

Frequently Asked Questions (FAQs) for OTM-50

1. Can I use OTM-50 for testing to evaluate the performance of emerging destruction technologies for PFAS remediation?

Yes. However, it is possible that new emerging technologies are designed specifically to destroy PFAS but do not destroy other components present in the feed. OTM-50 is a trace level analytical method: Its performance can be hampered by the presence of non-trace levels of organic or inorganic components. As such, it is imperative that the feed and expected emissions are completely characterized prior to sampling.

2. Can I use a mechanical flow controller, like those used to collect ambient samples, to regulate the sample flow into the canister instead of a critical orifice?

No. Mechanical flow controllers have a regulator incorporated in them that reduces the vacuum at the sample inlet to extend the constant flow pressure range of the sampler. Because this vacuum is significantly less than the vacuum generated by the bypass pump, the sampler will not function properly. Additionally, the flow-paths of mechanical flow controllers have a substantial amount of surface area for sample interaction. They also typically include polymeric materials that can adsorb organic and inorganic constituents of the sample stream. This may lead to measurement bias and can make the flow controller difficult to clean for reuse.

3. Do I need to collect a full 4 to 5 L gas sample along with a smaller volume if the gas stream will require dilution for analysis?

No. If the gas stream is sufficiently characterized so that collection of a smaller volume of gas allows for accurate measurements of the VFCs of interest, then a critical orifice of lesser flow rate may be employed to reduce the sample volume collected. However, this approach may impact the ability to perform the procedures outlined in Section 11.3: "Reporting of Unknown Peaks". In this case, the tester/facility should consult their regulatory authority before testing to confirm a sample volume reduction is acceptable.

4. How are sources to distinguish between a volatile fluorinated compound (VFC) that may be present in flue gas as a distinct chemical compound versus a VFC that is present in flue gas as a product of incomplete PFAS combustion? Is the intent of the method to measure VFCs that are representative of PICs of PFAS?

There is not a way to distinguish between the sources of VFCs present in the flue gas unless the composition of the destruction method's influent is known. The method is intended to measure all target VFCs present in the emissions, including PICs/PIDs as well as industrial compounds of interest. These groups are not mutually exclusive and many of the current 30 target compounds fall into both categories.

5. Can SUMMA canisters be used for sampling? Section 6.0 (Equipment and Supplies) states that the suitability of SUMMA canisters has not been evaluated for the method (6.1.10). Does EPA

intend to complete an evaluation of SUMMA canisters, and what would you expect in terms of stability/applicability?

Early in the development and application to OTM-50, we did use SUMMA canisters as these were the canisters that were available to us at the time. The silicon ceramic coating is more prevalent and more inert than the traditional SUMMA passivation, so we do not plan to complete an evaluation of SUMMA canisters and we do not know what to expect in terms of stability or applicability. To use SUMMA canisters for OTM-50, laboratories would need to conduct their own investigations and show that all performance criteria in OTM-50 can be met.

6. Do canisters need to be individually checked after cleaning when the sample concentrations are high (9.3.5)?

The laboratory is responsible for ensuring the cleanliness of the canisters after undergoing the batch cleaning procedure. The degree of cleanliness may depend on the method MDLs, the requirements of the testing program, or the levels of VFCs expected in the samples.

If batch canister cleaning and certification is deemed acceptable for a sampling program, and a selected canister from the batch certification fails the performance criteria after cleaning, then it may be necessary to check each canister in the batch. The laboratory may also choose to clean the canisters a second time. A canister that sampled a high concentration may be intentionally selected as the batch representative or all the canisters from the batch may be individually checked if the laboratory prefers.

7. Do the silanized critical orifices for controlling the sample flow rate get clean checked prior to reuse, perhaps when sample concentrations are high?

No, the silanized critical orifices do not get clean checked prior to use. The cleaning procedure is provided in 8.4.2. The orifices are checked for flow before testing to verify flow rate and to ensure there is no clogging. If it is preferred further checks or more rigorous cleaning can be done before use. Ultimately, the orifice cleanliness is confirmed as part of the sampling system background QC check.

8. Should the cleaning procedure of the glassware for the sampling train (moisture/acid gas conditioning) be based on the procedure for OTM-45 to make sure that all PFAS are adequately removed (8.4.1)?

This is a valid suggestion. What's presented in OTM-50 are the procedures that have been shown to work. The low surface energies and low boiling points of these nonpolar VFCs should, generally, simplify the cleaning procedure. The primary difference is that the glassware is not baked to the same, higher temperatures contained in OTM-45. The glassware cleaning procedure in OTM-45 can be used for OTM-50 but is not required at this time.

9. Why are the sample lines heated to 120 °C towards the bypass pump (8.5.6.1)? Is this to protect the pump?

Heated sample lines are only used with the Direct VFC Sampling System (see Figure OTM-50-1) and only in instances where the moisture content is $\leq 3\%$ v/v. Moisture is not removed in this configuration. The actual operating temperature for sampling does not exceed 250 °F/121 °C and can be as low as 5 - 10 °C above the duct or stack temperature. Unheated lines are used from the exit of the orifice sample tee to the bypass pump.

10. Why isn't a dehumidifier/silica tower included in the sampling train?

The volume of gas withdrawn from the sampling port is not large enough to warrant it. The canister only samples a portion of this gas stream and drying of the gas for a dry gas meter is not needed.

11. Did you test volatilization from the applied PFA lines? Our experience with PFA tubing indicates that extended heating may not be effective (via OTM-45).

We have not seen contamination from the heated PFA lines that have been purged as described. Possible off-gassing is determined by the sampling system background (9.1.1), where a sample is collected while flowing UHP air or nitrogen through the entire sampling system, which includes the heated PFA lines, if used. This is performed following cleaning of the PFA heated lines, where the lines are heated to the maximum operating temperature and purged for at least 2 hours. The sample line cleaning temperature exceeds the maximum operating temperature for sampling. OTM-50's targets are different from OTM-45's targets, and the highly volatile VFCs may just get purged faster than the polymer processing aids.

12. Do the PFA sample lines have to be heated for 2 hours for every test or just at first use (8.4.3.1)? Is this step to off-gas existing VFCs from the line so they do not off-gas during the test?

Heating and purging sample lines is only required at first use for 2 hours. You do not need to purge the sample lines between runs, but you do need to clean them to remove contaminants. Best practice suggests purging them prior to the first test at a site. You could also use a different line in between tests.

The purpose of the cleaning is to condition them and purge any VFCs in the transfer line material itself as well as for any VFCs that may be retained from an actual sample collection. Note that the heated transfer lines are heated well above the maximum sampling temperature (120 °C) during cleaning (e.g., ≥ 150 °C/300 °F). The actual cleanliness of the heated transfer line is not assessed separately prior to use but is assessed as part of the sampling system background QC check.

13. Are used lines blank checked between use to evaluate carryover?

The system background sample is used to check for train contamination. Lines and glassware that were all prepared in the same fashion do not need to be rechecked after the one train setup. If the same train is to be used for multiple samples without the normal cleaning procedures, then another blank would be recommended using the used train to ensure no carryover.

14. Why is the relative humidity (RH) probe heated up to 180°C (6.1.11)?

This has to do with the range of function of the RH probe. To enable the use of a proper RH probe, it must be capable of functioning at temperatures of ≥ 180 °C.

15. Is the OTM-50 sampling train complementary with the OTM-45 sampling train? Most applications/studies (e.g., on incinerators) will be interested in the full PFAS scope (both >C4 and <C3 compounds).

Combining the two trains is not something EPA would envision. These are separate methods. Operating both trains simultaneously and independently is possible.

16. Are there specific CO₂ and individual acid gas thresholds that EPA has observed that are of concern? The method specifies a threshold for moisture (>3%) whereby a specific sampling methodology should be used, but a threshold for acid gases has not been provided (1.1.1). Are acid gas readings required data?

There are no CO₂ and acid gas thresholds that we know of. The impingers reduce the acid gases to manageable levels (without impingers the canisters and analytical equipment can be substantially harmed when acid gases are present). We have been able to quantitate the target compounds in samples with as high as 12% CO₂. It is important to know the CO₂ concentration because it was found to be an interferent with certain targets and knowing the sample CO₂ concentration informs analytical approaches to ensure the data quality parameters are met. Acid gas readings are not required data. But if acid gases are present, impingers must be used.

17. Should glass lines or borosilicates be used instead of coated stainless-steel lines in the sampling configurations (6.2.2.1.2)? Couldn't the coated stainless steel go bad quickly?

While glass is preferred, experiments have shown that silicon ceramic coated steel is superior to raw stainless steel. Over time, the coating on the stainless steel could be compromised by acid gases. We have not had the opportunity to perform paired trains with silicon ceramic coated steel and a glass liner concurrently. However, it has been noted that silicon-ceramic-lined stainless steel should not be heated above 80 °C as damage to the surface coating due to oxidation may occur, leading to active sites on the surface of the steel (see TO-15a).

18. Should the impingers also be analyzed for mass balance in case some of the VFCs with lower partial pressure condense out in the impingers during sample collection?

Analysis of impinger catch in the acid gas water managed OTM 50 sampling train is not required. If a mass balance is desired, the impingers contents may be analyzed for water soluble targets (sample train rinses could also be considered). A procedure for the analysis of the impinger contents has not been developed yet, although application of water or waste methods for short chain water soluble PFAS may have application.

19. What should the final vacuum in the canisters be after sampling? What should the sampler do if the final vacuum after sampling is outside of the recommended range?

In most cases a 4 - 5 L sample size is ideal. That would be equivalent to 68 - 85 kPa (10 - 5 in. Hg vacuum) final pressure. A sample over 5 L will likely not be representative of the source, as the pressure differential across the critical orifice will reach a point where the sampling flow rate will greatly decrease. If the pressure is lower (more vacuum) than expected, a smaller sample volume was collected. Collecting a smaller volume does not invalidate a sample and may be performed if high concentrations are expected. Smaller sample volumes may increase detection limits. A larger volume (higher pressure or less vacuum) would indicate that a leak or potentially nonlinear sampling rates may have occurred. In this case, another OTM-50 sample should be collected to resample the source. If an additional sample is not collected, the data must be flagged indicating that a leak is suspected that may affect the results.

20. Why must samples be analyzed within 30 days if longer stability can be demonstrated (11.1.5)?

Samples must be analyzed within 30 days to be consistent with the hold times for other EPA canister methods (TO-15a). While longer stability has been demonstrated for the calibration standards, we have not evaluated the stability of samples collected from moist, acid gas process gas. Matrix effects that cause reactions with targets may decrease stability. More research on sample stability needs to be conducted.

21. What flow rate should be used for the Direct VFC Sampling System (OTM-50-1)?

The same flow rate should be used for both systems. The bypass gas is limited to 1 L/min. No testing has been performed to determine if there are any problems caused by using lower bypass sampling rates, e.g., adsorption of higher boiling point targets.

Canister orifice sampling rates should follow standard stack sampling integration times (approximately 1 hour per sample). Other canister sampling rates could be used, (i.e., for grab samples) but no testing has been performed to determine if there are any problems caused by higher canister flow rates, e.g., adsorption of higher boiling point targets.

22. Can you provide a chart of temperature versus orifice size versus canister volume, especially when using cold sampling lines? You will have different mass captured due to temperature difference unless you specify a certain sampling rate to accommodate for the difference.

We found it helpful to test the flow rate of the orifice with an extra evacuated canister and a flow meter at the sampling location. Often orifices of the same "size" provide different flow rates.

23. Can you provide more information on internal standards and calibration standards?

Multiple internal standards can be used to monitor instrument performance. Target compounds can be purchased as individual standards and mixed by laboratories, or a mixed compressed standard may be purchased given sufficient lead time for the vendor. Several vendors now supply mixed OTM-50 calibration standards.

24. Can calibration standards be diluted with humidified nitrogen instead of zero air (10.1.2)?

Perhaps, but we prefer that zero air be used instead of nitrogen to best match the composition of field samples.

25. Can different volumes be used for field sample analysis (11.2)?

Different injection volumes can only be used to analyze field samples if the calibration and CO₂ bias check has been performed for each volume as described in the method.

26. Is loop injection allowed for higher concentration samples or analytes that may break through the trap?

Yes, provided the calibration and other quality checks are performed in the same way as the samples are analyzed. Variable volume injections have been addressed in the method. Loop injections would likely only be for double digit or higher parts-per-million concentrations and limit the application greatly. A high concentration sample can be diluted in an additional canister to allow analysis of more types of samples with only one calibration and QC procedures.

27. Was there a particular sample or set of conditions in which you saw issues with the trifluoromethane under (11.2.1)?

Yes, the issues with trifluoromethane are related to a specific set of instrumental conditions. We observed that a long purge time on a sorbent-packed focusing trap sometimes causes issues with trifluoromethane recovery.

28. Do LBs analyzed before the initial calibration (ICAL) have to meet performance criteria (10.7.3.1)?

Yes, it is necessary that the LB run directly before the calibration standards meets the performance criteria. Additional instrument blanks or air blanks may be run before the ICAL to ensure that the system has been flushed prior to running the LB.

29. Why does CF₄ appear to be 100x higher than the other compounds in the calibration bias assessment (Table OTM-50-6) when it is only 10x higher in the VFC calibration standard?

CF₄ was evaluated based on 20 mL injection volumes of the VFC standard while all other compounds were evaluated using 200 mL injection volumes. A lower injection volume was utilized for CF₄ due to its low breakthrough volume on the trap. Since CF₄ is present at a 10-fold higher concentration than the remaining compounds in the standard and was injected at a lower volume, the CF₄ concentration is 100-fold higher in the evaluations performed at U.S. EPA.

30. Is the CCV response factor used to quantify target compounds? Does this depend on the calibration curve fit selected during ICAL?

Yes, the initial CCV response factors for a sequence are used to quantitate the target compounds in this method if linear calibration curves are used for the ICAL. If a quadratic

equation is used, then the ICAL curves are used for quantitation and the CCV must be within +/- 20% of the theoretical concentration.

31. Are the concentrations in the calibration standard range before or after 3x dilution? Should the concentrations be of the diluted samples/standard, or of the original samples as received? Do we need to correct for dilutions?

The concentrations in the calibration standard range are representative of the actual amount of VFCs in the canister when they are prepared. Samples may be analyzed with or without dilution or pressurization. If samples are diluted/pressurized, these dilutions will need to be corrected for during data analysis. Each canister may have a different dilution factor depending on its pressure after sampling and exactly how much it is pressurized before instrumental analysis. For higher concentration samples, dilution is required to bring samples into the calibration range. EPA prefers samples to be analyzed in the linear range of the calibration curve.

32. Can you explain how the MDLs were determined in Table OTM-50-2? The lowest level standard is usually used to determine MDLs using 7 replicate injections, but the lowest CF₄ standard was shown as 50 ppbv. Normally the MDL can be reported as no more than 10x lower than the test concentration, yet Table OTM-50-2 shows CF₄ at 0.03 ppbv, which is more than 1000x lower.

The MDLs were determined using the standard deviation of eight injections from four canisters prepared at 0.0125, 0.025, 0.050, and 0.125 ppbv (CF₄ only) multiplied by the student's t-test for 99% confidence with n-1 degrees of freedom (2.998). MDLs were determined using the 0.0125 ppbv canister unless the target compound could not be detected at that concentration. When a standard deviation between replicate injections was not available, the MDL was estimated at the spiking level (3-5:1 signal-to-noise visual). If a target compound had numerical results in the LB in some of the replicate injections, but not all, then the MDL was set to the highest LB concentration result. If all LBs had numerical results for the target analyte in replicate injections, the MDL was calculated using the standard deviation of the LB concentrations multiplied by the student's t-test for 99% confidence with n-1 degrees of freedom (2.998) and added to the average concentration of the LB. The MDL for CF₄ was determined using a 0.125 ppbv calibration standard, so the determined MDL of 0.030 ppbv is within the range of 10x lower than the test concentration and not 1000x lower.

33. Do you have suggested MDL levels?

No, we do not have suggested MDL levels. MDLs will vary depending on the type of mass spectrometer that is used and the method parameters. Table 50-2 shows MDLs we have achieved using a quadrupole mass spectrometer.

34. Section 15.0 (Waste Mgmt) is reserved. Does the Agency intend to offer guidance for the proper management of potentially PFAS contaminated wastes resulting from this test method?

No formal guidance for PFAS waste management is included at this time. The filter, the impinger water, and tubing that will not be reused are the main wastes from sampling. Many sources

could have other substances in the emissions that may be harmful. It is best to dispose of the materials following the guidelines for the other potential hazardous materials that may be present.

35. What do I do if the lowest calibration point fails QC criteria for a few target analytes in the ICAL?

If some, but not all, of the target analytes are not within $\pm 20\%$ of its true value at the lowest calibration point, then that calibration point is outside of the linear range for that compound. A higher calibration point must be used to establish the QRL for compounds outside of $\pm 20\%$ of the ICAL.

36. Does the operating temperature of the orifice affect sample flow rate?

We have considered the effects of temperature as well as sample gas composition on orifice sample flow rates and have determined these effects to be minor relative to method performance requirements. Based on orifice sampling temperatures of 20 °C (VFC Canister Sampling System with Water/Acid Gas Management) and 120 °C (maximum temperature of the Direct VFC Sampling System), the theoretical sample flow rates would differ by <5%. The theoretical sample flow difference is even less when comparing ambient gas composition to combustion gas composition.