APPLICATION NOTE AN148

ASTM D5769 Standard test method for determination of benzene, toluene, and total aromatics in finished gasolines by GC-MS.

KEY WORDS : Aromatics, Benzene, Toluene, gasoline

INTRODUCTION

After the petroleum refining process it is important to assess the gasoline quality and to see if the fuel regulations are met. The ASTM D5769 describes a method to determine Benzene, Toluene and total aromatics in finished gasolines using a gas chromatograph (GC) in combination with a Mass Spectrometer (MS).

This application is applicable on the SCION Instruments 4X6 in combination with the SCION Instruments single quad (SQ). But the analysis was performed on the SCION Instruments 8X00 GC series with the new 8700 SQ mass spectrometer shown in figure 1.

Figure 1. SCION Instruments 8X00 GC with SQ-MS.

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EXPERIMENTAL

This analysis can be implemented on the 8300-GC and the 8500-GC platform. The analysis was performed on the SCION Instruments 8500-GC analyser equipped with SQ MS and SCION 8400PRO autosampler.

After the refinery process it is important to inspect the quality of the product(s) to see if the fuel meets the regulations set for the gasoline products.

The ASTM D5769 is a simple method for the determination of benzene, toluene and total aromatics in gasoline. With this method it is also possible to measure gasolines that contain alcohols and ethers (oxygenates) as additives. It has been determined that common oxygenates found in finished gasolines do not interfere with the analysis.

This method uses a multipoint calibration consisting of at least five levels. Specified deuterated hydrocarbons are recommended as internal standards. This application note uses the recommended: Benzene-d6, Ethylbenzene-d10 and Naphtalene-d8 as internal standard. For toluene it is also possible to use Toluene-d8 as an extra internal standard.

The method has been tested for the following concentration ranges in liquid volume percent. Benzene 0.1 to 4.0 %; Toluene 1 to 13%; C_6 to C_{12} aromatics 10 to 42%.

RESULTS

All the results were calculated according to the described method ASTM D5769.

The precision of the method was obtained by ten consecutive injections. The concentration used varied for every component.

It was shown that the repeatability (RSD%) for almost all components were below 2%. Table 4 shows the repeatability for each of the components.

Table 2. Instrumentation operating conditions.

Injector	Splitless 250:1, 250 °C
Column	SCION 1-MS
Oven Program	160°C (0 min), 3°C/min to 120°C (0 min) 10°C/min to 250°C
Carrier	Helium: Linear velocity 35 (50°C)
Inj. Volume	0.2 µl
Autosampler	8400PRO
Software	MS work station
MS transfer line temperature	270°C
Ion source temperature	220°C
Ionization mode	EI
Scan start	0.5
Scan mode	Full Scan

All the chromatographic peaks were identified with the NIST library. Figure 3 shows six examples of these target peaks from a standard containing all the components.

The calibration curves for each component were made from certified standards. All components had a correlation coefficient (R^2) greater than 0.9991, except 2-Methyl-naphthalene which had a correlation of 0.9982.

According to the ASTM D5769 every component should have a correlation coefficient of a least 0.99 or better. This means that all the components meet the requirements.

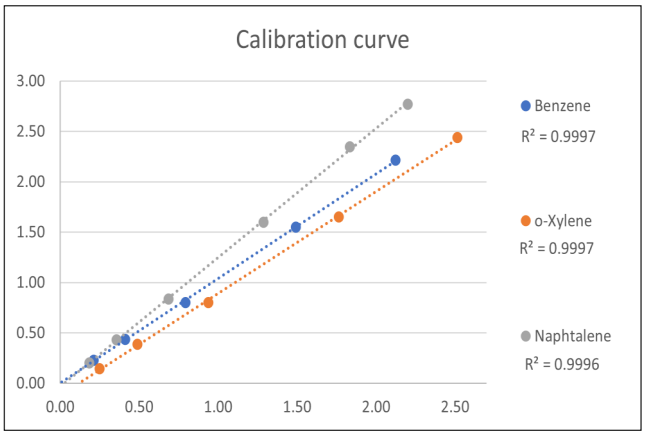

Figure 2. Calibration curve example of three components.

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Figure 2 shows an example of the calibration curves of Benzene, o-Xylene and Naphthalene, in addition the correlation coefficients of each component are shown in table 4.

From the linearity the limit of detection (LOD) and limit of quantitation (LOQ) were calculated. These values can also be found in table 4.

The Quality control sample was pre-prepared, the average concentrations are shown in table 3. The left column shows the concentration on the certificate and the right shows the measured concentration. All concentrations are shown in percentage (%) except 1.4-Diethylbenzene, that is shown in µg/ml. According to ASTM D5769 the values obtained should not deviate more than 5%, except 1.2.4.5-Tetramethylbenzene and Naphthalene those are set on a max deviation of 10% The values in table 3 are all within these limits

Table 3. Results of the Quality Control sample

QC component	QC (Certified) %	QC (measured) %
Benzene	1.000	1.001
Toluene	9.000	9.092
Ethylbenzene	2.970	2.826
m-Xylene	2.997	2.913
o-Xylene	2.946	2.878
1.2.4-Trimethylbenzene	2.946	2.640
1.2.3-Trimethylbenzene	2.983	2.836
1.4-Diethylbenzene (ug/ml)	100.1	95.64
1.2.4.5-Tetramethylbenzene	1.998	2.059
Naphthalene	1.000	1.021

The gasoline sample was spiked with internal standard and after that injected in the GC-MS. The calculated results of the sample are shown in table 4.

Table 4. Results of the different components

	R^2	LOD mg/100g	LOD %	LOQ mg/100g	LOQ %	RSD %	Sample %
Benzene	0.9997	76.9	0.08	236.7	0.24	0.93	0.76
Toluene	0.9996	353.7	0.35	1071	1.07	1.07	9.21
Ethylbenzene	0.9993	119.0	0.12	351.3	0.35	0.81	1.97
m/p-Xylene	0.9992	180.3	0.18	546.4	0.55	1.08	4.30
o-Xylene	0.9996	115.2	0.12	348.9	0.35	0.92	3.02
(1-Methylethyl)-benzene	0.9997	70.0	0.07	212.1	0.21	1.69	<0.21
Propyl-benzene	0.9997	68.3	0.07	206.8	0.21	1.66	0.42
1-Methyl-3-ethylbenzene	0.9997	60.4	0.06	183.2	0.18	1.16	1.41
1-Methyl-4-ethylbenzene	0.9996	55.8	0.06	169.0	0.17	1.17	0.62
1.3.5-Trimethylbenzene	0.9997	61.4	0.06	186.1	0.19	1.43	0.64
1-Methyl-2-ethylbenzene	0.9997	67.1	0.07	203.2	0.20	1.21	0.49
1.2.4-Trimethylbenzene	0.9994	109.9	0.11	333.1	0.33	1.31	2.06
1.2.3-Trimethylbenzene	0.9997	69.2	0.07	209.6	0.21	2.02	0.45
Indan	0.9997	48.1	0.05	145.7	0.15	0.97	<0.15
1.4-Diethylbenzene	0.9995	59.0	0.06	178.9	0.18	1.25	<0.18
n-Butylbenzene	0.9995	56.7	0.06	171.8	0.17	1.46	<0.17
1.2-Diethylbenzene	0.9998	39.3	0.04	119.1	0.12	1.68	<0.12
1.2.4.5-Tetramethylbenzene	0.9991	86.9	0.09	263.4	0.26	1.68	<0.26
1.2.3.5-Tetramethylbenzene	0.9999	22.9	0.02	69.5	0.07	1.56	0.13
Naphthalene	0.9997	41.6	0.04	125.9	0.13	1.24	<0.13
2-Methyl-naphthalene	0.9982	112.2	0.11	340.0	0.34	1.98	<0.34
1-Methyl-naphthalene	0.9996	54.5	0.06	165.1	0.17	2.09	<0.17

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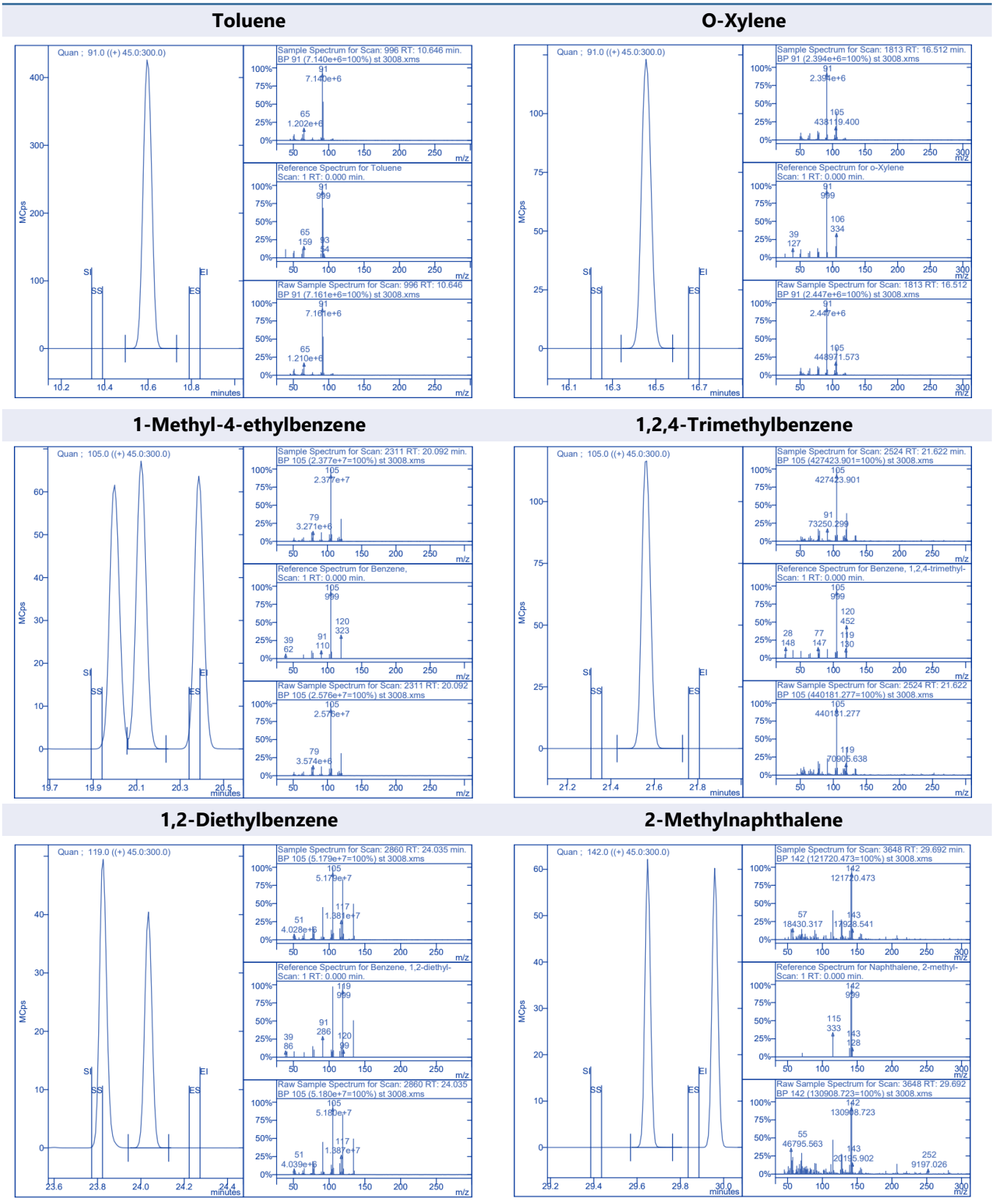

Figure 3. Target compound example peaks.

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CONCLUSION

The Scion 8X00-GC analyser equipped with a split/ spitless injector, Scion Instruments column and new 8700 SQ mass spectrophotometer is capable of performing ASTM D5769 in a way that complies to the method.

The equipment of the 8X00-GC analyser is pre determined, for ordering information or customisation, please contact your local sales representative.

Although the 4X6-GC series is not used in this application it is possible to perform this analysis on the SCION Instruments 4X6 GC series.

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