Analysis of Gasoline Blends and Finished Gasolines using Reformulyzer® M4 according to ASTM D6839 & EN ISO 22854 - OPIONA Mode

- **Fast Analysis in 60 minutes**
- **In compliance with key methods EN ISO 22854 and ASTM D6839**

Keywords:
Reformulyzer , Group-Type Analysis, iso/normal separation, OPIONA

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.

Typical modes used	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	X		X			X				
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										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 below 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. Paraffins and Naphthenes pass the Olefin- and 5A trap where Olefins are trapped on the Olefin trap and nParaffins on the 5A trap. Further separation of Saturates is on the 13X Column resulting in a carbon number distribution.

By using multiple valves and columns the Aromatics, PolyNapthenes and Alcohols are analyzed on a Boiling Point Column in two different Aromatic fractions. The 5A trap is desorbed after the Ether fraction and all nParaffins are separated on the 13X Column. The first Aromatic fraction is analyzed on the Boiling Point Column. The Olefin trap will desorb next with the 5A trap in flow so all nOlefins are trapped. Other Olefins pass unretained and are separated on the 13X column. Second Aromatic fraction is analyzed between Olefin fraction and nOlefin fraction. Finally the 5A trap is desorbed and nOlefins are separated on the 13X Column.

The Micropacked traps and columns are located in the left side and have separate heater elements for individual temperature programming. This allows heating and/or cooling of traps simultaneous, resulting in total analysis runtime of 60 minutes.

From (min)	To (min)	Components	Column route
0	12	C4 to C11 N+P	1st Polar column fraction on 13X Column
12	15	Ethers	Trapped Ethers via E/A-trap to Boiling Point Column
15	16	Saturates > 185°C	Backflush Boiling Point Column
16	27	C4 to C11 nP	Desorbtion of 5A trap on 13X Column
27	29	C6 to C8 A and pN	2nd Polar Column fraction via E/A-trap to Boiling Point Column
29	30	Saturates > 185°C	Backflush Boiling Point Column of 2nd Polar Column fraction
30	40	C4 to C11 CO+O	Backflush desorption of Olefin trap on 13X Column with 5A trap in flow
40	49	Alcohols + C8 to C10 A	3rd Polar Column fraction via E/A-trap to Boiling Point Column
49	50	Aromatics > 185°C	Backflush Boiling Point Column of 3rd Polar Column fraction
50	60	C4 to C11 nO	Desorption of 5A trap on 13X Column

Table 2: Reformulyzer M4 OPIONA Mode

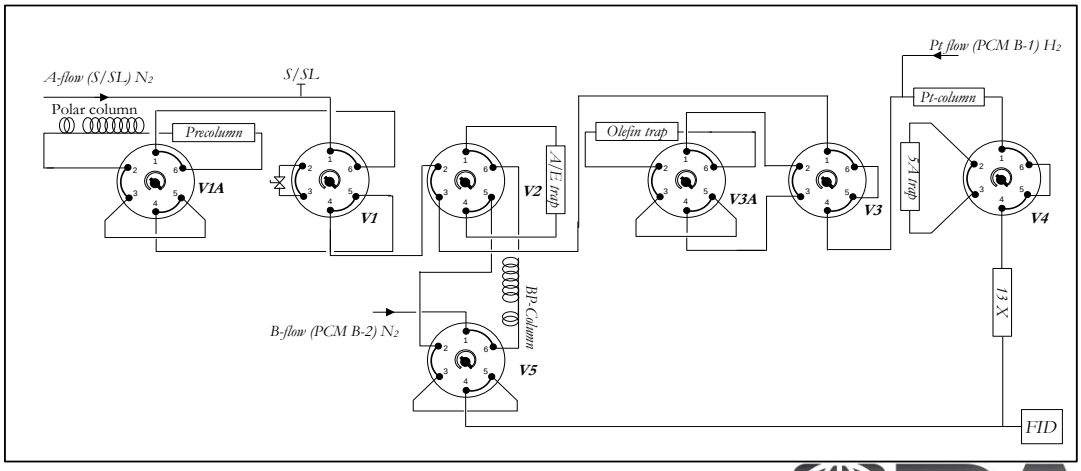

Figure 1: Reformulyzer M4 Flow Diagram

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Gravimetric Blend 512 and Gasoline N Certified Reference Materials (CRM) were analyzed using the Reformulyzer M4 in OPIONA mode.
Representative chromatograms are shown below and typical report outputs from the analysis for the CRM are in Tables 3 and 4.
Reported are compositions in Weight% and Volume% and list component class by carbon number as well as the totals for the different groups and the totals per carbon number.

Chromatograms show clear group separations for i/n-Paraffins, Naphthenes, Aromatics, i/n-Olefins and Oxygenates, and %Weight and %Volume by carbon numbers are well within specifications for this particular CRM.

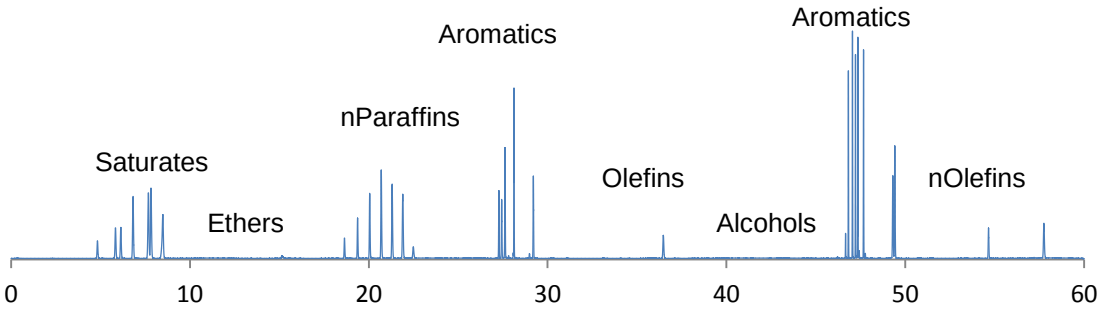

Figure 2: Reference Sample Gravimetric Blend (50.16.512) in OPIONA mode

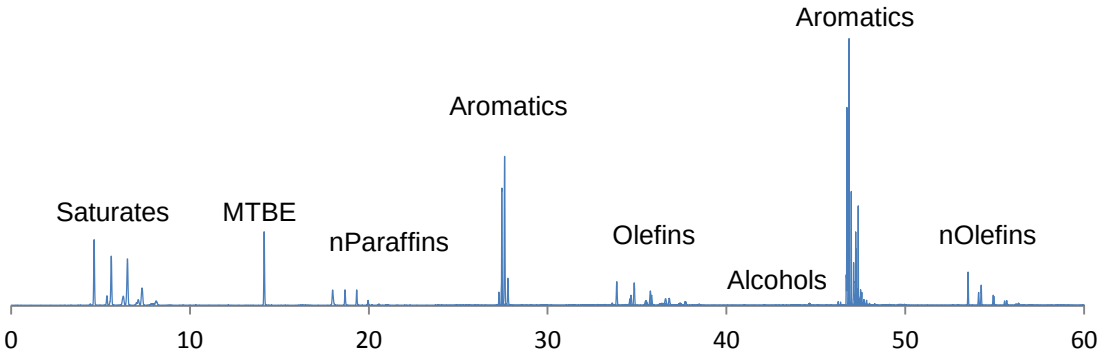

Figure 3: Gasoline K CRM (00.02.045) in OPIONA mode

Normalized weight percent results

Cnr	Naph.	i-Par.	n-Par.	Arom.	Cycl Ol.	i-Olef.	n-Olef.	Oxyg.	Total
2								0.03	**0.03**
3									
4		0.03				0.35	0.05	0.07	**0.50**
5	0.12	6.65	2.20		0.20	2.44	2.40	10.08	**24.09**
6	1.02	5.74	1.47	1.20	0.71	2.43	1.56		**14.13**
7	1.70	6.36	1.39	11.85	0.90	1.85	0.83		**24.88**
8	1.17	2.96	0.45	15.42	0.53	1.12	0.39		**22.04**
9	0.47	0.96	0.11	9.57	0.20	0.52	0.12		**11.95**
10		0.23		1.26		0.08			**1.57**
11+		0.25		0.48					**0.73**
Poly	0.05								**0.05**
Total	**4.53**	**23.18**	**5.62**	**39.78**	**2.54**	**8.79**	**5.35**	**10.18**	**100.00**

Table 3: Reporting Gasoline N Weight%

Normalized volume percent results

Cnr	Naph.	i-Par.	n-Par.	Arom.	Cycl Ol.	i-Olef.	n-Olef.	Oxyg.	Total
2								0.03	**0.03**
3									
4		0.04				0.44	0.06	0.06	**0.60**
5	0.12	8.04	2.64		0.19	2.82	2.77	10.17	**26.75**
6	1.02	6.56	1.67	1.03	0.69	2.69	1.72		**15.38**
7	1.69	6.99	1.53	10.29	0.86	1.99	0.90		**24.25**
8	1.14	3.16	0.49	13.39	0.50	1.18	0.41		**20.27**
9	0.45	1.00	0.12	8.25	0.19	0.54	0.13		**10.68**
10		0.23		1.07		0.08			**1.38**
11+		0.24		0.41					**0.65**
Poly	0.04								**0.04**
Total	**4.46**	**26.26**	**6.45**	**34.44**	**2.43**	**9.74**	**5.99**	**10.26**	**100.00**

Table 4: Reporting Gasoline N 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 60 minutes to produce reliable results in OPIONA mode with full iso/normal separation for paraffins and olefins.

Specifications		
Scope / Separation Range	Finished gasoline Reformer feed Reformate Straight naphtha FCC naphtha/Olefins Isomerates Alkylate 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		
According Methods	ASTM D6839, EN-ISO22854, ASTM D5443, IP566, SH/T 0741, GB/T 28768-2012	
Ordering Information		
CCG3500A	Reformulyzer M4 120V	
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; ACs Turn-Key Application solutions include the AC Reformulyzer ® , SimDis, Hi-Speed RGA and Customized instruments.