Frequently Asked Questions (FAQs) for OTM-50

1. **Is the target list of 30 compounds aimed at incinerator compounds and products of incomplete combustion/destruction (PICs/PIDs)?**

   OTM-50 is intended to measure a variety of volatile fluorinated compounds (VFCs), 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.

2. **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.

3. **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. Is there any experience with SUMMA canisters?**

   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. However, we did not evaluate their performance. The silicon ceramic coating is more prevalent and more inert than the traditional SUMMA passivation, so we have not performed further evaluations.

4. **Does EPA intend on complete an evaluation of SUMMA canisters? What would you expect in terms of stability/applicability?**

   No, EPA does 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.

5. **Do canisters get batch certified clean between uses?**

   Yes, the canisters are batch certified clean between use. One canister from every cleaning batch is analyzed as a lab blank to check for cleanliness.

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

   No, it is not necessary to individually check every canister, unless the selected canister from the batch certification after cleaning fails the performance criteria. In this case, other canisters from the batch will need to be checked and the entire batch may need to be cleaned 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?**

   The orifices are rinsed with water and methanol. Then dried in a vacuum oven at 50-70 °C and 16-33 kPa. The water and methanol should remove most PFAS that may form the targets and the vacuum oven ensures that the volatile compounds are evaporated. So far, the blanks from orifices cleaned in this way have been clean. 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. **Have stability problems with the VFC compounds been observed?**

   No, we have not observed issues with stability of the VFC compounds. A stability study was conducted for the 30 VFCs presented in Table OTM 50-1. In this study, a 20 ppbv VFC calibration standard (200 ppbv CF_4) was assessed over a period of 23 weeks. Most compounds met performance criteria of recovery within +/- 30% over this duration. Table OTM-50-8 presents the results of this study.

9. **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?**

   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.

10. **Why are the sample lines heated to 150°C towards the bypass pump? 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 ≤3% v/v. Moisture is not removed in this configuration. The actual operating temperature for sampling does not exceed 250 °F/121 °C. Unheated lines are used from the exit of the orifice sample tee to the bypass pump.

11. **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.

12. **Did you test volatilization from the applied TFA lines?**

    Yes, this is accomplished during the determination of 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.

13. **Why is it required to heat PFA tubing for at least 2 hours to limit VFC off-gassing? Our experience with PFA tubing indicates that extended heating may not be effective (via OTM-45). Can the Agency share the testing results that were used to inform the selection of a 2-hour heating threshold as referenced in the method? Are you heating the lines and purging them to off-gas existing VFCs from the line so they do not off-gas during the test? Reason is unclear.**

    See the answer to question 12. We have not seen contamination from the heated PFA lines that have been purged as described. The targets are different from OTM-45's targets, and the highly volatile VFCs may just get purged faster than the polymer processing aids.

14. **Why isn't a field blank included? Have you looked at ambient concentrations, contamination risk and potential leakage from heated TFA linings?**

    We believe the determination of the sampling system background includes an assessment of the potential contamination from the heated PFA lines. A separate test of just the lines has not been attempted at this time, as acceptable quality control checks have been observed from the sampling system background samples.

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

    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.

16. **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. From a technical standpoint, the incompatibilities appear minor.

17. **Are there specific CO_2 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.**

    There are no 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 targets in samples with as high as 12% CO_2. It is important to know the CO_2 concentration because it was found to be an an interferent with certain targets and knowing the sample CO_2 concentration informs approaches to ensure the data quality parameters are met.

18. **Are acid gas readings also required data? If so, would the data be limited to SO_2 and HCl?**

    No, acid gas concentrations are not required data.

19. **Should glass lines or borosilicates be used instead of coated stainless-steel lines in the sampling configurations? 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.

20. **Should the heated filter be glass or can quartz be used?**

    A glass filter housing should be used. We use an inconel filter support. The filters should be glass or quartz fiber filters.

21. **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.

22. **What should the final vacuum in the canisters be after sampling?**

    In most cases a 5 L sample size is ideal. That would be equivalent to 85 kPa (5 in. Hg vacuum) final pressure.

23. What should the sampler do if the final vacuum after sampling is outside of the recommended range?

If the pressure is lower (more vacuum) than expected a smaller sample volume was collected. A smaller volume collected does not invalidate a sample and may be performed if high concentrations are expected. Smaller sample volume 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 taken to resample the source. Worst case if an additional sample is not collected, the data must be flagged indicating that a leak is suspected that may affect the results.

24. Why must samples be analyzed within 30 days if longer stability can be demonstrated?

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.

25. 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. Bypass gas is limited to 1 L/min. No testing has been performed to determine if there are any problems caused by 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.

26. 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.

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

Availability of gaseous mixed standards for OTM 50 is an ongoing topic that EPA is following. OTM 50 is clear about multiple internal standards that 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.

28. Can calibration standards be diluted with humidified nitrogen instead of zero air?

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

29. Can different volumes be used for field sample analysis?

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.

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

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.

31. Why is water being added to the canister field samples?

We have removed the requirement to add water to field samples prior to analysis. The addition of water was a remnant from the use of SUMMA canisters.

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

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.

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

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.

34. Why does CF_4 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?

CF_4 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 CF_4 due to its low breakthrough volume. Since CF_4 is present at a 10-fold higher concentration than the remaining compounds in the standard and was injected at a lower volume, the CF_4 concentration is 100-fold higher in the evaluations performed at U.S. EPA.

35. **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.

36. **Is the CCV response factor used to quantify compounds that are not in the calibration standard?**

    No, the CCV response factor is not used to quantify compounds that are not present in the calibration standard. Unknown peaks present in samples that are not in the calibration standard are reported along with their retention times and peak areas, but these are not given quantitative values.

37. **Section 1.2 says the method is applicable to concentrations up to 300 ppbv. Is that before or after 3x dilution?**

    Section 1.2 indicates that this upper range of 300 ppbv is for undiluted samples. The method is applicable for samples that fall into the calibration range of the method. 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.

38. **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.

39. **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 CF_4 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 CF_4 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 (CF_4 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 CF_4 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.

40. 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 does present MDLs we have been able to achieve using a quadrupole mass spectrometer.

41. 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.

42. 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 ±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 ±20% of the ICAL.

48. Is the heating of the PFA heated lines and purging them to off-gas existing VFCs from the line so they do not offgas during the test?

OTM-50 has been revised to clarify the procedure for cleaning the heated transfer lines (Section 8.4.3) – both new and after use. 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.

43. Do the lines have to be heated for 2 hours for every test or just at first use?

Heating and purging is only required at first use for 2 hours. You do not need to purge them 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.

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

The system background sample is to show that the cleaned train does not have any 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 to ensure no carryover.

45. Is the Agency aware of acceptable alternatives to heating PFA tubing for 2 hours that would eliminate the VFC risk?

We are not aware of any methods that are easier. If another method provides clean blanks, then that method can be used.

46. Do you have any data to back up the off-gassing/adsorption from Viton and Telfon? They're common materials so it would be interesting to look at conditions under which off-gassing and adsorption had occurred to try and understand more. Off-gassing from Viton has been seen at >200 °C but more data would be great to have.

We do not have data about off-gassing/adsorption about of these polymers.

49. **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.