June 19, 2014

Mr. Adrian Hanley
U.S. Environmental Protection Agency
1200 Pennsylvania Ave, NW
Mail Code 4303T
Washington, DC 20460

Re: Analysis Requirements and pH Preservation for Acrolein and Acrylonitrile Methods

Dear Mr. Hanley,

The Environmental Laboratory Advisory Board (ELAB or Board) is a standing Federal Advisory Committee Act board that advises the U.S. Environmental Protection Agency (EPA or Agency). The Board's Charter states that it is to provide consensus advice, information and recommendations on issues related to EPA measurement programs and facilitate operation and expansion of a national environmental laboratory accreditation program.

ELAB welcomed EPA's revision of Method 624 for the determination of acrolein and acrylonitrile in the last Methods Update Rule (MUR) published on May 18, 2012. In addition to the changes made in 2012, the Board would like to recommend supplementary changes to the method that could be addressed in the upcoming MUR in 2014.

1. The recommended preference of Method 624 versus Method 603.

Section 1.2 of Method 624 states that Method 624 may be extended to screen for acrolein and acrylonitrile, but that the preferred method is Method 603. ELAB suggests changing this statement to "…acrolein and acrylonitrile should preferably be analyzed by Method 624." Method 624 is superior to Method 603 for this testing and used by the laboratory community more often than Method 603. Some of the rationalization to promote Method 624 over Method 603 includes:

- Method 603 uses a flame ionization detector. This is a nonselective detector and will respond to any organic compound. If acrolein and acrylonitrile are present in a sample, there also is the possibility of finding significant concentrations of various other hydrocarbons. Hence, the potential for false positives and false negatives caused by interferences can be high.
    - For example, a false negative could be caused by the presence of a large, masking hydrocarbon eluting at a slightly different retention time than acrolein or acrylonitrile, making it difficult to see the target peak when present at a lower concentration.
- The purge conditions in Method 603 (85^{o}C for 15 minutes) can transfer very large quantities of water to the instrument, which hinders the analysis of acrolein and acrylonitrile.

2. Preservation requirement for acrolein and acrylonitrile.

The Board has discussed the pH preservation requirement and provides information (attached) to support ELAB's suggestion that EPA consider the removal of preservation at pH 4–5. Removal of the pH requirement for acrolein and acrylonitrile will:

- Eliminate the problem of field adjustment of samples to pH 4–5, which is very challenging.
- Facilitate implementation and management of method specifications by laboratories.
- Reduce cost to laboratories without compromising data quality.
- Provide harmonization with SW846 Update V, Chapter 4, which no longer contains the preservation requirement of pH 4–5 for acrolein and acrylonitrile.

Failure of laboratories to comply with the current pH requirement often results in data of good quality being unnecessarily invalidated. ELAB suggests that EPA consider removing the pH preservation requirement for acrolein and acrylonitrile and instead make the preservation requirement identical to that for purgeable aromatic hydrocarbons, which preserves samples below pH 2.

Thank you for your consideration. The Board looks forward to your comments and feedback on this issue. Please know that you are welcome to attend any of ELAB's monthly teleconferences to discuss these topics in detail.

Respectfully,

Patsy Root
Chair, Environmental Laboratory Advisory Board

cc: ELAB Board
Attachments: "Propose change to Table II – REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES."

Date: 11/22/10
To: OW-Docket@EPA
From: URS Corporation
Subject: Docket ID No. EPA-HQ-OW-2010-0192

Propose change to Table II – REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

FROM

Parameter number / name	Container	Preservation	Maximum holding time
Table IC – Organic Test			
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤ 6°C[18], 0.008% $Na_2S_2O_3$[5], pH to 4-5[10]	14 days[10]

TO

Parameter number / name	Container	Preservation	Maximum holding time
Table IC – Organic Test			
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤ 6°C[18], 0.008% $Na_2S_2O_3$[5], HCL to pH < 2	14 days

Table II should be revised from the draft version to include changes in preservation requirements for acrolein and acrylonitrile. It is difficult and burdensome to preserve samples in the field to the limited pH range specified (i.e., pH 4-5) for analysis of acrolein and acrylonitrile. Typically, analysis for acrolein and acrylonitrile is performed in conjunction with analysis of a larger list of volatile organic compounds (ex., the priority pollutant volatile list). In lieu of preserving the samples to a pH 4-5, another preservation option for acrolein and acrylonitrile is to collect an unpreserved sample and analyze within 3 days of collection. This option increases the analytical costs (laboratory analyzes a preserved and unpreserved sample if additional parameters are requested) as well as creates hardship on the laboratory to meet the accelerated hold time. Acrolein and acrylonitrile were included in a spiking study to assess preservation requirements for these compounds to alleviate these issues.

Study Details:
On behalf of DuPont, Lancaster Laboratories, Inc. of Lancaster, Pennsylvania, performed a volatile spiking study in preserved and unpreserved water samples. The compounds, acrolein, acrylonitrile, vinyl chloride, styrene, and 2-chloroethyl vinyl ether, were spiked at a concentration of 100 ug/L into the following:

- three preserved (with HCL to pH <2) deionized water samples
- three unpreserved deionized water samples

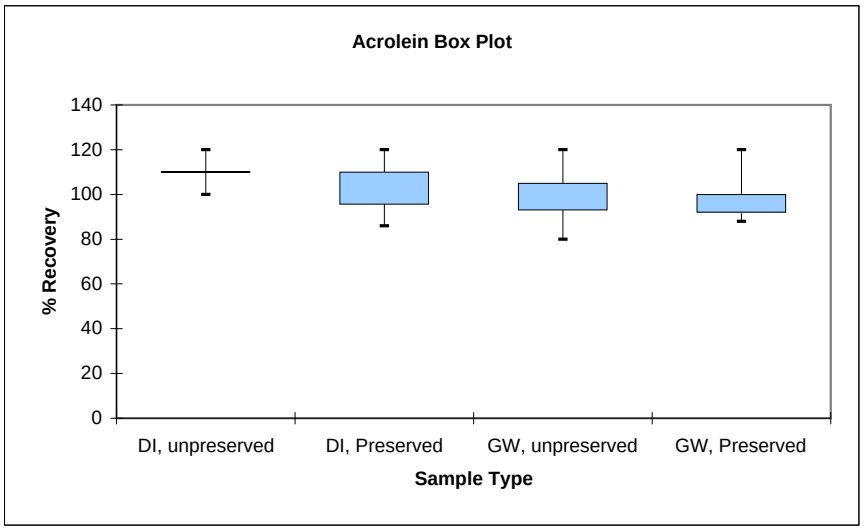
- three preserved (with HCL to pH <2) groundwater samples
- three unpreserved groundwater samples

Each of the 12 samples was analyzed every other day starting on Day 0 and ending on Day 16. With the exception of 2-chloroethyl vinyl ether in the preserved samples, acceptable recoveries (70-130%) were observed for all compounds in both matrices. As a result, we believe the preservation criteria for acrolein and acrylonitrile can be modified to read "Cool, $\leq 6°C^{18}$, 0.008% $Na_2S_2O_3^5$, HCL to pH < 2" and the maximum holding time criteria be modified to read "14 days".

2-chloroethyl vinyl ether, styrene, and vinyl chloride were also included in the spiking study to address an update to Table 4-1 of SW-846, Chapter 4, which calls for unpreserved samples for these three compounds. Since acceptable recoveries were observed in the preserved samples from Day 0 to Day 16 for acrolein, acrylonitrile, styrene, and vinyl chloride, we believe samples can be preserved with HCL to pH<2 and analyzed within 14 days. We do agree with EPA on submitting an unpreserved sample for the analysis of 2-chloroethyl vinyl ether.

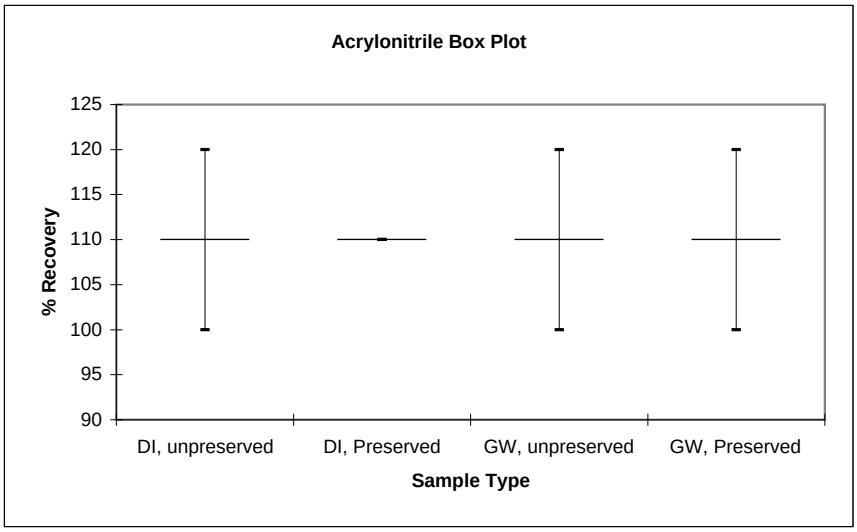
The supporting data has been included for your review.

DuPont / Lancaster Laboratories VOC Spiking Study Results - Spike Percent Recovery



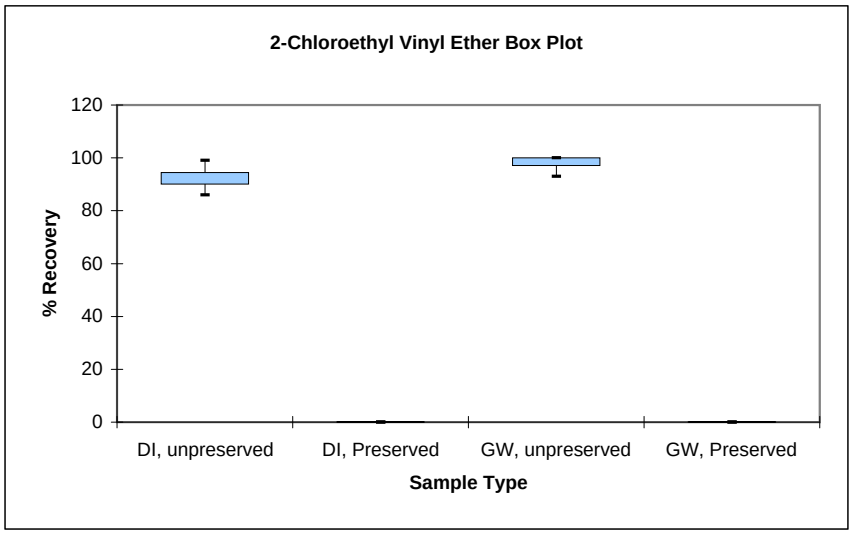
Day, Sample #	Acrolein, DI, unpreserved % Recovery	Acrolein, DI, Preserved % Recovery	Acrolein, GW, unpreserved % Recovery	Acrolein, GW, Preserved % Recovery
Day 0, #1	110	110	120	110
Day 0, #2	110	110	110	120
Day 0, #3	110	120	110	110
Day 2, #1	110	110	110	110
Day 2, #2	120	110	110	110
Day 2, #3	110	110	110	100
Day 4, #1	110	100	100	100
Day 4, #2	110	110	100	97
Day 4, #3	110	100	100	98
Day 6, #1	110	100	100	100
Day 6, #2	110	97	100	93
Day 6, #3	110	100	100	94
Day 8, #1	120	97	97	94
Day 8, #2	110	96	94	91
Day 8, #3	110	89	92	90
Day 10, #1	110	110	94	90
Day 10, #2	110	100	96	92
Day 10, #3	100	94	85	100
Day 12, #1	120	87	81	92
Day 12, #2	120	86	80	89
Day 12, #3	100	87	91	88
Day 14, #1	100	110	91	100
Day 14, #2	110	110	96	110
Day 14, #3	120	91	100	94
Day 16, #1	100	95	100	92
Day 16, #2	110	98	91	93
Day 16, #3	120	100	110	88

	DI, unpreserved	DI, Preserved	GW, unpreserved	GW, Preserved
median	110	100	100	94
1st quartile	110	95.5	93	92
min	100	86	80	88
max	120	120	120	120
3rd quartile	110	110	105	100



Day, Sample #	Acrylonitrile, DI, unpreserved % Recovery	Acrylonitrile, DI, preserved % Recovery	Acrylonitrile, GW, unpreserved % Recovery	Acrylonitrile, GW, preserved % Recovery
Day 0, #1	120	110	120	120
Day 0, #2	120	110	110	110
Day 0, #3	110	110	120	110
Day 2, #1	110	110	110	110
Day 2, #2	110	110	110	110
Day 2, #3	110	110	110	110
Day 4, #1	110	110	110	110
Day 4, #2	110	110	110	110
Day 4, #3	110	110	110	110
Day 6, #1	110	110	110	110
Day 6, #2	110	110	110	110
Day 6, #3	110	110	110	110
Day 8, #1	100	110	100	110
Day 8, #2	100	110	110	110
Day 8, #3	110	110	100	110
Day 10, #1	110	110	110	110
Day 10, #2	110	110	110	110
Day 10, #3	110	110	110	110
Day 12, #1	110	110	110	110
Day 12, #2	110	110	110	110
Day 12, #3	110	110	110	110
Day 14, #1	110	110	110	110
Day 14, #2	110	110	110	110
Day 14, #3	110	110	110	100
Day 16, #1	110	110	110	100
Day 16, #2	110	110	110	100
Day 16, #3	110	110	110	100

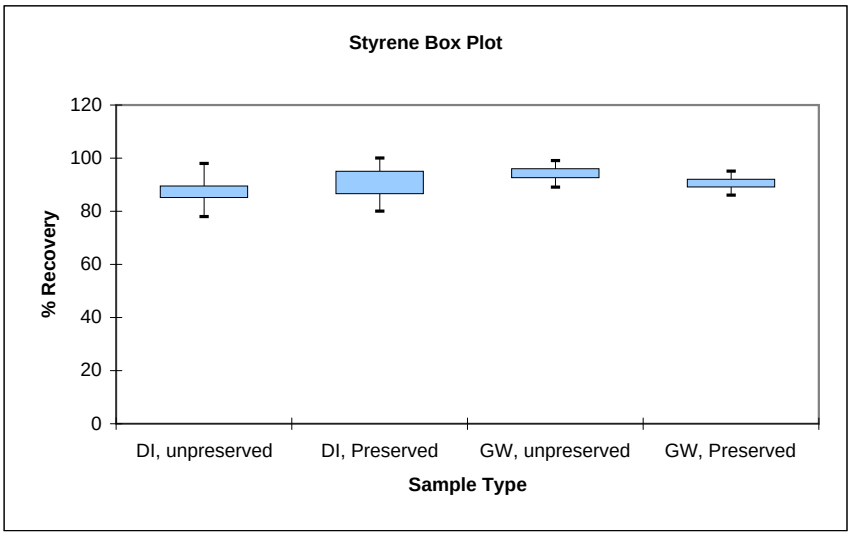
	DI, unpreserved	DI, Preserved	GW, unpreserved	GW, Preserved
median	110	110	110	110
1st quartile	110	110	110	110
min	100	110	100	100
max	120	110	120	120
3rd quartile	110	110	110	110



Day, Sample #	2-Choroethyl Vinyl Ether, DI, unpreserved % Recovery	2-Choroethyl Vinyl Ether, DI, Preserved % Recovery	2-Choroethyl Vinyl Ether, GW, unpreserved % Recovery	2-Choroethyl Vinyl Ether, GW, Preserved % Recovery
Day 0, #1	97	0	98	0
Day 0, #2	96	0	98	0
Day 0, #3	96	0	100	0
Day 2, #1	89	0	94	0
Day 2, #2	89	0	95	0
Day 2, #3	90	0	93	0
Day 4, #1	88	0	95	0
Day 4, #2	90	0	94	0
Day 4, #3	90	0	96	0
Day 6, #1	90	0	98	0
Day 6, #2	92	0	97	0
Day 6, #3	91	0	97	0
Day 8, #1	94	0	98	0
Day 8, #2	94	0	97	0
Day 8, #3	95	0	97	0
Day 10, #1	90	0	99	0
Day 10, #2	91	0	100	0
Day 10, #3	91	0	100	0
Day 12, #1	92	0	100	0
Day 12, #2	92	0	100	0
Day 12, #3	94	0	100	0
Day 14, #1	86	0	100	0
Day 14, #2	94	0	100	0
Day 14, #3	96	0	100	0
Day 16, #1	94	0	99	0
Day 16, #2	99	0	100	0
Day 16, #3	97	0	100	0

	DI, unpreserved	DI, Preserved	GW, unpreserved	GW, Preserved
median	92	0	98	0
1st quartile	90	0	97	0
min	86	0	93	0
max	99	0	100	0
3rd quartile	94.5	0	100	0

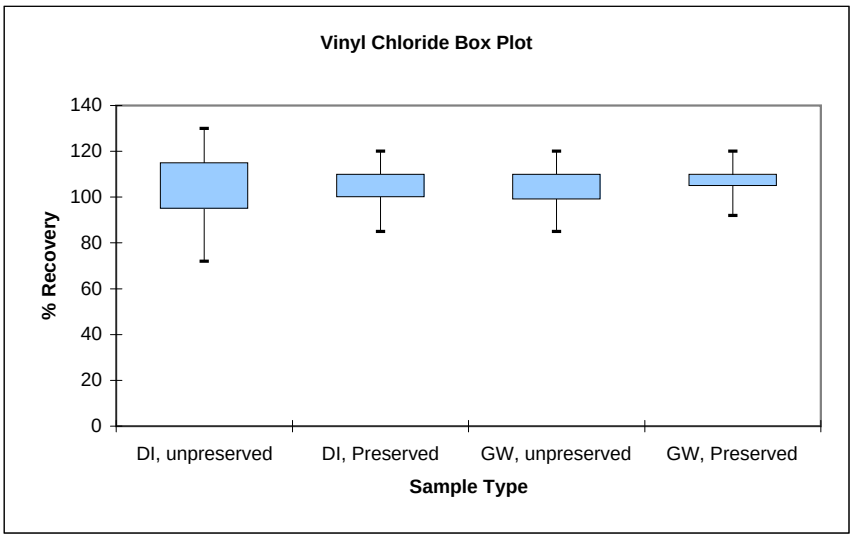
DuPont / Lancaster Laboratories VOC Spiking Study Results - Spike Percent Recovery



Day, Sample #	Styrene, DI, unpreserved % Recovery	Styrene, DI, Preserved % Recovery	Styrene, GW, unpreserved % Recovery	Styrene, GW, Preserved % Recovery
Day 0, #1	89	89	96	92
Day 0, #2	90	91	95	92
Day 0, #3	90	87	96	91
Day 2, #1	87	87	95	89
Day 2, #2	87	87	94	90
Day 2, #3	86	88	95	89
Day 4, #1	87	85	93	87
Day 4, #2	86	84	93	86
Day 4, #3	85	83	93	86
Day 6, #1	85	85	92	90
Day 6, #2	84	82	90	89
Day 6, #3	85	80	90	90
Day 8, #1	88	87	93	89
Day 8, #2	88	86	91	89
Day 8, #3	87	94	89	87
Day 10, #1	87	98	94	92
Day 10, #2	86	97	94	95
Day 10, #3	85	95	94	95
Day 12, #1	85	99	93	92
Day 12, #2	82	100	92	94
Day 12, #3	82	98	92	93
Day 14, #1	78	95	99	93
Day 14, #2	97	94	98	90
Day 14, #3	98	96	97	91
Day 16, #1	96	93	96	90
Day 16, #2	96	95	98	87
Day 16, #3	92	93	97	88

	DI, unpreserved	DI, Preserved	GW, unpreserved	GW, Preserved
median	87	91	94	90
1st quartile	85	86.5	92.5	89
min	78	80	89	86
max	98	100	99	95
3rd quartile	89.5	95	96	92

DuPont / Lancaster Laboratories VOC Spiking Study Results - Spike Percent Recovery



Day, Sample #	Vinyl Chloride, DI, unpreserved % Recovery	Vinyl Chloride, DI, Preserved % Recovery	Vinyl Chloride, GW, unpreserved % Recovery	Vinyl Chloride, GW, Preserved % Recovery
Day 0, #1	130	120	110	110
Day 0, #2	110	110	110	110
Day 0, #3	120	110	110	110
Day 2, #1	110	110	110	110
Day 2, #2	110	110	110	100
Day 2, #3	110	110	100	96
Day 4, #1	110	100	100	100
Day 4, #2	110	100	100	96
Day 4, #3	110	96	100	92
Day 6, #1	100	98	100	120
Day 6, #2	100	92	99	120
Day 6, #3	100	85	99	120
Day 8, #1	110	98	120	120
Day 8, #2	110	98	110	120
Day 8, #3	110	120	110	110
Day 10, #1	90	110	91	110
Day 10, #2	88	110	91	110
Day 10, #3	86	110	88	110
Day 12, #1	88	110	88	110
Day 12, #2	83	120	88	110
Day 12, #3	78	110	85	110
Day 14, #1	72	110	120	110
Day 14, #2	120	110	120	110
Day 14, #3	130	110	120	110
Day 16, #1	120	110	110	110
Day 16, #2	120	100	120	100
Day 16, #3	120	100	120	100

	DI, unpreserved	DI, Preserved	GW, unpreserved	GW, Preserved
median	110	110	110	110
1st quartile	95	100	99	105
min	72	85	85	92
max	130	120	120	120
3rd quartile	115	110	110	110