APPLICATION NOTE

MultiTek® Analysis of Sulfur and Nitrogen in Ethyl Alcohol by UV Fluorescence and Chemiluminescence

- **Rapid and Accurate Determination of Chemically Bound Nitrogen and Sulfur**
- **Fully Automated Combustion System**
- **Sample Versatility**
- **MultiTek® Performance Verification**

Keywords:
MultiTek®, Total Nitrogen, Total Sulfur Chemilluminescence, and Ultraviolet Fluorescence, EN 15486, ASTM D5453, D4629, and D4806

INTRODUCTION

Denatured ethanol is a widely used commodity in many countries as a fuel source, exceeding the consumption of gasoline in some economies. Ethanol is a commodity that has a vast array of usage, but is strictly regulated in the fuels industry because of its physical characteristics, cost of production and transportation. which in turn have enacted strict product specifications for blending with gasoline as a fuel source.

Reaction:

The principal of operation for nitrogen analysis begins with the complete, high temperature oxidation of the entire sample matrix as illustrated in the first equation. The sample is combusted with oxygen at a temperature of 1050°C. The oxidation products include CO_2, H_2O, NO, SO_2, and various other oxides (designated MO_X below). The combustion gases are routed through a membrane drying system to remove all water and then to the nitrogen detector module for quantification.

1) $R\text{-}N + R\text{-}S + O_2 \rightarrow CO_2 + H_2O + NO + SO_2 + MO_x$

According to the second equation, the NO is contacted with O_3 (ozone), produced by an onboard generator, to form NO_2 (metastable nitrogen dioxide).

2) $NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + hv + O_2$

The SO_2 is exposed to ultraviolet radiation of a specific wavelength as shown in equation (3). This radiation is re-released in the form of sulfur fluorescence. This fluorescence is detected by a photomultiplier tube (PMT) and is proportional to the amount of sulfur in the original sample.

3) $SO_2 + hv' \rightarrow SO_2^* \rightarrow SO_2 + hv''$

Nitrogen and sulfur calibration standards are analyzed to produce calibration curves. When samples of unknown nitrogen/sulfur content are analyzed, the MultiTek Software compares the raw sample data to the calibration curve to generate and report nitrogen/sulfur concentrations.

EXPERIMENTAL CONDITIONS

Instrumentation:

Antek MultiTek® Vertical, and Antek Model 748 Autosampler.

APPLICATION NOTE

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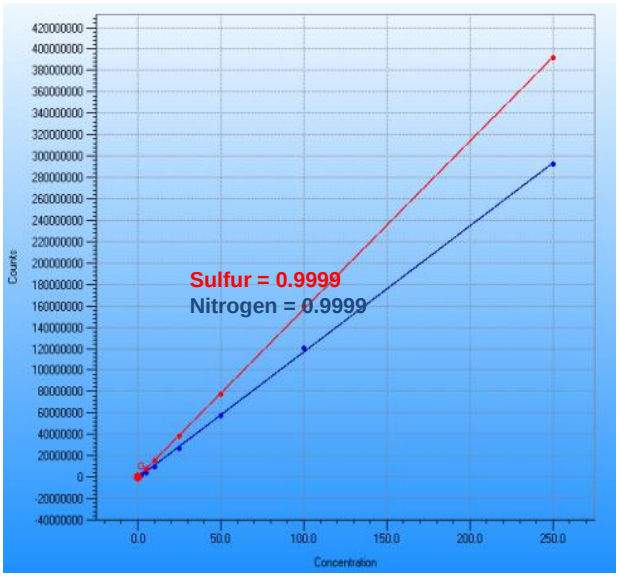
Instrument Parameters:

Sample Fill Volume (mg)	10
GFC1 – Ar/He (ml/min)	130.0
GFC2 – Pyro O_2 (ml/min)	450.0
GFC3 – Ozone O_2 (ml/min)	35.0
GFC4 – Carrier O_2 (ml/min)	25.0
Furnace (°C)	1050
Cycle Time (mm:ss)	4:00
N-Detector Cooler (°C)	5.00
N-PMT High Voltage (V)	625
S-PMT High Voltage (V)	675



The calibration standards were prepared in 99.5% reagent grade ethanol in order to minimize variations between the calibration standards and sample matrix. The calibration curve was then evaluated by using ASTM Proficiency Testing Program Samples as statistical performance monitors in assessing how close the sample values are to the robust mean.

Correlation of Test Data:

Four samples of known nitrogen content were analyzed against the calibration plot. The sulfur results were then evaluated against the data provided by all laboratories participating in the ASTM Fuel Ethanol program. The z-scores were calculated to assess where the sample concentrations fell statistically in comparison to a large population of test facilities. The results are as follows:

Calibration Standard Concentration (µg/ml):w	N Average Area Counts (n=5):	S Average Area Counts (n=5)
0	223266	353274
0.5	852970	599714
1.0	1529376	825457
2.5	3888545	2148139
5.0	7777089	4369930
10.0	15165756	9512291
25.0	38486824	27189767
50.0	77639025	57864494
100.0	159451412	120432676
250.0	391767100	292592689

Sample Identification:	Robust Mean Sulfur (ppm):	Lab Results Sulfur (ppm):	Z-Score:
ASTM ETOH0808	2.62	2.29	-0.4
ASTM ETOH1104	1.29	1.09	-0.6
ASTM ETOH1108	2.17	1.84	-0.6
ASTM ETOH1112	1.81	1.51	-0.7

The following plots illustrate the sample peaks for the sulfur and nitrogen analysis. Each table provides the expected concentration for each sample and provides a calculated z-score for each.

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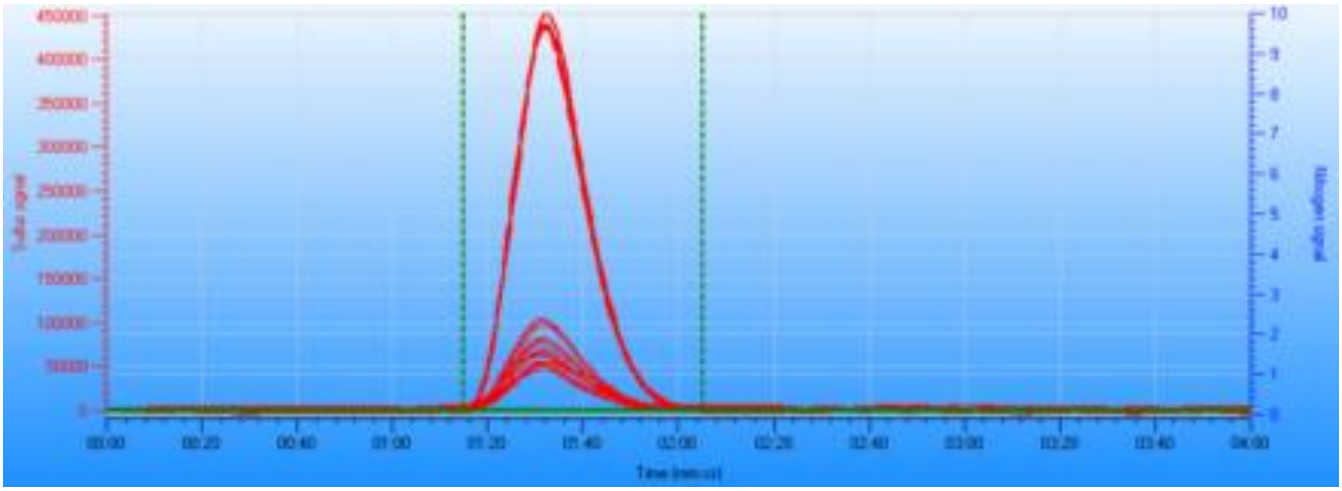

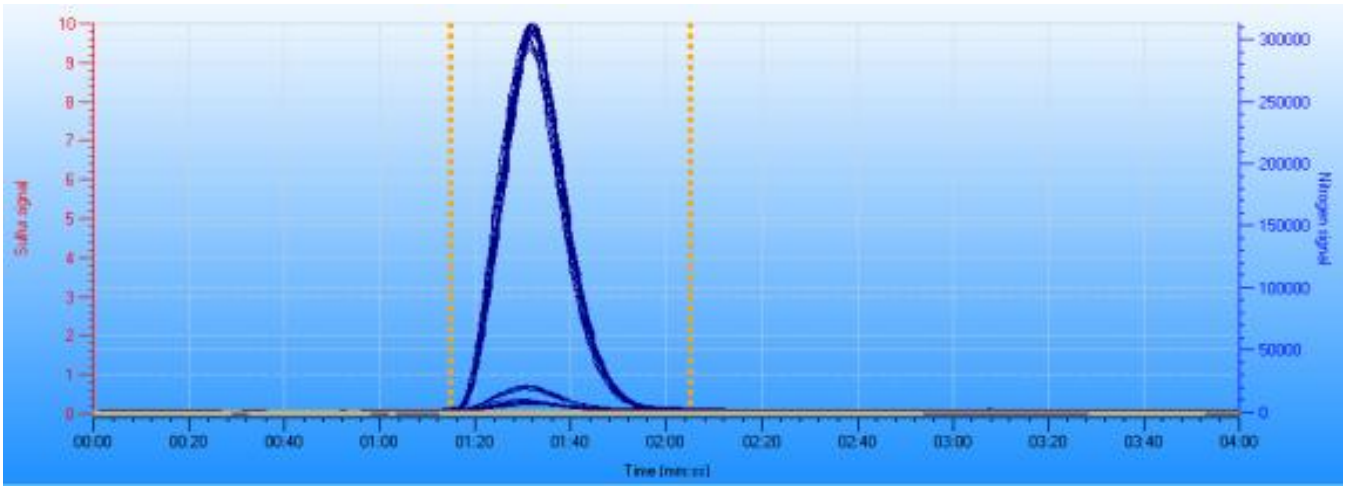

There currently aren't any proficiency program results to monitor the nitrogen concentrations for ethyl alcohol. This currently does not allow a statistical performance comparison for nitrogen results.

Sample Identification:	Robust Mean Nitrogen (ppm):	Lab Results Nitrogen (ppm):	Z-Score:
ASTM ETOH0808	N/A	8.72	N/A
ASTM ETOH1104	N/A	0.88	N/A
ASTM ETOH1108	N/A	0.88	N/A
ASTM ETOH1112	N/A	1.21	N/A

CONCLUSION

The analysis of fuel ethanol demonstrates that fast (4-minutes per injection) and accurate results can be produced for a dynamic range (0-250ppm) of sulfur and nitrogen. Higher ranges are also possible with the use of higher concentration calibration standards. The MultiTek offers excellent sample versatility and a fully automated combustion solution for monitoring finite product specifications of ethanol products.

The Antek MultiTek® is the only instrument on the market that combines sulfur, nitrogen, and halides analysis all in one. Compact, powerful, automated, and able to analyze gas, liquid, or solid samples, it's the perfect solution to today's increasing demand worldwide for fast, accurate detection and analysis of contaminants, and corrosive elements. Because MultiTek® delivers precise results with high sensitivity and unmatched versatility, it's a valuable process optimization tool that will deliver faster ROI and a better bottom line.

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