MEETING TIER III PERFORMANCE BASED MEASUREMENT APPROACH CRITERIA FOR MEASURING LOW LEVEL SULFUR BY ASTM D5453 IN AUTOMOTIVE FUELS

INTRODUCTION

This poster gives an overview of the requirements that are needed to meet the TIER III regulation and to show example data of the the analytical performance of sulfur in gasoline measurements according to the TIER III program. The Environmental protection agency (EPA) TIER III program has come into effect per January 1st 2017 for all major gasoline producers and importers. The TIER III program is a follow up of the previous TIER II program with changes to the maximum allowable sulfur content and the introduction of the use of the performance based measurement system (PBMS).

ANTEK: MultiTek Sulfur configuration

IMPORTANCE

EPA claims that the introduction of the TIER III program will generate an annual prevention by 2030 of 2000 premature deaths, 2200 asthma attacks and up to 50000 respiratory illness in children. Total health related benefits will be between $6.7 – 19 Billion dollars annually. The proposed reductions in sulfur for gasoline will achieve immediate emissions reductions and health benefits from the existing automotive fleet, and in time it will support the general air quality.

PERFORMANCE BASED

The Performance based measurement system (PBMS) which was previously introduced with TIER II is now mandatory. By using the PBMS, EPA specifies a set of processes and limitations. Part of this PBMS is the validation of the data by meeting the Accuracy and Precision criteria and performing continuous SQC measurements with reference material.

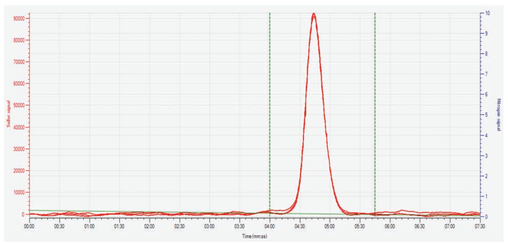

Figure 1: Typical 10 ppm sulfur peak.

PRECISION

For precision calculation a commercially available sulfur standard was analyzed over a period of 20 days. The maximum allowable standard deviation computed from the results must be less than or equal to 1.5 times the repeatability ''r'' divided by 2.77, where ''r'' equals the ASTM repeatability of ASTM D7039. Passed if Δ Stdev ≤ Max. Stdev.

PRECISION																				
Day	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
QC 1	1.19	1.22	1.16	1.37	1.18	1.15	1.17	1.26	1.30	1.18	1.21	1.20	1.17	1.18	1.21	1.13	1.14	1.13	1.14	1.13
QC 2	4.96	4.93	4.98	4.93	4.95	4.96	4.92	4.95	4.87	4.83	4.81	4.82	4.83	4.91	4.88	4.91	4.92	4.90	4.89	4.93
QC 3	8.16	8.22	8.07	8.25	8.06	7.97	8.26	7.82	7.88	7.68	7.98	7.92	7.96	8.01	8.09	8.21	8.20	8.22	8.28	8.31

QC 1	
Ref. Value	1.20
Mean	1.19
STDEV	0.06
RSD %	5.04
Max. STDEV	0.31
Passed?	passed

QC 2	
Ref. Value	5.0
Mean	4.90
STDEV	0.05
RSD %	0.97
Max. STDEV	0.67
Passed?	passed

QC 3	
Ref. Value	8.20
Mean	8.08
STDEV	0.17
RSD %	2.08
Max. STDEV	0.87
Passed?	passed

Table 1: Example of precision calculation, all concentrations are in mg/kg

ACCURACY

Table 1 shows typical data from the calculation of the accuracy where a sulfur standard was measured 10 times in a continuous sequence.

The average deviation from the standard is compared to the calculated maximum accuracy.

ACCURACY						
Replicate	QC 1	Δ	QC 2	Δ	QC 3	Δ
1	1.227	0.027	5.054	0.054	7.904	0.296
2	1.266	0.066	4.973	0.027	8.058	0.142
3	1.146	0.054	4.925	0.075	7.792	0.408
4	1.102	0.098	4.957	0.043	7.682	0.518
5	1.153	0.047	4.951	0.049	7.883	0.317
6	1.334	0.134	4.945	0.055	8.022	0.178
7	1.170	0.030	4.965	0.035	7.863	0.337
8	1.167	0.033	5.030	0.030	7.839	0.361
9	1.225	0.025	5.092	0.092	7.852	0.348
10	1.176	0.024	5.038	0.038	8.224	0.024
Mean Δ	0.054		0.50		0.293	
Max. Δ	0.224		0.88		0.632	
Ref. Value	1.20		5.00		8.20	
Passed?	passed		passed		passed	
PASS Criteria	if Δ CoA ≤ Max. Δ					

Table 2: Example of accuracy calculation, all concentrations are in mg/kg

STANDARD QUALITY CONTROL

Each laboratory that is measuring according to the EPA TIER III regulation, shall need to setup a quality control system in accordance to ASTM D6299. This includes a mandatory instrument validation on accuracy and precision with a minimum of 3 times a year. In addition an "I"-Chart shall be constructed to monitor the instrument performance.

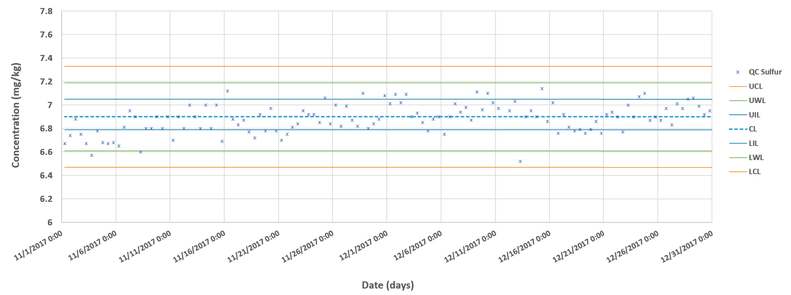

Figure 2: Typical 'i' chart for SQc

INSTRUMENTATION

The data presented is generated on a MultiTek Sulfur analyzer from PAC. The MultiTek Total combustion elemental analyzer can determine total sulfur concentration in a wide range of sample matrices. The principle of operation for sulfur analysis begins with the combustion of the sample. The sample is combusted with oxygen at a temperature of 1050°C. Oxidation products include CO_2, H_2O, NO, SO_2 The combustion gasses are routed through a membrane drying system to remove all water and then to the sulfur UV-fluorescence detector module(s) for quantification.

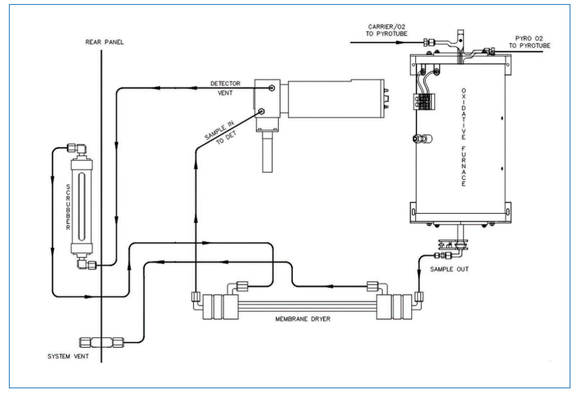

Figure 3: Flow path overview MultiTek Sulfur

CONCLUSION

The data presented shows that the MultiTek can be used for the measurement of total sulfur in gasoline products for certification purposes according to the EPA TIER III regulations.

For more information please contact us at http://www.paclp.com