

PREPRINT EXTENDED ABSTRACT

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The Analysis of Reformulated Gasolines
Using Fast Gas Chromatography / Mass Spectrometry

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The requirement that all reformulated gasoline (RFG) sold in the United States be analyzed by gas chromatography / mass spectrometry (GC/MS) for aromatic content presents a unique challenge and opportunity for petroleum analytical analyses. A fast GC/MS method was developed which encompasses or surpasses not only the basic EPA performance requirements for analysis of total aromatics, but will simultaneously measure individual aromatics and oxygenates in reformulated gasolines. Furthermore, the combined procedure requires only 10 minutes of instrument and computational time. In contrast, ASTM Method D 5769 generally takes 90 minutes just to measure total aromatic content. The measurements of oxygenates, benzene, and toluene also compare favorably to the standard ASTM methods. The method matches the precision and accuracy of ASTM Method D3606, a GC/GC method, which is the only current acceptable method for individual aromatics in RFG. Furthermore, it can measure methyl t-butyl ether (MTBE) and t-amyl methyl ether (TAME) as accurately as ASTM D5599, the approved OFID method for oxygenates.

The fast chromatography method meets all of the requirements of the EPA and ASTM methods. The EPA primarily list performance objectives requiring GC/MS and 2% overall accuracy. The ASTM Method does not restrict the chromatography or types of internal standards. The Texaco Method has procedural enhancements which enable it to expand the basic scope of these methods beyond total aromatics and to surpass their precision and accuracy while maintaining performance requirements of both the EPA and ASTM methods. These enhancements are:

- The additional use of deuterated surrogate, toluene, which is not required, but allowed by the ASTM method.
- The use of micro-bore capillary gas chromatography, which reduces greatly processing time, and prevents ion saturation of the mass spectrometer source.
- More appropriate selection of quantitation ions, which enhances precision and accuracy without changing any operating procedures.

Since toluene is generally the most abundant individual aromatic hydrocarbon component in gasoline, its accurate measurement is critical. (The EPA requires that total aromatics in RFG be measured to the within 2% of the theoretical value.) Benzene is a poor choice as an internal standard for toluene for two reasons. First, benzene is found in commercial gasolines at a much lower level than toluene. (~0.1-.5% vs. ~10%) Second, benzene has a very different mass spectral fragmentation pathway. It lacks a benzylic carbon-carbon bond. The addition of a deuterated toluene surrogate at an appropriate concentration ensures its accurate measurement.

Typical calibration curves illustrating benzene and toluene are shown in Figures 1 and 2. Both curves are essentially linear over the entire concentration range with correlation coefficients approaching 1.0.

The use of micro-bore and mini-bore capillary GC columns for quantitative analysis provides a number of advantages over conventional capillary columns. In addition to the decreased elution time provided by the more efficient separation, the decreased capacity of these columns may be used to increase the dynamic range of the mass spectrometer, thus improving calibration linearity and accuracy. The smaller inside surface area and shorter length of these columns leads to a much reduced phase bleed level in the ion source, lengthening the time between ion source cleanings and, therefore, instrument recalibration. The decreased gas flow through the narrow-bore columns greatly improves the gas load into the ion source, as well as simplifying the running of these columns at high split ratios for neat samples such as gasolines.

Figure 3 shows the comparison of the chromatography using a conventional capillary column and a micro-bore capillary column in the region of C₃-benzenes (trimethyl benzenes, ethyl methyl benzenes, and propyl benzenes). Note that there is no loss of chromatographic resolution or change in the relative ion abundances, but the GC retention time has been reduced from 38 minutes to 6 minutes.

Ten full mass range scans across each GC peak are necessary for adequate precision. The mass spectrometry should be capable of scanning from 45 to 250 amu every 0.1 seconds. Most modern commercial instruments can achieve this rate. The Texaco method has been implemented on four different mass spectrometers from three different vendors.

Table 1 shows typical repeatability for this method (generally the standard deviations are less than 0.5). The EPA requires accuracy within 2.0% of the actual value. Figure 4 shows a comparison of benzene data using this method, which was collected on four different GC/MS systems.

Comparison to other standard methods.

Figure 4 also compares the analysis of benzene in gasoline using ASTM Method D3606 (a GC/GC column switching method, which is the only current acceptable method for individual aromatics in RFG) and the Texaco GC/MS Method. The results of both methods is essentially identical. (However, the Texaco Method also simultaneously measured all the individual aromatics, their total sum, and oxygenates.)

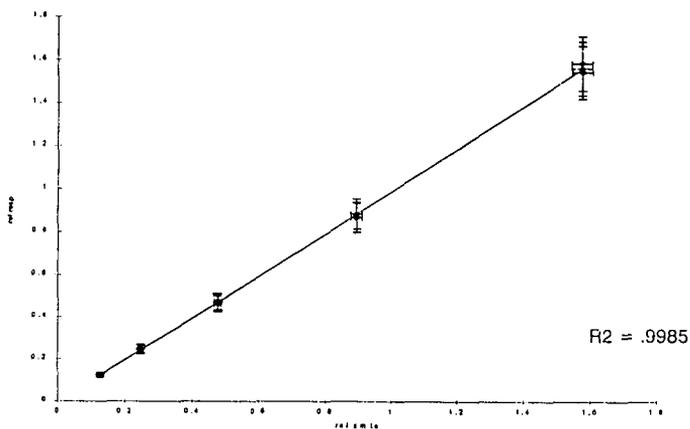
Table 2 compares the analysis of total aromatics in gasoline using the Texaco fast GC/MS method with the ASTM Method D1319, using fluorescent indicator adsorption open column liquid chromatography (FIA), ASTM Method D5769 (the routine total aromatic method using GC/MS), and ASTM D5580 Method (a GC/GC column switching method being adopted by CARE). The FIA method is not precise, but it is on average accurate. The average of 65 different laboratories produced results essentially the same as the Texaco fast GC/MS Method. The routine ASTM D5780 generally will result in somewhat lower total aromatics, since the method does not currently consider the differences in mass spectral response factors between carbon and hydrogen benzylic losses in the heavier alkyl aromatic region. For example pentamethyl benzene molecular ion has a very different relative response factor to that of the pentyl benzene.

Figure 5 compares the analysis of MTBE and TAME using the fast GC/MS method and the ASTM Method D5599 (OFID). Again, the Texaco Method results are essentially the same as the OFID results. Again, it must be noted that these results were obtained simultaneously with the measurements of benzene, toluene, and total aromatics.

Benzene Calibration

figure 1

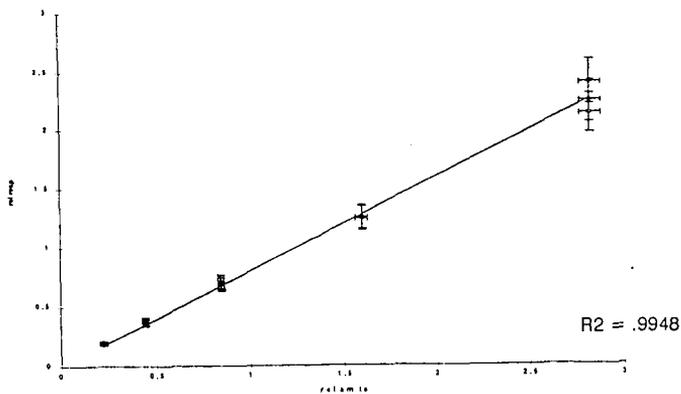
Benzene m/z 78 (0.1 to 5 wt%) vs. Benzene-d6 m/z 83,84 (2 wt%)



Toluene Calibration

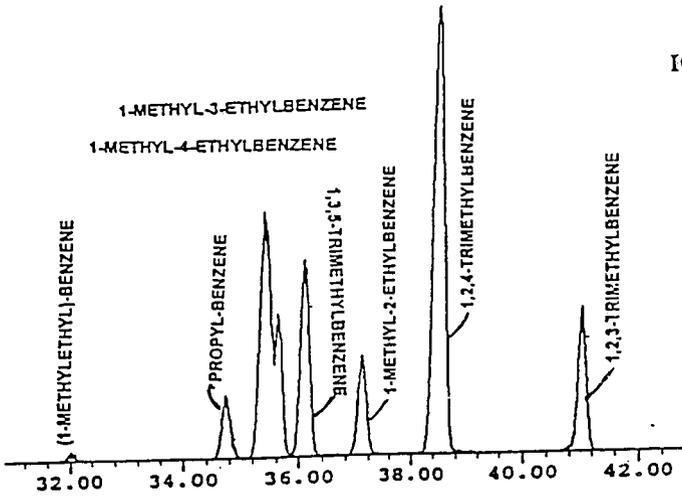
figure 2

Toluene m/z 92 (2 to 20 wt%) vs. Toluene-d8 m/z 99,100 (7 wt%)



Generally used version of ASTM Method
SIR Chromatogram

figure



Texaco Version SIR Chromatogram
(still meets all EPA and ASTM requirements)

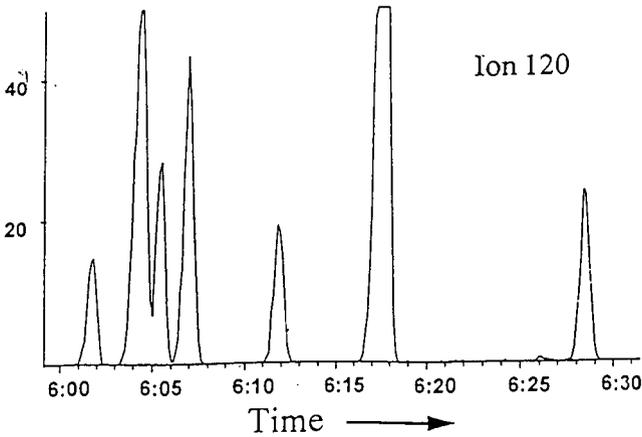


figure 4

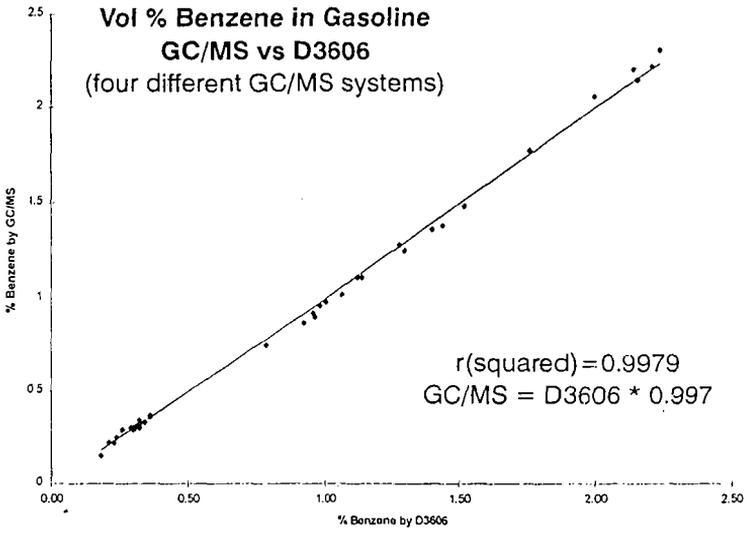
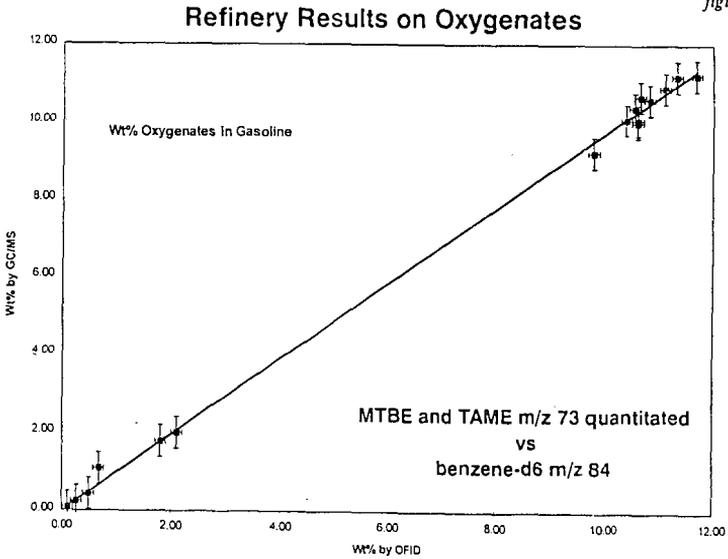


figure 5



Sample Precision

table 1

Compound	#1	#2	#3	#4	Average	Std Dev
Benzene	1.13	1.16	1.20	1.15	1.16	0.03
Toluene	8.60	8.45	8.66	8.28	8.55	0.23
ethyl benzene	2.30	2.30	2.34	2.18	2.28	0.07
m.p. xylene	5.04	5.09	5.23	5.04	5.10	0.09
o-xylene	1.73	1.71	1.77	1.64	1.71	0.05
cumene	0.07	0.09	0.08	0.07	0.08	0.01
propyl benzene	0.36	0.39	0.36	0.37	0.37	0.01
m-ethyl toluene	1.15	1.18	1.20	1.20	1.18	0.02
p-ethyl toluene	0.70	0.72	0.68	0.70	0.70	0.02
1,3,5-trimethyl benzene	0.69	0.60	0.69	0.58	0.59	0.01
o-ethyl toluene	0.38	0.36	0.36	0.38	0.37	0.01
1,2,4-trimethyl benzene	1.73	1.72	1.71	1.73	1.72	0.01
1,2,3-trimethyl benzene	0.32	0.33	0.34	0.32	0.33	0.01
indan	0.55	0.56	0.55	0.59	0.56	0.02
C4 benzenes (cymenes)	0.11	0.08	0.11	0.12	0.10	0.01
C4 benzenes (straight chain)	1.49	1.46	1.50	1.47	1.48	0.02
C4 benzenes (tetramethyl)	0.29	0.29	0.27	0.26	0.28	0.01
C5 benzenes	0.08	0.09	0.08	0.08	0.08	0.01
naphthalene	0.19	0.20	0.20	0.20	0.20	0.01
C5 benzenes	0.22	0.22	0.20	0.22	0.21	0.01
2-methyl naphthalene	0.18	0.18	0.18	0.18	0.18	0.00
1-methyl naphthalene	0.07	0.08	0.08	0.06	0.07	0.01
TAME	0.0	0.0	0.0	0.0	0.0	0.0
MTBE	11.5	11.2	11.5	11.4	11.4	0.1
Total Aromatics	27.46	27.25	27.69	26.82	27.30	0.37

table 2

		Jul-95		
<u>Aromatics</u>				
ASTM FIA (Corrected)	25.46	+/-	2SD 3.76	N 65
Texaco fast GC/MS	25.60			
routine ASTM D5769 GC/MS	20.94	+/-	2.00	27
ASTM 5580	27.20	+/-		2
<u>Benzene</u>				
ASTM 3606	0.63	+/-	0.12	50
Texaco fast GC/MS	0.65			
routine ASTM D5769 GC/MS	0.63	+/-	0.10	20
ASTM 5580	0.59			2
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		Aug-95		
<u>Aromatics</u>				
ASTM FIA (Corrected)	21.09	+/-	2SD 4.06	N 49
Texaco fast GC/MS	19.32			
routine ASTM D5769 GC/MS	17.47	+/-	3.12	33
ASTM 5580	19.73	+/-	1.96	3
<u>Benzene</u>				
ASTM 3606	0.29	+/-	0.04	56
Texaco fast GC/MS	0.29			
routine ASTM D5769 GC/MS	0.30	+/-	0.02	25
ASTM 5580	0.26	+/-	0.02	3
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		Sep-95		
<u>Aromatics</u>				
ASTM FIA (Corrected)	13.59	+/-	2SD 2.08	N 54
Texaco fast GC/MS	13.88			
routine ASTM D5769 GC/MS	12.79	+/-	1.58	34
ASTM 5580	14.41	+/-	2.14	3
<u>Benzene</u>				
ASTM 3606	0.26	+/-	0.08	58
Texaco fast GC/MS	0.27			
routine ASTM D5769 GC/MS	0.28	+/-	0.06	28
ASTM 5580	0.23			2