AC Analytical Controls' Reformulyzer M4 expands its capabilities on gasoline analysis in revised ASTM D6839-21 and ISO 22854

- ASTM D6839/ISO 22854 updated with an expanded and extended concentration range of oxygenates and aromatics
- ASTM D6839 updated to include correlations to other gasoline standards
- Reformulyzer (D6839) allowed to report benzene content to EPA as per PBMS

Keywords: ASTM D6839, Reformulyzer M4, Gasoline, EPA, ISO 22854

Introduction:

The AC Reformulyzer is one of the most used analyzers worldwide to determine the total aromatic, total olefin, benzene, oxygen content, and oxygenates in finished gasoline, with an active global installed base of over 500 instruments. Many international fuel specifications refer to the Reformulyzer-compliant methods ISO 22854 or ASTM D6839.

Refineries in the United States are subjected to Environment Protection Agency (EPA) regulations that specify single parameter analysis methods for total aromatics, total olefin, and benzene content as measured by ASTM D1319, D3606, D5580, D4815, D5599, and D5769.

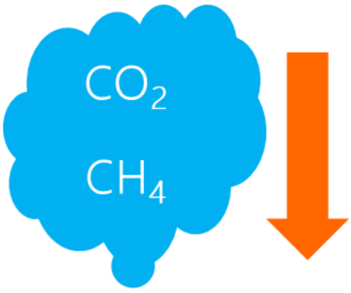
To extend the versatility of the AC Reformulyzer, AC Analytical Controls expanded its already extensive analytical measurement range for oxygen content, specific oxygenates, and specific aromatics, as future changes in gasoline composition are expected. The Reformulyzer now also includes correlations to the traditional EPA ASTM methods in the ASTM D6839.

As part of its research and development process to expand the Reformulyzer capabilities, AC analytical Controls applied the outcome of two studies:

- Interlaboratory Study (ILS) organized by PAC which included over 60 participating laboratories worldwide to extend the concentration range of selected oxygenates, benzene, and toluene.

- Method comparison study of ASTM D6839 versus D3606, D5769, D5580, D1319, and D6550 based on real-life samples from the ASTM Proficiency Test Program from 2004 to 2019.

Interlaboratory Study - Extending the Measurement Range

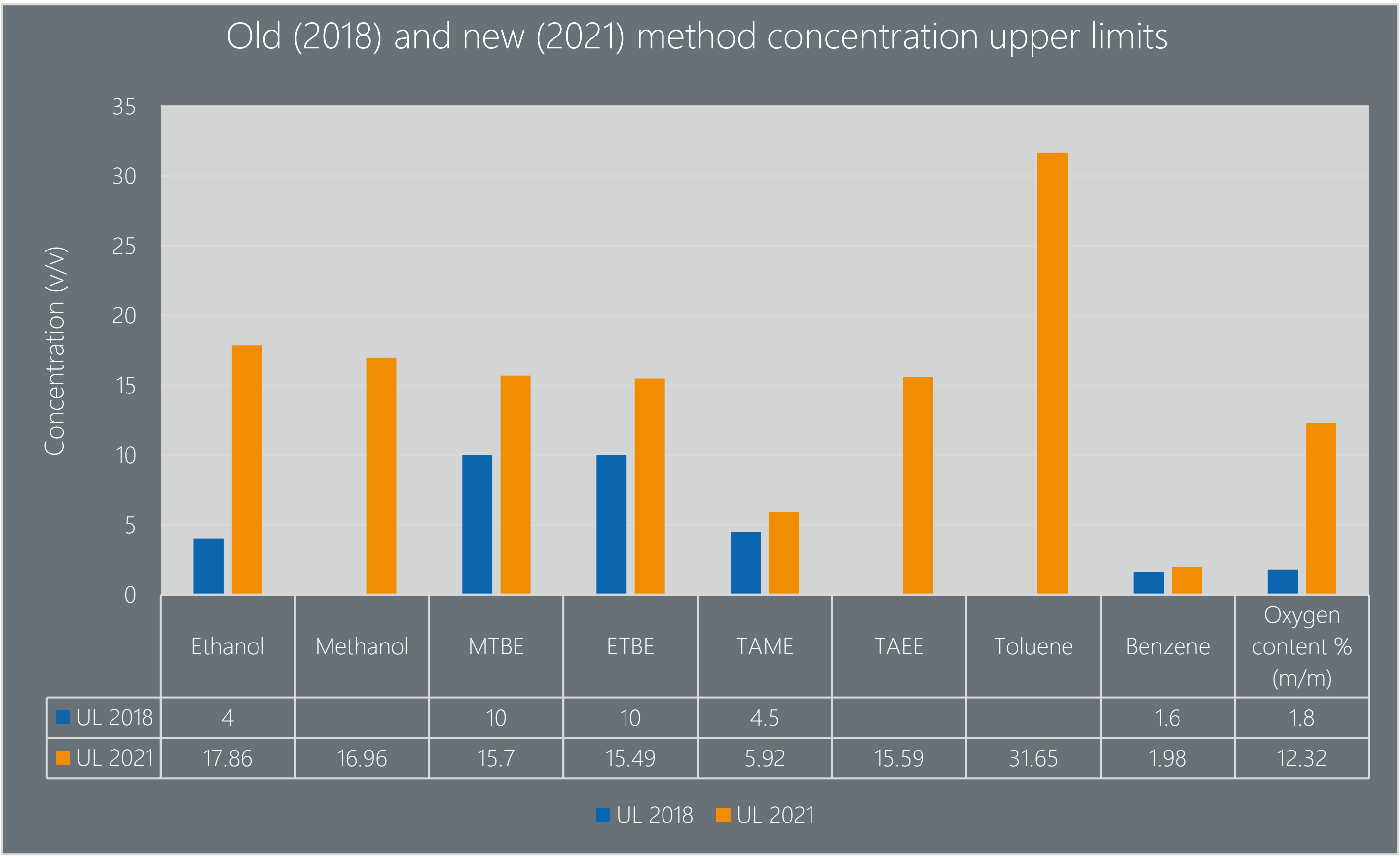


Governments around the world are setting tighter legislation on greenhouse gas emissions. To comply with these new laws, the automotive industry is focused on reducing their car and truck emissions. One of their research programs, in collaboration with the petroleum industry, investigates how fuel composition can be changed to meet future greenhouse gas specifications while maintaining a superior driving experience.

Overall, the trend is to blend higher concentrations of various oxygenates like (bio) ethanol, (bio) methanol, MTBE, ETBE, TAME and TAEE into a finished gasoline.

Recognizing these changes in fuel composition, AC Analytical Controls began preparing an ILS in 2019 to add, update and extended the concentration range for oxygen content and selected oxygenates and aromatics in ASTM D6839 and ISO 22854. The ILS samples were measured by more than 60 laboratories worldwide in 2020 and the statistical outcome of the ILS permitted us to update the concentration range for the listed components and oxygen content shown in table 1.

The updated concentration range in ASTM D6839 was accepted in April 2021. The official release of the updated ASTM D6839 will follow shortly. The ISO 22854 is expected to follow later in 2021.



	Ethanol	Methanol	MTBE	ETBE	TAME	TAEE	Toluene	Benzene	Oxygen content % (m/m)
UL 2018	4		10	10	4.5			1.6	1.8
UL 2021	17.86	16.96	15.7	15.49	5.92	15.59	31.65	1.98	12.32

Table 1: Upper limit of oxygen content, benzene, toluene and various oxygenates in ASTM D6839-18 vs new 2021

ASTM PTP Comparison Study - Correlations

United States refiners must comply with and report according to EPA (Environment Protection Agency) regulation methods. The EPA's Performance Based Monitoring System (PBMS) allows the use of results from alternative methods that are correlated with the EPA referee methods with the main requirement that the correlations are made in accordance with ASTM D6708.

The Reformulyzer method ASTM D6839 is considered an alternative method. Correlations with the EPA method and other typical gasoline property methods would be a great addition to the use of the Reformulyzer application for gasoline testing.

Real-life results from the ASTM Proficiency Test Program from 2004 to 2019 were used to compare the results between the Reformulyzer (D6839) and other ASTM test methods D3606, D5580, D5769, D1319 & D6550.

Typical Methods	Scope
ASTM D1319 - Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption	This test method covers the determination of hydrocarbon types over the concentration ranges from 5 to 99 volume % aromatics, 0.3 to 55 volume % olefins, and 1 to 95 volume % saturates in petroleum fractions that distill below 315°C.
ASTM D3606 - Determination of Benzene and Toluene in Gasoline	This test method covers the determination of benzene and toluene in finished motor and aviation spark ignition fuels by gas chromatography.
ASTM D5580 - Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography	This test method covers the determination of benzene, toluene, ethylbenzene, the xylenes, C9 and heavier aromatics, and total aromatics in finished motor gasoline by gas chromatography.
ASTM D5769 - Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry	This test method covers the determination of benzene, toluene, other specified individual aromatic compounds, and total aromatics in finished motor gasoline, including gasolines containing oxygenated blending components, by gas chromatography/mass spectrometry (GC/MS).
ASTM D6550 - Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography	This test method covers the determination of the total amount of olefins in blended motor gasolines and gasoline blending stocks by supercritical-fluid chromatography (SFC). Results are expressed in terms of mass % olefins. The application range is from 1 to 25 mass % total olefins.
ASTM D6839 - Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography	This test method covers the quantitative determination of saturates, olefins, aromatics, and oxygenates in spark ignition engine fuels by multidimensional gas chromatography. Each hydrocarbon type can be reported either by carbon number or as a total.

Table 2: Overview of gasoline composition ASTM methods.

The method used for this comparison is ASTM D6708 - Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material. By following this statistical method, a statement about the expected difference in results of the two test methods can be made. If there is a difference or bias between the two test methods a correction or correlation can be applied and is accepted in the industry.

The statistical study resulted in relations for benzene, total aromatics, and total olefins between the Reformulyzer (D6839) and other ASTM methods (D1319, D3606, D5580, D5769 and/or D6550).

The ASTM balloting process for adding these additional correlations in the Reformulyzer method is completed. The correlations for benzene, total aromatics, and total olefins between the Reformulyzer (D6839) and other ASTM methods (D1319, D3606, D5580, D5769 and/or D6550) are accepted and will be part of the next version of the D6839 method.

1. Scope*

1.1 This practice covers statistical methodology for assessing the expected agreement between two standard test methods that purport to measure the same property of a material, and deciding if a simple linear bias correction can further improve the expected agreement. It is intended for use with results collected from an interlaboratory study meeting the requirement of Practice D6300 or equivalent (for example, ISO 4259). The interlaboratory study must be conducted on at least ten materials that span the intersecting scopes of the test methods, and results must be obtained from at least six laboratories using each method.

Overall, the results from the Reformulyzer show no or only very small bias between methods. Most noticeable is the benzene content, where there is no bias between D6839 and D5769 as well as D5580. This shows how well the Reformulyzer correlates as a full PIONA gasoline composition analyzer to other single parameter methods. See table 3 for the overview of added correlations.

Correlation	Equation
ASTM D5769 Benzene content	**predicted Y = X** Where: X = result obtained by Test Method D6839-18 predicted Y = a predicted outcome by Test Method D5769-20
ASTM D3606 (B) Benzene content	**bias-corrected X = predicted Y = X-0.0114** Where: X = result obtained by Test Method D6839-18 bias-corrected X = predicted Y = a predicted outcome by Test Method D3606-20e1 Procedure B Test result range: 0.52 to 1.67 vol%.
ASTM D5580 Benzene Content	**predicted Y = X** Where: X = result obtained by Test Method D6839-18 predicted Y = a predicted outcome by Test Method D5580-20e1 Test results range from 0.52 to 1.53 vol%
ASTM D1319 Total Aromatics	**bias-corrected X = predicted Y = X − 1.0376** Where: X = result obtained by Test Method D6839-18 bias-corrected X = predicted Y = a predicted outcome by Test Method D1319-19
ASTM D5580 Total Aromatics	**bias-corrected X = predicted Y = 0.9772*X + 0.6419** Where: X = result obtained by Test Method D6839-18 bias-corrected X = predicted Y = a predicted outcome by Test Method D5580-15(2020)
ASTM D5769 Total Aromatics	**bias-corrected X = predicted Y = X − 1.6964** Where: X = result obtained by Test Method D6839-18
ASTM D6550 Total Olefins	**predicted Y = X** Where: X = result obtained by Test Method D6839-18 predicted Y = a predicted outcome by Test Method D6550-20

Table 3: ASTM D6839 correlation overview

EPA Fuel Regulation

As of January 1st, 2021, the EPA regulation for reformulated gasoline has been streamlined to only four parameters that need reporting:

- Reid Vapor Pressure (D5191)
- Oxygen Content (D5599)
- Sulfur Content (D7039)
- Benzene Content (D5769)

Until 2021, the referee procedure for measuring benzene content was D3606 but has been changed to D5769. The benzene content in reformulated gasoline should have an average concentration of 0.62 vol%, with a maximum average concentration of 1.30 vol%.

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 60, 63, 79, 80, 1042, 1043, 1065 and 1090

[EPA–HQ–OAR–2018–0227; FRL–10014–97–OAR]

RIN 2060–AT31

Fuels Regulatory Streamlining

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

This is excellent news for United States customers, as the correlation for D5769 is included in the D6839 with a measurement range of 0.52 – 1.67 vol%. Following EPA's Performance-based Measurement System (PBMS), the Reformulyzer can now be used as an alternative method to report benzene content to the EPA.

The correlation equation is ASTM D6839 = ASTM D5769 meaning **no bias correction is required**.

Conclusion

From the outcome of the Interlaboratory Study as well as the method comparison study per ASTM D6708, one can only conclude that the goal to make the AC Reformulyzer a more versatile applied analyzer has been accomplished.

The increased concentration range for the various oxygenates and aromatics as well as oxygen content makes the Reformulyzer ready for the future as the increased oxygenate content expected in fuel specifications will fall in the concentration range of the ASTM D6839 / ISO 22854 method.

This increased concentration range, together with the addition of correlations with other ASTM methods in the Reformulyzer method D6839 makes the Reformulyzer the most versatile analyzer for gasoline testing on the market. More specifically the correlation to D5769 allows the Reformulyzer be used to report benzene content to the EPA.

PAC is at the forefront of gasoline testing, staying in close contact with its customers to anticipate changes in the market and fuel specification. This could not have been accomplished without the help and support of our loyal and trusted customers around the world who participated in the ILS. A special thank you to all participants.

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