Evaluating Preservation Requirements for Acrolein and Acrylonitrile in Aqueous Matrices

The results of a study sponsored by the

Environmental Monitoring Coalition

March 2, 2022

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1. Executive Summary

In 40 CFR 136, Table II and Table 4-1 in SW-846, the EPA established aqueous sample preservation and holding time requirements for acrolein and acrylonitrile that differ significantly from those of other volatile organic compounds that are measured by the same EPA method, either Method 624.1 or 8260D.

The need to employ different sample preservation methods for these analytes results in a significant reduction in productivity for the laboratory community. It requires that samplers and laboratories collect and handle separate samples for these two analytes rather than being able to use the same sample for all the needed method 624.1 and Method 8260 analytes. Current regulatory requirements for acrolein and acrylonitrile specify that samples be preserved to a pH of between 4 and 5 and be analyzed within 14 days. For most volatile organic compounds in water, samples are preserved to pH ≤2 and analyzed within 14 days. In addition, preserving samples to a pH between 4 and 5 is virtually impossible to achieve in the field without compromising the sample volatiles so samples are commonly over or under preserved.

This report documents the results of a study that demonstrated that using pH ≤2 preservation for samples to be analyzed for acrolein and acrylonitrile is clearly better than the currently required pH 4 – 5 preservation, and that there is no need to have different requirements for these two analytes. This report also shows that samples that are not acidified can provide unacceptable results for acrolein much shorter than the current 3-day holding time.

Since the main concern is with acrolein and acrylonitrile in aqueous samples being analyzed in support of the Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA) regulatory programs, the work focused on matrices of concern to these regulatory programs.

While the focus was on determining if using pH ≤2 preservation would be suitable for acrolein and acrylonitrile, what would happen if no preservation was used was also evaluated.

Since the longest holding time for VOCs is 14 days, sample stability was only studied over 14 days.

2. Background

In 40 CFR 136, Table II and in Table 4-1 in SW-846, the EPA established aqueous sample preservation and holding time requirements for acrolein and acrylonitrile that differ significantly from those of other volatile organic compounds.

The need to employ different sample preservation methods for these analytes results in a significant reduction in productivity for the laboratory community. It requires that samplers and laboratories collect and handle separate samples for these two analytes rather than being able to use the same sample for all the needed method 624.1 and Method 8260 analytes.

Current regulatory requirements specify that samples be preserved to a pH of between 4 and 5 and be analyzed within 14 days (Table 1). For most volatile organic compounds in water, samples are preserved to pH ≤2 and analyzed with 14 days.

Table 1. Current EPA Sample Preservation Requirements

Analytes	Preservation	Holding time
Purgeable Halocarbons	Cool, < 6°C, 0.008% $Na_2S_2O_3$, HCl to pH ≤2[1]	14 days.
2-Chloroethylvinyl ether	Cool, < 6°C, 0.008% $Na_2S_2O_3$	14 days.
Purgeable aromatic hydrocarbons	Cool, < 6°C, 0.008% $Na_2S_2O_3$, HCl to pH ≤2[1]	14 days[1]
Acrolein and acrylonitrile	Cool, < 6°C, 0.008% $Na_2S_2O_3$; Adjust pH to 4-5[2]	14 days[2]

Notes:

1. If the sample is not adjusted to pH ≤2, then the sample must be analyzed within seven days of sampling.

2. The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

As can be seen from this table, both the CWA in 40 CFR 136 and the RCRA Program's SW-846 specify a different preservation for acrolein and acrylonitrile than for other VOCs.

In November 2010, the former EPA Environmental Laboratory Advisory Board (ELAB) cited data that demonstrated the stability of acrolein and acrylonitrile in both deionized water and groundwater for 16 days, whether preserved to a pH $\leq$2 or unpreserved. EPA concluded the information insufficient to justify the requested change.

To improve laboratory productivity and reduce the chance of inadvertent errors, the Environmental Monitoring Coalition (EMC) worked with individuals from the EPA Office of

Science and Technology (OST) and the Office of Land and Emergency Management OLEM) to design a study to determine whether the more usual preservation and holding time standards are applicable to these analytes.

The study included six aqueous matrices that would pose a challenge to analyte stability.

The objective of this study is to demonstrate that sample preservation of pH ≤ 2 is as effective as, if not better, then the currently required pH 4 – 5 preservation for acrolein and acrylonitrile, enabling these two analytes to be measured concurrently with the other analytes in Methods 624.1 or 8260.

3. Study Management

The study was conducted under the auspices of the Environmental Monitoring Coalition (EMC) and was managed by a Task Group consisting of:

Study Team

- Richard Burrows, Eurofins TestAmerica
- William Lipps, Shimadzu Scientific Instruments
- Brad Meadows, Babcock Laboratories
- Judy Morgan, Pace Analytical
- Jerry Parr, The NELAC Institute
- David Friedman, David Friedman Consulting (Task Manager)

Participating Laboratories

The following laboratories volunteered their time to generate the data for the study.

- Eurofins Lancaster Environmental, Lancaster, PA
- Babcock Laboratories, Riverside, CA
- Pace Analytical, Mt. Juliet, TN

EPA Participation

The assistance of the following EPA scientists in planning and conducting the study by, among other things, helping to select and, in some cases, obtain the needed samples is greatly appreciated.

- Adrian Hanley, Office of Water
- Lemuel Walker, Office of Water
- Troy Strock, Office of Resource Conservation and Recovery

Study Schedule

Samples were collected and analyzed from March to July 2021.

4. Study Design

Samples were collected from six (6) sources representing matrices of interest in the Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA) programs.

CWA Matrices

- Effluent from a publicly owned treatment works (POTW)
- Surface water (SW)
- Two wastewater samples from an industrial facility or influent from a wastewater treatment plant treating industrial wastewater (IW-1 and IW-2)

RCRA Matrices

- Landfill leachate (LL)
- Groundwater with high hardness (GW)

Upon arriving at the laboratory, an aliquot of each sample was analyzed to determine the "native" level of acrolein and of acrylonitrile and to determine other chemical and physical properties of the water samples.

The remaining samples of each matrix were then split into three 2-Liter aliquots. One aliquot was immediately preserved with 1:1 HCl to pH $\leq$2.; one preserved with 1:1 HCl to a pH of 4.0 – 5.0; and one aliquot was left unpreserved. Each of the aliquots was then used to fill 25 40-mL VOA vials. Each VOA vial was then spiked with acrolein and acrylonitrile so that the concentration of acrolein and of acrylonitrile in the vial was approximately 100 ppb.

Each type of preservation was then analyzed in quintuplicate (number of replicates = 5) on Days 0, 3, 7, 10 and 14 using EPA Method 624.1.

Before beginning any sample analysis, each participating laboratory was instructed to ensure and document that their analytical system (i.e., analyst, equipment, methodology) detected acrolein and acrylonitrile at levels of 5.0 ug/L for acrolein and acrylonitrile in reagent water and the LOQ was no higher than 10 ug/L.

The laboratories were directed to report the results of the analyses of each sample (the individual results) and the results of their analytical QC data using a defined protocol. They were also instructed to provide an EPA Contract Laboratory Program Level 4 type data package so that a 3rd party reviewer could use the data package to reproduce the results from the raw data.

The results of the testing were evaluated by:

(1) Calculating the average results and Relative Standard Deviation (RSD) for the subsamples preserved at pH ≤2; at pH 4.0 – 5.0; and unpreserved to evaluate within-laboratory precision;

(2) Comparing the concentration of each compound in each sample to the Method 624.1 LCS Lower Control Limit (LCL) of 60% for CWA matrices and 39% (acrolein) and 63% (acrylonitrile) for RCRA matrices[1]; and

(3) Looking at the concentration of acrolein and of acrylonitrile with all three types of preservation at 14 days.

About Control Limits
Neither Method 624.1 nor 8260D specify control limits for acrolein and acrylonitrile. Section 8.4.5 Method of 624.1 states "The laboratory should use 60 -140% as interim acceptance criteria for recoveries of spiked analytes that do not have recovery limits specified in Table 7." The Department of Defense has established limits of 39-155% for acrolein and 63- 135% for acrylonitrile in aqueous matrices.

Note: The goal of this study was not to establish holding times, but rather to determine if the pH ≤2 preservation and 14-day holding times for other volatiles could be used for acrolein and acrylonitrile.

[1] Quality Systems Manual (QSM) for Environmental Laboratories, Revision 5.3. June 2019

5. Results

5.1 Data Quality Indicators

Data Quality Indicators (DQIs) include precision, accuracy (bias), representativeness, comparability, and completeness (PARCC).[2] Sensitivity is frequently added to this list. Representativeness and comparability are not appropriate for this effort.

5.1.1 Precision

In general, the precision of the laboratory work averaged under 10%. A 16% RSD for acrolein in the leachate sample is primarily due to 10 of the 40 replicates being below the Reporting Limit (RL) of 10 ug/L. There were similar issues with the IW1 sample with 28 of 30 results under the RL. Finally, the Day 0 results for acrylonitrile in the surface water sample had a bi-modal distribution. The first 2 replicates had values of 135 ug/L, consistent with no loss of the analyte. The last 2 had an average of 29 ug/L, equivalent to the rest of the samples from day 3 to day 14. This analysis sequence began at 10:16 am with the 4 and 5 replicates being analyzed over an hour later, suggesting the acrylonitrile degraded as the samples warmed up.

Table 2. Study Sample Precision Data

Matrix	Mean Relative Standard Deviation, % (75 Replicates each unless otherwise specified)	
	Acrolein	**Acrylonitrile**
POTW Effluent	6.7	2.8
Surface Water (SW)	3.7 (n = 24)	8.6 (n = 72)
Industrial Wastewater 1 (IW1)	14 (n = 30)	4.2
Industrial Wastewater 2 (IW2)	6.7 (n = 53)	6.8
Landfill Leachate (LL)	16	4.0
Groundwater (GW)	6.0	2.8

5.1.2 Bias

Bias can be estimated by the recovery of acrolein and acrylonitrile in Laboratory Control Samples (LCS), by the recovery of surrogate compounds in each sample, and by Method Blanks (MB).

[2] Guidance on Data Quality Indicators. EPA QA/G5i. September 2001

Table 2. Study Bias Data

Analyte	Mean Recovery, %					
LCS	**POTW**	**SW**	**IW1**	**IW2**	**LL**	**GW**
Acrolein	90	88	90	124	90	95
Acrylonitrile	91	125	92	122	91	95
Surrogates						
1,2-Dichloroethane-d4	106	95	103	103	101	102
4-Bromofluorobenzene	100	97	96	99	106	97
Toluene-d8	101	103	99	100	104	103
Method Blanks						
Acrolein, ug/L	ND	ND	ND	ND	ND	ND
Acrylonitrile, ug/L	ND	ND	ND	ND	ND	ND

The values above provide confidence that the sample results contained in this report are a good estimate of the true concentration. See Appendix C for more details about these quality control samples.

5.1.3 Sensitivity

The sensitivity of the results can be estimated by the Method Detection Limit (MDL) and Reporting Limit (RL) for each analyte by each laboratory.

Table 3. Method Detection Limits and Reporting Limits

Analyte	MDL, ug/L			RL, ug/L		
	Lab A	**Lab B**	**Lab C**	**Lab A**	**Lab B**	**Lab C**
Acrolein	1.9	1.0	2.5	10	10	50
Acrylonitrile	4.0	0.2	0.67	10	1.0	10

5.1.4 Completeness

The goal was to have 75 data points for each matrix (5 days x 3 preservation techniques x 5 replicates) x 6 matrices for 2 analytes for a total of 900 data points. There were 15 outlier data points removed, 6 from the surface water and 9 from industrial wastewater 2. See Tables C-2 and C-6. These all appear to be blunders associated with the spiking levels (not spiked; 2x spike) as the surrogate recoveries were all within control limits, except for replicate 1 on day 14 of industrial wastewater 2 at pH 2 for acrolein where no result as reported as the compound was not included in the analyte list. Thus these data can be considered 98% complete.

As shown in Appendix C, over 1,200 data points were collected for surrogate spikes and Laboratory Control Samples. All of these data met the acceptance criteria except for 2 results for 1,2-dicchloroethane-d4.

5.2 Additional Information About Samples

Table 4. Results for Indicator Parameters

Sample	Initial pH	TSS (mg/L)	Hardness (mg/L)	Turbidity	Oil & Grease (mg/L)	Alkalinity (mg/L)
POTW Effluent	4.5	7.4	194		3.0J	104
Surface Water		7.3	154	7.8	ND	152
Wastewater 1	9.2	57	1300	31	4.1	140
Wastewater 2		39	81	80	ND	69.8
Landfill Leachate	1.7	59	1060	80	4.8	631
Groundwater	8.0	2	150	3.1	3.6	140

Table 5. Additional Analytes Found in Samples (ug/L)

Sample	Volatile Analytes Detected
POTW Effluent	
Surface Water	
Industrial Wastewater 1	Bromoform (0.27), chloroform (1.1), dibromochloromethane (0.29), Toluene (0.50)
Landfill Leachate	
Industrial Wastewater 2	
Groundwater	1,1-Dichloroethane (0.6/0.2), Tetrachloroethane (24), 1,2-Dichloroethene (0.14), Trichloroethene (3.6)

It should be noted that no native acrolein or acrylonitrile was found in any of the samples.

5.3 Results for Acrolein

Figures 1 through 6 present the results for acrolein in each of the various aqueous media when the sample was not preserved, was preserved to pH ≤2, and when preserved to meet the current requirements of pH 4 - 5. Each figure shows the mean of 5 replicate measurements performed on days 0, 3, 7, 10, and 14 in ug/L. A Lower Control Limit is also graphically shown as percent recovery. Since all samples were spiked at 100 ug/L, this control limit is equivalent to 60 ug/L for CWA and 39 ug/L for RCRA. Method 624.1 does not have criteria for acrolein for either the LCS or matrix spike, but states 60-140% may be used until the laboratory generates data. Method 8260 D does not have QC acceptance for acrolein for either LCS or matrix spikes. The Department of Defense (DOD) has established limits of 39-155%. Figures 7-9 show the same results summarized across all media.

Note: 2 ug/L was used as a default value for all not detected results for illustration only.

Figure 1. Acrolein in POTW Effluent

pH 2; pH 4 – 5; No preservative Lower Control Limit

For acrolein in the POTW effluent, the pH ≤2 and pH 4-5 both met the 60% lower control limit (LCL) with recoveries around 80%. With no preservative, results were below 60% by Day 3.

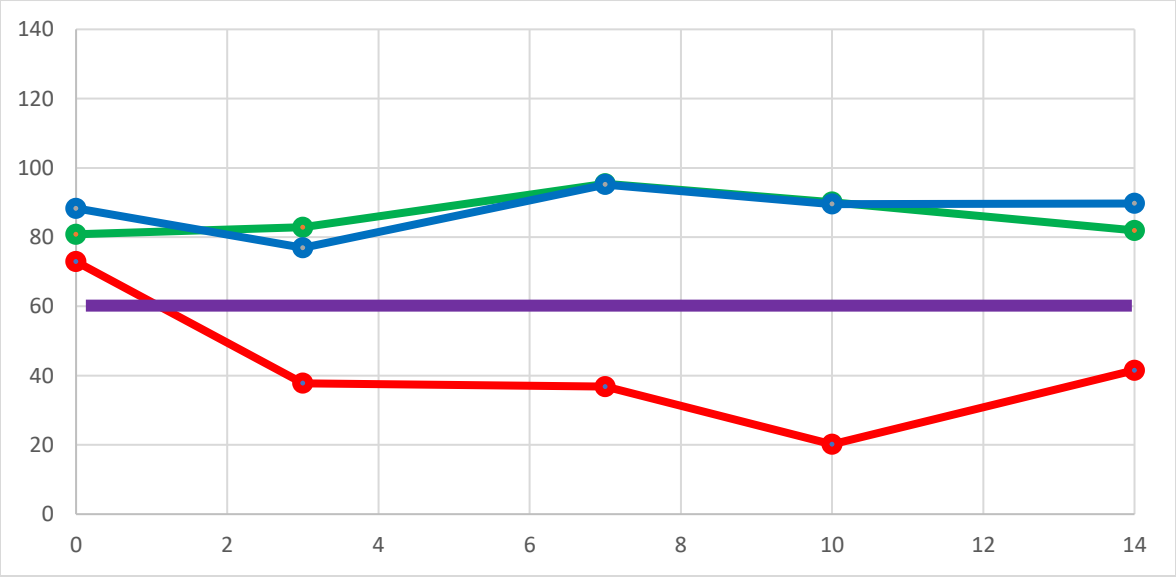
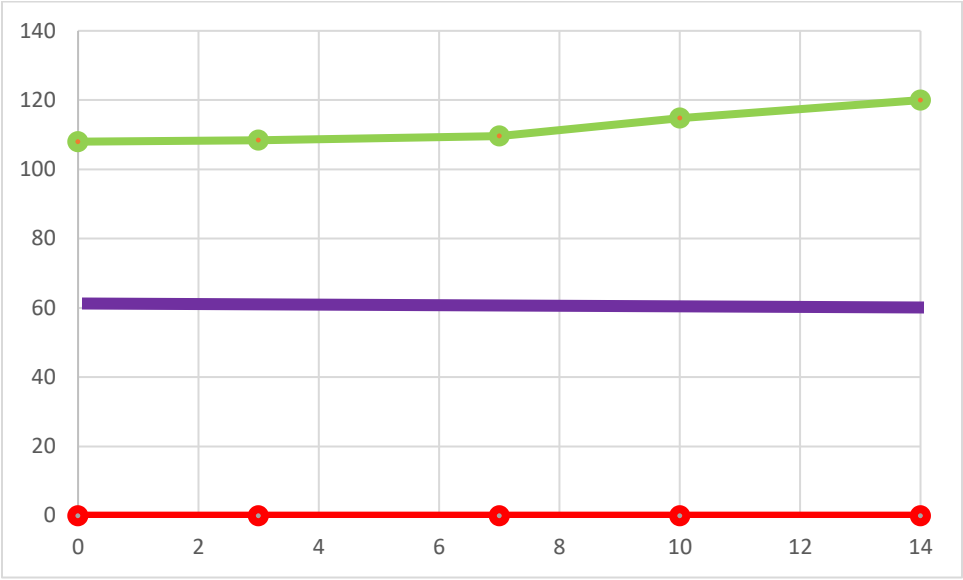


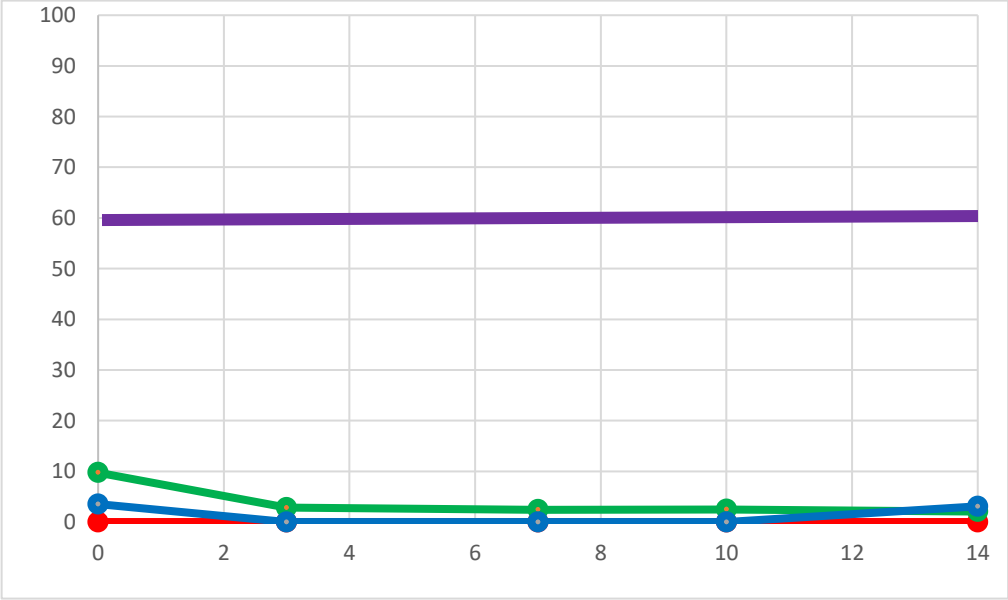
Figure 2. Acrolein in Surface Water



pH 2; pH 4 – 5; No preservative Lower Control Limit

In the surface water, acrolein was stable in the pH ≤2 samples, however, without preservation and at pH 4-5, the acrolein seemed to disappear instantly.

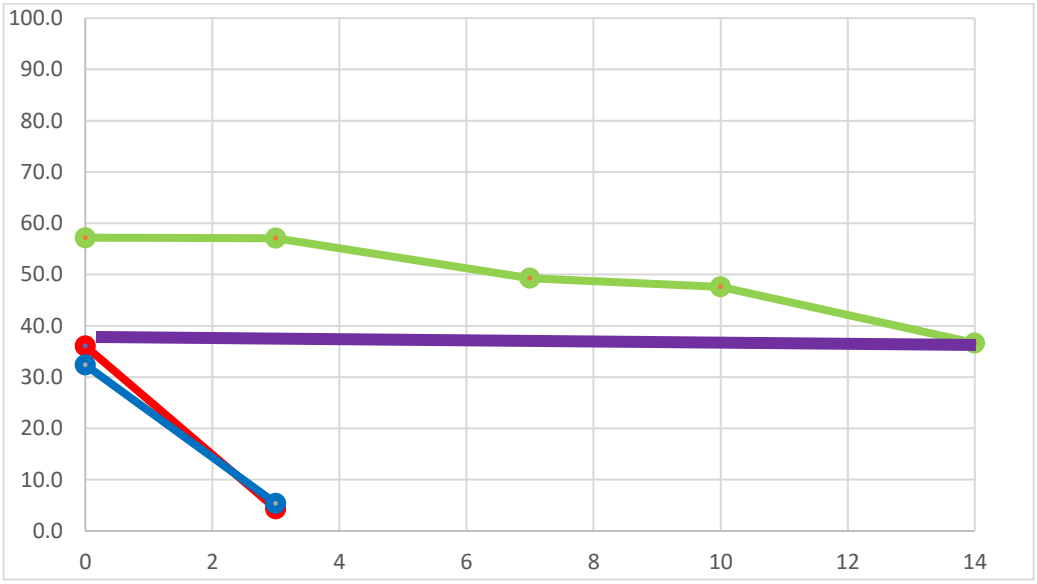
Figure 3. Acrolein in Wastewater 1



pH 2; pH 4 – 5; No preservative Lower Control Limit

In the first industrial wastewater effluent, none of the preservation methods adequately preserved acrolein after even one day, much less after 14 days.

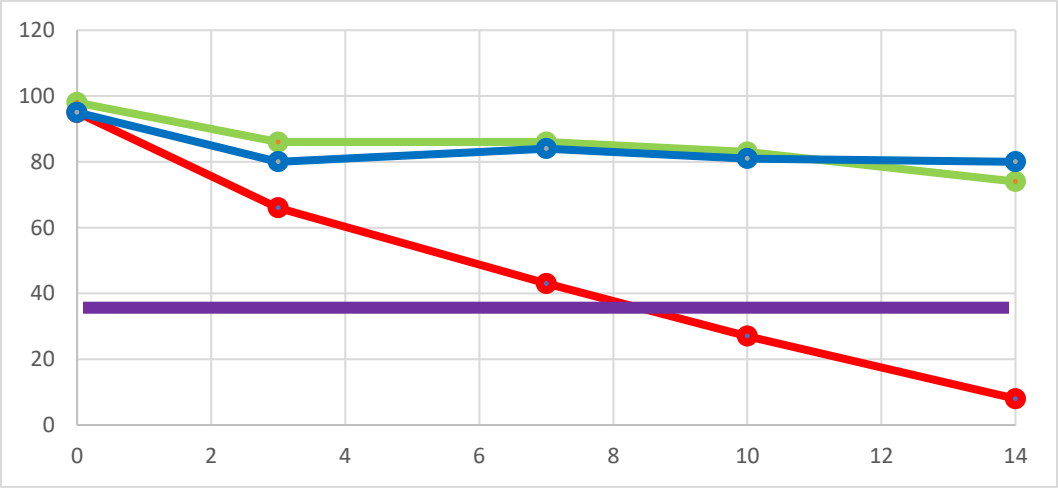
Figure 4. Acrolein in Landfill Leachate



pH 2; pH 4 – 5; No preservative Lower Control Limit

In the landfill leachate, preservation at pH ≤2 is significantly better than either no preservation or acidification to pH 4 - 5 and meets a 14-day holding time for the 39% LCL established by DOD. Even though the pH ≤2 sample began with a low recovery, the decrease in concentration from just under 60 µg/L to 40µg/L indicates a 14-day holding time is met.

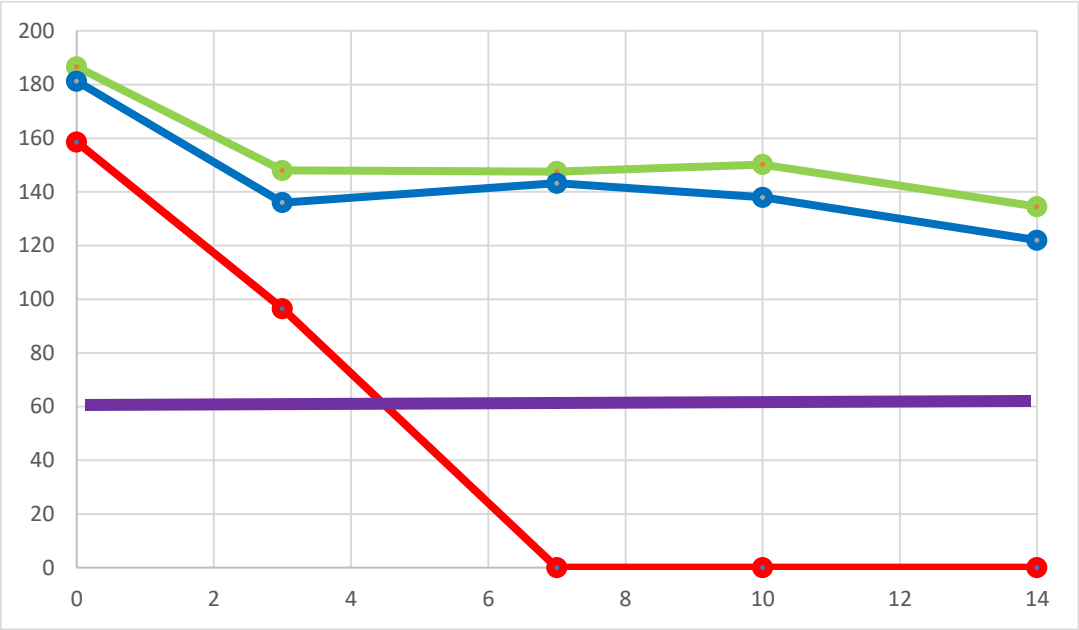
Figure 5. Acrolein in Groundwater



pH 2; pH 4 – 5; No preservative Lower Control Limit

For the groundwater sample, without preservation the acrolein rapidly degrades. With either pH ≤2 or pH 4 – 5 preservation, the sample maintains a 14-day holding time.

Figure 6. Acrolein in Wastewater 2



pH 2; pH 4 – 5; No preservative Lower Control Limit

Without acidification, the concentration of acrolein degraded to an unacceptable level very quickly and was not detectable at 7 days. With either acidification, the concentration remains in the acceptable range at 14 days. However, pH ≤2 reservation yields slightly better results than the current pH 4 – 5 requirement.

Figure 7. Acrolein without Preservation Across Media

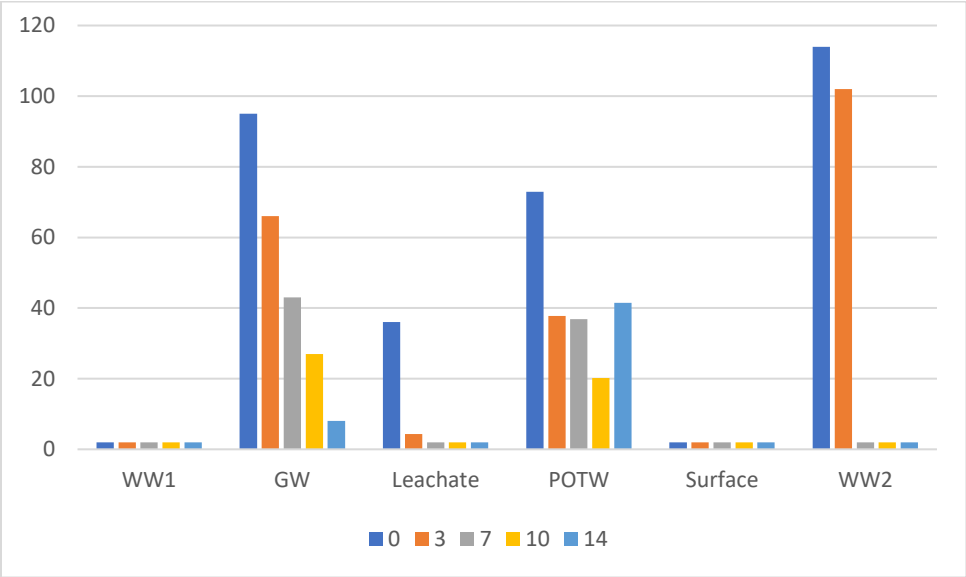
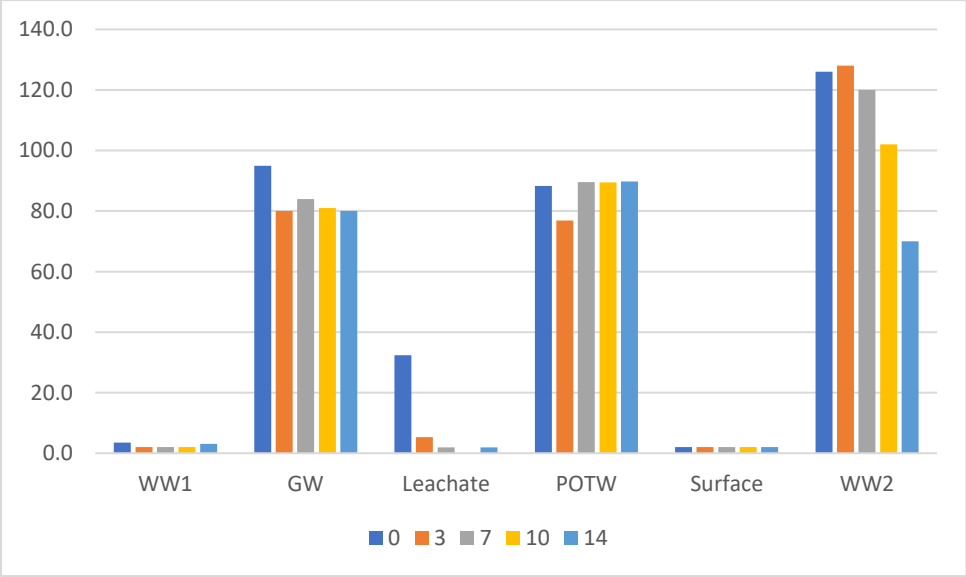


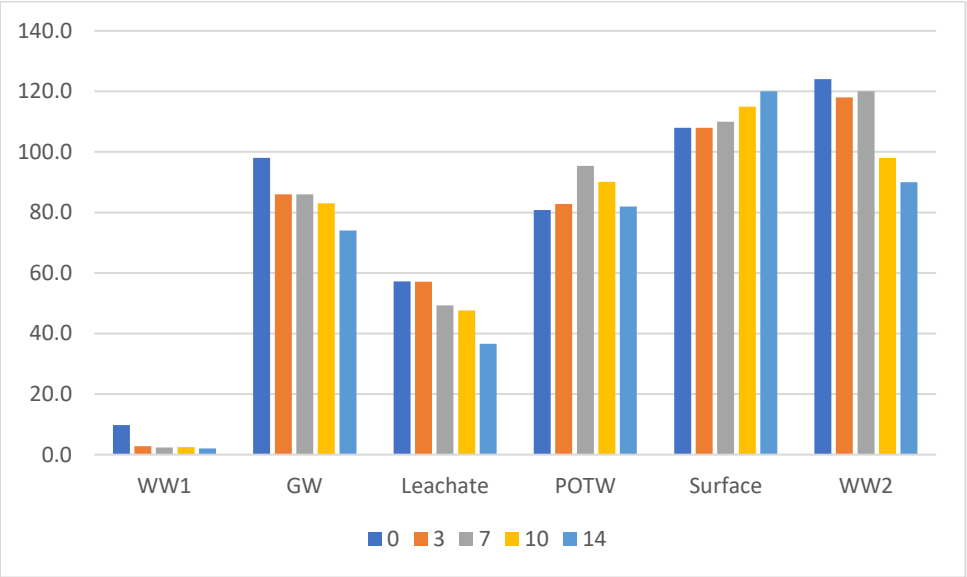
Figure 7 displays the acrolein results for unpreserved samples. It is readily apparent that without preservation, acceptable results will not be achieved, even at Day 0.

Figure 8. Acrolein pH 4 -5 Preservation Across Media



With acidification to pH 4 – 5, for three of the matrices, the recovery at 14 days is still unacceptable.

Figure 9. Acrolein pH ≤2 Preservation Across Media



Preservation to pH ≤2, yields better results than the currently approved preservation to pH 4 -5, even for the outlier IW1 matrix which had an obvious interference (most likely something in the samples that immediately reacted with the spiked acrolein) and the leachate sample which also seems to react with the acrolein.

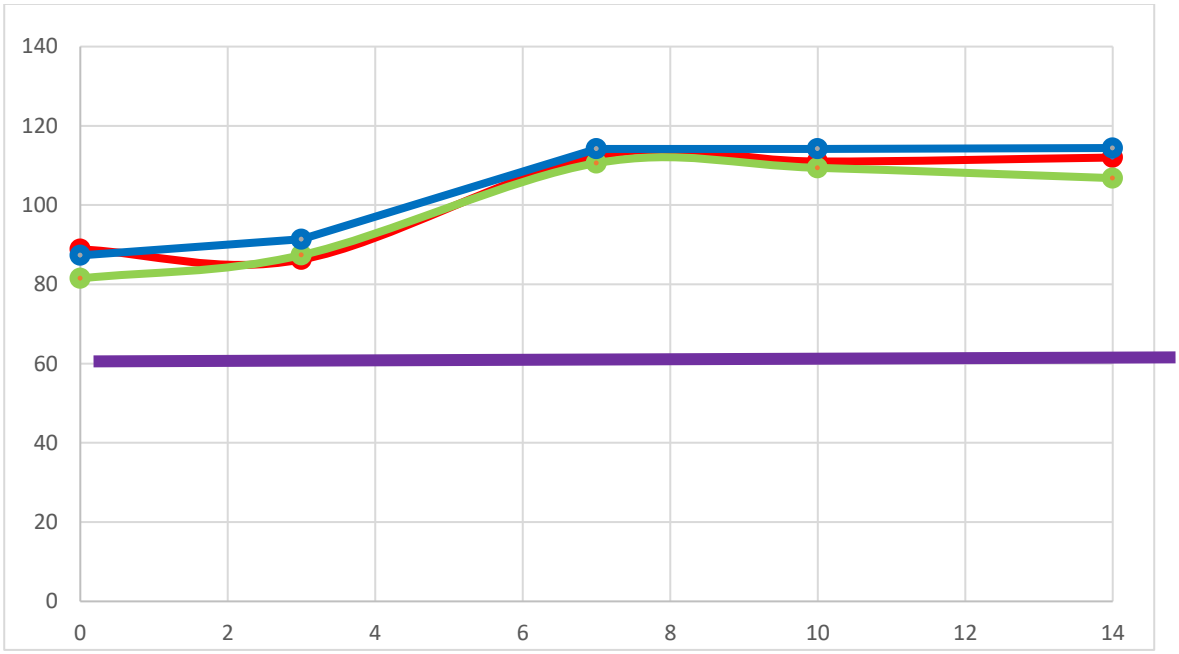
Acrolein Summary

- IW1 reacted with the spiked acrolein with poor recoveries regardless of preservation. Even in this matrix, the slightly higher results for the pH ≤2 samples indicate it is the better preservative.
- Excluding Wastewater 1,
  - Only 5 of the 23 unpreserved samples had acceptable recoveries.
  - 14 of the 23 samples had acceptable recoveries at pH 4-5.
  - 22 of the 23 samples had acceptable recoveries at pH 2. The only result that did not meet the LCL was the Day 14 leachate sample with a recovery of 37%, slightly below the 39% limit. However, since this sample also reacted with the original spiked acrolein for a Day 0 concentration of 60 µg/L, the 37 µg/L remaining at Day 14 indicates that a 14-day holding time is valid.

5.4 Results for Acrylonitrile

Figures 10 through 15 present the results for acrolein in each of the various aqueous media when the sample was not preserved, was preserved to pH ≤2, and when preserved to meet the currently approved requirements of pH 4 - 5. Each figure shows the mean of 5 replicate measurements performed on days 0, 3, 7, 10, and 14 in ug/L. A Lower Control Limit is also graphically shown as percent recovery. Since all samples were spiked at 100 ug/L, this control limit is equivalent to 60 ug/L for CWA samples and 63 ug/L for RCRA matrices. Method 624.1 does not have criteria for acrolein for either the LCS or matrix spike but states 60-140% may be used until the laboratory generates data. Method 8260 D does not have QC acceptance for acrolein for either LCS or matrix spikes. The Department of Defense (DOD) has established limits of 63-135 %. Figures 16-18 show the same results summarized across all media.

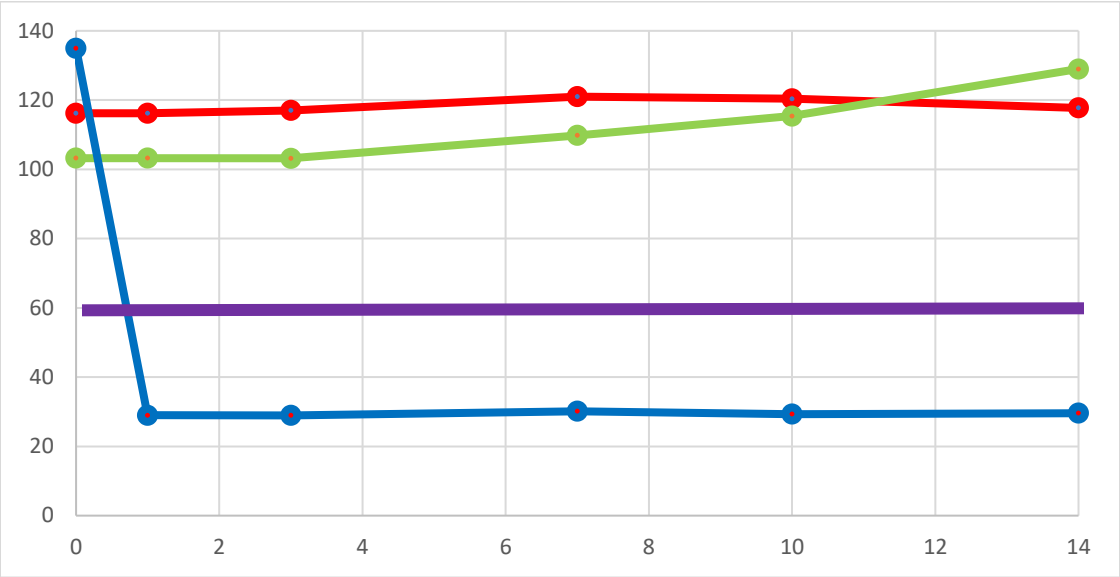
Figure 10. Acrylonitrile in POTW Effluent



pH 2; pH 4 – 5; No preservative Lower Control Limit

For the POTW effluent, even if samples are not preserved, acrylonitrile is stable over 14 days. There was no significant difference between preservation and non-preservation and recoveries hovered around 90%.

Figure 11. Acrylonitrile in Surface Water

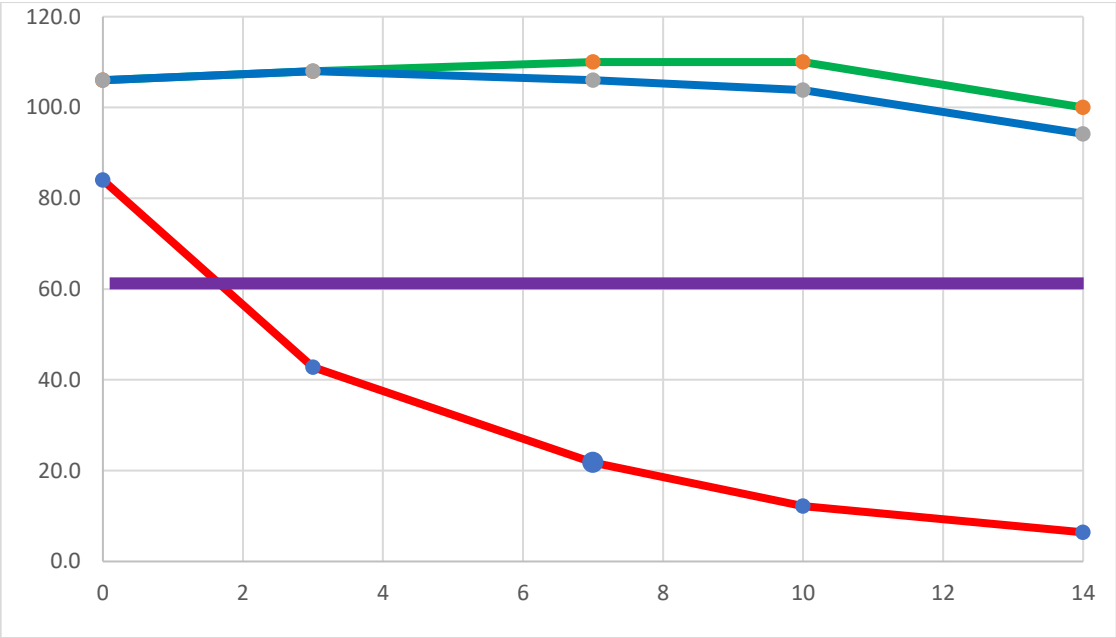


pH 2; pH 4 – 5; No preservative Lower Control Limit

In the surface water acrylonitrile was stable enough for acceptable results at 14 days at pH ≤2 and with no preservation but dropped below the acceptable limit at Day 1 for the pH 4-5 samples.

Note: Because of the bi-modal distribution of results in Day 0, the mean of the first 2 replicates was plotted as Day 0 while the mean of the last 2 was plotted as Day 1.

Figure 12. Acrylonitrile in Wastewater 1

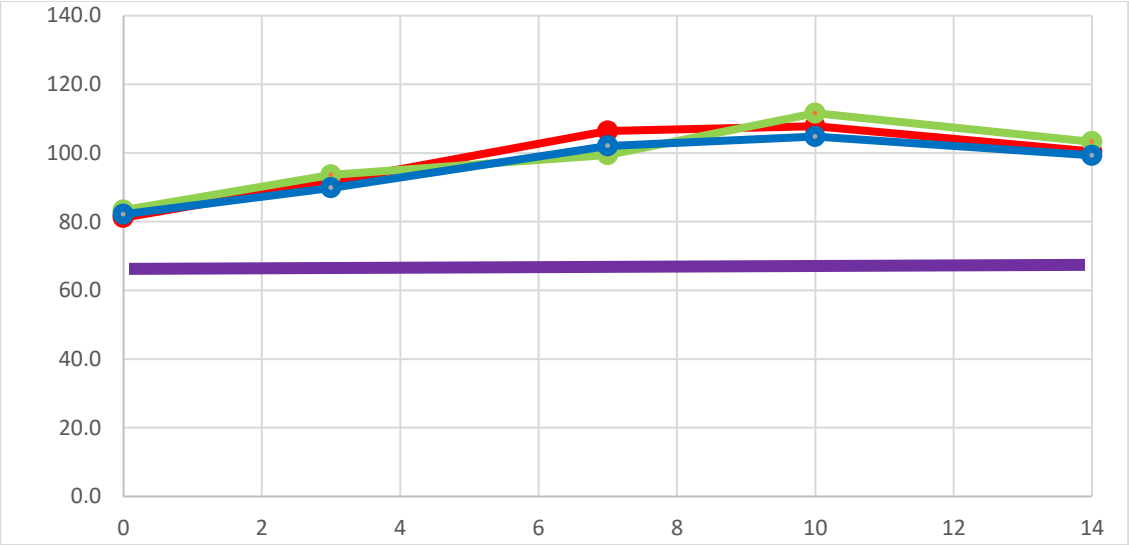


pH 2; pH 4 – 5; No preservative Lower Control Limit

In the IW1 effluent, the acrylonitrile is stable when the sample was acidified either to a pH of ≤2 or 4 -5.

Without preservation, however, the acrylonitrile recovery dropped drastically within two days.

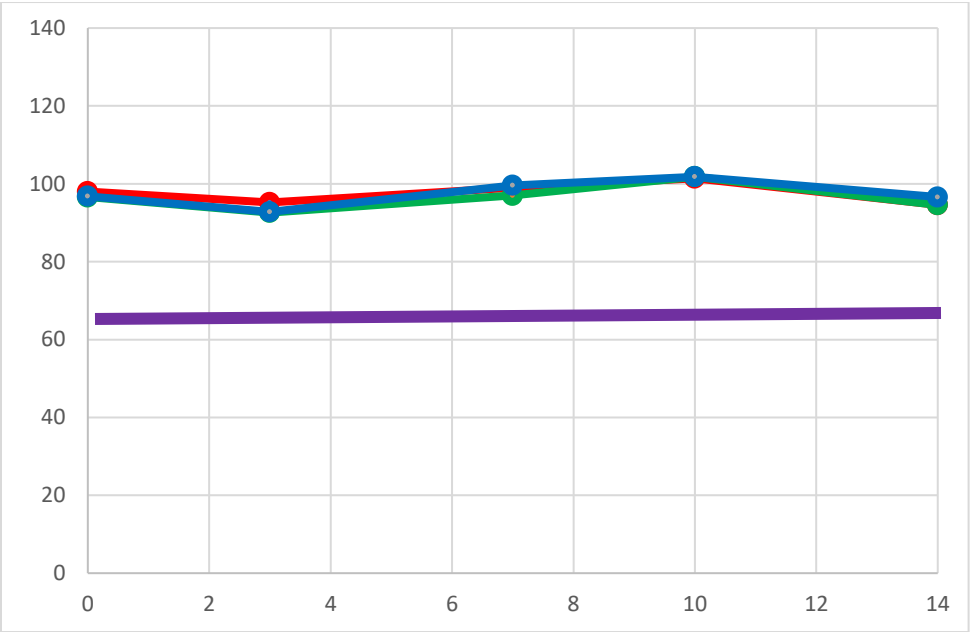
Figure 13. Acrylonitrile in Landfill Leachate



pH 2; pH 4 – 5; No preservative Lower Control Limit

In the landfill leachate acrylonitrile is stable for 14-days regardless of preservation.

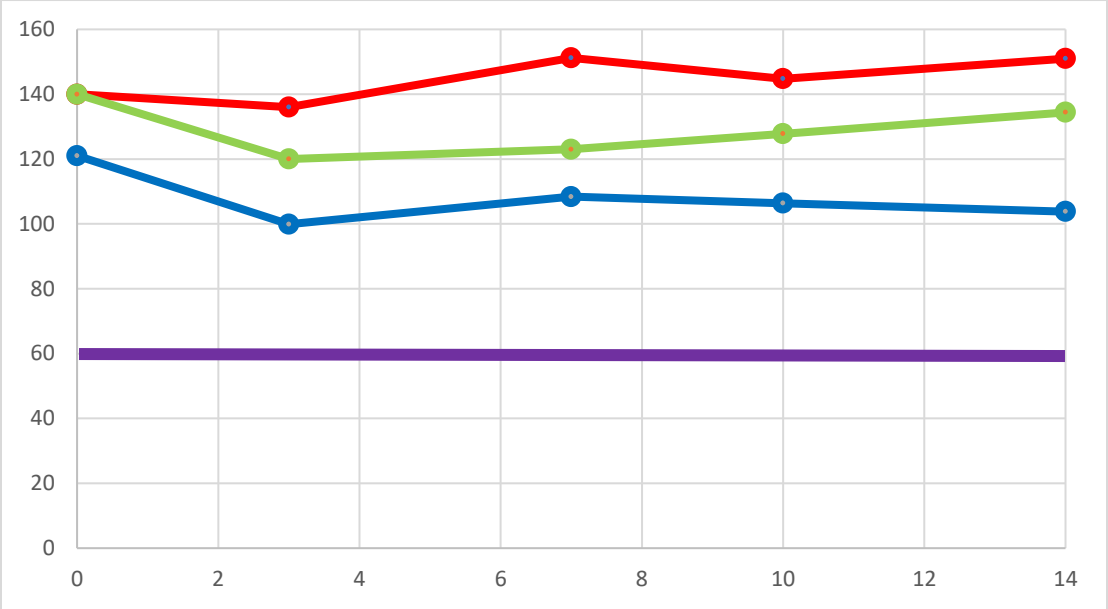
Figure 14. Acrylonitrile in Groundwater



pH 2; pH 4 – 5; No preservative Lower Control Limit

Similarly, with the groundwater sample, acidification is not needed to maintain the acrylonitrile in the sample over the 14 days.

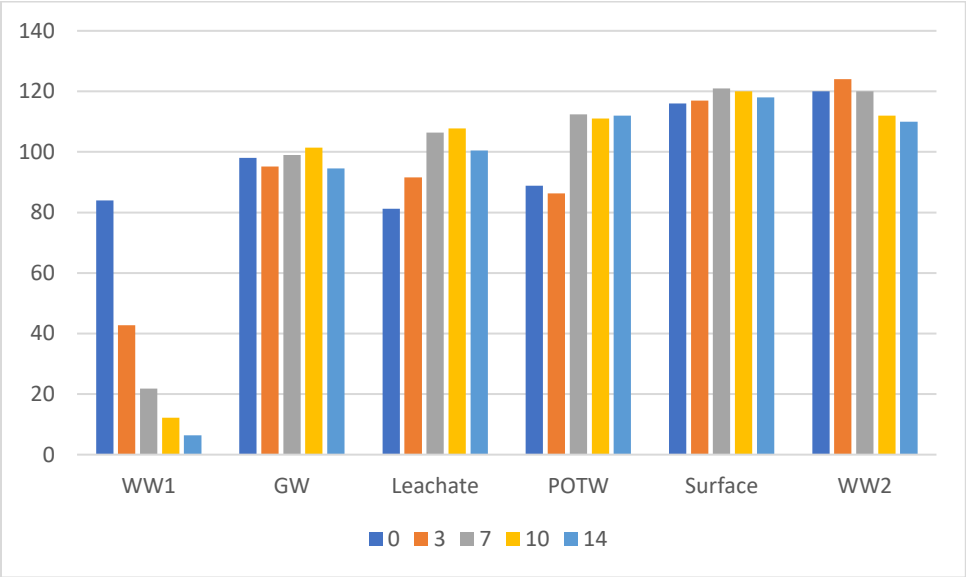
Figure 15. Acrylonitrile in Wastewater 2



pH 2; pH 4 – 5; No preservative Lower Control Limit

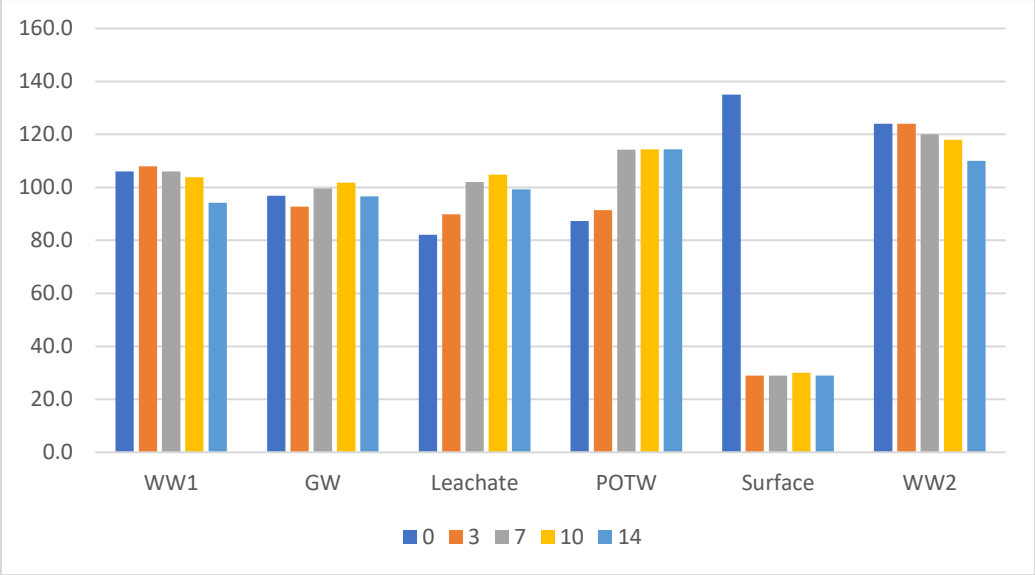
Finally, in IW2 the acrylonitrile concentration remained unchanged at all preservation types. Referring to the data in Table C-6, the mean concentration across 72 replicates was 126 ug/L with a standard deviation of 20 ug/L.

Figure 16. Acrylonitrile without Preservation Across Media



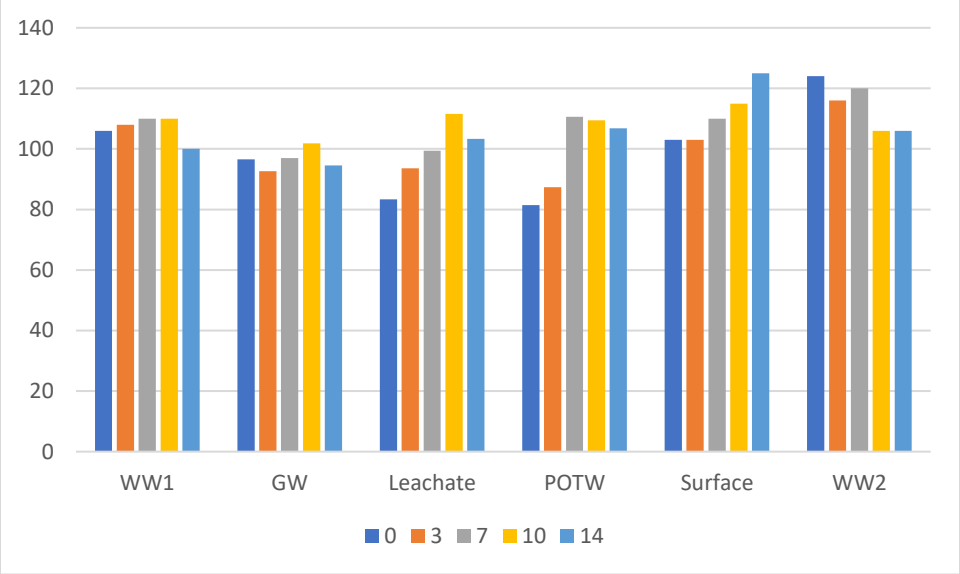
With the exception of IW1, the acrylonitrile is stable enough to yield acceptable results at 14 days, even without preservation. As with acrolein, rapid analyte loss was found in IW1.

Figure 17. Acrylonitrile pH 4 – 5 Across Media



Overall, acrylonitrile is fairly stable in the samples with acidification to pH 4 – 5; however, equivalent or better results are obtained by preservation at pH ≤2 (Figure 18).

Figure 18. Acrylonitrile pH 2 Preservation Across Media



All results had acceptable recoveries at 14 days if the sample is acidified to pH ≤2.

Acrylonitrile Summary

For acrylonitrile, all of the acidification requirements evaluated provided acceptable results for all matrices at 14 days, with the exception of the surface water sample at pH 4-5. However, with IW1, not acidifying the samples yielded unacceptable results.

6.0 Conclusions

- pH $\leq$2 preservation for acrolein and acrylonitrile yielded better results than the currently approved pH 4 – 5 requirements.
- There can be a rapid loss of acrolein with no preservation implying that samples need to be preserved in the field quickly. Even though the currently approved pH 4 -5 acidification is better than non-acidification. the pH adjustment is difficult to perform adequately possibly resulting in under-preserved samples.
- For acrolein, with pH $\leq$2 acidification, even after a 14-day holding time, acrolein recoveries are at least 80%, except for one of the industrial wastewaters, where the acrolein was lost almost immediately.
- For acrylonitrile, the approved pH 4-5 preservation showed minimal loss for the 14-day holding time, however recoveries were as good as, or better, when preserved at pH $\leq$2.
- This study showed that in a variety of water matrices, allowing a pH $\leq$2 sample preservation for acrolein and acrylonitrile would better maintain a 14-day holding time and not compromise the resulting analyses.
- Samples preserved to a pH $\leq$2 and held for 14 days before analysis would generally meet the default EPA Method 624.1 recovery criteria of 60 – 140% and the DOD criteria of 39-153% for acrolein and 63-135% for acrylonitrile. In addition, preservation at pH $\leq$2 would enable the determination of acrolein and acrylonitrile concurrently with all of the other analytes in each respective method.
- Unpreserved samples showed significant loss within 1-3 days for 4 of the 6 sample types for acrolein. We suggest EPA recommend that preservation take place immediately after sampling. Since it is difficult to adjust samples to a pH of 4 – 5 with HCl, this short holding time of unpreserved samples further supports the recommendation to allow preservation with HCL at pH $\leq$2.

Appendix A

Acrolein/Acrylonitrile Holding Time Re-evaluation

Study Plan

Background

On June 19, 2014, the former U. S. Environmental Protection Agency (EPA or the Agency) Environmental Laboratory Advisory Board (ELAB) sent a letter to the Agency requesting that EPA Method 624 be modified with respect to the preservation and holding time requirements for acrolein and acrylonitrile (Attachment A). Specifically, ELAB requested that: (a) the requirement to preserve samples at a pH of 4-5 be eliminated and instead make the preservation requirement identical to that for purgeable aromatic hydrocarbons, which preserves samples below pH 2, and (b) that the allowable maximum holding time be extended to 14 days.

In their letter, ELAB cited data from an email sent to the EPA Office of Water Docket on November 11, 2010 (Docket I.D. No. EPA-HQ-OW-2010-0192). This data, from URS Corporation, demonstrated that acrolein and acrylonitrile were stable in both deionized water and groundwater whether the samples had not been preserved or had been preserved with HCl to pH 2. Samples were shown to be stable for, at least, 16 days.

The Environmental Monitoring Coalition (EMC) was recently formed of organizations and individuals active in environmental monitoring. Members include experts from commercial environmental testing laboratories, state laboratory associations, state regulatory agencies, other trade associations, academia, federal and state agencies, data users, and environmental monitoring vendors including consulting firms and laboratory assessment bodies.

The EMC focuses on developing consensus recommendations to federal and state agencies and stakeholder groups that will reflect the opinions and positions of its constituents on issues that include but are not limited to:

- Validating and implementing methods for sample collection and for biological, chemical, radiological, and toxicological analyses;
- Standards and guidance for developing scientifically rigorous, statistically sound, and representative environmental measurements;
- Encouraging the performance approach in environmental monitoring and regulatory programs;
- Employing a quality systems approach that ensures that environmental monitoring data are of known and documented quality; and

- Facilitating the operation and expansion of a national environmental laboratory accreditation program.

Since EPA has not acted on the ELAB request due to a lack of sufficient data demonstrating the validity of the requested change, the EMC is undertaking a study to collect the additional data needed for EPA to justify the requested change.

The objective of the study will be to demonstrate that acidification of samples to pH ≤2 preserves the acrolein and acrylonitrile concentration in water samples as well as the current 40 CFR Part 136, and SW-846 acidification to pH 4 – 5 requirement. A secondary objective will be to confirm the efficacy of the current preservation and holding time guidance.

It is the goal of the EMC that the EPA Offices of Water and of Resource Conservation and Recovery adopt the requested preservation and holding time recommendations in their respective programs.

Overview of Study Design and Objectives

1. Samples will be collected from six (6) sources representing matrices of interest in the Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA) programs.

2. Upon arriving at the laboratory, an aliquot of each sample will be analyzed to determine the "native" level of acrolein and of acrylonitrile and to determine other chemical and physical properties of the water samples.

3. The remaining samples of each matrix will then be split into three 2-Liter aliquots. One aliquot will immediately be preserved with 1:1 HCl to pH ≤2; one to a pH of 4.0 – 5.0; and one aliquot will be left unpreserved. Each of the aliquots will then be used to fill, at least, (40) forty-40 mL VOA vials. Each VOA vial will then be spiked with acrolein and acrylonitrile so that the concentration of acrolein and of acrylonitrile in the vial is approximately 100 ppb.

4. Each type of preservation will then be analyzed in quintuplicate (number of replicates = 5) on Days 0, 3, 7, 10 and 14 using EPA Method 624.1.

5. The results of the testing will be evaluated by: (1) Plotting the average results for the three subsamples preserved at pH ≤2; at pH 4.0 – 5.0; and unpreserved to ascertain relative loss of analyte trends; (2) by comparing the percentage of the compound remaining in the sample to the Method 624.1 LCS acceptance criteria of 60 – 140% of the initial (i.e., Day 0) concentration; (3) using the Student's t-test to determine if there is any statistically significant

difference between preservation at pH ≤2; preservation at pH 4.0 – 5; or unpreserved, and (4) looking at the concentration of acrolein and of acrylonitrile all three types of preservation at 14 days.

6. Once the study has been completed and found to support the requested changes, a report detailing the study and its results will be submitted to EPA's Offices of Water and Resource Conservation and Recovery with a request that the appropriate changes to their methodology be made.

Details of Analysis Plan

1. Eight (8) one-liter samples of each waste will be collected for the preservation study plus additional samples of each waste for determining Oil & Grease, TSS, Hardness, Alkalinity, Turbidity, and Initial VOCs, will be collected from the following six types of facilities representing various matrices of interest to the Clean Water Act and Resource Conservation and Recovery Act regulatory programs. The wastes to be employed are:
   (a) Effluent from a publicly owned treatment works (POTW)
   (b) Surface water (SW)
   (c) Wastewater from an industrial facility or influent from a wastewater treatment plant treating industrial (IW-1)
   (d) Landfill leachate (LL)
   (e) Groundwater with high hardness (GW)
   (f) Wastewater from an industrial process or the influent from a wastewater treatment plant treating industrial waste (IW-2)

   These six (6) matrices are expected to have properties that will challenge sample stability and cover the variety of aqueous matrices of concern to the two regulatory programs. They were selected with the assistance of the EPA study representatives.

   Samples will be collected, using routine facility procedures, by either wastewater or landfill facility personnel or by representatives of the participating laboratories and shipped to the appropriate laboratory so that the laboratory receives the samples within 24 hours using the fastest practicable method of transportation. All samples will be kept cold (<6° C) during shipping.

2. Before beginning any sample analysis, each participating laboratory will ensure and document that their analytical system (i.e., analyst, equipment, methodology) can detect

acrolein and acrylonitrile at levels of 5.0 ppb for acrolein and acrylonitrile in reagent water and the LOQ is no higher than 50 ppb.

3. Each laboratory will receive 16 liters total, eight (8) liters of each of two matrices.

4. When a laboratory receives the samples, the laboratory shall first analyze a subsample of each matrix to determine its "native" or background concentration of acrolein and acrylonitrile; the concentration of the other Method 624.1 listed VOC compounds; and for hardness, turbidity, alkalinity, oil and grease, and Total Suspended Solids.

5. Once the "native" concentration has been determined, the remaining samples of each matrix will be used to prepare three, 2-liter aliquots (Figure 1). One of the aliquots will be left unpreserved, one preserved to pH ≤ 2, and one preserved to pH 4.0 – 5.0. (The pH of all three aliquots will be measured using a pH meter and the results documented. (Care shall be taken to ensure that all samples and spiking materials are kept below 6 ° C during the aliquoting and spiking procedures and when the VOA vials are not being analyzed.)

6. As soon as the laboratory has divided up and preserved the matrix samples, each of the three aliquots shall be further subdivided into, at least, thirty 40 mL portions and placed into VOA vials and sealed. Each VOA vial will then be spiked with acrolein and with acrylonitrile so that the concentration of acrolein and of acrylonitrile in the vial is approximately 100 ppb.

7. As soon as spiking is completed, five VOA vials of each preservation type and of each matrix shall be analyzed to determine the Day = 0 levels. The remaining VOA vials shall be stored at <6 ° C until needed for analysis on Days 3, 7, 10 and 14.

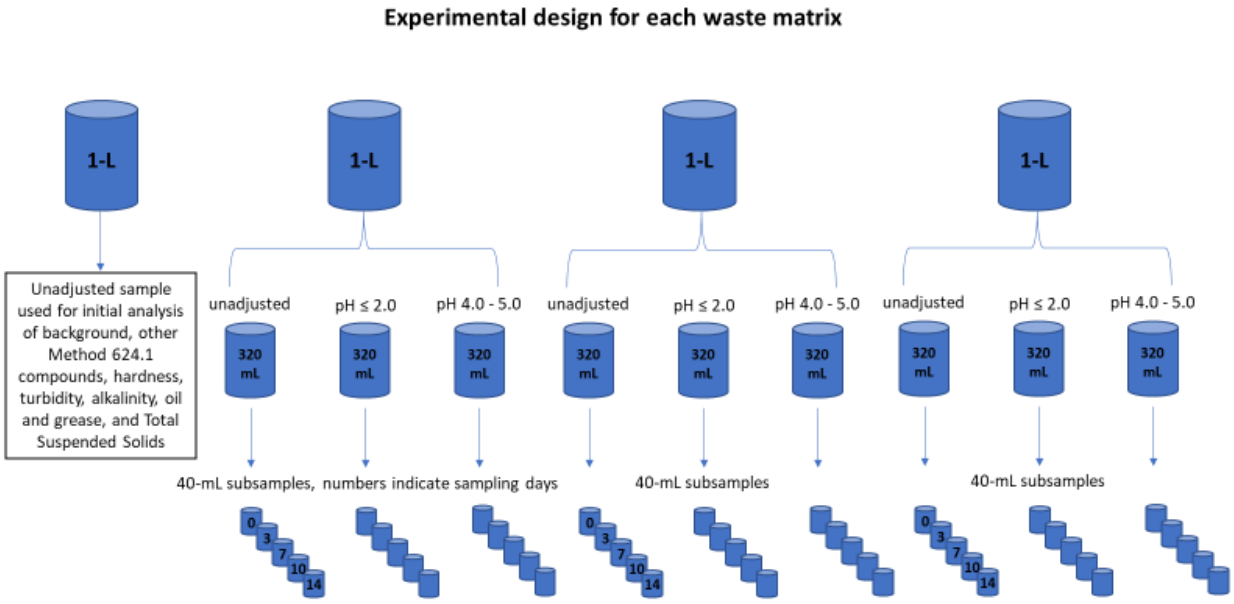


Figure 1. Each laboratory will receive 8-L of each waste they are to analyze, plus additional samples appropriate for determining Oil & Grease, TSS, hardness, Alkalinity, Turbidity, and initial VOC concentration. From each waste source, the 8 L sample will be divided into four 2-L bottles. Three of the four bottles will be treated with the requisite preservation, and then each 2-liter bottle will be subdivided into 40-ml VOA vials. The VOA vials will then be spiked with acrolein and acrylonitrile (The extra 2-L bottle of sample is kept in storage in case the laboratory needs it.). Five 40-mL subsamples from each pH treatment group will be analyzed on Day 0, 3, 7, 10, and 14.

See table below for distribution details. Laboratories shall analyze these samples in batches as they would normal commercial samples.

Table 1. Distribution of Matrix Samples

Lab	POTW	SW	IW-1	LL	GW	IW-2
1	X			X		
2		X	X			
3					X	X

6. Analyses of the samples will be performed in quintuplicate on Days 0, 3, 7, 10, and 14. This will mean each laboratory would analyze 5 subsamples (VOA vials) of each matrix and of each type of preservation on each scheduled day of the study for both acrolein and acrylonitrile. Laboratories shall employ Method 624.1 for the analyses.

7. Laboratories will report the results of the analyses of each sample (the individual results) and the results of their analytical QC data using the attached spreadsheet. They will also provide an EPA Contract Laboratory Program Level 4 type data package to support the regulatory change process so that a 3rd party reviewer could use the data package to reproduce the results from the raw data. The analytical results and the data package should be sent electronically to David Friedman@cox.net using the spreadsheet in Appendix D. Note: The full data package need only be provided for the acrolein and acrylonitrile analyses.

Determination of Validity of Requested Change

1. The four objectives of the study are:

(a) to determine if acidification of samples to pH ≤2 preserves the samples as well as the currently specified acidification to pH 4.0 – 5.0;

(b) to determine if either the current or the requested preservation permits the samples to remain valid for 14 days;

(c) to determine if preservation is needed for the samples to remain suitable for analysis over 14 days;

(d) to confirm that using the current preservation and holding time requirements will yield valid analytical results.

2. Before submitting the data to EPA, the results of the study will be looked at in several ways to ascertain if the proposed preservation and holding times are appropriate to obtaining valid analytical results. These include:

(1) The average concentration of acrolein and of acrylonitrile of the quintuplicate results on each waste/preservation combination will be compared to the method 624.1 recovery acceptance criteria of 60 – 140% (Appendix C) at each study time period. If the concentrations are within the method 624.1 acceptance criteria, the preservation method employed for that particular sample will be deemed to have been effective. If the Day 14 concentration of the pH ≤2 samples are found to be within the acceptable range, then the validity of a 14-day holding time will be considered to have been demonstrated.

(2) The average concentration of acrolein and of acrylonitrile will be compared at each day of analysis to see if there is a statistical difference between the two preservation methods and the unpreserved sample. It will be deemed that there is a statistical difference if the average (mean) concentration of one preservation method is less than the average concentration of another preservation (no preservation is considered one type of preservation) to a level of confidence of 95% (i.e., that there is less than a 5% probability that the concentration in one sample is lower than that of another).

(3) The average recovery for each method of preservation against time will be plotted to identify trends and to ascertain whether there is any apparent difference between the preservation/non-preservation approaches.

Study Implementation and Management

a. This study is being conducted under the auspices of the EMC. The EMC is responsible for managing the study, and David Friedman, on behalf of the EMC, is responsible for the day-to-day management of the effort. He can be contacted at 703-389-3821 or at friedmanconsulting@outlook.com.

b. The following individuals have participated in the design of this study:
- Richard Burrows
- William Lipps
- Brad Meadows
- Judy Morgan
- Jerry Parr

c. The following laboratories and the individual in each laboratory managing their organization's efforts are:
- Babcock Laboratories, Brad Meadows
- Eurofins Laboratories, Richard Burrows
- Pace Laboratories, Judy Morgan

d. Representing the EPA and helping to design the study and ensure that appropriate matrices were employed were:
- Adrian Hanley, Lemuel Walker and Sarah Burket, EPA Office of Water
- Troy Strock, Office of Resource Conservation and Recovery

Study Schedule

a. Finalize study plan (February 3, 2021)
b. Identify sources of matrix samples (February, 2021)
c. Shipping containers and bottles shipped to sources of samples (February, 2021)
d. Sample collection (February, 2021)
e. Samples received at laboratories (March 22, 2021)
f. Samples baseline tested, aliquoted, preserved, and Day 0 analyses performed (March, 2021)
g. Day 3 analyses performed (March, 2021)
h. Day 7 analyses performed (March, 2021)
i. Day 10 analyses performed (March, 2021)
j. Day 14 analyses performed (March, 2021)
k. Data package to David Friedman (April, 2021)
l. Data analysis to Task Group (May, 2021)
m. Task Group meeting (May, 2021)
n. Draft report to Task Group (June, 2021)
o. Task group meeting (June, 2021)
p. Second draft report to Task Group and to EMC for their review and comment (July, 2021)
q. Finalize report (July, 2021)
r. Send report and data package to EPA (August, 2021)
s. Presentation at 2021 NEMC (August, 2021

ATTACHMENT B

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°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,

P Root

Patsy Root
Chair, Environmental Laboratory Advisory Board

cc: ELAB

Appendix B. Analytical Results

The six tables which follow present the individual sample results for every replicate, along with the mean concentration, standard deviation, and percent relative standard deviation (RSD)

Table B-1 POTW

	Acrolein, ug/L					Acrylonitrile, ug/L				
Preservation	**0**	**3**	**7**	**10**	**14**	**0**	**3**	**7**	**10**	**14**
Initial	ND					ND				
Neutral	72.9	37.3	50	18	44	93.1	87.5	111	112	115
Neutral	74.1	34.3	33.7	17.7	48.9	90	83.5	115	110	113
Neutral	73	38.5	47.5	20.7	42.4	87	84.4	115	114	109
Neutral	65.3	40.6	24.9	21.5	41.4	83	86.8	109	108	114
Neutral	79.3	38.2	28.1	22.9	30.9	91	89.2	112	111	109
Mean	72.9	37.8	36.8	20.2	41.5	88.8	86.3	112	111	112
StdDev	5.00	2.29	11.4	2.2	6.60	3.93	2.32	2.61	2.24	2.83
RSD, %	6.9	6.1	30.8	11.2	15.9	4.4	2.7	2.3	2.0	2.5
pH2	83.1	84.6	95.2	87.9	83.2	78.9	87.3	109	108	111
pH2	81.7	87.6	95.6	90.3	82.5	80	92.6	111	110	105
pH2	80.2	80.4	94.9	91.7	82.6	85.9	85.7	109	111	105
pH2	76	82.1	95.4	89.6	81.1	82.7	87.8	112	108	108
pH2	83.1	79.6	95.9	91	80.2	79.9	83.5	112	110	105
Mean	80.8	82.9	95.4	90.1	81.9	81.5	87.4	110	109	107
StdDev	2.95	3.27	0.38	1.46	1.23	2.84	3.37	1.52	1.34	2.68
RSD, %	3.6	3.9	0.4	1.6	1.5	3.5	3.9	1.4	1.2	2.5
pH 4-5	91.2	77.2	96.7	86.2	91.6	94.3	88.2	117	111	116
pH 4-5	87.5	77.1	95.8	88.1	89.1	85.6	89.5	118	113	114
pH 4-5	86.7	77.3	97.8	96.2	87	86.4	91.7	118	117	115
pH 4-5	90.7	76.4	96.2	82.9	89	89.4	91.3	118	112	114
pH 4-5	85.4	76.6	89.3	94.2	91.9	80.8	96.1	116	118	113
Mean	88.3	76.9	95.2	89.5	89.7	87.3	91.4	117	114	114
StdDev	2.54	0.40	3.36	5.55	2.04	4.98	3.00	0.89	3.11	1.14
RSD, %	2.9	0.5	3.5	6.2	2.3	5.7	3.3	0.8	2.7	1.0

Table B-2 Surface Water

Preservation	Acrolein, ug/L					Acrylonitrile, ug/L				
	Day 0	Day 3	Day 7	Day 10	Day 14	Day 0	Day 3	Day 7	Day 10	Day 14
Initial	ND					ND				
Neutral	ND	ND	ND	ND	ND	113	118	106	120	113
Neutral	ND	ND	ND	ND	ND	116	122	117	118	117
Neutral	ND	ND	ND	ND	ND	121	115	2.6U*	125	120
Neutral	ND	ND	ND	ND	ND	115	111	138	119	121
Neutral	ND	ND	ND	ND	ND	116	119	123	120	1.1U*
Mean						116	117	121	120	118
StdDev						2.9	4.2	13.3	2.7	3.6
RSD, %						3	4	11	2	3
pH2	111	113	110	116	110	105	105	112	117	117
pH2	109	106	108	113	110	105	100	110	113	116
pH2	103	108	110	117	208*	99.2	103	110	119	216*
pH2	107	105	108	113	128	102	103	106	112	140
pH2	110	110	112	115	131	105	105	111	116	143
Mean	108	108	110	115	120	103	103	110	115	129
StdDev	3.2	3.2	1.7	1.8	11.3	2.6	2.0	2.3	2.9	14.5
RSD, %	3	3	2	2	9	3	2	2	2	11
pH 4-5	ND	ND	ND	ND	ND	135	29.5	30.3	28.8	29.4
pH 4-5	ND	ND	ND	ND	ND	135	28.5	29.8	26.7	30.1
pH 4-5	1940*	ND	ND	ND	ND	1870*	28.2	29.9	30	30.1
pH 4-5	ND	ND	ND	ND	ND	30.4	29.3	30.5	31.1	28.4
pH 4-5	ND	ND	ND	ND	ND	27.3	29.2	30.2	30	29.9
Mean						82	29	30	29	30
StdDev						61	0.6	0.3	1.7	0.7
RSD, %						75	2	1	6	2

* Outlier not included in Mean calculation

U Detected below Reporting Limit

Table B-3. Groundwater

	Acrolein, ug/L					Acrylonitrile, ug/L				
Preservation	**0**	**3**	**7**	**10**	**14**	**0**	**3**	**7**	**10**	**14**
Initial	ND					ND				
Neutral	90	62	47	36	17	94	93	98	110	95
Neutral	98	68	48	32	15	100	100	100	97	95
Neutral	96	64	44	36	18	100	96	98	100	97
Neutral	90	61	45	32	13	96	91	100	100	93
Neutral	95	66	43	27	8	100	96	99	100	93
Mean	93.8	64.2	45.4	32.6	14.2	98	95.2	99	101	94.6
StdDev	3.63	2.86	2.07	3.71	3.96	2.83	3.42	1.00	4.98	1.67
RSD, %	3.9	4.5	4.6	11.4	27.9	2.9	3.6	1.0	4.9	1.8
pH2	91	84	77	80	79	93	95	91	99	98
pH2	96	84	85	84	72	97	92	100	100	94
pH2	98	82	81	85	77	98	90	100	110	93
pH2	95	81	81	81	78	97	92	94	100	95
pH2	98	86	86	83	74	98	94	100	100	93
Mean	95.6	83.4	82	82.6	76	96.6	92.6	97	101	94.6
StdDev	2.88	1.95	3.61	2.07	2.92	2.07	1.95	4.24	4.60	2.07
RSD, %	3.0	2.3	4.4	2.5	3.8	2.1	2.1	4.4	4.5	2.2
pH 4-5	98	81	84	86	92	97	93	100	100	95
pH 4-5	94	86	84	79	95	95	96	99	99	100
pH 4-5	93	86	85	87	76	94	94	100	100	94
pH 4-5	96	82	81	86	81	98	92	99	110	98
pH 4-5	95	80	84	81	80	100	89	100	100	96
Mean	95.2	83	83.6	83.8	84.8	96.8	92.8	99.6	102	96.6
StdDev	1.92	2.83	1.52	3.56	8.23	2.39	2.59	0.55	4.60	2.41
RSD, %	2.0	3.4	1.8	4.3	9.7	2.5	2.8	0.5	4.5	2.5

Table B-4. Leachate

	Acrolein, ug/L					Acrylonitrile, ug/L				
Preservation	**0**	**3**	**7**	**10**	**14**	**0**	**3**	**7**	**10**	**14**
Initial	ND					ND				
Neutral	38.6	3.8	ND	ND	ND	79.6	91	103	113	100
Neutral	39	6.6	ND	ND	ND	82.5	92.2	106	109	98.8
Neutral	33.8	3.5	ND	ND	ND	79.9	89.4	107	109	99.4
Neutral	32.4	4.0	ND	ND	ND	79.9	92.4	110	105	102
Neutral	36.5	3.7	ND	ND	ND	84	92.8	106	103	102
Mean	36.1	4.3				81.2	91.6	106	108	100
StdDev	2.91	1.28				1.97	1.38	2.51	3.9	1.49
RSD, %	8.1	29.6				2.4	1.5	2.4	3.6	1.5
pH2	59.1	54.7	55.4	58.8	36.9	85	93.4	103	127	96.4
pH2	53.8	55.5	54.4	41.7	34.9	81.3	90.1	104	110	101
pH2	59.9	57.9	50.7	40.5	35.4	89.4	91.2	102	111	106
pH2	60.4	58.1	50.4	48.8	38.4	81.6	96.8	109	104	106
pH2	52.8	59.2	35.6	48.2	37.6	79.5	96.7	79.2	106	107
Mean	57.2	57.1	49.3	47.6	36.6	83.4	93.6	99.4	112	103
StdDev	3.61	1.90	7.97	7.29	1.47	3.92	3.08	11.6	9.07	4.50
RSD, %	6.3	3.3	16.2	15.3	4.0	4.7	3.3	11.7	8.1	4.4
pH 4-5	38.4	3.5	ND	ND	ND	82.6	88.3	108	103	98
pH 4-5	32.6	3.0	ND	ND	ND	79	87.2	104	109	102
pH 4-5	30.2	4.6	ND	ND	ND	79.8	85.5	98.9	105	100
pH 4-5	30.4	9.6	ND	ND	ND	85.4	96.3	99.8	104	98.5
pH 4-5	30.4	6.0	ND	ND	ND	84	92	99.6	103	98.1
Mean	32.4	5.4				82.2	89.9	102	105	99.3
StdDev	3.50	2.65				2.72	4.32	3.9	2.49	1.70
RSD, %	10.8	49.4				3.3	4.8	3.8	2.4	1.7

Table B-5. Industrial Wastewater 1

	Acrolein, ug/L					Acrylonitrile, ug/L				
Preservation	**0**	**3**	**7**	**10**	**14**	**0**	**3**	**7**	**10**	**14**
Initial	ND					ND				
Neutral	ND	ND	ND	ND	ND	80	45	22	12	6.5 U
Neutral	ND	ND	ND	ND	ND	84	40	20	13	6.6 U
Neutral	ND	ND	ND	ND	ND	88	43	22	12	6.4 U
Neutral	ND	ND	ND	ND	ND	88	43	22	12	6.1 U
Neutral	ND	ND	ND	ND	ND	80	43	23	12	6.5 U
Mean						84	42.8	21.8	12.2	6.42
StdDev						4.00	1.79	1.10	0.45	0.19
RSD, %						4.8	4.2	5.0	3.7	3.0
pH2	14	4.4U	2.6 U	2.3 U	2.1 U	100	110	110	120	100
pH2	11	3U	2.1 U	2.3 U	ND	110	110	110	110	100
pH2	7.1U	2.5 U	3 U	2.8 U	2.1 U	110	110	110	100	100
pH2	8.5U	2.2 U	2.1 U	2.3 U	ND	100	110	110	110	100
pH2	8.1U	2.1 U	2.3 U	2.8 U	2 U	110	100	110		100
Mean	9.74	2.84	2.42	2.5	2.00	106	108	110	110	100
StdDev	2.78	0.94	0.38	0.27	0.10	5.48	4.47	0.00	8.16	0.0
RSD, %	29	33	16	11	5.0	5.2	4.1	0.0	7.4	0.0
pH 4-5	3.4 U	ND	ND	ND	ND	110	110	110	99	94
pH 4-5	3.7 U	ND	ND	ND	ND	100	110	100	110	91
pH 4-5	3.7 U	ND	ND	ND	ND	100	110	100	100	95
pH 4-5	3.5 U	ND	ND	ND	3 U	110	110	110	110	91
pH 4-5	3.4 U	ND	ND	ND	3.2 U	110	100	110	100	100
Mean	3.54				2.38	106	108	106	103.8	94.2
StdDev	0.15				0.66	5.48	4.47	5.48	5.67	3.70
RSD, %	4.3				27.8	5.2	4.1	5.2	5.5	3.9

U Result below Reporting Limit of 10 ug/L

Table B-6. Industrial Wastewater 2

	Acrolein, ug/L					Acrylonitrile, ug/L				
Preservation	**0**	**3**	**7**	**10**	**14**	**0**	**3**	**7**	**10**	**14**
Initial										
Neutral	157	103	50	ND	ND	21.4*	139	148	143	153
Neutral	163	95.6	ND	ND	ND	21.4*	136	145	141	155
Neutral	149	80.8	ND	ND	ND	131	135	150	61.2	136
Neutral	159	96.9	ND	ND	ND	143	134	159	149	134
Neutral	165	106	ND	ND	ND	146	136	154	146	177
Mean	159	96				140	136	151	145	151
StdDev	6.2	9.7				7.9	1.9	5.4	3.5	17.4
RSD, %	4	10				6	1	4	2	12
pH2	174	156	153	159	**	142	208*	128	133	171
pH2	227	144	150	150	152	203*	120	124	129	143
pH2	164	151	146	148	132	124	117	121	128	122
pH2	211	82.4	141	151	130	177	130	116	127	121
pH2	157	141	148	143	124	117	113	126	122	115
Mean	187	148	148	150	135	140	120	123	128	134
StdDev	30.7	6.8	4.5	5.8	12.2	26.8	7.3	4.7	4.0	23.0
RSD, %	16	5	3	4	9	19	6	4	3	17
pH 4-5	196	145	145	136	4.6U*	122	103	112	109	101
pH 4-5	190	138	141	2.6U*	127	117	101	107	105	107
pH 4-5	197	142	148	140	117	146	103	110	109	104
pH 4-5	684*	134	144	3.1	124	588*	92.9	109	103	106
pH 4-5	142	121	138	61.5	120	99.1	99.6	104	106	101
Mean	181	136	143	138	122	121	100	108	106	104
StdDev	26.3	9.4	3.8	2.8	4.4	19.3	4.2	3.0	2.6	2.8
RSD, %	15	7	3	2	4	16	4	3	2	3

* Outlier excluded from calculations

** Compound not listed on target analyte list.

U Value below reporting limit

Appendix C Quality Control (QC) Data

The level four data packages were reviewed to ensure criteria such as tuning criteria, performance checks, and initial calibrations all met method requirements. The two tables below and the figures which follow provide information about surrogate spikes and Laboratory Control Samples.

Table C-1 Laboratory Control Sample Results

Matrix	Acrolein		Acrylonitrile	
	Mean Recovery, %	RSD, %	Mean Recovery, %	RSD, %
POTW	90	11.3	91	11.6
Surface Water	88	9.8	125	2.7
Industrial Water 1	90	10.3	92	8.3
Industrial Water 2	124	6.4	122	2.8
Leachate	90	11.2	91	11.6
Ground water	95	5.9	95	5.6

Note: The summary above reflects the results from 30 LCS samples containing acrolein and acrylonitrile. All results met control limits.

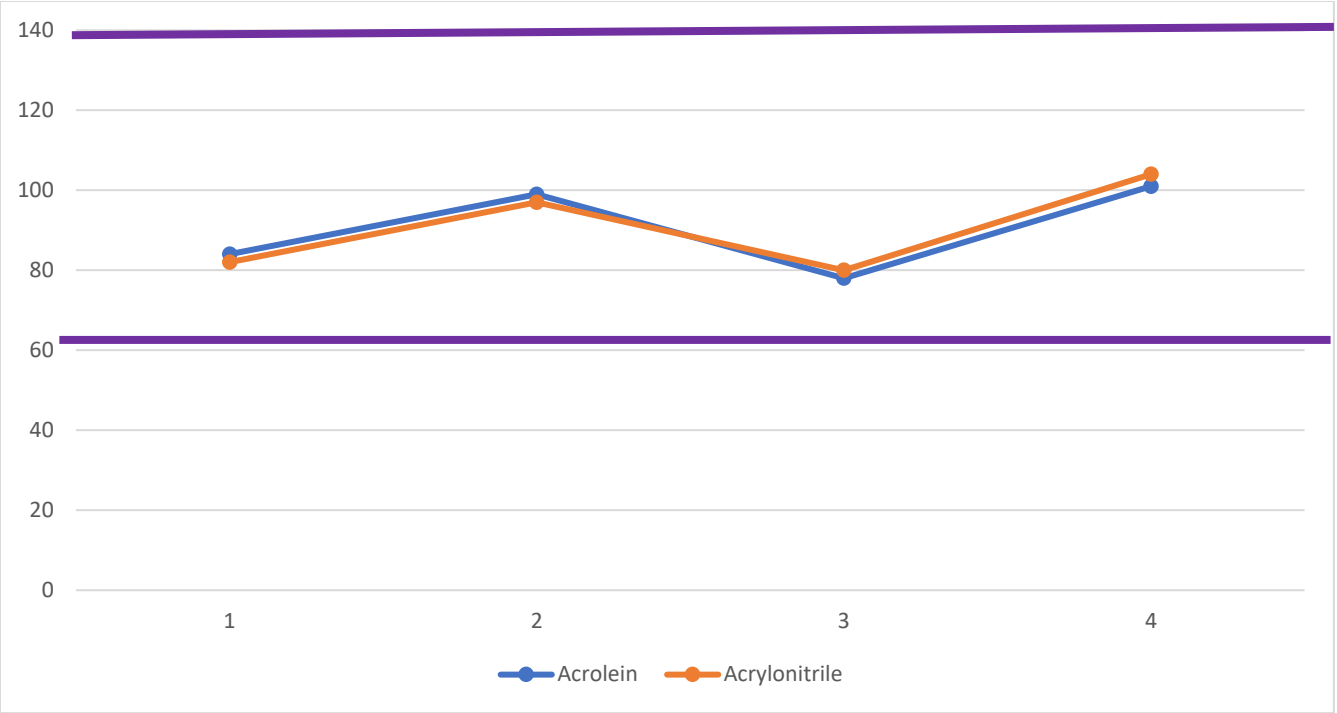
Table C-2 Surrogate Results

Matrix	1,2-Dichloroethane-d4		4-Bromofluorobenzene		Toluene-d8	
	Mean Recovery, %	RSD, %	Mean Recovery, %	RSD, %	Mean Recovery, %	RSD, %
POTW	106	2.8	100	1.4	101	1.5
Surface Water	103	2.4	97	1.7	101	1.6
Industrial Water 1	103	4.4	106	3.3	99	3.3
Industrial Water 2	100	2.8	99	1.4	105	1.5
Leachate	101	3.0	106	2.0	104	0.75
Ground water	102	2.2	97	1.5	93	0.9

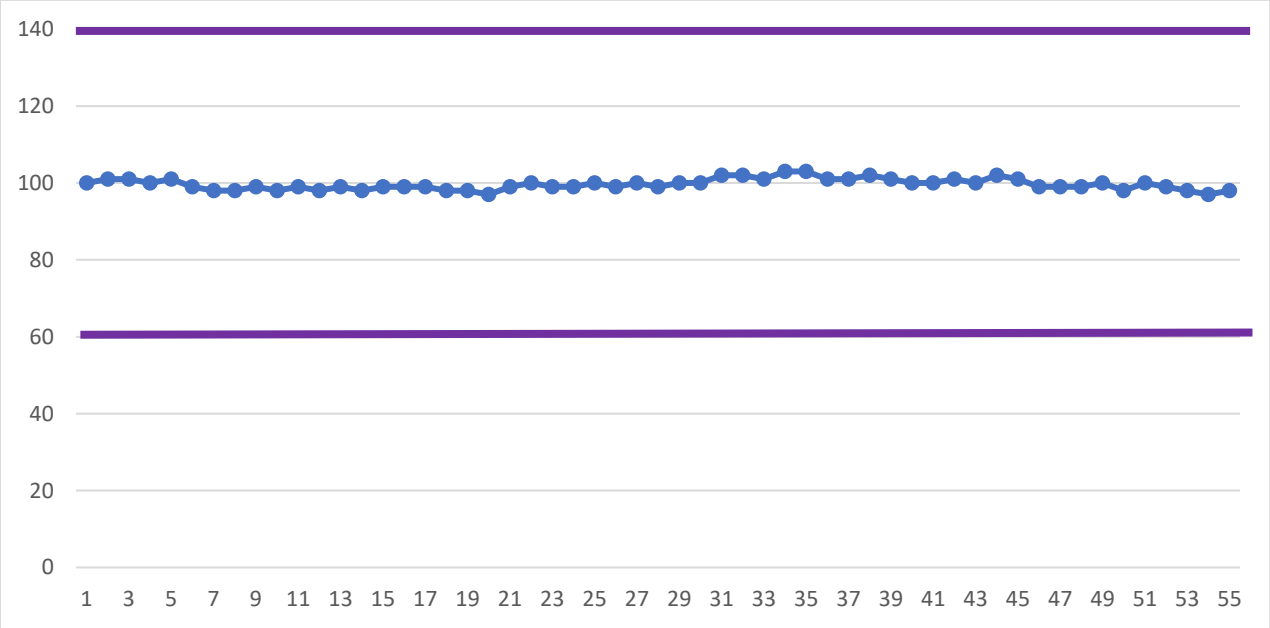
Note: The summary above reflects the results from 419 analyses for each surrogate that met the control limits for each compound. There were 2 failed results for 1-2-dichloroethane d4 for wastewater 2 at pH 2 at Day 3 and Day 14 at 336% and 182%. The narrative with these samples indicated “sample foaming” and the chromatograms showed a very large “peak” from 2.5 to 5 minutes. The replicates bracketing these two samples did not exhibit the same behavior. In summary, 99.8 % of the surrogate recoveries were within control limits.

Figures D-1 to D-4. QC Results for POTW Sample

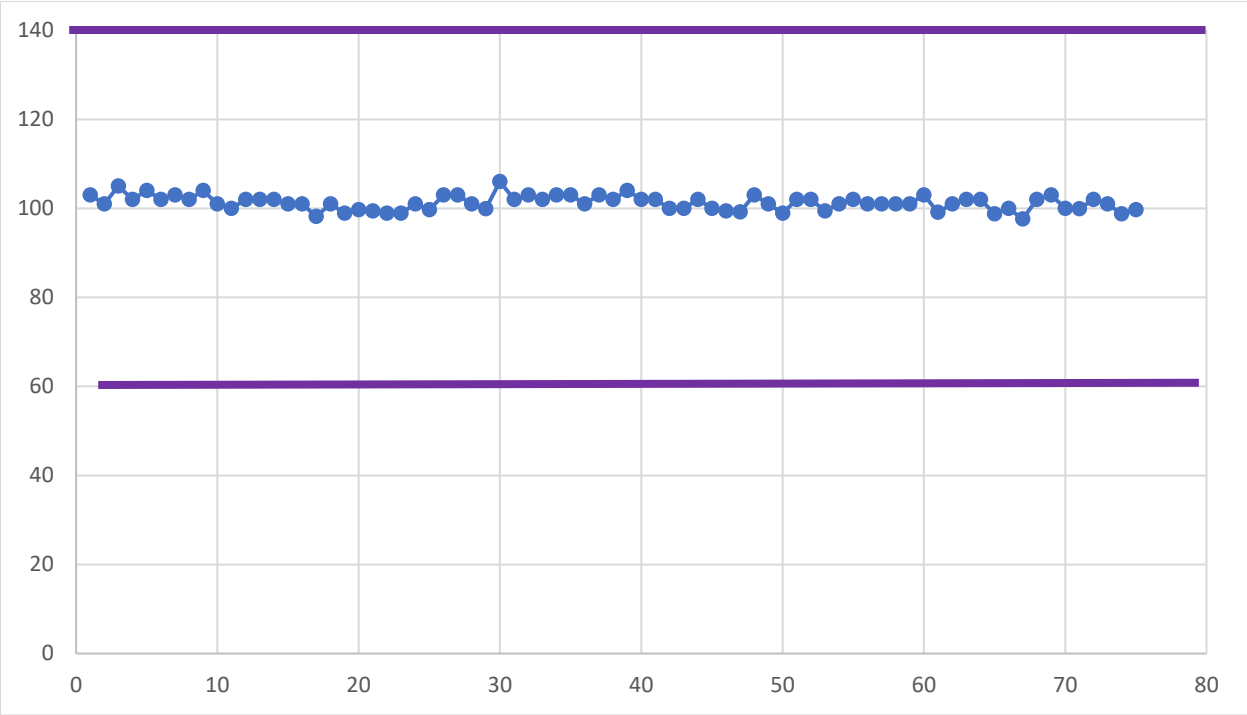
D.1. LCS Recoveries



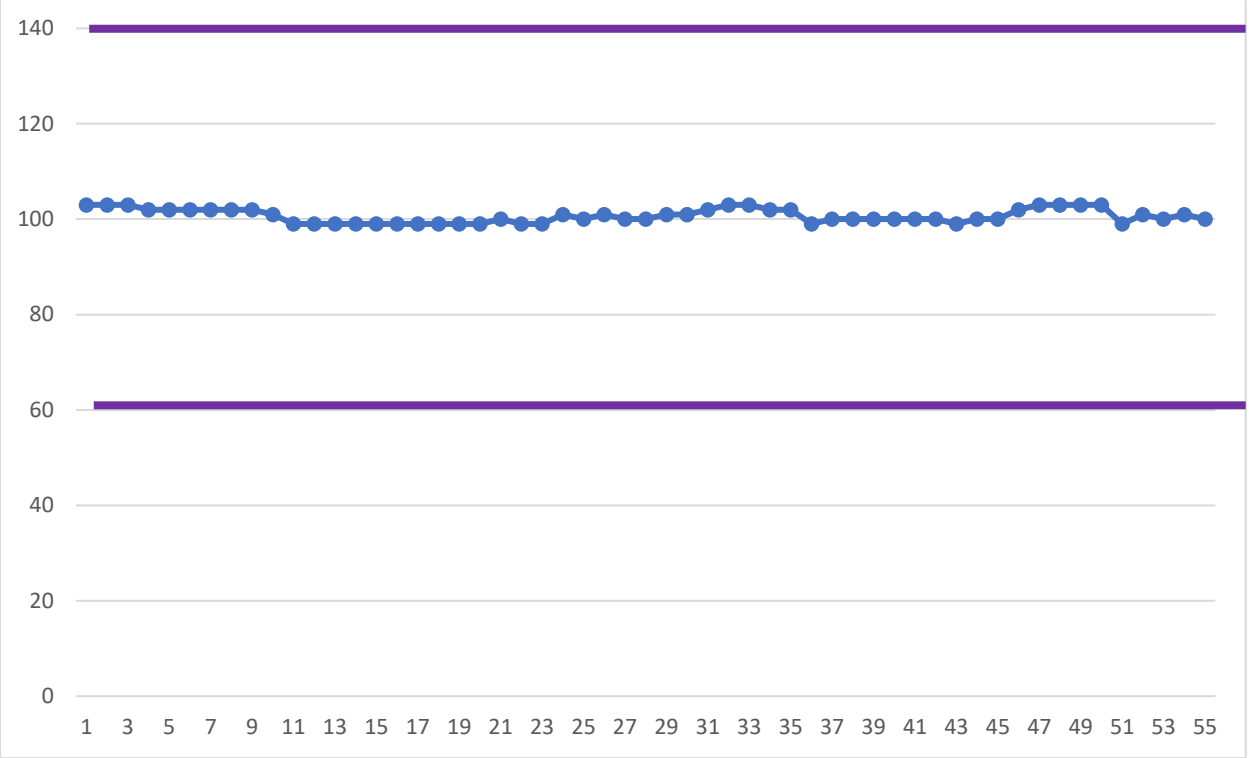
D.2. 1.2-Dichloroethane-d4



D.3. 4-Bromofluorobenzene (Surr)

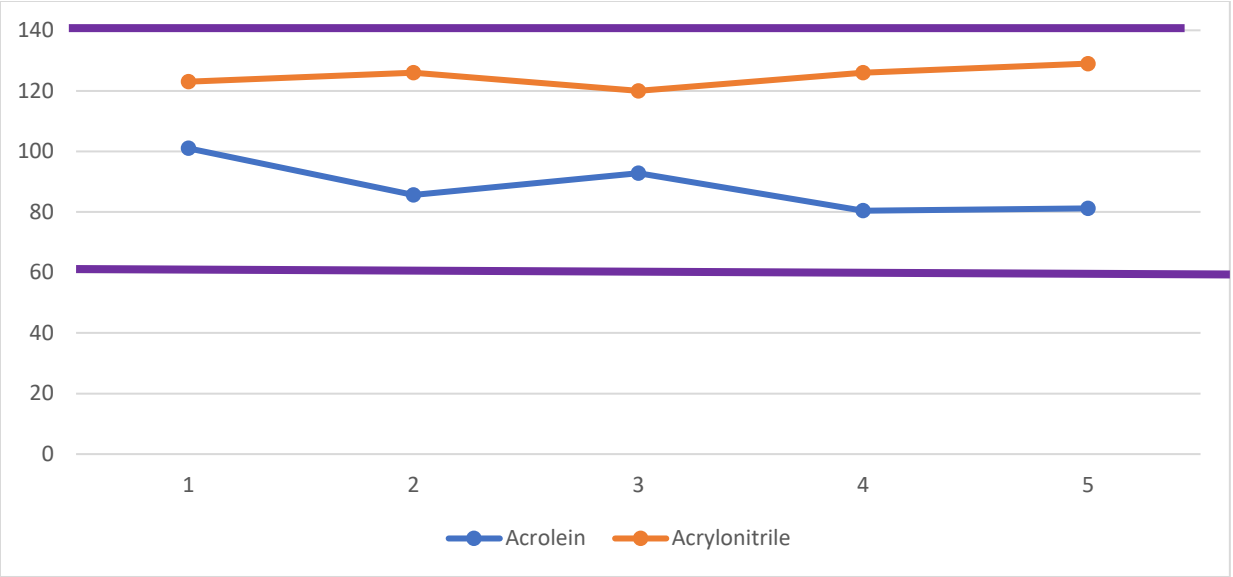


D.4. Toluene-d8

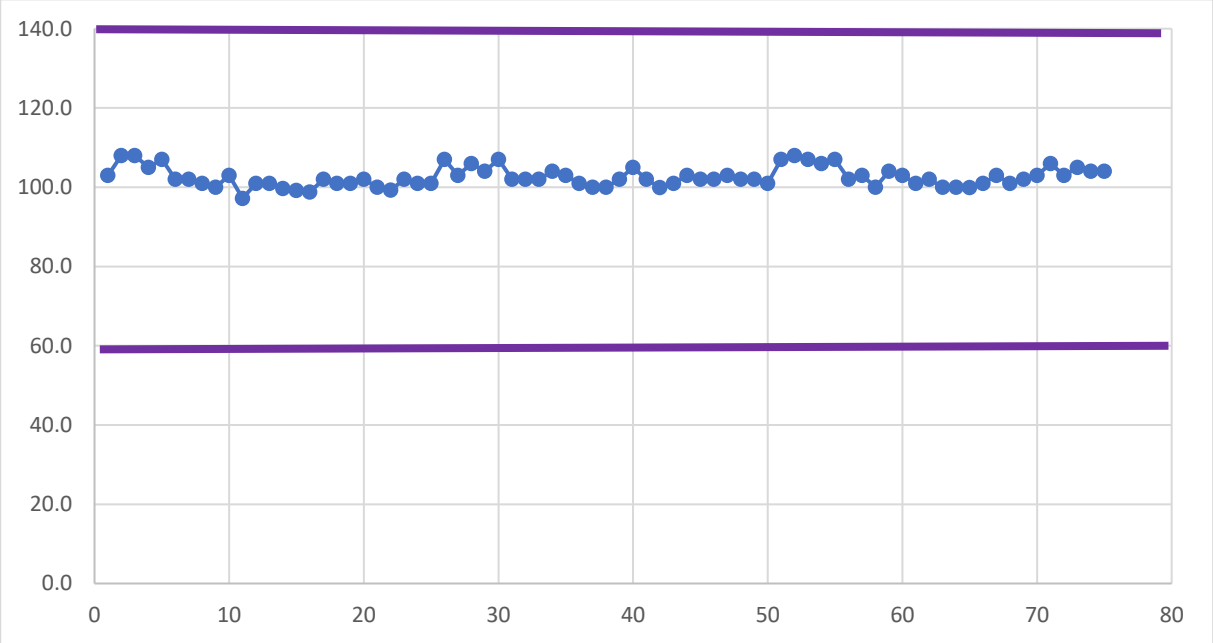


Figures D-5 to D-8. QC Results for Surface Water Sample

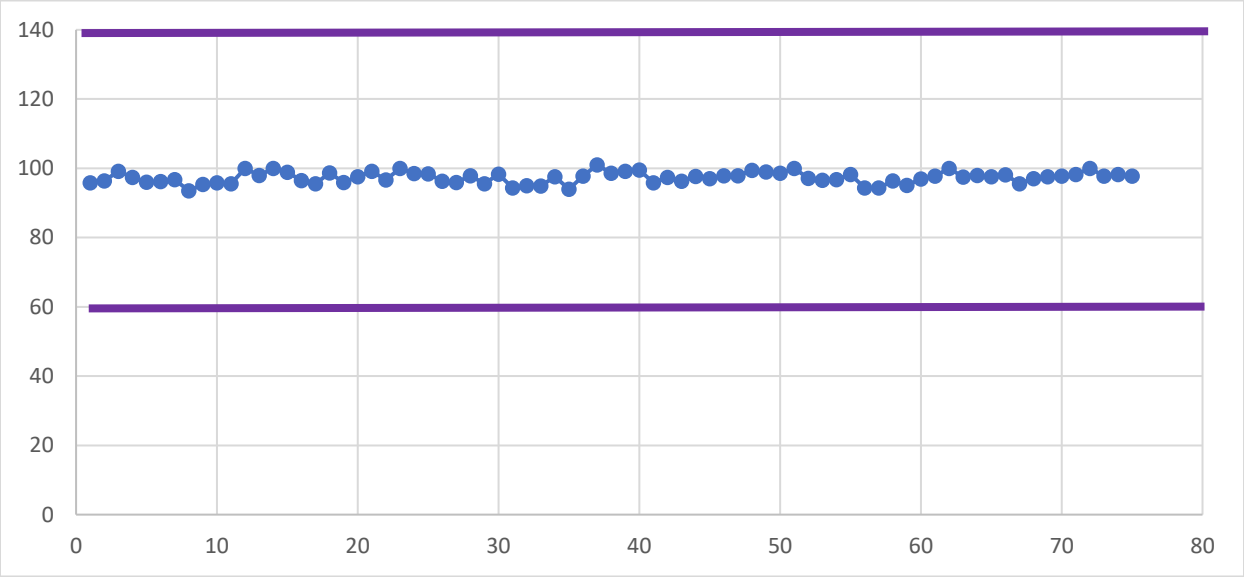
D.5. LCS Recoveries



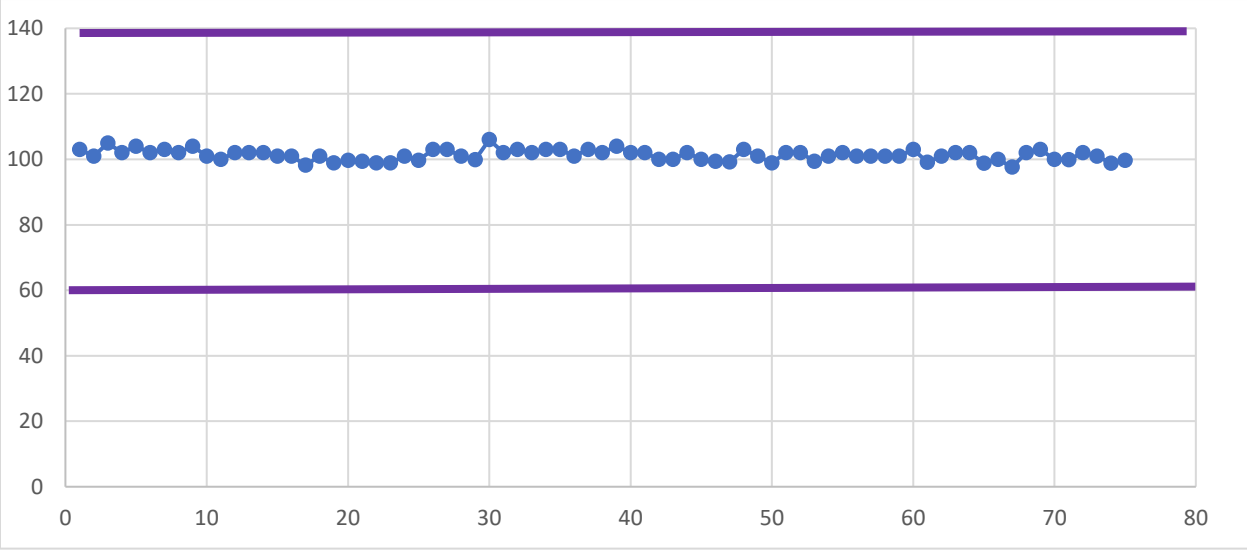
D.6. 1.2-Dichloroethane-d4



D.7. 4-Bromofluorobenzene (Surr)

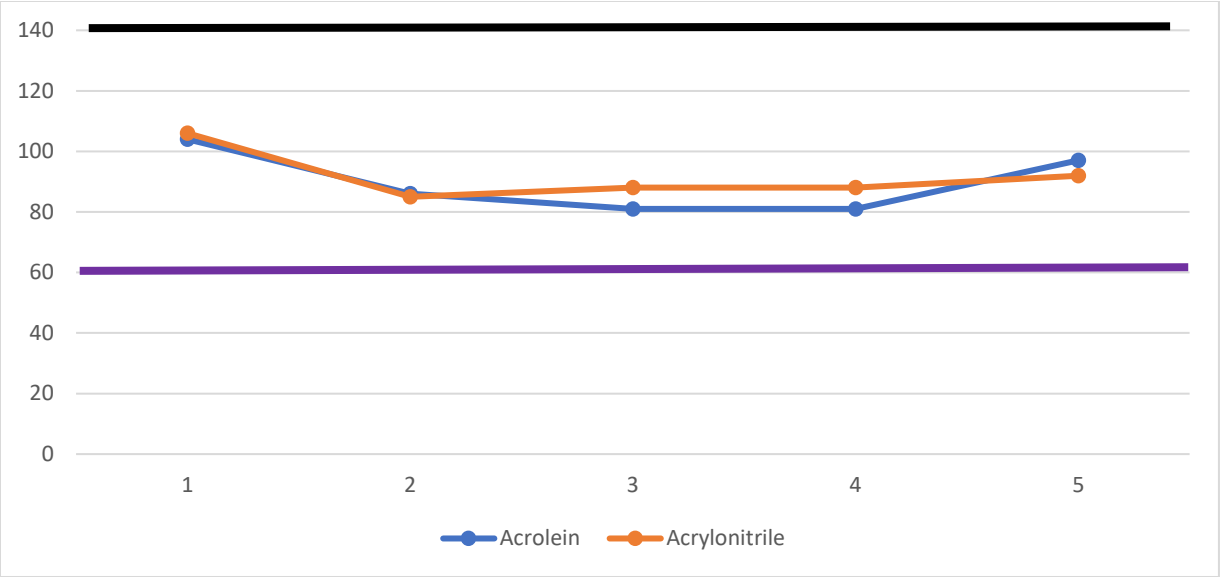


D.8. Toluene-d8

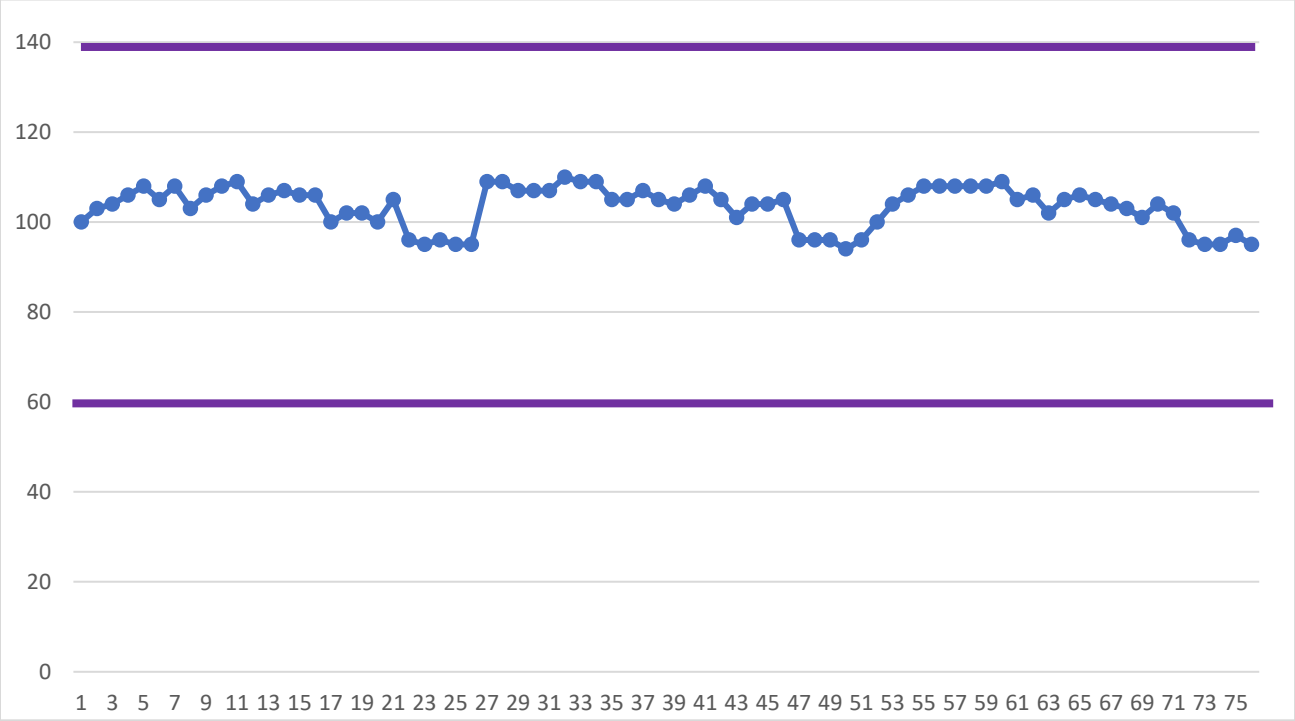


Figures D-9 to D-12. QC Results for Industrial Wastewater 1

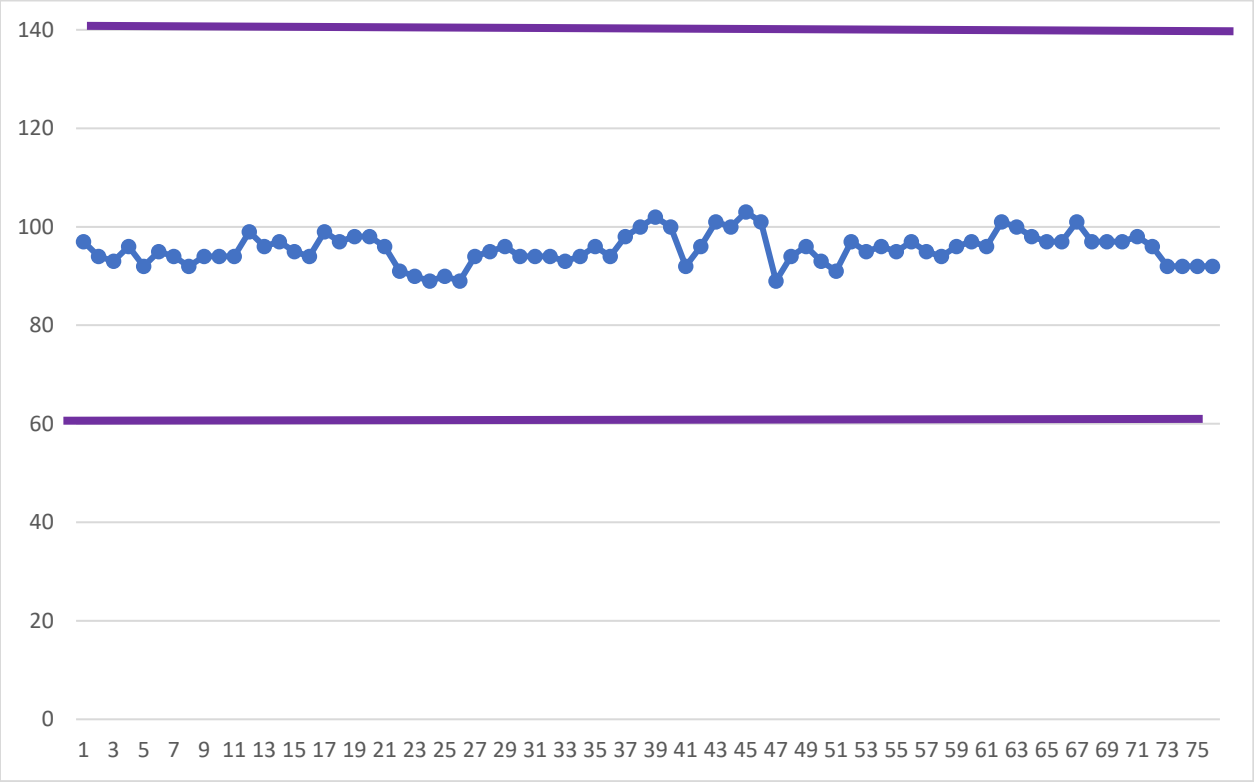
D.9. LCS Recoveries



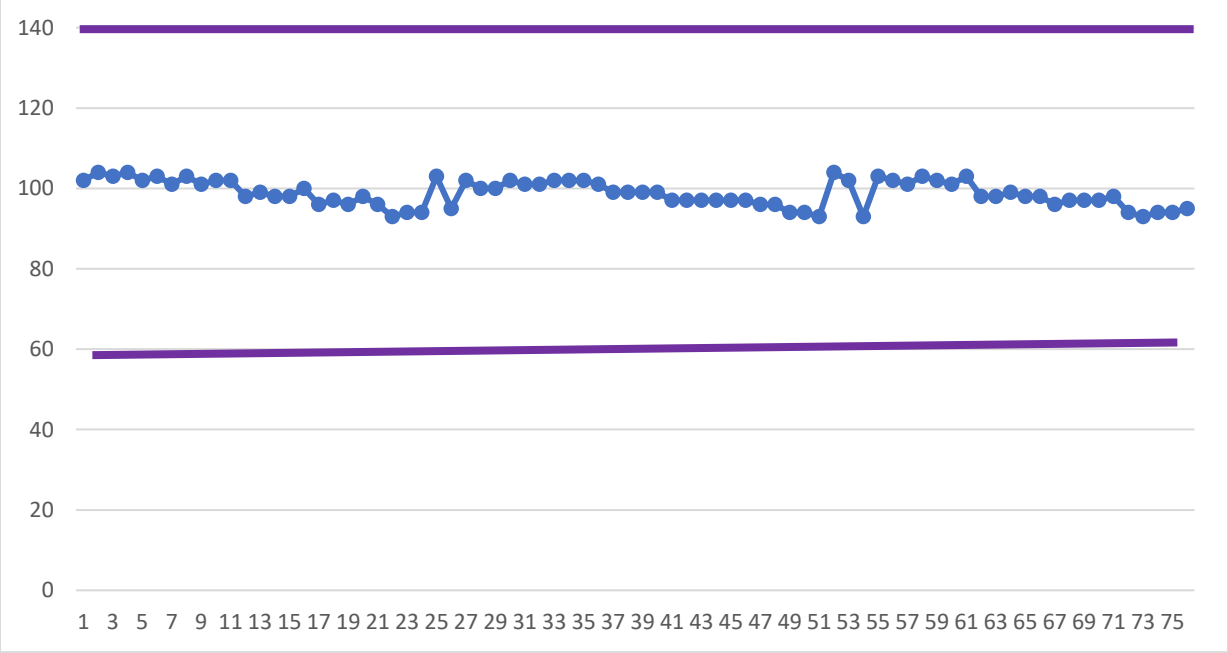
D.10. 1.2-Dichloroethane-d4



D.11. 4-Bromofluorobenzene (Surr)

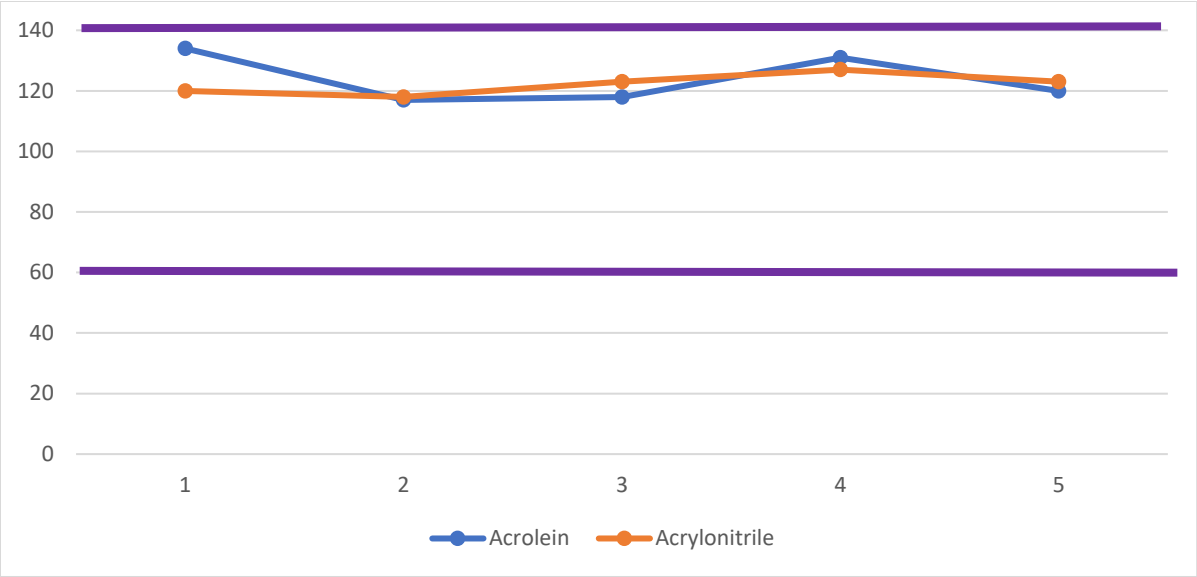


D.12. Toluene-d8

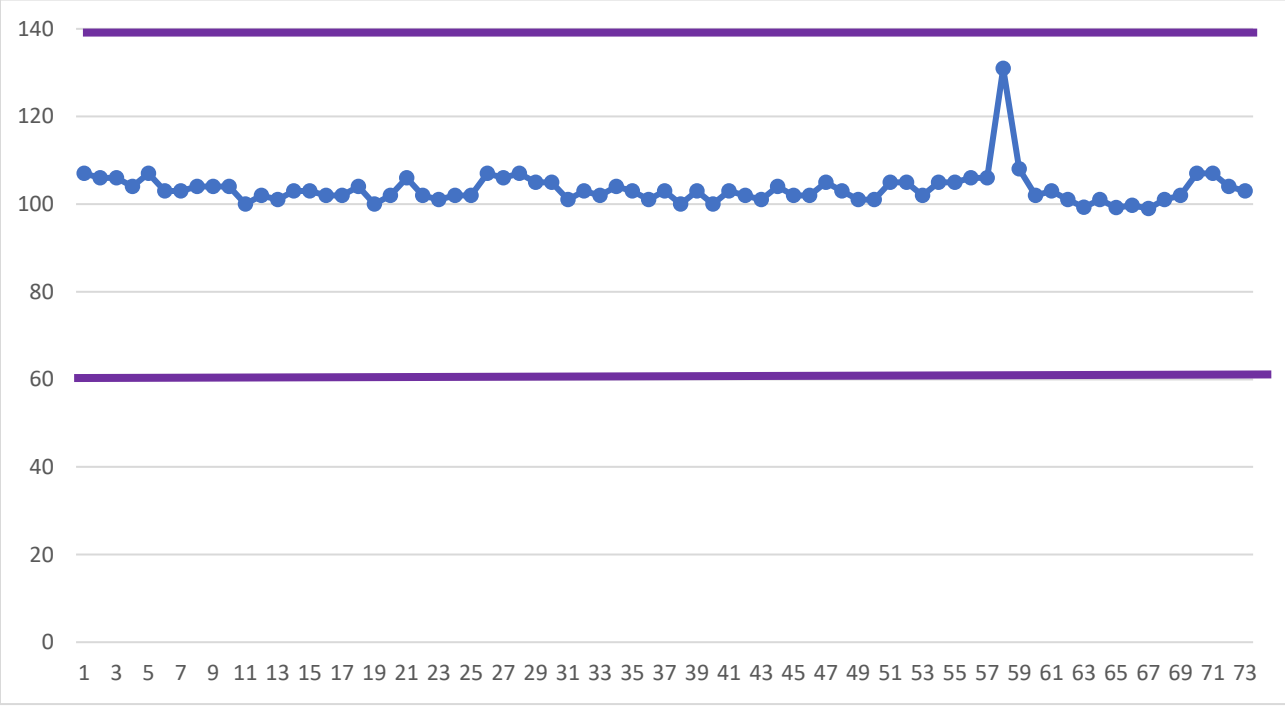


Figures D-13 to D-16. QC Results for Industrial Wastewater 2

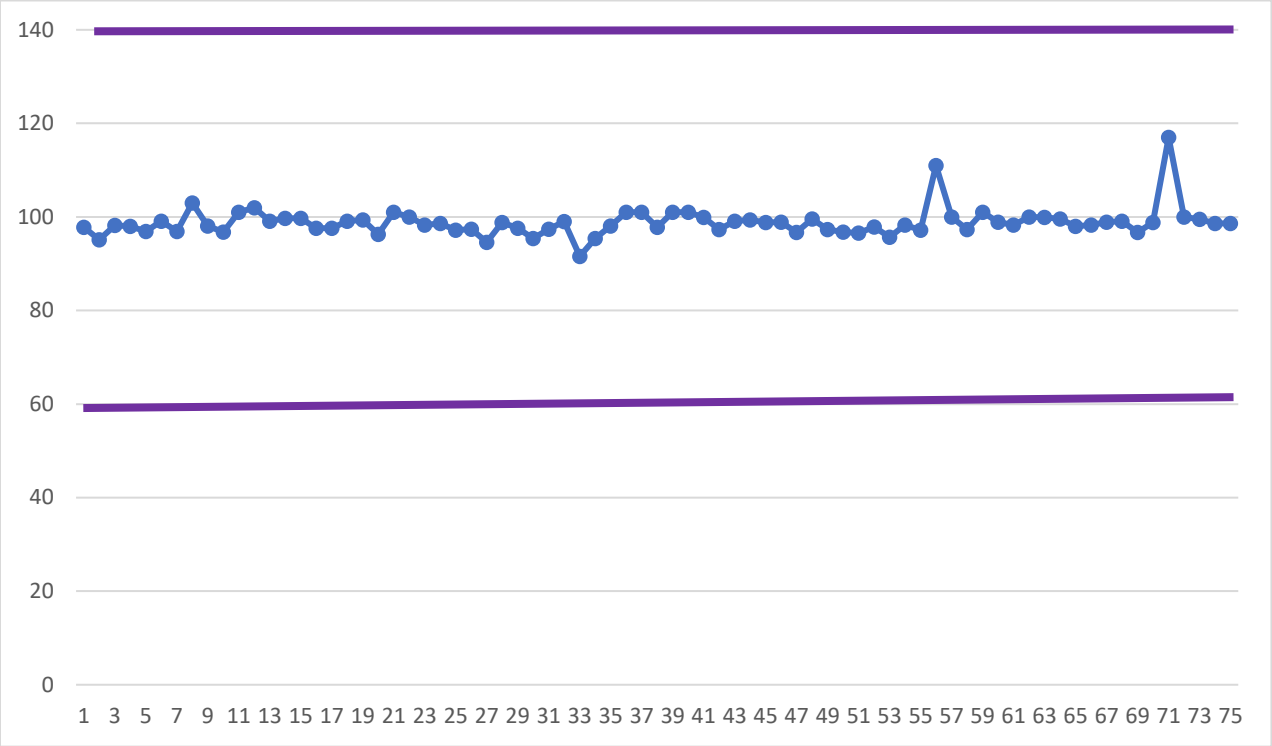
D.13. LCS Recoveries



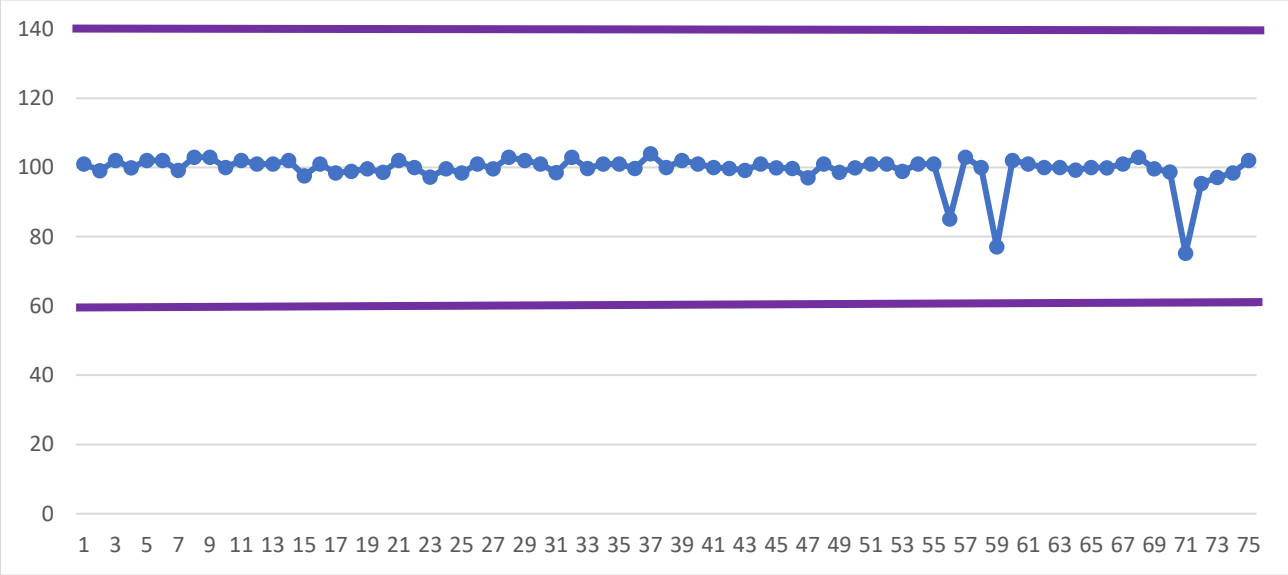
D.14. 1.2-Dichloroethane-d4



D.15. 4-Bromofluorobenzene (Surr)

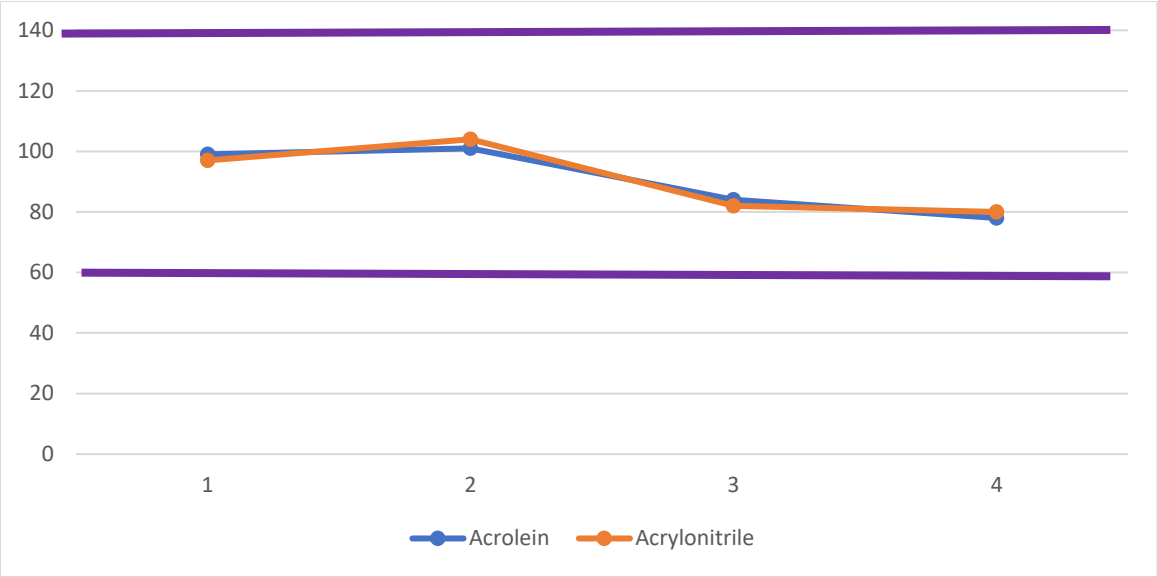


D.16. Toluene-d8 (Surr)

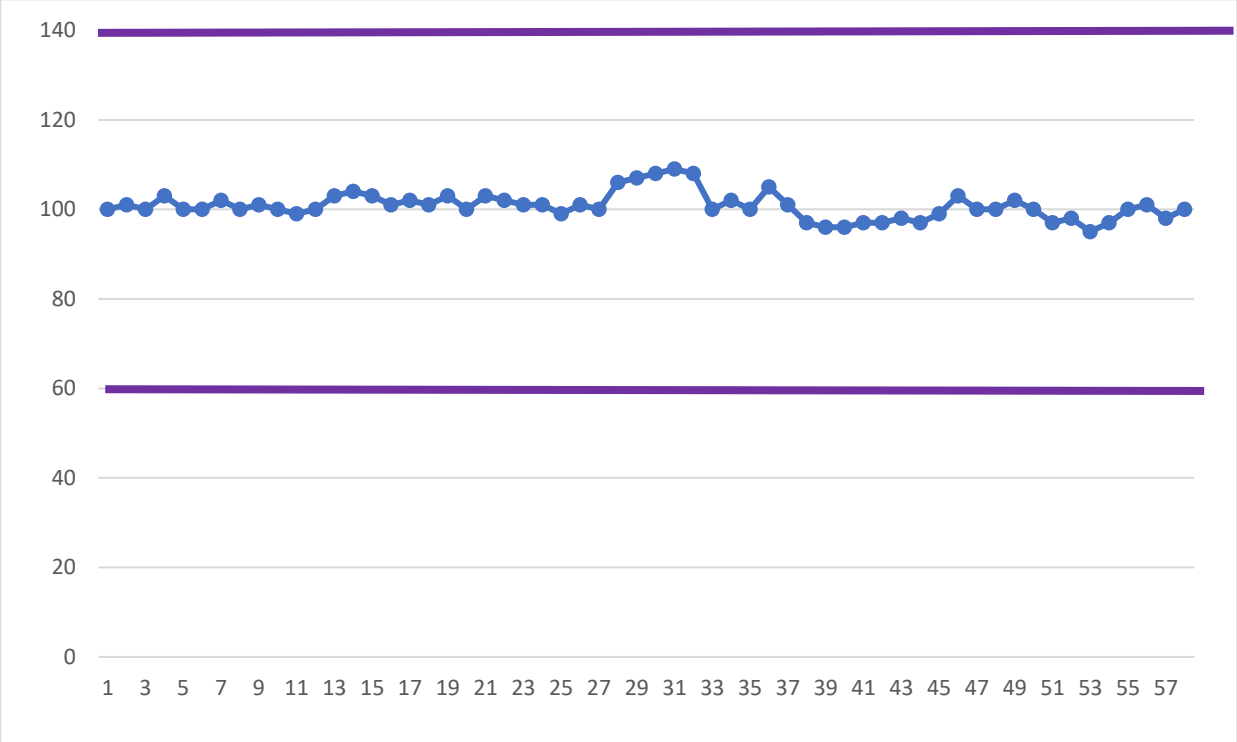


Figures D-17 to D-20. QC Results for Leachate Sample

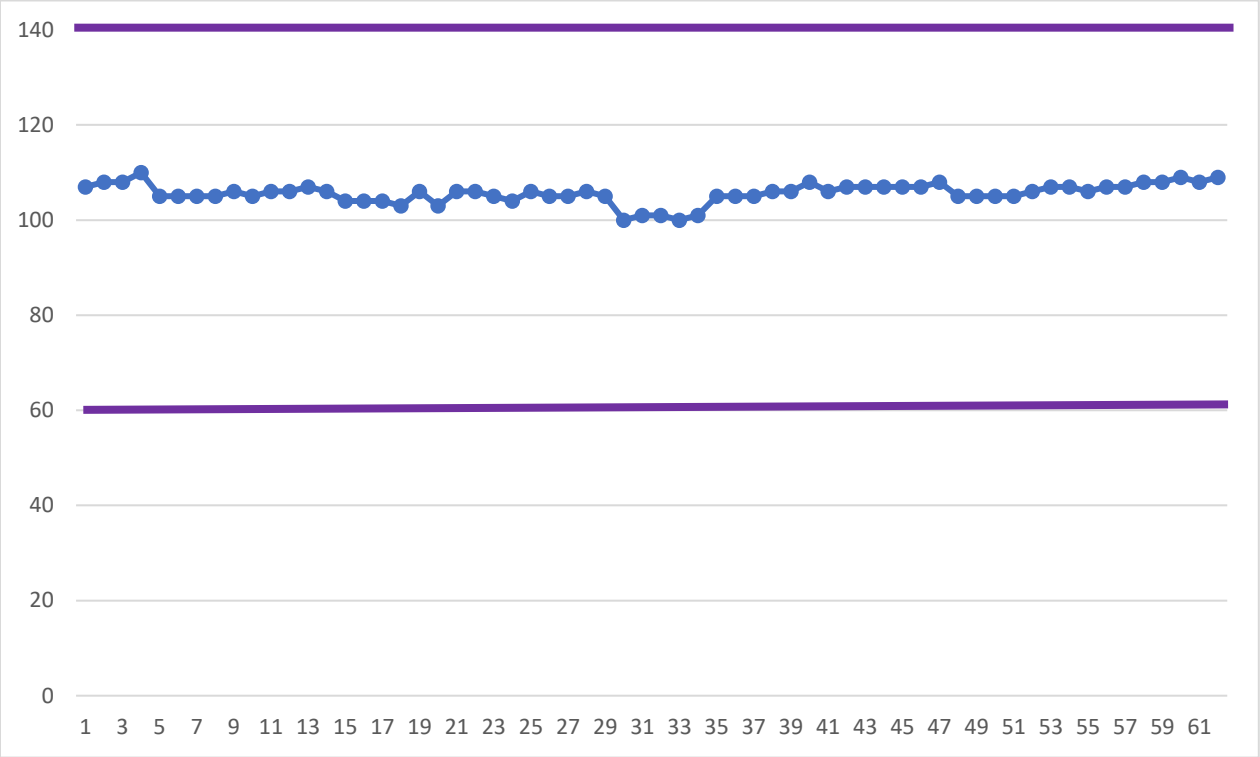
D.17. LCS Recoveries



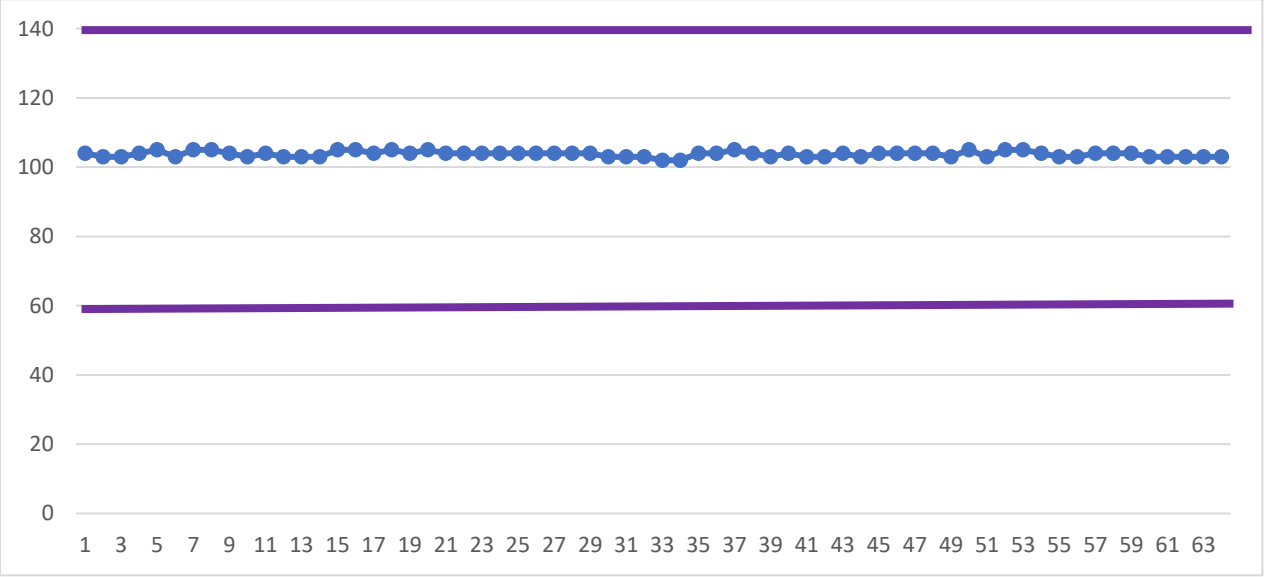
D.18. 1.2-Dichloroethane-d4



D.19. 4-Bromofluorobenzene (Surr)

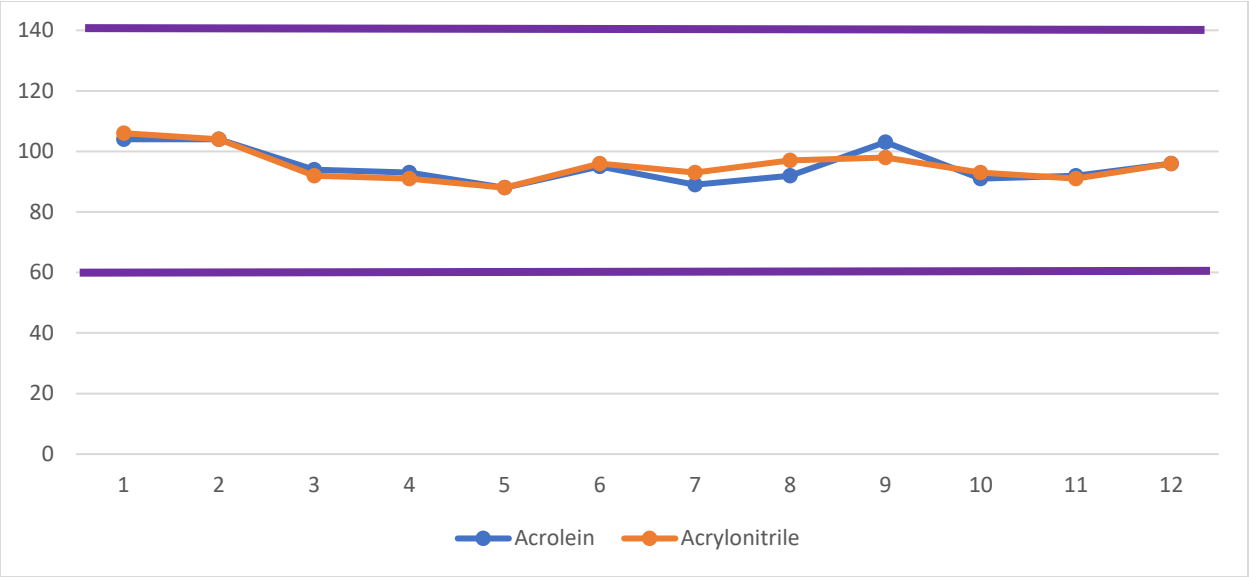


D.20. Toluene-d8

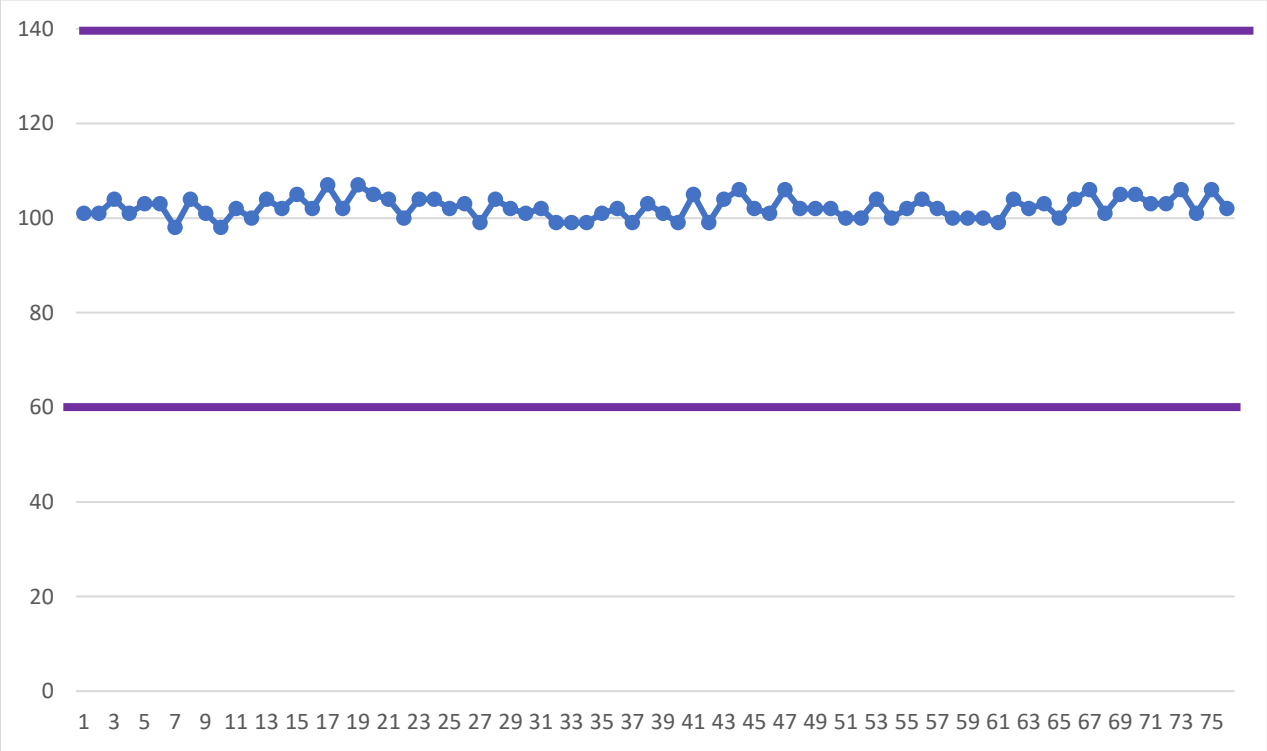


Figures D-21 to D-24. QC Results for Ground Water Sample

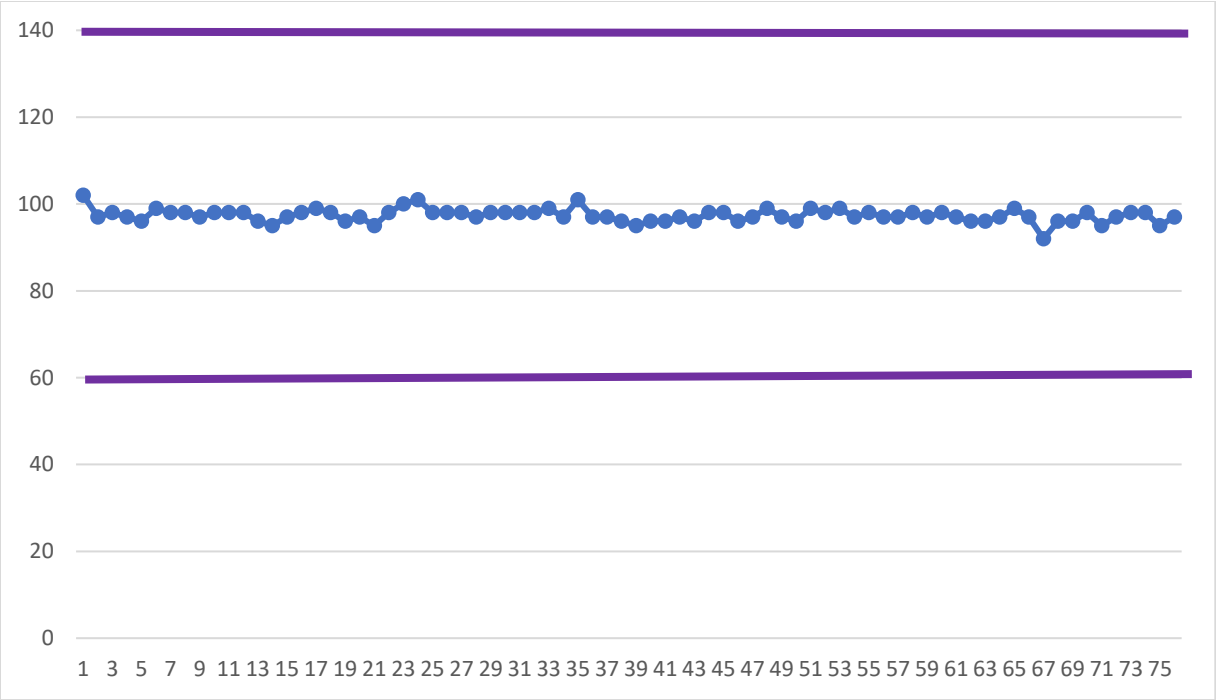
D.21. LCS Recoveries



D.22. 1.2-Dichloroethane-d4



D.23. 4-Bromofluorobenzene (Surr)



D.24. Toluene-d8