

US EPA ARCHIVE DOCUMENT



May 16, 2018

Jennifer Orme-Zavaleta (EPA Science Advisor)
United States Environmental Protection Agency
Ariel Rios Building (MD 4101M)
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

RE: Preservation of Wastewater Samples Tested for Acrolein and Acrylonitrile

Dear Dr. Orme-Zavaleta:

The Environmental Laboratory Advisory Board (ELAB or Board), a standing Federal Advisory Committee Act board that advises the U.S. Environmental Protection Agency (EPA or Agency), sent a letter on June 19, 2014 to EPA's Mr. Adrian Hanley, advising EPA that the Clean Water Act preservation requirement for acrolein and acrylonitrile of pH 4-5 was unnecessary, and preserving such samples to pH <2 was sufficient. EPA responded in the comments associated with the 2015 Method Update Rule (Docket EPA-HQ-OW-2014-0797) that this requested was not adopted "because EPA does not have data to demonstrate that acrolein would not be degraded in wastewater samples at pH values other than 4 - 5." ELAB is reiterating its request to change the preservation requirements. Attached are the results of two studies performed on treatment plant effluent wastewater samples spiked with acrolein and acrylonitrile and tested over a holding time of 7-14 days. Both studies showed that only about half of the acrolein was retained for 7-14 days at either pH 4-5 or pH <2. Therefore, there was no advantage to pH 4-5 preservation over pH <2, and therefore it should be eliminated as a requirement.

Field adjustment of samples to pH 4-5 is very challenging and samples for volatile organics are routinely preserved to pH <2. Eliminating the pH 4-5 requirement would reduce cost without compromising data quality.

ELAB appreciates the opportunity to provide this information in support of meeting Agency's program goals. Please let us know if you would like ELAB to perform additional review of this topic.

Respectfully,
Michael F. Delaney

Michael F. Delaney, Ph.D.
Chair, Environmental Laboratory Advisory Board

cc: ELAB Board
Thomas O'Farrell, ELAB Designated Federal Official

Attachment:
Acrolein Preservation Data from the Massachusetts Water Resources Authority and the Sanitation Districts of Los Angeles County

Acrolein& Acrylonitrile Study by Method 603/624 (heated purge GC-MS)

A&A Spike true value is 50ppb.

Day 1 02/22/16			Day 2 02/23/16			Day 7 02/29/16		
LFB			LFB			LFB		
Acrolein- 112%	Acrylonitrile- 99%	Surrogate- 97%	Acrolein- 115%	Acrylonitrile- 98%	Surrogate- 100%	Acrolein 108%	Acrylonitrile 98%	Surrogate- 99%
Neutral spiked			Neutral spiked			Neutral spiked		
Acrolein- 46%	Acrylonitrile- 105%	Surrogate- 98%	Acrolein- 23%	Acrylonitrile- 99%	Surrogate- 99%	Acrolein 6.5%	Acrylonitrile 88%	Surrogate- 104%
pH 2 spiked			pH 2 spiked			pH 2 spiked		
Acrolein- 71%	Acrylonitrile- 90%	Surrogate- 100%	Acrolein- 57%	Acrylonitrile 105%	Surrogate- 101%	Acrolein 50%	Acrylonitrile 87%	Surrogate- 99%
pH 4 spiked			pH 4 spiked			pH 4 spiked		
Acrolein- 63%	Acrylonitrile 103%	Surrogate- 98%	Acrolein- 55%	Acrylonitrile- 103%	Surrogate- 100%	Acrolein 55%	Acrylonitrile 88%	Surrogate- 105%

The Massachusetts Water Resources Authority (MWRA) Department of Laboratory Services conducted a small preservation/holding time study for Acrolein and Acrylonitrile in 2016. Samples of the Deer Island Treatment Plant final wastewater effluent were spiked with the two target compounds at 50 ug/L. Some samples were left at ambient pH (about pH 6.5). Some samples were preserved at pH 2 and 4. Samples were held in 40 mL septum-capped VOA vials at <6 C until analysis. Samples were tested the same day, the next day, and 7 days later using heated purge and trap GC-MS analysis following EPA Method 603. The surrogate was 1,2-Dichloroethane-d4. The laboratory fortified blank (LFB) consisted of the two target compounds spiked into laboratory reagent water.

The wastewater final effluent samples consisted of primary and secondary treatment, chlorination with hypochlorite, and dechlorination with bisulfite. The samples had no detectable total chlorine residual.

Acrolein was stable in the LFB, but degraded quickly in the final effluent sample. Preservation at pH 2 and pH 4 were comparable, and better than no pH preservation, but half of the acrolein was lost in 7 days.

Acrylonitrile was fairly stable in all samples.

From this small experiment, there is no evidence that preservation of acrolein at pH 4 is preferable to preservation at pH 2. The EPA NPDES regulation (40 CFR 136) would allow unpreserved samples to be analyzed within three days without pH adjustment, but under the conditions of this experiment most of the acrolein would already be lost.

These analyses were performed by Raisa Goldin, MWRA Chemist.

Summarized by Mike Delaney, MWRA Lab Director (www.mwra.com, mike.delaney@mwra.com, 617-660-7801).

Acrolein/Acrylonitrile Stability Study

Provided by Huy Do

Supervising Scientist / QA Manager at Sanitation Districts of Los Angeles County

From: Do, Huy [mailto:hdo@lacsds.org]
Sent: Wednesday, April 04, 2018 7:23 PM
To: Delaney, Mike <Mike.Delaney@mwra.com>
Cc: 'mahesh.pujari@lacity.org' <mahesh.pujari@lacity.org>
Subject: RE: Acrolein preservation for EPA Methods 603 and 624

Mike,

Attached is a summary of the experiments that our lab conducted in 2011. The first experiment was performed in May of 2011, and the second experiment was performed approximately one month later to show that the data was reproducible. I would like to point out that these were simple internal experiments that the lab conducted to gain a better understanding of the effects of pH adjustments on acrolein and acrylonitrile. It was not our intention to use the data for regulatory purposes and therefore, not all factors were considered in the design of these experiments. Please note that pH 5 in the tables means unpreserved sample – the lab used DI water in the preparation of these samples and the analyst noted that the pH of DI water was around 5 (I am not sure why the analyst decided to check the pH of DI water – it is definitely not a recommended practice).

The laboratory prepared 2.0 L of a 20 ug/L acrolein standard and 2.0 L of a 20 ug/L acrylonitrile. One liter of each standard was left unpreserved and the second liter of each standard was pH adjusted to <2 using HCl. These standards were then transferred to 40 mL VOA vials and stored in the refrigerator until analysis. The analysis was performed according to EPA 624.

Please do not hesitate to let me know if you have any questions or need additional information.

Thanks,
Huy

ACROLEIN / ACRYLONITRILE STABILITY STUDY
 Agilent 6890N/5973N O.I. 4560 Archon 2552

May 2011

May 20 11
 study

MATRIX: Water
 CONCENTRATION: 20 ug/L

DATE	DAY	ACROLEIN				ACRYLONITRILE			
		pH 5 (ug/L) %Rec		pH <2 (ug/L) %Rec		pH 5 (ug/L) %Rec		pH <2 (ug/L) %Rec	
3-May-11	0	17.4	87.0	18.0	90.0	19.0	95.0	19.5	97.5
4-May-11	1	18.8	94.0	---	---	20.8	104.0	---	---
5-May-11	2	No data - Agilent instrumentation out of service - filament #1 open							
6-May-11	3	16.5	82.5	15.5	77.5	19.6	98.0	21.7	109
7-May-11	4	---	---	---	---	---	---	---	---
8-May-11	5	---	---	---	---	---	---	---	---
9-May-11	6	No data - Agilent instrumentation out of service - P/T							
10-May-11	7	No data - Agilent instrumentation out of service - replace source							
11-May-11	8	No data - Agilent instrumentation out of service - replace source							
12-May-11	9*	13.4	67.0	10.8	54.0	18.6	93.0	18.8	94.0
13-May-11	10	---	---	---	---	---	---	---	---
14-May-11	11	---	---	---	---	---	---	---	---
15-May-11	12**	16.3	81.5	10.4	52.0	18.8	94.0	18.6	93.0
16-May-11	13 a.m.	15.8	79.0	11.3	56.5	19.2	96.0	18.8	94.0
16-May-11	13 p.m.	16.6	83.0	10.6	53.0	18.7	93.5	18.4	92.0
17-May-11	14	15.9	79.5	10.1	50.5	18.3	91.5	18.5	92.5

* Exceeded 12 hours

** Acidified sample exceeded 12 hrs

ACROLEIN / ACRYLONITRILE STABILITY STUDY
 Agilent 6890N/5973N O.I. 4560 Archon 2552

June 2011

ES
6/30/11

MATRIX: Water
 CONCENTRATION: 20 ug/L

DATE	DAY	ACROLEIN				ACRYLONITRILE			
		pH 5 (ug/L) %Rec		pH <2 (ug/L) %Rec		pH 5 (ug/L) %Rec		pH <2 (ug/L) %Rec	
1-Jun-11	0	19.4	97.0	18.0	90.0	19.5	97.5	18.9	94.5
2-Jun-11	1	17.6	88.0	15.8	79.0	18.6	93.0	18.0	90.0
3-Jun-11	2*	16.3	81.5	15.0	75.0	17.0	85.0	17.4	87.0
4-Jun-11	3	---	---	---	---	---	---	---	---
5-Jun-11	4	---	---	---	---	---	---	---	---
6-Jun-11	5	---	---	---	---	---	---	---	---
7-Jun-11	6	16.1	80.5	11.6	58.0	18.3	91.5	18.0	90.0
8-Jun-11	7***ex	15.0	75.0	10.9	54.5	17.2	86.0	17.0	85.0
9-Jun-11	8 ^{ex}	16.4	82.0	10.9	54.5	18.4	92.0	18.5	92.5
10-Jun-11	9	---	---	---	---	---	---	---	---
11-Jun-11	10	---	---	---	---	---	---	---	---
12-Jun-11	11 ^{ex}	14.7	73.5	11.4	57.0	19.3	96.5	18.9	94.5
13-Jun-11	12**ex	17.2	86.0	10.6	53.0	18.4	92.0	18.5	92.5
14-Jun-11	13	---	---	---	---	---	---	---	---
15-Jun-11	14 ^{ex}	15.6	78.0	9.9	49.5	19.4	97.0	19.1	95.5
16-Jun-11	15	18.2	91.0	10.3	51.5	20.0	100.0	19.8	99.0

*Surrogate recovery fail low - 82% (no acid); 86% (acidified); QA limit 90%

**Surrogate recovery fail low - 88% (no acid); acidified sample within QA limit (90%)

***Surrogate recovery fail low - 88% (no acid and acidified); QA limit 90%

ex - Sample run past 12 hours

June 2011
study