

A close-up photograph of several bright green leaves on a thin brown branch, set against a blurred background of more foliage and a bright sky. The leaves are in sharp focus, showing their veins and serrated edges.

VOC and Carbonyl Sampler Certification for NATTS

**Presented by:
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Background: What/Why of Certification

- A process to determine the amount and type of bias introduced by air sampling devices (samplers) into ambient air measurement methods TO-15A (VOCs) and TO-11A (carbonyls).
- Collect samples of zero gas and spiked gas under controlled conditions into VOC canister and carbonyl cartridge media and analyzed by their respective methods.
- The analytical results then shows the effects the samplers have on the samples they generate.

NATTS TAD Sampler Certification references

- VOC: Section 4.2.3.5 (pp. 70-72) (TAD, Rev 3)
Section 4.2.3.3 (pp. 89-92) (TAD, Rev 4)

- Carbonyl: Section 4.3.7.1.1 (pp.104-105) (TAD, Rev 3)
Section 4.3.7.1.1 (pp. 158-162) (TAD, Rev 4)

ERG Certification System



Certification System Construction

- Humidified Nitrogen zero gas (TAD Rev. 3)
 - Changing to Zero Air (TAD Rev. 4)
- Stainless steel humidification chamber
- Mass flow controllers for spiked sample stream generation
- Separate challenge and zero manifolds, both heated

Canister Sampler Certification Procedure

- Purge overnight w/ zero gas
- Known Standard Challenge test (3 hrs or 24 hrs)
 - Tier 1 compounds
- Purge overnight w/ zero gas
- Zero Check test

Tier 1 Compounds – VOCs

- Vinyl Chloride
- 1,3-Butadiene
- Ethylene Oxide
- Acrolein
- Chloroform
- Benzene
- Carbon Tetrachloride
- Trichloroethylene
- Tetrachloroethylene

Carbonyl Procedure

- Purge overnight w/ zero gas
- Zero Check test
- Purge overnight w/ zero gas
- Known Standard Challenge test (3 hrs or 24 hrs)
 - Tier 1 compounds

Tier 1 Compounds – Carbonyls

- Formaldehyde
- Acetaldehyde

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VOC Sampling Unit Certification (Positive and Negative Bias Check)

Sampler Certified: **ERG(C):AT/C-5-CHAL-CH1**
Sampler Certification date: _____

This sampler is intended to be used for the collection of VOC compounds.

Statement about annual certification:

Positive bias check:

Positive bias check for this VOC sampling unit was performed by collecting a 24-hour sample of humidified UHP nitrogen. Each channel of each VOC sampler was verified.

The zero check was performed by simultaneously providing humidified (50 to 70% RH) hydrocarbon- and oxidant-free UHP nitrogen to the sampling unit for collection onto a canister and to a separate reference canister connected directly to the supplied nitrogen gas source.

The humidified zero gas flow was performed over 24 hours to simulate field sampling time period through the sampling unit into the zero challenge canisters.

Analysis for target compounds showed all Tier 1 core compounds in the zero challenge canister were not greater than 0.2 ppbv or 3x MDL (whichever is lower) higher than the reference canister. The remaining core compounds also met these criteria.

Know Standard challenge certification:

The standard challenge gas is supplied to the challenge manifold by dilution of a gas mixture of VOCs via dynamic dilution with humidified UHP nitrogen. The manifold is connected to the sampling unit inlet, a reference canister, and a rotameter acting as a vent to ensure that the manifold remains at ambient pressure.

Analysis by GC/MS for target compounds must demonstrate that each VOC in the challenge sample is within 15% of the concentration in the reference sample.

Each sampler is prepared individually.

Certified for 12 months after date documented above.

QA Coordinator

Date

VOC Results!



Zero Certification Report - VOCs

TO-15 Method Blank and Annual Canister Certification Blank

		Reference	Channel 1		Channel 2				
Data File Name		L22A%017.D	L22A%018.D		L22A%019.D				
Operator		CAK IS 1E18003	CAK IS 1E18003		CAK IS 1E18003				
Acq. Method File		2010006.M	2010006.M		2010006.M				
Sample Name		2012804-01	2012802-01		2012802-02				
Misc Info		ZEROREF012822	ATC4-ZERO-CH1		ATC4-ZERO-CH2				
#	Name	Amount (ppbv)	Amount (ppbv)	PASS*	Amount (ppbv)	PASS*	Blank Criteria @	2021 MDL	3x MDL
1)	IS-Hexane-d14			na		na	na	na	na
2)	Acetylene	0.02	0.00	Y	0.00	Y	0.200	0.110	0.330
3)	Propylene	0.03	0.03	Y	0.04	Y	0.200	0.130	0.390
4)	Dichlorodifluoromethane	0.01	0.00	Y	0.00	Y	0.0732	0.0244	0.0732
5)	Chloromethane	0.02	0.00	Y	0.01	Y	0.152	0.0507	0.152
6)	Dichlorotetrafluoroethane	0.00	0.00	Y	0.00	Y	0.0210	0.0070	0.0210
7)	Vinyl Chloride	0.00	0.00	Y	0.00	Y	0.0258	0.0086	0.0258
8)	1,3-Butadiene	0.00	0.00	Y	0.00	Y	0.0495	0.0165	0.0495
9)	Ethylene Oxide	0.03	0.00	Y	0.03	Y	0.0783	0.0261	0.0783
10)	Bromomethane	0.00	0.00	Y	0.00	Y	0.0303	0.0101	0.0303
11)	Chloroethane	0.00	0.00	Y	0.00	Y	0.0318	0.0106	0.0318
12)	Acetonitrile	0.00	0.02	Y	0.00	Y	0.1575	0.0525	0.1575
13)	Acrolein	0.09	0.12	Y	0.17	Y	0.200	0.102	0.306
14)	Trichlorofluoromethane	0.01	0.00	Y	0.00	Y	0.0414	0.0138	0.0414
15)	Acrylonitrile	0.00	0.00	Y	0.00	Y	0.0513	0.0171	0.0513
16)	1,1-Dichloroethane	0.00	0.00	Y	0.00	Y	0.0262	0.0087	0.0262
17)	Methylene Chloride	0.09	0.00	Y	0.00	Y	0.2000	0.1030	0.3090

Known Standard Challenge Report - VOCs



VOC Known Standard Challenge Certification NATTS Tier I Compounds

	Reference	Channel 1			Channel 2		
Data File Name	L22DU008.D	L22DU013.D			L22DU014.D		
Operator	CAK IS 1E18003	CAK IS 1E18003			CAK IS 1E18003		
Acq. Method File	2040001.M	2040001.M			2040001.M		
Sample Name	2042027-01	2042030-01			2042030-02		
Misc Info	CHALREF042022	ATC4-CHAL-GH1			ATC4-CHAL-GH2		
Compound Name	Amount (ppbv)	Amount (ppbv)	% Recovery of target	PASS (Y/N)	Amount (ppbv)	% Recovery of target	PASS (Y/N)
Vinyl Chloride	1.07	1.11	103.5	Y	1.08	101.0	Y
1,3-Butadiene	1.10	1.12	101.3	Y	1.10	99.7	Y
Acrolein	0.82	0.88	107.1	Y*	0.81	98.9	Y*
Chloroform	1.05	1.06	101.5	Y	1.05	100.3	Y
Benzene	1.05	1.07	102.2	Y	1.08	102.4	Y
Carbon Tetrachloride	0.98	0.98	99.9	Y*	0.98	100.0	Y*
Trichloroethylene	1.07	1.09	101.5	Y	1.08	100.9	Y
Tetrachloroethylene	1.10	1.11	100.5	Y	1.11	101.0	Y



TO-15(A) Canister Sampler Acceptability

Zero Check

- Each target conc < Zero Reference concentration + (3 x MDL **or** 0.2 ppbv)
(TAD Rev. 3)
 - *Each target conc < Zero Reference concentration + (0.03 ppbv **or** 3 x MDL) (TAD Rev. 4)*
OR means use the lower value of the two

Known Standard Challenge

- 85-115% recovery of target compounds vs. reference (TAD Rev. 3)
 - *Less than reference conc ± 15.1 % recovery (TAD Rev. 4)*

Corrective Action - Canister

- Zero Check and Canister Challenge Certification

- TAD Rev. 3

- Tier 1 targets: certification must pass prior to sampling
- Non-Tier 1 targets: results must be qualified in AQS if sampling proceeds with failing results (SB flag)

- TAD Rev. 4

- Certification must pass prior to sampling but if deployed must be flagged (SB and associated LK or LL flag). Failing Zero Challenge compounds above 5 x MDL are invalidated (null qualifier EC flag).

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Carbonyl Sampling Unit Zero Check (Positive Bias Check)

Sampler Certified: **CO38584-Zero-Ch1**
Sampler Certification date: **2/22/2018**

This sampler is intended to be used for the collection of carbonyl compounds.

Statement about annual certification:

Positive bias check for this carbonyl sampling unit was performed by collecting a 24-hour sample of humidified UHP nitrogen. Each channel of each carbonyl sampling instrument was verified. The portion of the flow path comprising the ozone denuder/scrubber and DNPH cartridge was verified as non-biasing.

The zero check was performed by simultaneously providing humidified (50 to 70% RH) hydrocarbon- and oxidant-free UHP nitrogen to the sampling unit for collection onto a cartridge and to a separate reference cartridge connected directly to the supplied nitrogen gas source.

The humidified zero gas flow was performed over 24 hours to simulate real world conditions, into the reference cartridge and through the sampling unit into the zero challenge cartridge.

Analysis for target compounds in the zero challenge cartridge showed that each compound is ≤ 0.2 ppbv greater than the reference cartridge. Comparison to the reference cartridge permits evaluating the contribution of the sampling unit irrespective of cartridge background contamination.

We prepare each sampler individually.

Certified for 12 months after date documented above.

Jennifer C. Nash
QA Coordinator

May 29, 2018
Date

The positive bias check was performed following the annual recharge or replacement of the ozone scrubber/denuder.

■ Carbonyl Results!



Zero Certification Report - Carbonyls



Carbonyl Sampler Unit Zero Check (Positive Bias Check)

Certification Blank

(ppbv)

Data File ID	ZeroRef081720	AT/C7-Ch1	Meets Criteria	AT/C7-Ch2	Meets Criteria
Sample date	8/17/20	8/17/20		8/17/20	
Date Analyzed	8/18/20	8/18/20	(Y/N)	8/18/20	(Y/N)
Formaldehyde	0.062	0.046	Y	0.047	Y
Acetaldehyde	0.019	0.016	Y	0.016	Y
Acetone	0.019	0.013	Y	0.015	Y
Propionaldehyde	0.019	0.018	Y	0.017	Y
Crotonaldehyde	ND	ND	Y	ND	Y
Butyraldehyde	0.007	0.006	Y	0.007	Y
2-Butanone	0.005	0.004	Y	0.005	Y
Benzaldehyde	0.004	0.003	Y	0.003	Y
Valeraldehyde	ND	ND	Y	ND	Y
Hexaldehyde	0.003	ND	Y	ND	Y

Acceptance Criteria for each compound is ± 0.2 ppbv greater than the reference cartridge.



Carbonyl Sampler Acceptability

Zero Check

- Each target conc < Zero Reference + 0.2 ppbv (TAD Rev. 3)
 - *Each target conc ≤ Zero Reference + 0.2 ppbv (TAD Rev. 4)*

Known Standard Challenge (Highly Recommended) (TAD Rev. 4)

- *Less than reference conc ± 15.1 % recovery (TAD Rev. 4)*

Corrective Action - Carbonyls

- Zero Check and Carbonyl Challenge Certification
 - TAD Rev. 3
 - Blank certification must pass prior to sampling showing \leq reference cartridge conc + 0.2 ppbv
 - TAD Rev. 4
 - Certification must pass prior to sampling but if deployed must be flagged (SB and associated LK or LL flag). Failing Zero Challenge compounds above 5 x MDL are invalidated (null qualifier EC flag).


Certification Prerequisites

- MFC Calibrations
- Ozone scrubber replacement
- Miscellaneous maintenance
- Double check your internal connections!

Expected Time Frame

- Should expect for the certification to take between 2-6 weeks, depending on how quickly it certifies
- Canister and carbonyl certifications done separately. Why? Acetonitrile.
- Obstacles to a successful certification
 - VOC Known Standard Challenge: acrolein & carbon tetrachloride recoveries
 - VOC Zero Test: Any compound
 - Carbonyl Zero Test: Leaks

Sending Samplers to ERG? Fill out this form, please

 Rev. 01-2022	
<small>601 Keystone Park Drive, Suite 700, Morrisville, NC 27560</small> SAMPLER CHAIN OF CUSTODY	
Sampler Information	Sampler Model: _____ Inventory Number: _____ Serial Number: _____ Relinquished by: _____ Date: _____ Required Analyses: <input type="checkbox"/> VOC (TO-15) <input type="checkbox"/> SNMOC (PAMS) <input type="checkbox"/> Carbonyls (TO-11A)
VOC/SNMOC Certification (TO-15, PAMS)	<small>Check all that apply</small> Certification Tests Required: <input type="checkbox"/> NA <input type="checkbox"/> Zero Check <input type="checkbox"/> Single Channel <input type="checkbox"/> Known Standard Challenge <input type="checkbox"/> Dual Channel Choose One: <input type="checkbox"/> BTEX Compounds <input type="checkbox"/> NATTS Tier 1 Compounds (See NATTS TAD Rev.3)
Carbonyls Certification (TO-11A)	<small>Check all that apply</small> Zero Check Certification: <input type="checkbox"/> NA <input type="checkbox"/> Channel 1 Ports: 1 <input type="checkbox"/> 2 <input type="checkbox"/> 3 <input type="checkbox"/> 4 <input type="checkbox"/> 5 <input type="checkbox"/> 6 <input type="checkbox"/> 7 <input type="checkbox"/> 8 <input type="checkbox"/> <input type="checkbox"/> Channel 2 <input type="checkbox"/> Channel 3
Certification Report Remittance	Sampler Certification reports are included in the package with the sampler when it is returned. A copy of the report should also be emailed to: 1.) _____ 3.) _____ 2.) _____ 4.) _____
Lab Receipt (E HQ use only)	Received by: _____ Date: _____ Receipt Condition (Circle): GOOD FAIR NEEDS REPAIR Explain: _____ _____

Comments: _____

Sampler Shipping

- Samplers need to be packed well for shipment!!
- 28.3g prevention = 0.453kg cure

Damage, Inc.



References

- NATTS Technical Assistance Document, Revision 3
 - https://www3.epa.gov/ttnamti1/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf
- NATTS Technical Assistance Document, Revision 4
 - <https://www.epa.gov/system/files/documents/2022-08/NATTS-TAD-Revision-4-Final-July-2022-508.pdf> (AMTIC website)

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Questions?

