Assessing overall quality of analysis of per- & poly-fluorinated alkyl substances (PFAS) by LC/MS/MS technique at KY-DEPS Lab

Part A: Drinking Water (Ref. 537.1)

April 30, 2021

Abstract

The quality of analysis of PFAS by LC/MS/MS technique for drinking water is assessed via statistical analysis (DES9401) of quality control data. This study suggests that the overall QC data quality of this analysis is good despite some failures in LFB and LFM samples. The high failure rates in LFM samples could be explained in terms of matrix effects. The good quality of analysis is also indicated by very good average percent recoveries for VA, FA/A1, LFB and LFM samples for all target analytes.

Summary of Analysis

Average Percent Recovery of QC Samples

The following table shows the average percent recoveries (PR) of LFB, LFM, CCV (A1 & A2), VA and LOQ samples (only target analytes and surrogates are presented):

Table 1. Average percent recovery data for the target analytes of this method.

Analyte	LFB-PR	LFM-PR	FA-PR	A1/A2-PR	VA-PR	LOQ-PR
ADONA	102.0	99.1	101.0	100	99.2	100
HFPO-DA	110.1	101.0	99.4	98.7	99.7	103
HFPO-DA (Surrogate)	106.4	111.0	98.7	96.9	96.7	100
PFBS	70.8	96.1	100.3	100	93.2	105
PFDA (Surrogate)	97.7	126.2	97.4	96.8	94.1	101
PFHpA	102.4	102.6	101.3	100	100.2	110
PFHxA (Surrogate)	98.9	97.2	101.7	102	97.2	103
PFHxS	114.3	101.0	100.9	101	93.1	103
PFNA	120.4	103.0	98.3	100	94.2	107
PFOA	111.1	98.5	100.5	99.4	93.0	108
PFOS	110.4	99.4	101	99.7	94.8	108
Control Limits	70-130	70-130	70-130	70-130	70-130	50-150

With the exception of VA (where 5 analytes have fewer than 20 data points for averaging), all analytes in each QC component have more than 30 data points for averaging. Above table suggests that all target analytes, on average, have acceptable percent recoveries.

Average QC-data Quality

When quality scores for various QC components of an analyte are averaged, we get average analyte quality score. For any analyte, a score below 70 but above 50 indicates that there is, at least, one failure per QC component. In this analysis (see the following bar diagram), we have three analytes (surrogates) with quality scores above 50% but below 70%. All target analytes performed well since their quality scores are above 70%. The average of all scores is greater than 70%, which indicates that the method, on average, performed good. Standard deviation generally indicates the variation of scores among all QCs: higher the value, larger is the variation of performances of various QCs for a particular analyte.

**AVG Analyte's QC Score/Stdev: $6065**
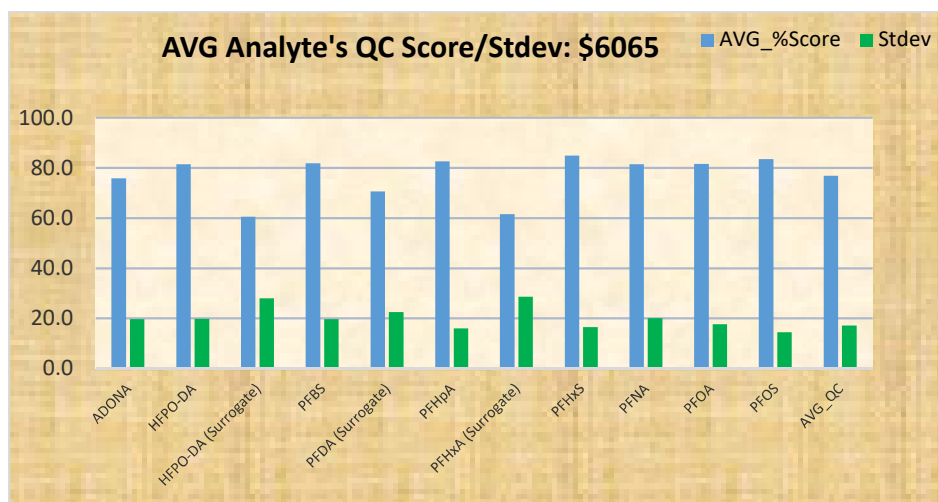
Average QC Score

By examining the average performances of all QCs, we find that matrix spike recoveries have, at least, two failures per analyte. For the LFB, the average scores indicate that there is at least one failure per analyte. In addition, for FA, CCV, VA, C1 and MB samples, there is no failure for any target analyte.


AVG QC Scores/Stdev:$6065
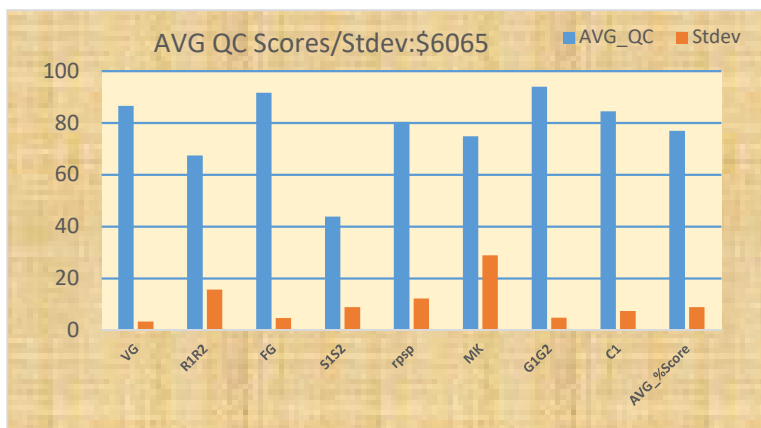
Details

1. VA

For this QC component, those analytes that have fewer than 20 points are not assessed. The following bar diagram shows that six analytes (which have 20 or more data points for the assessment) performed very well with quality score at or above 80% for each analyte.
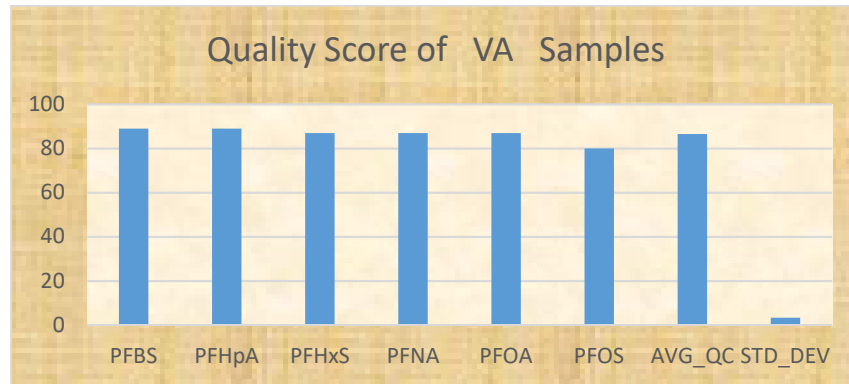

Usually, a quality score ≥ 80% means data quality is very good with no failure; anything below 50 is below average indicating two or more failures. A value of quality score in the range of 50-70 means there is at least one failure. The following is a control chart for PFOS:
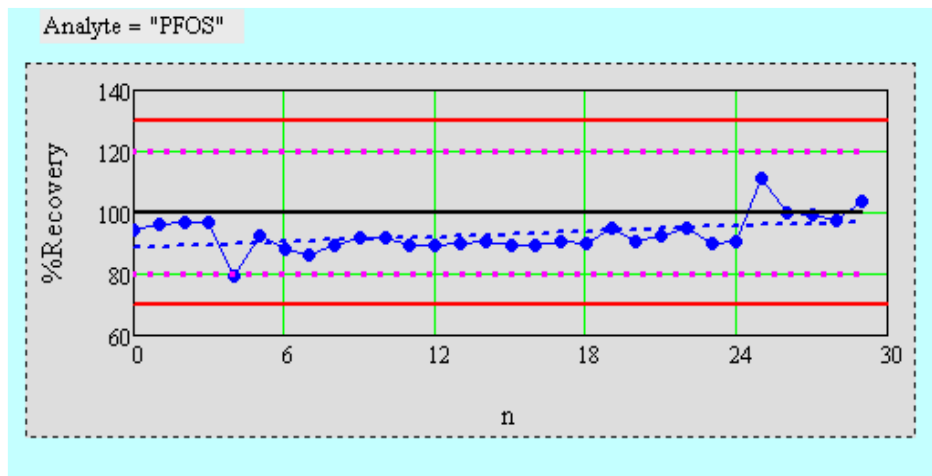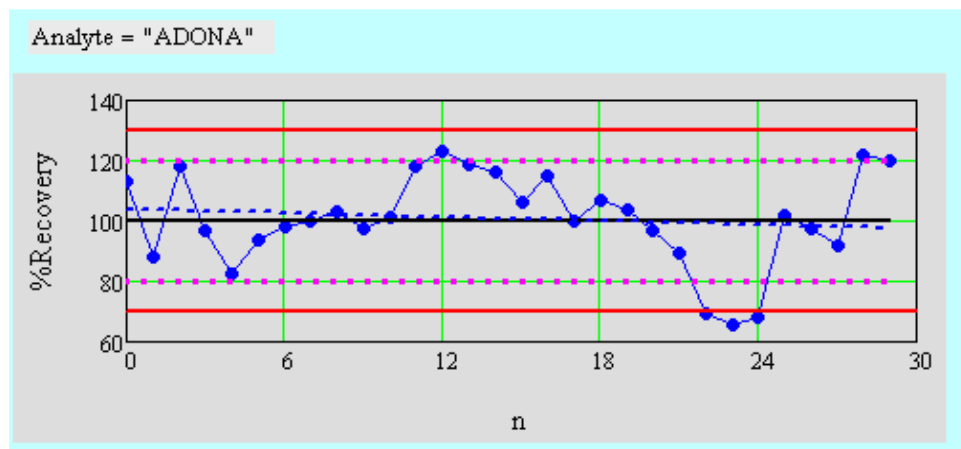
2. LFB

For this QC component, where L1 and L2 recovery data are combined, the performance is average. Out of 11 analytes (including surrogates), two analytes have at least two failures (out of past 30 data points).
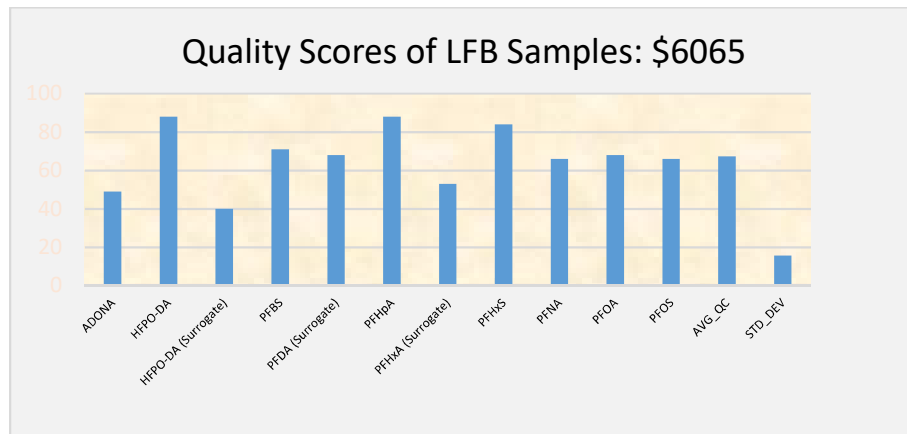

Here is the control chart for ADONA:

Obviously, three failures observed here are marginal. Here is the summary of the full statistical analysis:

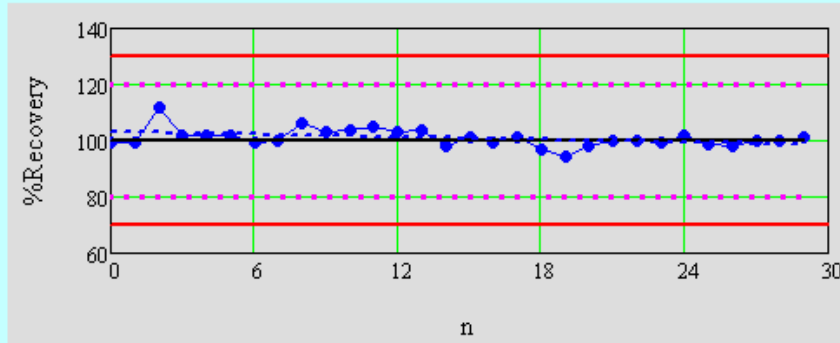|		0	1	2
	0	"DES$6065"	"ADONA"	"R1 R2"
	1	"# Unusual Data Omitted"	0	"No unusual data"
	2	"# Data for Long-Term"	39	" LT_Q: < AVG"
	3	"%Overall Failure Rate"	7.69	"OOC Data present"
	4	"Time of Long-term Data"	"02/02/2019"	"02/24/2021"
	5	"Time of Stat Data"	"08/16/2019"	"02/24/2021"
	6	"# True Outliers Rejected"	0	"No Outliers"
	7	" Size -Stat Analysis "	30	"Size Ideal "
SUMM =	8	"AVG Recov = "	100.7%	"Mean ~ Exptd "
	9	"St Dev ="	15.5	"Improve ! VAR > EXPTD "
	10	"Normality = "	"YES"	"Data Normal "
	11	"MK Trend = "	"NO"	"No Trend ! Great! "
	12	"Skewness = "	-0.66	"Data Skewed: Improve "
	13	"Kurtosis ="	0.14	" Peaked cf. NormDist "
	14	"Process Capability Index ="	1.34	" Cpk OK "
	15	"Warning I, II, III Present ? "	" Present "	"Only WN III present "
	16	" # MIN _Q Failed "	3	" > 2 Failures: Unacceptable"
	17	" Staistical Properties"	"GOOD "	"Good ; OK "
	18	"6 Sigma_QUALITY"	"AVG "	"AVG 6 Sigma Quality"
	19	"QUALITY %SCORE"	49.32	" Improve "

3. FA

In this case, most analytes performed very well and the average QC quality is very good. This is displayed in the following bar diagram:
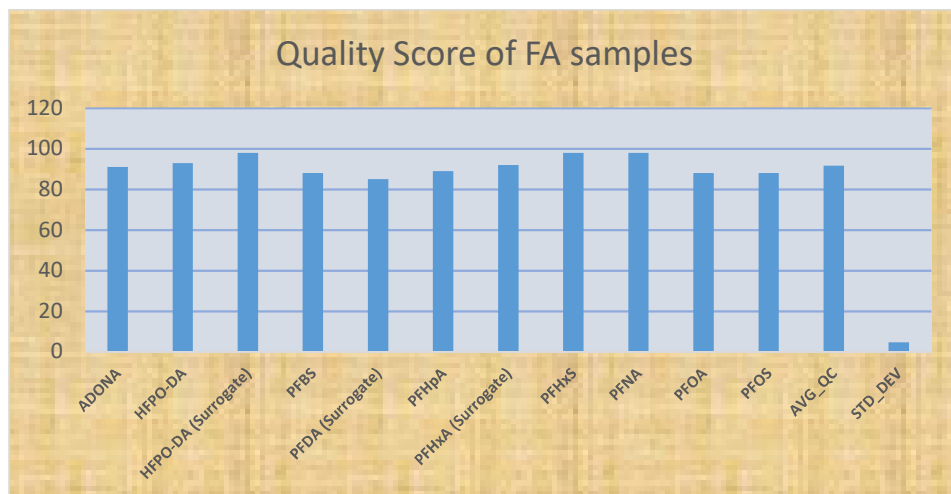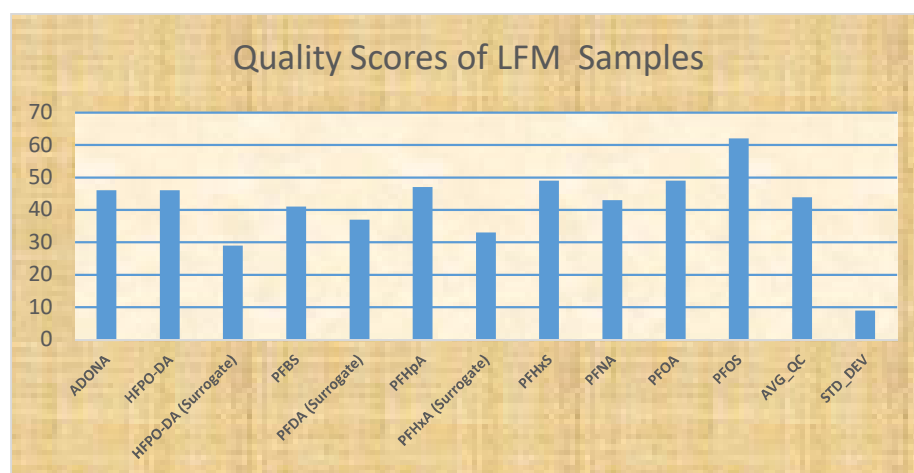

Here is one example with PFOA:

Analyte = "PFOA"

		0	1	2
	0	"DES$6065"	"PFOA"	"FG"
	1	"# Unusual Data Omitted"	0	"No unusual data"
	2	"# Data for Long-Term"	49	" LT_Q: EXC "
	3	"% Overall Failure Rate"	0	" No Failure-Great!"
	4	"Time of Long-term Data"	"01/21/2019"	"02/25/2021"
	5	"Time of Stat Data"	"10/07/2019"	"02/25/2021"
	6	"# True Outliers Rejected"	0	"No Outliers"
	7	" Size -Stat Analysis "	30	"Size Ideal "
SUMM =	8	"AVG Recov = "	100.99	"Mean ~ Exptd"
	9	"St Dev ="	3.22	" Grreat! VAR < EXPTD "
	10	"Normality = "	"YES"	"Data Normal "
	11	"MK Trend = "	"YES - d"	"Slight Trend! ~OK"
	12	"Skewness = "	1.22	"Data Skewed: Improve "
	13	"Kurtosis ="	3.96	" Peaked cf. NormDist "
	14	"Process Capability Index ="	6.63	" Cpk EXC ! "
	15	"Warning I, II, III Present ? "	" Present "	"Only WN I present"
	16	" # MIN _Q Failed "	0	" No Failure: Great ! "
	17	" Staistical Properties "	"AVG "	"AVG; ~OK "
	18	"6 Sigma_QUALITY"	"EXC "	" EXC 6 Sigma Quality !"
	19	"QUALITY %SCORE"	87.5	"Good+"

4. LFM

In this case, most analytes have more than two failures (out of past 30 points) as indicated by less than 50 quality scores for most analytes. This could be explained in terms of matrix effects.

Quality Scores of LFM Samples

Here is one example:

Analyte = "ADONA"
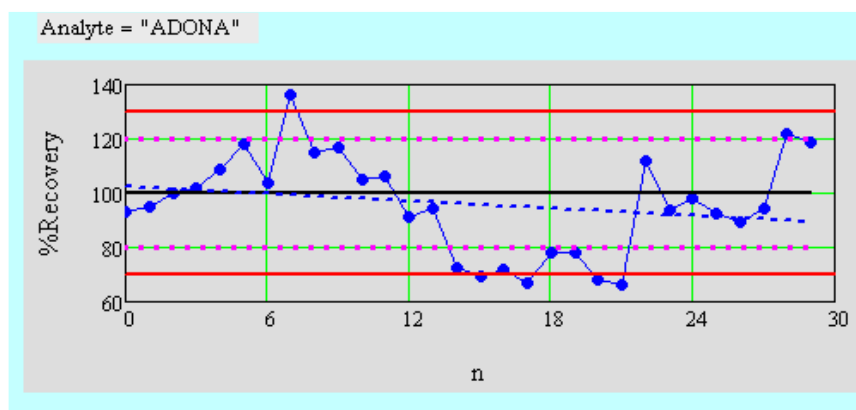
However, most failures in this example are very marginal.

5. Precision

Here precision data from LFB and LFM duplicates (RP and SP) are combined to make sure that the number of data points used for each case is at least 20. The overall quality score for this combined QC component is about 80, indicating that precision of measurements for this method is very good.

Precision from Duplicate Runs of LFB/LFM Samples
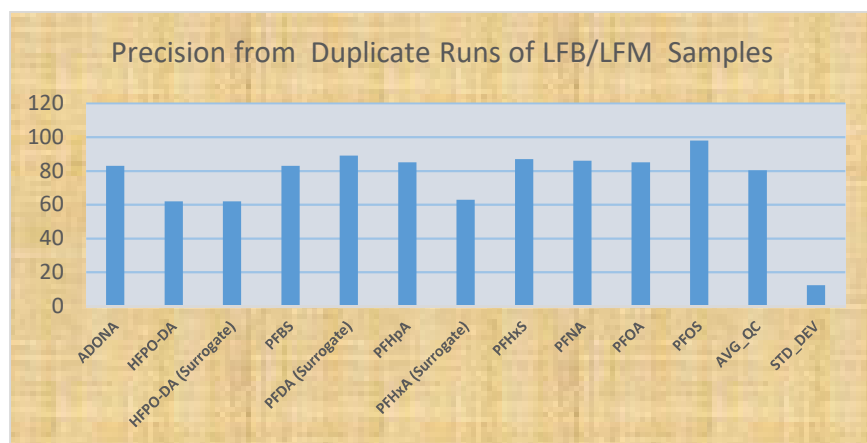
Here, only three compounds (two of them are surrogates) scored below 70 %, but above 60%. All other compounds scored above or near 80%. Here is one control chart for HFPO-DA:


Analyte = "HFPO-DA"
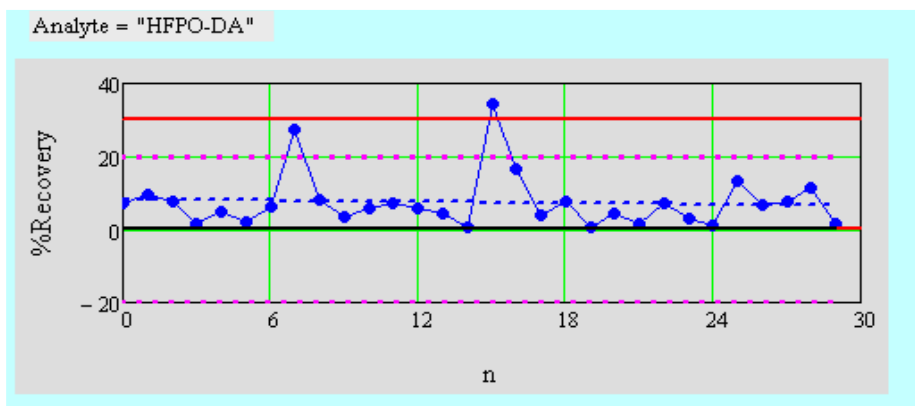
6. MB data

All MB data performed very well (score > 80%) as shown by the following diagram. Lower scores are only observed for the surrogates where spikes are added (they are not blank in the true sense and their evaluation is based on 70-130 limits).
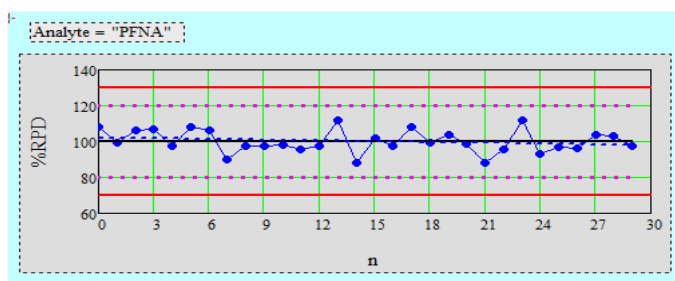
Quality Scores of MB samples/ Surrogate Recovery
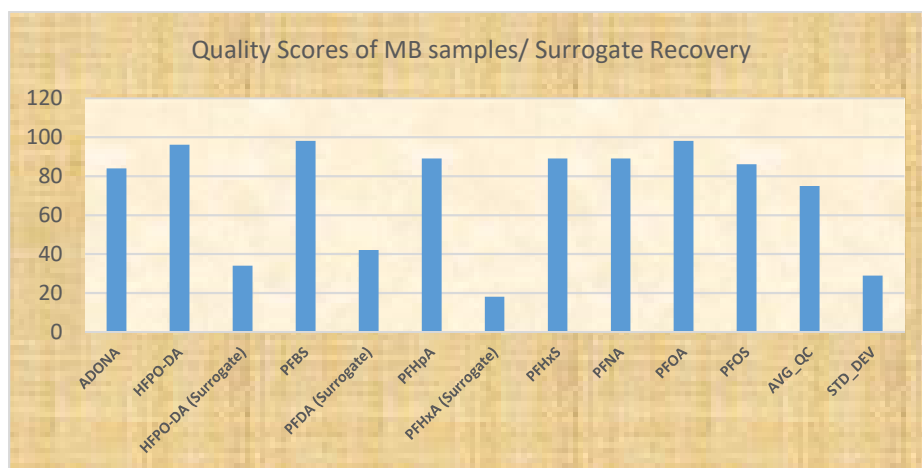
7. CCV (A1, A2)

CCV samples (A1 and A2 are combined) have excellent average quality scores (>90%), meaning that all analytes – on average – have performed very well.


Quality scores of CCV Samples (A1/A2)
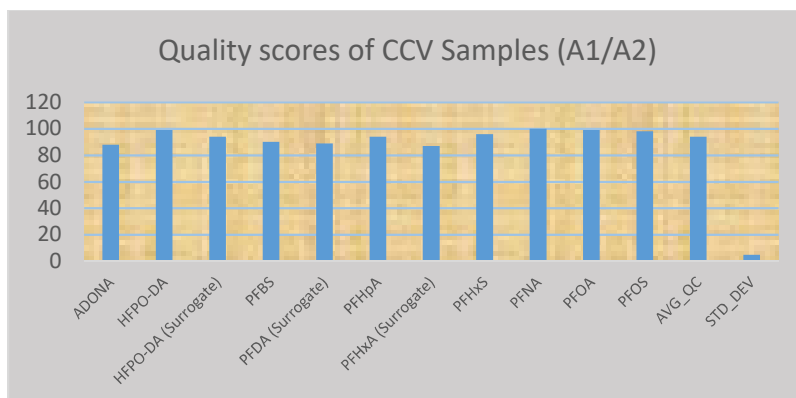
Here are the control chart and summary of statistical analysis for PFNA:

Analyte = "PFNA"

	0	1	2
0	"DES$6065"	"PFNA"	"G1g2"
1	"# Unusual Data Omitted"	0	"No unusual data"
2	"# Data for Long-Term"	43	" LT_Q: EXC "
3	"%Overall Failure Rate"	0	" No Failure-Great!"
4	"Time of Long-term Data"	"01/16/2019"	"02/24/2021"
5	"Time of Stat Data"	"08/16/2019"	"02/24/2021"
6	"# True Outliers Rejected"	0	"No Outliers"
7	" Size -Stat Analysis "	30	"Size Ideal "
8	"AVG Recov = "	100.15	"Mean ~ Exptd "
9	"St Dev ="	6.37	" Grreat! VAR < EXPTD "
10	"Normality = "	"YES"	"Data Normal "
11	"MK Trend = "	"NO"	"No Trend ! Great! "
12	"Skewness = "	0.06	" ~ Not Skewed "
13	"Kurtosis ="	-0.45	" Flat cf. NormDist "
14	"Process Capability Index ="	2.06	" Cpk EXC ! "
15	"Warning I, II, III Present ? "	"Absent"	"Great ! "
16	" # MIN _Q Failed "	0	" No Failure: Great ! "
17	" Staistical Properties"	" EXC "	" EXC; OK + "
18	"6 Sigma_QUALITY"	"EXC "	" EXC 6 Sigma Quality !"
19	"QUALITY %SCORE"	100	"EXC+"

SUMM =

8. LOQ

Most analytes for the LOQ samples performed very well. Only one analyte (surrogate) performed average with one failure:

Quality Score of LOQ Recovery Samples

Analyte = "HFPO-DA (Surrogate)"
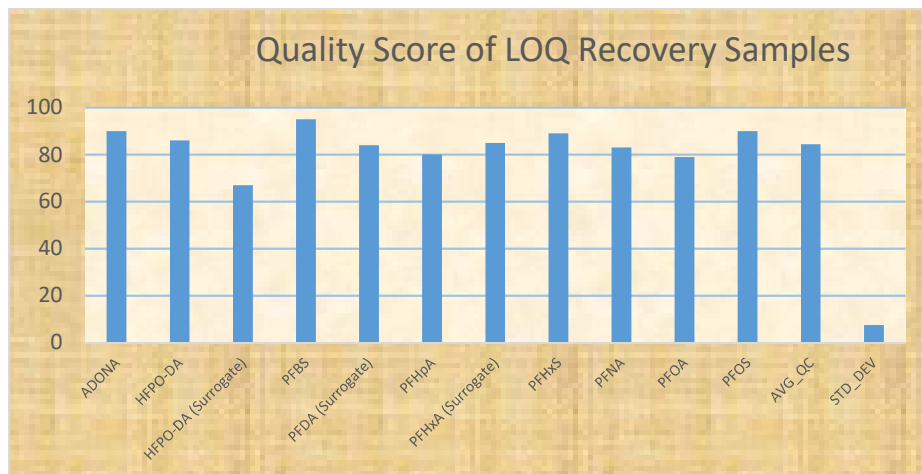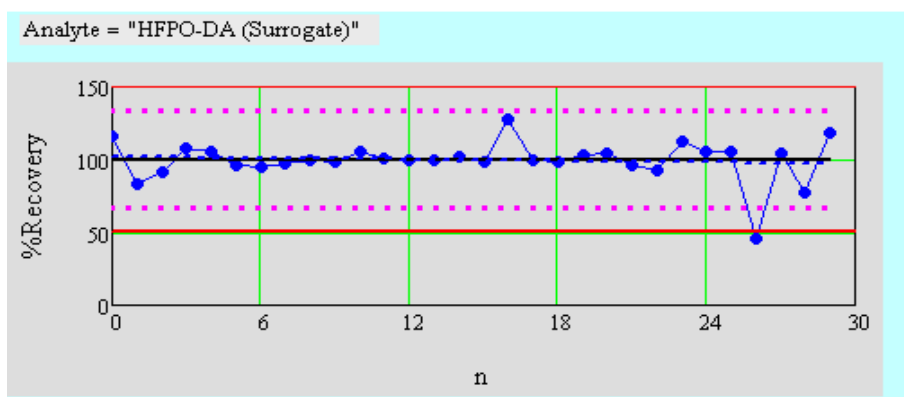
Conclusion

By considering all factors, this method, on average, is performing well. Some failures in LFB samples are not expected, and hence all efforts should be made to improve it. Though matrix effects could explain the lower LFM recoveries, further improvements of their performances are highly desired.

Assessing overall quality of analysis of poly-fluorinated alkyl substances (PFAS) by LC/MS/MS technique at KY-DEPS Lab

Part B: Non-potable Water (Ref. 8327)

Abstract

The quality of analysis of PFAS in non-potable water by LC/MS/MS technique is assessed via statistical analysis (DES9401) of quality control data. This study- with a limited number of data points- suggests that the overall QC data quality of this analysis is good. For this method, the failure rates for LFM samples are lower than those in the DW method for all target analytes. The average percent recovery data for VA, FA/A1/A2, LFB and LFM samples suggest a good performance of this method.

Summary of Results

For this analysis ($6060), not enough QC data points are available to make a good statistical assessment. However, in some cases, similar QC data are combined to make the sample size suitable (n ≥20) for the analysis. Here is the initial assessment on the quality of QC data for the analytes of interests of this method:

**Table 1**. Average percent recovery data for the target analytes of this method.

| Analyte	VGIG	R1R2	FG	S1S2	g1g2
ADONA	105	101	108	91.5	108
HFPO-DA	92.9	97	107	79.6	106
HFPO-DA (Surrogate)	104	112	107	92.2	118
PFBS	104	107	107	95.4	108
PFBS (Surrogate)	101	124	106	118	106
PFHpA	99.3	110	108	100	108
PFHpA (Surrogate)	105	124	111	114	108
PFHxS	102	107	105	94.2	106
PFHxS (Surrogate)	105	123	108	115	111
PFNA	103	104	107	96.4	105
PFNA (Surrogate)	105	119	107	112	108
PFOA	102	106	105	96.2	108
PFOA (Surrogate)	103	122	108	113	108
PFOS	102	104	109	92.6	105
PFOS (Surrogate)	101	115	105	113	106
Sizes(Surrogate, Analyte)	14,24	19,23	16,17	9,11	9,9
Control Limits	70-130	70-130	70-130	70-130	70-130

This table suggests that average percent recovery for each analyte, for each QC component, lies within the method prescribed control limits.

Statistical Quality Assessment

The following bar diagram shows the average statistical quality scores of all target analytes and surrogates:

AVG Analyte Quality Assessment:$6060
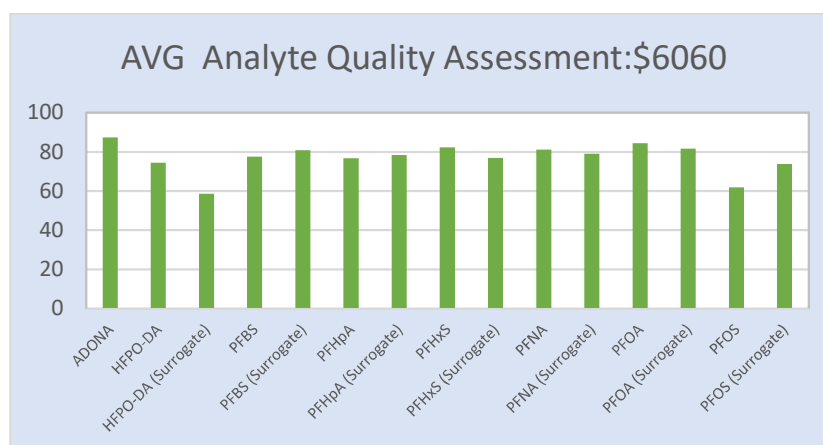
In this analysis, similar QCs are combined to get enough data (at least, n=14) to run the program for the statistical assessment. This diagram also indicates that most analytes performed good as indicated by quality scores >70% for most analytes. Again, the main limitation is the absence of sufficient data (n ≥20) for a good statistical assessment. Hence, at this point we should be cautiously optimistic about the overall performance of this method. The following bar diagram shows the average performances of some QCs of this method:


AVG QC Score:$6060
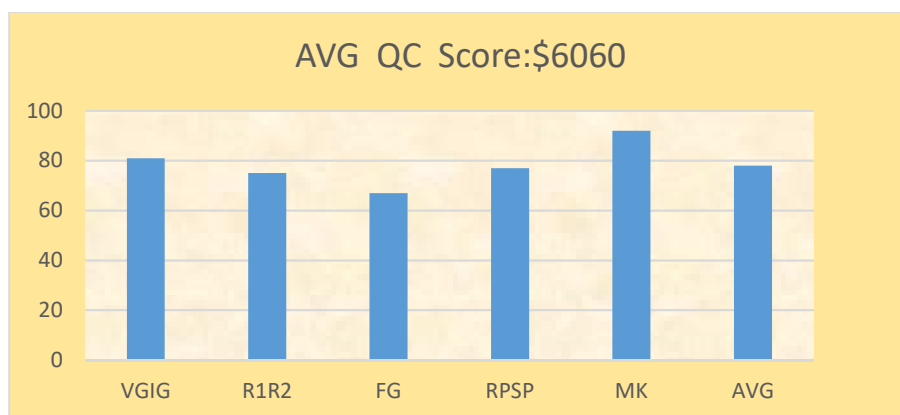
An average of all QC scores near 80% indicates that the overall QC performance of this method is good.

Details

1. VA/IA

The following diagram shows the performance of VA/IA (VA and IA data are combined) samples for all target analytes and surrogates. The average of all scores is over 80%, which suggests a good overall performance of this method.

Quality Assessment of VA/IA:$6060
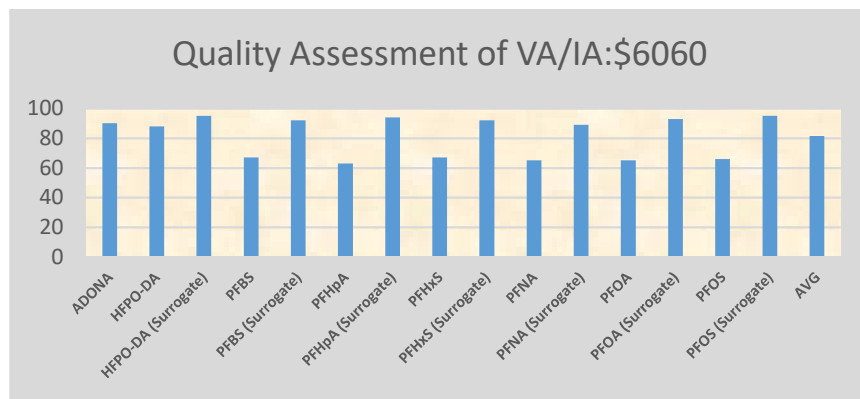
Here are the control chart and summary of statistical analysis for one analyte, PFOA:

Analyte = "PFOA"
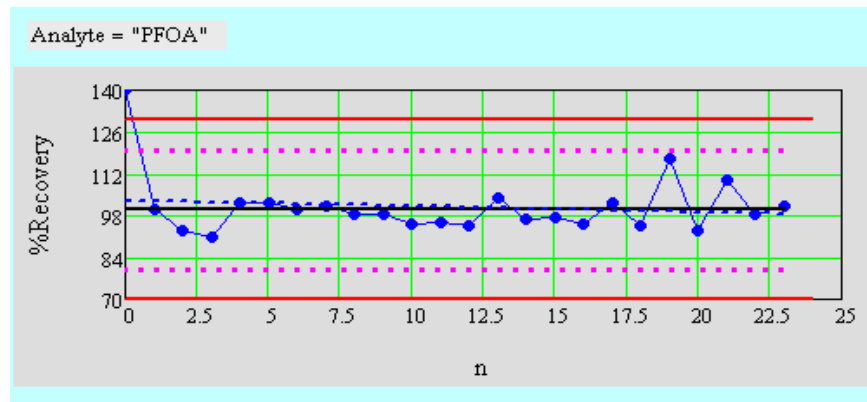
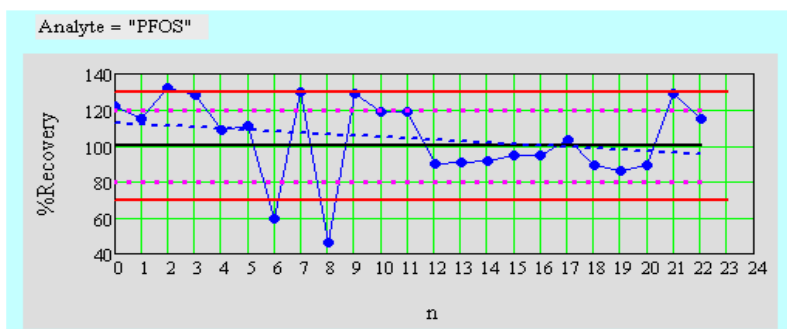|		0	1	2
	0	"DES$6065"	"PFOA"	"VGIG"
	1	"# Unusual Data Omitted"	0	"No unusual data"
	2	"# Data for Long-Term"	27	" LT_Q: < AVG"
	3	"% Overall Failure Rate"	3.7	"OOC Data present"
	4	"Time of Long-term Data"	"03/18/2020"	"03/03/2021"
	5	"Time of Stat Data"	"05/12/2020"	"03/03/2021"
	6	"# True Outliers Rejected"	0	"No Outliers"
	7	" Size - Stat Analysis "	24	"Size still ~ OK! "
	8	"AVG Recov = "	100.83	"Mean ~ Exptd "
SUMM =	9	"St Dev ="	10.09	"Improve ! VAR > EXPTD "
	10	"Normality = "	"NO "	" Data not-normal "
	11	"MK Trend = "	"NO"	"No Trend ! Great! "
	12	"Skewness = "	2.86	"Data Skewed: Improve "
	13	"Kurtosis ="	9.96	" Peaked cf. NormDist "
	14	"Process Capability Index ="	3.72	" Cpk EXC ! "
	15	"Warning I, II, III Present ? "	" Present "	"Only WN I present"
	16	" # MIN _Q Failed "	1	" 1 Failure ~OK! "
	17	" Staistical Properties"	"AVG "	"AVG; ~OK "
	18	"6 Sigma_QUALITY"	"EXC "	" EXC 6 Sigma Quality !"
	19	"QUALITY %SCORE"	65.47	"AVG +"

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A single failure at the beginning of this analysis lowered the score significantly. By omitting the first point, the score becomes 85. Since there is no valid reason to omit the first point, it was included in the assessment.

2. LFB (L1/L2)

For LFB samples, a few analytes performed below average which lead to a lower than 80% quality score. However, the average score greater than 70% is an indication of good overall performance of LFB samples.
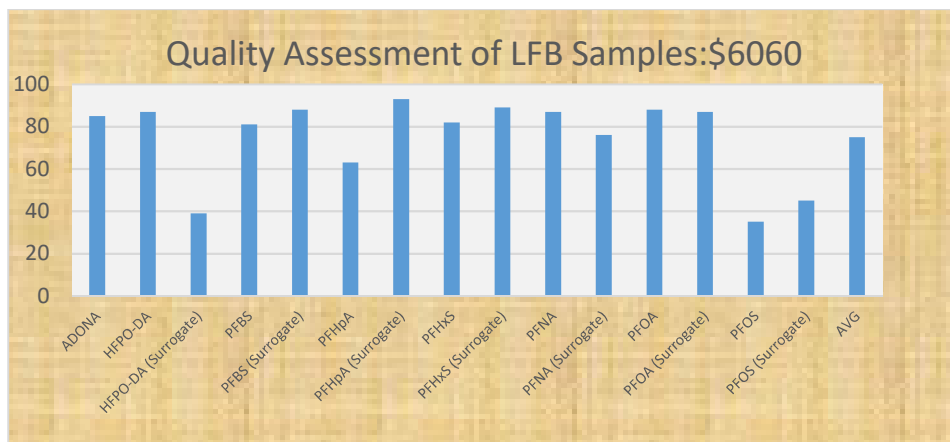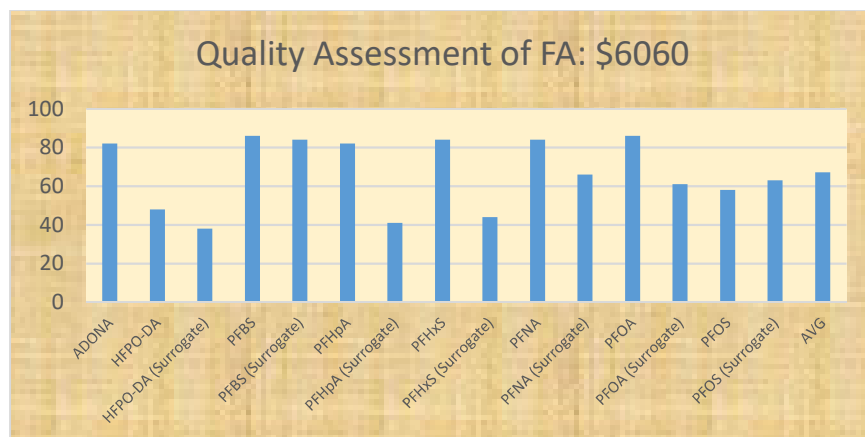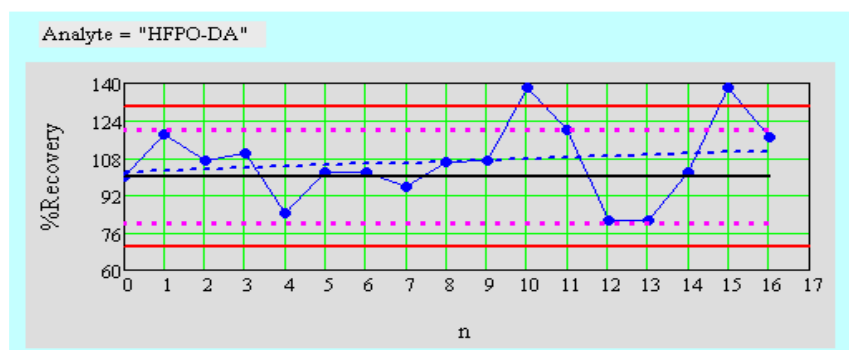

Here is one example (PFOS):

		0	1	2
	0	"DES$6065"	"PFOS"	"R1 R2"
	1	"# Unusual Data Omitted"	0	"No unusual data"
	2	"# Data for Long-Term"	23	" LT_Q: < AVG"
	3	"% Overall Failure Rate"	13.04	"OOC Data present"
	4	"Time of Long-term Data"	"05/12/2020"	"03/04/2021"
	5	"Time of Stat Data"	"05/12/2020"	"03/04/2021"
	6	"# True Outliers Rejected"	0	"No Outliers"
	7	" Size - Stat Analysis "	23	"Size still ~ OK! "
SUMM =	8	"AVG Recov = "	104	"Mean ~ Exptd "
	9	"St Dev ="	22.56	"Improve ! VAR > EXPTD "
	10	"Normality = "	"YES"	"Data Normal "
	11	"MK Trend = "	"YES - d"	"Trend High! CHK QC "
	12	"Skewness = "	-0.89	"Data Skewed: Improve "
	13	"Kurtosis ="	0.69	" Peaked cf. NormDist "
	14	"Process Capability Index ="	0.46	"Cpk not OK"
	15	"Warning I, II, III Present ? "	" Present "	"Only WN II present "
	16	" # MIN _Q Failed "	3	" > 2 Failures: Unacceptable"
	17	" Statistical Properties"	" < AVG "	" <AVG; Improve ! "
	18	"6 Sigma_QUALITY"	"AVG "	"AVG 6 Sigma Quality"
	19	"QUALITY %SCORE"	34.96	" Improve "

3. FA

For this QC component, sample size is less than 20 (n=16-17), making assessment less reliable. Usually, target analytes performed better than the performances of surrogates. However, HFPO-DA is an exception as indicated by the following bar diagram.
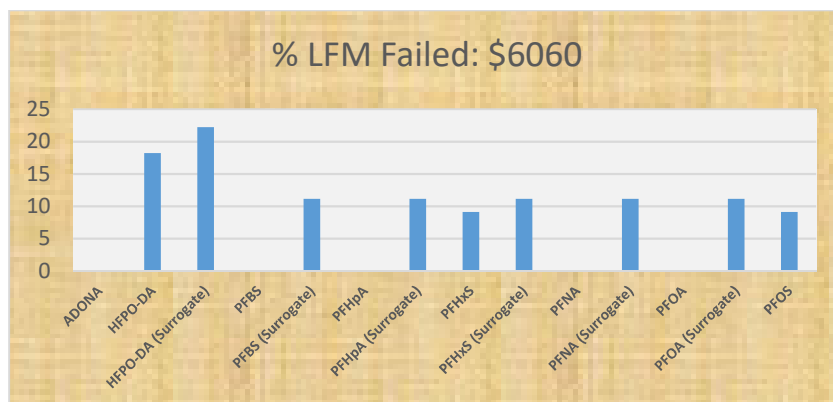

Quality Assessment of FA: $6060

Here are the control chart and summary of statistical analysis for HFPO-DA:

Analyte = "HFPO-DA"

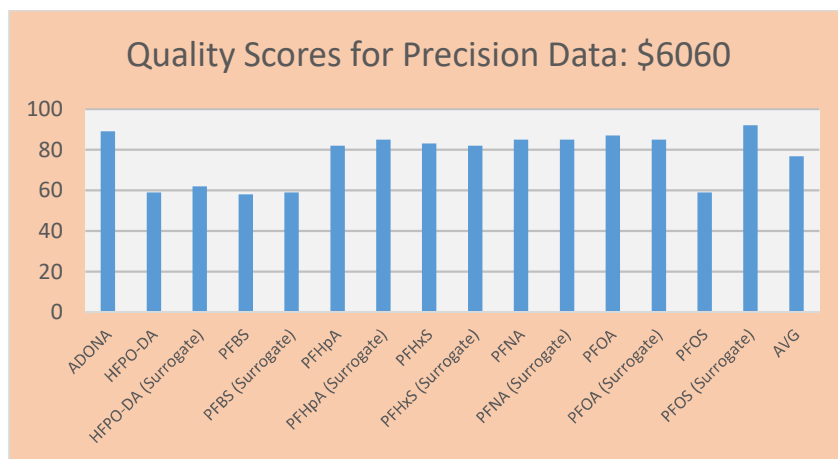|	0	1	2
0	"DES$6065"	"HFPO-DA"	"FG"
1	"# Unusual Data Omitted"	0	"No unusual data"
2	"# Data for Long-Term"	17	" LT_Q: < AVG"
3	"%Overall Failure Rate"	11.76	"OOC Data present"
4	"Time of Long-term Data"	"03/19/2020"	"03/04/2021"
5	"Time of Stat Data"	"03/19/2020"	"03/04/2021"
6	"# True Outliers Rejected"	0	"No Outliers"
7	" Size -Stat Analysis "	17	" Size < 20 ! Not OK!"
8	"AVG Recov = "	106.44	"Mean ~ Exptd "
9	"St Dev ="	16.61	"Improve ! VAR > EXPTD "
10	"Normality = "	"YES"	"Data Normal "
11	"MK Trend = "	"NO"	"No Trend ! Great!"
12	"Skewness = "	0.36	" Skewed Slightly"
13	"Kurtosis ="	0.07	" Peaked cf. NormDist "
14	"Process Capability Index ="	0.55	"Cpk not OK"
15	"Warning I, II, III Present ? "	"Absent"	"Great ! "
16	" # MIN _Q Failed "	2	" 2 Failures: Improve "
17	" Staistical Properties"	"GOOD "	"Good ; OK "
18	"6 Sigma_QUALITY"	"AVG "	"AVG 6 Sigma Quality"
19	"QUALITY %SCORE"	47.92	"NA; n < 20) "

SUMM = (label spanning rows 9–10 on the left)

4. **LFM**

For LFM samples, we do not have enough data points (n=9-11) for running the program for the statistical assessment; however, the following bar diagram would give an idea about the failure rate of various analytes. Obviously, most target analytes have lower failure rates.
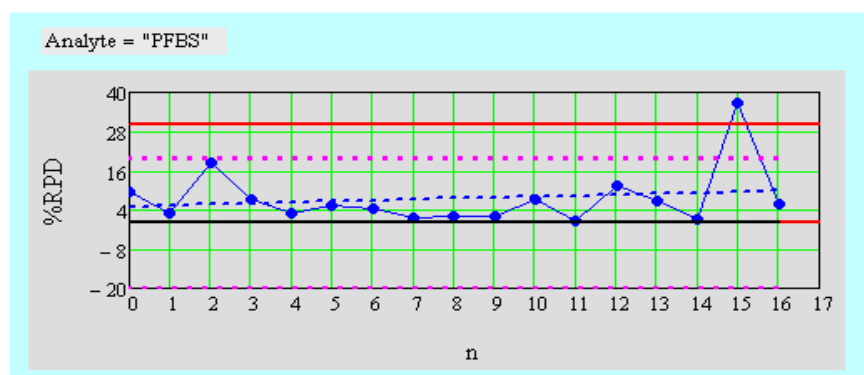

% LFM Failed: $6060

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5. Precision

Precision data (RP & SP) are obtained from the duplicate runs of LFB and LFM samples. These data are combined to get enough data to run the program for a statistical assessment (mostly n=17).


Quality Scores for Precision Data: $6060

Here are the control chart and summary of statistical analysis for PFBS:

Analyte = "PFBS"

|	0	1	2
0	"DES$6065"	"PFBS"	"rpsp"
1	"# Unusual Data Omitted"	0	"No unusual data"
2	"# Data for Long-Term"	17	" LT_Q: < AVG"
3	"%Overall Failure Rate"	5.88	"OOC Data present"
4	"Time of Long-term Data"	"05/12/2020"	"03/04/2021"
5	"Time of Stat Data"	"05/12/2020"	"03/04/2021"
6	"# True Outliers Rejected"	0	"No Outliers"
7	" Size -Stat Analysis "	17	" Size < 20 ! Not OK!"
8	"AVG Precision"	7.45	"Slight mean shift! "
9	"St Dev ="	8.73	" Grreat! VAR < EXPTD "
10	"Normality = "	"NO "	" Data not-normal "
11	"MK Trend = "	"NO"	"No Trend ! Great! "
12	"Skewness = "	2.65	"Data Skewed: Improve "
13	"Kurtosis ="	8	" Peaked cf. NormDist "
14	"Process Capability Index ="	0.82	"Cpk not OK"
15	"Warning I, II, III Present ? "	" Present "	" > 1 Warnings "
16	" # MIN _Q Failed "	1	" 1 Failure ~OK! "
17	" Staistical Properties"	" < AVG "	" <AVG; Improve ! "
18	"6 Sigma_QUALITY"	"Good "	" Good 6 Sigma Quality ! "
19	"QUALITY %SCORE"	57.93	"NA; n < 20) "

SUMM =

6. MB

For method blank, we have only 14 data points for the analytes and less for the surrogates. However, surrogates are not included here for the assessment. The following diagram indicates that MB samples performed very well.

Quality Assessment for MB: $6060
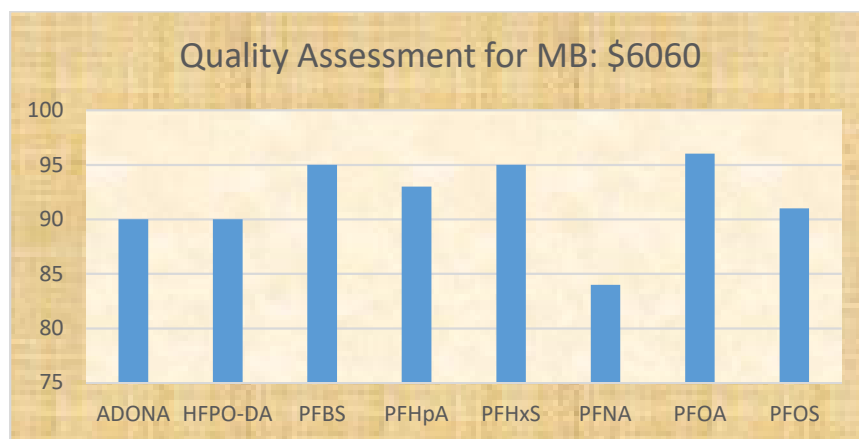
7. CCV

The CCV (A1/A2) samples performed well in terms of the number of samples that failed to meet the method requirements after eliminating one set of data as outlying observations. Only two surrogates have one failure out of eight observations.

% CCV Samples (A1/A2) Failed:$6060
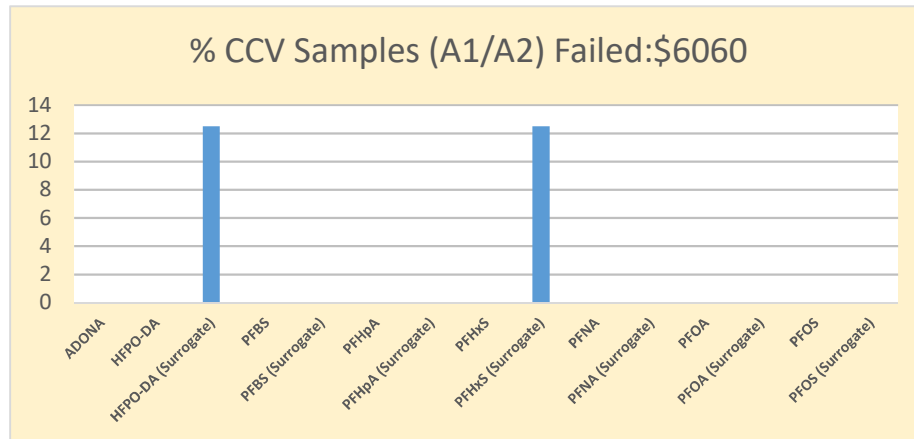
Conclusion

Despite the limitation of using less than 20 data points for most QCs, this study finds that QC data of all target analytes of this method are performing well. If the average quality score for each QC component is analyzed, we find that FA sample is performing somewhat lower than our expectation. No assessment for CCV samples (A1/A2) was possible other than comparing their average percent recoveries against their control limits and percentage data failed to meet the method requirements. In these respects, CCV samples (A1/A2) are performing well. The average recoveries for all other QC samples are quite satisfactory.