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# Health assessment of gasoline and fuel oxygenate vapors: Generation and characterization of test materials

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## ABSTRACT

In compliance with the Clean Air Act regulations for fuel and fuel additive registration, the petroleum industry, additive manufacturers, and oxygenate manufacturers have conducted comparative toxicology testing on evaporative emissions of gasoline alone and gasoline containing fuel oxygenates. To mimic real world exposures, a generation method was developed that produced test material similar in composition to the re-fueling vapor from an automotive fuel tank at near maximum in-use temperatures. Gasoline vapor was generated by a single-step distillation from a 1000-gallon glass-lined kettle wherein approximately 15–23% of the starting material was slowly vaporized, separated, condensed and recovered as test article. This fraction was termed vapor condensate (VC) and was prepared for each of the seven test materials, namely: baseline gasoline alone (BGVC), or gasoline plus an ether (G/MTBE, G/ETBE, G/TAME, or G/DIPE), or gasoline plus an alcohol (G/EtOH or G/TBA). The VC test articles were used for the inhalation toxicology studies described in the accompanying series of papers in this journal. These studies included evaluations of subchronic toxicity, neurotoxicity, immunotoxicity, genotoxicity, reproductive and developmental toxicity. Results of these studies will be used for comparative risk assessments of gasoline and gasoline/oxygenate blends by the US Environmental Protection Agency.

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## 1. Introduction

In 1994, the Environmental Protection Agency (EPA) issued a final rule under the Clean Air Act (CAA) which adds new health effects information and testing requirements to the Agency's existing registration program for motor vehicle fuels and fuel additives (Registration of Fuels, 2013: § 79.56; Clean Air Act, 2012). The rule, referred to as the "211(b)" rule, required additional actions that must be taken to register or maintain product registration. Under the new registration program, producers of current and new motor vehicle fuel and fuel additives are required to provide information and test results to EPA regarding the composition of emissions from their products and the potential effects of these emissions on the public health and welfare. These new data requirements supplemented the existing registration requirements.

To help fulfill the new 211(b) requirements for gasoline and diesel fuel, the American Petroleum Institute organized the 211(b) Research Group ("Research Group"). The Research Group is an unincorporated group of over two hundred fuel, oxygenate, and fuel additive manufacturers affiliated by contractual obligation to meet the Tier 1 and Tier 2 testing requirements of Section 211(b)(2) and 211(e) of the Clean Air Act.

The Research Group's purpose was to address two of the three categories of fuel outlined in the 211(b) rule (40 CFR 79.56). Membership in the Research Group is open to any company which has an interest in the registration of these products with EPA. The Research Group tested; (1) "baseline" fuel groups which contain no elements other than carbon, hydrogen, oxygen, nitrogen and sulfur, and for gasoline contain less than 1.5% oxygen by weight, and for diesel contain less than 1.0% oxygen, and (2) "non-baseline" fuel groups which contain only the elements listed above but are either derived from nonconventional sources of oil, or contain in excess of 1.5% or 1.0% oxygen by weight for gasoline and diesel respectively. Oxygenates in non-baseline fuel groups tested by the Research Group were; ethanol (EtOH), tertiary-butyl alcohol (TBA), methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME) and di-isopropyl ether (DIPE).

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The Research Group's testing scope does not include a third category of fuel groups, namely atypical fuel groups, which consist of fuels or fuel additives that contain elements other than carbon, hydrogen, oxygen, nitrogen and sulfur.

The toxicology studies required under Alternative Tier 2 of the 211(b) Rule are based on inhalation exposure to the evaporative emissions from baseline gasoline or oxygenated gasolines. The health endpoints included assessments for subchronic toxicity, neurotoxicity, genotoxicity, immunotoxicity, developmental toxicity, reproductive toxicity, and chronic toxicity/carcinogenicity. The results of chronic toxicity testing of gasoline and gasoline combined with MTBE have already been reported (Benson et al., 2011) and reported elsewhere in this issue are the findings for subchronic toxicity testing (Clark et al., 2014), genotoxicity (Schreiner et al., 2014), neurotoxicity (O'Callaghan et al., 2014), immunotoxicity (White et al., 2014), reproductive toxicity (Gray et al., 2014), and developmental toxicity testing in mice and rats (Roberts et al., 2014a, 2014b).

Generation of the evaporative emissions described in the original 211b rule at CFR 79.57(f)(2) required the construction of an "evaporative emissions generator (EEG)". The EEG was to be filled no more than 40% full with the fuel to be tested. The EEG was to be heated to 130 °F and the generated vapor was to be well mixed and used for inhalation exposures. The size and number of EEGs were to be varied to adjust the chamber atmosphere concentrations. No more than 7% of the fuel volume was to be lost during vapor generation and the fuel in the EEG was to be replaced at the end of each day. Those original rule requirements imposed significant logistical and safety issues for the toxicology testing facilities and the Research Group. Because of those issues, the Research Group undertook development of an alternative method for generating the evaporative emissions. The alternative method developed to generate and characterize the test articles used in the toxicology studies are reported in this paper.

## 2. Methods and materials

The gasoline (e.g., baseline gasoline) used to generate all the test articles is patterned after the reformulated gasoline summer baseline fuel as specified in CAA section 211(k)(10)(B)(i) (40 CFR 79.55). The specifications and blending tolerances for that gasoline are listed in Table 1 as well as the actual values for the first lot of baseline gasoline blended.

The additive types included in the CAA baseline gasoline specifications and the actual treat rates used for this testing program are also listed in Table 1. The test articles used in the inhalation toxicity studies are vapor condensates prepared from baseline gasoline and baseline gasoline plus oxygenate blends using the method described below. The method used to generate the vapor condensate test articles was developed at Chevron Energy Technology Company (Richmond, CA). Generation of the test articles was done using commonly accepted petroleum engineering practices.

### 2.1. Baseline gasoline and oxygenate blending

Baseline gasoline meeting CAA requirements was blended by Phillips 66 Petroleum – Specialty Chemicals (Borger, TX). Over the duration of the program, three lots of CAA compliant baseline gasoline were blended. The first lot (RF-A-BG) was used to develop an alternative method for generating the vapor condensate (test article) to be used in the 211(b) Rule testing. The second lot (API 99-01) was used to splash-blend each of the six gasoline/oxygenate blends and prepare the vapor condensate test articles for all the studies described in this series of papers. The oxygenates used were procured by Phillips 66 Petroleum from various commercial

**Table 1**
Baseline gasoline fuel properties.

| Property | ASTM method | EPA specifications [a] | RF-A-BG [b] |
|---|---|---|---|
| API gravity | D 4052 | 57.4 ± 0.3 | 57.7 |
| Sulfur, ppm | D 4294 | 339 ± 25 | 320 |
| Benzene, volume % | GC | 1.53 ± 0.3 | 1.44 |
| RVP, psi | D 323 | 8.7 ± 0.3 | 8.7 |
| Octane, (R + M)/2 | D 2699 D 2700 | 87.3 ± 0.5 | 87.5 |
| Distillation parameters: | D 86 | | |
| 10%, °F | | 128 ± 5 | 126 |
| 50%, °F | | 218 ± 5 | 216 |
| 90%, °F | | 330 ± 5 | 332 |
| Hydrocarbon type (volume %) | D 1319 | | |
| Aromatics | | 32.0 ± 2.7 | 31.7 |
| Olefins | | 9.2 ± 2.5 | 11.6 |
| Saturates | | 58.8 ± 2.0 | 56.7 |
| Additive types: | | | Treat rate used (lbs/1000 barrels) |
| Required | | Deposit control | 107 |
| | | Corrosion inhibitor | 5 |
| | | Demulsifier | 2 |
| | | Anti-oxidant | 5 |
| | | Metal deactivator | 1 |
| Permissible | | Anti-static | 0.5 |

[a] 40 CFR79.55.
[b] Phillips 66 petroleum data.

sources and included methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), t-butyl alcohol (TBA), and ethanol (EtOH). The oxygen content of the various fuel blends was the maximum allowed under EPA regulations at the time of preparation. For MTBE, ETBE, TAME and DIPE the oxygen content target was 2.7 wt. %. For EtOH and TBA the oxygen content target was 3.7 wt. %. The third lot (API 02-08) of baseline gasoline was used to generate additional baseline gasoline vapor condensate to complete the chronic/carcinogenicity study.

### 2.2. Determining headspace vapor compositions

The compositional target for the test articles made using the alternative method were determined by analyzing the equilibrium headspace of sealed 20 ml vials filled 40% full with baseline gasoline or the gasoline/oxygenate blends. This volume was consistent with the original 1994 CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. Duplicate samples were prepared and analyzed on the same day. The sealed vials were submerged up to the cap in a 130 °F water bath for 10 min at which time they were inverted three times and replaced for 5 min more. The headspace vapor composition was determined by gas chromatography (GC). A Hewlett Packard 19395A headspace sampler was programmed to withdraw a headspace sample at this time and transfer it through a heated line to a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a non-polar fused silica capillary column. The injection volume of headspace vapor was 1 mL into 30 psi helium carrier gas at an injection temperature of 250 °C (split flow 200 mL/min). The oven temperature program is proprietary information.

The material eluting from the column was quantified using a flame ionization detector at 250 °C (H$_2$ 30 mL/min; Air 300 mL/min). Data was collected by an EZChrom Data System and individual compounds identified by proprietary techniques (Chevron SE-30). Analysis of liquid fuel samples was done with the same gas chromatography technique but the sample volume injected was

1 uL. Data from the Chevron SE-30 analysis is expressed as volume percent in this paper to facilitate comparisons with data from ExxonMobil (method described below) that is expressed as area percent.

## 2.3. Large scale vapor condensate generation

To produce the quantity of vapor condensate test articles necessary to complete the 211(b) Alternative Tier 2 Testing program, a large scale batch method was developed. It required filling a glass-lined 1000 gallon kettle (Pfaudler, Rochester, NY) with approximately 800 gallons of baseline gasoline or gasoline/oxygenate blend. The sample was slowly heated and stirred for up to 72 h as the liquid temperature was raised to approximately 150 °F, resulting in a vapor temperature of approximately 130 °F. The vapor leaving the kettle traveled downward to a chilled receiver vessel were it was condensed and collected as liquid. Additional vapor traps chilled in dry ice/isopropanol captured any the remaining vapor that didn't condense in the receiver. The chilled condensate from the receiver and additional trap material were then uniformly mixed, transferred to 5-gallon or 70-gallon LPG-type containers (Manchester Tank, Franklin, TN) and shipped to the toxicology testing laboratories as required. For the G/ETBE and G/DIPE vapor condensates, butylated hydroxytoluene (Sigma–Aldrich) was added at a concentration of 10 ppm to prevent formation of oxygenate peroxides.

## 2.4. Analysis of vapor condensate samples

A sample of each vapor condensate was sent to ExxonMobil Biomedical Sciences, Inc., (Annandale, NJ) for compositional analysis using a method that could be adapted by multiple toxicology testing facilities. Eighteen hydrocarbons and the six oxygenates were chosen as the reference analytes to be quantified. The analysis procedures followed US EPA Good Laboratory Practice Standards (40 CFR Part 79.60, 1994). Initially a gas chromatography–flame ionization detector method was developed using a Supelco Petrocol DH 150 capillary column (150 m × 0.25 mm; 1.0 μm film thickness). It used a 0.5 uL injection volume of vapor condensate (plus 1 uL of a reference compound mixture) into a Perkin Elmer XL Autosystem with an injector temperature of 225 °C (split flow 370 mL/min) and helium carrier gas at 65 psi. The oven temperature program was 35 °C hold 130 min; ramp @ 2 °C/minute to 200 °C. The detector temperature was 225 °C ($H_2$:air ratio of 45:450 mL/min). Data collection was done using a Perkin Elmer Nelson Turbochrom instrument. Using those instrument conditions, this method was capable of resolving each of the 18 reference hydrocarbons from each other and from four of the six oxygenates. A second method using a Supelco Petrocol DH Octyl capillary column (100 m × 0.25 mm; 0.5 μm film thickness) was used to separate the MTBE/2,3-dimethylbutane and the DIPE/n-hexane pairs that could not be resolved on the Petrocol DH 150 capillary column. The instrument conditions for this second method are identical to the first except for a lower helium carrier gas pressure of 40 psi.

The results of the ExxonMobil GLP-compliant method were used to establish the reference composition for the test articles. The results are expressed as "area percent" to facilitate comparison among multiple laboratories. The analytical measurements of the vapor condensates by the toxicology testing facilities also conformed to GLP-requirements and analysis for the individual hydrocarbons were consistent with those measured by ExxonMobil. This paper summarizes the compositional data obtained by both the non-GLP method (Chevron SE-30) and the GLP-compliant method (ExxonMobil).

## 3. Results

Analysis of the equilibrium vapor in the headspace of 20 ml vials at 130 °F provided the target concentration of the various oxygenates desired during the large scale batch preparations. Table 2 shows those target concentrations and the measured concentration of oxygenate achieved in the test articles. The rank-order of the oxygenate concentration in the equilibrium vapor and the test article was maintained by the large scale batch process used by the Research Group.

Table 3 compares the carbon number distribution of whole baseline gasoline with its 130 °F equilibrium vapor and the baseline gasoline vapor condensate test article.

Table 4a compares the hydrocarbon types and other properties of whole gasoline with its equilibrium vapor and the baseline gasoline vapor condensate test article. Key differences between whole gasoline and the vaporized gasoline are the significantly greater concentration of C4 and C5 constituents and depletion of C7–C12 aromatic constituents in the vapor condensate. The equilibrium

**Table 2**
Equilibrium vapor target and test article measured concentrations of fuel oxygenates.

| Oxygenate | Target concentration (volume %)[a] | Reference concentration (area %)[b] |
|---|---|---|
| TAME | 10.6 | 11.9 |
| EtOH | 12.4 | 13.3 |
| ETBE | 14.2 | 16.3 |
| TBA | 14.3 | 16.5 |
| DIPE | 16.5 | 17.8 |
| MTBE | 19.3 | 21.3 |

[a] Chevron SE-30.
[b] ExxonMobil.

**Table 3**
Carbon number distribution of whole and vaporized gasoline.[a]

| Carbon number | Whole baseline gasoline (volume %) | Equilibrium vapor at 130 °F (volume %) | Baseline gasoline vapor condensate (volume %) |
|---|---|---|---|
| 3 | 0 | 0 | 0.1 |
| 4 | 4.7 | 27.1 | 20.6 |
| 5 | 16.3 | 40.9 | 46.4 |
| 6 | 18.5 | 18.8 | 21.6 |
| 7 | 19.1 | 8.0 | 9.0 |
| 8 | 20.2 | 4.0 | 2.2 |
| 9 | 10.6 | 0.8 | 0.2 |
| 10 | 6.0 | 0.2 | 0 |
| 11 | 2.8 | 0 | 0 |
| 12 | 1.8 | 0 | 0 |

[a] Chevron SE-30.

**Table 4a**
Chemical characterization of whole and vaporized gasoline.[a]

| Physical chemical parameter | Whole RF-A-BG gasoline | RF-A-BG equilibrium vapor at 130 °F | Baseline gasoline vapor condensate test article |
|---|---|---|---|
| Paraffins (volume %) | 47.5 | 79.5 | 76.6 |
| Olefins (volume %) | 9.4 | 12.1 | 13.8 |
| Cycloparaffins (volume %) | 6.0 | 2.8 | 5.9 |
| Aromatics (volume %) | 34.3 | 5.5 | 3.7 |
| Benzene (volume %) | 1.4 | 1.0 | 1.2 |
| Number of constituents | 380 | 242 | 131 |
| Average molecular weight | 95.9 | 73.2 | 73.8 |
| Specific gravity 60/60 | 0.752 | 0.650 | 0.651 |

[a] Chevron SE-30 analysis.

**Table 4b**
Chemical characterization of the vapor condensate test articles.[a]

| Physical chemical parameter | Baseline gasoline | G/EtOH | G/TBA | G/MTBE | G/ETBE | G/TAME | G/DIPE |
|---|---|---|---|---|---|---|---|
| Paraffins (volume %) | 76.6 | 67.4 | 63.5 | 59.5 | 63.1 | 66.2 | 63.3 |
| Olefins (volume %) | 13.8 | 12.6 | 13.5 | 12.5 | 13.2 | 14.2 | 12.8 |
| Cycloparaffins (volume %) | 5.9 | 2.0 | 3.3 | 2.2 | 2.7 | 3.0 | 2.4 |
| Aromatics (volume %) | 3.7 | 2.5 | 4.4 | 3.2 | 3.8 | 4.4 | 3.5 |
| Benzene (volume %) | 1.2 | 0.9 | 1.3 | 1.0 | 1.1 | 1.2 | 1.1 |
| Oxygenate (volume %) | 0 | 15.4 | 15.4 | 22.7 | 17.2 | 12.2 | 17.9 |
| Average molecular weight | 73.8 | 65.9 | 72.1 | 73.7 | 77.1 | 77.2 | 76.5 |
| Specific gravity 60/60 | 0.651 | 0.665 | 0.678 | 0.668 | 0.669 | 0.670 | 0.663 |

[a] Chevron SE-30 analysis.

vapor and vapor condensate are also less complex and have a lower average molecular weight and specific gravity. Table 4b compares the hydrocarbon types and other properties of all the test articles used in the testing program.

Using a large scale batch process at a single location allowed the Research Group to safely produce the large quantities of test article required. The magnitude of the operation is evident from the volumes shown in Table 5. Over fifty-five thousand gallons of whole gasoline was required to make almost ten thousand gallons of test article(s).

To help achieve consistency in the GC analysis between several toxicology testing facilities, a reference method conducted under GLP procedures was developed by ExxonMobil. As part of that development effort, a comparison of results between the Chevron SE-30 method and the ExxonMobil method was done.

**Table 5**
Percentage of whole gasoline recovered as vapor condensate by a large scale batch process.

| | Whole gasoline | Vapor condensate | Percentage (%) |
|---|---|---|---|
| Baseline gasoline | 20,356 gallons | 3332 gallons | 16 |
| G/EtOH | 4028 gallons | 616 gallons | 15 |
| G/TBA | 4052 gallons | 966 gallons | 23 |
| G/MTBE | 15300 gallons | 2723 gallons | 17 |
| G/ETBE | 3916 gallons | 719 gallons | 18 |
| G/TAME | 4022 gallons | 826 gallons | 20 |
| G/DIPE | 3903 gallons | 630 gallons | 16 |
| Total quantities | 55,577 gallons | 9812 gallons | |

**Table 6**
Results of baseline gasoline vapor condensate analysis by two gas chromatography methods.

| Compound | Chevron SE-30 (Volume-percent)[a] | ExxonMobil (Area-percent) |
|---|---|---|
| Isobutane | 4.0 | 2.8 |
| n-Butane | 15.4 | 13.1 |
| Isopentane | 34.8 | 34.8 |
| n-Pentane | 13.1 | 13.7 |
| Trans-2-pentene | 2.6 | 2.6 |
| 2-Methyl 2-butene | 3.8 | 3.9 |
| 2,3-Dimethylbutane | 1.7 | 1.7 |
| 2-Methylpentane | 5.9 | 6.8 |
| 3-Methylpentane | 3.5 | 3.9 |
| n-Hexane | 3.2 | 3.1 |
| Methylcyclopentane | 1.7 | 1.6 |
| 2,4-Dimethylpentane | 1.1 | 1.1 |
| Benzene | 1.6 | 2.2 |
| 2-Methylhexane | 1.2 | 1.2 |
| 2,3-Dimethylpentane | 1.3 | 1.2 |
| 3-Methylhexane | 1.3 | 1.4 |
| Isooctane | 1.5 | 1.5 |
| Toluene | 2.2 | 3.3 |

Analysis of sample RF-A-BG.
[a] These compounds are normalized to 100%.

The results in Table 6 demonstrate that the two GC methods are comparable for the 18 hydrocarbons speciated by the ExxonMobil method. For that comparison the Chevron SE-30 data for those 18 hydrocarbons was normalized to 100%. The Chevron SE-30 method actually separated and quantified 131 peaks from the baseline gasoline vapor condensate. Those 18 hydrocarbons made up over 81% of the sample volume.

The results of the ExxonMobil analysis of the seven test articles are shown in Table 7. The vapor condensate from the three lots of baseline gasoline are similar. Only the second lot (API 99-01) was used to prepare the test articles used in the studies reported in this series of papers. The toxicology testing facilities were required to periodically perform similar GC analysis on the chamber air to confirm that they consistently achieved an atmosphere of completely "re-vaporized" test article over the duration of the study.

## 4. Discussion

The original EPA method required the inhalation test atmosphere of "evaporative emissions" to be generated from whole gasoline in situ at the toxicology testing laboratory. The logistic and safety issues associated with that requirement prompted the Research Group to develop an alternative method. The method developed by the Research Group was submitted to EPA for approval before the start of the Alternative Tier 2 testing program. The advantages of the alternative method included: (1) the handling and heating of large quantities of gasoline were done at a petroleum company research facility with technical staff who routinely handle flammable materials, (2) by adding nitrogen gas under slight pressure to the 5-gallon LPG-type container, the toxicology testing facilities could continuously meter out the amount of test article necessary, wholly re-vaporize it, and introduce the vapor into the exposure chambers, (3) the vapor condensate test material provided adequate inhalation exposure concentrations (e.g., up to 50% of the lower explosive limit), (4) the test material atmosphere was uniform throughout the exposure duration at all the toxicology testing laboratories, and (5) the vapor condensate composition was more similar to the 130 °F equilibrium vapor composition than the vapor achieved using the method described in the original rule (data not presented, see EPA Docket, 1997).

To test the proposed alternative evaporative emissions generation method, API sponsored a developmental toxicity evaluation of unleaded gasoline vapor condensate in the rat outside the CAA 211b test rule (Roberts et al., 2001). The success of that study and the advantages of the alternative method persuaded EPA to approve the Research Group's proposed methodology as part of the Alternative Tier 2 Rulemaking (EPA Docket, 1998). The test articles generated and characterized by the methods described were used at three different toxicology testing facilities to conduct the testing required by the Alternative Tier 2 Fuel and Fuel Additive regulations.

**Table 7**
Reference method analysis of vapor condensate test articles.

| Compounds | RF-A-BG Baseline gasoline | API 99-01 Baseline gasoline | API 02-08 Baseline gasoline | G/EtOH | G/TBA | G/MTBE | G/ETBE | G/TAME | G/DIPE |
|---|---|---|---|---|---|---|---|---|---|
| Isobutane | 2.8 | 3.6 | 2.1 | 2.2 | 3.0 | 2.2 | 2.0 | 1.9 | 2.0 |
| n-Butane | 13.1 | 15.2 | 19.9 | 11.6 | 9.9 | 11.1 | 10.6 | 10.4 | 11.5 |
| Isopentane | 34.8 | 35.1 | 32.1 | 34.0 | 25.2 | 31.0 | 32.5 | 33.6 | 32.2 |
| n-Pentane | 13.7 | 13.2 | 5.4 | 10.2 | 11.6 | 9.1 | 9.8 | 10.3 | 9.6 |
| t-2-Pentene | 2.6 | 2.5 | 2.4 | 2.1 | 2.1 | 2.0 | 2.1 | 2.3 | 2.1 |
| 2-Methyl-2-butene | 3.9 | 3.8 | 3.3 | 3.1 | 3.2 | 2.9 | 3.2 | 3.4 | 3.1 |
| 2,3-Dimethylbutane | 1.7 | 1.6 | 6.2 | 2.2 | 1.6 | 0.9 | 1.4 | 1.5 | 1.3 |
| 2-Methylpentane | 6.8 | 6.3 | 9.6 | 5.1 | 6.1 | 4.5 | 5.1 | 5.6 | 4.5 |
| 3-Methylpentane | 3.9 | 3.6 | 6.8 | 2.9 | 3.8 | 2.6 | 2.9 | 3.2 | 2.7 |
| n-Hexane | 3.1 | 3.0 | 1.2 | 2.4 | 3.4 | 2.1 | 2.4 | 2.6 | 1.8 |
| Methylcyclopentane | 1.6 | 1.5 | 0.7 | 1.2 | 1.6 | 1.1 | 1.3 | 1.4 | 1.0 |
| 2,4-Dimethylpentane | 1.1 | 1.0 | 0.6 | 1.0 | 1.0 | 0.9 | 1.0 | 1.2 | 1.0 |
| Benzene | 2.2 | 2.1 | 1.9 | 1.6 | 2.0 | 1.5 | 1.8 | 2.0 | 1.8 |
| 2-Methylhexane | 1.2 | 1.1 | 1.7 | 1.1 | 1.3 | 1.0 | 1.1 | 1.2 | 1.1 |
| 2,3-Dimethylpentane | 1.2 | 1.1 | 1.0 | 1.1 | 1.3 | 1.0 | 1.1 | 1.3 | 1.1 |
| 3-Methylhexane | 1.4 | 1.3 | 2.3 | 1.2 | 1.5 | 1.1 | 1.3 | 1.5 | 1.3 |
| Isooctane | 1.5 | 1.3 | 0.7 | 1.3 | 1.5 | 1.2 | 1.4 | 1.5 | 1.4 |
| Toluene | 3.3 | 3.0 | 2.6 | 2.4 | 3.4 | 2.5 | 2.7 | 3.2 | 2.6 |
| EtOH | | | | 13.3 | | | | | |
| TBA | | | | | 16.5 | | | | |
| MTBE | | | | | | 21.3 | | | |
| ETBE | | | | | | | 16.3 | | |
| TAME | | | | | | | | 11.9 | |
| DIPE | | | | | | | | | 17.8 |

Values reported as area percent.

## Conflicts of interest

Michael Henley was an employee of Chevron Energy Technology Company; API requested and paid for work. Daniel Letinsky was an employee of ExxonMobil Biomedical Sciences, Inc. and financial support for conducting the analytical characterizations of the gasoline test materials was solicited and paid for by AP. John Carr was an employee of Chevron Energy Technology Company; API requested and paid for work. Mario Caro was an employee of Chevron Energy Technology Company; API requested and paid for work. Wayne Daughtrey was an employee of ExxonMobil Biomedical Sciences, Inc. and financial support for conducting the analytical characterizations of the gasoline test materials was solicited and paid for by API. Russell White was an employee of American Petroleum Institute while the manuscript was written (current employer); and White was an employee of Chevron Energy Technology Company during the method development phase detailed in the paper.

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