Improving Accuracy in the Determination of Aromatics in Gasoline by Gas Chromatography–Mass Spectrometry

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Abstract

Petroleum industry studies show that the total aromatics content of a gasoline as determined by ASTM Standard Test Method D5769, "Determination of Benzene, Toluene, and Total Aromatics in Finished Gasoline by Gas Chromatography/Mass Spectrometry", is consistently lower than results obtained using other standard test methods. Sources of this bias are investigated, and practical modifications to D5769 to reduce the bias are proposed.

Introduction

With the Clean Air Act Amendments of 1990, Congress mandated that the Environmental Protection Agency (EPA) promulgate regulations requiring that gasoline sold in certain parts of the country be reformulated to reduce vehicle emissions of toxic and ozone-forming compounds. These regulations would also prohibit conventional gasoline sold in the rest of the country from becoming more polluting than it was in 1990. The final rule (1) delineating the standards for gasolines became effective January 1, 1995.

To certify that a fuel complies with the standards for reformulated gasoline (RFG), it must be shown that the fuel contains a minimum of 2.0 mass percent oxygen and a maximum of 1.00 volume percent benzene. The fuel must also achieve the emissions reductions specified for its intended geographic location. The emissions performance of a fuel is calculated using equations derived from one of two emissions models described in the final rule. The "Complex Model", mandated after January 1, 1998, requires the input of a number of fuel parameters (physical properties and chemical composition), each of which must be measured by a specific test method designated by the EPA.

One of the input parameters for the "Complex Model" is the total aromatics content of the fuel. The EPA has stipulated that total aromatics be determined by gas chromatography with mass spectrometric detection (GC–MS) (2) and has included the framework for such a method in the RFG final rule. To help ensure the consistent implementation of the loosely defined EPA method, petroleum

Table I. Comparison of Consensus Values for Total Aromatics Content by ASTM D5769, D1319, and D5580

ASTM sample number	Total aromatics content (% volume)*			Relative % difference	
	D5769	D1319	D5580	D5769 versus D1319	D5769 versus D5580
RFG 9609	22.8	24.1	23.3	–5.4	–2.1
RFG 9610	15.7	20.3	20.1	–22.7	–21.9
RFG 9611	19.5	20.7	21.2	–5.8	–8.0
RFG 9612	22.0	23.6	23.4	–6.8	–6.0
RFG 9701	13.8	15.0	16.0	–8.0	–13.8
RFG 9702	20.2	22.7	23.5	–11.0	–14.0
RFG 9703	26.5	28.5	28.7	–7.0	–7.7
RFG 9704	17.3	19.7	18.8	–12.2	–8.0
RFG 9705	16.9	19.5	19.8	–13.3	–14.6
RFG 9706	23.5	25.8	25.6	–8.9	–8.2
RFG 9707	23.6	29.6	28.9	–20.3	–18.3
RFG 9708	33.3	35.8	37.2	–7.0	–10.5

* Values from monthly reports of the ASTM Interlaboratory Crosscheck Program for Reformulated Gasoline using the ASTM method.

industry scientists, under the auspices of ASTM (formerly the American Society for Testing and Materials), developed a standard test method that meets the requirements of the EPA approach. The ASTM designation for that method is Standard Test Method D5769, "Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry" (3). The vast majority of aromatics determinations for RFG certification are being performed in accordance with its specifications.

Most of the test methods designated by the EPA for determining RFG parameters provide precision and accuracy that are sufficient for the needs of the RFG program; however, the accuracy of ASTM D5769 is suspect. Consensus results (Table I) from an ASTM proficiency test program (4) clearly show that the total aromatics content of a fuel as determined using D5769 is consistently lower than those values obtained using two other ASTM standard test methods, D1319 (5) and D5580 (6). The relative difference in calculated total aromatics content for individual samples is significant, ranging from –2% to –23%. For this sample set, the bias of the results using D5769 relative to either of the other two methods is approximately –11%.

This negative bias relative to the other methods does not prove that D5769 is inaccurate. In fact, both D1319 and D5580 are known to be subject to interferences which could result in erroneously high values for total aromatics content. Furthermore, the accuracy of D5769 can not be unequivocally determined because of the lack of suitably complex reference materials with known aromatics content. Nevertheless, there is great cause for concern that such a large bias exists, and there is sufficient reason to believe that at least part of the bias is attributable to shortcomings in D5769.

One potential shortcoming lies in the very fact that D5769 is a target component analysis. The total aromatics content of a fuel is calculated by summing the concentrations of individual aromatic compounds that appear in a predefined target component list. Inaccuracies in the calculated total aromatics content could arise if a fuel contains aromatic species that are not included in this target list. An incomplete list would result in a negative bias, such as the one between D5769 results and results obtained using D1319 and D5580. This potential shortcoming, along with the presence of this negative bias, formed the impetus for a study designed to investigate potential sources of error in D5769 and to develop and test modifications to correct them.

Experimental

Instrumentation

All analyses were performed on a Hewlett-Packard (Wilmington, DE) HP 6890 GC equipped with an HP 5973 mass selective detector (MSD). The GC was fitted with a capillary split/splitless injection port, and flow was controlled using an electronic pneumatic control system. The MSD was fitted with a 250-L/s turbomolecular high-vacuum pump and was connected to the GC using a capillary direct GC–MSD interface. System control, data acquisition, and data processing were achieved using HP G1701AA MSD Productivity ChemStation Software (version A.03.01) in gasoline analysis mode on a DOS platform. Specific GC and MS conditions are presented in Table II.

Samples

Four sets of samples were analyzed in various aspects of this study. One set was composed of five gasoline blendstocks: light straight run (LSR) naphtha, reformate, coker naphtha, fluid catalytic cracking unit (FCCU) naphtha, and the heavy-end fraction of FCCU naphtha (heavy cat naphtha, or HCN). A second sample set consisted of the saturate, aromatic, and olefin fractions of these five blendstocks, separated and isolated using an extension of the ASTM D1319 protocol. The third and largest set of samples consisted of the 21 gasoline fuels used in various ASTM round-robin studies (7). The final set was a collection of six samples from an ASTM proficiency test program that were selected for their wide range of total aromatics concentrations.

Test method

All tests were conducted using the precepts of ASTM D5769, with the exception of those performed on the fractionated gasoline blendstocks. D5769 is an internal standard method that uses three perdeuterated internal standards: benzene-d_6, ethylbenzene-d_{10}, and naphthalene-d_8. Targeted aromatic components are calibrated with respect to one of these internal standards. The total aromatics content of a fuel is calculated by summing the

Table II. GC–MSD Conditions

Component	Condition
GC	
Column	60 m × 0.25-mm i.d., df 1.0 µm dimethylpolysiloxane
Injector	capillary split/splitless
Injector split ratio	1500:1
Injection size	0.1 µL
Injector temperature	280°C
Injection port liner	SGE 4-mm i.d. HP Focusliner
Syringe	5-µL, 23 guage needle
Septum	high pressure Merlin Microseal
Oven temperature program	80°C for 0.67 min, to 250°C at 6°C/min
Carrier gas	helium
Carrier gas flow program	0.5 mL/min for 0.4 min, to 1.0mL/min at 3 mL/min^2
GC–MSD interface	
Interface	capillary direct
Temperature	270°C
MS	
Type	quadrupole mass filter
Mode	scan
Scan range	75 to 175 daltons
Scan rate	3.62 s^{-1}
Source temperature	230°C
Analyzer temperature	106°C
Ionization mode	electron impact
Ionization voltage	70 eV

concentrations of these individual targeted components. The five fractionated gasoline blendstocks were analyzed not to determine their aromatic content but to identify the aromatic species and potential interferences that they contained. For this reason, the

internal standards were not added to these five samples and quantitative results were not obtained.

Results and Discussion

Potential sources of error in ASTM D5769

Investigation of ASTM D5769 revealed two potential sources of error that could greatly impact method accuracy. First, the target component list used for the calculation of the total aromatics content of a fuel may be incomplete. It does not currently account for more highly unsaturated aromatic compounds, nor does it account for higher-boiling aromatics that can be present in some gasoline blendstocks. Second, D5769 lacks a criterion to ensure that data acquisition has continued until all sample material has eluted from the GC column. Without this criterion, inappropriate GC conditions might be used or data acquisition might be terminated prematurely or both. Both of these shortcomings can negatively impact method accuracy by leading to erroneously low values for the total aromatics content of a gasoline.

Sources of error and suggested modifications

Studies which showed that these potential sources of error were likely to affect the accuracy of D5769 results were designed and performed. Consequently, two modifications to correct these sources of error were developed and tested.

Modification #1: Expanding the target component list

The D5769 target component list is currently limited to C_6 through C_{12} alkyl benzenes, indane, alkyl indanes, naphthalene, and methyl naphthalenes (Table III). Conspicuously absent from this target list are aromatic hydrocarbons with substituted groups that contain additional degrees of unsaturation, such as indenes and olefino-benzenes. The D5769 target list also omits tetralins, biphenyls, and higher molecular weight indanes and naphthalenes. These additional types of aromatic compounds are expected to be present in some blendstocks used to produce conventional and reformulated gasolines.

FCCU naphtha is a common gasoline blendstock. This cracked product contains both olefinic and aromatic species. Therefore, the heavy-end fraction of FCCU naphtha (HCN) is likely to contain high concentrations of the types of aromatic species not targeted by D5769. For this reason, the aromatic fraction of HCN was selected for GC–MS analysis to test for the presence of these additional aromatic species. Analyzing only the aromatic fraction ensured that any species subsequently identified as untargeted components were sure to be aromatic. The analysis showed that HCN did in fact contain many aromatic species that are not included in the D5769 target component list (Figure 1). Subsequent GC–MS analysis of samples containing the aromatic fraction of four additional gasoline blendstocks showed that they too contained additional aromatic species that are not in

Table III. D5769 Target Component List*
Benzene
Methylbenzene
Ethylbenzene
1,3-Dimethylbenzene
1,4-Dimethylbenzene
1,2-Dimethylbenzene
(1-Methylethyl)-benzene
Propyl-benzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
1,3,5-Trimethylbenzene
1-Methyl-2-ethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Indan
1,4-Diethylbenzene
Butylbenzene
1,2-Diethylbenzene
1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
Pentamethylbenzene
Naphthalene
2-Methyl-naphthalene
1-Methyl-naphthalene
Uncalibrated indans
Uncalibrated C_{10}-benzenes[†]
Uncalibrated C_{11}-benzenes[†]
Uncalibrated C_{12}-benzenes[†]

* From Annual Book of ASTM Standards (8).
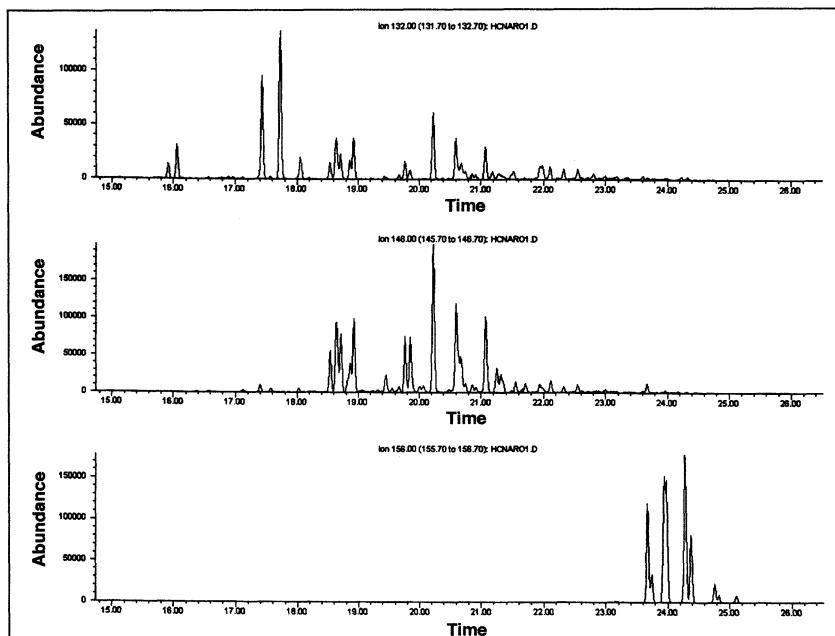[†] Alkyl-substituted benzenes only.

Figure 1. GC–MS analysis of the aromatic fraction of HCN showing the presence of mass 132, 146, and 156 aromatics, three of several aromatic components in HCN that are not accounted for in ASTM D5769.

the D5769 target list. Table IV provides a summary of the additional aromatic compound types identified in these samples. This list includes only those aromatic species that were identified in at least one blendstock at levels that were later found to be 0.01% by weight or higher.

Because these common gasoline blendstocks contain aromatic species not targeted by D5769, the calculated total aromatic content of a gasoline containing any of them will be erroneously low. Expanding the target list to include these additional aromatic components would improve the accuracy of D5769. A proposed expanded list is presented in Table V. This table also specifies the values for four parameters that are required by D5769 to quantitate components in the target list: quantitation ion, calibration curve, integration window, and specific gravity. Some of these values are already specified in D5769; others were determined using methods that are outlined in the section of this paper titled "Implementing the expanded target list".

Modification #2: Specifying an end-of-run criterion

ASTM D5769 provides approximate GC–MS operating conditions (8). For the most part, selecting values for critical GC and MS parameters is left to the discretion of the individual analyst. It is also left to the analyst to identify the "end" of the chromatographic analysis for their selected conditions: the point when all material has eluted from the GC column and it is acceptable to terminate data acquisition. Properly identifying this end-of-run point is especially important when implementing the proposed expanded target list. Many of the additional components in this list are higher-boiling species that could easily be unaccounted for if inappropriate instrument conditions were specified. As a standard test method, D5769 should provide a criterion for accurately and reproducibly selecting this end-of-run point. Currently, it does not.

One possible choice for such a criterion would be to select a compound that is known to elute after all expected components of a gasoline sample and to specify that data acquisition must continue until the elution of that end-of-run marker compound. One suitable compound for this end-of-run marker is n-hexadecane. Figure 2 shows that it elutes well after the last detectable compounds in five different gasoline blendstocks. Another advantage of using n-hexadecane is that chromatographic conditions (Table II) can be adjusted to ensure that it elutes before a significant rise in the chromatographic baseline resulting from column bleed. This improves the signal-to-noise ratio and helps with the integration of higher-boiling aromatic components.

Implementing the expanded target list

Four parameters are required by D5769 to quantitate each component in the target list. First, a quantitation ion must be selected. This quantitation ion is used for both component detection and the determination of area response. Second, an appropriate calibration curve must be used for quantitation. In the case of uncalibrated components, the calibration curve of one of the calibrated components must be selected. Third, an integration window must be defined. An appropriate window will ensure an accurate total area that is free from interfering species. Fourth,
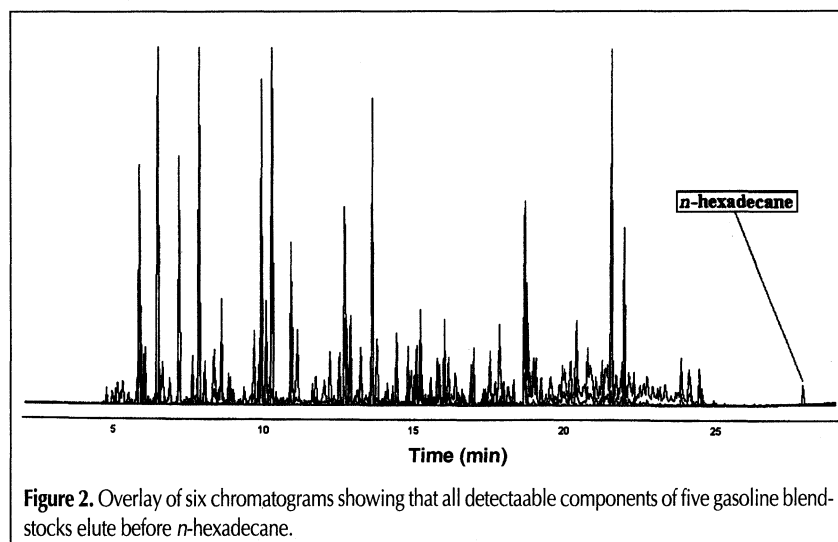

Figure 2. Overlay of six chromatograms showing that all detectaable components of five gasoline blendstocks elute before n-hexadecane.

Chemical formula	Nominal molecular weight	Examples	Blendstocks containing these compounds*
C_8H_8	104	Styrene	coker
C_9H_8	116	Indene	FCCU, HCN, reformate
$C_{10}H_{10}$	130	Methylindenes	FCCU, HCN, reformate
$C_{10}H_{12}$	132	Methylindanes, tetralin	coker, FCCU, HCN, LSR, reformate
$C_{11}H_{12}$	144	Ethylindenes, dimethylindenes	FCCU, HCN
$C_{11}H_{14}$	146	Methyltetralins, ethylindanes, dimethylindanes	coker, FCCU, HCN, LSR, reformate
$C_{12}H_{10}$	154	Biphenyl	HCN
$C_{12}H_{12}$	156	Ethylnaphthalenes, dimethylnaphthalenes	FCCU, HCN, reformate
$C_{12}H_{14}$	158	Methylethylindenes, trimethylindenes	HCN
$C_{12}H_{16}$	160	Trimethylindanes, ethyltetralins, dimethyltetralins	FCCU, HCN
$C_{13}H_{12}$	168	Methylbiphenyls	HCN
$C_{13}H_{14}$	170	Methylethylnaphthalenes, trimethylnaphthalenes	FCCU, HCN, reformate
$C_{13}H_{18}$	174	Methylethyltetralins, tetramethylindanes, diethylindanes	FCCU, HCN

Table IV. Aromatic Species Present in Various Gasoline Blendstocks that Are Not Targeted by D5769

* Abbreviations: coker, coker naphtha; FCCU, fluid catalytic cracking unit naphtha; HCN, heavy-end fraction of FCCU naphtha; LSR, light straight run naphtha; reformate, reformer naphtha.

a specific gravity, used to convert calculated mass percent to volume percent, must be identified or estimated.

In most cases, these parameters are well-defined for components in the current D5769 target list. For those components without well-defined values, and for the additional aromatic species in the proposed target list, these values must be defined. The methods used to determine the values for these parameters are described in the following sections.

Selecting quantitation ions

In most cases, D5769 specifies the use of the molecular ion as the quantitation ion for each component; however, there are exceptions. In order to standardize the choice of quantitation ion, the molecular ion was used exclusively for components in the proposed target list (Table V).

Selecting calibration curves for uncalibrated components

In D5769, each component in the target list is quantitated using a multi-point calibration curve. Selecting an appropriate calibration curve for uncalibrated components is difficult because of the nature of MS analysis. Different compounds fragment differently, producing vastly different detector responses.

Table V. Proposed Target Compound List and Values for Parameters Required by D5769 for Quantitation

Proposed target compounds	Quantitation ion	Assigned calibrated compound	Integration window start after	Integration window end before	Specific gravity
Calibrated compounds					
Benzene	78	benzene	identified by retention time		0.8845
Toluene	92	toluene	identified by retention time		0.8719
Ethylbenzene	106	ethylbenzene	identified by retention time		0.8717
m- and *p*-Xylene	106	*m*- and *p*-xylene	identified by retention time		0.8676*
o-Xylene	106	*o*-xylene	identified by retention time		0.8843
1-Methylethylbenzene	120	1-methylethylbenzene	identified by retention time		0.8668
n-Propylbenzene	120	*n*-propylbenzene	identified by retention time		0.8670
1-Methyl-3-ethylbenzene	120	1-methyl-3-ethylbenzene	identified by retention time		0.8695
1-Methyl-4-ethylbenzene	120	1-methyl-4-ethylbenzene	identified by retention time		0.8661
1,3,5-Trimethylbenzene	120	1,3,5-trimethylbenzene	identified by retention time		0.8705
1-Methyl-2-ethylbenzene	120	1-methyl-2-ethylbenzene	identified by retention time		0.8855
1,2,4-Trimethylbenzene	120	1,2,4-trimethylbenzene	identified by retention time		0.8807
1,2,3-Trimethylbenzene	120	1,2,3-trimethylbenzene	identified by retention time		0.8992
Indane	118	indane	identified by retention time		0.9696
1,4-Diethyl- and *n*-butylbenzene	134	1,4-diethyl- and *n*-butylbenzene	identified by retention time		0.8654†
1,2-Diethylbenzene	134	1,2-diethylbenzene	identified by retention time		0.8843
1,2,4,5-Tetramethylbenzene	134	1,2,4,5-tetramethylbenzene	identified by retention time		0.8918
1,2,3,5-Tetramethylbenzene	134	1,2,3,5-tetramethylbenzene	identified by retention time		0.8946
Naphthalene	128	naphthalene	identified by retention time		1.180
2-Methylnaphthalene	142	2-methylnaphthalene	identified by retention time		1.093
1-Methylnaphthalene	142	1-methylnaphthalene	identified by retention time		1.0244
Uncalibrated compounds					
Styrene	104	2-methylnaphthalene	identified by retention time		0.9111
Indene	116	2-methylnaphthalene	identified by retention time		0.998
Biphenyl	154	2-methylnaphthalene	identified by retention time		0.868
Uncalibrated compounds groups					
$C_{10}H_{10}$ Uncalibrated aromatics	130	2-methylnaphthalene	ethylbenzene-d_{10}	naphthalene-d_8	0.985
$C_{10}H_{12}$ Uncalibrated aromatics	132	1,2-diethylbenzene	ethylbenzene-d_{10}	naphthalene-d_8	0.930
$C_{10}H_{14}$ Uncalibrated aromatics	134	1,2-diethylbenzene	ethylbenzene-d_{10}	naphthalene-d_8	0.877
$C_{11}H_{12}$ Uncalibrated aromatics	144	1,2-diethylbenzene	ethylbenzene-d_{10}	*n*-hexadecane	0.969
$C_{11}H_{14}$ Uncalibrated aromatics	146	1,2-diethylbenzene	ethylbenzene-d_{10}	2-methylnaphthalene	0.937
$C_{11}H_{16}$ Uncalibrated aromatics	148	1,2-diethylbenzene	ethylbenzene-d_{10}	*n*-hexadecane	0.874
$C_{12}H_{12}$ Uncalibrated aromatics	156	1,2-diethylbenzene	1-methylnaphthalene	*n*-hexadecane	1.011
$C_{12}H_{14}$ Uncalibrated aromatics	158	1,2-diethylbenzene	ethylbenzene-d_{10}	*n*-hexadecane	0.959
$C_{12}H_{16}$ Uncalibrated aromatics	160	1,2-diethylbenzene	ethylbenzene-d_{10}	*n*-hexadecane	0.942
$C_{12}H_{18}$ Uncalibrated aromatics	162	1,2-diethylbenzene	ethylbenzene-d_{10}	*n*-hexadecane	0.867
$C_{13}H_{12}$ Uncalibrated aromatics	168	2-methylnaphthalene	1-methylnaphthalene	*n*-hexadecane	1.017
$C_{13}H_{14}$ Uncalibrated aromatics	170	1,2-diethylbenzene	1-methylnaphthalene	*n*-hexadecane	1.002
$C_{13}H_{18}$ Uncalibrated aromatics	174	1,2-diethylbenzene	naphthalene	*n*-hexadecane	0.931

* Calculation based on $2/3$ *m*-xylene and $1/3$ *p*-xylene.
† Calculation based on $1/2$ 1,4-diethylbenzene and $1/2$ *n*-butylbenzene.

This makes it potentially inappropriate to use the calibration curve of one component for the quantitation of another. This is especially true if the detection method uses only a single quantitation ion rather than the total ion current of each compound (which is the case with D5769). Additional complexity arises from the fact that many of the uncalibrated components in the proposed target list are not individual compounds but groups of aromatic isomers with significantly different fragmentation characteristics.
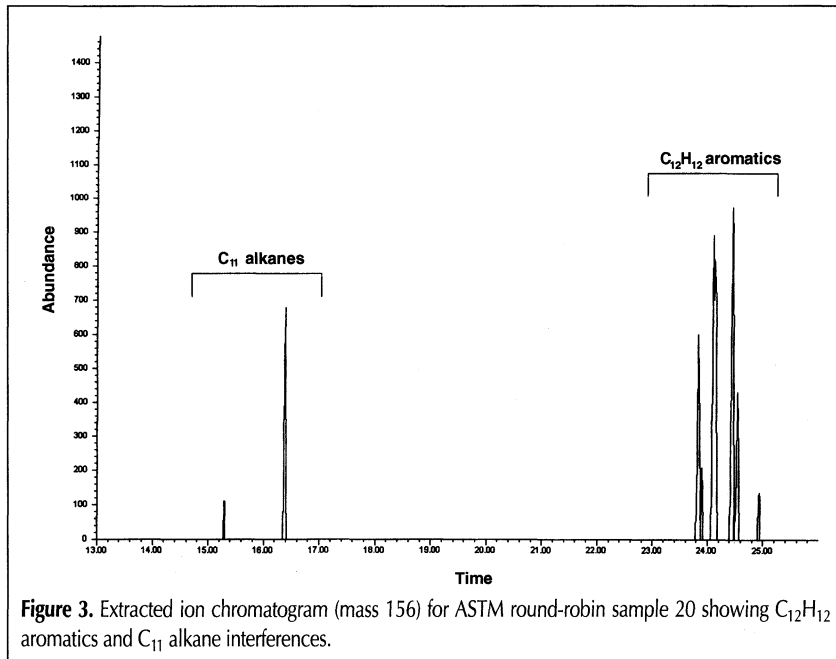
The fragmentation characteristics of components within each of the uncalibrated compound groups must be taken into consideration when determining which calibration curve will be used for quantitation. A key factor to consider is the percentage of the total ion current represented by the quantitation ion for the average individual component in the uncalibrated compound group. For example, 1-methylindene and 3-methylindene are two compounds in the $C_{10}H_{10}$ uncalibrated aromatics group. The quantitation ion represents 22.5% of the total ion current for 1-methylindene and 25.0% for 3-methylindene (9), making the simple average 23.8%. The calibrated component whose curve is selected for quantitation of the $C_{10}H_{10}$ uncalibrated aromatics group should have a quantitation ion that is as close as possible to 23.8% of its total ion current. Two possible calibrated components that could be selected are 2-methylnaphthalene and 1,2-diethylbenzene. Of the two, 2-methylnaphthalene is a better choice because its quantitation ion is 29.7% of its total ion current, whereas the quantitation ion of 1,2-diethylbenzene is only 9.5% of its total ion current (9). This approach served as the basis for selecting the most appropriate calibrated compound for the quantitation of each uncalibrated aromatic group in the proposed target list (Table V).

Selecting integration windows

Quantitating each uncalibrated component in the proposed target list requires the accurate determination of its total area. Most uncalibrated components in the proposed target list consist of multiple aromatic isomers rather than a single aromatic compound. For those component groups, the total area is calculated by summing the individual areas of uncalibrated isomers within a specified time range or integration window in the chromatographic run.

Selecting an appropriate integration window for some uncalibrated components in the target list is complicated by the presence of interfering

Figure 3. Extracted ion chromatogram (mass 156) for ASTM round-robin sample 20 showing $C_{12}H_{12}$ aromatics and C_{11} alkane interferences.

Figure 4. Results for 21 ASTM round-robin samples showing an increase in the calculated aromatics content using the modified D5769 approach.
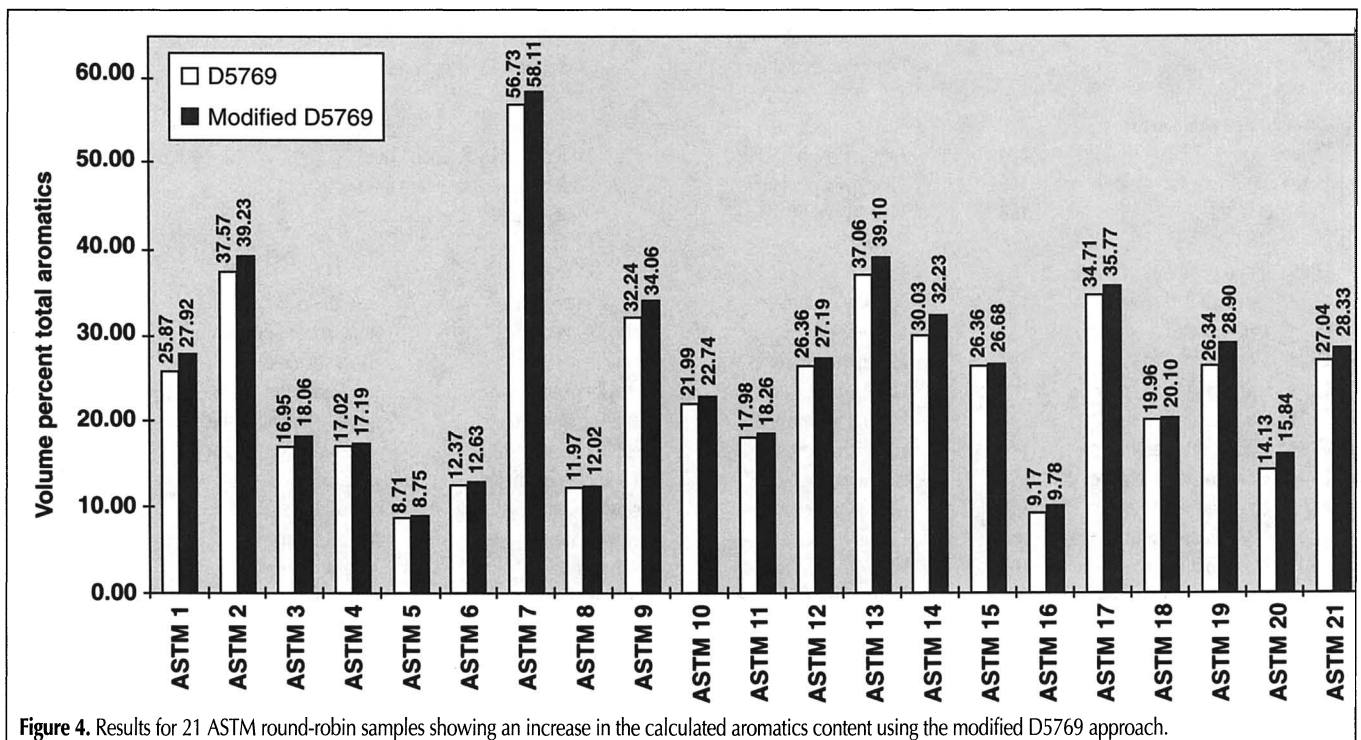
species in the fuel. In the case of $C_{11}H_{16}$ uncalibrated aromatics, no interfering species were found in any of the samples tested; therefore, the integration window could encompass the entire chromatographic run. On the other hand, there are potential interfering species for the $C_{12}H_{12}$ uncalibrated aromatics, such as C_{11} alkanes (Figure 3). Ideally, an integration window should be defined to include all $C_{12}H_{12}$ aromatics while excluding C_{11} alkanes and other interfering species in the fuel.

Defining the integration window for each uncalibrated compound group in the proposed target list required the GC–MS analysis of the saturate, aromatic, and olefin fractions of five gasoline blendstocks. These analyses were used to identify the retention times of aromatic isomers and potentially interfering species. This retention time information was used to define integration windows that included aromatic isomers but limited the presence of interfering species. The beginning and end of each integration window was then referenced to compounds in the calibration set. Referencing these windows to calibrated compounds eliminated the need for the separate analysis of a complex retention time standard and ensured the consistent definition of these windows when the conditions in Table II were used. Table V lists the integration window defined for each uncalibrated aromatic group in the proposed target list.

Assigning specific gravities

In D5769, the specific gravity value for each targeted component is necessary to convert percent mass to percent volume. Data presented in Thermodynamic Research Center (TRC) tables (10) were used to identify or estimate the specific gravity for each component in the proposed target list (Table V). For individual compounds listed in the TRC tables, the stated specific gravity was used. For individual compounds not listed, the specific gravity was estimated by extrapolating or interpolating TRC density data. For compound groups, a specific gravity was calculated based on the simple average of specific gravities for isomers in that group. Specific gravities for those isomers were identified or estimated using TRC data.

Effect of modifications on calculated total aromatics content

In order to assess the impact that the two proposed modifications have on D5769 results, three sets of samples were analyzed. These three sets included the twenty-one ASTM D5769 round robin samples, the six ASTM proficiency test program samples, and the five gasoline blendstocks. Each set was analyzed using the standard D5769 protocol with the operating conditions shown in Table II. Total aromatics results calculated using the standard D5769 target list were compared with those obtained using the expanded target list and calculation parameters specified in Table V. Whenever possible, these data were compared with total aromatics results obtained by ASTM D1319.

ASTM round robin samples

The round robin samples were analyzed in order to assess the impact of the proposed modifications on a large sample set. As the data in Figure 4 show, the modified D5769 approach provided higher total aromatics values than the standard D5769 protocol for all 21 samples in this set.

ASTM proficiency test program samples

Because no consensus D1319 and D5580 results were available for the round-robin samples, a set of six ASTM proficiency test program samples was analyzed to assess the bias between D5769 and other standard test methods. Robust mean data for D1319 and D5580 were available for the samples in this set. The data in Figure 5 show that, when using the modified approach, the bias between D5769 and other standard test methods was reduced. The average relative difference between D1319 and D5769 results decreased from −10.0% to −5.6% by implementing the modified D5769 approach. Likewise, the average relative difference between D5580 and D5769 results decreased from −11.0% to −6.7% using the proposed modifications.

Gasoline blendstocks

The modified D5769 method accounts for aromatic species with additional degrees of unsaturation that standard D5769 does not. For this reason, it is expected that the total aromatics content of cracked blendstocks would show some of the
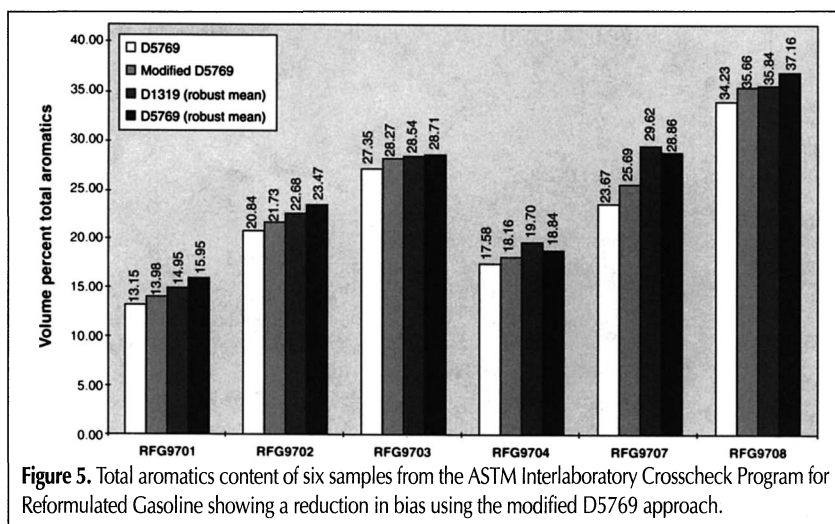

Figure 5. Total aromatics content of six samples from the ASTM Interlaboratory Crosscheck Program for Reformulated Gasoline showing a reduction in bias using the modified D5769 approach.
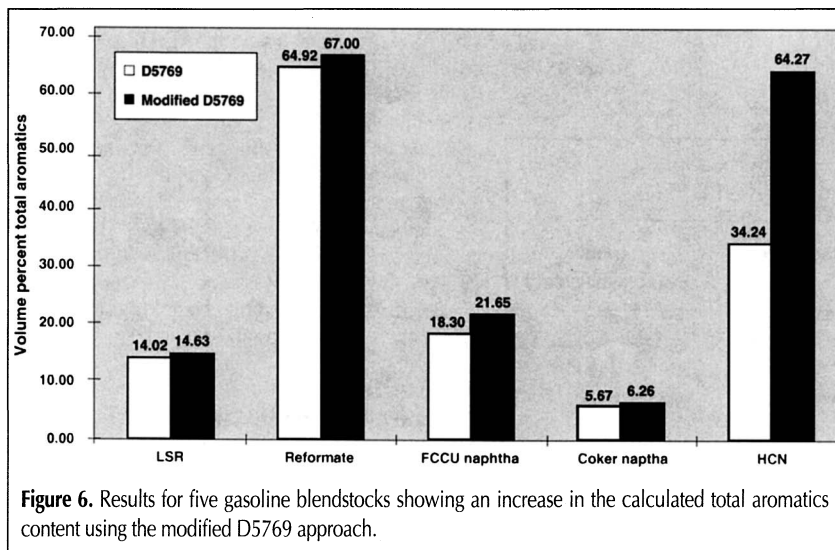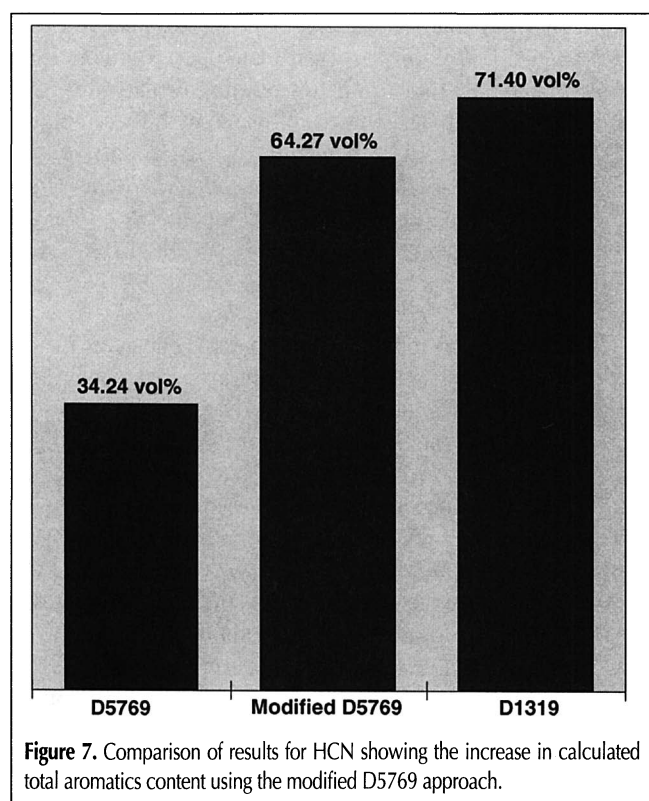

Figure 6. Results for five gasoline blendstocks showing an increase in the calculated total aromatics content using the modified D5769 approach.

largest increases using the modified approach. In order to test this premise, five gasoline blendstocks were analyzed (Figure 6). The relative differences between standard D5769 and modified D5769 results for these samples are presented in Table VI. As expected, those blendstocks produced using either thermal or catalytic cracking processes (coker naphtha, FCCU naphtha, and HCN) showed significantly larger increases than the non-cracked blendstocks (LSR and reformate). As an extreme case, HCN showed an 88% increase in the total aromatics content using modified D5769, leading to a substantial reduction in the difference between D5769 and D1319 results (Figure 7).

Conclusion

This study shows that two simple modifications to ASTM Standard Test Method D5769 can improve accuracy in the deter-

mination of the total aromatics content of a fuel. First, the target component list should be expanded to include additional aromatic species not currently targeted by D5769. A detailed analysis of various gasoline blendstocks helped to identify which aromatic species should be added to the target component list. Second, an end-of-run criterion should be implemented to ensure the accurate and reproducible selection of the end of the chromatographic run (the point where all material has eluted from the GC column and when it is acceptable to terminate data acquisition). Specifying that data acquisition must continue through the elution of n-hexadecane has been shown to be an acceptable end-of-run criterion. Implementing these changes brings D5769 results into closer agreement with those obtained using other standard test methods.

Figure 7. Comparison of results for HCN showing the increase in calculated total aromatics content using the modified D5769 approach.

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Table VI. Comparison of Total Aromatics Content of Five Gasoline Blendstocks as Determined by ASTM D5769 and Modified D5769

Blendstock	Total aromatics by D5769	Total aromatics by modified D5769	Relative percent difference
LSR	14.02	14.63	4.35
Reformate	64.92	67.00	3.20
FCCU*	18.30	21.65	18.28
Coker†	5.67	6.26	10.41
HCN*	34.24	64.27	87.72

* Catalytically cracked blendstock.
† Thermally cracked blendstock.