



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAY 9 2005

OFFICE OF
AIR AND RADIATION

W.S. Stewart
Environmental Section Supervisor, Permitting and Programs
Chemicals and Refinery Complex
ExxonMobil Refining & Supply Company
Beaumont Refinery
P.O. Box 3311
Beaumont, TX 77704-3311

Re: Request to use an alternative fuel sampling methodology to calculate SO₂ emissions, for Units 61STK1, 61STK2, and 61STK3 at the Beaumont Refinery (Facility ID (ORISPL) 50625)

Dear Mr. Stewart:

The United States Environmental Protection Agency (EPA) has reviewed the June 18, 2004 petition submitted by ExxonMobil Refining and Supply Company (ExxonMobil) under §75.66, in which ExxonMobil requested to use an on-line gas chromatograph to measure the hourly hydrogen sulfide (H₂S) content of the refinery fuel gas, in order to calculate sulfur dioxide (SO₂) emissions for Units 61STK1, 61STK2, and 61STK3 at the Beaumont, Texas Refinery. EPA denies the petition, for the reasons given below.

Background

ExxonMobil is currently constructing three identical cogeneration units i.e., Units 61STK1, 61STK2, and 61STK3, at its Beaumont Refinery in Beaumont, Texas. Each unit consists of a natural gas-fired combustion turbine and a heat recovery steam generator (HRSG). Each HRSG has an auxiliary combustion source ("duct burner"), which will fire both natural gas and refinery fuel gas (RFG). The combustion turbines drive electrical generators, and the HRSGs provide steam for use within the refinery.

According to ExxonMobil, Units 61STK1, 61STK2, and 61STK3 are subject to the Acid Rain Program. Therefore, ExxonMobil is required to continuously monitor and report SO₂, NO_x, and CO₂ emissions and heat input for these units, in accordance with 40 CFR Part 75.

ExxonMobil currently monitors the H₂S content of the refinery fuel gas, using on-line gas chromatographs. In the June 18, 2004 petition, ExxonMobil requested approval to use H₂S data from its on-line gas chromatographs to meet the SO₂ monitoring requirements of Appendix

D to Part 75. For non-traditional gaseous fuels such as RFG, section 2.3.3 of Appendix D requires hourly sampling of the total sulfur content of the fuel, either by using an on-line gas chromatograph or by taking manual samples, unless a 720-hour demonstration is provided under Section 2.3.6 of Appendix D, showing that the gaseous fuel qualifies for less-frequent sampling.

As an attachment to the June 18, 2004 petition, ExxonMobil provided 720 hourly average measurements of the H₂S content of the RFG and 30 measurements of the total sulfur content of the fuel, for each of the two RFG sources that will feed the new cogeneration units, i.e., the South Drum and the North Drum. The South Drum will be the primary source of the RFG, although on occasion, gas from the North Drum may be routed through the South Drum to the HRSGs, if necessary.

The H₂S data were collected with the plant's on-line gas chromatographs, and the total sulfur samples were taken manually, once per day over a 30-day period, using ASTM Method D3246. These data were intended to demonstrate that the H₂S content of the RFG is representative of its total sulfur content and that, for the purposes of the Acid Rain Program, hourly H₂S measurements could be used, instead of the hourly total sulfur measurements required by Part 75, to calculate the SO₂ emissions from Units 61STK1, 61STK2, and 61STK3.

EPA's Determination

EPA denies ExxonMobil's petition to use hourly measurements of the H₂S content of the RFG at the Beaumont Refinery to calculate the SO₂ emissions from Units 61STK1, 61STK2, and 61STK3. This denial is based on the results of an analysis of the demonstration data provided by ExxonMobil with the June 18, 2004 petition. EPA performed a series of statistical tests (i.e., "F-test", "correlation analysis", "Student's t-test", and "Bias Test") in order to examine the feasibility of using the H₂S content of the RFG to represent the total sulfur content of the fuel. The overall results of these statistical analyses, which are summarized below, fail to show a reasonable correlation or consistency between the H₂S content of the RFG and the total sulfur content.

F-test

The F-test provides a measure of the probability that two sets of data have the same variance. Variance describes the "spread" of the data or variation from the mean. For two data sets to be considered comparable, they must have equivalent variances. For each of the RFG sources (i.e., the North and South Drum), EPA compared 30 manual total sulfur samples to 30 corresponding¹ hourly average H₂S values. The two data sets were assumed to be normally distributed and independent of each other. To conclude that the variances of the data sets are reasonably equivalent, the calculated F-value must be less than the "critical" F-value of 1.87 obtained from an F-distribution table at the 95 percent confidence level with (n-1) degrees of freedom. The North Drum passed the test, with an F-value of 0.060. However, the calculated F-value of the South Drum was 1.969, which exceeded the critical value. Therefore the H₂S and

¹ I.e., the average H₂S concentration for the same clock hour in which the manual total sulfur sample was taken.

total sulfur data sets for the South Drum did not demonstrate a reasonable equivalence of variances and cannot be considered similar.

Correlation Analysis

The coefficient of correlation (r) is a quantitative measure of the degree of linear agreement or uniformity between two data sets. It represents the direction and strength of the relationship between the two data sets. To demonstrate a reasonable correlation, an "r" value of 0.80 is considered acceptable. For each of the RFG sources, EPA determined an r value, based on the 720 hourly H_2S readings and the 30 total sulfur samples. However, neither the data from the South Drum (r value of 0.532), nor the North Drum data (r value of 0.220), demonstrate an acceptable amount of correlation between the H_2S and total sulfur readings. Thus, the H_2S measurements do not consistently correlate with the total sulfur measurements.

Student's t-test

This statistical test is used to determine if there is a significant difference in the sample means of two data sets. The student's t-test compares the actual difference between the two means in relation to data variation (expressed as the standard deviation of the difference between the means). If the calculated t-value exceeds the tabulated value at the 95 percent confidence level with $(n-2)$ degrees of freedom, then the means are significantly different. According to the student's t-test, there is a significant difference in sample mean values for the North Drum. This test is only valid when the population variances are considered equivalent. Due to the unequal variances in the South Drum as demonstrated by the F-test, a difference could not be detected and therefore the results of this test are inconclusive for the South Drum.

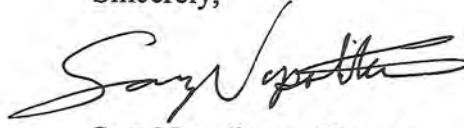
Bias Test

A bias test demonstrates whether one data set consistently differs from another data set, therefore allowing the two data sets to be equalized by using a multiplying factor. In other words, the bias test might be able to demonstrate that the 30 total manual sulfur samples differed from the 720 hourly H_2S readings by a constant amount. However, the bias test is only applicable if the samples are shown to be similar and correlatable through other statistical tests such as the F-test, Student's t-test, and correlation analysis. Therefore the bias test was not used to demonstrate equivalence between the H_2S and the total sulfur values.

Based on all these statistical test results, EPA concludes that on-line measurement of the H_2S content of the RFG at the Beaumont Refinery does not adequately characterize the total sulfur content of the fuel. Apparently, there are additional sulfur compounds in the fuel besides H_2S . Therefore, for the purposes of calculating SO_2 emissions from Units 61STK1, 61STK2, and 61STK3, the total sulfur sampling requirements in section 2.3.3 of Appendix D must be fully met for the refinery fuel gas. ExxonMobil must analyze the total sulfur content of the RFG at the required frequency, either by using an on-line gas chromatograph capable of measuring the total sulfur content or by performing manual sampling, as appropriate.

EPA's determination relies on the accuracy and completeness of the information provided in ExxonMobil's June 18, 2004 petition and the supporting data provided with the petition. This determination is appealable under Part 78. If you have any questions regarding this correspondence, please contact Travis Johnson at (202) 343-9018. Thank you for your continued cooperation.

Sincerely,

A handwritten signature in black ink, appearing to read "Sam Napolitano", with a stylized flourish at the end.

Sam Napolitano, Director
Clean Air Markets Division

cc: Joyce Johnson, Region, EPA Region VI
Sandy Simko, Texas Department of Environmental Quality
Travis Johnson, CAMD