

Enhanced TN/TS Performance data of TSHR 7000 series with small sample volumes

Introduction

Running total sulfur and nitrogen analysis in liquid hydrocarbons in today's QC and routine laboratories are very common and in a significant number of cases require precise, reliable and fast analysis data. With our TSHR 6000 and 7000 series TN/TS/TX analyzers in conjunction with HR 7000 series Liquids Autosampler we have defined a high sample volume of 80 ul as a default value.

In order to reduce analysis time further, improve productivity and be in fully compliance with typical sample volume definitions as set in ASTM D5453 method, we have carried out tests to prove the performance of this analysis.

This Note described the total sulfur and nitrogen performance data with use of low sample volumes such as 10 and 20 ul, on a TN/TS 7000 instrument with HR 7000 liquid autosampler and a test of use typical sample volumes to verify the calibration curves performance as per ASTM D5453 method.

Within Athena software a dedicated method with typical settings for injection volumes upto 20 uL and reduced total cycle (analysis) time less than 5 minutes has been defined.

TN/TS 7000 with HR 7000

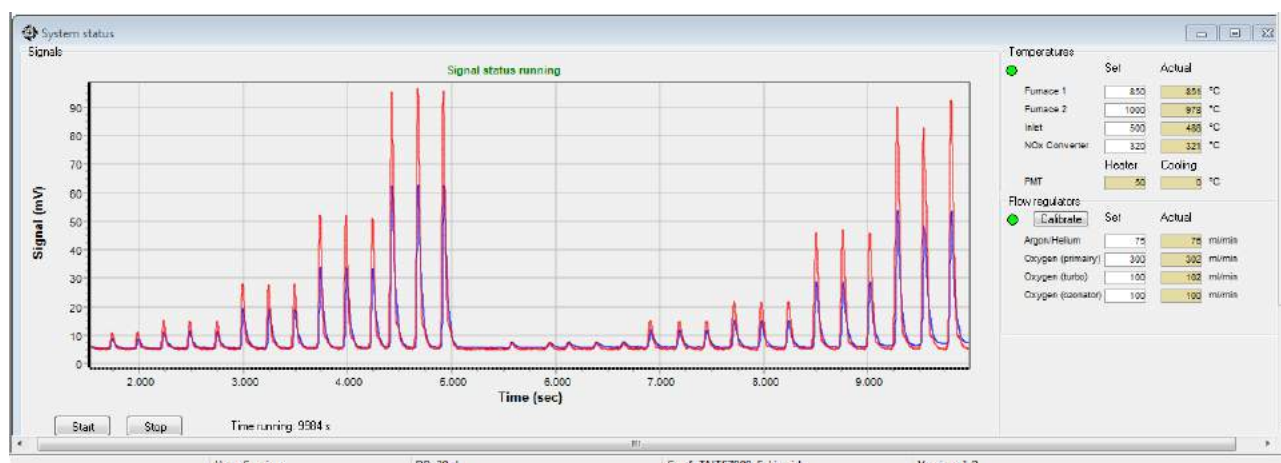
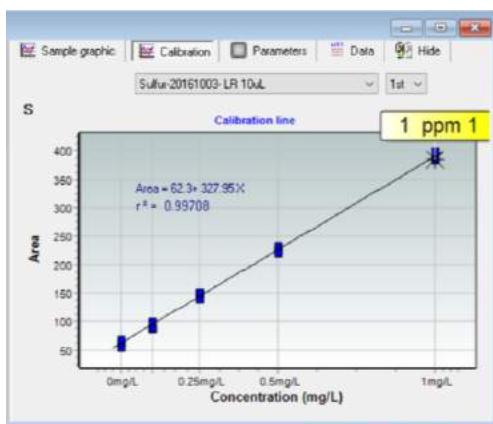


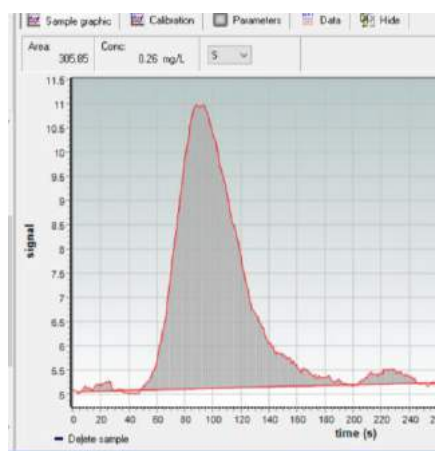
Figure 2 System status with typical instrument settings and real time measurements

Calibration line I (0 – 1 ppm) comparison data

TOTAL SULFUR						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	< 0,05	N/A	< 0,05	N/A	<0,03	N/A
0,1 ppm	0,09	25	0,09	25,6	0,09	4,0
0,25 ppm	0,26	8,4	0,25	3,8	0,25	3,8
0,5 ppm	0,50	3,8	0,51	0,8	0,50	1,2
1 ppm	1,00	2,4	1,00	1,3	1,00	0,6
R ²	0,9971		0,9988		0,9995	



Sulfur Cal line with 10 uL sample volume



Sample curve 0,25 ppm with 20 uL volume

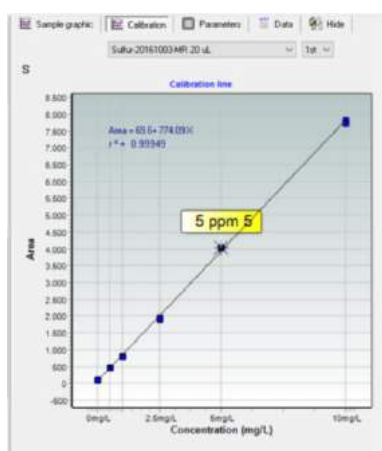
TOTAL NITROGEN						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	<0,05	N/A	< 0,05	N/A	<0,03	N/A
0,1 ppm	0,06	27	0,09	14,6	0,07	20
0,25 ppm	0,25	14	0,23	12,7	0,25	1,6
0,5 ppm	0,54	0,9	0,52	0,7	0,52	2,8
1 ppm	0,98	1,5	1,00	2,9	0,99	0,6
R ²	0,9897		0,9935		0,9990	

Comments:

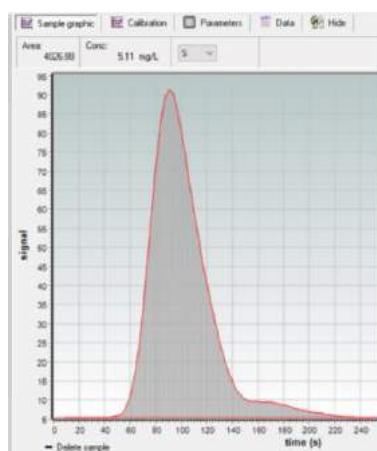
The above data shows a significant difference in repeatability between low sample volumes of 10 and 20 uL and the large sample volume of 80 uL and also improvements on the RSD's for respective concentrations. We can conclude that for trace level analysis below 0.5 ppm, it's recommended to use 80 uL which will give more accurate results for both sulfur and nitrogen.

Calibration line II (0 – 10 ppm) comparison data

TOTAL SULFUR						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	< 0,05	N/A	0,05	25,0	0,08	3,0
0,5 ppm	0,51	3,2	0,51	2,0	0,54	3,1
1,0 ppm	1,00	4,4	0,94	1,9	0,95	0,6
2,5 ppm	2,53	1,3	2,4	1,5	2,47	1,3
5 ppm	5,07	2,3	5,13	0,2	5,06	0,3
10 ppm	9,98	0,3	9,97	0,7	10,0	0,2
R ²	0,9997		0,9995		0,9996	



Sulfur Cal line with 20 uL sample volume



Sample curve 5 ppm with 20 uL volume

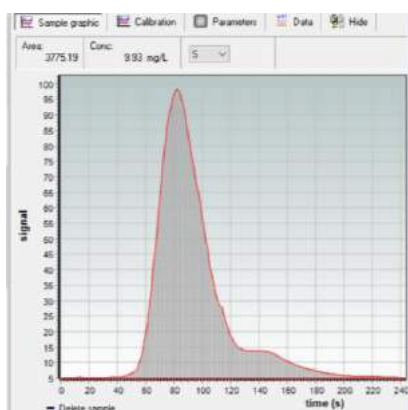
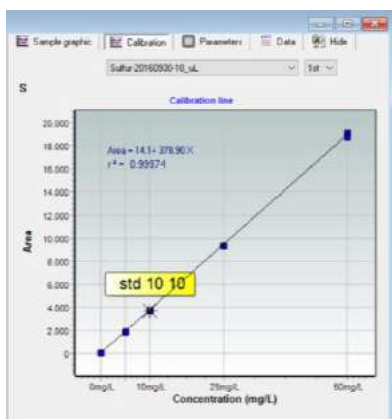
TOTAL NITROGEN						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	0,13	40	0,15	6	0,16	6,0
0,5 ppm	0,55	2,5	0,56	3,2	0,57	1,2
1,0 ppm	0,94	0,4	0,94	2,3	0,94	0,5
2,5 ppm	2,40	2,2	2,39	2,2	2,44	1,9
5 ppm	4,90	0,9	4,89	1,3	4,92	0,8
10 ppm	10,1	0,3	10,1	0,4	10,1	0,2
R ²	0,9993		0,9990		0,9992	

Comments:

The correlation and linearity for the obtained results of total sulfur and nitrogen content is very similar for all 3 different sample volumes in this low ppm range. The RSD's improve a bit when the sample volume is increased but in general it does meet the requirements as below 5%.

Calibration line III (0 – 50 ppm) comparison data

TOTAL SULFUR						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	0,26	16,3	0,27	8,5	0,29	4,7
5 ppm	5,00	0,5	5,04	0,3	4,98	0,5
10 ppm	9,86	0,7	9,77	0,3	9,80	0,2
25 ppm	24,7	0,1	24,6	0,9	25,0	0,6
50 ppm	50,1	1,1	50,2	0,4	50,2	2,2
R ²	0,9997		0,9997		0,9992	



Sulfur Cal line with 10 uL sample volume

Sample curve 10 ppm S with 20 uL volume

TOTAL NITROGEN						
Volume	10 uL		20 uL		80 uL	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
blank	0,28	12,3	0,28	7,5	0,41	3,0
5 ppm	4,86	0,4	4,82	0,4	4,83	0,7
10 ppm	9,77	0,9	9,76	0,7	9,73	0,6
25 ppm	25,0	0,2	25,0	0,9	25,3	0,3
50 ppm	50,1	0,5	50,1	0,4	50,4	0,4
R ²	0,9998		0,9998		0,9998	

Comments

Based on above obtained results we can conclude that the use of small sample volumes (10 and 20 uL) has minimum impact to the performance of this working range (0 – 50 ppm). So this means that for routine measurements in the range of 0 – 50 ppm, 20 uL sample size give good repeatability and will help drive productivity for customer convenience.

ASTM D5453 calibration data

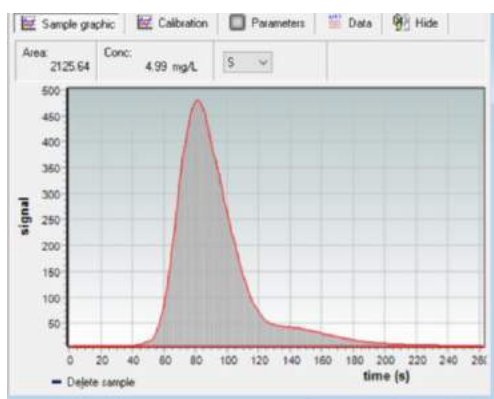
This method defined 3 calibration lines (Curves I, II and III) with the following concentrations and sample volumes:

Standard	Curve I	Curve II	Curve III
1	0.5	5	100
2	1.0	25	500
3	2.5	50	1000
4	5.0	100	
5	10.0		
Sample size	20 uL	10 uL	5 uL

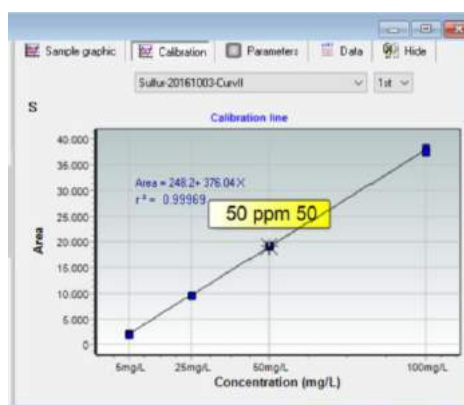
According above defined curves, we have prepared calibration standards with the respective concentrations and use the given sample sizes to analyze these as three replicates at the TSHR TN/TS 7000 model analyzer with HR 7000 sampler. The results obtained from these standards are given below. Curves I and II were measured in standard range of UV-F detector and curve III in high range of TS-UVF detector.

TOTAL SULFUR CALIBRATION LINES - ASTM D5453						
Standard	Curve I		Curve II		Curve III*	
	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %	Mean (mg/L)	RSD %
1	0,51	2,0	4,78	8,9	104	0,7
2	0,94	1,9	25,0	0,5	492	1,3
3	2,4	1,5	50,5	0,8	1004	2,0
4	5,13	0,2	99,8	1,2		
5	9,97	0,7				
R ²	0,9997		0,9997		0,9990	

*high range setting UV-F detector



Sample graph of 5 ppm S with 10 uL injection volume



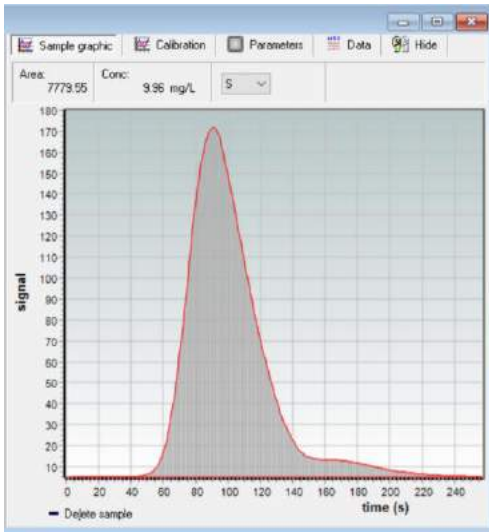
Calibration line 0 – 100 ppm

Comments.

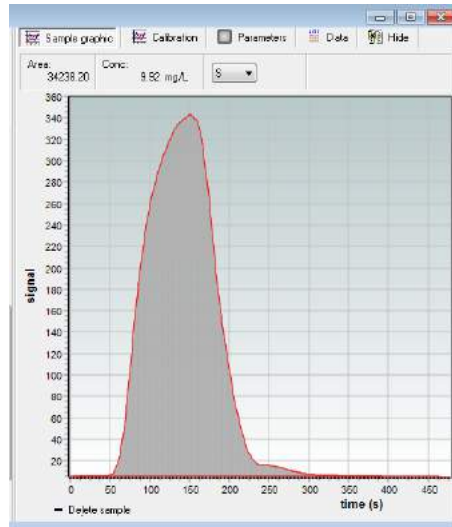
The results of curves I and II gives a good linearity and repeatability when using reduced sample volumes, as defined in ASTM D5453 method, at the TSHR TN/TS 7000 instrument.

Curve III measure in high range setting of the UV-F detector shows also a good correlation and the use of only 5 uL gives a reasonable RSD for the 3 concentrations.

Examples of analysis times for a 10 ppm Sulfur between 20 and 80 uL injection volumes:



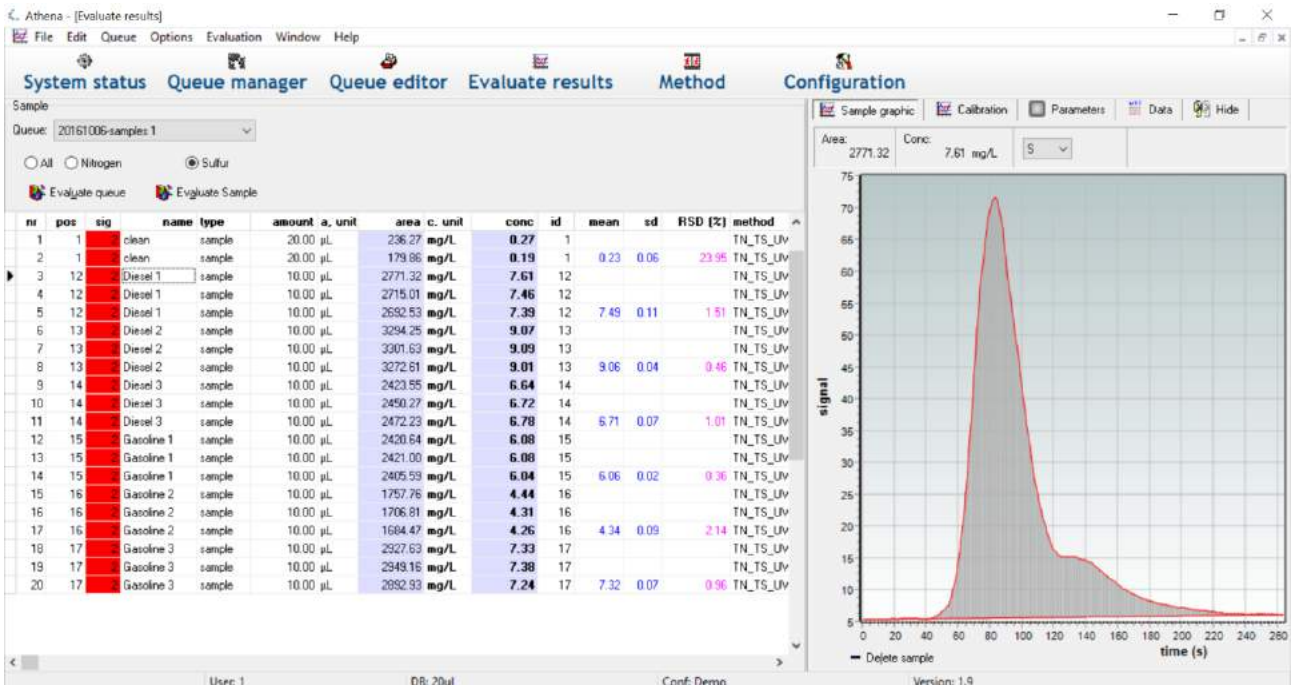
20 uL injection volume: < 5 minutes



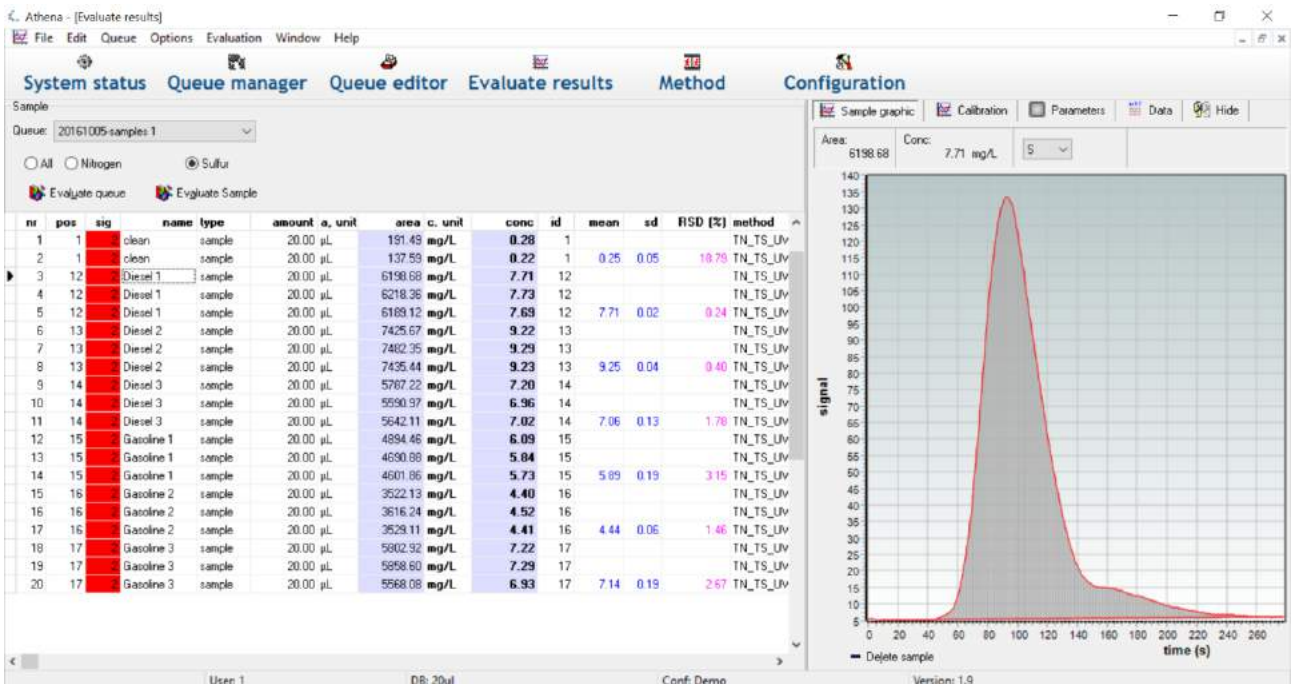
80 uL injection volume: 7 minutes

Total Sulfur Analysis of Diesel and Gasoline samples using small sample volumes.

Below given table and graphs shows the performance data of using 10 and 20 ul sample volumes to compare the sulfur concentrations in a set of diesel and gasoline samples.



Sulfur data using 10 uL sample volume for Diesel and Gasoline samples



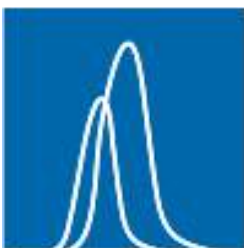
Sulfur data using 20 µL sample volume for Diesel and Gasoline samples

Summary

Based on above experiments and test data we can conclude that the TSHR TN/TS 7000 series in conjunction with the HR 7000 Liquids Autosampler series, is capable of handling low sample volumes as 10 and 20 µL with precise sulfur/nitrogen data which results into the following features and benefits:

- Short Analysis times: less than 5 minutes which results in productivity savings
- Excellent performance data and fully compliance with ASTM D5453 / D4629 methods
- Lower costs of operation because of shorter analysis times

For Trace Level Sulfur/Nitrogen analysis (ppb) it's still recommended to use high sample volume (e.g. 80 µL) to obtain accurate results and low RSD's.



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