

Analysis of Tertiary-amyl-ethyl Ether (TAE) and C8 Ethers in Finished Gasolines using Reformulyzer[®] M4

- **Fast Analysis in 39 minutes**
- **In compliance with key methods EN ISO 22854 and ASTM D6839**

Keywords:

Reformulyzer , Group-Type Analysis, Gasoline, TAE and C8 Ethers



INTRODUCTION

With the introduction of the 4th generation AC Analytical Controls (AC) Reformulyzer M4, group type analysis of gasolines and its precursors & blend streams has become easier and much faster than before.

The Reformulyzer M4 benefits from the use of capillary/Micropacked columns and traps, resulting in unprecedented speed of analysis, the widest analytical range and excellent precision. It complies with key methods EN ISO 22854 and ASTM D6839 and derived methods.

Depending on the sample stream or product, a range of analytical modes can be used, ensuring shortest possible runtimes, and data as required for that specific product. See Table 1.

This application note describes the quantitative determination of hydrocarbon types and oxygenates in Gasoline Blends and Finished Gasolines using the AC Reformulyzer M4 including determination of C7 and C8 ethers.

	PNA	OPNA	PIPNA	PONA	PIONA	PIANO	OPIONA	GASOLINE	FAST GROUP TYPE	E85
Light Straight Run Naphtha	X		X			X				
Heavy Straight Run Naphtha	X		X			X				
Depentanized Bottom Reformate	X		X			X				
FCC Light/Med/Heavy				X	X					
Visbreaker				X	X					
Alkylate / Isomerate			X							
Gasoline Blend							X	X	X	
Gasoline w. Oxygenates		X					X	X		
E85, E20, E10										X
Analysis Time	25	30	30	30	55	40	60	39	15	39

Table 1: Reformulyzer M4 Analysis Modes vs Product Streams

INSTRUMENTAL

The determination of different hydrocarbon types and oxygenates is achieved by separation and elution on a series of designed traps and columns. The flow diagram for Reformulyzer M4 is shown in Figure 1, and the analysis schedule used for this specific method is in Table 2. The Polar Column separates the Paraffins and Naphthenes from the Aromatics while Heavy Aromatics and Alcohols are retained on the Pre-Column. Ethers pass unretained and are trapped on the Ether/Alcohol-trap to be analyzed on the Boiling Point column. The Backflush time in Ether fraction is extended by 1.2 minute ensuring any C8 Ethers are eluting in the Ether fraction. Paraffins and Naphthenes pass the Olefin trap where Olefinic components are trapped. Further separation of Saturates by carbon number is achieved on the 13X Column. By using multiple valves and columns the Aromatics, PolyNaphthenes and Alcohols are analyzed on a Boiling Point Column in two different Aromatic fractions. Between two aromatic fractions the Olefin trap is desorbed in backflush and Olefins are separated on 13X column. The Micropacked traps and columns, located in the left side have separate heater elements for individual temperature programming. This allows simultaneous heating and/or cooling of traps, resulting in total runtime of 39 minutes. Extending Backflush time for Ethers does not affect runtime

From (min)	To (min)	Components	Column route
0	12	C4 to C11 N+P	1 st Polar column fraction on 13X Column
12	16.5	Ethers	Trapped Ethers via E/A-trap to Boiling Point Column
16.5	18.5	Saturates > 185°C	Backflush Boiling Point Column
18.5	26	C4 to C11 CO+O	Backflush desorption of Olefin trap on 13X Column
26	29	C6 to C8 A and pN	2 nd Polar Column fraction via E/A-trap to Boiling Point Column
29	30	Saturates > 185°C	Backflush Boiling Point Column of 2 nd Polar Column fraction
31	37	Alcohols + C8 to C10 A	3 rd Polar Column fraction via E/A-trap to Boiling Point Column
37	39	Aromatics > 185°C	Backflush Boiling Point Column of 3 rd Polar Column fraction

Table 2: Reformulyzer M4 Gasoline High Ether method

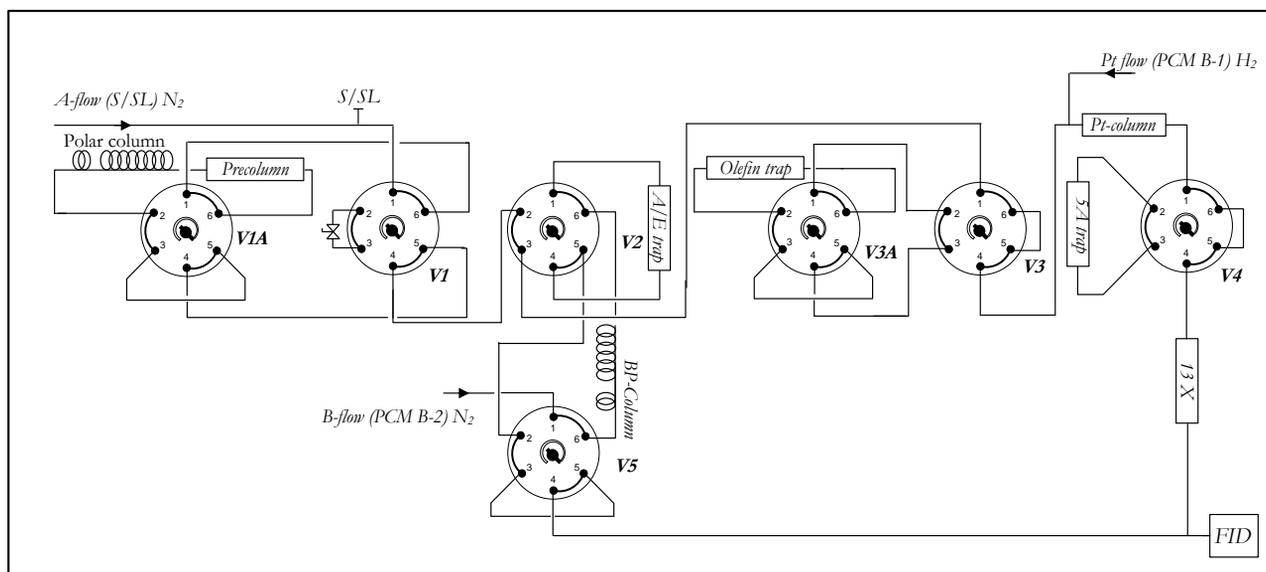


Figure 1: Reformulyzer M4 Flow Diagram

A gasoline sample with different Ethers including C8 Ethers was analyzed using the Reformalyzer M4 in Gasoline mode with extended ether fraction.

A Representative chromatogram is shown below and results compositions in Weight% and Volume% are in Tables 3 and 4.

Results are reported by component class by carbon number as well as their respective group totals.

Chromatograms show clear group separations for C7 (TAAE) and C8 ethers in a modified Gasoline Mode, allowing these components to be reported additional to other oxygenates such as ETBE or Ethanol from the same analysis.

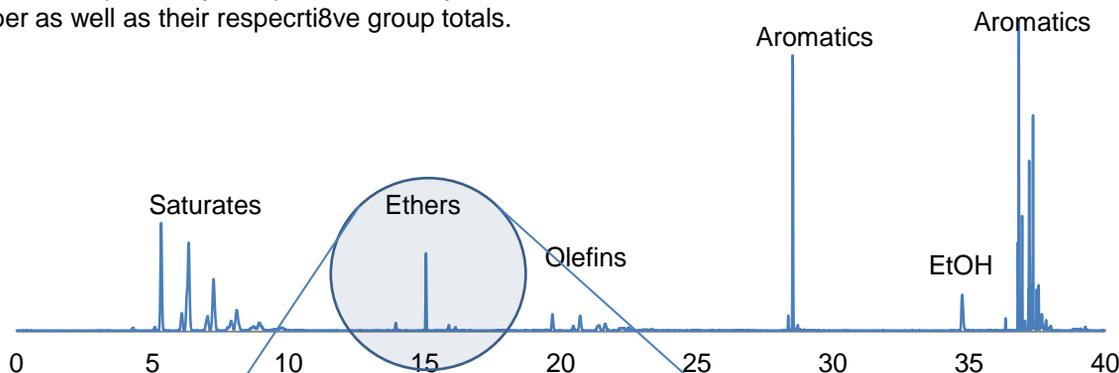


Figure 2: Sample with TAAE and C8 Ethers in Gasoline mode

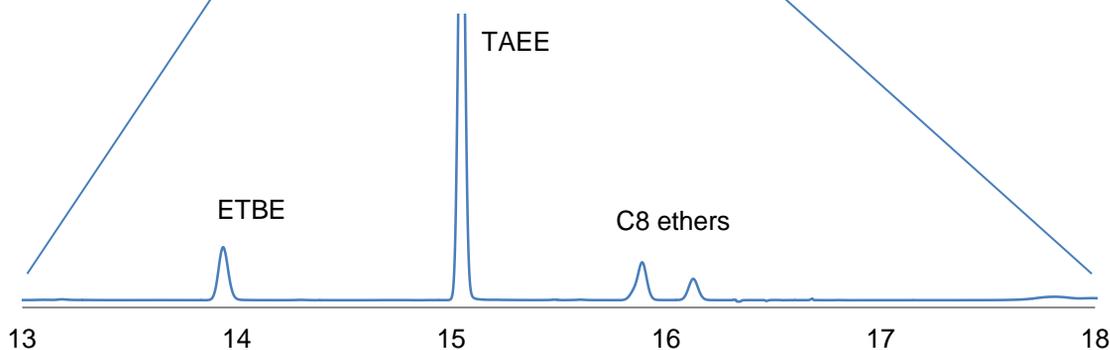


Figure 3: Ether fraction with C8 ethers in Gasoline mode

Normalized weight percent results

Cnr	Naph.	Paraf.	Arom.	Cycl Ol.	Olef.	Oxyg.	Total
1						0.10	0.10
2						7.18	7.18
3						0.03	0.03
4		0.19			0.03	0.12	0.34
5	0.24	8.71		0.06	1.35	0.03	10.39
6	1.68	10.95	0.49	0.38	1.41	0.72	15.63
7	1.86	6.15	9.55	0.80	0.79	4.68	23.83
8	1.58	3.03	12.48	0.56	0.40	0.78	18.83
9	0.89	1.45	17.36	0.25	0.20		20.15
10	0.29	0.72	1.08	0.06	0.06		2.21
11+		0.57	0.62				1.19
Poly	0.12						0.12
Total	6.66	31.77	41.58	2.11	4.24	13.64	100.00

Table 3: Reporting Gasoline High Ethers Weight%

Normalized volume percent results

Cnr	Naph.	Paraf.	Arom.	Cycl Ol.	Olef.	Oxyg.	Total
1						0.10	0.10
2						6.94	6.94
3						0.03	0.03
4		0.25			0.04	0.11	0.40
5	0.25	10.68		0.06	1.58	0.03	12.60
6	1.70	12.72	0.42	0.37	1.59	0.75	17.55
7	1.87	6.87	8.42	0.77	0.86	4.68	23.47
8	1.56	3.29	11.01	0.53	0.42	0.77	17.58
9	0.86	1.53	15.21	0.23	0.21		18.04
10	0.28	0.75	0.93	0.06	0.06		2.08
11+		0.57	0.54				1.11
Poly	0.10						0.10
Total	6.62	36.66	36.53	2.02	4.76	13.41	100.00

Table 4: Reporting Gasoline High Ethers Volume%

CONCLUSION

The Reformulyzer M4 provides reports group type data in full accordance with key methods EN ISO 22854 and ASTM D6839.

Weight% and Volume% profile reports are generated grouping naphthenes, paraffins, olefins, aromatics and oxygenates by carbon number as well as the totals of the different groups and the totals by carbon number.

Through the use of Capillary and Micropacked columns and Traps The Reformulyzer M4 takes only 39 minutes to produce reliable results in Gasoline mode.

Small modification of the standard gasoline Mode allows for the additional analysis of TAEE and C8 Ethers without compromise to all other components or runtime.

Specifications		
Scope / Separation Range	Reformer feed Reformate Straight naphtha FCC naphtha / <u>olefins up to 75%</u> Isomerates Alkylate Finished gasoline E20+/E85	Paraffins C4-C11 Isoparaffins C4-C11 Olefins C4-C11 Naphthenes C5-C11 Aromatics C6-C11 Oxygenates C1-C6 (includes Methanol, Ethanol, n-Propanol, i-Propanol, t-Butanol, i-Butanol, 2-Butanol, tert-amylalcohol, MTBE, ETBE, DIPE, TAME)
Method Compliance		
Accordinging Methods	ASTM D6839, EN-ISO22854, ASTM D5443, IP566, IP526, EN14517, SH/T 0741, GB/T28768	
Ordering Information		
CCG3500A	Reformulyzer M4 110V	
CCG3500B	Reformulyzer M4 200V	
CCG3500C	Reformulyzer M4 230V	

Table 5: Reformulyzer M4 Specifications & Ordering Information

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; AC's Turn-Key Application solutions include the AC Reformulyzer®, SimDis, Hi-Speed RGA and Customized instruments.