Application Note: 42035

Ultra low-level analysis of Total Nitrogen and Total Sulfur in hydrocarbons with the TN/TS 3000 analyzer

Key Words

- Hydrocarbons
- Total Nitrogen
- Total Sulfur
- TN/TS 3000

Introduction

Governments all over the world have set the maximum Sulfur content in organic fuels for the present and near future. Sulfur in the automotive fuels is one of the major causes of smog. Experts expect that the Nitrogen content in fuels will attract more attention to protect the environment even more now the Sulfur content is regulated. The content of Sulfur and Nitrogen is also important for the productivity of refineries. Catalysts in the refinery processes lose efficiency by the poisoning effects of Sulfur and Nitrogen. Refineries need to monitor the Total Nitrogen and Total Sulfur content in the feedstock to tune the processes at the highest stage of efficiency.

Thermo Electron Corporation developed the TN/TS 3000 analyzer for the ultra-low concentration analysis of Sulfur and Nitrogen in petrochemical products. The TN/TS 3000 measures both Sulfur and Nitrogen simultaneously, making the analysis of Total Nitrogen and Total Sulfur in hydrocarbons very efficient. The very high sensitivity makes it possible to measure the Total Nitrogen and Total Sulfur content at low ppb level. This application note describes the sensitivity, linearity and reproducibility of the TN/TS 3000 analyzer in the range of 0 to 100 µg/L of Nitrogen and Sulfur in xylene.

Referenced Documents

The TN/TS 3000 Total Sulfur/Nitrogen Analyzer from Thermo, complies with the following standard methods for this particular application:

ASTM D5453	Standard Test Method for determination of Total Sulfur in light hydrocarbons, motor fuels and oils by ultraviolet fluorescence.
ASTM D4629	Standard Test Method for determination of trace Nitrogen compounds in light hydrocarbons by chemiluminescence

Principle of operation

A stock solution of 1,000 mg/L Nitrogen (element source is pyridine) and 1,000 mg/L Sulfur (element source is thiofene) in xylene is the basis for the samples. Diluting the stock standard results in a set of samples ranging from 25 µg/L to 1000 µg/L. The auto sampler injects each sample into the analyzer 10 times to show the reproducibility of the analyzer. Table 1 lists the settings of the analyzer, table 2 and table 3 list the expected concentration of each sample for Sulfur and Nitrogen.

Oxygen injection	325 mL/min
Argon injection	100 mL/min
Oxygen combustion	100 mL/min
Oxygen ozonator	100 mL/min
Furnace temp. I	1000 °C
Furnace temp. II	1000 °C
Injection speed	1 µL /sec
Sample volume	100 µL

Table 1: System settings

Results

Figure 1 shows a typical response for Nitrogen 40 µg/L. Table 2 and table 3 list the results for the samples. The results include the mean integrated detector signal, the standard deviation and the relative standard deviation of the ten integrated detector signals per sample.

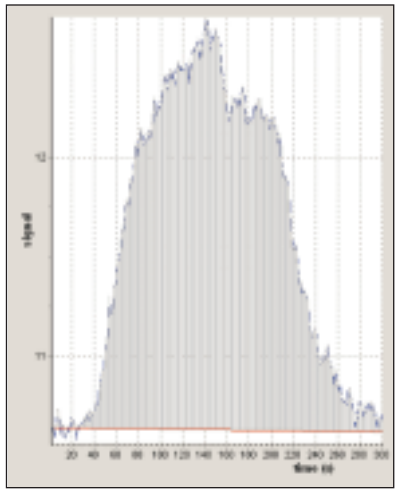

Figure 1. Integrated response for Nitrogen

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SAMPLE CONCENTRATION (µg S/L)	MEAN AREA (mV*S)	STDEV (µg S/L)	RSD (%)
0	46.2	1.26	100.12
25	135.3	1.1	4.2
30	157.1	0.5	1.6
40	192.1	0.8	2.1
50	230.7	0.6	1.2
60	263.1	0.9	1.5
70	303.0	0.8	1.2
80	343.9	0.9	1.1
100	423.5	0.8	0.7

Table 2: Response for Sulfur (n=10)

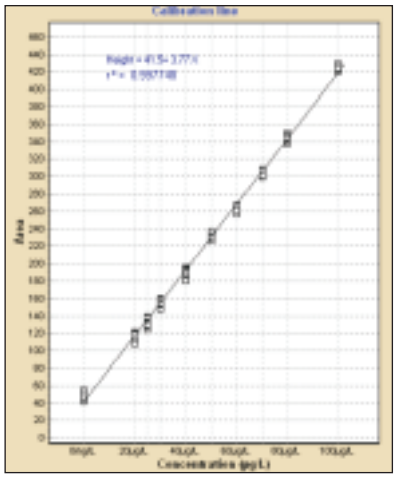
SAMPLE CONCENTRATION (µg N/L)	MEAN AREA (mV*S)	STDEV (µg N/L)	RSD (%)
0	239.8	0.4	-163.0
25	273.3	0.8	3.0
30	280.2	0.8	2.6
40	294.8	1.0	2.4
50	306.4	1.4	2.8
60	320.0	0.5	0.8
70	330.4	1.5	2.3
80	347.0	0.9	1.1
100	373.5	1.3	1.3

Table 3. Response for Nitrogen (n=10)

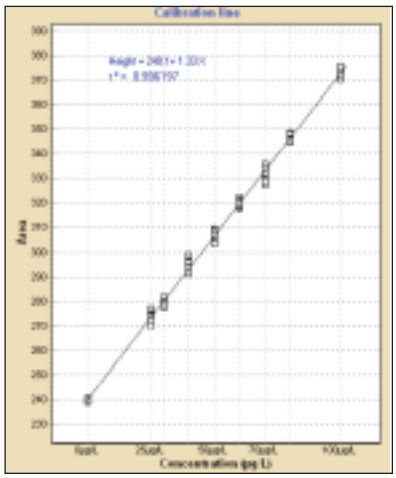
Discussion

Table 2 and table 3 list the reproducibility of the Sulfur and Nitrogen analysis. The RSDs are smaller than 5%, even for 25 µg/L. Likely 25 µg/L is not the lowest concentration in the working ranges of the Sulfur and the Nitrogen detectors.

The results of the samples show linear responses for Sulfur and Nitrogen, as shown in graph 1 and 2 respectively. The regression coefficients (r^2) of the lines are 0.9977 for Sulfur and 0.9961 for Nitrogen, proving the linear responses statistically. Table 4 shows the calculated concentrations of the samples, using the linear regression equations for Sulfur or Nitrogen. The same table also compares the calculated concentrations of the samples to the expected concentration. The relative deviations show no trends and are smaller than the reproducibility of analysis itself.



Graph 1: Linearity for Sulfur



Graph 2. Linearity for Nitrogen

SAMPLE CONCENTRATION (µg/L)	CALCULATED CONCENTRATION (µg/L)		RELATIVE DEVIATION (%)	
	SULFUR	NITROGEN	SULFUR	NITROGEN
25	24.9	25.0	0.4	0.0
30	31.1	30.2	3.7	0.7
40	39.7	41.2	0.8	3.0
50	50.2	50.0	0.4	0.0
60	58.8	60.2	2.0	0.4
70	69.3	68.2	1.0	2.6
80	80.2	80.6	0.2	0.8
100	101.3	100.6	1.3	0.6

Table 4. Expected concentration compared to calculated concentration

Conclusions

The Sulfur and Nitrogen detector have excellent reproducibility in the ultra-low working range of 25 to 100 µg/L. More research is necessary to define the lowest concentration is this working range. The linearity for Sulfur as well as Nitrogen analyses on the TN/TS 3000 analyzer is very good.

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