

# Investigation of the effect of isopropanol in crude oil-in-water dispersions by fluorescence spectroscopy

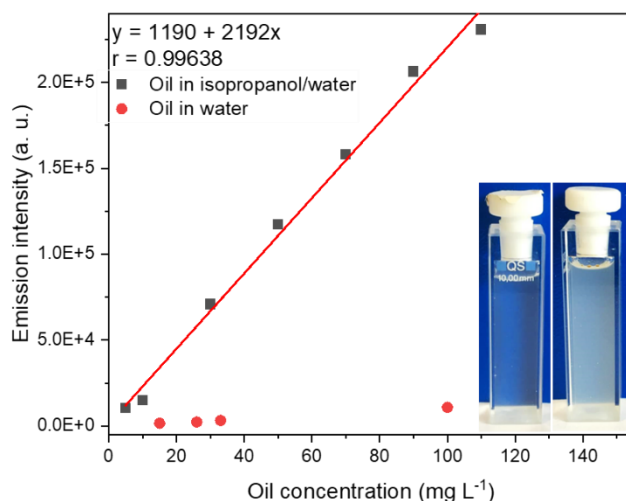
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Produced water (PW) is the main waste from offshore oil and gas extraction. Given the acute and chronic toxicity of dispersed and dissolved components present in PW, arises the need for constant monitoring to assure that the content of crude oil in water is lower than 30 mg L<sup>-1</sup>, as limited by the OSPAR convention for the North Sea. However, the analysis technique most recommended by regulations and conventions – gas chromatography – is rather expensive, time-consuming, and fails at determining the most toxic oil-derived components: dissolved species, mainly aromatic hydrocarbons. Hence, fluorescence-based sensors have emerged as promising alternatives to quantify crude oil in water for being low-cost, fast, and sensitive, and for providing information on both dissolved and dispersed species present in the oil. In the absence of a surfactant, oil droplets coalesce and cream as the sample shaking is ceased, and sometimes that happens faster than the emission spectrum scan rate. Consequently, the sample composition along the sensor light path changes during the spectral measurement in such a way that the signals collected in the first and last wavelengths correspond to different and transitory concentrations. Some sensor manufacturers suggest the addition of a small volume of isopropanol to oil-in-water dispersions due to its outstanding ability to stabilize emulsions, delaying the creaming of dispersed oil and leading to more reliable emission measurements, even when no surfactant is present. Even though isopropanol does not fluoresce, we aimed to investigate if the emission from crude oil in water could be affected by the addition of isopropanol. Our data set consisted of emission spectra of 182 samples of crude oil in water/isopropanol mixtures, with oil concentrations varying from 42 to 1271 mg L<sup>-1</sup> and isopropanol mass fractions in the mixtures ranging from 0 to 1. Some features extracted from the emission spectra were used as input for Principal Component Analysis, from which we observed that the samples clustered into three groups. The isopropanol content in each dispersion and consequently the dielectric constants were found to be the main underlying factors driving the shape and intensity of the emission spectra. In the range of 0.01 to 0.5 w/w of isopropanol, the samples became milky which cleared at higher isopropanol content. That milky haze observed when alcohol is added to the oil-in-water dispersion is known as the Ouzo effect, which happens in ternary mixtures of water, a miscible second solvent (here isopropanol), and a component that is highly miscible with the second solvent and poorly soluble in water. Additional experiments showed that significant changes in the spectral shapes and intensities were observed more as a function of the isopropanol content than of the actual oil concentration. Furthermore, the quantum yield of crude oil is highly dependent on the isopropanol-to-water proportion. This means that adding isopropanol to crude oil-in-water dispersions is not advisable for oil quantification purposes by fluorescence spectroscopy.



Correlation plots of oil concentrations and emission intensities ( $\lambda_{\text{excitation}} = 300 \text{ nm}$ ,  $\lambda_{\text{emission}} = 440 \text{ nm}$ ) of oil-in-water dispersions containing isopropanol (black squares) and without isopropanol (red circles). The inset pictures depict oil-in-water dispersions with 800 mg L<sup>-1</sup> of oil, containing isopropanol (right-hand side) and without isopropanol (left-hand side).