

THE DETECTION OF CRUDE OIL CONTAMINATION IN SYNTHETIC BASED DRILLING MUDS

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ABSTRACT

In response to a need for a simple compliance monitoring test for crude oil contamination in synthetic drilling muds an inexpensive and rig-worthy ultraviolet (UV)/chromatography method was developed. The method utilizes prepackaged silica gel solid phase extraction columns to separate various mud components from the synthetic base and crude oil contaminants using common organic solvents. The synthetic fluids along with any crude oil are eluted down the column. Observance of any UV induced fluorescence along the column can be attributed to crude oil contamination as synthetic base fluids do not contain fluorescent entities. Detection limits to 0.05 wt% crude oil contamination were found.

INTRODUCTION

The offshore drilling conditions in the Gulf of Mexico are demanding with water depths up to 6,000 feet through reactive clays and around salt formations often using deviated drilling techniques. These severe conditions require the use of inverse emulsion drilling muds or oil based muds (OBMs) that provide optimum drilling performance. In an invert emulsion mud, there is continuous outer organic phase that contains the mud solids and an internal aqueous phase dispersed (emulsified) as separate droplets. The continuous organic outer phase is water insoluble and thus reduces the amount of interaction of the drilling mud with water sensitive formations leading to better solids control, cuttings removal, hole stability and drilling rates.

Traditionally the invert emulsion muds used diesel or mineral oil for the organic phase, OBMs. However, on site discharge of drill cuttings from drilling rigs produced from wells using OBMs was banned in the early 1990's. This created a need and lead to the development of synthetic based muds (SBMs). These drilling muds are also inverse emulsions and provide the same or improved drilling characteristics as an OBM. A key advantage to their use is that the low toxicity of the synthetic fluid resolves many of the environmental issues associated with the use of invert muds and in particular allows for discharge of the drill cuttings. The low toxicity also reduces pollution hazards and worker exposure to diesel oil.

Current EPA regulations do not specifically address SBMs today but the EPA is working with industry groups, the American Petroleum Institute (API) and the National Oceans Industries Association (NOIA), to develop these regulations. An important compliance test needed for WBMs is one to detect crude oil contamination. The static sheen test developed for water based muds (WBMs) is ineffective for SBMs. The synthetic itself is lighter than water and can form a sheen giving a false positive. Also because the mud is an invert emulsion mud with a water insoluble external phase, the mud can stick to the drill cutting's surface and be carried to the seafloor hiding any contamination to produce a false negative. SBMs containing up to 20 wt% crude oil contamination have shown negative static sheen tests in lab tests. A joint API/NOIA analytical work group with EPA participation was formed to find a suitable test to determine crude oil contamination in SBMs. The suggested requirements for the analytical method were:

- comparable detection limits to static sheen test, 1 wt% crude
- suitable for rig site (rig motion, power fluctuations, rugged, small spaces)
- single pass/fail limit
- minimal false positives
- works with a variety of crude oils and synthetic base oils
- easy operation (minimal training required)
- reasonable costs.

Using these criteria, a simple effective chromatographic test method using black light fluorescence detection for crude oils was developed. It uses readily available rugged equipment, prepackaged activated silica solid phase extraction columns, and common solvents. The test meets the detection requirements and is easy to run using minimal space and simple equipment.

EXPERIMENTAL

Determination of Crude Oil Contamination in Drilling Fluids - Field Method

The method is intended for the on-site measurement of total crude oil in new or contaminated drilling fluids. It relies upon fluorescence of the aromatics in the crude oil for detection and measurement of crude oil contamination. Aromatics are visualized by fluorescence on an active silica column during separation from other components of the sample. The liquid portion of the drilling fluid is separated from the mud solids by settling. Centrifugation may be necessary in rare cases to separate the liquid and solids. One drop of the liquid is carefully placed on an active silica solid phase extraction (SPE) column using a pipet or medicine dropper. One half ml. of isopropanol is added and the column is placed under a black (mercury vapor UV) light. The fluorescing aromatics in the sample are observed as they move down the column and the concentration of crude is determined by visual comparison of the sample fluorescence with that of standards prepared in hexadecane solvent from the suspect crude. Alternatively the fluorescence intensity can be compared to a polynuclear aromatic standard reference, such as phenanthrene. This might be done in those cases where no samples of the potential crude contaminant exist, as is the case when drilling through new formations.

The apparatus consists of solid phase extraction (SPE) columns packed with active silica. For this work we used SPE columns manufactured by J.T. Baker and marketed by a number of distributors. They were used as received. These columns will become deactivated if saturated by water, so they should be kept carefully sealed from atmospheric humidity until a few minutes before use. A 300mw black light emitting wavelength 254 nm was used for visualization. Isopropanol was purchased as chromatographic grade. Phenanthrene and hexadecane were reagent grade.

This work was part of a collaborative test study to determine the best ways to identify crude contamination of drilling muds. Sixty samples of muds were prepared from five different crude oils and three different fluids by a drilling company. The fluids used to prepare the samples were enhanced mineral oil fluids (EMO), internal olefin fluids (IO), and linear alpha olefin-ester fluids (LAO). Crude oil concentrations in the prepared samples were 0.5%, 1%, 2% and 5% v/v. Samples of the presumably crude-oil free mud were also provided. The crudes were chosen for variety. Four of the five crudes were fairly typical, fluoresced strongly, and could be easily detected. Most crudes would be expected to behave in this way. The fifth crude, labeled crude D, was extremely light and possessed little aromatic content. Instead of the normal brown to black color it was yellow, suggesting that it was more typical of a condensate than a real crude. Gas chromatographic analysis confirmed that the crude contained only the light fraction, and was thus not typical of what might be encountered while drilling.

In this work the fluorescence intensity was used to determine the presence or absence of crude oil, and to rank the samples in order of crude concentration. Presence of crude was defined as observing a fluorescence intensity equal to or greater than that of a 0.5% solution of the same crude diluted with hexadecane and analyzed in the same way. A sample of the uncontaminated mud was also run to define a blank level.

RESULTS

In order to define a detection limit for the method, a series of dilutions of phenanthrene in hexadecane were run. These experiments showed the limit of detectability for the method to be approximately 50ppmw/v phenanthrene.

As mentioned above, one of the crudes, the crude labeled D, used in preparing the samples was, in actuality, a condensate and not a realistic sample. The aromatics level in this crude was very low and greater difficulty was encountered in detection of this crude than any of the others.

Drilling fluids typically also contain additives which may fluoresce. These additives are often very polar structures. Samples of all three fluids showed varying levels of a fluorescing material which was strongly retained at the top of the silica column and resolved chromatographically in the SPE column from the crude oil aromatics. All twenty spiked samples of the enhanced mineral oil fluids tested positive for at least 0.5% crude oil. All of the samples fluoresced at levels consistent with their crude oil concentration. The blank mud showed no fluorescence, except for the small band at the top of the column, presumably due to the additive fluorescence. Each of the crude oil/mud samples also showed the additive fluorescence band at the top of the column.

When the internal olefin (IO) based mud was analyzed, it was found that the blank mud containing supposedly no crude actually contained a small amount of fluorescing material. Analysis of the mud liquid phase by GC-MS showed that the mud was contaminated with polycyclic aromatics (PAH's). It was later discovered that this mud actually was a field mud. The presence of PAH's created a significant blank fluorescence which had to be considered in evaluating the actual samples. However interference was minimal and analysis of all twenty spiked IO samples showed all samples to test positive for at least 0.5% crude, except for 2 of the 0.5% samples, which were only marginally positive. One of the two samples was the 0.5% sample of the condensate, crude D.

The LAO-ester fluid mud samples were also prepared from the same used mud as the IO samples. All spiked LAO samples tested clearly positive again with the exception of the 0.5% sample of crude condensate D.

CONCLUSIONS

All samples correctly tested positive at the required 1.0% level. The test resulted in clear positive results for all but three of the sixty spiked samples at the 0.5% level. Two of the three questionable results were for the atypical crude D, in reality a condensate. Only one of the sixty spiked samples would have been judged erroneously to be below the 0.5% level, and that was the 0.5% LAO sample of crude D. Two of the three supposedly clean muds were found by this method in fact to be contaminated with low levels of crude oil. This was confirmed by GC-MS analysis of the mud fluid and by admission of the preparer that the mud had already been used in a formation. The test is thus very sensitive, sensitive enough to detect ppm levels of crude oil in muds. For accuracy in predicting contamination at or above a certain level, a comparison or reference standard, such as a solution of crude oil or phenanthrene, must be used. Any sample producing fluorescence above that standard is judged to test positive.

This method has several advantages:

- It is capable of being used at the drilling site since it requires minimal equipment and training and uses inexpensive and safe equipment and material
- It is rapid (<5 minutes), simple, and inexpensive
- It works with all synthetic fluids and gives no false positives at the 0.5% level. Polar surfactants which fluoresce do not interfere because they are chromatographically separated from the fluorescing crude components.
- The threshold limit for positive report can be set at any level above about 0.1% crude oil because of the sensitivity of the method.