

DETERMINATION OF TOTAL SULFUR IN REFINED PRODUCT PIPELINES

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ABSTRACT

Low sulfur fuel specifications are presenting tremendous challenges to the refining industry. Distribution of low sulfur motor fuels by pipelines presents yet another set of challenges. Ultra low sulfur diesel, ULSD, will be limited to 15 parts per million sulfur (ppm S) by weight (wt/wt), by mid 2006. It is expected that ULSD will necessarily be transported in a common pipeline system with 1,000 to 3,000 ppm S (wt/wt) distillates, such as, jet fuel. The opportunity for sulfur contamination of the ULSD diesel is enormous. Rapid, precise and on-line determination of total sulfur will provide a means for sulfur contamination detection in the fuel distribution system. A unique approach was used to perform laboratory simulations of pipeline interfaces between high and low sulfur fuels. Response time and analytical performance of an on-line method for determination of total sulfur in refined product pipelines will be reviewed.

INTRODUCTION

The United States Environmental Protection Agency (USEPA), and other environmental regulatory agencies have promulgated regulations requiring dramatic reductions in motor fuel sulfur content. The regulations will most immediately impact highway motor fuels. In the U.S., sulfur content of highway diesel fuel will be reduced from 500 ppm S (wt/wt) to 15 ppm S (wt/wt) by mid 2006.¹ The average sulfur content of gasoline will be limited to 30 ppm S (wt/wt) beginning early 2006.² Off-road, marine and locomotive diesel fuel will contain 500 ppm S (wt/wt) to approximately 3000 ppm S (wt/wt).³ Jet fuel will also contain several thousand ppm sulfur for the foreseeable future. The low sulfur diesel and gasoline are typically referred to as "clean fuels". The vast majority of clean fuels and high sulfur fuels are distributed from refineries to product terminals in refined product pipelines. A pipeline operator may send a batch of clean fuel directly behind a batch of

high sulfur fuel. These fuels will mix in the pipeline to form what is typically referred to as pipeline interface or transmix, see Figure 1. Detection of an ultra low sulfur diesel, ULSD, and off road diesel interface will likely require on-line sulfur measurements. The primary property difference between high sulfur and ULSD is sulfur content. Therefore, other methods of interface detection, such as, density measurement are considered to be unreliable.⁴

The clean fuel regulations have substantially increased the sulfur content differential between highway fuels and various off road fuels. Today the sulfur content of highway diesel averages approximately 300 ppm S (w/w) while off-road diesel can be as high as 3000 ppm S (wt./wt.), a 10:1 difference.³ The sulfur content difference between ULSD, 15 ppm S (wt./wt.) and off road diesel could be as high as 200:1. The average sulfur content of low sulfur gasoline will be 30 ppm S (wt./wt.), the sulfur content differential between it and off road fuels could be as high as 100:1. The potential for sulfur contamination of clean fuels will increase dramatically as the clean fuel regulations take effect. In addition to interface detection, pipeline operators anticipate that on-line sulfur concentration measurements will be needed prevent sulfur contamination of clean fuels as a result of pipeline dead legs and other unexpected contamination sources. The challenges of the on-line sulfur concentration measurements at refined product pipeline terminals are many. The primary challenge is to provide a very fast response to changes in sulfur concentration. It is expected that changes in sulfur concentration must be reported in 60 seconds or less.

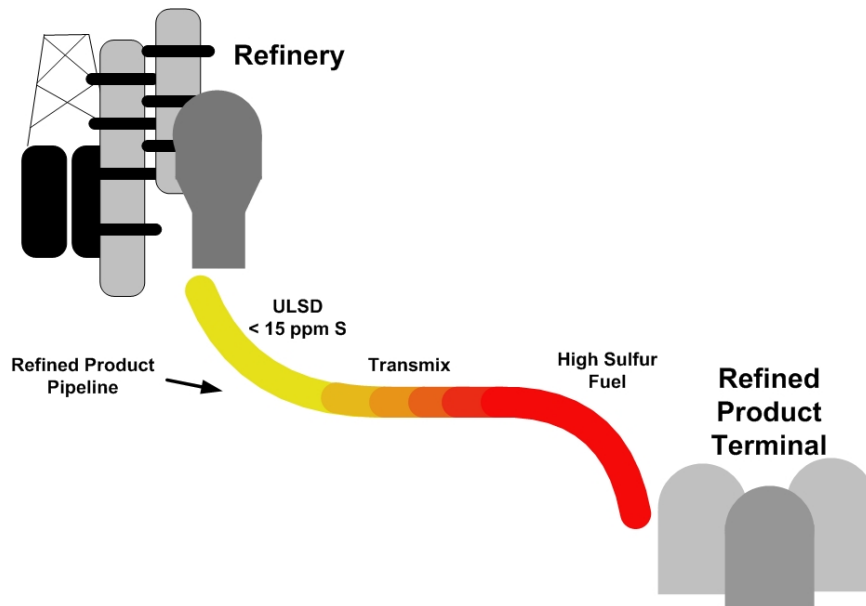


FIGURE 1 – REFINED PRODUCT PIPELINE INTERFACE

DEFINITION OF ANALYZER RESPONSE TIME

Reliable detection of pipeline interfaces or sulfur contamination will require an on-line sulfur analyzer with a rapid response time. Analyzer response time must be characterized relative to a known change in sulfur concentration. We propose that the analyzer's initial response to a sulfur concentration change, **X**, and the analyzer's final response time (time to stabilize at a new sulfur concentration), **Y**, must be considered. These analyzer response times are defined as shown in Figure 2:

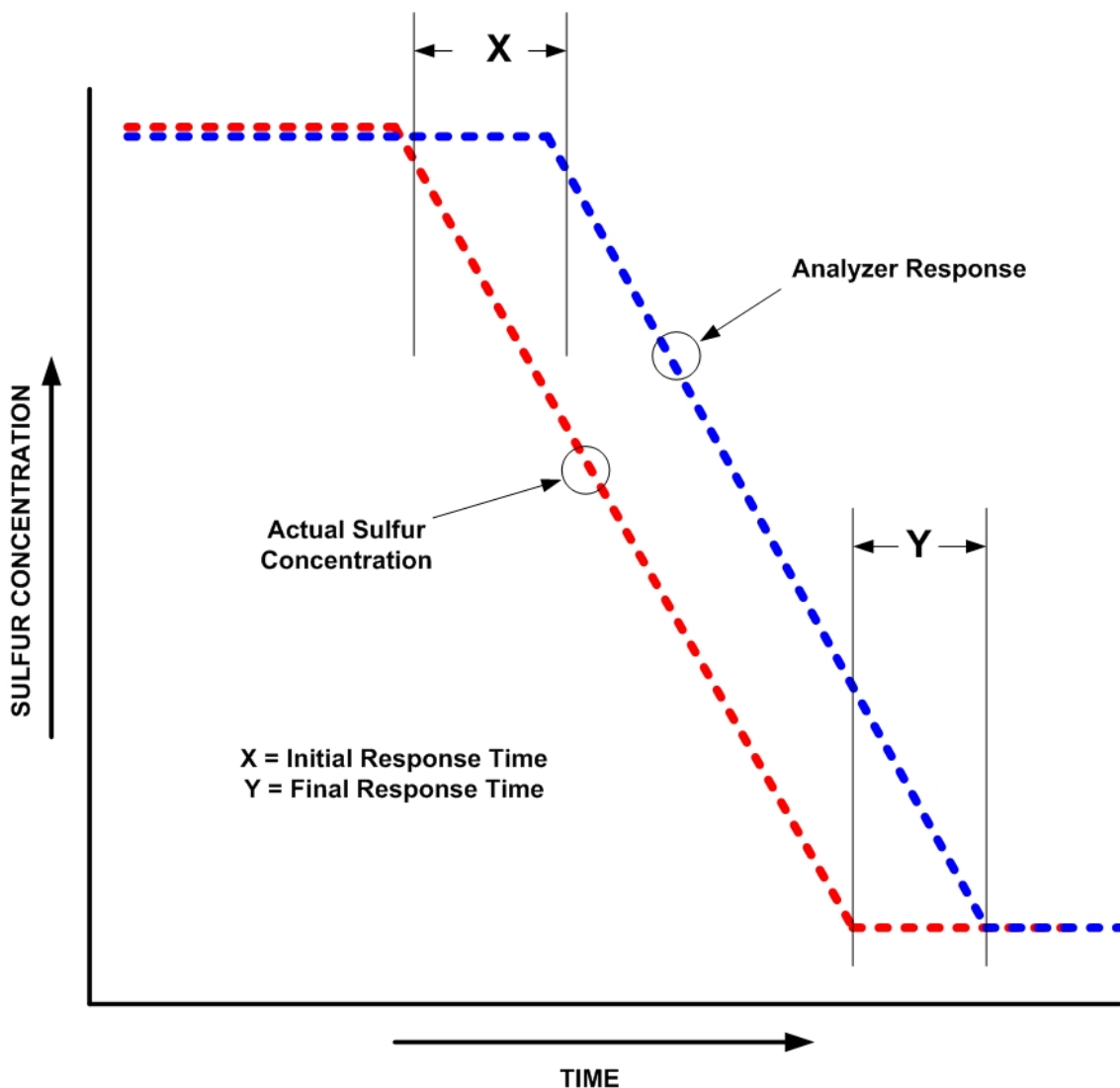


FIGURE 2 – DEFINITION OF ANALYZER RESPONSE TIME

APPARATUS FOR DETERMINATION OF ANALYZER RESPONSE TIME

A test apparatus that enabled the calculation of the actual sulfur concentration as a function of time was constructed to determine the on-line analyzer's response time. This test apparatus has allowed precise determination of the analyzer's response to simulated pipeline interfaces and "slugs" of pipeline sulfur contamination. Figure 3 illustrates the configuration of the test apparatus.

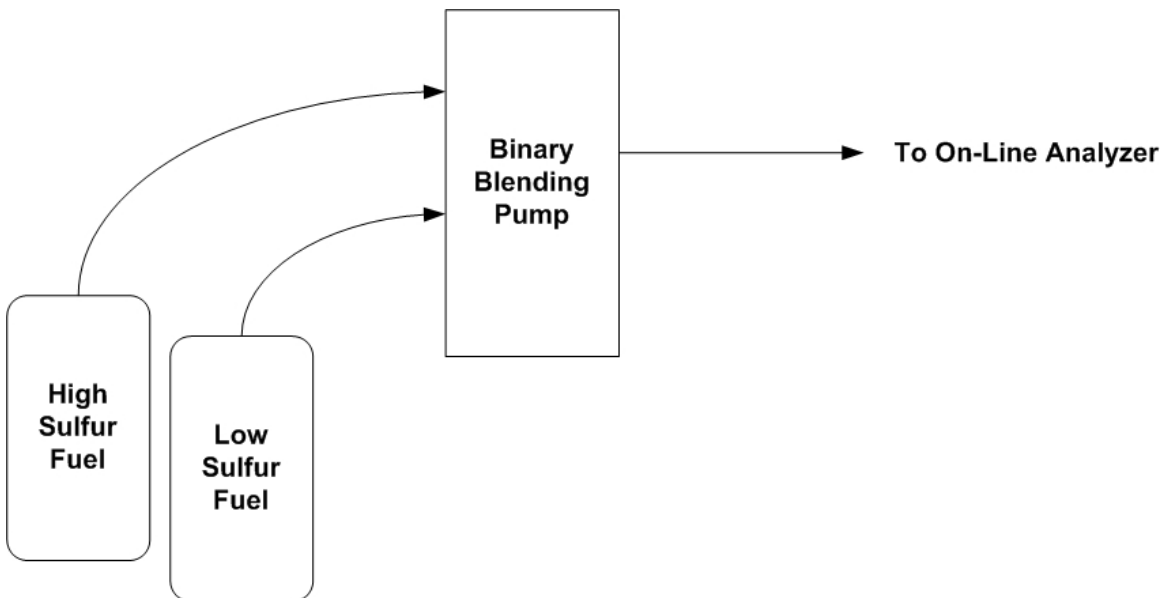


FIGURE 3 – TEST APPARATUS CONFIGURATION

The output of the binary blending pump was directed to the inlet of Thermo Electron's on-line total sulfur analyzer, the SOLA II. This analyzer measures motor fuel total sulfur content by sample combustion, then by pulsed ultraviolet fluorescence spectrometry (PUVF).⁵ New samples are introduced to the analyzer once every 15 seconds, for refined product pipeline applications. Each 15 second sample is mixed with air and then combusted. All motor fuel sulfur compounds are converted to sulfur dioxide (SO₂), during the combustion process. The amount of SO₂ formed is quantified by the PUVF spectrometer. The result of this process is a batch total sulfur concentration output representative of pipeline conditions. Essentially, the analyzer is reporting the rate of total sulfur concentration change in the pipeline. This unique method for the on-line analysis of total sulfur enables the rapid detection of pipeline interfaces and "slugs" of pipeline sulfur contamination.

The binary blending pump can be programmed to simulate a variety of potential sulfur concentration profiles that might be expected in refined product pipeline. The actual sulfur concentration as a function of time can be determined from the blending pump's program. The following response times were determined:

- a) Response when sulfur concentration is changing from high to low.
- b) Response when sulfur concentration is changing from low to high.
- c) Response to a “slug of sulfur contamination”.

The pump’s dead time, time required for a new sample to travel from pump to the analyzer’s injection valve, was determined as follows:

The total observed response time can be described as:

$$R_{PS} = R_S + R_P \quad (1)$$

Where;

R_{PS} = total observed response time

R_S = analyzer response time (X or Y)

R_P = time required to deliver new sample from pump to injection valve

Assuming that R_P is a linear function of the total pump flow then for pump flow rates of 2.5 ml/min and 5.0 ml/min we have:

at 5.0 ml/min:

$$R_{PS1} = R_S + R_P \quad (2)$$

and at 2.5 ml/min:

$$R_{PS2} = R_S + 2R_P \quad (3)$$

By substitution and rearrangement we have:

$$R_P = R_{PS2} - R_{PS1} \quad (4)$$

The blending pump was programmed to deliver a 5.0 minute linear change from 322.1 ppm S to 6.5 ppm S at total flow rates of 5.0 ml/min and 2.5 ml/min. At 5.0 ml/min R_{PS1} was measured as 80 seconds. At 2.5 ml/min R_{PS2} was measured as 100 seconds. The estimated pump “dead time”, R_P , is 20 seconds.

RESPONSE TIME MEASUREMENTS

Figure 4-6 illustrate response time measurements from high to low sulfur fuel, low to high sulfur fuel and a simulated “slug” of sulfur contamination, respectively. Figure 7 summarizes the analyzer’s response to a typical pipeline interface from a very high sulfur

diesel to ULSD. In each case two analyzer signals are plotted. The signal labeled “Analyzer Interface Signal” is used for high speed detection of pipeline interfaces or pipeline sulfur contamination. The signal labeled “Analyzer Quality Control(QC), Signal” is used for precise measurement of fuel sulfur concentration. The analyzer is equipped with “at-line” analysis capability to enable the manual, off-line, analyses of tank, barge and/or truck samples. These analyses are typically performed at times when pipeline interfaces are not expected and the “Analyzer QC Signal” is used to certify the sulfur content of these samples. The pump dead time, 20 sec., is subtracted from each response time measurement.

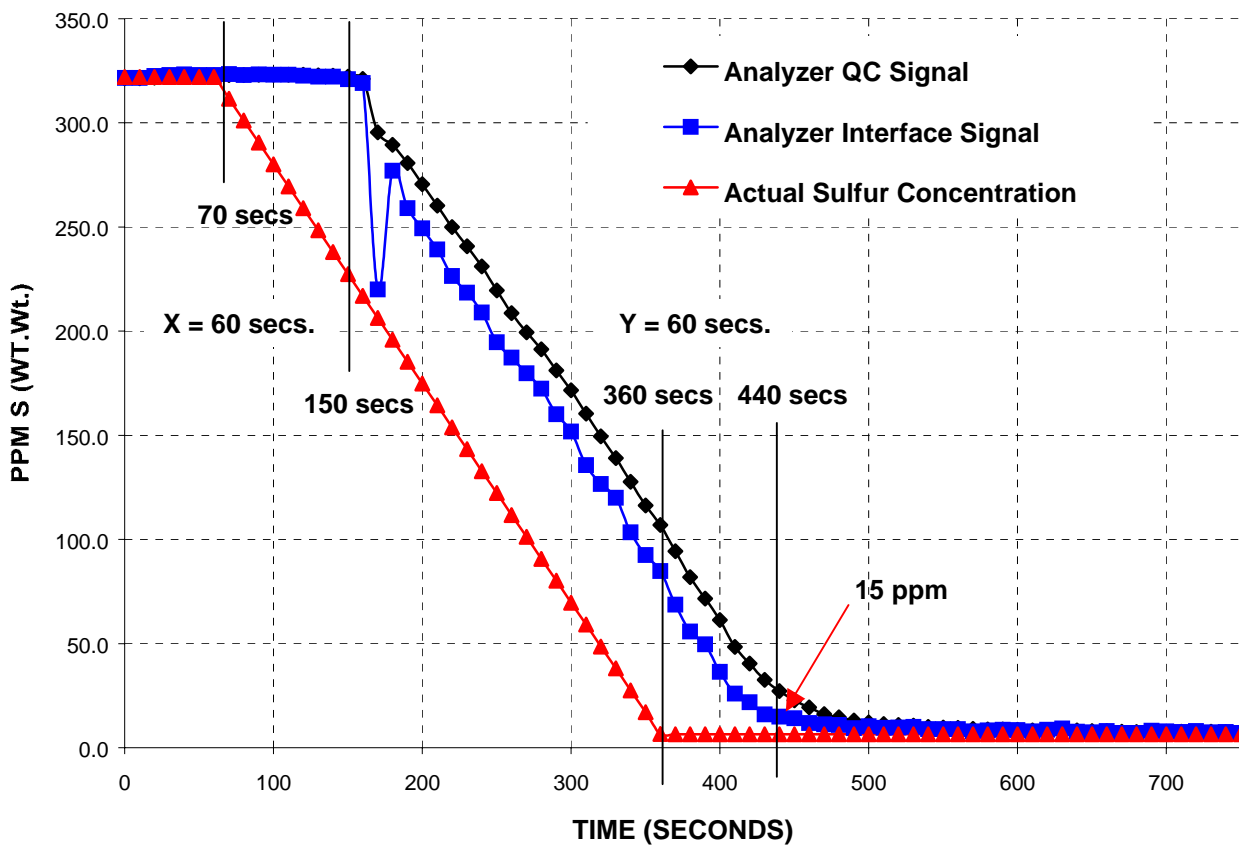


FIGURE 4 – FIVE MINUTE LINEAR INTERFACE FROM 322.1 PPM S TO 6.5 PPM S

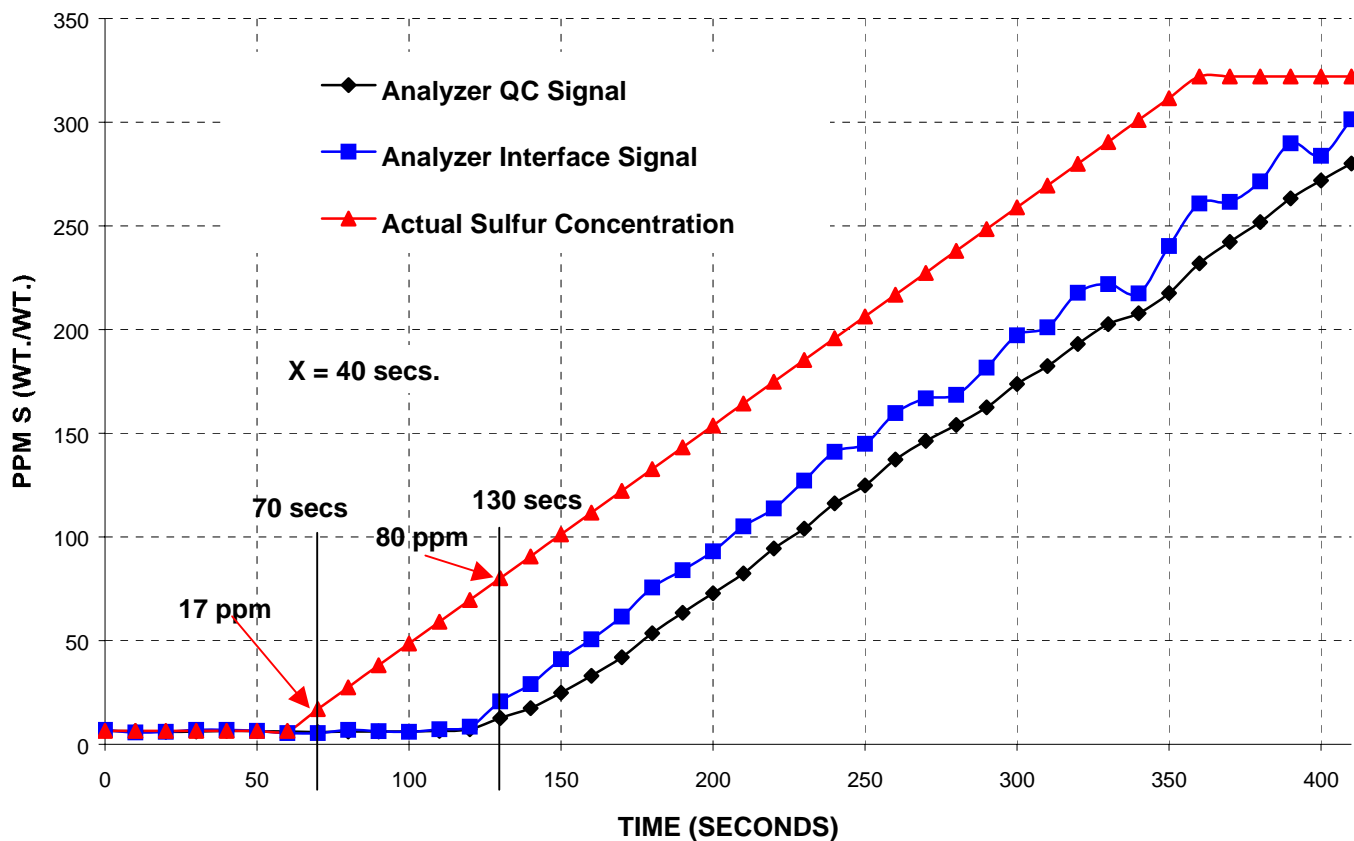


FIGURE 5 – FIVE MINUTE LINEAR INTERFACE FROM 6.5 PPM S TO 322.1 PPM S

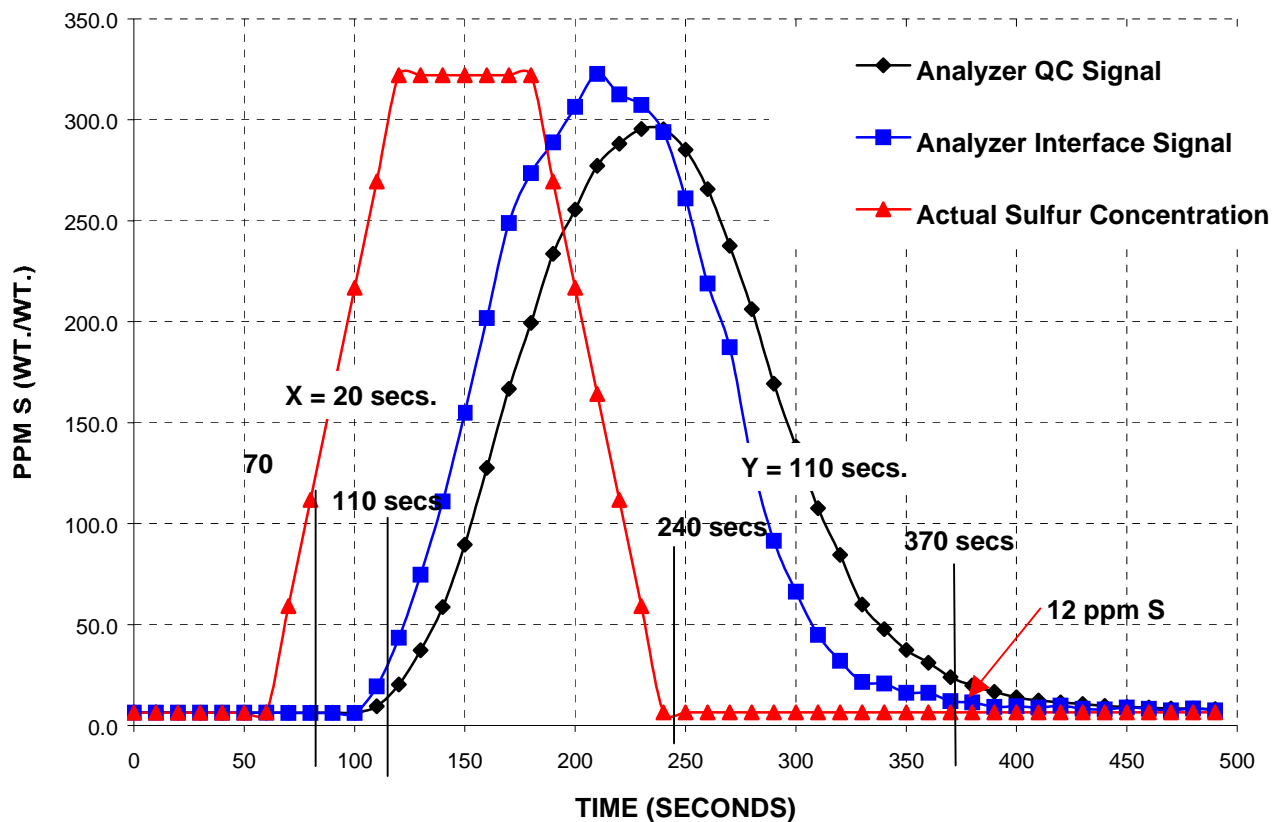


FIGURE 6 – ANALYZER RESPONSE TO “SLUG” OF SULFUR CONTAMINATION (ONE MINUTE LINEAR CHANGE FROM 6.5 PPM S TO 322.1 PPM S, HOLD 322.1 PPM S FOR ONE MINUTE, THEN ONE MINUTE LINEAR CHANGE FROM 322.1 PPM S TO 6.5 PPM S)

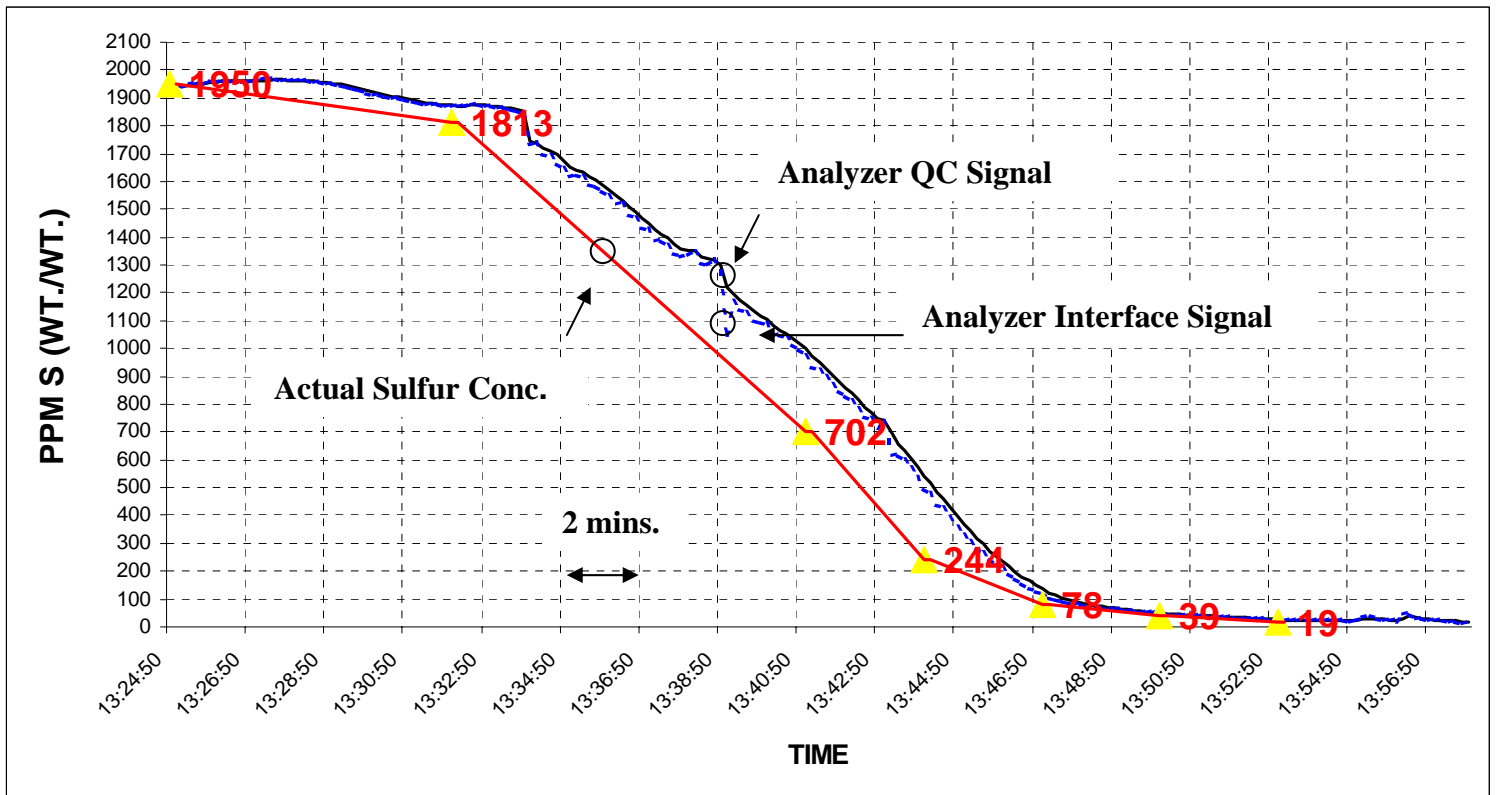


FIGURE 7 – ANALYZER RESPONSE TO TYPICAL PIPELINE INTERFACE

CONCLUSIONS

The response time of a unique on-line total sulfur analysis method was evaluated using a binary blending pump that enabled the simulation of pipeline interfaces and sulfur contamination. Initial response times from 20-60 seconds were proven. The variability of response times is likely dependent upon the rate of pipeline sulfur concentration change and the time at which the sulfur concentration change is presented to the analyzer. The analyzer introduces a new sample for analysis once every 15 seconds, therefore, if a pipeline sulfur concentration change occurs immediately following the introduction of a new sample one can expect a minimum analyzer response delay of 15 seconds. The rate of actual sulfur concentration change in figure 4 is slower than that shown in figure 6. The initial response time in figure 4 is 60 seconds versus 20 seconds for figure 6. Since the delay of 15 seconds between sample introductions will not account for all of the response time difference we conclude that the analyzer's response time is faster when the rate of pipeline sulfur concentration change is greater. These results indicate that this unique batch method of total sulfur analysis can provide an excellent representation of refined product pipeline sulfur concentration profiles.

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