ASTM D19.06 SUBCOMMITTEE

STUDY REPORT FROM THE TESTING OF ADDITIONAL INDUSTRIAL WASTEWATER MATRICES IN SUPPORT OF ASTM STANDARD D7575 FOR USEPA's RECONSIDERATION OF THIS METHOD IN THE FORTHCOMING METHOD UPDATE RULE

Prepared for:
United States Environmental Protection Agency
Office of Water
Engineering and Analytical Support Branch

November, 2011

INTRODUCTION

This report is in response to the United States Environmental Protection Agency (EPA) Office of Water, Engineering and Analytical Support Branch request to conduct and provide test results from additional industrial water matrices in support of its reconsideration of ASTM Standard D7575 (Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination) for inclusion in EPA's forthcoming Method Update Rule (MUR).

The remainder of this document provides the details of the study and results that were obtained.

STUDY NAME

The name of this study was: "Testing of Additional Industrial Wastewater Matrices in Support of USEPA Reconsideration of ASTM Standard D7575 in the Forthcoming Method Update Rule."

STUDY DIRECTION AND SPONSOR

This study was performed under the direction of ASTM D 19 Water. The study was sponsored and managed voluntarily by the technical members of the ASTM D19.06 Sub-committee for ASTM Standard D7575.

STUDY DESIGN

Summary

The design of this study was similar to those in the previous single-laboratory studies used for standardization of ASTM D7575. In summary, wastewater from applicable industries acceptable to the study objectives were collected according to standard EPA protocols and shipped to the OSS laboratory for initial screening of oil and grease by ASTM Standard D7575 to ensure the concentration within the sample was within the range of the method. The industrial matrices that passed this screening were then sent to a designated laboratory for oil and grease determination by EPA Method 1664 and ASTM Standard D7575. Upon completion of sample analyses, ASTM D19.06 sub-committee has reviewed the results and prepared this written study report for submission to EPA's Engineering and Analytical Support Branch.

Sample Matrices

Per the objective of the study plan, three specific industrial matrices were collected. The sample collection process followed the sampling procedures of EPA's Freon replacement studies during the development of EPA 1664, whereby one large single grab was collected and sample bottles were split from that original grab while being mixed. The three specific matrices were of the following categories:

- Sample #1: Petroleum Refining and Related Industries – SIC 29: The matrix obtained was from a large refinery facility that processes raw crude oil into multiple petroleum products including petroleum and grease-related products.

- Sample #2: Food and Kindred Products Manufacturers – SIC 20: The matrix obtained was from a large food and restaurant complex whose sample stream has constituents of animal greases and oils from both beef and pork sources.

- Sample #3: Chemicals and Allied Products – SIC 28: The matrix obtained here is from the process stream of a large chemical manufacturer that falls within EPA's regulation category of organic chemicals, plastics, and synthetic fibers (OCPSF).

Study Methods

The two methods used for this study were EPA Reference Method 1664 (hexane liquid/liquid extraction) and ASTM Standard D7575.

It is worth noting that through the course of this study ASTM D7575-10 was updated to ASTM D7575-11. The update process (ASTM work item WK34733) included language suggestions supplied to the subcommittee by USEPA that helped strengthen the method and its procedures. The changes followed the ASTM method revision and voting process. The changes (including an editorial change from an industry member of ASTM) were unanimously approved by ASTM D19 members.

Study Laboratories

The laboratories identified for this study included OSS for initial screening of matrices to ensure that they were within the operating range of D7575 and a centralized commercial laboratory in New England performing EPA Method 1664 and ASTM D7575 for oil and grease on the same collected industrial matrix samples.

Standardized Quality Control Tests

START-UP TESTING:

The independent laboratory and independent laboratory technician chosen were already qualified to perform EPA 1664. Prior to ASTM D7575 testing, however, the independent laboratory technician had to prove to be proficient with performing ASTM D7575. Thus, the following steps were successfully performed:

a) Training by OSS
b) Calibration – *per ASTM D7575 Section 12.2.*
    a. The technician successfully calibrated the instrument and determined a linear function to convert FTIR response peak height at or near 2920 wavenumbers to oil and grease mg/L. That equation was determined to be:

   b. Total Oil and Grease (mg/L) = 146.295*(peak height) – 0.217

c) Determination of technician Lower Detection Limit (LDL) and Method Detection Limit (MDL) – *per ASTM D7575 Section12.4.*
   a. The technician received an LDL of 1.69 mg/L and an MDL of 5.37 mg/L.

d) Demonstration of initial performance of recovery (IPR) – *per ASTM D7575 Section 12.5.*
   a. The technician successfully passed the IPR with 88.1% average recovery and relative standard deviation of 9.1%

MATRICES:

In this study, the three matrices of interest were subjected to the following standardized quality control (QC) and comparative tests, for each of the two methods:

- Calibration verification (once per batch [e.g. 20 samples] per day of testing) – *per ASTM D7575 Section 14.1 and EPA 1664 Section 9.5.*
- Field matrix sample in triplicate – *per ASTM D7575 Section 14 and EPA 1664 Section 11.*
- Field matrix sample spike (hexadecane and stearic acid per EPA Method 1664 protocol) – *per ASTM D7575 Section 12.8 and EPA 1664 Section 9.3.*
- Field matrix sample spike duplicate (hexadecane and stearic acid per EPA Method 1664 protocol) – *per ASTM D7575 Section 12.8 and EPA 1664 Section 9.3.*
- Reagent blank (one per batch [e.g. 20 samples] per day of testing) – *per ASTM D7575 Section 12.7 and EPA 1664 Section 9.4.*
- Laboratory Control Spike (one per batch [e.g. 20 samples] per day) – *per ASTM D7575 Section 12.6 and EPA 1664 Section 9.6.*
- Laboratory Control Spike Duplicate (one per batch [e.g. 20 samples] per day) – *per ASTM D7575 Section 12.6 and EPA 1664 Section 9.6.*

Statistical Analysis and Results

Precision of Triplicate Field Sample Analyses – Triplicate analyses of each matrix were tested for precision by calculating the percent relative standard deviation (standard deviation divided by the mean concentration X 100).

Accuracy and Precision of Matrix Spike and Matrix Spike Duplicate Analyses - The matrix spike and matrix spike duplicate (MS/MSD) test was used to assess method performance in the sample matrix. Analytes of interest (hexadecane and stearic acid) were added to a field sample aliquot that was then thoroughly homogenized and split into two spiked replicate aliquots for analysis. One of these replicates was identified as the matrix spike sample and the other was identified as the matrix spike duplicate sample. The recovery of the analytes relative to the spike concentration was determined in each sample. Accuracy was measured from the difference in determination of the spiked sample and unspiked field sample divided by the spiked amount,

multiplied by 100. The precision of the determinations was assessed by measuring the relative standard deviation of recovery.

Accuracy and Precision of Laboratory Control Spike and Laboratory Control Spike Duplicate - The laboratory control spike and laboratory control spike duplicate (LCS/LCSD) test was used to assess method performance in a controlled reference matrix. Analytes of interest (hexadecane and stearic acid) were added to reagent water that was then thoroughly homogenized and split into two spiked replicate aliquots for analysis. One of these replicates was identified as the laboratory control spike sample and the other was identified as the laboratory control spike duplicate sample. The recovery of the analytes relative to the spike, were determined in each sample. Accuracy was determined from the average of the two recoveries of spiked samples divided by the spiked amount, multiplied by 100. The precision of the determinations was assessed by measuring the relative standard deviation of recovery.

The statistical results for the study matrices are provided in **Appendix A**.

Appendix A – provides the data and analysis for each of the three primary study matrices. The results include:

a) Calibration Verification
b) Method Blank
c) Laboratory Controls
d) Triplicates
e) Matrix Spikes

of each study matrix.

Appendix B – provides plots of the data associated with all aspects of recent ASTM D7575 versus EPA 1664 comparability studies. These plots include:

Chart 1: Difference in average results between ASTM D7575 and EPA 1664. This plot includes data from ASTM D7575 development, auxiliary data provided to EPA per their request, and this Notice of Data Availability study. It should be noted that the **average difference across all matrices = 0.6 mg/L**. Note that in this chart the 'industrial laundry (1664 interferent issues)' non-point reflects that TPH measurement is used instead of total oil and grease because of a known interferent issue with surfactants in this matrix.

Chart 2: ASTM D7575 vs. EPA 1664 Laboratory Control Sample (LCS) comparability plots from both ASTM D7575 development and this Notice of Data Availability Study.

Chart 3: ASTM D7575 vs. EPA 1664 Matrix Spike (MS) plots from both ASTM D7575 development and this Notice of Data Availability Study.

Conclusion

ASTM D19 Subcommittee for ASTM D7575 has successfully executed a comparative study in response to the United States Environmental Protection Agency (EPA) Office of Water, Engineering and Analytical Support Branch request to conduct and provide test results from additional industrial water matrices in support of its reconsideration of ASTM Standard D7575 (Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination) for inclusion in EPA's forthcoming Method Update Rule (MUR).

The study focused on providing comparability data (ASTM D7575 versus EPA 1664) on three matrices of interest to EPA (SICS Code 29 – Petroleum Refining, SIC Code 20 – Food – including animal greases and oils, and SIC Code 28 – OCPSF). For these matrices, testing included:

a) Calibration verification
b) Method Blank
c) Laboratory Control and Laboratory Control Duplicate
d) Triplicate analysis

and

e) Matrix Spike and Matrix Spike Duplicate.

Comparability data between ASTM D7575 and EPA 1664 has been provided in Appendix A.

With the exception that EPA 1664 failed to adequately capture matrix spikes for the petroleum refining matrix, both methods demonstrated documented QC test performance.

Consistent with previous ASTM D7575 versus EPA 1664 testing and as concluded in previous statistical comparisons, results from this study (see Appendix B plots) show comparability between ASTM D7575 and EPA 1664. These previous comparisons can be found at the EPA Docket site:

1) http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OW-2010-0192-0163
    a. Document ID: EPA-HQ-OW-2010-0192-0163
    b. Attached file #1: "*Supplemental Data and Statistical Analysis in Support of Method Equivalence of ASTM D7575 Solventless Oil and Grease and EPA Method 1664A*",
    c. Document Type: Public Submission
    d. This is comment on Proposed Rule: Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures
    e. Docket ID: EPA-HQ-OW-2010-0192
    f. Submitted to Docket 12/21/2010

2) http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OW-2010-0192-0135

a. Document ID: EPA-HQ-OW-2010-0192-0135
b. Attached file #1 0900006480bba5b3.pdf. *"ASTM D19.06 Sub-committee, D-19 Water Inter-Laboratory Study to Establish Precision Statements for ASTM WK23240 – Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination"*
c. Document Type: Public Submission
d. This is comment on Proposed Rule: Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures
e. Docket ID: EPA-HQ-OW-2010-0192
f. Submitted to Docket 12/21/2010

APPENDIX A – MATRICES RESULTS

MATRIX #1 Petroleum Refining and Related Industry - SIC 29 - Large Refinery Facility that Processes Raw Crude Oil into Multiple Petroleum Products including Grease Products

		CALIBRATION VERIFICATION						METHOD BLANK				LABORATORY CONTROL						TRIPLICATES		MATRIX SPIKE					
		ASTM D7575			EPA 1664			ASTM D7575		EPA 1664		ASTM D7575			EPA 1664			ASTM D7575	EPA 1664	ASTM D7575			EPA 1664		
	BOTTLE	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	LCS Value (mg/L)	Recovery %	79%-113% Pass?	LCS Value (mg/L)	Recovery %	78%-114% Pass?	Triplicate Value (mg/L)	Triplicate Value (mg/L)	Matrix Spike Value (mg/L)	Recovery %	70%-126% Pass?	Matrix Spike Value (mg/L)	Recovery %	78%-114% Pass?
Cal. Ver.	N/A	39.14	39.14	YES	40	40	YES																		
Blank	BLANK							-1.14	YES	0.3	YES														
LCS	LCS											41.5			37										
LCSD	LCSD											39.4			35.5										
LCS AVE												40.5	101.13%	YES	36.3	90.63%	YES								
LCS SD												1.45			1.06										
Triplicate #1	T0101																	15.6	13.6						
Triplicate #2	T0102																	15.3	15.0						
Triplicate #3	T0103																	16.6	19.2						
Triplicate Ave																		15.8	15.9						
Triplicate RSD																		4.37%	18.26%						
MS	T0104																			64.4			31.1		
MSD	T0105																			58.2			28.8		
MS AVE																				61.3			29.9		
MS AVE RECOVERY																					113.7%	YES		35.0%	NO

MATRIX #2 Food and Kindred Product Manufacturers - SIC 20 - Large Food and Restaurant Complex Sample Containing Animal Greases and Oils from both Beef and Pork

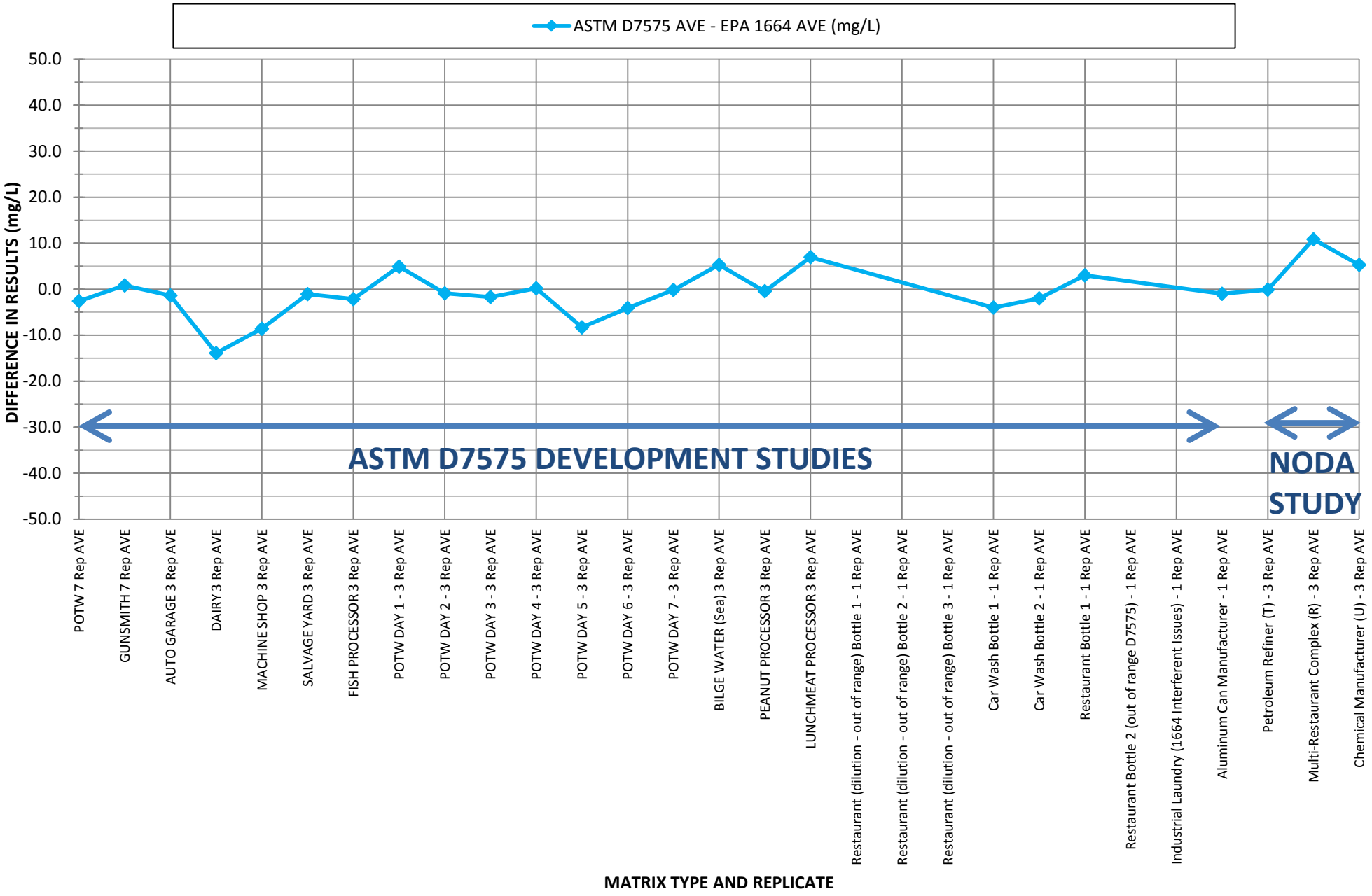
		CALIBRATION VERIFICATION						METHOD BLANK				LABORATORY CONTROL						TRIPLICATES		MATRIX SPIKE					
		ASTM D7575			EPA 1664			ASTM D7575		EPA 1664		ASTM D7575			EPA 1664			ASTM D7575	EPA 1664	ASTM D7575			EPA 1664		
	BOTTLE	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	LCS Value (mg/L)	Recovery %	79%-113% Pass?	LCS Value (mg/L)	Recovery %	78%-114% Pass?	Triplicate Value (mg/L)	Triplicate Value (mg/L)	Matrix Spike Value (mg/L)	Recovery %	70%-126% Pass?	Matrix Spike Value (mg/L)	Recovery %	78%-114% Pass?
Cal. Ver.	N/A	39.58	39.14	YES	40	40																			
Blank	BLANK							-0.51	YES	0.3	YES														
LCS	LCS											33.9			37.0										
LCSD	LCSD											31.7			36.0										
LCS AVE												32.8	81.93%	YES	36.5	91.25%	YES								
LCS SD												1.55			0.71										
Triplicate #1	R0101																	45.4	37.6						
Triplicate #2	R0102																	51.6	37.2						
Triplicate #3	R0103																	48.8	38.5						
Triplicate Ave																		48.6	37.8						
Triplicate RSD																		6.33%	1.69%						
MS	R0104																			95.89877			73.0		
MSD	R0105																			101.3117			73.8		
MS AVE																				98.6			73.4		
MS AVE RECOVERY																					125.0%	YES		89.2%	YES

MATRIX #3 Chemicals and Allied Products - SIC 28 - Large Chemical Manufacturer that Falls within EPA's Regulation Category for OCPSF

		CALIBRATION VERIFICATION						METHOD BLANK				LABORATORY CONTROL						TRIPLICATES		MATRIX SPIKE					
		ASTM D7575			EPA 1664			ASTM D7575		EPA 1664		ASTM D7575			EPA 1664			ASTM D7575	EPA 1664	ASTM D7575			EPA 1664		
	BOTTLE	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Calibration Verification Value (mg/L)	Calibration Standard Value (mg/L)	Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	Blank Value (mg/L)	< LDL (1.69 mg/L) Pass?	LCS Value (mg/L)	Recovery %	79%-113% Pass?	LCS Value (mg/L)	Recovery %	78%-114% Pass?	Triplicate Value (mg/L)	Triplicate Value (mg/L)	Matrix Spike Value (mg/L)	Recovery %	70%-126% Pass?	Matrix Spike Value (mg/L)	Recovery %	78%-114% Pass?
Cal. Ver.	N/A	39.58	39.14	YES	40	40	YES																		
Blank	BLANK							-0.51	YES	0.3	YES														
LCS	LCS											33.9			37.0										
LCSD	LCSD											31.7			36.0										
LCS AVE												32.8	81.93%	YES	36.5	91.25%	YES								
LCS SD												1.55			0.71										
Triplicate #1	U0101																	36.4	29.2						
Triplicate #2	U0102																	34.5	31.0						
Triplicate #3	U0103																	35.9	30.7						
Triplicate Ave																		35.6	30.3						
Triplicate RSD																		2.80%	3.21%						
MS	U0104																			71.46743			65.1		
MSD	U0105																			64.15265			63.4		
MS AVE																				67.8			64.3		
MS AVE RECOVERY																					80.6%	YES		84.9%	YES

APPENDIX B – ASTM D7575 VS EPA 1664 COMPARABILITY CHARTS

ALL COMPARATIVE STUDIES: D7575 vs. EPA 1664 Differences in Results (mg/L)
(average difference across all matrices = 0.6 mg/L)
does not include data from test results out of ASTM D7575 range

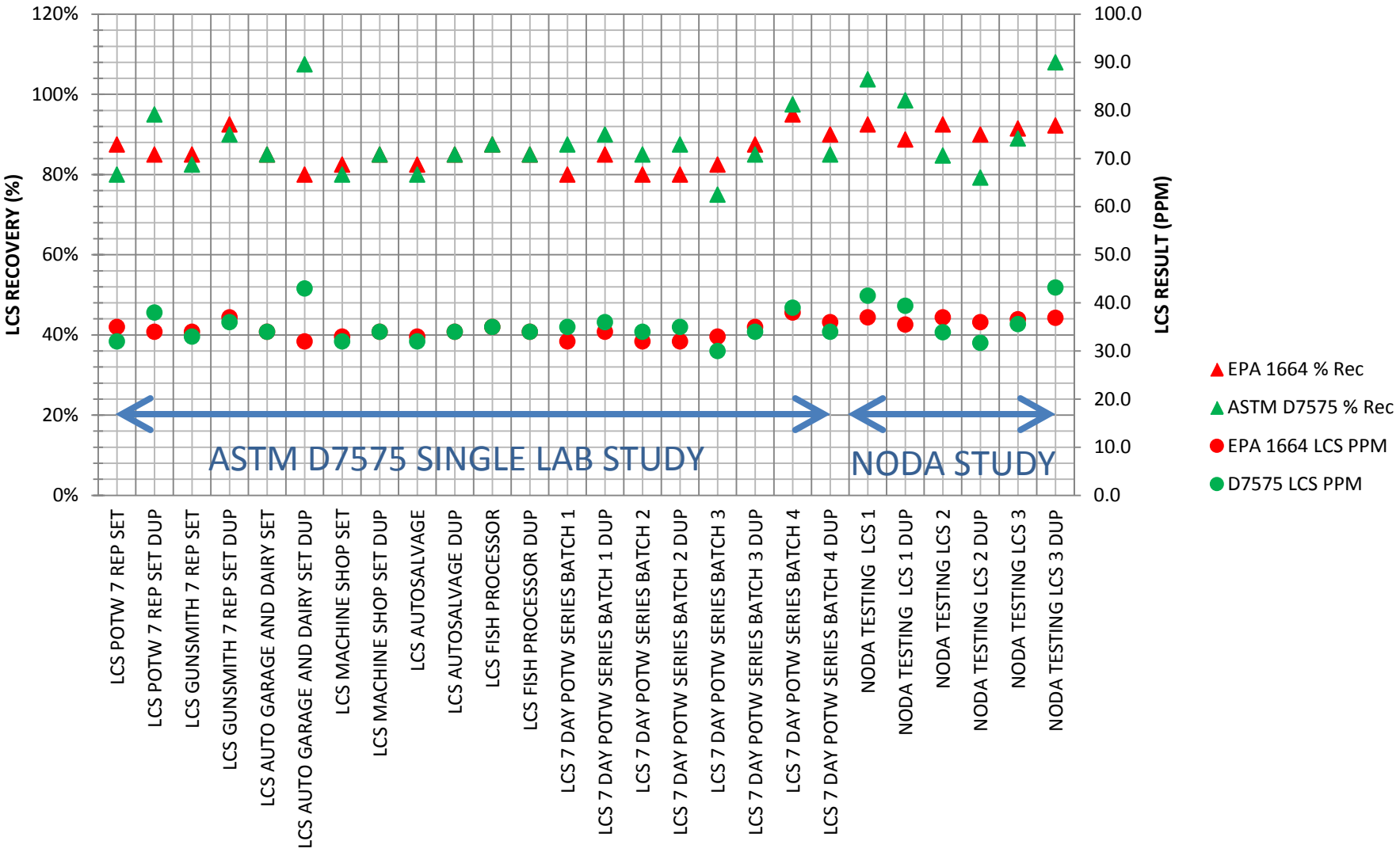


ASTM D7575 vs EPA 1664 Comparative Study

Laboratory Control Samples

ASTM D7575 (ave=88.4% recovery)

EPA 1664 (ave=86.5% recovery)



ASTM D7575 vs EPA 1664 Comparative Study Matrix Spike Recovery

ASTM D7575 (ave=98% recovery) >> EPA 1664 (ave=71% recovery)