Comparison Table of Acceptance Criteria for EPA Method TO-15A (September 2019) to NATTS Technical Assistance Document (TAD) Revision 3 (October 2016)

May 27, 2020

TO-15A				NATTS TAD Rev 3
Parameter	**Description and Details**	**Required Frequency**	**Acceptance Criteria**	
Zero-air challenge of analytical instrument systems	Test of instrumentation to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the preconcentrator to verify that the analytical instrument and all connections are sufficiently clean	At installation prior to initial use of the instrument	Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or preferably not detected (see Section 9.3.1)	Omitted
Known-standard challenge of analytical instrument systems	Test to demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias)	At installation prior to initial use of the instrument	Verifies that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations (see Section 9.3.2)	Omitted
Zero-air challenge of autosamplers associated with analytical instrument systems	After establishing the initial calibration (ICAL), each port of the autosampler is tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections	Prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples	Each target VOC's concentration should be < 20 pptv or preferably not detected (see Section 9.3.3)	Omitted
Known-standard challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds or negative bias)	Prior to initial use and upon replacement of transfer lines	Each target VOC's concentration within ±15% of theoretical concentration (see Section 9.3.3)	Omitted
Canister leak check	Verification that canisters are leak-free by performing a pressure decay test of a canister pressurized to approximately 203 kPa absolute (29.4 psia) over the course of several days	Prior to initial use and recommended periodically thereafter (e.g., every 3 years)	Remove from service and repair any canister that exhibits a pressure change ≥ 0.69 kPa/day (see Section 9.4.1)	Identical (≤ 0.1 psi/day) [Section 4.2.4.1.1.1]

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Zero-air challenge of canisters for qualification	Test of canisters to determine that they remain acceptably clean (show acceptably low positive bias) over the course of a known time period, typically 30 days or the laboratory holding time, by filling with humidified zero air (not nitrogen)	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and a subsequent time period (e.g., 30 days), each target VOC's concentration ≤ 20 pptv at 101.3 kPa absolute (14.7 psia) (refer to Table 10-3 and Section 9.4.2)	Strongly Recommended Annually Permits nitrogen Must be < 3xMDL or 0.2 ppbv (200 pptv), whichever is lower, at each timepoint [Section 4.2.4.1.1.1]
Known-standard challenge of canisters for qualification	Test of canisters to determine bias by filling with a known reference standard (approximately 100 to 500 pptv) prepared in humidified zero air (not nitrogen) and analyzing	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and subsequent analysis at 30 days or typical laboratory holding time, each target VOC's concentration must remain within ±30% of theoretical concentration (see Section 9.4.3)	Strongly Recommended Annually Permits nitrogen Concentration range 0.3 to 2 ppbv (300 to 2000 pptv) Must recover within 70 to 130% of theoretical at each timepoint [Section 4.2.4.1.1.2]
Zero-air challenge of sampling devices/systems	Assessment of positive bias of sampling system by collecting humidified zero air through the sampling device/system and comparing it to the reference sample collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples	Analysis must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample (see Section 9.5.2)	To be conducted annually following maintenance and calibration Permits nitrogen in addition to zero air Target VOCs in challenge sample must not be > 3xMDL or 0.2 ppbv (200 pptv), whichever is lower, more than the co-collected reference sample [Section 4.2.3.5.1]
Known-standard challenge of sampling devices/systems	Assessment of bias of sampling system by collecting a known reference standard (approximately 100 to 500 pptv) through the sampling device/system and comparing it to the reference standard collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples or damaging sample matrices that may impact the activity of the flow path surfaces	Each target VOC's concentration within ±15% of concentrations in the reference sample (see Section 9.5.3)	To be conducted annually following maintenance and calibration Permits nitrogen in addition to zero air as diluent gas Target VOCs in challenge sample must be within ±15% difference of the concentration measured in the co-collected reference sample [Section 4.2.3.5.2]

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Purge gas check	Analysis of canister cleaning purge gas to ensure contaminants are acceptably low	Verified upon initial setup and in the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, or following maintenance of zero-air generator	Each target VOC's concentration < 20 pptv (see Section 10.1.1)	Each target VOC < 3xMDL or < 0.2 ppbv (200 pptv), whichever is lower [Section 4.2.4.2.3]
Canister cleaning batch blank	Analysis of a sample of humidified diluent gas in a canister from a given batch of clean canisters to ensure acceptably low levels of VOCs in the batch of cleaned canisters	One or more canisters from each batch of cleaned canisters (chosen canister should represent no more than eight total canisters) Alternatively, each canister checked for cleanliness	Upon analysis 24 h after filling, each target VOC's concentration should meet the canister blank acceptance criterion in Table 10-3 (i.e., ≤ 20 pptv at 101.3 kPa absolute, 14.7 psia) (see Section 10.2)	One canister per cleaning batch (batch size not specified, recommended as one canister per ten cleaned). At sample collection pressure, each target VOC < 3xMDL or < 0.2 ppbv (200 pptv), whichever is lower [Section 4.2.4.2.4]
Dilution blank (DB)	Canister filled with clean, humidified diluent gas that is used to dilute samples; indicates that diluent gas and dilution apparatus do not contribute target VOCs to the samples; the DB should not be prepared through a dilution system used for preparing standards	Ideally one DB is prepared and analyzed with each set of samples that are diluted, and at minimum one DB is prepared and analyzed when source and/or filters are changed	DB should be sufficiently clean such that no positive bias is imparted to the samples; each target VOC's concentration should be < 20 pptv (see Section 12.2).	Criteria not specified [Section 4.2.7]
Holding time	Duration from end of sample collection or canister preparation to analysis	Each field-collected or laboratory QC (standard or blank) canister	≤ 30 days unless longer stability can be demonstrated (see Section 13.4)	As soon as possible after collection, not to exceed 30 days [Section 4.2.1]
MS tune check, as applicable	May be accomplished by injection of 1 to 2 ng bromofluorobenzene (BFB) for tune verification of quadrupole or ion trap MS detector	Prior to ICAL and prior to each day's analysis	Abundance criteria for BFB listed in Table 14-2 (see Section 14.4.2)	Does not apply to time-of-flight (TOF) or ion trap MS Frequency: Prior to ICAL and every 24 hours of analysis thereafter. Abundance criteria for BFB in Table 4.2-2 [Section 4.2.8.5]
Retention time (RT)	RT of each IS and target compound	All qualitatively identified compounds and internal standards	IS compounds within ±2 s of their mean ICAL RTs (see Section 15.1.1) Target VOCs within ±2 s of their mean ICAL RTs (see Section 16.2)	IS compounds must be within ± 0.33 minutes of the average RT determined from the ICAL [Section 4.2.8.5.4] Target VOCs must be within ±0.06 relative retention time (RRT) units of the average from the ICAL [Section 4.2.8.5.2.2]

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Internal standards (IS)	Deuterated or other compounds not typically found in ambient air co-analyzed with samples to monitor instrument response and assess matrix effects	Co-analyzed along with all calibration standards, laboratory QC samples, and field-collected samples	Area response for each IS compound preferably within ±30% of the average response as determined from the ICAL and may not exceed ±40% (see Section 15.1.2)	Area response for each IS compound must be within ±40% of the average response determined from the ICAL [Section 4.2.8.5.4]
Initial calibration (ICAL)	Analysis of a minimum of five calibration levels (minimum eight levels if using quadratic regression) covering approximately 20 to 5000 pptv	Before sample analysis; following failed BFB tune check (as applicable), failed IS criteria, or failed CCV criteria; or when changes/maintenance to the instrument affect calibration response	Average RRF ≤ 30% RSD and each calibration level within ±30% of theoretical concentration; for quadratic or linear curves, coefficient of determination (r^2) ≥ 0.995, and each calibration level within ±30% of theoretical concentration (see Section 15.2.3)	Recommended calibration range 0.03 to 5 ppbv (30 to 5000 pptv). Minimum 5 points, recommend more if employing quadratic regression model Average RRF ≤ 30% RSD and each calibration level within ±30% of theoretical concentration; for quadratic or linear curves, coefficient of determination (r^2) ≥ 0.995, and each calibration level within ±30% of theoretical concentration [Section 4.2.8.5.2.2]
Second source calibration verification (SSCV)	Analysis of a secondary source standard in the lower third of the calibration curve to verify ICAL accuracy for each target analyte	Immediately after each ICAL	Measured concentrations of VOCs should be within ±30% of theoretical concentration (see Section 15.3.1)	Concentration not specified Frequency and acceptance criteria identical Additionally allows for RRF of each compound to be within ±30% of the ICAL mean RRF [Section 4.2.8.5.2.3]
Continuing calibration verification (CCV)	Analysis of a known standard in the lower third of the calibration curve to verify ongoing instrument calibration for each target analyte	Prior to analyzing samples in an analytical sequence and at the end of a sequence; recommended after every 10 sample injections	Measured concentrations of VOCs within ±30% of theoretical concentration (see Section 15.3.2)	Concentration not specified Frequency is every 24 hours of analysis following successful calibration Acceptance criteria identical Additionally allows for RRF of each compound to be within ±30% of the ICAL mean RRF [Section 4.2.8.5.2.4]

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Instrument blank (IB)	Analysis of an injection where no sample or standard is introduced to the preconcentrator to preliminarily demonstrate the carrier gas and instrument are sufficiently clean to begin analysis	Prior to ICAL and at the beginning of an analytical sequence	Each target VOC's concentration should be < 20 pptv (see Section 15.3.3.1)	Recommended Each target VOC < 3xMDL or < 0.2 ppbv (200 pptv), whichever is lower [Section 4.2.8.5.2.2]
Method blank (MB)	Canister filled with clean, humidified gas; indicates that target VOCs and potential interferences are at acceptably low levels in the system as a whole; the MB is to help assess overall quality of the data	Prior to and following the ICAL and prior to the initial daily CCV/SSCV	This should demonstrate acceptably low carryover in the analytical system prior to analysis of samples; each target VOC's concentration should generally be < 20 pptv (see Section 15.3.3.2)	Frequency required once each analysis batch of 20 or fewer field collected samples Each target VOC < 3xMDL or < 0.2 ppbv (200 pptv), whichever is lower [Section 4.2.8.5.2.5]
Calibration blank (CB)	Canister filled with clean, humidified diluent gas; indicates that diluent gas and dilution apparatus do not contribute target VOCs, i.e., positive bias to the ICAL is acceptably low; may also serve as zero point in the ICAL	Prepare one CB with each set of calibration standard canisters and analyze with each ICAL	CB should be sufficiently clean such that little or no positive bias is imparted to the calibration (see Section 15.3.3.3)	Omitted
Method precision	Duplicate samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through the same sampling inlet (e.g., a rack-mounted system that employs one inlet to fill two canisters at the same time; this determines the precision of the sampling and analysis processes OR Collocated samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through two separate sampling inlets (e.g., two mechanical flow control devices (MFCDs) that are individually attached to two canisters); this determines the precision of the sampling and analysis processes	Applicable to the collection of samples: collect approximately 5% of total samples or minimum of three samples	Precision ≤ 25% relative percent difference (RPD) of target VOCs in the compared samples when both measurements are ≥ fivefold MDL (see Section 15.3.4)	For sites collecting precision samples, must be 10% of primary sample frequency Acceptance criteria identical [Section 4.2.2]

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Instrument precision	Precision is determined from repeated analyses of a gas sample from one canister; replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision	One replicate analysis with each analytical sequence or 5% of field samples in each analytical sequence, whichever is greater	Precision ≤ 25% RPD for target VOCs when both measurements are ≥ fivefold MDL (see Section 15.3.4)	Recommended as one per analysis batch or one per 20 sample injections, whichever is greater Acceptance criteria identical [Sections 4.2.2.2 and 4.2.8.5.2.5]
Field blank	Canister filled with clean, humidified diluent gas transported to the field site(s) with field collected samples; indicates that sample handling practices do not contaminate samples	*Optional*: prepared for transport with field-collected samples; frequency determined by method user	Each target VOC's concentration should be approximately 20 pptv or less (see Section 15.3.5)	Omitted
Field spike	Canister filled with humidified standard gas at a concentration in the lower third of the calibration curve and transported to the field site(s) with field collected samples; indicates that sample handling practices do not deteriorate sample integrity	*Optional*: prepared for transport with field-collected samples; frequency determined by method user	Measured concentrations of VOCs within ±30% of theoretical spiked concentrations (see Section 15.3.5)	Omitted
Audit accuracy	Analysis of an independently prepared audit standard to determine analytical accuracy	Annually at a minimum	Within ±30% of accepted reference value (see Section 15.3.6)	Audit performed through NATTS PT program must show bias within ±25% of study NATTS Laboratory mean [Section 2.1.4.1]
Preconcentrator leak check	Pressurize or evacuate the canister connection to verify as leak-free	Each canister connected to the instrument prior to analysis	< 3.4 kPa (0.5 psi) change per minute or as recommended by the manufacturer (see Section 16.1.2)	Must be ≤ 0.2 psi/minute or meet manufacturer specifications [Section 4.2.8.5.2.1]
Method detection limit (MDL)	Establishes the minimum amount of a target analyte distinguishable above background with 99% confidence; determined from spiked canisters and MB canisters	Annually at a minimum	MDLs are recommended to be < 20 pptv or should meet program goals (see Table 17-2 for example MDLs)	Determined annually Minimally 7 method blank and 7 spiked canisters; prepared over 3 separate dates and analyzed over 3 separate dates Determined MDLs must be ≤ NATTS MDL Measurement Quality Objective [Section 4.2.5]

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MDL confirmation sample	Known standard prepared at approximately onefold to fivefold the determined MDL_{sp} to confirm the determined MDL is reasonable	Not required but recommended for MDLs determined as the MDL_{sp} (and not for those determined as the MDL_b)	Recommended recovery within 40% to 160% or other in-house defined limits (see Section 17.8)	Identical [Section 4.1.3.1]
Compound Identification *(Not listed in TO-15A Table 18-1)*	Criteria that must be met to positively identify a target compound Refer to Section 16.2	Each target VOC	1. Compound RT must be within ±2s from ICAL average RT 2. At least one qualifier ion must be within ±30% *relative* abundance of the average abundance of the quantitation ion established in the initial calibration 3. Signal-to-noise ratio > 3:1, preferably > 5:1 4. Quantitation ion and qualifier ion must be co-maximized (peak apexes within 1 scan of each other) Permits positive identification by experienced analyst when any of these four criteria is not met. Rationale for such positive identification should be documented and reported data should be flagged to indicate identification criteria were not met	1. Compound RT must be within the assigned RT window 2. Does not specify *relative abundance, otherwise identical* 3. S:N identical 4. Co-maximization identical Permits analyst interpretation of signal to noise and co-maximization as well as positive identification for experienced analyst with documented rationale [Section 4.2.8.5.3]