they are not going to develop ethylene oxide over time and skew your results? In this section, we will explore where ethylene oxide may be coming from and how to prevent its formation.

Because higher levels of ethylene oxide correlated with higher levels of background contamination and this was only seen in canisters containing humidified air, it has been postulated that ethylene oxide is formed by the breakdown of larger carbon compounds when exposed to oxygen through reactions catalyzed by humidity [3]. This means that rigorous cleaning using humid air for extended periods and multiple evacuation/pressurization cycles could remove the nontarget contaminants that, in the presence of the humid air of a field sample, could react to form background ethylene oxide.

In Figure 4 (see page 6), we demonstrate the effectiveness of a good cleaning protocol. First, two air canisters were cleaned following a standard procedure. After seven days of storage, an observable ethylene oxide signal was detected. Then, the same canisters were cleaned more rigorously using a proprietary process and tested again. No ethylene oxide was detected after seven days, demonstrating that after the more stringent cleaning process they were suitable for ethylene oxide monitoring projects. However, even scrupulous cleaning may not completely eliminate all background contamination in all situations, so exact cleaning procedures should be determined in each lab to ensure effectiveness for their particular testing needs and levels of background contamination.

As discussed previously, in addition to a cleaning routine that uses humid air, it is important to evaluate canisters that are to be used for ethylene oxide analysis for the presence of more than the targeted analytes for your study. Evaluate full scan data to look for evidence of nontarget contaminates that may be the source of ethylene oxide growth over time. If your instrument is capable of collecting both SIM and scan data in a single analysis, take advantage of that capability to see what evidence might be lurking in the full scan view. Finally, as much as practical, ensuring that ethylene oxide analysis occurs as quickly as possible after sample collection will help minimize the amount of background ethylene oxide that develops during sample storage.

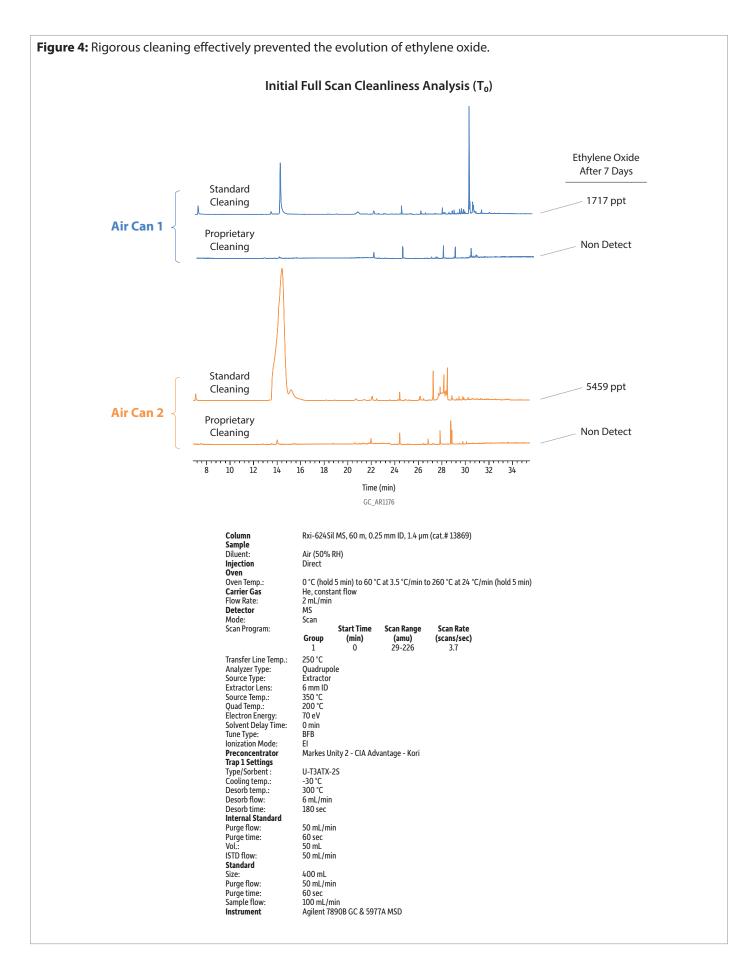
Don't Miss Signs That Air Canisters Are Too Dirty for Ethylene Oxide Analysis

In summary, it is not always easy to get air canisters clean enough for field sampling, but using dry, inert gas and only monitoring target compounds makes it even harder to tell if an air canister is suitable for use. To make sure you are aware of nontarget contaminants that could affect ethylene oxide analysis, always use humid air in method development, validation, and check procedures to ensure that those results will reflect what actual samples experience under real-world conditions. Using full scan mode can also help reveal the presence of nontarget contamination that might be contributing to the formation of ethylene oxide over time in the humid air of field samples. By employing rigorous cleaning, using humidified air fill gas, and checking full scan data in addition to SIM, you can minimize positive bias when adding ethylene oxide to existing volatiles analysis methods.

References

- [1] J. Jinot, D. Bayliss, J. Fritz, H.D. Kahn, N. Keshava, R. McGaughy, R. Subramaniam, L. Valcovic, S. Valimiri, Evaluation of the inhalation carcinogenicity of ethylene oxide, U.S. Environmental Protection Agency (2016). https://cfpub.epa.gov/ncea/iris/iris_documents/toxreviews/1025tr.pdf
- [2] Sulfur compound stability in air sampling canisters: how fill gas choice affects method accuracy, Restek Corporation (2020). https://www.restek.com/en/technical-literature-library/articles/sulfur-compound-stability-in-air-sampling-canisters-how-fill-gas-choice-affects-method-accuracy/
- [3] J. Hoisington, J.S. Herrington, Rapid determination of ethylene oxide and 75 VOCs in ambient air with canister sampling and associated growth issues, Separations 8(3) (2021). https://www.mdpi.com/2297-8739/8/3/35/htm







Ashcroft 2074 Digital Pressure Gauge

- Accuracy to +/- 0.25%.
- Range of 30 "Hg vacuum to 60 psi pressure.
- LCD display (5-digit).
- 10 engineering units available.
- Auto-off timers.
- Battery powered: uses two AA batteries (included).

High-accuracy test gauges are recommended for verifying the vacuum/pressure in canisters before and after sampling. This battery-powered digital gauge has all-metal wetted parts in an IP 65 weatherproof case. It has a battery life of over 400 hours (with a battery-level indicator), can store min/max values, and all of its functions can be password protected.

Description	qty.	cat.#
Ashcroft 2074 Digital Pressure Gauge	ea.	24268

Not CE approved.



24268

Specifications:
Accuracy: ±0.25% full-scale terminal point
Fittings: 1/4" NPT
Diameter: 3"
Material: Stainless Steel
Temp. Limits: 14°F to 140°F (-10°C to 60°C)
Wetted Materials: 316L and 17-4 Ph stainless steel

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Superior Performance—an Excellent Restek Value.

- Provide accurate integrated sampling without a sampling pump.
- Siltek-treated components ensure accurate sampling of active components.
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Air sampling canisters sold separately.

Description	Flow Capacity	Material	Orifice Size	qty.	cat.#
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	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
Deserting Ata Consulting Wit	8–15 mL/min	Siltek Treated	0.0020"	kit	24162
Passive Air Sampling Kit	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.







RAVE Diaphragm Valves

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- Proven long life—durable design is engineered to exceed 15,000 cycles.
- Leak-free performance—each and every valve is helium leak tested to 1x10-6 mL/sec.
- Effortless operation—easily finger turn to achieve full valve closure (only 10 in-lb).
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- RAVE valves are standard on our full line of SilcoCan, TO-Can, and miniature air sampling canisters.
- Also available for Entech air canisters.

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



Canisters are the gold standard for ambient VOC monitoring.

Can Volume	Dimensions: height x sphere diameter	Weight
1 liter	8.5 x 5.25" (21.6 x 13.3 cm)	2.25 lbs (1.02 kg)
3 litar	11 5 v 7 25"	3 50 lbc

Dimensions/Weights of Air Canisters

(29.2 x 18.4 cm) (1.59 kg)
6 liter 12.5 x 9.25" 5.75 lbs (2.61 kg)
15 liter 17.0 x 12.25" 11.75 lbs (5.33 kg)

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.
- High-quality, metal-to-metal seal, 2/3-turn valve with stainless-steel diaphragms prevents sample adsorption for more accurate results.
- Canisters and valves made of 304 and 316 stainless steel to withstand the rigors of field work.
- Both 2-port and 3-port valves are available; 3-port valve includes -30" Hg/60 psi vacuum/pressure gauge (other gauges available).
- Featuring the proven long life, leak-free performance, and effortless operation of the new RAVE valve—learn more.

Description	Modification	Volume	qty.	cat.#
	2-Port RAVE Valve	1L	ea.	27400
	2-Port Siltek-Treated RAVE Valve	1L	ea.	27401
	3-Port RAVE Valve with Gauge*	1L	ea.	27402
	3-Port Siltek-Treated RAVE Valve with Gauge*	1L	ea.	27403
	without Valve	1L	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
ilcoCan Canister	without Valve	3 L	ea.	22091
oncocan Canister	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).



TO-Can Air Sampling Canisters with RAVE Valve

- Proprietary electropolished surface maintains compound stability.
- High-quality, metal-to-metal seal, 2/3-turn valve with stainless-steel diaphragms prevents sample adsorption for more accurate results.
- Both 2-port and 3-port valves available; 3-port valve includes -30" Hg/60 psi vacuum/ pressure gauge (other gauges available).
- SUMMA canister equivalent.
- Featuring the proven long life, leak-free performance, and effortless operation of the new RAVE valve—learn more.

Description	Modification	Volume	qty.	cat.#
	2-Port RAVE Valve	1L	ea.	27416
	3-Port RAVE Valve with Gauge*	1L	ea.	27417
	without Valve	1L	ea.	22094
	2-Port RAVE Valve	3 L	ea.	27418
	3-Port RAVE Valve with Gauge*	3 L	ea.	27419
TO-Can Canister	without Valve	3L	ea.	22095
10-can canister	2-Port RAVE Valve	6 L	ea.	27420
	3-Port RAVE Valve with Gauge*	6 L	ea.	27421
	without Valve	6 L	ea.	22096
	2-Port RAVE Valve	15 L	ea.	27422
	3-Port RAVE Valve with Gauge*	15 L	ea.	27423
	without Valve	15 L	ea.	22097

^{*}Range of standard gauge is -30" Hg to 60 psi.

Do not exceed canister maximum pressure of 40 psig (2.75 bar).



Can Volume	Dimensions: height x sphere diameter	Weight
1 liter	8.5 x 5.25" (21.6 x 13.3 cm)	2.25 lbs (1.02 kg)
3 liter	11.5 x 7.25" (29.2 x 18.4 cm)	3.50 lbs (1.59 kg)
6 liter	12.5 x 9.25" (31.8 x 23.5 cm)	5.75 lbs (2.61 kg)
15 liter	17.0 x 12.25" (43.2 x 31.1 cm)	11.75 lbs (5.33 kg)

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High-capacity, fully automated, easy-to-use canister cleaning oven dramatically increases lab efficiency.

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- Compliant to most documented government and standard methods.
- Powerful 6i pump can achieve 50 mTorr in <25 minutes for twelve 6-L canisters; higher power 10i option also available.
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- Fully assembled and ready to use.

Description	Туре	Voltage	Certification/ Compliance	qty.	cat.#	
TO-Clean Oven	Edwards nXDS6i Dry Scroll Pump	120 V, 60 hz	CE	ea.	26379	
	Edwards nXDS6i Dry Scroll Pump	220/230 V, 50/60 hz	CE	ea.	26380	
w/Oil Free Pump	Edwards nXDS10i Dry Scroll Pump	120 V, 60 hz	CE	ea.	26381	
	Edwards nXDS10i Dry Scroll Pump	220/230 V, 50/60 hz	CE	ea.	26382	

 $Shipping: FedEx\ Ground, unless\ otherwise\ requested.\ Costs\ vary\ depending\ on\ ship-to\ location.$



Specifications Dimensions: 44" H x 48" W x 27" D Weight: 525 lb Certification: CE

ordering notes

Note: Ovens are built on demand; therefore, a ten-week lead time is required on all orders.

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27330

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Description	Certification/ Compliance	Dimensions	Flow Capacity	Туре	qty.	cat.#
	CE, NIST	5.7" h x 2.4" w x 1.1" d	0-50 sccm	Color Display	ea.	27330
Portable Mass Flow	CE, NIST	5.7" h x 2.4" w x 1.1" d	0-50 sccm	Monochrome Display	ea.	27331
Calibrator, Whisper Series	CE, NIST	5.7" h x 2.4" w x 1.1" d	0-500 sccm	Color Display	ea.	27332
Series	CE, NIST	5.7" h x 2.4" w x 1.1" d	0-500 sccm	Monochrome Display	ea.	27333
	CE, NIST	4.1" h x 2.4" w x 1.1" d	0-50 sccm	Color Display	ea.	27334
Lab-Based Mass Flow Calibrator, Whisper Series	CE, NIST	4.1" h x 2.4" w x 1.1" d	0-50 sccm	Monochrome Display	ea.	27335
	CE, NIST	4.1" h x 2.4" w x 1.1" d	0-500 sccm	Color Display	ea.	27336
	CE, NIST	4.1" h x 2.4" w x 1.1" d	0-500 sccm	Monochrome Display	ea.	27337

^{*}Restek Recommends: Recalibrate your Alicat flow calibrator once every year to maintain lifetime warranty. Prolonged failure to recalibrate your unit may result in increased error. To always get the most accurate measurements, contact Restek Customer Service to send in your flow calibrator for service, recertification, and recalibration (cat.# 26462).



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^{**} Note: Handling, removing, or replacing the battery will void the Alicat warranty.