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Subject: Characterization of Quik-Foam (Draft for review and comment)
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Characterization of Quik-Foam:

Quik-Foam is a commercially available foaming agent distributed by Baroid Industrial Drilling Products, a product line of Halliburton. The MSDS describes it as a proprietary blend of alcohol ethoxy sulfates (AES) in an ethanol/isopropyl alcohol (IPA) mixture. LANL and EES have a particular interest in further characterizing this material as it is commonly used with other drilling additives in the drilling of ground water characterization wells. Understanding the composition of Quik-Foam will help in determining the potential impact, if any, on the chemistry of the well waters being characterized.

Volatile / Semi volatile Components of Quik-Foam:

The MSDS indicates that the composition of Quik-Foam is made up of ethanol and isopropyl alcohol (IPA) (totaling as much as 20% by weight) and AES surfactants. A simple weight loss difference was used to determine the weight percent composition of volatile / semi volatile and the non volatile fractions by carefully drying the material under mild heating at 60 °C under reduced pressure. Results were a consistent with 50% weight loss leaving a non-volatile waxy residue presumably consisting of an AES mixture.

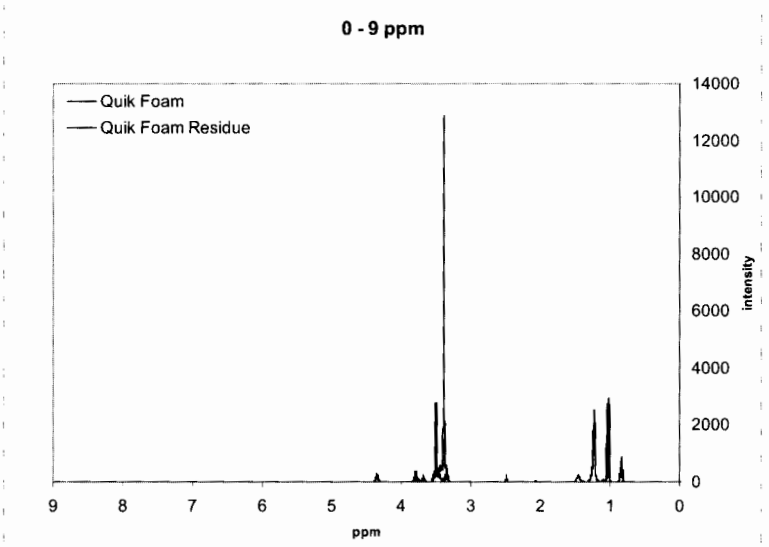

Figure 1. Quik Foam and Quik Foam Residue - 1H NMR Analysis

Proton NMR of Quik-Foam and Quik-Foam Residue:

Proton NMR of the Quik-Foam as received and after drying are shown in Figure 1 and confirms the presence of both ethanol and IPA. In addition, water was observed, which makes up the balance of weight loss from the volatile / semi volatile fraction. The

resonances from these components disappear upon drying. Expansion of the NMR spectra between 1.0-1.07 ppm shows the ethanol and IPA region (Figure 2). Since molar amounts are directly proportional to peak area, the integration of these areas gives a method for directly determining the relative ratios of the two alcohols. With the additional integration of water at 3.4 ppm a molar ratio of ethanol:IPA:water of 1.9:1.0:18.8 was obtained with this mixture, making up approximately 50% by weight of the Quik-Foam.

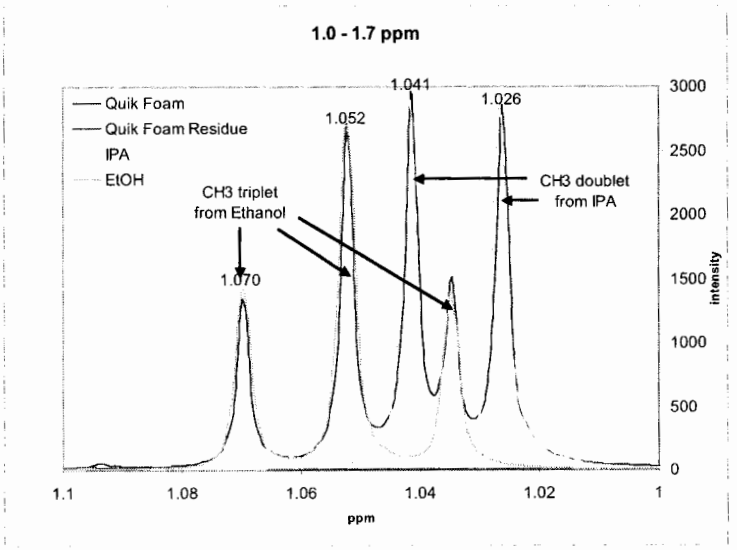

Figure 2.

The spectra details in the overlay of Quik-Foam, the Quik-Foam residue, ethanol, and IPA are shown in Figure 3 and in Figure 4 for the regions 0.5-1.7 ppm and 3.0-4.0 ppm indicating the resonances of each individual contributor to the spectrum.

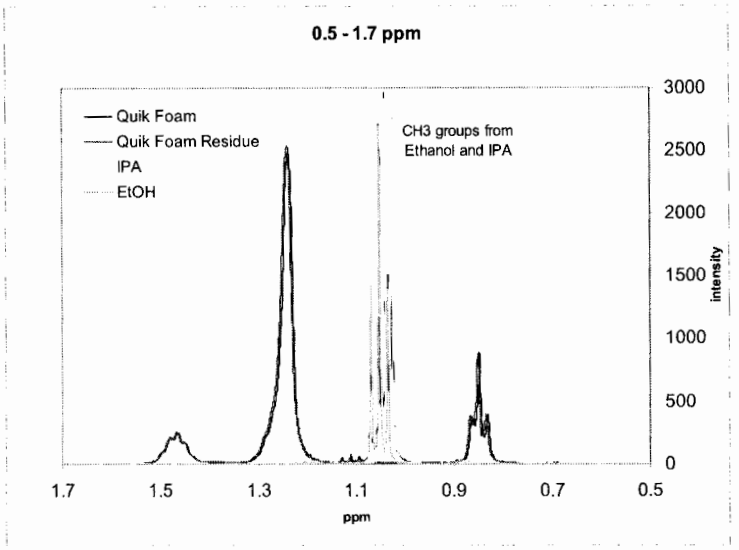

Figure 3.

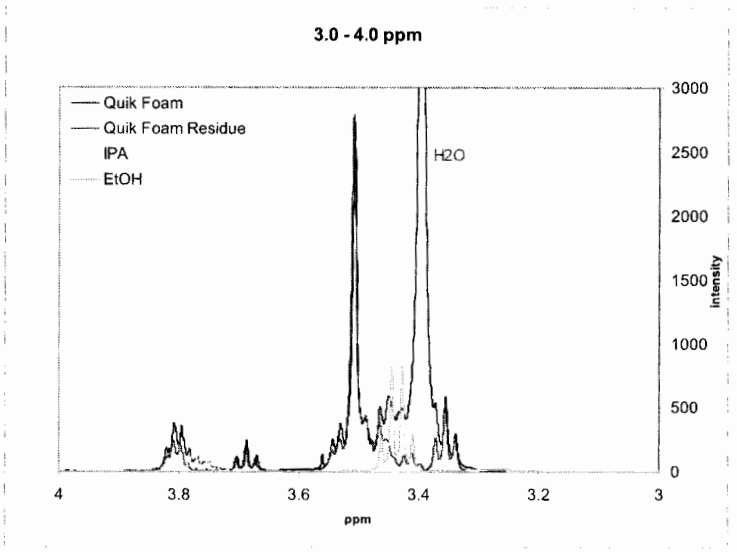

Figure 4.

Shifts in proton resonances in NMR are very sensitive to the chemical environments in which the protons (hydrogen nuclei) are found. Their shift, in reference to an internal standard, offers a lot of information on the chemical environment or structure. The residue spectrum in Figure 5 is consistent with alkyl/ alcohol ethoxy sulfates with an alkyl tail. In addition the spectrum indicates that the residue consists of two to three distinct surfactant compounds, which is consistent with the wording in the MSDS indicating a mixture of AES materials.

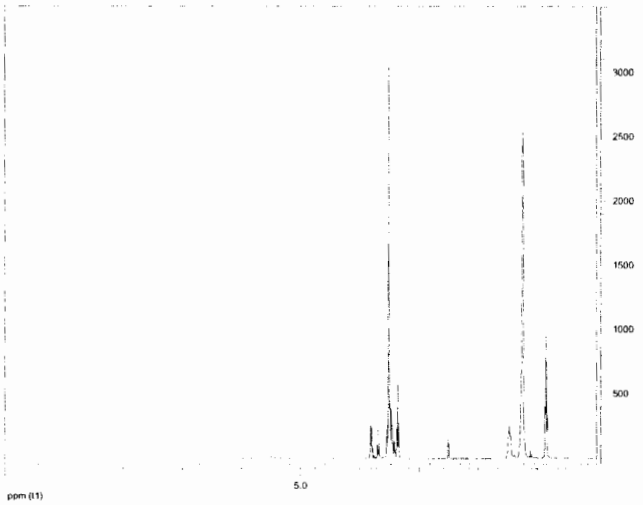

Figure 5. Proton NMR of Quik-Foam Residue

TGA-MS Analysis with DTGA of the Quik-Foam Residue:

Thermogravimetric analysis (TGA) allows a material to be characterized by plotting weight loss (ie decomposition) against temperature. It allows one to determine a material's thermal stability. The TGA for the Quik-Foam residue (Figure 6) indicates a very rapid weight loss between 100-300 °C in which approximately 76% of its initial

mass was lost. This low temperature of decomposition excludes gas chromatography (GC) as a technique for separation, isolation, and identification of the individual components. For characterization and identification of the components of the Quik-Foam residue, a non destructive separation method

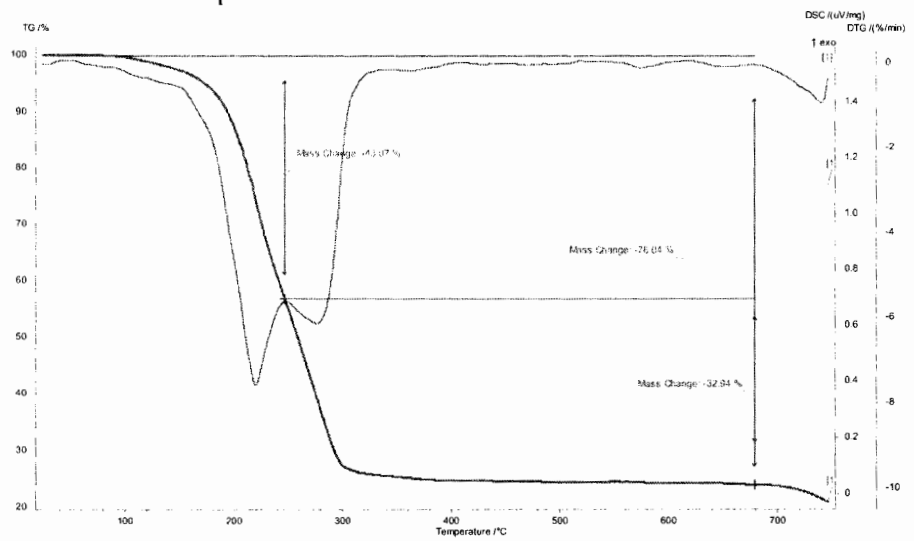

Figure 6

LC-MS of the Quick-Foam Residue:

Liquid chromatography-mass spec (LC-MS) was the method used for separation of the Quik-Foam residue into individual components. Optimization of the separation gave the chromatogram in Figure 7 which was collected in the electrospray negative mode. The chromatogram indicates the separation of three components with the elution of the highest molecular weight material first (9.59 min) and that of the lowest molecular weight material last (12.74 min).

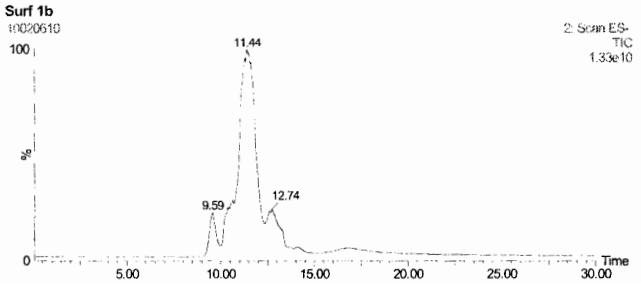

Figure 7. LC Chromatogram of the Quik-Foam residue.

The mass spectra of each of these individual components (Figure 8) have a number of similarities in their mass fragment losses which suggest that, while different in molecular weights, the chemical composition and structure are very similar. Each of the three show repeated losses of 44 mass units from the molecular ion peak which is consistent with the loss of ethylene oxide ($O\text{-}CH_2CH_2$). These are the repeat units found

in alcohol ethoxy sulfates. The number of these units lost is an indication of how many of these repeat units are found in the structure. In addition each of the three mass spectra have a mass fragment at 96-97 for loss of a sulfate (SO_4) and a mass fragment at 80 for loss of SO_3 .

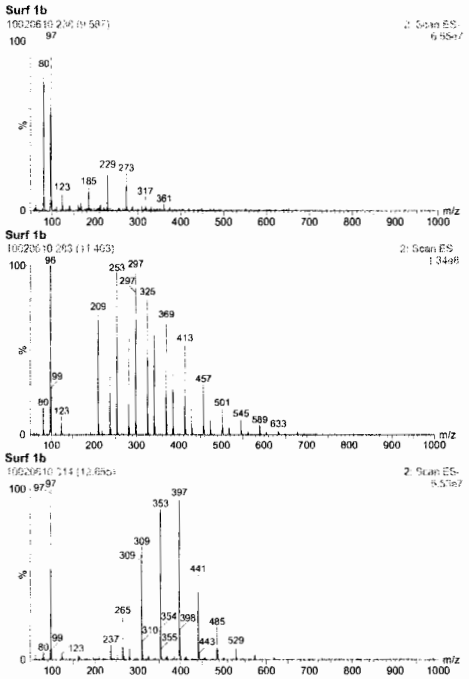

Figure 8. Mass spectra of the three Quick-Foam residue components

Based on the characterization results, two of the three compounds that make up the composition of the Quik-Foam residue have been assigned a chemical structure. The first which eluted at 11.44 min with a molecular mass of 633 is decyl nona(ethyleneoxide) sulfate (Figure 9a) and the second is dodecyl hexa(ethyleneoxide) sulfate (Figure 9b). Identifying the third compound which was the first to elute presented a problem due to an anomaly. Its spectrum indicates a molecular mass of 361 but, if this were the case, being the smallest mass, it should have eluted last. Speculation is that the mass of this compound is much greater but that the compound did not survive the mass spectrometer intact.

$$H_3C—(CH_2)_9—(OCH_2CH_2)_9—OSO_3^-$$

a.

$$H_3C—(CH_2)_{11}—(OCH_2CH_2)_6—OSO_3^-$$

b.

Figure 9. a. decyl nona(ethyleneoxide) sulfate
b. dodecyl hexa(ethyleneoxide) sulfate

Quik-Foam Summary:

The following summary points can be made based on the characterization of the Quik-Foam and its residue using NMR, TGA, LC-MS and gravimetric analysis:

- Quik-Foam is comprised of a mixture of surfactant compounds which are present at 50% by weight.
- The remaining 50% is made up of ethanol, IPA and water in a molar ratio of 1.9:1.0:18.9 as determined by integration in the proton NMR.
- The Proton NMR of the residue is consistent with a mixture of alkyl alcohol ethoxy sulfates.
- TGA shows onset of decomposition of the Quik-Foam residue at 100 ^{o}C with a mass loss of 76% at 300 ^{o}C.
- LC-MS identifies 3 components in the Quik-Foam residue with structures having been assigned to two of the three components as determined by the molecular ion peak and the mass fragments.
- All three mass spectra are consistent with alkyl alcohol ethoxy sulfates.
- The third unidentified component is probably the highest molecular weight component; however it is unstable to the mass spectrometer so that a molecular ion peak is not observed.