Agilent 4815 GC Oxygenates Analyzer for the Analysis of Gasoline per ASTM D-4815-04

Application Note

Energy & Fuels

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Introduction

Oxygenated compounds can be present in various hydrocarbon matrices either because they were purposely added (e.g. gasoline) or because they are naturally present or formed during catalytic processes such as polymer production. In gasoline, oxgenated compounds are added as “anti-knock” agents to increase octane number and decrease emissions by replacing organo-lead compounds.

The type and concentration of oxygenated compounds must be measured in reformulated gasolines as part of ongoing product quality assessment and to confirm that oxygenated components have been added in the correct amounts according to regulatory requirements (e.g. California Air Resources Board). ASTM D4815 is often chosen as the standard method of choice for the determination of oxygenated compounds.

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Product Features

Optimized for the analysis of oxygenated compounds in gasoline by ASTM D-4815

The system is configured and fully tested at the factory to ensure that it provides data in compliance with the requirements of the standard method. Agilent will then install the system and check its performance in your laboratory.

An easy to use, sophisticated solution

The industry proven Agilent GC and software is a very powerful combination and key in generating reliable results. The 4815 GC Oxgenates Analyzer yields excellent results regardless of the operator's skill level.

Operational procedures are fully documented

All Agilent GC analyzers not only include proven GC hardware and software but are also preloaded with analysis methods and documentation specific to those methods.

Comprehensive single vendor "solution"

Agilent is the only GC supplier that has a proven legacy of providing complete solutions without relying on third parties. The hardware, software, application optimization, documentation, installation and support services are all provided by Agilent.

Analyzer Overview

The 4815 GC Analyzer is specially configured, consisting of two analysis columns, a split/splitless capillary injector, a 10 port rotary valve and single Flame Ionization Detector (FID). For the best results the use of an automatic liquid sampler is highly recommended. (See Figure 1 for configuration detail detail). The system is optimized to provide results in accordance with the ASTM D4815 method.

Operational parameters, including gas flows, are controlled electronically. Individual ethers and alchohols are quantified in gasoline, including MTBE, ETBE, TAME, DIPE, C1-C4 alcohols and tert-amyl alcohol. Individual ether components are measured from 0.1 to 20.0 mass %. The individual alcohols are measured from 0.1 to 12.0 mass %.

The analysis works as follows:

1. The sample is introduced to the system via the split/splitless capillary inlet, vaporized and transferred to the first column (Agilent J&W CP-TCEP for Alcohols in Gasoline; micro-packed) where the lower boiling/non-polar components are separated from higher boiling/polar components. The lower boiling components (those eluting prior to methylcyclopentane) are then flushed to vent.

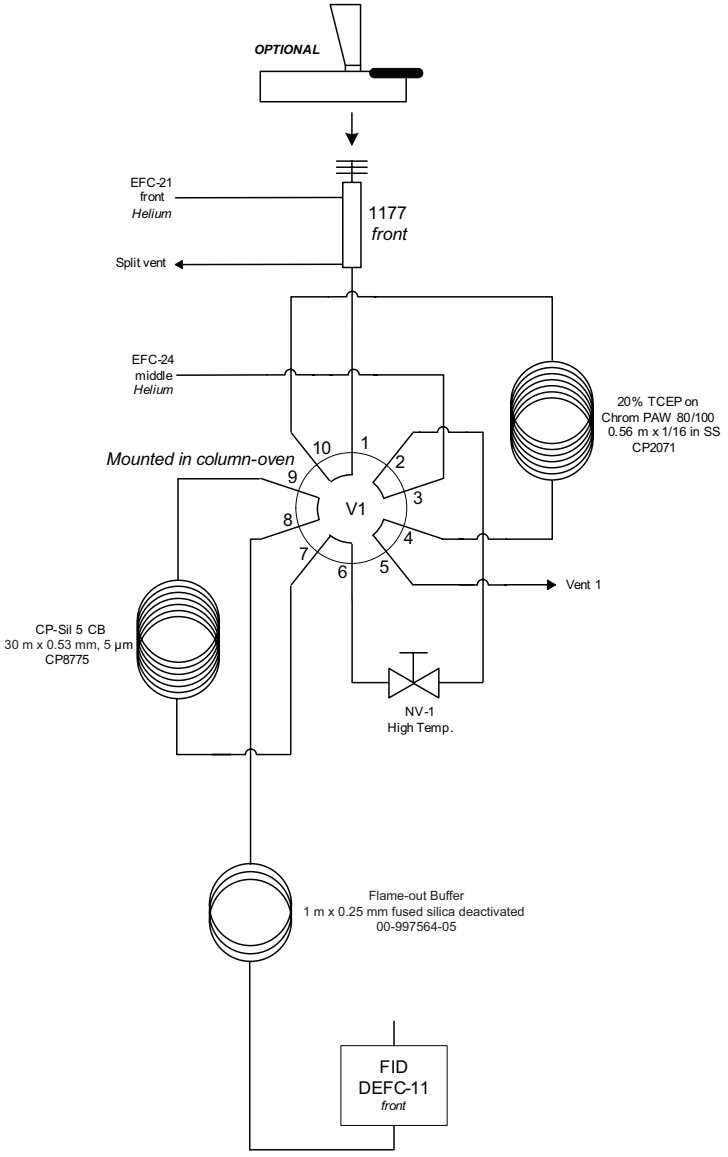
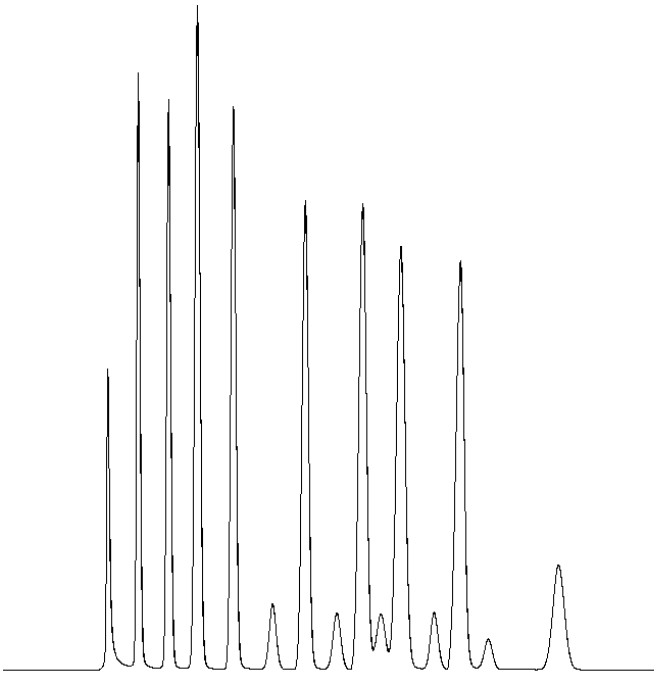


Figure 1. 4815 System Configuration Diagram

2. At a pre-determined time, the valve is switched and the higher boiling/polar components retained on the first column are backflushed onto the second (capillary) column (Agilent J&W CP-Sil 5CB) which has also been placed in the analysis path. The components of interest are then eluted on the second column, separated based on individual boiling point and detected via the FID.

Once benzene and TAME have fully eluted, the second column is backflushed and the remaining components are vented. Electronic flow control is used to increase the column pressure to accelerate elution of the remaining components as a composite peak, helping to reduce the overall sample analysis time. A typical chromatogram is shown in Figure 2.



Peak Identities

1. ***Methanol***
2. ***Ethanol***
3. ***Isopropanol***
4. ***tert-Butanol***
5. ***n-Propanol***
6. ***MTBE***
7. ***sec-Butanol***
8. ***DIPE***
9. ***iso-Butanol***
10. ***ETBE***
11. ***Tert Amyl Alcohol***
12. ***DME***
13. ***n-Butanol***
14. ***Benzene***
15. ***TAME***

Calibration is performed using several concentrations of a multi-component standard mixture with varying measured amounts of each of the oxygenated compounds. DME (1,2-dimethoxyethane) is added to each of the calibration standards. The system automatically generates a calibration curve for each analyte and computes linearity data. The samples are analyzed and each of the oxygenates are automatically quantified and a results report printed at the end of each analysis cycle. Typical performance results are shown in Table 1.

Figure 2. 4815 - Typical Chromatogram

Table 1. Typical Repetition for 15 Consecutive Samples

	Peak Area Counts per Target Analyte					
Analysis Run Number	**ETBE**	**MTBE**	**DIPE**	**TAME**	**Methanol**	**Ethanol**
1	1091607	1055853	1006944	2723971	2314775	4502637
2	1092548	1056604	1006333	2729622	2314607	4508744
3	1089694	1053480	1003985	2722182	2311682	4504657
4	1075404	1040368	989958	2689793	2288325	4457518
5	1094391	1057769	1008441	2737793	2327095	4521321
6	1082492	1047466	994728	2710139	2302127	4488649
7	1081258	1046027	995978	2706787	2306457	4489523
8	1086955	1051162	1001150	2721315	2321677	4505866
9	1078448	1043422	992506	2701805	2302820	4485725
10	1078209	1043115	992645	2703248	2310069	4485939
11	1097805	1058447	1011330	2745709	2361642	4548321
12	1095479	1058130	1009374	2741334	2344727	4540612
13	1074047	1039164	989716	2691657	2292032	4450770
14	1070283	1035161	984098	2677596	2294149	4452828
15	1074517	1035223	988866	2695103	2292921	4452076
Mean Area Count	1084209.133	1048092.733	998403.4667	2713203.6	2312340.333	4493012.4
Std Dev	8971.9	8435.5	8833.6	20479.8	20227.0	30748.1
RSD	0.83%	0.80%	0.88%	0.75%	0.87%	0.68%

These data represent typical results.

For further information, contact your local Agilent Sales Office.

Reference

ASTM D4815-04, Standard Test Method for the Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C1 to C3 Alcohols in Gasoline by Gas Chromatography; American Society for Testing and Materials, Philadelphia, PA.

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