DISPERSANT EFFECTIVENESS TESTING ON WATER-IN-OIL EMULSIONS AT OHMSETT

For

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Disclaimer

Executive Summary

The objective of this study was to determine the effectiveness of chemical dispersants when applied to water-in-oil emulsions and to determine if similar viscosity limits exist for successful dispersion of emulsions as for un-emulsified crude oils.

Preliminary tests were completed in the small-scale wave tank at SL Ross. Full-scale tests were completed at Ohmsett-The National Oil Spill Response Test Facility in Leonardo, New Jersey.

Tests were conducted with Corexit 9500 and Corexit 9527 dispersants. Four oils were selected for testing based on their availability and known tendency to form water-in-oil emulsions. The oils used were Endicott crude oil, Sockeye crude oil and two heavy fuel oil mixes; IFO 30 and IFO 120 blends.

The viscosities of the emulsions used in the small-scale test program ranged from 1210 cP to 78,380 cP. These 50% water content emulsions were made using a paint stirrer and a technique developed in a previous study (SL Ross 2005). Corexit 9500 and Corexit 9527 generated negligible dispersion (less than 12%) on emulsions with viscosities of 2630 cP and higher when applied at a 1:20 dispersant-to-oil ratio (DOR). Corexit 9527 was marginally more effective than Corexit 9500 on the lower viscosity emulsions but neither dispersant achieved a dispersant effectiveness (DE) greater than 42% for any of the emulsions tested. The fresh oils were all dispersible (DE between 66% and 100%) with Corexit 9500 in the small-scale tests. Summaries of these results are found in Figure 1 and Table 2.

Nineteen large-scale dispersant effectiveness tests were completed at the Ohmsett facility in December 2005, on emulsions of the same four oils used in the small scale testing. Emulsions for the large-scale tests were generated using two different procedures. In one method the emulsions were formed by slowly mixing salt-water into samples of the oil in a drum using a mechanical stirrer similar to the method used in the small-scale testing. This technique for emulsion formation was developed in an earlier study (SL Ross 2005) and was found to produce emulsions with entrained water drop characteristics similar to emulsions formed in breaking wave conditions. The second set of emulsions was formed on the surface of the Ohmsett tank.

Quantities of the oil were placed on the water and breaking waves were introduced to the tank. The breaking wave action was continued until a water-in-oil emulsion formed. Example micro-photographs of the two types of emulsions can be seen in Appendix B.

In the large-scale Ohmsett tests the dispersants were not effective (less than 13%) on the emulsions with viscosities above 10,000 cP and were only marginally effective (less than 40%) on emulsions between 4000 and 10,000 cP. Detailed test results from the Ohmsett test program are found in Table 4 and Figure 4.

In a number of the tests completed at Ohmsett the estimate of the amount of oil collected at the end of the test exceeded the amount released for the test. It is likely that errors in the measurements of the high water contents in the final collected emulsions are the causes of these discrepancies. Test samples were disposed of before these results could be confirmed.

Duplicate tests were completed for two test cases (Endicott on-tank emulsion with Corexit 9500) and IFO 30 mechanical emulsion and Corexit 9500). The DE values for the Endicott tests were similar (6.5 % and 12.8%) but there was a significant difference in the IFO 30 test results (9.6% and 31.4%). While it is not known for certain what the cause of the discrepancy is, it is possible that it is also due to the methods used to determine the water content in oil sampled at the end of the test. The methods used to determine water contents for high water content samples should be investigated and refined in future tests.

In-water oil concentration and oil drop sizes were measured during the test program using a laser particle size analyzer (LISST) towed at a depth of 1.5 meters below the calm water surface. The oil concentration and drop size measurements made using the LISST did not consistently correlate with the measured dispersant effectiveness. The LISST data is provided in Appendix A. This is in contrast to other dispersant effectiveness tests completed where there was a good correlation (SL Ross 2006b). The poor correlation in this study may have been because the LISST device is only recording a portion of the dispersed oil cloud in each pass and with the poor oil dispersion encountered in this test program the dispersed oil cloud was patchier than in other tests. As a result the LISST data may not be representative of the overall dispersion in these tests, in all cases.

Visual ranking of dispersant effectiveness was successful in qualitatively differentiating the dispersant effectiveness in only 55% of the tests. The four "false positive" visual rankings (tests #7, #11, #12 and #3) all occurred in tests where Corexit 9500 was used. The reason for this is not clear. The trends in the LISST oil drop size and concentration results do not provide a clear explanation for the false positive visual results.

The dispersant effectiveness (DE) estimates from the Ohmsett tank tests are generally higher than those from the SL Ross tank. The higher DE values from Ohmsett are likely due to the higher wave energies that are achieved at Ohmsett when compared to the SL Ross tank. A comparison of the DE estimates from the two test series is provided in Figure 5.

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Dispersant Effectiveness Testing On Water-In-Oil Emulsions

1. Objective

The objective of the work was to determine the effectiveness of chemical dispersants applied to water-in-oil emulsions made with crude oils of varied origin.

2. Background

The use of chemical dispersants in US waters is on the verge of achieving a similar status to that of conventional booming and skimming countermeasures. US Coast Guard oil spill response equipment requirement guidelines (Summary Report of Public Workshop for Response Plan Equipment CAPs http://www.uscg.mil/vrp/reg/caps.shtml) mandate that a dispersant application capability must be included in spill response plans for those regions where dispersant pre-authorization has been established and dispersants are included in the plan holder's response capabilities. As industry gears-up its ability to apply dispersants the number of spill incidents where dispersants will be considered will increase. There will be an increased need to know when dispersants will likely be effective on different oil types to assist in the dispersant-use decision-making process.

Presently there is a lack of good data and knowledge on the dispersibility of water-in-oil emulsions under at-sea conditions. A previous study at Ohmsett has shown that oils with viscosities less than 6500 cSt are dispersible and that oils with viscosities higher than 30000 cSt are not (SL Ross 2006). Oil viscosity proved to be a good indicator of likely dispersant effectiveness in these tests. The primary goal of the current study was to determine the dispersibility of water-in-oil emulsions made from various oils to see if similar viscosity limits for successful dispersion exist for emulsions.

3. Small-Scale Testing

Fourteen small-scale dispersant effectiveness tests were completed in the SL Ross wave tank in late November and early December of 2005 just prior to the Ohmsett test program.

3.1 Oils, Emulsions and Dispersants Tested

Tests were completed with Corexit 9500 and Corexit 9527 dispersants. Four oils were selected for testing based on their availability and known tendency to form water-in-oil emulsions. The oils used were Endicott crude oil, Sockeye crude oil and two heavy fuel oil mixes; IFO 30 and IFO 120 blends. Water-in-oil emulsions were made using a paint stirrer and a technique developed in a previous study (SL Ross 2005). The viscosities of the emulsions used in the small-scale test program are shown in Table 1. The parent oil viscosities, measured at 100 s^{-1} shear rate, varied from 340 to 1340 cP. The emulsion viscosities ranged from 1210 cP to 78,380 cP.

Table 1 Physical Properties of Oils Used in Small-Scale Testing

Crude Oil Name	Viscosity (cP at 8.5 °C)				
	2 s^{-1}	10 s^{-1}	30 s^{-1}	100 s^{-1}	
Endicott					
fresh	-	-	1296	570	
6% weathered	-	-	2064	1000	
50% wc		-	2633	1210	
IFO 30					
Fresh	-	-	370	340	
50% wc	-	-	1880	1570	
IFO 120	-				
Fresh	-	-	1175	1340	
50% wc	29,370	23,060			
Sockeye					
Fresh			780	1020	
50% wc	11,600	10,160	9350	-	
70% wc	78,380	10,000[a]			

[a]emulsion likely broke in cup during measurement

3.2 Methods

The small-scale tank tests were completed on the oils shown in Table 1 to provide an indication of the dispersibility of each of these oils prior to large-scale testing at Ohmsett. Dispersant effectiveness tests were completed using SL Ross's small-scale test tank. The test apparatus and detailed methods used in this testing can be found in an earlier report (SL Ross 2003a). All tests were completed with the wave paddle set to 34 rpm that generated a wave height of approximately 20 cm. The tank water temperature was about 9 °C throughout the test program. This was the water temperature that was predicted for the Ohmsett tank based on the scheduled test dates and previous years water temperature records. Dispersant was applied to the oil or emulsions by hand using a syringe to ensure proper dosage onto the thick slicks. The overhead spray boom was not used due to the large number of passes that would have been required to achieve the target dispersant dosage of 1 part dispersant to 20 parts of emulsion (1:20 DOR). Waves were on during the dispersant application to best simulate the conditions that would be present during the Ohmsett test program. Waves were applied for a 20-minute period and the emulsion remaining within the containment zone was collected immediately after the water surface calmed. The amount of oil collected was compared to the initial amount used to determine the dispersant's effectiveness.

3.3 Test Results

The results from the small-scale testing are provided in Table 2 and Figure 1. The results show trends in effectiveness as a function of emulsion viscosity and dispersant type. Emulsions with viscosities of 2630 cP and higher had negligible dispersion when dispersant was applied at a 1:20 DOR. Corexit 9527 was marginally more effective than Corexit 9500 on the Endicott, IFO 30 and IFO 120, 50% water content emulsions. The fresh oils were all dispersible with Corexit 9500.

Table 2 Small-Scale Tank Test Results

Oil Name	Viscosity (cP) (15°C @ 30 s^{-1})	% Dispersed	
		9527	9500
Endicott			
fresh	1300	-	66
6% weathered	2060	-	3
6% weathered & 50% wc	2630	12.3	3.3
IFO 30			
Fresh	370	-	100
50% wc	1880	42	21
IFO 120			
Fresh	1175	-	-
50% wc	29,370 [a]	4.5	3.1
Sockeye			
Fresh	780	-	95
50% wc	11,600 [a]	0	0
70% wc	78,380 [a]	0	0

[a] viscosity measured at 2 s^{-1}

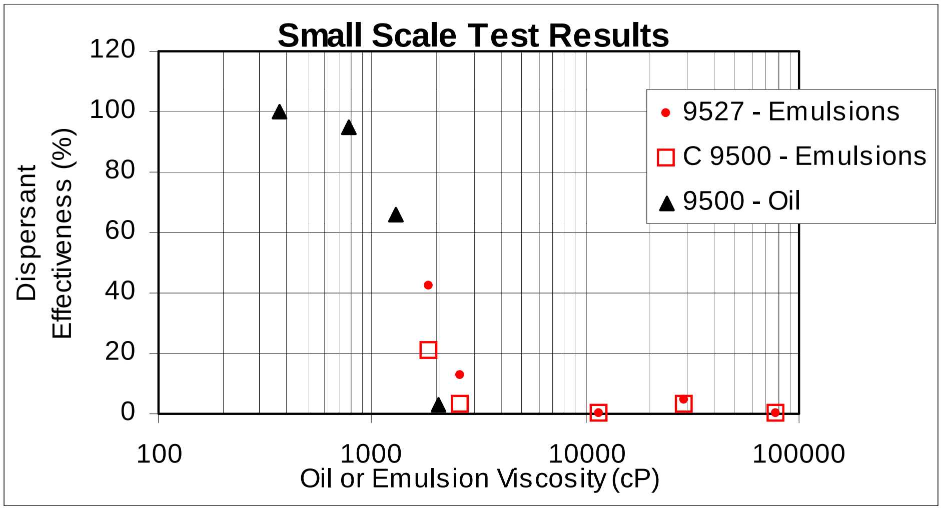

Figure 1 Small-Scale Tank Test Dispersant Effectiveness versus Oil Viscosity

4. Large-Scale Tank Testing at Ohmsett

4.1 Oils, Emulsions and Dispersants Tested

Nineteen large-scale dispersant effectiveness tests were completed at the Ohmsett facility in December 2005, on emulsions of the same four oils used in the small scale testing; Sockeye, Endicott, IFO 30 and IFO 120. Corexit 9500 and 9527 dispersants were used in all tests.

Emulsions were generated using two different procedures. In one method the emulsions were formed by slowly mixing salt-water into samples of the oil in a drum using the mechanical stirrer shown in Figure 2. This technique for emulsion formation was developed in an earlier study (SL Ross 2005) and was found to produce emulsions with entrained water drop characteristics similar to emulsions formed in breaking wave conditions. The second set of emulsions was formed on the surface of the Ohmsett tank under more realistic conditions. Samples of the oil were placed on the water and breaking waves were introduced to the tank. The waves were stopped when the oil reached the end containment barrier and the oil was moved back to the opposite end of the tank. The waves were then re-started. This process was continued until a water-in-oil emulsion formed. Oil samples were taken periodically and viewed under a microscope to monitor the emulsion progress.

Figure 2 Mechanical Stirrer Used to Make Water-in-Oil Emulsions

The viscosities, densities and water contents of the various oils and emulsions used in the final test matrix are provided in Table 3. Also include in this table are hypertext links to micro-photographs of these emulsions. The photographs of the mechanically formed emulsions show a similar water drop-size structure to those generated on the tank for the Endicott and Sockeye oils. The scale in the photographs represents approximately 10 micrometers per small division based on a photograph of a stage micrometer at the same magnification that can be seen in Appendix B at the following hypertext link (Scale).

Table 3 Physical Properties of Emulsions Used in Ohmsett Testing

Oil Name	Viscosity (cP)			Density (g/cm³ at 15°C)	Water Content (% by Volume)	Hypertext Link to Microphotographs of Emulsions
	10 s^{-1}	100 s^{-1}	Temp (°C)			
Sockeye						
Fresh	2084	2171	5	0.934	0	
On-Tank Emulsion	45,500	-	3.5	0.968	48	SOCKtank
Mechanically Mixed Emulsion	8638	5419	3	0.944	56	SOCKmech
Endicott						
Fresh	168	158	3.5	0.900	0	
Weathered	1280	525	5.5	0.919	0	
On-Tank Emulsion	3920	1973	3.5	0.924	50	ENDTank
Mechanically Mixed Emulsion	6069	2624	3.5	-	55	ENDmech
IFO 30						
fresh	1433	1089	3	0.940	0	
Mechanically Mixed Emulsion	7895	4670	3	-	55	IFO30mech
IFO 120						
fresh	12,578	5232	3	0.953	0	
Mechanically Mixed Emulsion	17,322	-	3	0.949	54	IFO120mech

4.2 Test Methods and Equipment

The dispersant effectiveness testing protocol developed over the past five years at Ohmsett was used in the testing. Detailed descriptions of the test protocol, and its development, and equipment used in the testing can be found in previous publications (SL Ross et al 2000a, 2000b, 2002a, 2002b, 2003a, 2003b, 2004, 2005). Significant improvements to the oil delivery system were implemented in the spring of 2005 to facilitate the discharge of viscous oils. Problems were encountered in delivering viscous oils in a previous test series (SL Ross. 2003a) and these modifications successfully addressed the problem.

The new oil discharge system includes:

1. a progressing cavity pump,
2. a pump speed control system,
3. a gravity fed oil hopper supply,
4. three-inch oil supply lines, and;
5. a stainless steel oil discharge manifold.

Oil is pumped into the hopper from drums or other supply tanks using the progressing cavity pump in reverse. The flow rate for this pump is precisely controlled by altering its rpm using the digital control module. The pump generates 0.19 gallons per minute per revolution of the pump. The quantity of oil discharged from the hopper is measured using a sonic probe mounted above the oil supply. Photographs of the oil supply system and oil discharge header are provided in Figure 3.

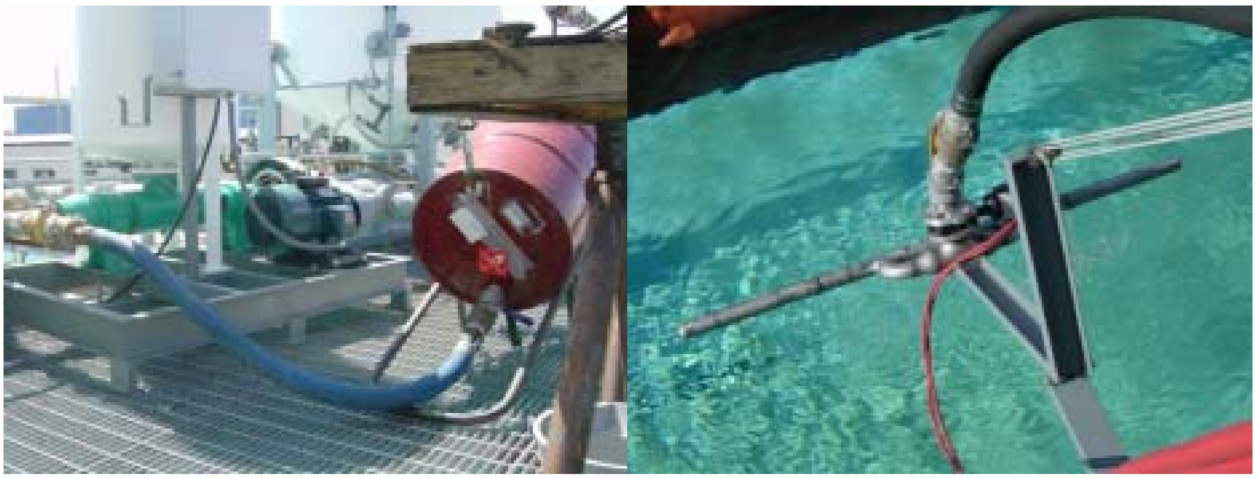

Figure 3 Oil Supply System and Discharge Header

The dispersant spray system used in the testing was the same as that used in previous dispersant tests at Ohmsett. Corexit 9500 and 9527 dispersants were used in all of the tests where dispersant was applied.

The basic test procedure used for all dispersant effectiveness tests is as follows.

1. A large oil containment area is established by placing booms across the tank at each end of the Ohmsett tank to isolate oil from the wave paddle and beaches.
2. The oil and dispersant are loaded into their respective supply tanks on the main bridge deck.
3. The main bridge is positioned at the southern quarter point within the boomed area. The wave paddle is started and the waves are allowed to develop to a stage just prior to the formation of breaking waves.
4. The wave paddle settings used in all of these tests were a 3.5 inch stroke and 34 to 35 strokes per minute.

5. The bridge is moved south at the required speed to achieve proper slick dimensions and dispersant application dosage (0.5 knots in this test series).
6. The oil is pumped at the required rate onto the surface through the discharge manifold mounted on the south side of the bridge (20 gpm in this test series).
7. The dispersant is applied onto the oil slick from the spray bar system mounted on the north side of the bridge in the same pass.
8. The waves are left on for 30 minutes and the wave paddle is stopped.
9. During the period of wave activity the LISST particle size analyzer is towed at a 1.5 meter depth through any dispersed oil cloud visible from the dispersion or under the surface oil slick if a cloud is not visible.
10. Once the waves are turned off the tank surface is allowed to calm.
11. The water spray from the bridge fire monitors is used to sweep any surface oil remaining on the water surface at the end of the test to a common collection area at one corner of the containment boom.
12. The oil is then removed from the water surface using a double-diaphragm pump and suction wand and placed in a collection drum.
13. An emulsion breaker is mixed into the contents of the drum and it is allowed to stand at least overnight. The majority of the free water present is decanted from the drum.
14. The remaining oil and water are well mixed and a sample is taken for water content and physical property determination.
15. The quantity of liquid in the drum is measured and the amount of oil determined by subtracting the amount of water as determined using the water content analysis.
16. The effectiveness of the dispersant is reported as the volume of oil discharged minus the amount collected from the surface all divided by the amount discharged.
17. Each test was video taped for future visual reference.

4.3 Dispersant Effectiveness Results

The test conditions and estimated Dispersant Efficiencies (DE) for all of the large-scale tank tests are summarized in Table 4. The air and water temperatures during the test program were generally within a few degrees of 0° C. Temperatures were considerably lower than usual for the month of December in New Jersey during the testing. As a result the large-scale tests were completed at lower temperatures than the small-scale testing completed in the SL Ross wave tank. The raw DE' values in theTable 4 were determined using the following simple formula: DE'= (volume spilled – volume collected from the surface) / volume spilled * 100.

The dispersant-to-oil ratios shown in Table 4 have been calculated based on the dispersant discharge flow rate and spray width, the oil flow rate, the oil slick width and the percent of the water surface within the oil slick width covered by oil.

The "control adjusted" DE value in Table 4 is the raw DE' value minus the amount of oil unaccounted for or lost in the control run (no dispersant) for that oil. The control adjusted DE values have been used in Figure 4. This plot shows the variation in dispersant effectiveness with emulsion viscosity for the two dispersants tested.

As seen in Table 4 and Figure 4 the dispersants were not effective on the emulsions with viscosities above 10,000 cP and were only marginally effective (less than 40%) on emulsions between 4000 and 10,000 cP.

Hypertext links are provided in Table 4 to video clip highlights of each of the tests. The video records can be viewed by double-clicking on a link when accessing this document through MS Word or Adobe Acrobat. The clips include small segments of video taken over the duration of the test and provide a good record of the behavior of the oil in each of the tests completed. It is highly recommended that they be viewed to get a full appreciation of the test program.

In a number of the tests completed at Ohmsett the estimate of the amount of oil collected at the end of the test exceeded the amount released for the test. It is likely that errors in the measurements of the high water contents in the final collected emulsions are the causes of these discrepancies. Test samples were disposed of before these results could be confirmed. In a number of cases the problem occurred in a control run. In these cases the DE' value for control adjustment purposes was set to 0.0. Negative DE values were plotted as zeros in Figures 4 and 5. Tests #11 and #12 (Endicott on-tank emulsion with Corexit 9500) and tests #14 and #15 (IFO 30 mechanical emulsion and Corexit 9500) were duplicate tests (same oil and dispersant). The DE values for the Endicott tests were similar (6.5 % and 12.8%) but there was a significant difference in the IFO 30 test results (9.6% and 31.4%). While it is not known for certain what the cause of the discrepancy is, it is possible that it is also due to the methods used to determine the water content in oil sampled at the end of the test, as described above.

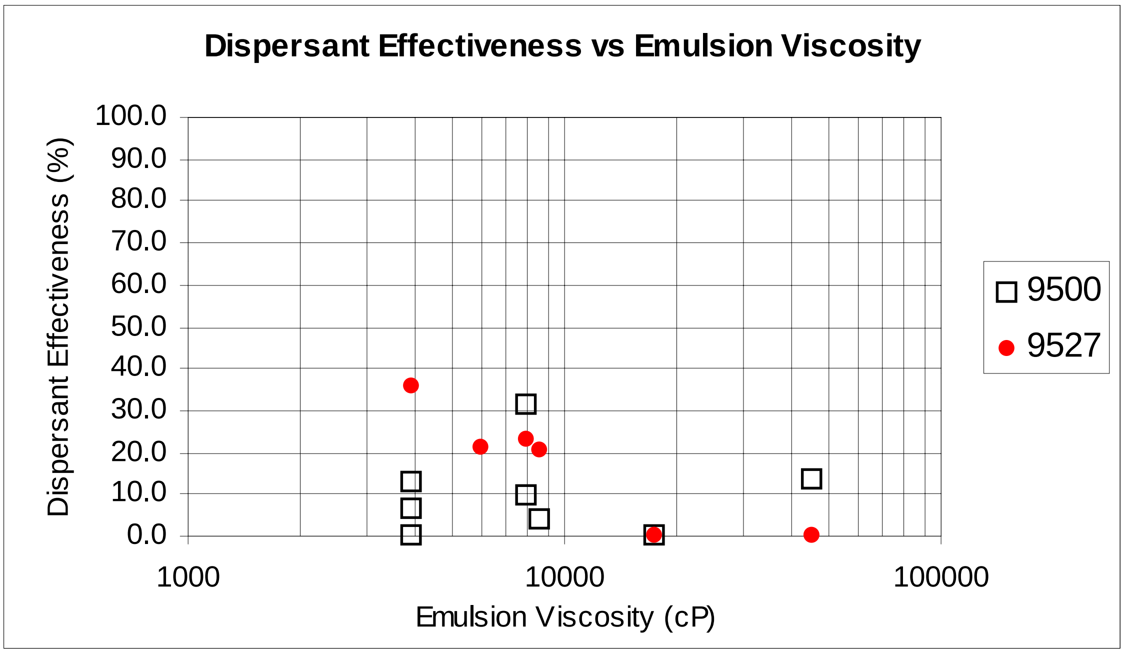

Figure 4 Dispersant Effectiveness vs Emulsion Viscosity in Ohmsett Tank Tests

In the large-scale tests Corexit 9527 was consistently but marginally more effective (DE between 20 and 35) than Corexit 9500 (DE between 0 and 13) on the emulsions with viscosities less than 10000 cP. However, Corexit 9500 was more effective on the most viscous oil tested (Sockeye on-tank 45,500 cP). Additional data is needed to confirm these possible trends.

Table 4 Test Condition and Results Summary for Ohmsett Tank Tests

Oil	Air Temp °C	Oil Temp °C	Water Temp °C	Emulsion Volume (liters)	Emulsion Viscosity $10s^{-1}$ 3.5°C	Dispersant Type	DOR	DE' (%)	DE (%)	Visual Dispersion Rank at times shown (minutes)			Links to Video Segments	Test #
										0-5	5–10	10-20		
Sockeye														
On-Tank Emulsion	2.8	2.2	0.6	90.8	45,500	Control	0	7.7	0.0	-	-	1		1
On-Tank Emulsion	3.9	2.8	2.8	75.7	45,500	9500	18	21.4	13.7	1	1	-	Test6.mpg	6
On-Tank Emulsion	2.2	4.4	2.8	76.5	45,500	9527	17	5.4	0.0	-	1	1	Test5.mpg	5
Mechanical Emulsion	2.8	3.3	2.8	73.8	8638	9500	18	3.6	3.6	3-4	1	1	Test7.mpg	7
Mechanical Emulsion	2.2	3.3	2.8	77.6	8638	9527	11	20.3	20.3	3	1	1	Test8.mpg	8
Endicott														
On-Tank Emulsion	-5.0	-6.1	1.7	73.8	3920	Control	0	22.8	0.0	1	1	1	Test9.mpg	9
On-Tank Emulsion	-1.7	5.6	2.2	74.2	3920	9500	11	29.3	6.5	3	3	1	Test11.mpg	11
On-Tank Emulsion	-2.2	3.3	2.2	79.5	3920	9500	10	35.6	12.8	3-4	2	1	Test12.mpg	12
On-Tank Emulsion	-3.9	-6.7	2.2	74.9	3920	9527	14	58.3	35.5	3-4	1	1	Test10.mpg	10
Mechanical Emulsion	2.8	3.3	3.3	81.4	6069	Control	0	-42.5	0.0	-	1	1	-	2
Mechanical Emulsion	2.8	0.0	3.3	77.6	6069	9500	12	0.2	0.2	2-3	1-2	1	Test3.mpg	3
Mechanical Emulsion	2.8	-0.6	0.6	75.7	6069	9527	6	20.8	20.8	3	1-2	1	Test4.mpg	4
IFO 30														
Mechanical Emulsion	-5.6	5.0	1.1	73.8	7895	Control	0	-1.8	0.0	1	1	1	Test13.mpg	13
Mechanical Emulsion	-5.0	4.4	1.1	70.0	7895	9500	22	31.4	31.4	3	2	1	Test14.mpg	14
Mechanical Emulsion	-4.4	3.3	1.1	70.8	7895	9500	14	9.6	9.6	-	-	-	Test15.mpg	15
Mechanical Emulsion	-2.2	1.7	1.1	77.6	7895	9527	21	22.7	22.7	3	2	1	Test16.mpg	16
IFO 120														
Mechanical Emulsion	0.0	5.0	0.6	77.6	17,322	Control	0	-11.7	0.0	1	1	-	Test19.mpg	19
Mechanical Emulsion	-2.8	5.6	0.6	75.3	17,322	9500	28	-8.1	0.0	1	1	1	Test17.mpg	17
Mechanical Emulsion	-1.1	6.7	0.6	74.6	17,322	9527	26	-31.5	0.0	1	1	1	Test18.mpg	18

Note: DE' is the dispersant effectiveness estimate prior to accounting for oil lost in the control run.

4.4 In-Water Oil Concentration Characterization

A LISST particle size analyzer was deployed throughout the test program to measure dispersed oil drop size distributions and concentrations. The peak oil concentration measured by the LISST during each test is reported in Table 5 along with the typical oil drop size Volume Median Diameters (VMD) or d50's measured during these peak concentrations. Graphs of oil concentration and drop size VMD as a function of time are provided in Appendix A. The graphs can be accessed by clicking on the hypertext links associated with the Test # identifier in Table 5.

Table 5 In-Water Oil Concentration and Volume Median Oil Drop Sizes

Oil	Emulsion Viscosity $10s^{-1}$ 3.5°C	Disperant Type	DOR	DE' (%)	DE (%)	LISST Peak Oil Conc.[1] (ppm)	VMD Range in Peak Oil Conc. (microns)	Test #
Sockeye								
On-Tank Emulsion	45,500	Control	0	7.7	0.0	40	75 to 250	1
On-Tank Emulsion	45,500	9500	18	21.4	13.7	50	<20	6
On-Tank Emulsion	45,500	9527	17	5.4	0.0	150	<25	5
Mechanical Emulsion	8638	9500	18	3.6	3.6	100	75 to 250	7
Mechanical Emulsion	8638	9527	11	20.3	20.3	150	75 to 250	8
Endicott								
On-Tank Emulsion	3920	Control	0	22.8	0.0	Background	<50	9
On-Tank Emulsion	3920	9500	11	29.3	6.5	100	75 to 350	11
On-Tank Emulsion	3920	9500	10	35.6	12.8	150	<25	12
On-Tank Emulsion	3920	9527	14	58.3	35.5	150	25 to 175	10
Mechanical Emulsion	6069	Control	0	-42.5	0.0	175	275 to 350	2
Mechanical Emulsion	6069	9500	12	0.2	0.2	50	<50	3
Mechanical Emulsion	6069	9527	6	20.8	20.8	75	<50	4
IFO 30								
Mechanical Emulsion	7895	Control	0	-1.8	0.0	Background	25 to 50	13
Mechanical Emulsion	7895	9500	22	31.4	31.4	75	<50	14
Mechanical Emulsion	7895	9500	14	9.6	9.6	125	<25	15
Mechanical Emulsion	7895	9527	21	22.7	22.7	150	25 to 200	16
IFO 120								
Mechanical Emulsion	17,322	Control	0	-11.7	0.0	Background	<25	19
Mechanical Emulsion	17,322	9500	28	-8.1	0.0	100	25 to 50	17
Mechanical Emulsion	17,322	9527	26	-31.5	0.0	250	25 to 50	18
Corexit 9500 - No Oil	-	9500	-	-	-	1200	275 to 325	20

[1]Background oil concentration readings were typically about 15 ppm.

In tests with a high dispersant effectiveness the peak oil concentrations measured should be well above the background level and the oil drops measured during the periods of peak oil concentration should be small (VMD's less than 75 microns). In tests with low dispersant effectiveness the opposites should be true (low peak oil concentration and/or large VMD drop size distributions). Unfortunately the in-water oil concentration measurements are not continuous in time and space so maximum oil concentrations in the water in any given test may or may not be recorded. Comparison of peak oil concentrations from test to test may not be a good discriminator of overall dispersant effectiveness. Small oil drop sizes in conjunction with elevated oil concentrations should correlate more closely with dispersant effectiveness. The results of Table 5 will be discussed with these thoughts in mind.

In all but two of the control tests (tests #1 and #2) the LISST did not detect any significant peaks in oil concentrations above background levels, therefore no significant dispersion of oil was detected. In control tests #1 and #2 elevated oil concentrations were recorded but the oil drop size distributions had large VMDs suggesting that the oil that was measured was only temporarily dispersed.

For the Sockeye emulsions, tests #5 and #6 had similar LISST results with both elevated concentrations and small oil drops during the period of elevated concentration. This would suggest that an elevated DE might have been measured in both of these tests. However, the measured DE for test #6 (Corexit 9500) was higher than test #5 (Corexit 9527). Tests #7 and #8 also had similar LISST results with elevated oil concentrations but with large oil drop sizes during the time of elevated concentrations. This suggests that both of these tests should have had similarly low DE results. However, test #8 (Corexit 9527) had a higher measured DE than test #7 (Corexit 9500) and a similar DE to test #6. It would appear that for tests with marginal DE that either the estimates for DE are not refined enough to properly distinguish between tests or the LISST data by itself are not a good indicator of the final DE. The type of dispersant used did not appear to significantly affect the outcome of the tests.

For the Endicott emulsions a similar comparison with similar results can be made using tests #12, #3 and #4. All of these tests had elevated in-water oil concentrations and small VMD oil drop distributions that should have led to elevated DE results. Test #12 and #4 had elevated DE values but test #3 did not. Endicott test #10 had the highest recorded DE (35.5%) but the oil drop sizes measured in this run were not consistently small when the oil concentration was high.

The same lack of trends is seen with the IFO 30 emulsions. Tests #14 and #15 both had LISST measurements that should be consistent with an elevated DE but only test #14 had a significant DE result. Test #16 had larger oil drops at the times of elevated oil concentrations than both #14 and #15 but the measured DE was greater than test #15.

The LISST oil concentration measurements for the IFO 120 emulsions are puzzling. The oil drop size distributions remained similar to background in both of the tests (test #17 and #18) with VMDs in the 25 to 50 micron range. Some of the highest oil concentration peaks were recorded in test #18 yet the DE measurements and visual observations both suggest no oil dispersion at all for this viscous emulsion (17,322 cP). When this was noticed during the test program the possibility that the dispersant might be influencing the LISST results was discussed and a final test was completed to investigate this possibility. In test #20 dispersant was sprayed onto the tank without an oil slick and the LISST was towed through the dispersant cloud. As can be seen test #20's graph of "oil concentration versus time" the peak concentrations recorded at the end of the test (values actually reached in excess of 1200 ppm) greatly exceeded those of all other tests but the drop sizes also exceeded those measured in all other tests (up to 375 microns). If the dispersant was influencing the oil concentration signal in the IFO 120 emulsion tests #17 and #18 then the drop size VMD's should also have been elevated in those tests (as in test #20) but they were not. The results of test #20 suggest that the LISST may be detecting dispersant in the water but the large drop sizes and high concentrations measured confuse the issue since these large values were not detected in any of the other 14 spray runs. More study is needed to determine the validity of test #20's results. The LISST's optical surfaces may have been contaminated in the latter stages of this test thus influencing the results. The Lisst operator did not notice the high concentration readings during the actual test and concluded that the dispersant was not affecting the performance of the LISST.

As described above, the oil concentration and drop size measurements did not consistently correlate with the measured dispersant effectiveness. This is in contrast to other dispersant effectiveness tests completed where there was a good correlation (SL Ross 2006b). The poor correlation in this study may have been because the LISST device is only recording a portion of the dispersed oil cloud in each pass and with the poor oil dispersion encountered in this test program the dispersed oil cloud was patchier than in other tests. As a result the LISST data may not be representative of the overall dispersion in these tests in all cases.

4.5 Visual Dispersion Estimates

A visual estimate of the dispersion outcome for each test was made using the method developed by Lewis (2004) during the 2003 U.K. dispersant trials completed in the English Channel. The reporting system developed by Lewis is shown in Table 6. The visual effectiveness estimates made during the current study are reported in Table 4. The visual assessments were made at three times during the test period: in the first 5 minutes of the test, between 5 and 10 minutes and at 10 to 20 minutes into the test.

Table 6 Method for Visually Assessing and Reporting Dispersant Effectiveness

Rank	Standard Phrase	Description
1	No obvious dispersion	Dispersant being washed off the black oil as white, watery solution leaving oil on surface. Quantity of oil on sea surface not altered by dispersant
2	Slow or partial dispersion	Some surface activity (oil appearance altered). Spreading out of oil. Larger droplets of oil (1 mm in diameter or greater) seen rapidly rising back to sea surface, but overall quantity appears to be similar to that before dispersant spraying
3	Moderately rapid dispersion	Quantity of oil visibly less than before spraying. Oil in some areas being dispersed to leave only sheen on sea surface, but in other areas still some oil present.
4	Very rapid and total dispersion	Oil rapidly disappearing from surface. Light brown plume of dispersed oil visible in water under the oil and drifting away from it

The common result in all of the observations was a dispersion rank of 1 at the end of all tests. This indicates that significant dispersion did not continue through to the end of any of the tests. Moderately rapid (rank 3) or very rapid (rank 4) dispersion of oil was noted in nine of the tests over the first five minutes. In five of these nine tests the estimated DE (20% or greater) was significantly greater than the tests with an initial ranking of 1 that had estimated DE's of 0 to 13.7%. This suggests that the visual ranking was successful in qualitatively differentiating the dispersant effectiveness in only 55% of the tests. The four "false positive" visual rankings (tests #7, #11, #12 and #3) all occurred in tests where Corexit 9500 was used. The reason for this is not clear. The trends in the LISST oil drop size and concentration results do not provide a clear explanation for the false positive results.

5. Comparison of Small-scale and Large-scale Test Results

A summary of the test conditions and test outcomes for both the small- and large-scale tests are provided in Table 7. Figure 5 shows a comparison of the results from the two facilities for the mechanically generated emulsions. The results from the Ohmsett tank tests are generally higher than those from the SL Ross tank (with one significant outlier). These higher DE values from Ohmsett are likely due to the higher wave energies that are achieved at Ohmsett when compared to the SL Ross tank. A direct comparison of emulsion viscosities between the two test series is not possible as different shear rates and temperatures were used in the viscosity measurements. Lower temperatures were used in the Ohmsett test measurements because the water temperature during the December tests was much lower than had been anticipated when the small-scale testing was completed. The emulsion viscosities were measured at temperatures close to the test water temperatures in both test series.

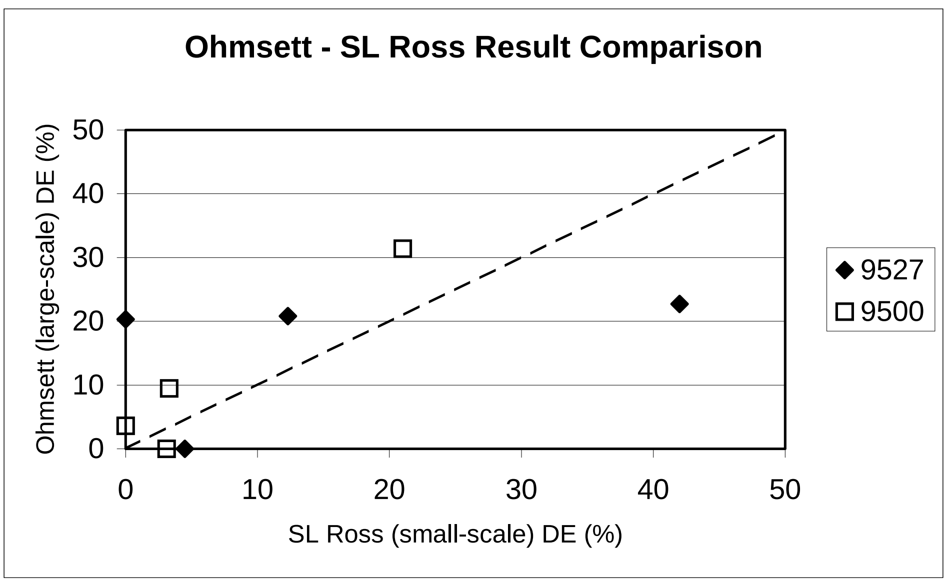

Figure 5 Comparison of Ohmsett (large-scale) and SL Ross (small-scale) DE Results

Table 7. Summary of Small- and Large-Scale Testing Results

Oil	% Water (vol)	Method of Emulsion Preparation	Viscosity (cP)				SL Ross Tank Testing DE (%)		Ohmsett Testing DE (%)			
							Corexit 9527 DOR 1:20	Corexit 9500 DOR 1:20	Corexit 9527		Corexit 9500	
			15°C 2 s^{-1}	15°C 30 s^{-1}	3.5°C 10s^{-1}	3.5°C 100s^{-1}			DOR	DE	DOR	DE
Endicott	50	Paint stirrer		2,630			12.3	3.3				
Endicott	56	Mechanical			6,069	2,624			1:6	20.8	1:12	0.2
Endicott	48	On-tank			3,920	1,973			1:14	35.5	1:11	6.5
Endicott	48	On-tank			3,920	1,973					1:10	12.8*
Sockeye	50	Paint stirrer	11,600				0	0				
Sockeye	56	Mechanical			8,638	5,419			1:11	20.3	1:18	3.6
Sockeye	48	On-tank			45,500	-			1:17	5.4	1:18	13.7
IFO 30	50	Paint stirrer		1,880			42	21				
IFO 30	55	Mechanical			7,895	4,670			1:21	22.7	1:22	31.4
IFO 30	55	Mechanical			7,895	4,670					1:14	9.6*
IFO 120	50	Paint stirrer	29,370				4.5	3.1				
IFO 120	54	Mechanical			17,322	-			1:26	0.0	1:28	0.0

- repeat test

6. Conclusions

The results from the small-scale testing show trends in effectiveness as a function of emulsion viscosity and dispersant type. Emulsions with viscosities of 2630 cP and higher had negligible dispersion (less than 12%) when dispersant was applied at a 1:20 DOR. The highest dispersant effectiveness achieved on a water-in-oil emulsion in the small-scale tests was 42%. Corexit 9527 was marginally more effective than Corexit 9500 on the Endicott, IFO 30 and IFO 120, 50% water content emulsions. The fresh oils (prior to emulsification) were all dispersible with Corexit 9500, the only dispersant tested on these oils.

In the large-scale Ohmsett tests the dispersants were not effective on the emulsions with viscosities above 10,000 cP and were only marginally effective (less than 40%) on emulsions between 4000 and 10,000 cP.

In a number of the tests completed at Ohmsett the estimate of the amount of oil collected at the end of the test exceeded the amount released for the test. It is likely that errors in the measurements of the high water contents in the final collected emulsions are the causes of these discrepancies. Test samples were disposed of before these results could be confirmed.

Duplicate tests were completed for two test cases (Endicott on-tank emulsion with Corexit 9500) and IFO 30 mechanical emulsion and Corexit 9500). The DE values for the Endicott tests were similar (6.5 % and 12.8%) but there was a significant difference in the IFO 30 test results (9.6% and 31.4%). While it is not known for certain what the cause of the discrepancy is, it is possible that it is due to the methods used to determine the water content in oil sampled at the end of the test, as described above.

The methods used to determine the water contents of the collected emulsion samples in this study may have been the primary source of error affecting the dispersant effectiveness estimates. The methods used to determine water contents for high water content samples should be investigated and refined in future tests.

The oil concentration and drop size measurements made using the LISST particle size analyzer did not consistently correlate with the measured dispersant effectiveness. This is in contrast to other dispersant effectiveness tests completed where there was a good correlation (SL Ross 2006b). The poor correlation in this study may have been because the LISST device is only recording a portion of the dispersed oil cloud in each pass and with the poor oil dispersion encountered in this test program the dispersed oil cloud was patchier than in other tests. As a result the LISST data may not be representative of the overall dispersion in these tests in all cases.

Visual ranking of dispersant effectiveness was successful in qualitatively differentiating the dispersant effectiveness in only 55% of the tests. The four “false positive” visual rankings (tests #7, #11, #12 and #3) all occurred in tests where Corexit 9500 was used. The reason for this is not clear. The trends in the LISST oil drop size and concentration results do not provide a clear explanation for the false positive visual results.

The dispersant effectiveness estimates from the Ohmsett tank tests are generally higher than those from the SL Ross tank for the mechanical emulsions of the same oils. These higher DE values from Ohmsett are likely due to the higher wave energies that are achieved at Ohmsett when compared to the SL Ross tank.

7. References

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SL Ross. 2006b. Dispersant Effectiveness Testing In Cold Water On Four Alaskan Crude Oils. Report to U.S. Minerals Management Service, 2006

Appendix A. Dispersed Oil Drop Size Distributions and Concentration

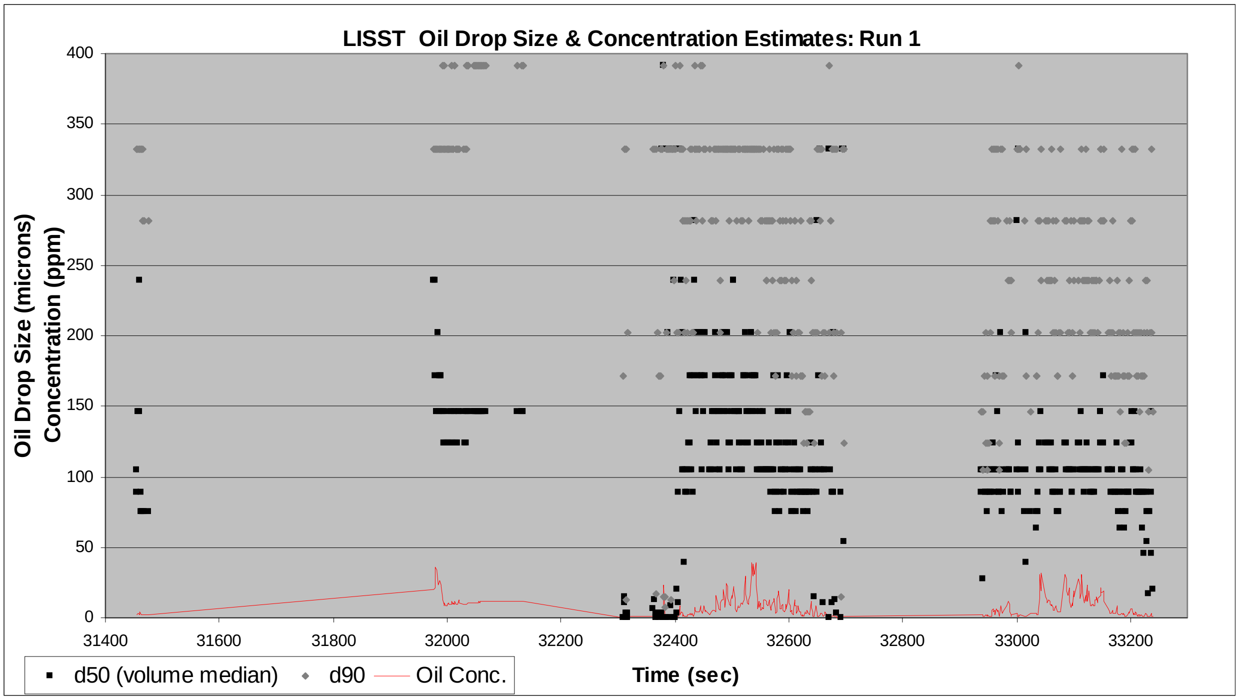
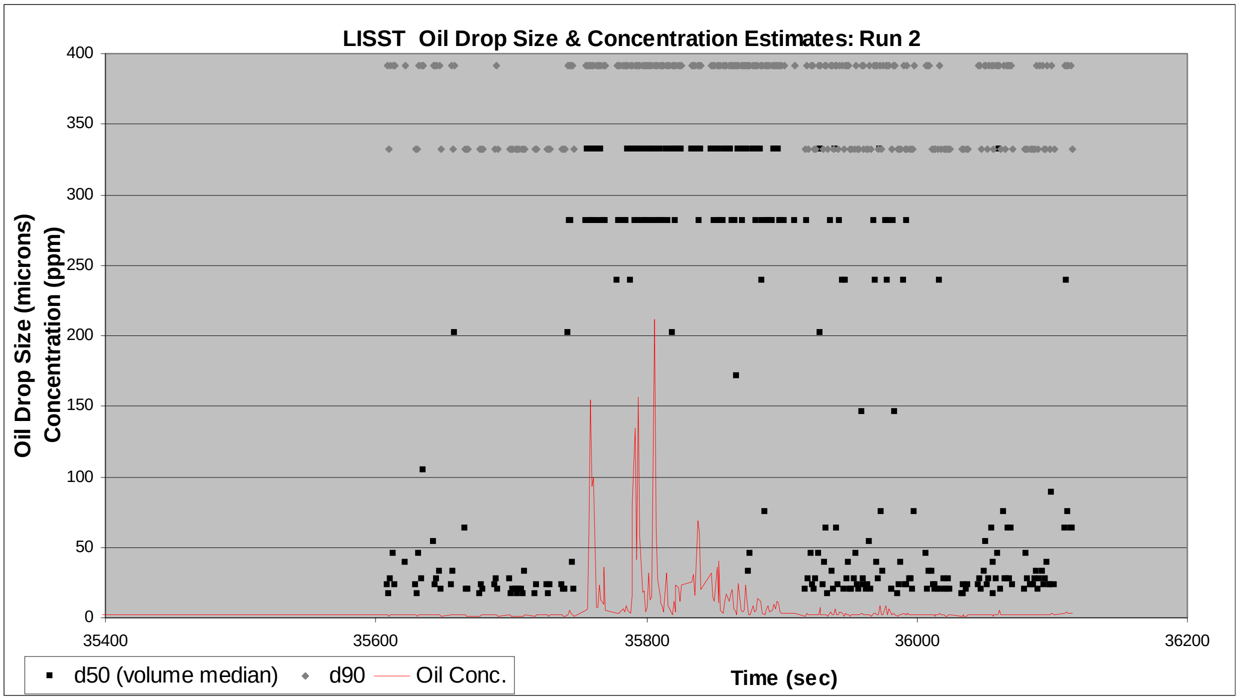


Figure A1 Test 1



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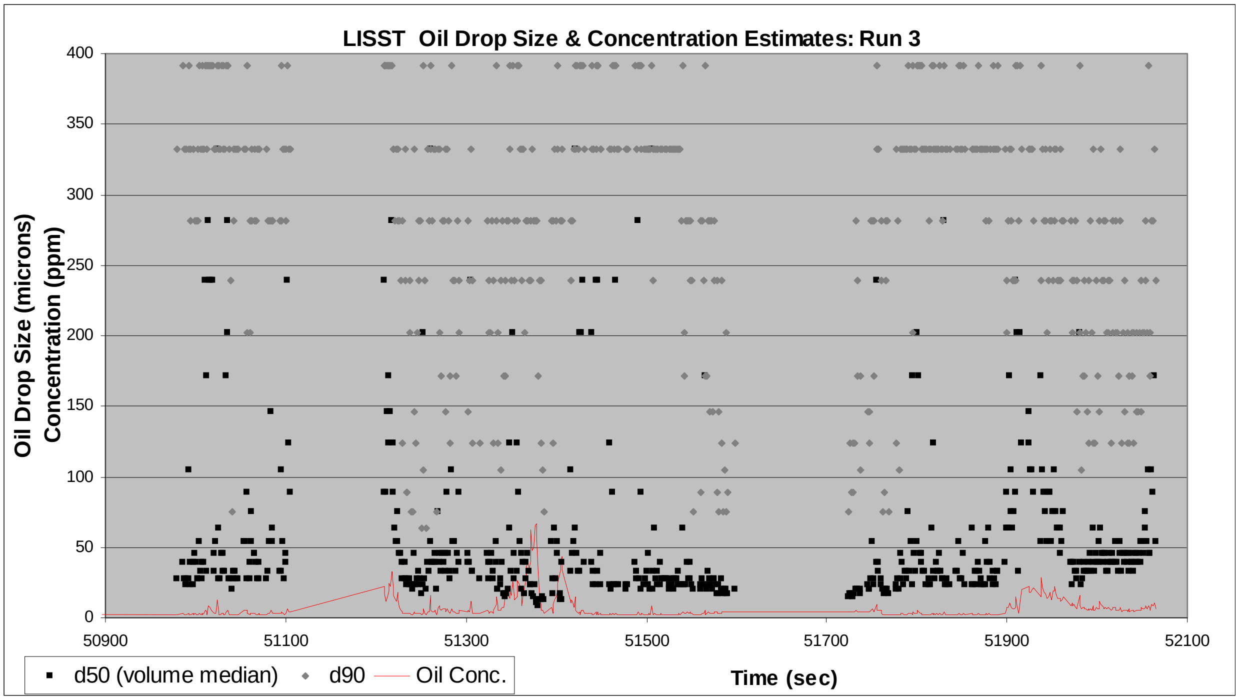

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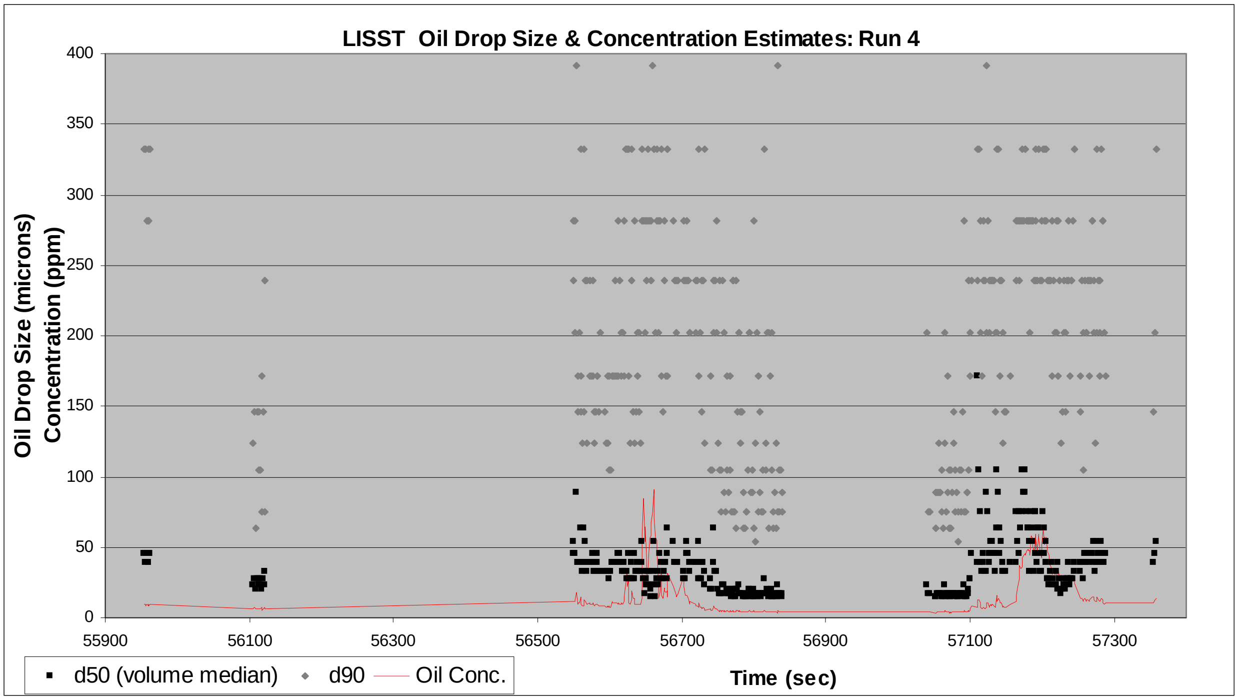
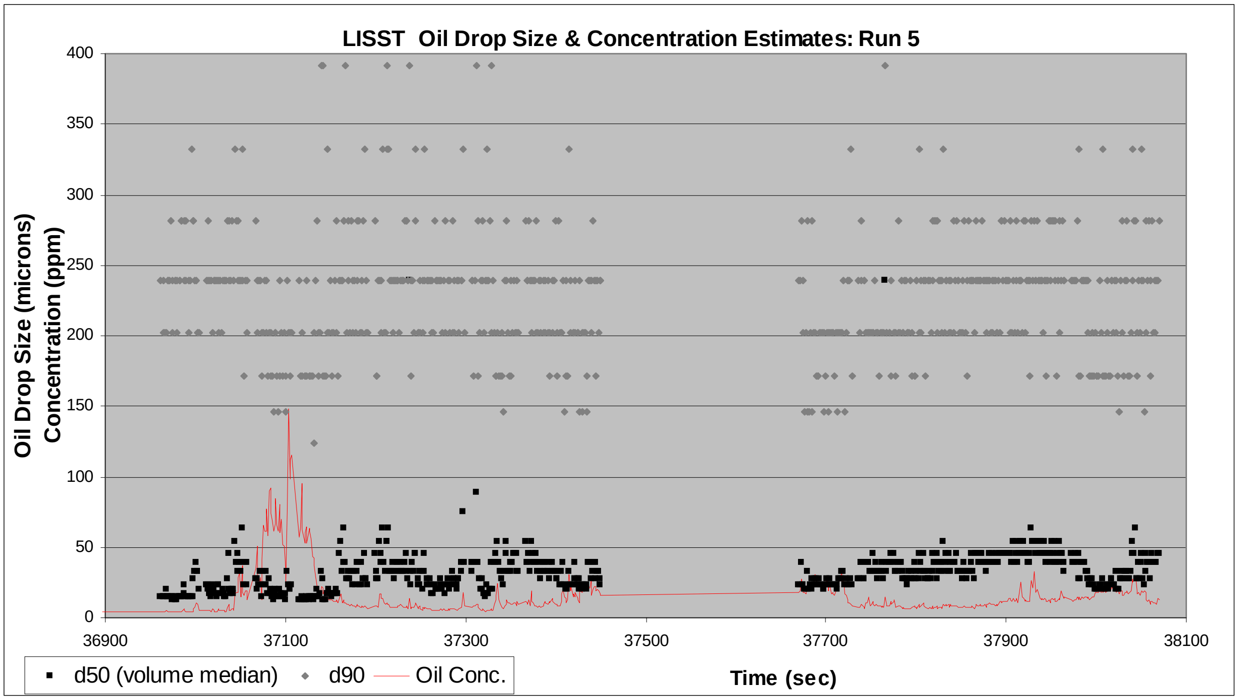


Figure A4 Test 4



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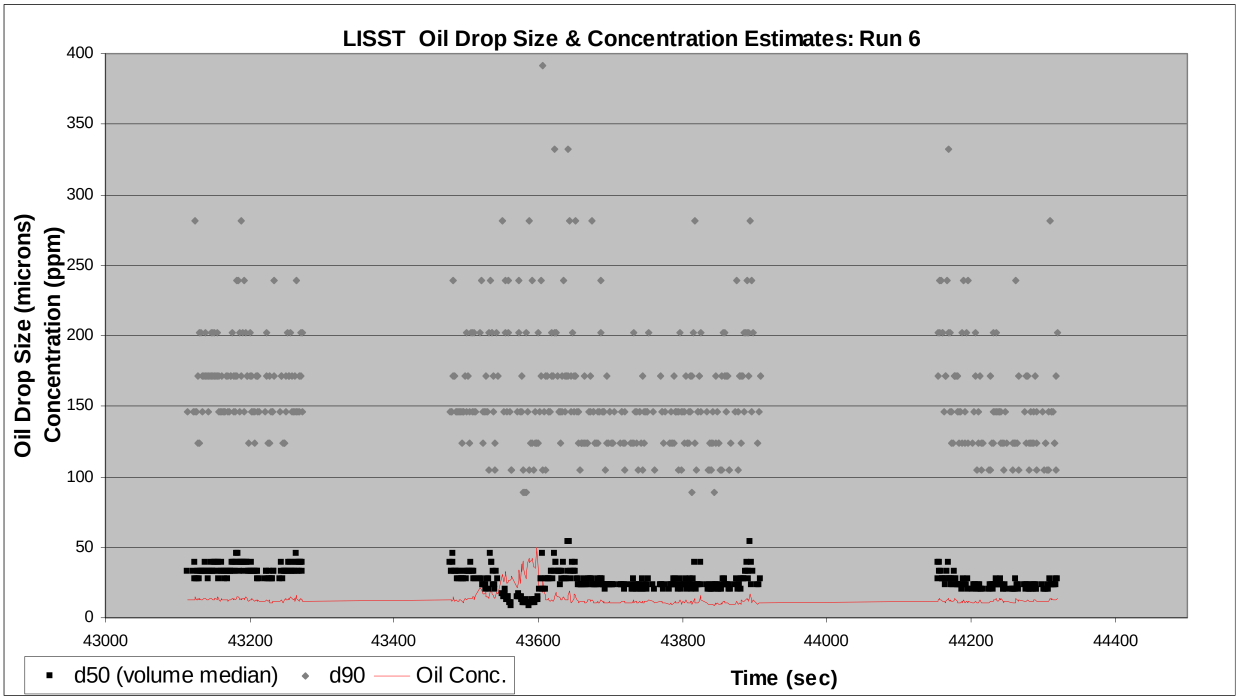

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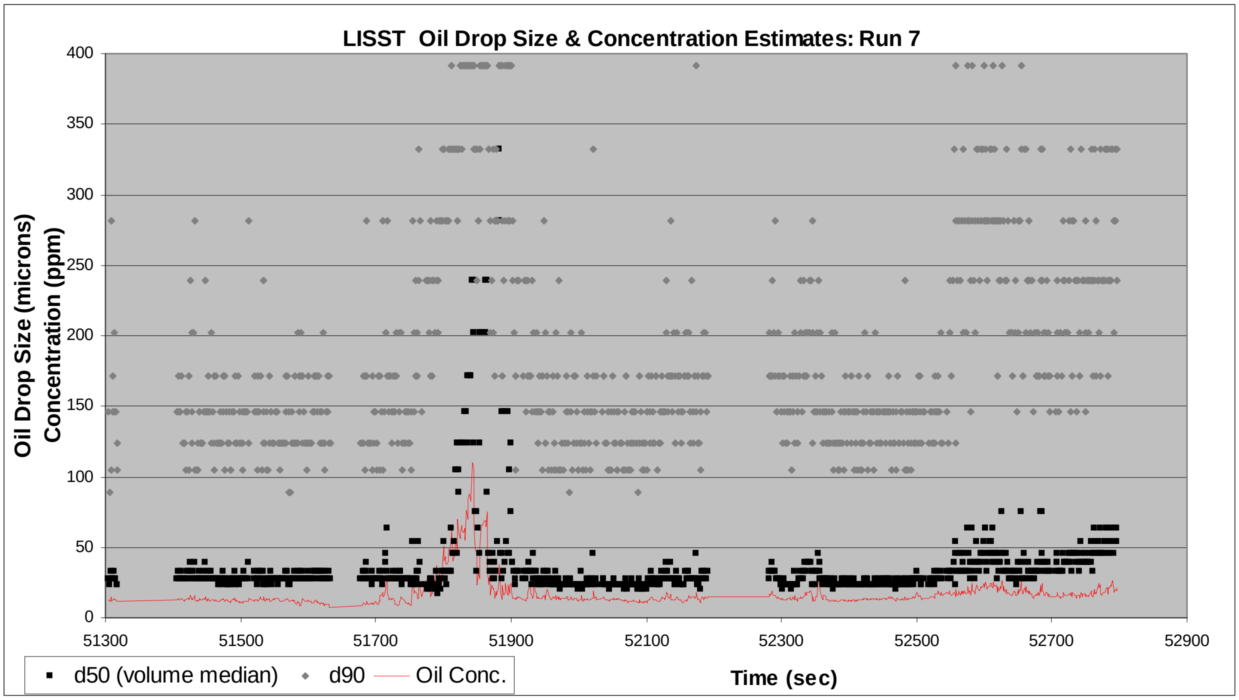
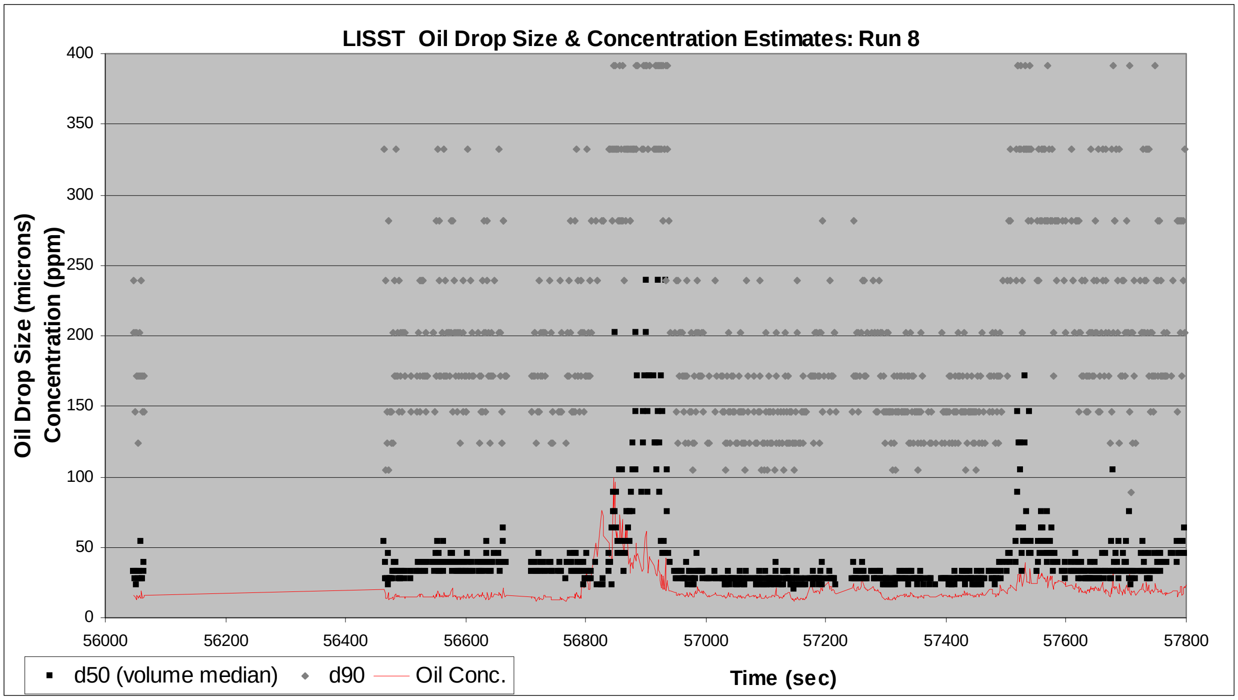


Figure A7 Test 7



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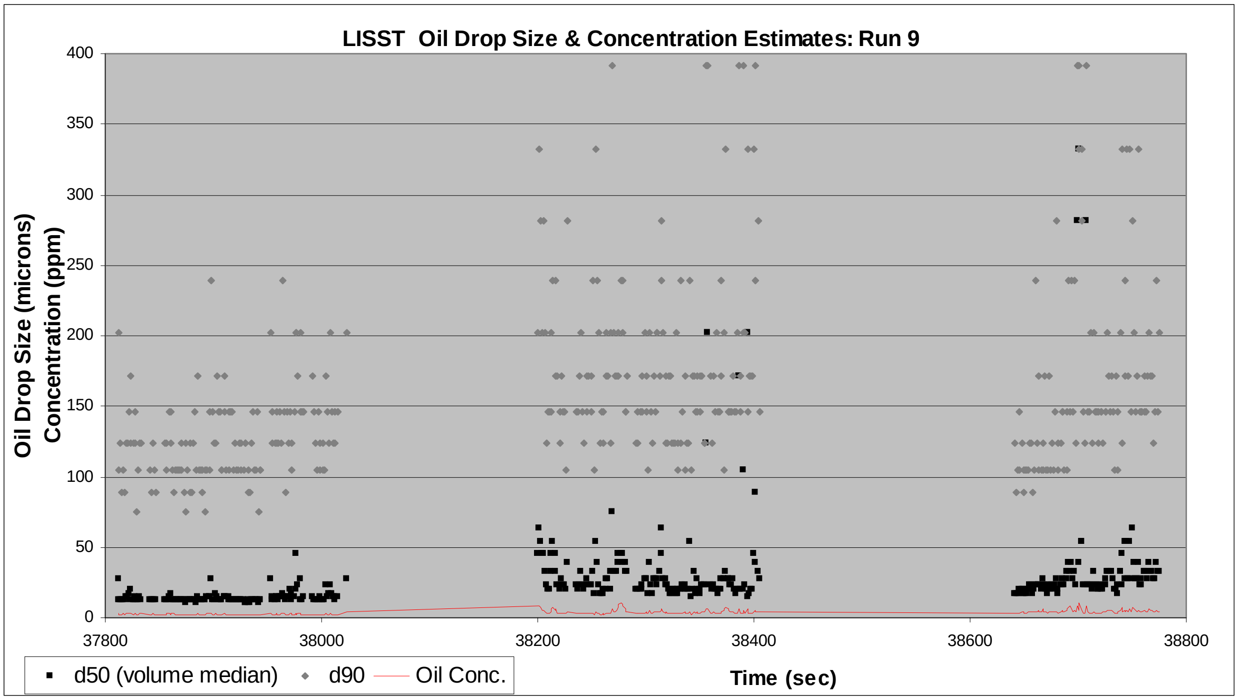

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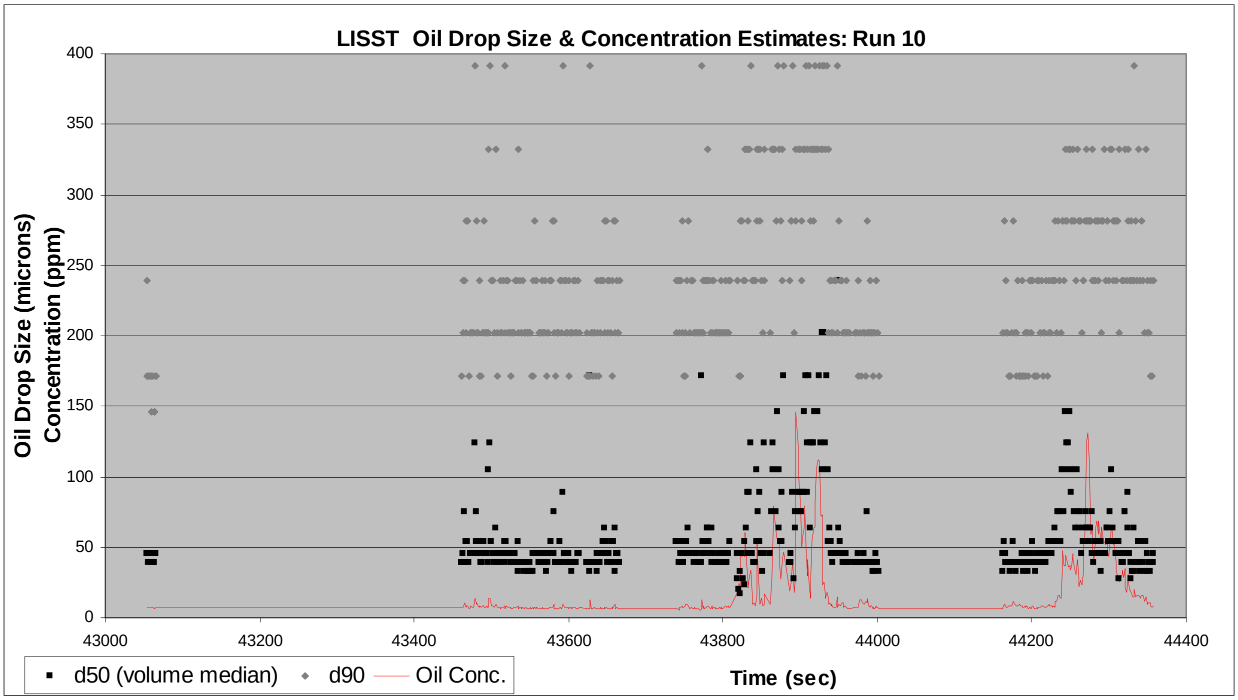
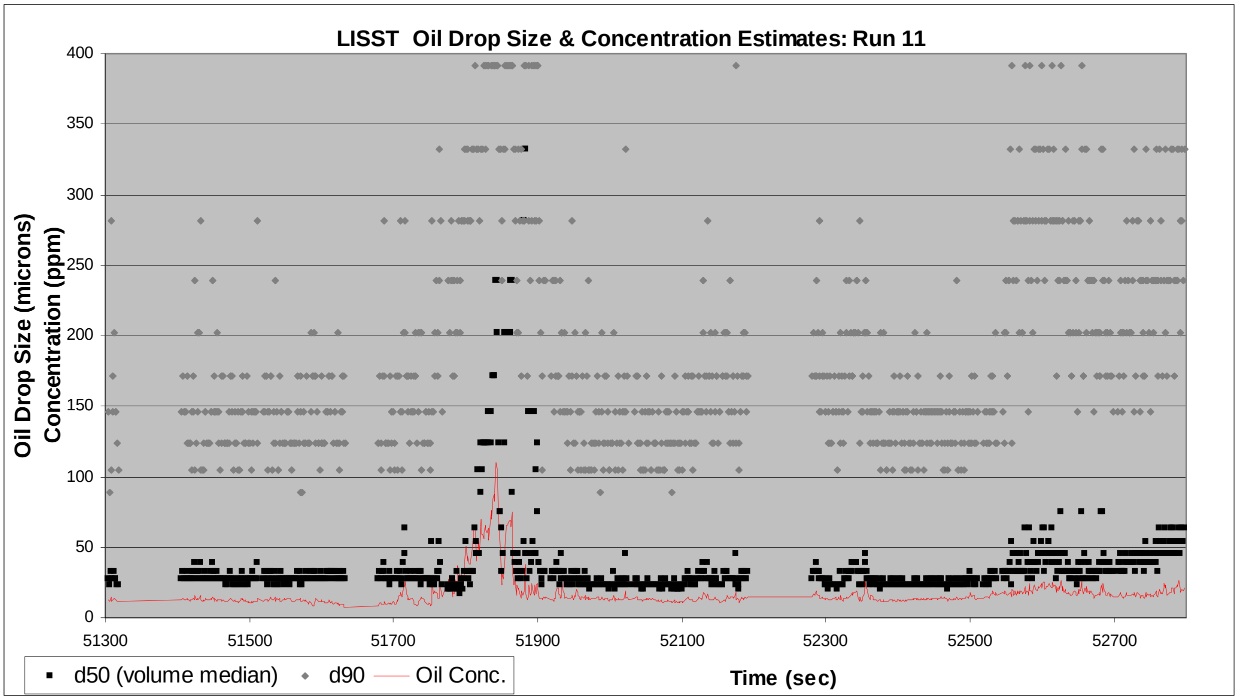


Figure A10 Test 10



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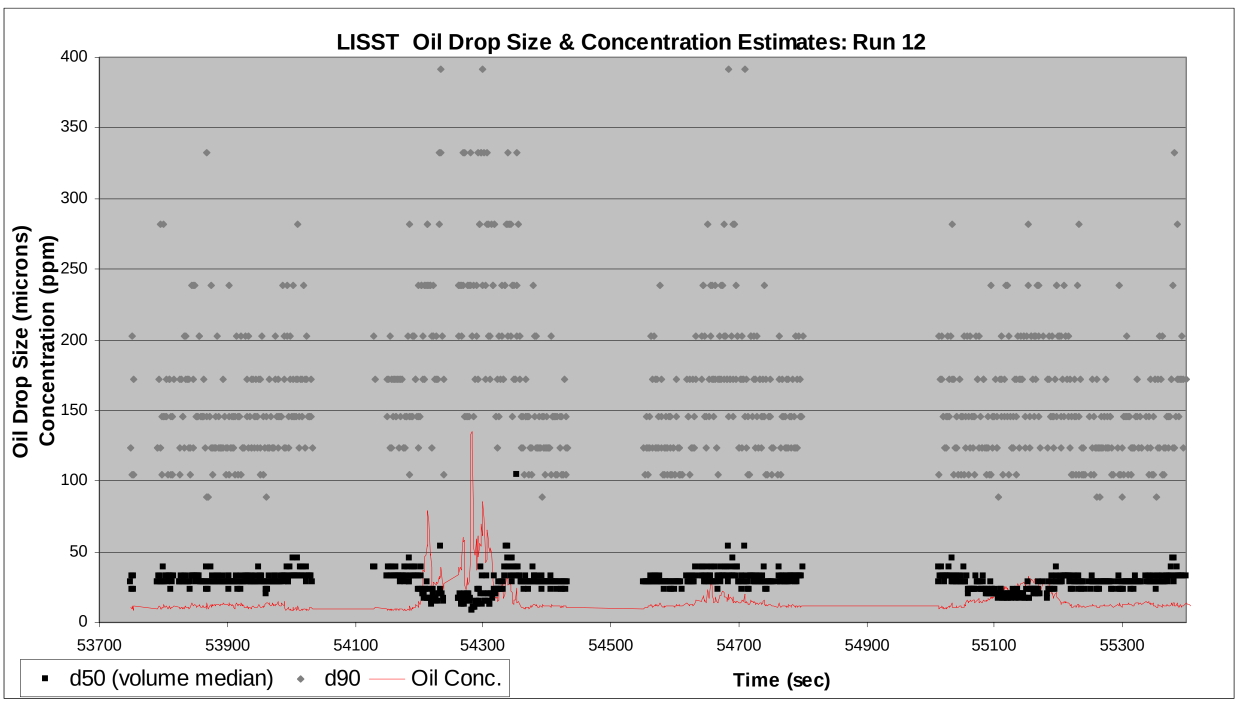


Figure 12 Test 12

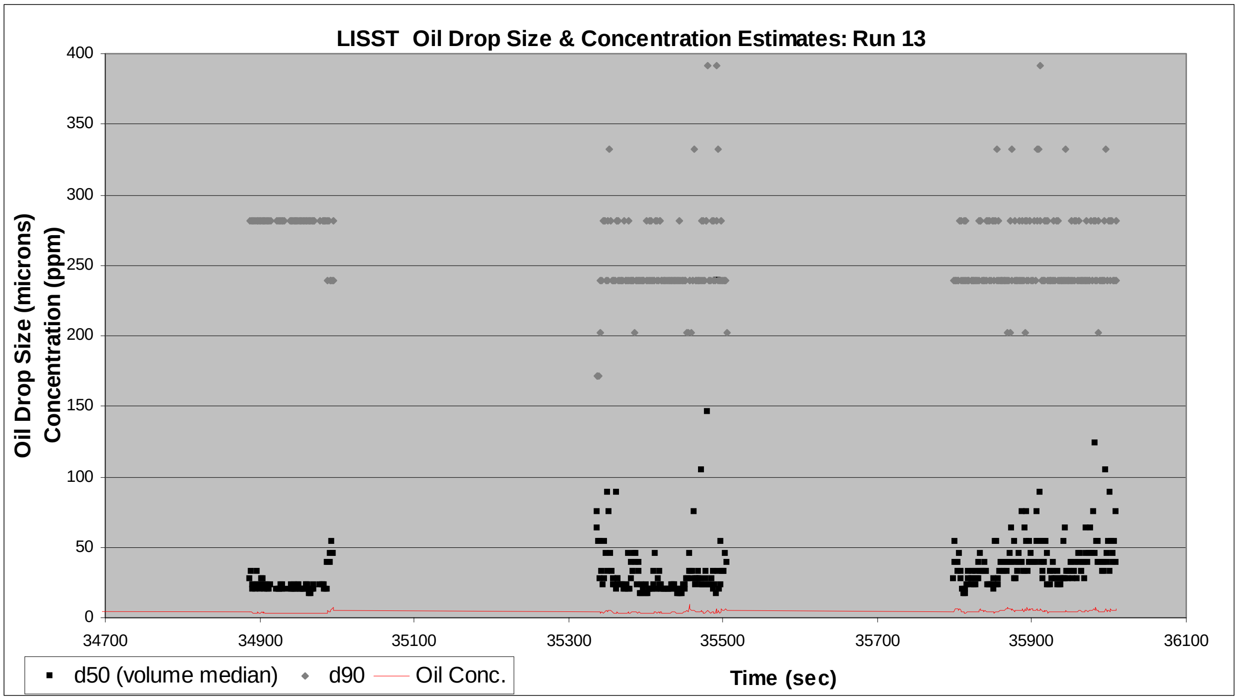
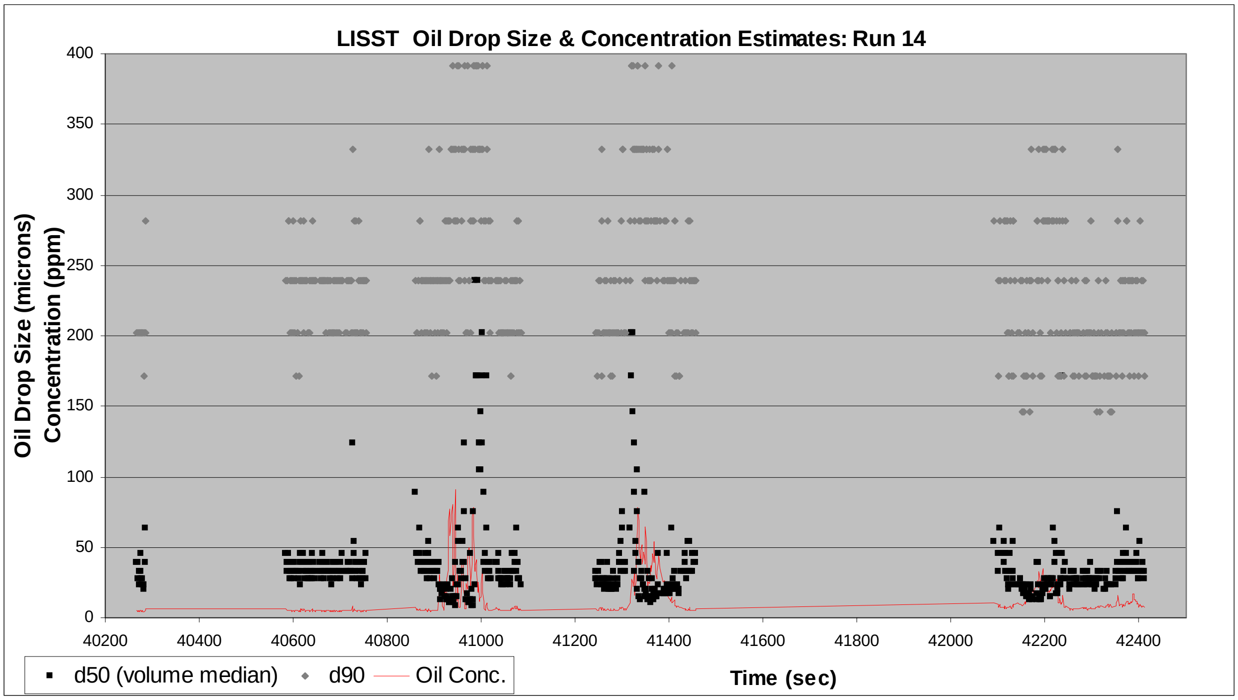


Figure A13 Test 13



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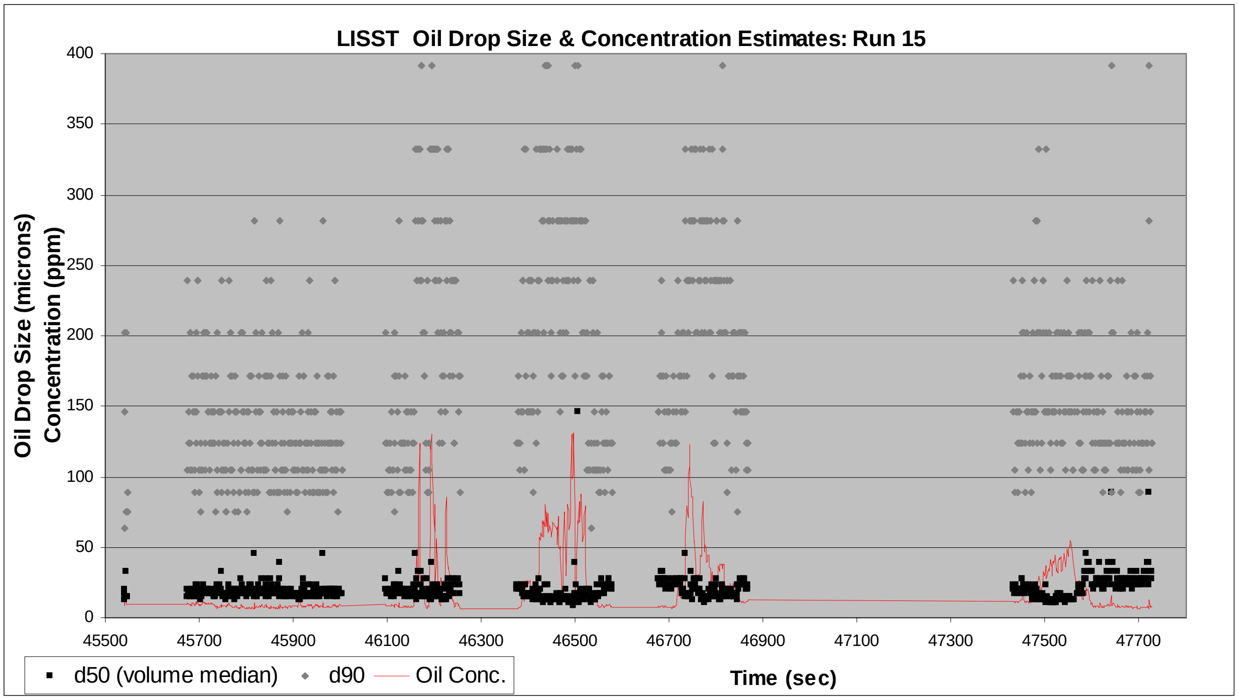

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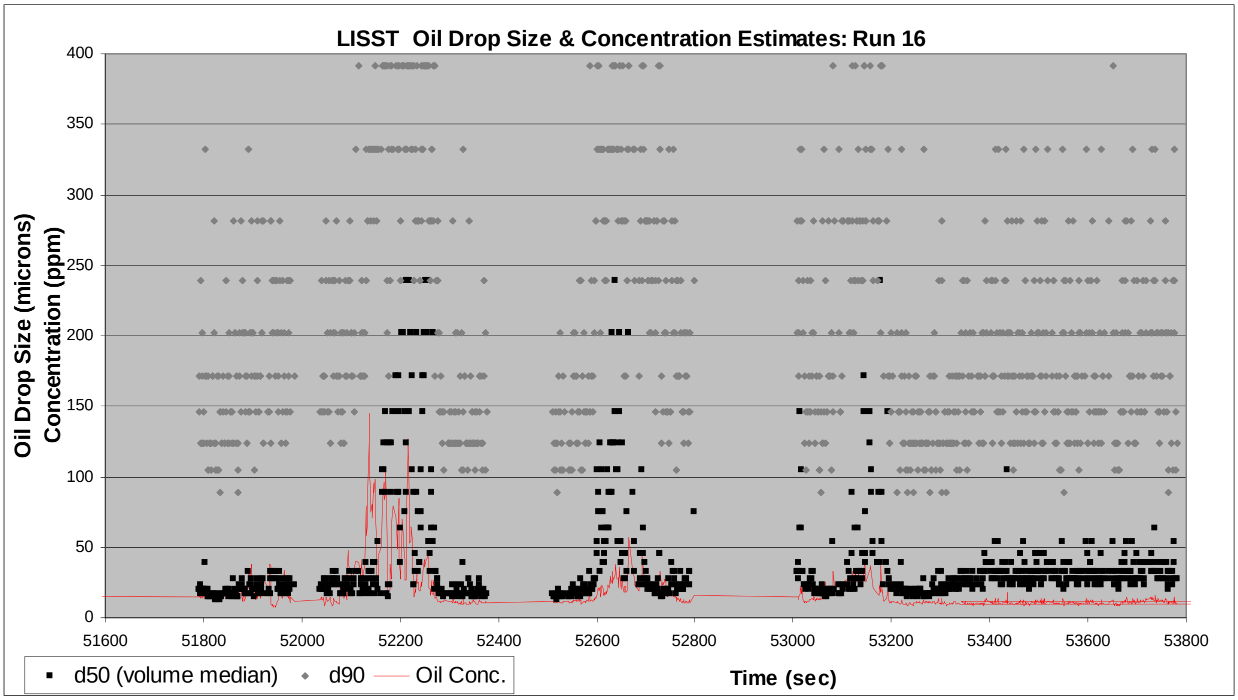


Figure A16 Test 16

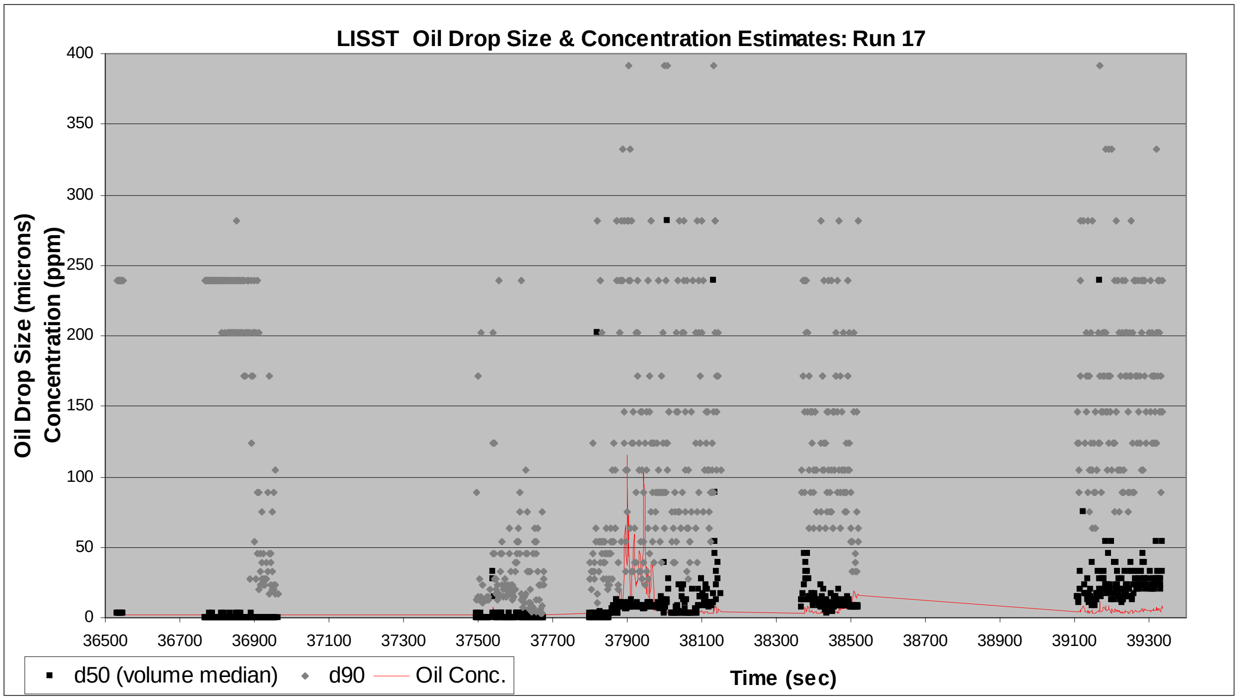


Figure A17 Test 17

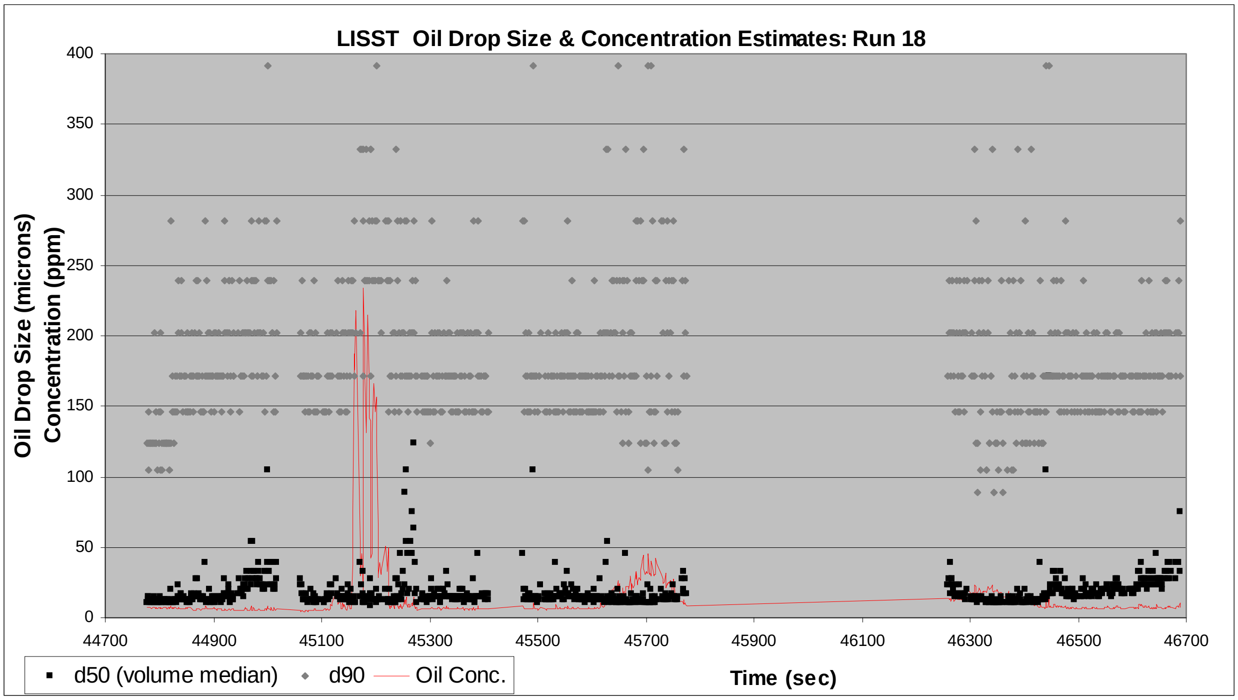


Figure A18 Test 18

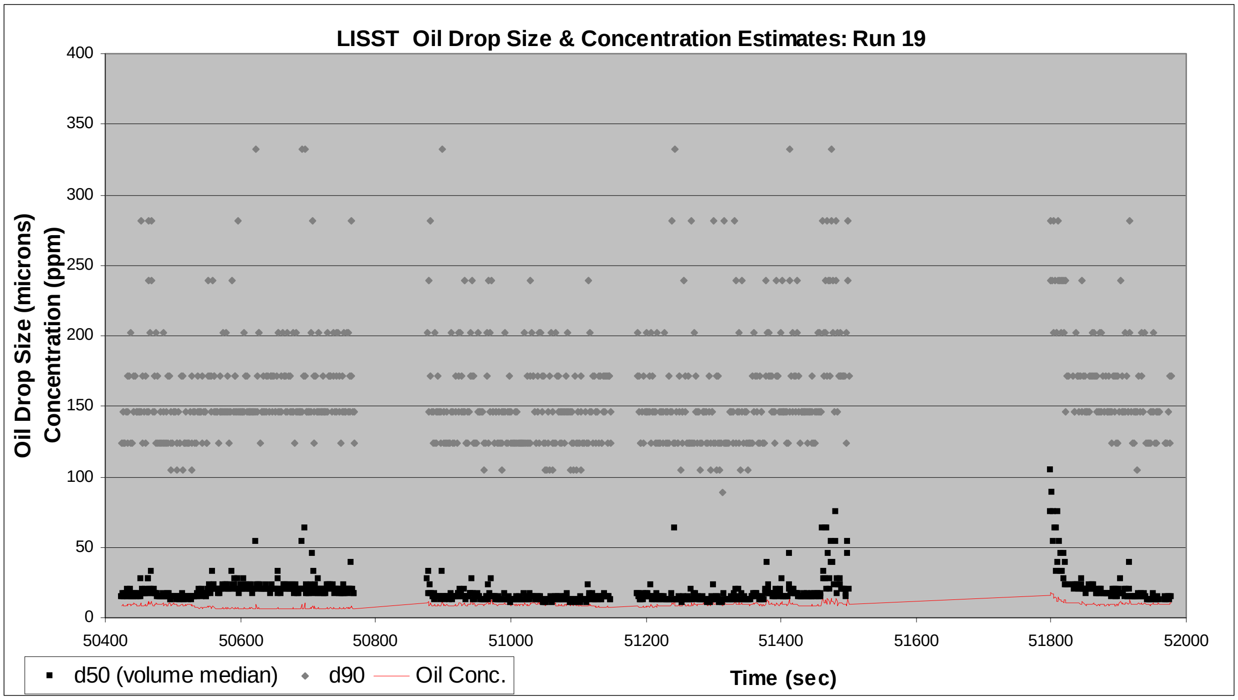


Figure A19 Test 19

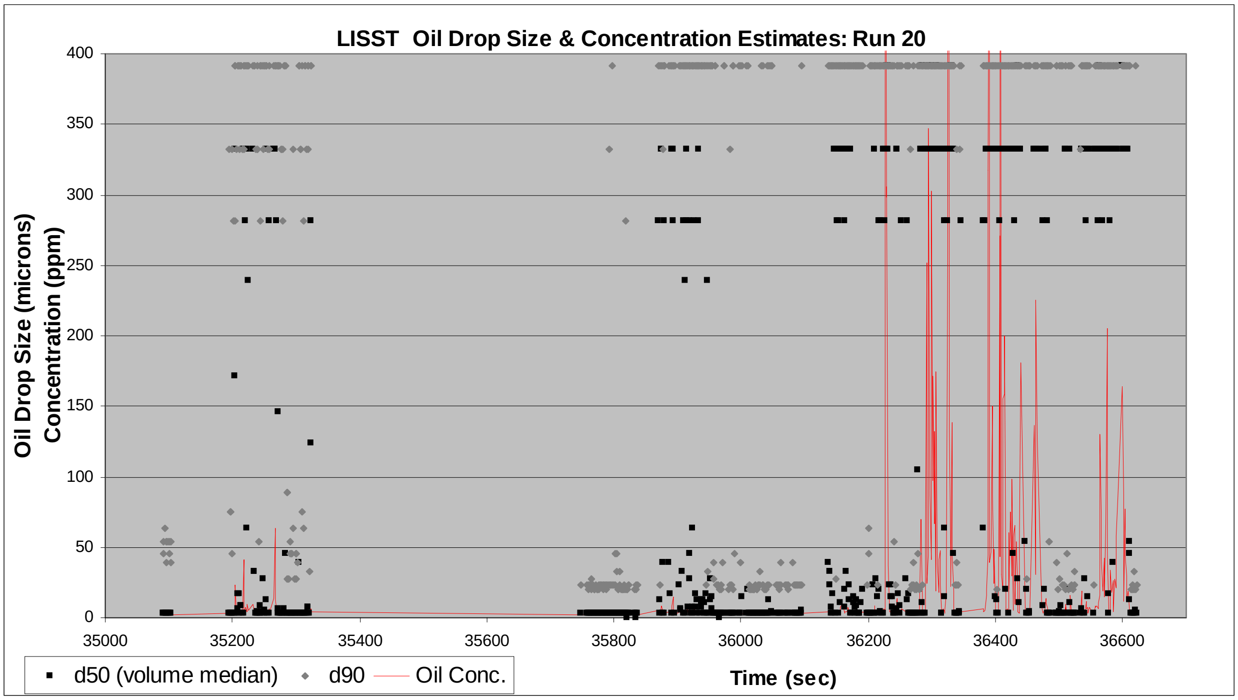
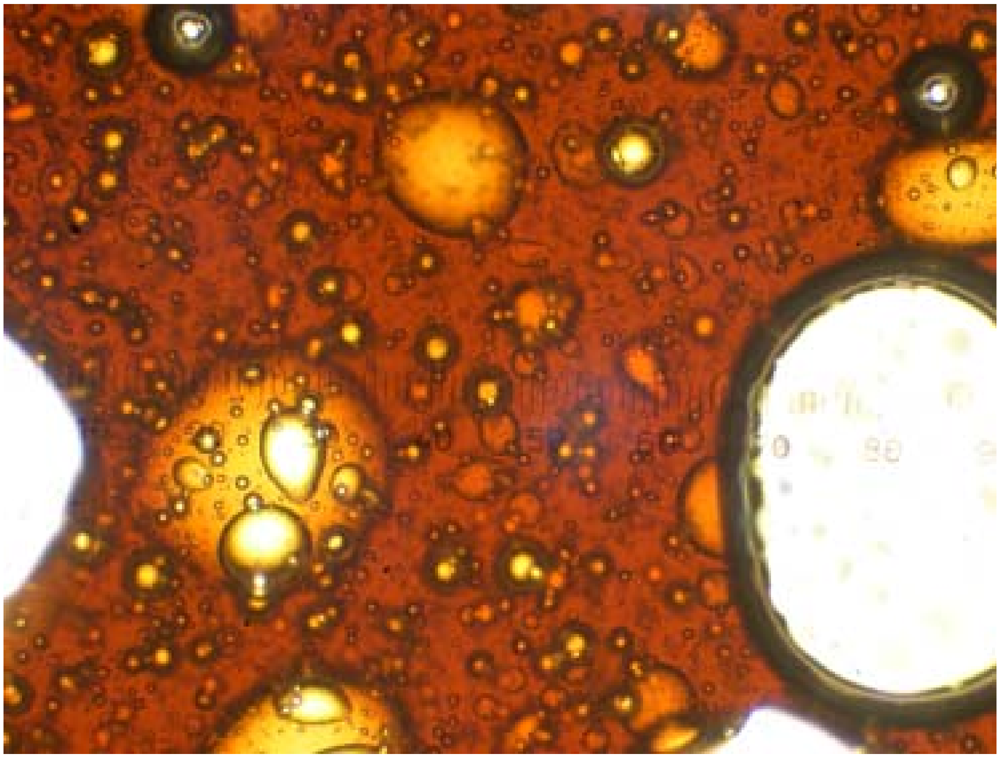


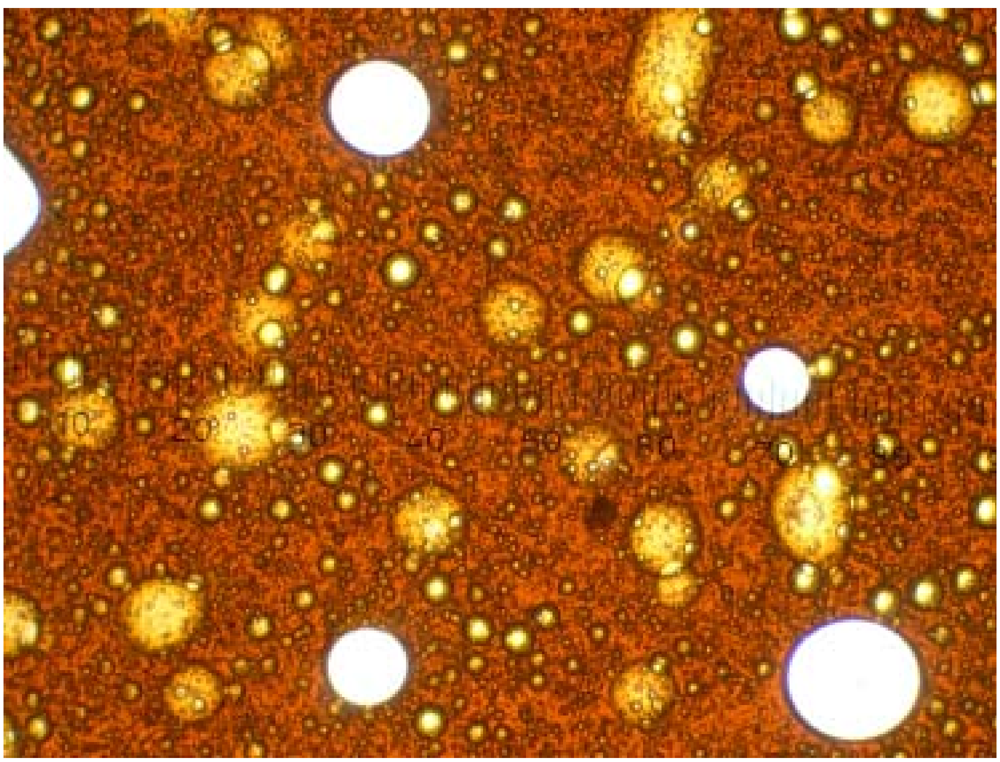
Figure A20 Test 20

Appendix B. Emulsion Micro-Photographs

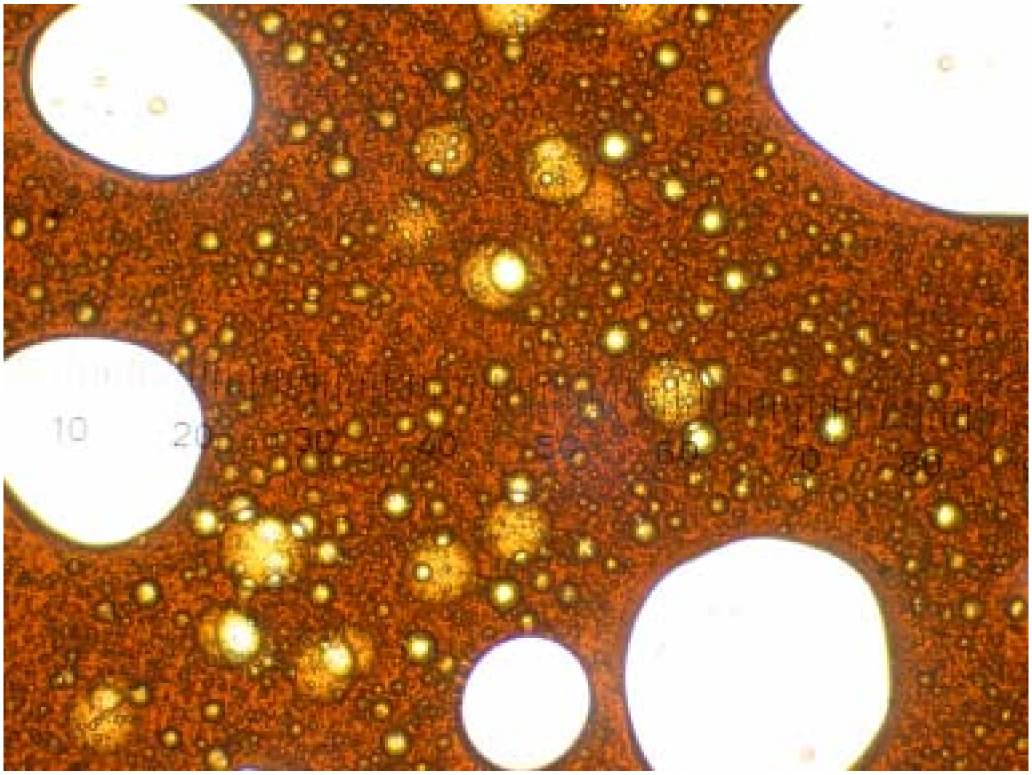
Endicott On-tank Emulsion



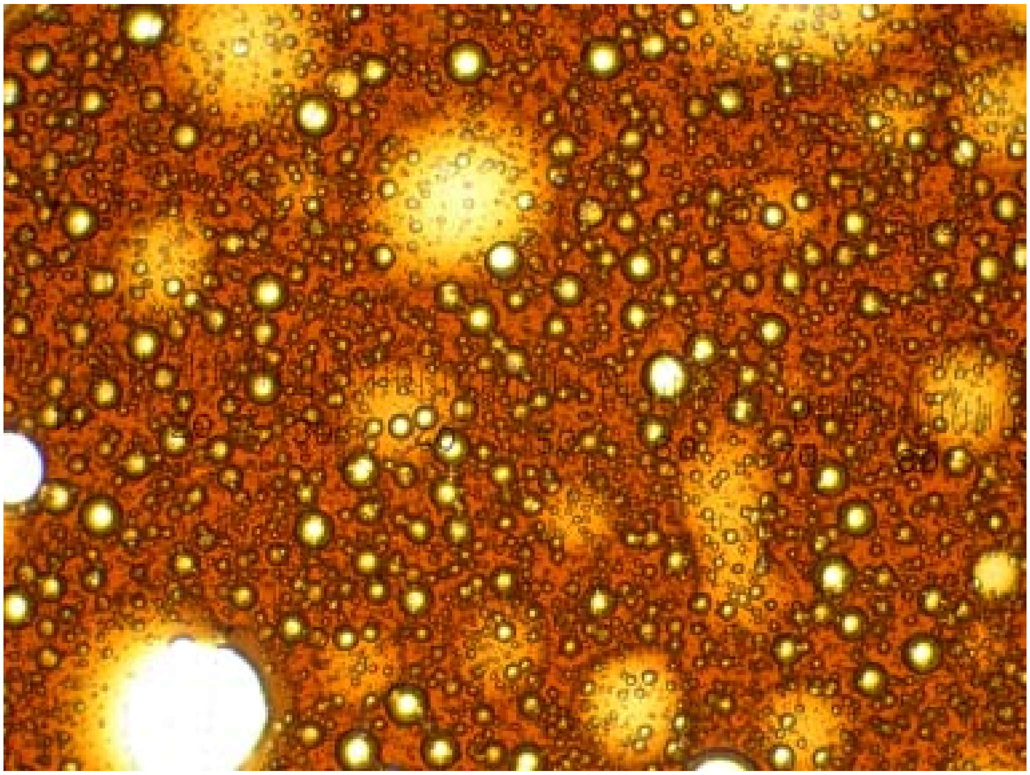
Endicott Mechanical Emulsion



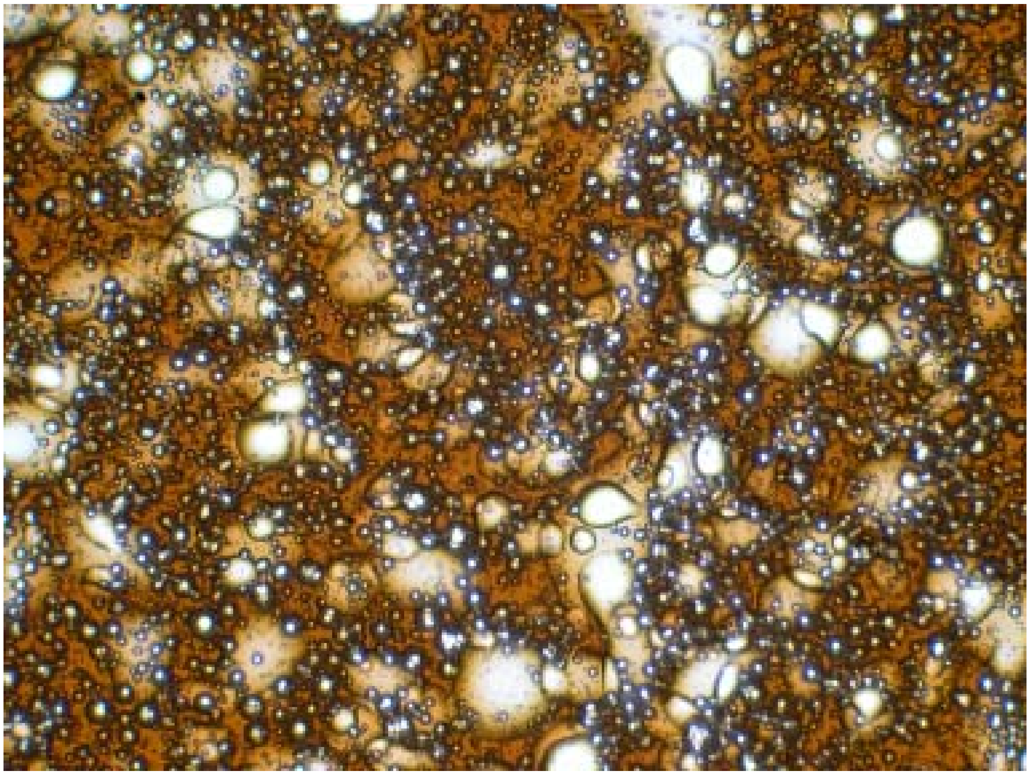
Sockeye On-tank Emulsion



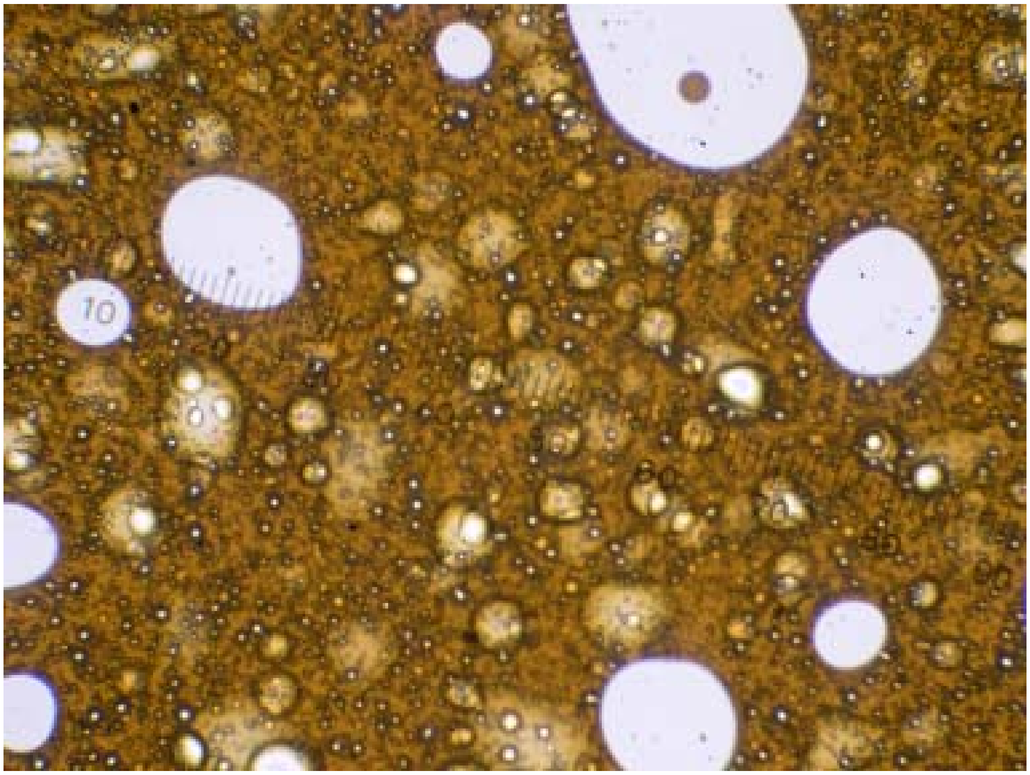
Sockeye Mechanical Emulsion



IFO 30 Mechanical Emulsion



IFO 120 Mechanical Emulsion



Scale Photo – Each fine division of the non-numbered satge micrometer is 10 micrometers. Distance from 10 to 20 on the numbered scale seen in the emulsion photos is about 100 microns.

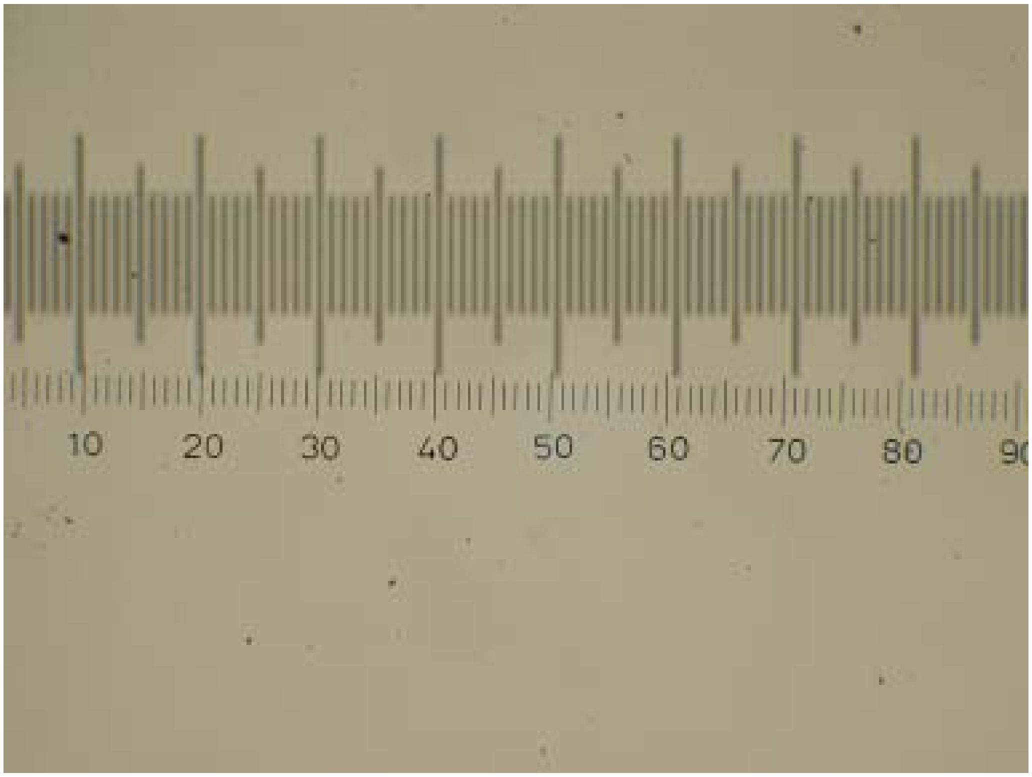


Photo of 1mm/100 Division Stage Micrometer with Eyepiece Reticle Installed (sharper, numbered scale) (60 units on eyepiece reticle = 585 microns on Stage Micrometer or 1 unit = 9.75 microns)