

# Improved Performance for the Analysis of Aromatics in Gasoline by ASTM Method D5769 Using the Agilent 5973 inert Gas Chromatography/Mass Spectrometry System

## Application

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### Abstract

**The new Agilent 5973 inert gas chromatography/mass spectrometry system can be used to measure high concentrations of aromatic compounds in gasoline using American Society of Testing and Materials Method D5769. This system provides improved linear calibrations when equipped with the optional extended linearity ion source kit. This makes Method D5769 easier and faster to set up, with more reliable results. The Agilent 5973 inert with the extended linearity source was also shown to quickly and easily pass the D5769 method performance tests for resolution, sensitivity, and spectral integrity.**

### Introduction

The levels of aromatic compounds in gasoline are adjusted upward or downward by refiners to comply with environmental regulations and to improve the properties and performance of the finished product. Due to the complex hydrocarbon matrix, it is difficult to chromatographically separate all aromatics from the other nonaromatic hydrocarbons. The American Society of Testing and

Materials (ASTM International) has developed Method D5769 that uses gas chromatography/mass spectrometry (GC/MS) to quickly separate, identify, and quantitate benzene, toluene, other specific and total aromatic hydrocarbons in gasoline [1]. This method is designed to measure these compounds between 0.1 and 42 weight percent.

One difficulty encountered when using Method D5769 is obtaining linear calibrations for compounds at concentrations higher than 10 weight percent. Modern GC/MS systems are designed to provide extremely low analytical sensitivity (ppm to ppb), with linear response over several orders of magnitude. However, when trying to analyze compounds at percent levels, the mass spectrometer electron ionization (EI) source can be saturated with sample, resulting in a nonlinear response over a relatively narrow concentration range.

There are a number of remedies to this issue that include custom mass spectrometer tuning, time programmed interface splitters, very small injections (<1  $\mu\text{L}$ ), very large split ratios (>1500:1), nonlinear curve fitting, and a specialized inlet pressure program [2]. These can be used individually or in combinations to meet the calibration requirements of the ASTM method. However, these approaches significantly add to the complexity of a method that is already very complex to successfully set up and run. The best solution to a detector response problem would be to have an EI source that is designed specifically for enhanced linearity.



The new Agilent Technologies 5973 inert GC/MS system has an EI source, constructed of a solid inert material, to provide high sensitivity for difficult samples containing pesticides, nitrophenols, and active sulfur compounds. At first glance, an instrument with this degree of sensitivity would not have the required linear dynamic range necessary to analyze aromatics in gasoline using Method D5769. However, the Agilent 5973 inert GC/MS system offers an optional extended linearity source kit that provides greater linear dynamic range for major compound analysis. This application note will demonstrate the improved performance of Method D5769 using this system.

## Experimental

The Agilent 5973 inert GC/MS system components used for this work are outlined in Table 1. Analysis conditions were set exactly as described by Method D5769 and are shown in Table 2. The ChemStation Autotune program was used to tune the Agilent 5973 inert. No changes were made to the electron multiplier voltage obtained by Autotune.

Method D5769 calibration standards were obtained from Accustandard (125 Market Street, New Haven, CT, USA). These standards contained all 23 aromatic compounds specified by the ASTM

**Table 1. Agilent 5973 inert Hardware Configuration for ASTM Method D5769**

<b>Agilent 5973 inert GC/MS hardware</b>	
G1778A	5973 inert with standard turbo pump and ChemStation
G2589-20045	Ultra large aperture drawout plate for extended linearity source
G1942N	6890N GC with capillary inlet and mass spectrometer direct capillary interface
G2613A	Agilent 7683 Automatic Liquid Injector (ALS) with nanoliter adapter
G2614A	100-sample tray for ALS
<b>Columns</b>	
Capillary column	1 $\mu$ m film HP-1, 60 m $\times$ 0.25 mm id (Agilent part number 19091Z-236)
<b>Consumables</b>	
Syringe	10 $\mu$ L fixed needle (Agilent part number 5181-1267)
Inlet liner	Split optimized, low pressure drop liner (Agilent part number 5183-4647)

**Table 2. Conditions for the GC/MS Analysis of Aromatics in Gasoline by ASTM Method D5769**

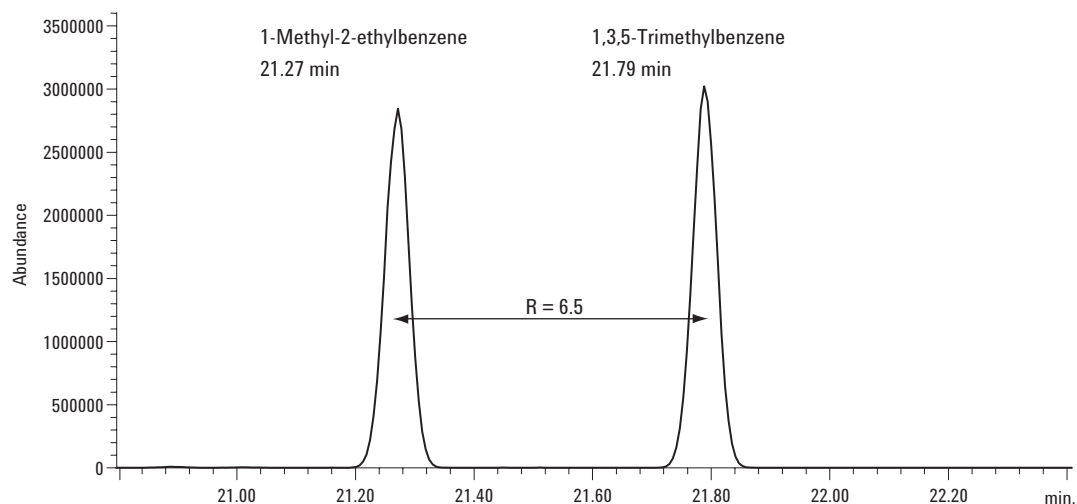
<b>GC Conditions</b>	
Carrier gas	Helium at 28.5 psig constant pressure mode 35 cm/s average linear velocity at 50 $^{\circ}$ C
Inlet	Capillary at 250 $^{\circ}$ C 250:1 split ratio
Oven temp	60 $^{\circ}$ C (0 min) 3 $^{\circ}$ C/min to 120 $^{\circ}$ C (0 min) 10 $^{\circ}$ C/min to 250 $^{\circ}$ C (0 min)
Injection size	0.2 $\mu$ L using a 10- $\mu$ L syringe
<b>Mass Spectrometer Conditions</b>	
GC/MS Interface	Direct capillary at 280 $^{\circ}$ C
Ion source	250 $^{\circ}$ C
Quadrupole	150 $^{\circ}$ C
Solvent delay	3 min.
Electron energy	70 eV
Emission current	35 amps
Scan range	45 to 300 Daltons
Sampling rate	2 <sup>3</sup> A/D
Scan speed	2.89 scans/s
Autotune	Standard

method along with four deuterated internal standards; benzene-d6, toluene-d9, ethylbenzene-d10, and naphthalene-d8. The calibration standards were used to construct a five-point calibration curve using the quantitation ions specified for each compound by the ASTM method. Other system performance tests for chromatographic resolution, mass spectral integrity, and sensitivity were performed using samples obtained from Accustandard that met ASTM Method D5769 requirements.

## Results and Discussion

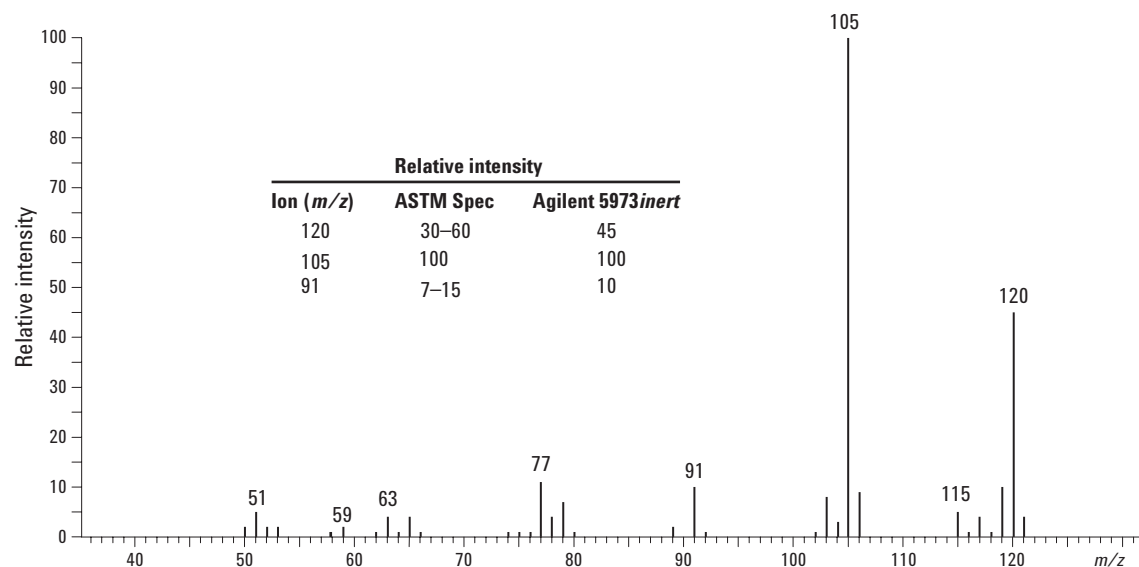
Since ASTM Method D5769 is a complex application, there are a number of system measures that must be met before calibration and sample analysis. First, the chromatographic resolution was tested under normal operating conditions using 1-methyl-2-ethylbenzene and 1,3,5-trimethylbenzene at 3 mass % each. The resolution between these two peaks must be greater than 2. Figure 1 shows that the resolution between these two compounds was 6.5 using the Agilent 5973 inert system, therefore exceeding the method requirements.

For a 0.01 mass % sample of 1,4-diethylbenzene, the signal-to-noise ratio must be at least 5 at mass 134. This sample was run with the Agilent 5973 inert system and the signal-to-noise ratio (peak-to-peak) was found to be 21.



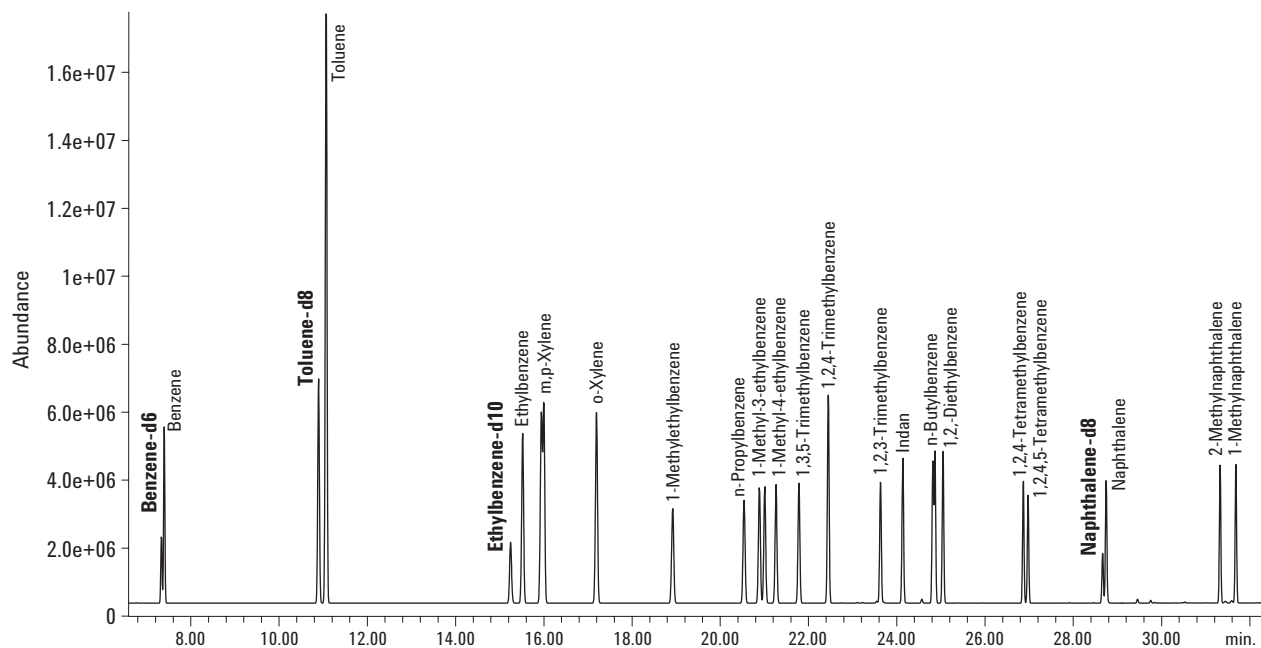
**Figure 1. The chromatographic resolution between 1-Methyl-2-ethylbenzene and 1,3,5-Trimethylbenzene exceeds the minimum requirement of 2.0 specified by ASTM method D5769.**

The mass spectral integrity performance was measured by running a 3 mass % sample of 1,2,3-trimethylbenzene. The spectrum of this compound must meet certain mass and relative abundance criteria to assure that the instrument is properly tuned and functioning. Figure 2 shows that this test was successfully met using the enhanced linearity Agilent 5973 inert.



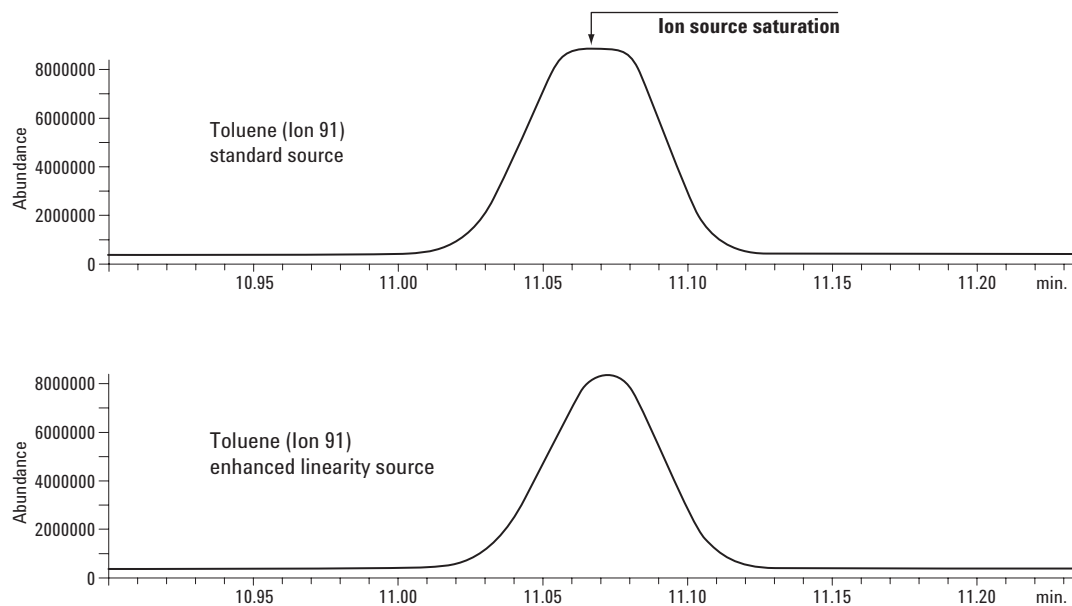
**Figure 2. For a 3 mass % of 1,2,3-trimethylbenzene sample, the spectral integrity requirements of the ASTM D5769 method are met using the Agilent 5973 inert enhanced linearity source.**

Calibration of the system was performed with standards containing 23 analytical compounds and four deuterated internal standards. The resulting five-point calibration curves for each aromatic compound spanned concentrations in gasoline of 0.1 to 42 weight percent. Figure 3 shows a total ion chromatogram (TIC) for one of these standard mixes.



**Figure 3. TIC of a calibration standard containing all 23 analytical compounds and four internal standards for the analysis of aromatics in gasoline.**

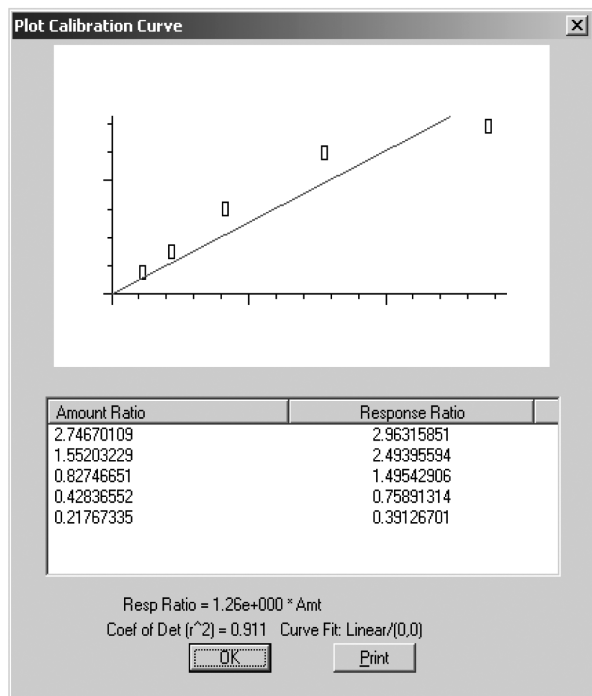
Reconstructed ion chromatograms (RIC) were made from characteristic ions for each calibrated compound. These RICs were integrated and the responses used to construct the calibration curves for each compound. Using conventional, high-sensitivity ion sources, the high-concentration standards can saturate the ion source, resulting in a “flat” or non-linear response for that compound. This effect is shown in Figure 4 for a 10 weight percent standard of toluene. In the upper chromatogram, the toluene RIC peak ( $m/z$  91) shows a “flat” top, indicating that the ion source contains too much toluene. However, by simply switching to the Agilent 5973 inert extended linearity source, the same toluene standard has the expected peak shape and response. This is shown in the lower chromatogram of Figure 4.



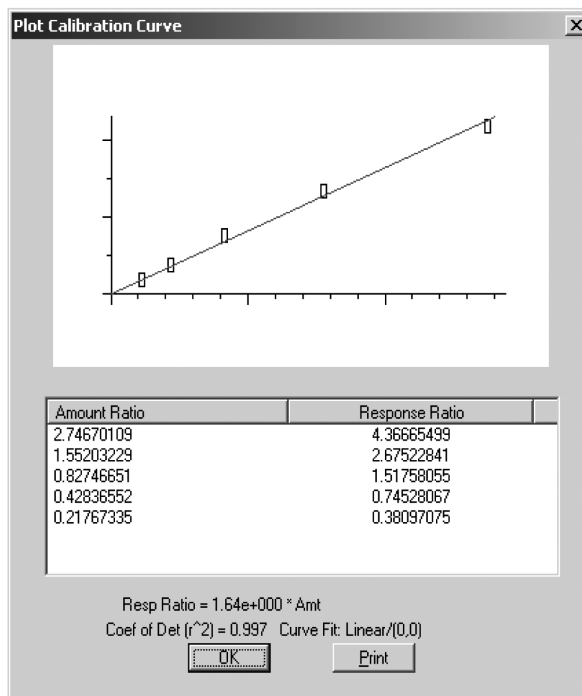
**Figure 4. RIC of  $m/z$  91 for the analysis of toluene. The upper chromatogram was obtained with the high sensitivity source of the Agilent 5973 *inert* system. The lower chromatogram shows the same standard run using an Agilent 5973 *inert* equipped with an enhanced linearity source.**

The result of this ion source saturation was calibration curves that do not meet the ASTM Method D5769 linearity specification. This problem was completely overcome when using the Agilent 5973 inert extended linearity source. Figure 5 shows a comparison of toluene calibration for the two different source designs on the Agilent 5973 inert.

**A. Standard Agilent 5973 inert source**



**B. Enhanced linearity Agilent 5973 inert source**



**Figure 5. Two toluene calibrations for ASTM Method D5769. A) the standard source does not meet the ASTM method requirements for linearity. B) using the enhanced linearity source, the requirements are easily achieved for toluene.**

## Conclusion

The new Agilent 5973 inert equipped with the optional extended linearity source kit was shown to meet or exceed all performance measures for the analysis of aromatics in gasoline by ASTM Method D5769. By quickly and easily obtaining linear calibration curves for percent level components, analysts using this method do not have to apply complex remedies such as specialized tuning, time programmed interface splitters, very small injections, very large split ratios, non-linear curve fitting, and specialized inlet pressure programs. More time can be spent running samples and producing analytical results.

## References

1. Annual Book of ASTM Standards, Vol. 05.03 "Petroleum Products and Lubricants (III), D 4928 - D 5950", ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
2. Leibrand, Roger J., "Latest Enhancements to the GC/MS Analysis of Gasoline by ASTM Method D-5769", Agilent Technologies publication 5966-2798E, December 1999. [www.agilent.com/chem](http://www.agilent.com/chem)

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