Technical Report

Multi-Laboratory Validation Study for Quantitation of Trifluoroacetate (TFA) by CAC-TFA-1.0

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1. Introduction:

1.1. Background

Trifluoroacetate (TFA) is an ultrashort-chain perfluoroalkyl substance (PFAS). It is the smallest of the perfluorinated carboxylates and considered fully mobile and highly persistent in the environment. TFA is stable in the environment and can persist in soil, water, and air for extended periods, likely to disrupt metabolic and endocrinal pathways and may cause developmental toxicity. TFA can form from the breakdown of a variety of chemicals, such as longer chain PFAS, pharmaceuticals, HFCs, and fire-fighting foams. Levels of TFA, and other ultra-short chain (USC) PFAS, are trending higher in aquatic environment and drinking waters due to their persistence. It has become more important to measure and monitor USC PFAS to assess the potential risks. The State Water Resources Control Board, Division of Drinking Water (DDW) has contracted CDFA's Center for Analytical Chemistry to develop a method for use in monitoring this compound in drinking water.

1.2. Method Summary

The analytical method for this study was validated and the single laboratory validation results are summarized in the following section. Refinements were made to that method based on the comments and results from the four participating laboratories in the multilaboratory validation study (MLVS). Those updates are released as CAC-TFA-1.1. This complete method is attached to this report as Appendix A.

The analytical method includes sample preparation and sample analysis procedures for raw and finished ground- and surface-sourced drinking water. The limited sample preparation includes spiking an isotopically labeled internal standard. The samples are directly injected into a liquid chromatography tandem mass spectrometer (LC/MS/MS) system for quantitative analysis.

1.3. Summary of the Single-Laboratory Study

The single-laboratory validation was performed by CDFA's Center for Analytical Chemistry Research and Development Unit (Sacramento, CA) (CAC-R&D), the laboratory originally contracted by State Water Resources Control Board, Division of Drinking Water (DDW) to develop a laboratory Standard Operating Procedure (SOP) for the analysis of TFA.

The single-laboratory validation study was intended to generate method performance data for the necessary aqueous matrices (surface and groundwater, raw and finished). Due to the ubiquitous nature of TFA, many of the near-MRL level spikes have exaggerated recoveries, sometimes over 500%. However, any of the test matrices that were spiked at least three times higher in concentration than their incurred level had acceptable recoveries between 70-130% when spiked greater than twice the MRL, and for the small number of samples that had very low levels of incurred TFA, MRL-level

spikes had recoveries between 50-150%. From these results it was decided to only include water sources with very low levels of background TFA in the MLVS.

The required instrumentation for this method has become commonplace in many full-service environmental laboratories. This availability, along with limited sample preparation, indicates that this method should be accessible, and possible to be implemented in a typical full-service environmental laboratory.

2. Study Management, Objectives, Design, and Implementation:

While this MLVS is not designed to support an alternate test procedure (ATP) application, the number of matrices and statistical analyses of the data reflect what would be required for an ATP for national use.

2.1. Study Management

Four laboratories (three commercial contract laboratories and one municipal water district laboratory) volunteered to participate in the study, under the authorization and stewardship from DDW. The four laboratories are listed in Table 2-1. All four laboratories contributed to the analysis of the aqueous matrices in this report (raw groundwater and finished groundwater-sourced drinking water). For the purposes of this study, the laboratories were randomly assigned numbers, which were used to maintain the anonymity of the results, these numbers do not correspond to their order of appearance in Table 2-1.

The CAC Quality Assurance unit (CAC-QA) oversaw the spiking of matrix and Proficiency Testing (PT) samples, and managed the shipment and received all data packages from the laboratories. Analytical standards were provided to the participating laboratories by CAC. Participating labs were also connected with a representative of Phenomenex Inc. who offered to provide LC columns for this study, if there was such a need. CAC-QA, with an established operational set-up and expertise to conduct PT schemes, prepared the PT samples shipped as part of this study, while CAC-R&D prepared the aqueous matrix samples.

CAC served as the method consultant to the MLVS and was available to clarify any questions or concerns.

Table 2-1. Participating Laboratories

Laboratory	Location	Role
Participating MLVS Labs		
Babcock Laboratories, Inc.	Riverside, CA	MLVS participant
Orange County Water District	Fountain Valley, CA	MLVS participant
Eurofins Environment Testing	Sacramento, CA	MLVS participant
McCampbell Analytical	Pittsburg, CA	MLVS participant
Ancillary Labs		
CDFA Center for Analytical Chemistry – Research and Development	Sacramento, CA	Single laboratory validation, preparation of matrix samples
CDFA Center for Analytical Chemistry – Quality Assurance	Sacramento, CA	Preparation of PT samples, evaluation of data

2.2. Study Objective and Design

The focus of the MLVS is to generate the necessary data to document the precision and accuracy and overall performance of the analytical method for quantitation of TFA in aqueous matrices. The primary objectives of this MLVS are to:

- Obtain data from aqueous matrices that are representative of the method's intended use.
- Obtain data from laboratories that are representative of those likely to use the method, but that were not directly involved in its development.
- Obtain feedback from laboratory users on the specifics of the method SOP.
- Use study data to evaluate the performance of the method.
- Develop QC acceptance criteria – average recovery and relative standard deviation – that will reflect method performance capabilities in real-world situations.

A brief description of the key points of this study design include:

- At least three laboratories, one of which is a municipal water laboratory.
- Two aqueous matrix samples from source and finished groundwater.
- Initial calibration of TFA by each laboratory.
- Initial Demonstration of Capability (IDOC) by each laboratory.
- Analyses of PT sample and matrix spike samples from each aqueous matrix.

This MLVS was conducted in two phases. The IDOC, which includes the initial calibration and verification of MRL level, and the method evaluation in the chosen aqueous matrices.

2.3. Matrix and Sample Selection

Two groundwater samples (one raw and one finished drinking water) were used for this phase of the MLVS. These were chosen to be representative of the expected real-world matrices analyzed by this method. These samples were collected from the Citrus Heights Water Treatment Plant. This location was chosen as it had previously been found to have very low incurred TFA levels, allowing it to be used for even the MRL-level spikes.

The MLVS was designed to include, for each water matrix analyzed, an 'unspiked' (native) sample, two replicates spiked at low concentration, and two replicates spiked at a mid-level concentration.

2.4. Selection of Spiking Levels and Aqueous Media

The sample matrices were collected by DDW. The chosen sample matrices were raw and finished water from the Citrus Heights Treatment Plant. The TFA spiking levels were chosen by CAC to be at the proposed MRL for the low-spike, and below 10 ppb for

the mid-spike. CAC-QA separately selected the PT spike level so that it would be blind to everyone participating, including all other CAC units.

2.5. Preparation of Study Samples

Aliquots of groundwater for each of the raw and finished sources were prepared as follows: The sample bottles delivered by DDW were allowed to come to room temperature and then inverted several times to ensure homogeneity. A 10mL matrix sample was prepared in a 30 mL amber leakproof HDPE bottle for each level. The water samples prepared and shipped by CAC were, for each matrix: one unspiked sample, duplicates at the MRL-spike level, and duplicates at the mid-spike level. After spiking, they were mixed well, sealed and stored in a refrigerator until they were packaged and shipped to the participating laboratories. The samples were shipped in ThermoSafe® insulated boxes with sufficient blue-ice packs to keep them cool, and a TempDot® sensor to ensure the samples stayed cold during transit.

As part of the MLVS, Proficiency Testing (PT) samples were also sent to the laboratories. An unknown spiked sample prepared by CAC-QA utilized reagent water as the matrix and shipped along with the study sample spikes. CAC-R&D analysts involved with the TFA method development had no participation in preparing these samples. CAC-QA also provided a PT sample to the CAC-R&D lab for analysis.

2.6. Storage Stability Study

During method development, a storage stability study was conducted to determine the hold time of TFA samples in finished tap water over the course of 28 days. The matrix samples were spiked in triplicate for this study, and triplicate tap water blanks were also stored at the same time. This allowed for the analysis of both the stability of the spiked TFA, but also the stability of any TFA concentration incurred. The data can be found in the method SOP in Appendix A, and the hold time was determined to be 28 days. The samples were stable through the end of the storage stability study.

3. Data Management, Data Validation, and Data Rules for Statistical Analysis:

3.1. Programmatic Overview

The data management process involved documented and approved instructions, meetings, consultation and communication when required, and review of laboratory packages. A “kickoff” meeting over Teams was scheduled to explain the expectations for the MLVS to the participating laboratories. Laboratories were provided with the method prior to the meeting in preparation and given the opportunity to review and get any questions or concerns clarified. They were also encouraged to ask questions via email or to schedule a one-on-one meeting throughout the MLVS as necessary. A written document containing the MLVS guidelines and passing QC criteria was also provided to the laboratories along with a data reporting template Excel workbook, to ensure uniform reporting.

3.2. Data Management

All result reporting forms, and raw data were submitted to CAC-QA via email. The labs were provided with an Excel workbook containing a sample handling sheet to document sample preparation and a template to report their analytical batch data and compute the IDOC results. The Excel template cells with embedded formulas were locked to prevent accidental corruption or unintended changes. The laboratories also submitted their instrument data such as chromatograms and transitions.

3.3. Data Validation

All data packages were reviewed by CAC-QA for completeness, compliance with the MLVS guidelines, and performance according to the QC metrics, see QC acceptance criteria in the SOP in Appendix A.

4. Calibration and Quantification:

Aqueous samples were analyzed by LC/MS/MS in MRM mode. The mass spectrometer was calibrated for masses to ensure the accuracy of the mass to charge ratio (m/z) values assigned to the instrument per the manufacturer's instructions. After the mass calibration had been verified, quantitative standards were used for a minimum five-point calibration for TFA.

4.1. Mass Calibration and Mass Calibration Verification

Each laboratory performed mass calibration and verification in accordance with their respective instrument manufacturer's instructions. The laboratories were instructed to use the same precursor and product ion masses (113/69), as TFA is very small and only has one reliable transition.

4.2. Initial Calibration

To provide each laboratory with the target analyte, CAC procured standards from Cabridge Isotope Laboratories, Inc. (CIL) and HPC Standards Inc, two commercial standards vendors. By providing the standards to all laboratories, the study variability that would have resulted from having each laboratory prepare standards was reduced. This also reduced the direct costs to each laboratory for their participation. The standards provided by CAC were used by the laboratories to create all calibration standards, calibration verification, and spiking solutions used in the MLVS. CAC-R&D and CAC-QA also used the same lot of standards to prepare the matrix samples and PT samples. In addition, CAC provided the laboratories an internal standard, procured from CIL.

Each laboratory calibrated their LC-MS/MS instrument using a series of calibration standards similar to those described in the method SOP (Appendix A); five to eight calibration levels between 0.040 ppb and 20.0 ppb. Each laboratory chose a different distribution of calibration levels. A minimum of five calibration standards was required for a valid analysis with the lowest calibration standard being at or below the MRL. The laboratories were allowed to use a linear or quadratic regression using peak areas and the internal standard technique. The SOP outlines calibration and quantification using an internal standard where TFA's response is compared to the isotopically labeled $^{13}C_2$-TFA.

Analytes at or below the MRL are required to be within ±50% of the true value, all other levels, within ±30% of the true value. Regression coefficients, r or r^2, were required to pass the following criteria: $r>0.995$, $r^2>0.990$. The relative standard error of the calibration curve needed to be less than or equal to 15%. An initial calibration was required to be submitted by each laboratory as part of the IDOC prior to receiving spikes/PT samples.

4.3. Calibration Verification and Instrument Sensitivity Check

Each laboratory analyzed multiple Continuing Calibration Check (CCC) samples in each batch to verify the integrity of the curve throughout the batch. The batch starts with a standard at the method MRL, followed by another CCC after every 10 samples, alternating between mid- and high-level calibration standards. MRL-level CCCs were required to recover within ±50% of their true value, mid- and high-level CCCs were required to recover within ±30% of their true value. No sample results were eliminated from the study due to CCC failures.

5. Initial Demonstration of Capabilities:

In addition to performing the initial calibration, laboratories submitted the results for IDOC. The IDOC included a precision and accuracy analysis, system background check, and MRL confirmation. In addition to those metrics discussed below, each laboratory also demonstrated satisfactory results for the chromatographic requirements (peak shape, change in retention time (RT), and internal standard area deviation from the calibration).

5.1. Demonstration of Precision and Accuracy (P&A) Results

Laboratories were required to spike seven replicate Laboratory Fortified Blanks (LFBs) fortified near the center of their calibration range. These LFBs were prepared and analyzed in the same manner as study samples, per the method. A percent relative standard deviation of less than 15% and a mean percent recovery of ±30% of the true value were the required criteria for this demonstration. All laboratories met these criteria.

5.2. Acceptable System Background

Five Laboratory Reagent Blanks (LRB) were run in the same batch as the LFBs for the P&A. The laboratories were required to have a background TFA level of less than one-third of their MRL. All laboratories satisfied this requirement, however Laboratory 4 originally only analyzed two LRBs and was directed to run the full five LRBs with their matrix samples as required by the study design.

5.3. Minimum Reporting Limit Verification Analyses

The Minimum Reporting Limit for TFA using this method was set by the method development (MD) laboratory at 0.085 ppb. The participating laboratories were required to confirm their MRLs using the MD level as an initial reference point. If the MRL confirmation fails initially, the labs were instructed to increase the concentration until the MRL confirmation passed. Seven LFBs were required to be spiked at the proposed MRL for confirmation using the formulas in the method.

Evaluation of the MRL data indicates that two laboratories confirmed the MRL at 0.085 ppb, one lab confirmed 0.075 ppb as the MRL, and the remaining lab at 0.250 ppb.

5.4. Quality Control Sample (QCS)

A QCS prepared from a standard from a different source to that of the calibration standards was also required as part of the IDOC. Each laboratory was sent standards from multiple vendors and allowed to choose which they would use as their primary standard and which would be their QCS. The QCS was prepared by the labs as a mid-level spike was used to confirm the accuracy of the calibration standards. The QCS must be within ±30% of the true value. All laboratories had passing QCS values indicating accurate calibration curves for this MLVS. Laboratory 1 spiked at 0.100 ppb,

Laboratories 2 and 3 spiked at 0.500 ppb, and Laboratory 4 spiked at 1.00 ppb, the recoveries are shown in Table 5-1.

Table 5-1. IDOC Results

Laboratory	Precision (%RSD)	Accuracy (Mean %)	System Background (Mean ppb)	MRL (ppb)	UPIR	LPIR	QCS
1	1.4%	94.7%	0.000	0.085	114.1%	68.8%	93.0%
2	3.0%	92.4%	0.000	0.075	146.1%	79.8%	90.5%
3	14.5%	97.9%	0.000	0.085	140.9%	71.7%	116.2%
4	3.7%	99.2%	0.000	0.250	145.0%	86.8%	106.8%

6. Water Matrix Results:

Each participating laboratory was sent ten matrix samples from the Citrus Heights Water Treatment Plant, five prepared from raw groundwater and five from finished groundwater. In addition to these ten samples, each lab was also sent a field reagent blank to analyze. The Citrus Heights Water Treatment Plant was chosen as the source of the matrix water for the current MLVS due to prior testing of its water by CAC-R&D showing it to have little native TFA concentration, and demonstrated not to interfere in the analysis. This was essential so that the laboratories would demonstrate their ability to analyze samples at their MRLs, given the ubiquitous nature of TFA, no other drinking water source among those tested during method development was evaluated to be without a native concentration of TFA.

6.1. TFA Concentrations in Unspiked Matrices

Each laboratory received one 10 mL sample of each unspiked matrix, raw and finished ground-sourced drinking water. All laboratories reported native concentrations of TFA well below one-third of their MRLs. These levels are included in Table 6-1.

6.2. Matrix Spike Results

The spike recovery data from all laboratories is also shown in Table 6-1. The raw and finished water matrices were spiked in duplicate at the proposed MRL-level (0.085 ppb) and at a mid-level (5.00 ppb).

The results were mixed for the MRL-level samples. Laboratory 3 had some samples with internal standard areas that deviated from the expected ±40% from the calibration set and had ND results for the MRL-level matrix samples. The MRL-level spikes were below Laboratory 4's confirmed MRL level of 0.250 ppb and are reported as estimates. Laboratory 1 had a single MRL-level sample (in raw groundwater) fall below the passing QC criterion of 50% recovery, but all their other MRL-level samples passed.

The results from all laboratories at the mid-level had recoveries ranging from 59.8%-122.6% recovery. Laboratory 3 had mid-level recoveries below the passing QC criterion 70% recovery.

6.3. PT Results

Each laboratory was sent a PT sample prepared by CAC-QA for analysis. PT sample ensemble with matrices were packaged in an insulated shipping box (such as ThermoSafe®) with ice packs ensuring standard integrity. All PT samples were shipped together to ensure process integrity and uniformity. Participating labs were given four weeks of time with results required to be sent to the CAC - QA. Table 6-2 denotes the results.

Table 6-1. Unspiked and Spiked Matrix Results

	Raw (ppb)					Finished (ppb)					
Laboratory	Unspiked	MRL Rep. 1	MRL Rep. 2	Mid-Level Rep. 1	Mid-Level Rep. 2	Unspiked	MRL Rep. 1	MRL Rep. 2	Mid-Level Rep. 1	Mid-Level Rep. 2	Field Blank
1	ND	0.059	0.040	3.676	3.775	ND	0.046	0.057	3.787	3.857	0.001
2	ND	0.072	0.052	6.129	5.810	ND	0.070	0.064	5.845	6.101	0.000
3	0.000[a]	0.000[a]	0.000[a]	3.197	3.061	0.000[a]	0.000[a]	0.000[a]	3.167	2.990	0.000
4	ND	0.034[b]	0.077[b]	5.474	5.035	ND	0.081[b]	0.074[b]	5.465	5.385	ND
CAC-R&D	ND	0.054	0.060	4.685	4.877	ND	0.056	0.054	4.774	4.941	ND

[a] Laboratory 3 had internal standard areas >140% of their calibration areas for some samples, resulting in the MRL level samples reporting as ND.

[b] MRL level spikes for laboratory 4 were below the confirmed MRL and are reported here as estimates.

Table 6-2. PT Results

Laboratory number	Target Value (ppb)	Recover Conc. (ppb)	Percent Recovery
1	2.700	2.319	85.9%
2	2.700	3.719	137.7%
3	2.700	0.818	30.3%
4	2.700	3.124	115.7%
CAC-R&D	2.700	2.912	107.9%

7. Summary:

7.1. Preparatory Batch QC

Per the CAC-TFA-1.0 method, an analysis batch consists of up to 20 field samples, a method blank, a continuing calibration check, laboratory fortified blank, and a laboratory fortified sample matrix and laboratory fortified sample matrix duplicate (or field duplicate) pair. A batch should begin, and end, with a continuing calibration check sample.

7.1.1. Method Blank

Method blanks, referred to as Laboratory Reagent Blanks (LRB) in this method, are included in the method to evaluate the potential for background contamination to be introduced during sample preparation in the laboratory. The TFA concentration in the LRB must be less than one-third the MRL. This requirement was met by all participating laboratories during the matrix and PT sample batches.

7.1.2. Ongoing Precision and Accuracy Analyses

Ongoing Precision and Accuracy samples, represented in this method by the batch LFB requirements, are included to evaluate the efficiency of the sample preparation processes over time. A LFB prepared in the same manner as the study samples is included in every preparation batch. CCC samples at mid- and high-levels are distributed throughout each batch as a check on calibration as well as ongoing accuracy. These CCCs were included in all laboratories' batches

This method also calls for the inclusion of Laboratory Fortified Sample Matrix (LFSM) and Laboratory Fortified Sample Matrix Duplicate (LFSMD), or a set of Field Duplicates (FD). LFSM and LFSMD are field samples, spiked with a known amount of TFA. FD are duplicate samples, collected at the same time in the field and treated identically through all sampling and laboratory procedures. These are included to check for any contamination from sample collection, preservation, storage and laboratory procedures in the samples of each batch. While not all labs included these samples during the MLVS, they should be included during routine use of this method.

7.1.3. Low-Level Ongoing Precision and Accuracy Analyses

Low-Level Ongoing Precision and Accuracy samples, the lowest-level CCC samples in the method, are included in each in the first analysis batch each day to evaluate method performance at the at the MRL. All laboratories except Laboratory 1 included a low-CCC in their matrix and PT sample batches.

7.2. Matrix Spike Analyses

Ongoing QC criteria of ±30% recovery when spiking ≥2*MRL, and ±50% recovery when spiking <2*MRL, (Appendix A, Section 9.2.4) was applied to evaluate the results. Excluding Laboratory 3, the mid-level spike results in both matrices were satisfactory,

and the MRL-level spike results were satisfactory for labs whose MRLs were lower than the spiking level (Laboratory 4's MRL was above the spiking level).

7.3. PT Result Analyses

All participating laboratories, including the CAC-R&D lab, performed the PT sample analysis satisfactorily, with the exception of Laboratory 3, based on the target amount and applying a PT requirement of the recoveries to be within ±40%. The overall recovery is 111.8 % and the RSD is evaluated to 19.1%. This calculation does not include Laboratory 3.

Although the ongoing QC criteria is set at ±30%, using a ±40% threshold for PT evaluation is realistic given the data variability, as indicated by the RSD of 19.1%. The elevated RSD suggests a moderate level of dispersion with the PT performance results. This dispersion can be seen as representative of the potential variability between labs based on the choices each laboratory made to optimize their chromatographic conditions.

8. Conclusions:

The objectives of this MLVS were achieved: validation of the CAC-TFA-1.0 method and the determination that the method can be implemented at a typical mid-sized full-service environmental laboratory. Overall, the data from the MLVS demonstrates that CAC-TFA-1.0, as written, is robust and is suitable for laboratories with similar instruments of different manufacturers and models. Points of additional clarity have been added to the SOP as version CAC-TFA-1.1. Specifically, it has been noted that the LFSM/LFSMD should be spiked greater than the native concentration of TFA instead of just at the mid-level of the calibration. Some corrections have also been made to Tables 10 and 11 in Section 17 to more accurately reflect the QC requirements listed in Section 9.

The results of the participating labs in this study have met the requirements stated in the method for:

- Mass Calibration and Verification
- Initial Calibration
- Calibration verification and sensitivity check
- Initial Precision and Accuracy
- Confirmation of MRL
- Batch QC samples

The suitability of the method to detect and quantify TFA in ground-sourced drinking water (both raw and finished) was successfully demonstrated through the analysis of spiked samples of those real-world matrix types. This suitability should also extend to raw and finished surface-sourced drinking water as well, though a surface source with a low enough native concentration of TFA to allow for MRL-level testing was unable to be found for this study. Method blank results demonstrated no bias from background contamination during sample preparation, though this remains a concern due to the increasing ubiquity of TFA. The Initial and Ongoing Recoveries and the Low-CV recoveries demonstrated that the QC acceptance criteria in the method were satisfactory for inclusion in the finalized method.

Finding a suitable background water matrix free of any incurred TFA could be very challenging and may require several pre-evaluations to ensure appropriate blank matrix material for this analysis. We encourage studies making use of this method to require the collection of Field Duplicate (FD) pairs, instead of LFSM/LFSMD pairs, to avoid needing to pre-analyze the field matrix to determine an appropriate spiking level. Instead ensure that the relative percent difference (RPD) between the FD pair meets the method QC requirements (Appendix A, Section 9.2.6).

9. References:

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Appendix A: Standard Operating Procedure for CAC-TFA-1.1

[Changes from CAC-TFA-1.0 to CAC-TFA-1.1 have been underlined.]

Appendix B: Guidelines for Interlaboratory Validation of Method CAC-TFA-1.0

Appendix C: Data Reporting Template for MLVS of Method CAC-TFA-1.0