Ultraviolet Fluorescence Spectroscopy (UVFS) of Oil In Seawater Near the Mississippi Canyon Wellhead Paul E. Kepkay, COOGER, DFO Canada

Introduction:

Ultraviolet fluorescence spectroscopy has proven to be a reliable way of estimating both the amount of oil suspended in seawater and how well the oil is dispersed. The primary means of obtaining an estimate of the degree of dispersion is to determine a fluorescence intensity ratio (FIR). This ratio is simply the intensity of fluorescence emission at 340 nm divided by the emission intensity at 455 nm.

Benchtop experiments in the laboratory have demonstrated that FIRs greater than a threshold ratio are poorly dispersed (with a dispersion efficiency of less than 20%). FIRs less than this threshold are well dispersed (with an efficiency of between 40 and 100%). Given that the threshold FIR may vary from place to place, it is probably better at this point to track FIR values as general indicators of increasing or decreasing dispersion.

Reported here are the results obtained from stations 13 and 16, located at the same co-ordinates before and after dispersant was deployed at depth at the wellhead between 04:50 on May 10 and 04:50 on May 11, 2010.

Methods:

Samples that had been acidified and preserved with 10% HCl were stored at low temperature. They were then transferred as 3.5 ml aliquots into plastic (methacrylate) cuvettes for fluorescence measurements in a Shimadzu RF5301 scanning fluorometer located at the BP Base in Port Fourchon. Each sample was subject to ultraviolet (UV) irradiation with the excitation energy fixed at 280 nm. Emission energy was then tracked and recorded as the fluorometer scanned between 300 and 545 nm.

The emission spectra were stored as Panorama fluorescence files and exported to an Excel workbook to plot the spectra and calculate/plot the fluorescence intensity ratio (FIR) for each spectrum.

Results:

The results obtained at stations 13 and 16 (located at 28.7254° North and 88.356° West) are plotted on the next two pages and indicate that both the spectra (Figure 1) and FIRs (Figure 2) changed after dispersant was applied at depth at the wellhead.

The spectra indicate that oil concentration was high at the sea surface and decreased rapidly with depth before dispersant was applied at the wellhead (Figure 1A). In contrast, after the dispersant was applied, the strongly reduced spectra (Figure 1B) indicate that oil concentration decreased considerably at the surface and increased slightly at 275 and 550 m. Both before and after application of the dispersant, the spectra (Figures 1A and B) indicate that there were very small amounts of oil located at depths of 275 and 550 m.

Before the application of dispersant, the fluorescence intensity ratios (FIRs) indicate that the efficiency of dispersion was high at the surface (with a low FIR of 5 at 0.5 m), decreasing to low

dispersion efficiency at depth (with a high FIR of 12 at 550m). After the application of dispersant, the pattern of dispersion efficiency changed, with high dispersion efficiencies at the surface and 550m, and low efficiencies at intermediate depths (1 and 275 m).





Spectra After Dispersant

Figure 1, UV fluorescence spectra of suspended oil at four depths before (A) and after (B) the application of dispersant at the wellhead in Mississippi Canyon. Note the strong decrease in oil concentration and the presence of oil (if only in small amounts) over all depths.

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FIR at Sampled Depths



Figure 2. Fluorescence intensity ratios (FIRs) of suspended oil at four depths at two stations occupied at the same location before and after the application of dispersant at the wellhead in Mississippi Canyon. High FIRs indicate low dispersion efficiencies and low FIRs indicate high efficiencies

Summary:

- Oil could be traced at all depths, with small amounts encountered at 275 and 550 m.
- Oil concentration decreased considerably after dispersant was applied at depth at the wellhead.
- Fluorescence intensity ratios (FIRs) increased with depth before application of dispersant at the wellhead, indicating that dispersion efficiency decreased with depth.
- After the application of dispersant, FIR was low and dispersion efficiency was high at the surface and 550 m. At intermediate depths of 1 and 275 m, FIR was high and dispersion efficiency was low.