



## Method for Determination of Residual Organo-Amine Salts in Aqueous Filtrates of Drilling Fluids

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### Abstract

Organo-amine salts (OAS) have been successfully used in aqueous-based drilling / drill-in fluids for stabilizing troublesome shale / gumbo formations and preventing gumbo adhesion to bottom-hole assemblies. Field operations requested a test procedure for determining residual organo-amine salts in aqueous filtrates. This procedure would provide better engineering control on product maintenance and system costs. The original test method, which used an organic solvent extraction with phenolphthalein for detection of organo-amine salts, was found to be ineffective due to the presence of lignosulfonate and lignite obscuring end test results. A new procedure has been developed, using an organic solvent extraction method and a spectrometer that measures the content of residual organo-amine salts by fluorescence. Lignosulfonate and lignite do not interfere with the measurement. This new method has been successfully utilized in field operations, providing the fluids engineer timely data for monitoring depletion rates of organo-amine salts while drilling. A cost-effective product maintenance program can be attained.

### Introduction

The primary emphasis of this research project was to develop a test procedure for determining residual OAS. A secondary emphasis was the in-depth investigation of how OAS performs. This was necessitated by the product application experience on a deepwater drilling fluid job. Although OAS appeared to be performing satisfactorily, the primary limitation was the inability to accurately determine residual product content with the original OAS test procedure (extraction method with phenolphthalein indicator). Test results were obscured by the presence of lignosulfonate and lignite, the two primary dispersants used in the mud system. However, eventual OAS treatment was excessive (up to 12 lb/bbl) while drilling the 17.5" interval. The operator expressed concerns as to whether OAS was truly available to

provide shale stabilization. Overall better control of cost for treatment maintenance of the drilling fluid system was sought.

### Qualitative Measuring with Phenolphthalein

Originally, a qualitative procedure was developed, using an extraction method for removing excess OAS in the API filtrate and then treating for a color change, denoting presence of the product. Quantification of OAS content was further determined by a solids-loading test matrix, using untreated bentonite as the contaminant and using the qualitative procedure. The point of color change at the corresponding incremental bentonite dosage was then correlated to the OAS concentration.

The qualitative procedure was, as follows:

- 1) Add 5 mL of filtrate to vial.
- 2) Add 5 drops (approximately 0.15 mL) of 50% caustic soda solution to same vial.
- 3) Add 2 mL of dichloromethane to same vial.
- 4) Mix 2 min and allow phases to separate.
- 5) Pour contents of vial into a 60-mL separatory funnel.
- 6) Collect bottom phase (dichloromethane) into a second vial.
- 7) Note: if a lignosulfonate additive is being used in the drilling fluid system, gently warm the second vial containing the bottom phase with warm water for one minute, taking care not to boil off the liquid.
- 8) Add 5 drops of phenolphthalein to second vial. Mix; if a pink color is developed, this is positive for presence of OAS.

If a positive result was obtained, it was recommended to conduct the following quantification procedure:

- 1) Add one leveled teaspoon (approximately 5 grams, representing 5 lb/bbl) of bentonite, to 350 mL of the drilling fluid.

- 2) Shear or mix for 5 minutes, ensuring the clay is well dispersed throughout.
- 3) Collect 5 mL of mud filtrate, using the standard API procedure.
- 4) Conduct the qualitative extraction procedure to determine presence of excess OAS.
- 5) If a pink color is developed, repeat the solids-loading test by adding another teaspoon of bentonite to the drilling fluid. Shear or mix the fluid, collect API filtrate and repeat the extraction test. Continue this format till no color change occurs.

Past laboratory research had determined the consumption rate of OAS to be 1 lb/bbl per approximately 4 lb/bbl bentonite or 16 lb/bbl gumbo shale or low gravity solids (assuming an average MBT of 20 for GOM shale, with bentonite typically being 80). Thus, if one were to do this procedure and find a result of positive pink color with the 5 lb/bbl bentonite-contaminated fluid but no color change with the 10 lb/bbl bentonite-contaminated fluid, an estimate of 1 lb/bbl excess OAS in the mud system could be assumed.

This procedure was successfully used for OAS applications in all polymeric non-dispersed systems. However, test results were found to be obscured by the presence of lignosulfonate and lignite, which were intentionally used as two primary dispersants in one particular lime hybrid mud system in question. Because this method was unsatisfactory, initial investigative efforts were made to improve the original phenolphthalein test, but with limited results.

#### **Sulfan Blue / Visible Spectrophotometer Study**

During the past project history, work then began on spectrographic analysis at visible light wavelengths. Another procedure was developed, using a Sulfan Blue dye transfer reagent/chloroform extraction method with a VIS spectrophotometer. This method is viable to be field-applicable for OAS systems containing no lignosulfonate or lignite. It is reasonably effective for determining OAS in an all-polymer system. This approach was used in the past for Gulf of Mexico deepwater applications. Using 11% sodium chloride solutions with increasing increments of OAS, Figure 1 demonstrates good response. However, lignite and lignosulfonate are problematic for this new procedure, not allowing for full extraction of OAS with both methylene chloride and chloroform. Attempts to acidize the whole mud with acetic acid and the mud filtrate with hydrochloric acid, in hopes of precipitating out lignite and lignosulfonate, failed to solve the problem.

After not seeing much success with that particular approach, it was accidentally discovered that the isolated OAS samples fluoresced, and subsequently, a linear correlation was found between the spectrometric count at a particular peak wavelength and the amount of OAS present.

#### **Fluorescence Spectrometer Research**

When the fluorescent characteristic of OAS was first observed, synthetic filtrates containing varying amounts of OAS with/without lignosulfonate and/or lignite were prepared and submitted to an outside laboratory. The results showed the feasibility of quantifying amines in a drilling fluid filtrate by fluorescence. Varying amounts of lignosulfonate did not interfere with OAS amine results. Results are graphically presented in Figure 2.

Based on these promising results, INTEQ Laboratories purchased a spectrometer to continue fluorescent studies. Fluorescence data from three experimental matrices were entered into a Quattro Pro spread sheet and a linear regression calculation performed. These test matrices were generated with increasing OAS content in 11% NaCl solutions with pH adjusted to 11. Two samples of OAS, referred to as A and B, were used to produce three experimental data sets as represented in Table 1 and Figure 3.

Intensive studies confirmed the fluorescent method worked, in spite of the presence of lignosulfonate and/or lignite, as shown in Table 2.

#### **Procedure for Quantitative Measuring by Fluorescence**

A filtrate sample is extracted with a chlorinated solvent to isolate the OAS component from the aqueous phase. The concentration of OAS is determined by its fluorescence property using an Ocean Optics DT2000 Spectrometer.

The procedure is, as follows:

##### **A. OAS Isolation**

- 1) Prepare solvent extraction vial by placing 4 mL of chloroform in vial.
- 2) Obtain mud sample and adjust the pH to above 9 if necessary.
- 3) Obtain 5 mL or more filtrate using standard API press.
- 4) Place 3 mL of filtrate in solvent extraction vial and mix vigorously for 2 min.
- 5) Allow phases to separate, centrifuge if necessary.

## B. OAS Measurement

- 1) Prepare fluorescence spectrometer and computer.
- 2) Remove the top water phase with a transfer pipet and place the lower phase of chloroform (CHCl<sub>3</sub>) solution in fluorescence cuvette.
- 3) Cap the cuvette and place in cuvette holder on the DT-1000 light source
- 4) Cover with box and allow fluorescence spectrum to stabilize on the computer screen. Computer visuals will change from something like Figure 4 to something like Figure 5.
- 5) With the cursor placed at 494 nm, read and record the count value at the bottom left of the computer screen. Computer visual should be like Figure 6.

The count intensity is related to the OAS concentration using the equation:

$$\text{OAS, lb/bbl} = \frac{\text{Count value} - 322}{459}$$

It should be noted that for somewhat different chemistries the optimum wavelength to take measurements may be different, and the equation for determining the amount of clay stabilizer may be different. That is, the peak wavelength of the fluorescent spectrum for a particular amine chemistry must be empirically observed, and the exact equation determined by linear regression analysis.

### Is OAS Available for Shale Stabilization?

Other effects observed in this study were the appearance of mud additives “consuming” OAS, based on spectrophotometric results. Various fluids were prepared with a specific concentration of OAS and a typical amount of one other additive. Filtrates were obtained and submitted for extraction. Results translated into one pound per barrel of additive appeared to absorb a measured amount of OAS. The levels of interaction are shown in Table 3.

The next phase of the project was to determine if OAS was truly available for clay stabilization. OAS chemistry is designed to inhibit hydration of clay by reducing water absorption, thus reducing swelling and dispersion. To determine if OAS was available, water solutions were prepared with lignosulfonate and/or lignite, with/without OAS. An amount of 35 lb/bbl commercial bentonite was added to each solution and sheared. Data summarized in Table 4 reveals that OAS is still available for inhibition of clay hydration, as evident by the low rheological properties and the high API fluid losses. Please note the significant performance of OAS alone, as compared to a

competitive clay stabilizer. It is surmised that a “sequestrant effect” of lignite and other additives with OAS is being observed, not a “consuming effect”. The ability of OAS to react with clay is far stronger than the bonding effects (whether they be hydrogen bonding, Van der Waals, etc.) with other additives.

### Cation Exchange Study

Bentonite was evaluated as a substrate for methylene blue (MBT) cationic exchange interaction with a mud filtrate containing OAS. A 20 lb/bbl non-treated bentonite slurry was prepared in deionized water and allowed to hydrate overnight. Synthetic filtrates, all prepared with 11% sodium chloride, included a blank, followed with increasing increments of 1 – 8 lb/bbl OAS and other filtrates containing chrome lignosulfonate or lignite or polymeric deflocculant, were tested.

The following MBT method was used:

- a. Add 2 ml of gel slurry to a flask.
- b. Dilute with 5 ml deionized water.
- c. Add 5 ml synthetic filtrate.
- d. Add 25 ml 3% hydrogen peroxide.
- e. Bring to low boil and digest for 15 minutes.
- f. Conduct MBT measurement.

A standard calibration graph showing residual OAS content in a filtrate versus equivalent bentonite concentration determined by MBT was plotted, as illustrated in Figure 7.

Also, as presented in Figure 8, chrome lignosulfonate and lignite with OAS lowered the expected MBT value corresponding to OAS at 7 lb/bbl. The polymeric deflocculant had no adverse effect. Citing the papers by B. Sithole and R. Guy<sup>1</sup> and by P. Cloos and R. D. Laura<sup>2</sup>, there is competition for cationic exchange clay sites between amines and additives like lignosulfonates and tannins.<sup>3, 4</sup> The mechanisms acting upon these sites though are different: lignosulfonates absorb, whereas amines show true cationic exchanging. Amines do have higher, stronger hydrogen bonding capability, thus inducing clay flocculation and overcoming dispersed clay characteristics provided by lignosulfonates. Lignitic additives have less effect upon the chemical properties of amines.

Interesting results were found in comparing the effectiveness of OAS against competitor products for reduction of cationic exchange capacities of bentonite. OAS was more effective than competitive products. The following data table shows the resultant MBT values (equivalent bentonite content).

Product amount:	INTEQ OAS	Competitor A	Competitor B
At 4 lb/bbl	12.5	13.8	15.6
At 8 lb/bbl	9.8	11.2	14.4

## Conclusions

A method has been found to determine residual OAS, in the presence of lignosulfonate and/or lignite. A fluorescence test procedure using a spectrometer was found to provide reproducible and reliable results. Even with varying lignosulfonate and/or lignite concentrations, residual OAS as low as 1 lb/bbl could be measured reproducibly. The fluorescence procedure, utilizing a laptop computer set-up, can be easily installed in a regional laboratory. Collected mud samples can be delivered on a timely basis, knowing the offshore transportation frequency to rigs. The procedure has been successfully used for several past offshore jobs utilizing OAS mud systems. Monitoring residual OAS in mud samples of the representative mud systems has been conducted in INTEQ Houston, New Orleans and Fourchon mud laboratories.

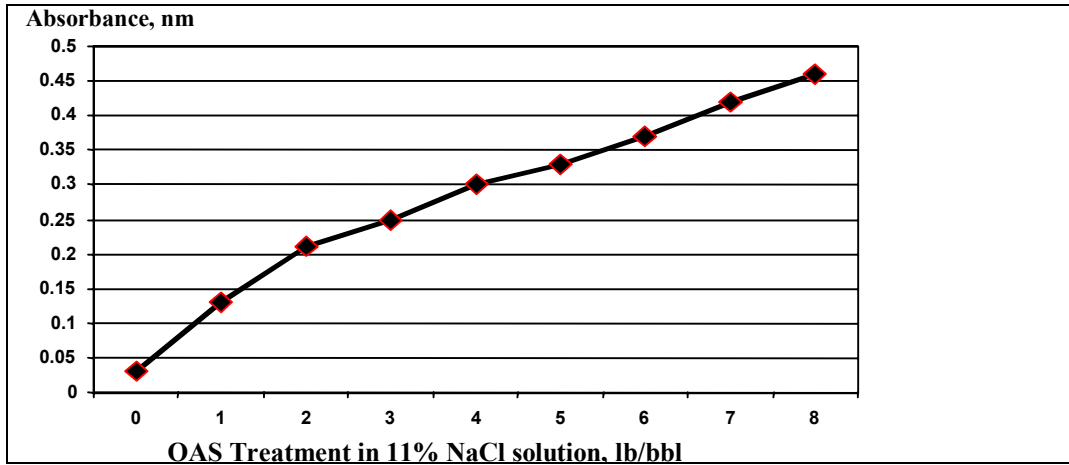
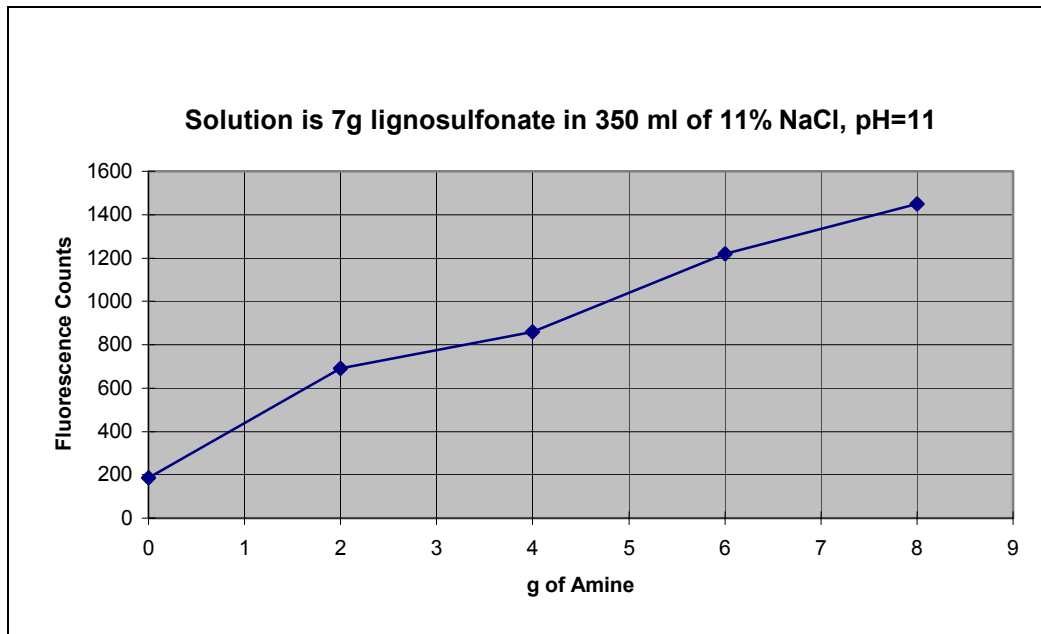
United States patent 6,194,216 has been granted for the test method.

## Acknowledgements

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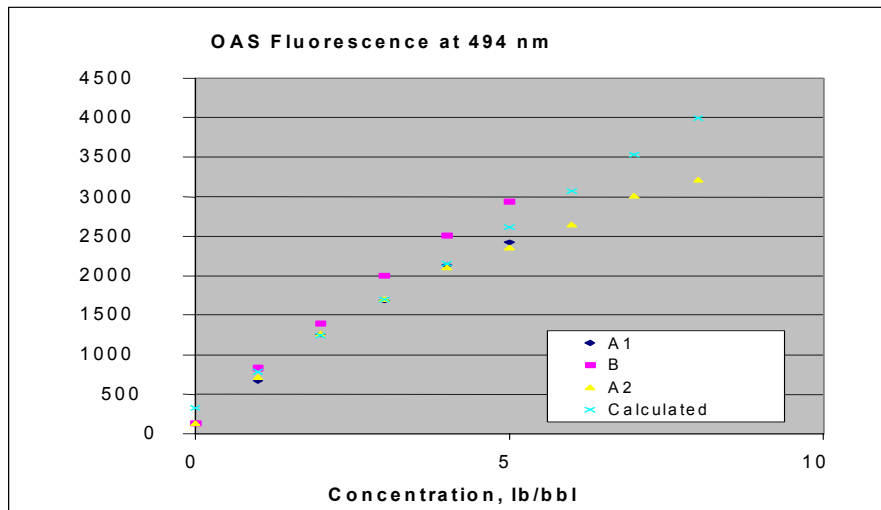
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**Figure 1: OAS absorbance in 11% sodium chloride solutions****Figure 2 Fluorescence versus OAS treatment**

**Table 1 Measured and calculated fluorescence readings**

OAS, lb/bbl	"A <sub>1</sub> " nm rdg	"A <sub>2</sub> ", nm rdg	"B", nm rdg	Calculated
0	135	135	135	322
1	672	715	830	781
2	1259	1260	1398	1240
3	1688	1700	1997	1699
4	2135	2110	2510	2158
5	2424	2360	2940	2617
6	—	2655	—	3076
7	—	3020	—	3535
8	—	3220	—	3994

**Figure 3 Fluorescence readings versus OAS concentration for Table 1 data**

The results showed a  $r^2$  of 0.946 and gave the equation:

$$\text{OAS, ppb} = (\text{Count} - 322) / 459$$

This equation is used in the standard method.

**Table 2 Residual OAS content, as determined by fluorescence**

Cr Lignosulfonate lb/bbl	Lignite lb/bbl	OAS lb/bbl (calculated)
0 (base fluid)	0 (base fluid)	3.4
3.5	0	3.5
7	0	3.2
0	2	3.2
7	7	2.6
7	10	3.4
7	20	3.0

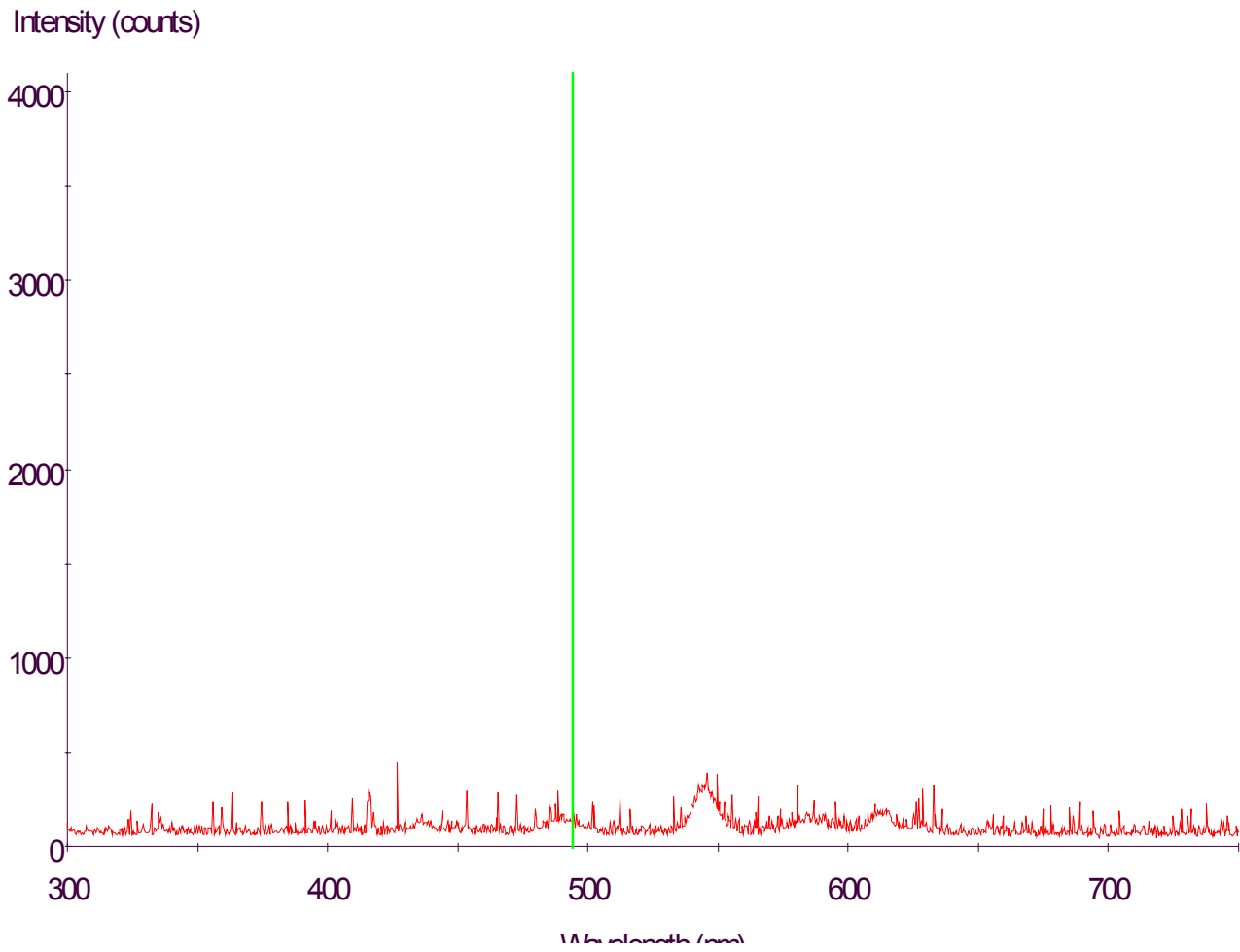
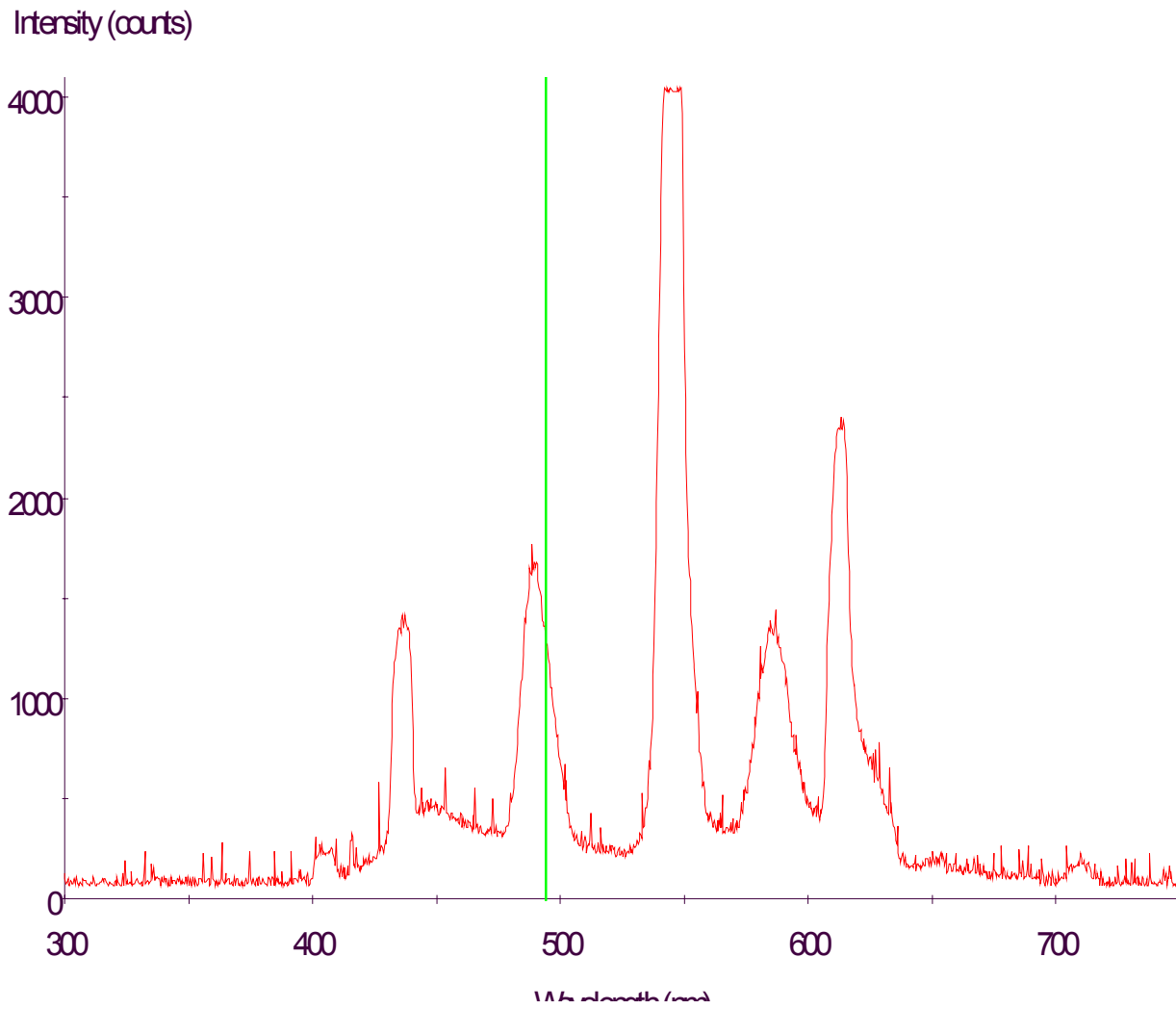
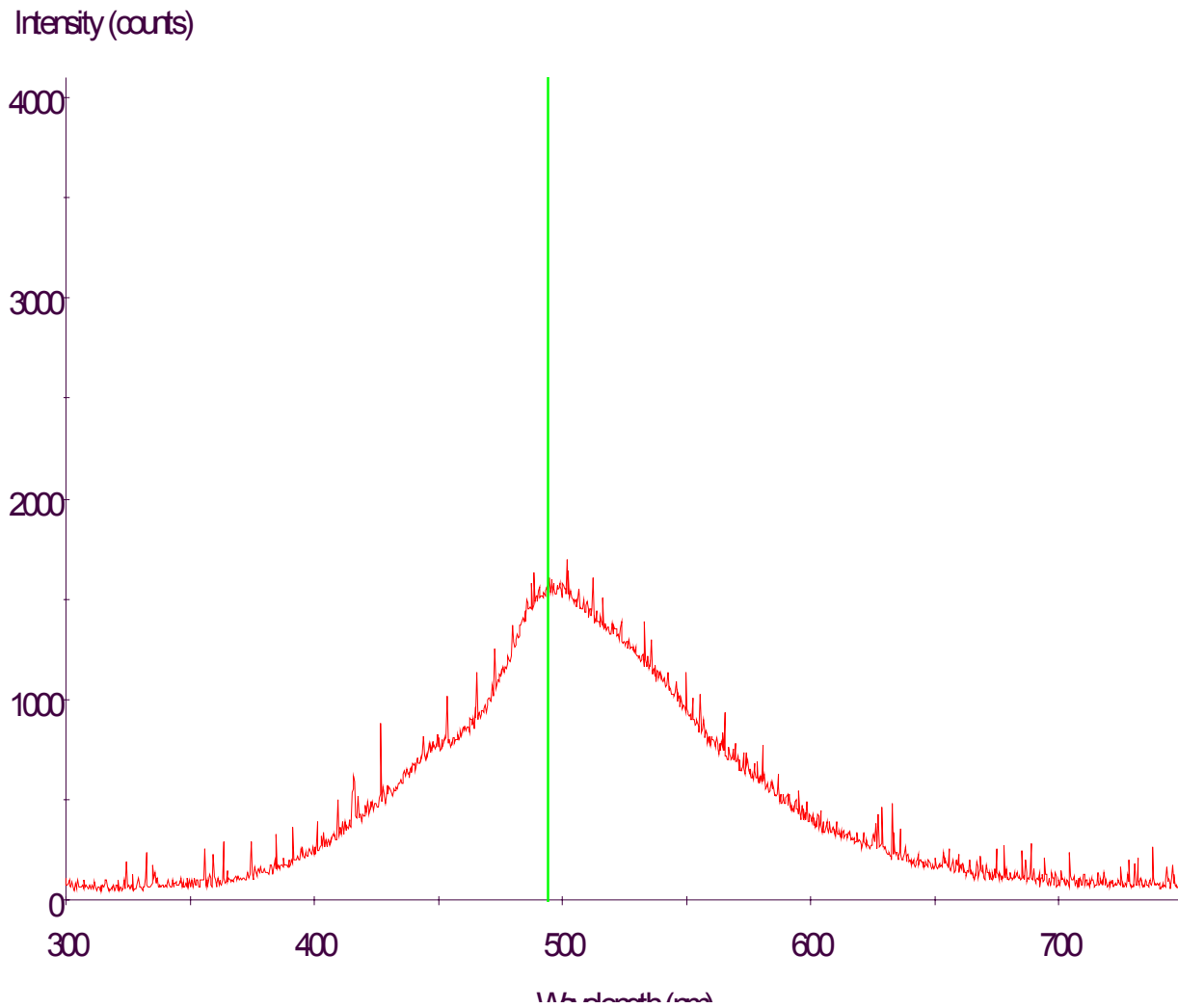
**Figure 4 Blank background fluorescence spectrum (x-axis wavelength in nm)**

Figure 5 Signal from fluorescence lights (x-axis wavelength in nm)





**Figure 6 OAS fluorescence spectrum (x-axis wavelength in nm)**

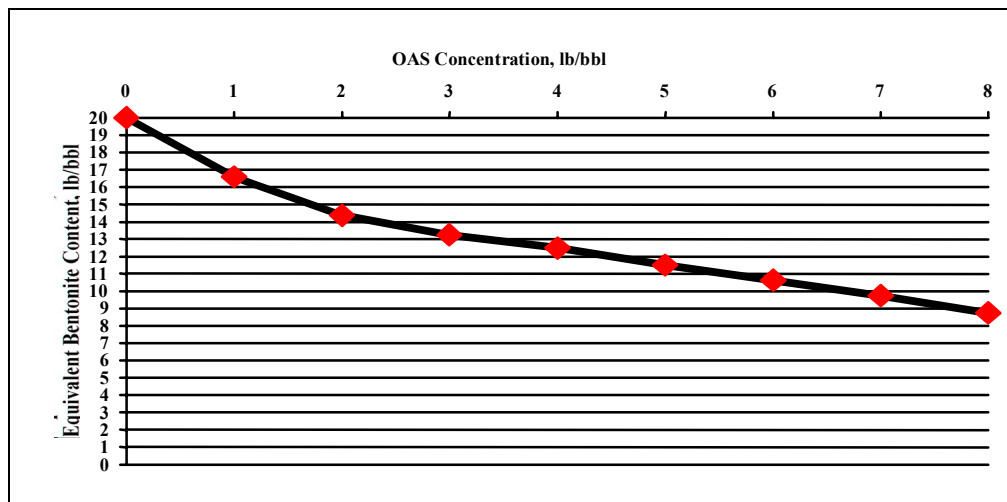
**Table 3 Interaction of mud additives with OAS**

Chrome Lignosulfonate	Lignite	Tannin	Polymeric Deflocculant	Derivatized Starch	PAC	PHPA
1.1 lb/bbl	1.2 lb/bbl	0.7 lb/bbl	0 lb/bbl	1.875 lb/bbl	4.0 lb/bbl	2.5 lb/bbl

**Table 4 Suppression of bentonite hydration**

<b>Materials:</b>										
Freshwater, bbl	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Lignite, lb/bbl		7.0	7.0				7.0			
Chrome Lignosulfonate, lb/bbl					7.0	7.0		7.0		
OAS, lb/bbl			7.0	7.0		7.0				
Competitor amine, lb/bbl							7.0	7.0	7.0	
Caustic (for pH of 11)		√	√	√	√	√	√	√	√	√
Bentonite, lb/bbl	35	35	35	35	35	35	35	35	35	35
<b>Properties:</b>										
600 rpm rdg	194	59	9	15	40	6	37	20	63	
300 rpm rdg	160	43	5	10	25	3	25	14	52	
200 rpm rdg	148	35	4	9	19	2	20	10	48	
100 rpm rdg	130	25	3	8	12	1	14	7	42	
6 rpm rdg	101	14	1	5	3	0	8	3	38	
3 rpm rdg	98	12	0	4	2	0	6	2	36	
Plastic viscosity, cp (75°F)	34	16	4	5	15	3	12	6	11	
Yield point, lb/100 ft <sup>2</sup>	126	27	1	5	10	0	13	8	41	
10 sec gel, lb/100 ft <sup>2</sup>	101	24	2	4	4	0	14	3	27	
10 min gel, lb/100 ft <sup>2</sup>	112	30	4	6	12	0	17	11	29	
API Filtrate, cm <sup>3</sup> /30 min	11	13	48	65	8	32	19	15	22	

**Figure 7 MBT determinations of 20 lb/bbl non-treated bentonite slurry with increasing OAS content**



**Figure 8 Effects of various additives upon MBT determinations of 20 lb/bbl non-treated bentonite slurry with increasing OAS content**

