

## Analysis of Iso- and n-Paraffins, Naphthenes, Iso- and n-Olefins and Aromatics (PIONA) using Reformulyzer<sup>®</sup> M4

- **Fast Analysis in 55 minutes**
- **In compliance with key methods EN ISO 22854 and ASTM D6839**

**Keywords:**

**Reformulyzer , Group-Type Analysis, PIONA**



### INTRODUCTION

With the introduction of the 4<sup>th</sup> 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 in Naphtha and Reformate streams 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 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
<b>Analysis Time</b>	<b>25</b>	<b>30</b>	<b>30</b>	<b>30</b>	<b>55</b>	<b>40</b>	<b>60</b>	<b>39</b>	<b>15</b>	<b>39</b>

Table 1: Reformulyzer M4 Analysis Modes vs Product Streams

## INSTRUMENTAL

The determination of hydrocarbon types in refinery streams 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 are retained on the Pre-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 and PolyNaphthenes are analyzed on a Boiling Point Column in two different Aromatic fractions. The 5A trap is desorbed after the first aromatic fraction and the nParaffins are separated on the 13X column. Next the Olefin trap is desorbed with the 5A trap in flow trapping the nOlefins. Cyclic and Iso-Olefins are separated on 13X Column. 5A trap is desorbed after second Aromatic fraction and nOlefins are separated on 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 55 minutes.

From (min)	To (min)	Components	Column route
0	12	C4 to C11 N+iP	1 <sup>st</sup> Polar column fraction on 13X Column
12	14.5	C6 to C8 A and pN	2 <sup>nd</sup> Polar Column fraction via E/A-trap to Boiling Point Column
14.5	16	Saturates > 200°C	Backflush Boiling Point Column of 2 <sup>nd</sup> Polar Column fraction
16	29	C4 to C11 nP	Desorption of 5A trap on 13X Column
29	40	C4 to C11 CO+iO	Desorption of Olefin trap with 5A in flow on 13X
40	42	C8 to C10 A	3 <sup>rd</sup> Polar Column fraction via E/A-trap to Boiling Point Column
42	43	Aromatics > 200°C	Backflush Boiling Point Column of 3 <sup>rd</sup> Polar Column fraction
43	55	C4 to C11 nO	Desorption of 5A trap on 13X Column

Table 2: Reformulyzer M4 PIONA method

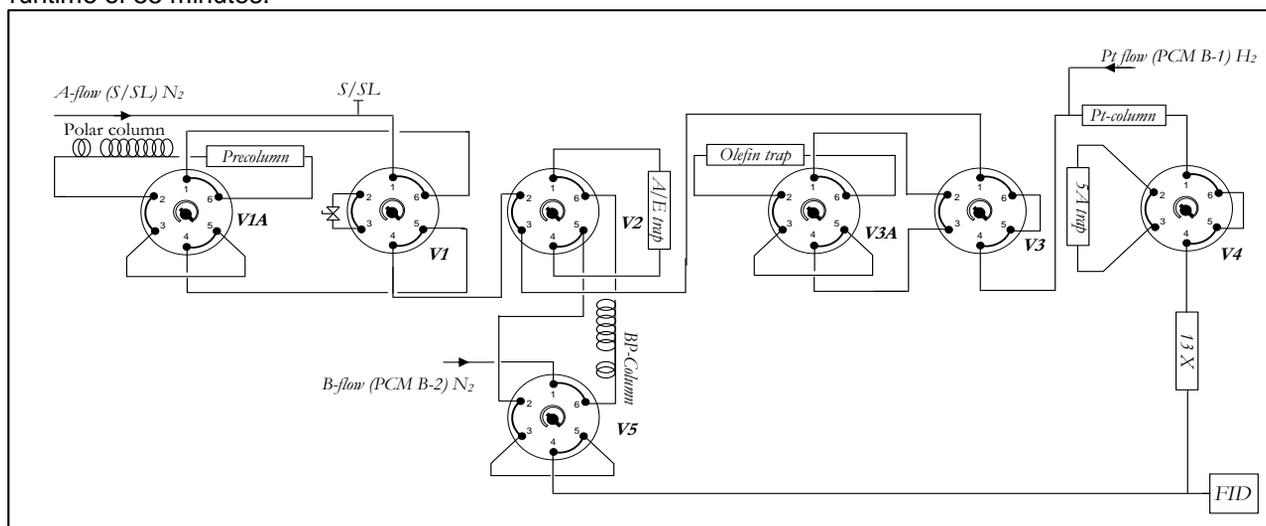
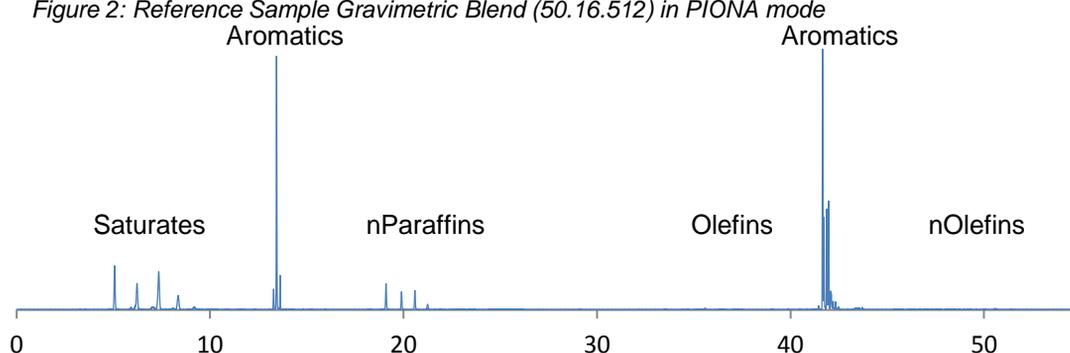
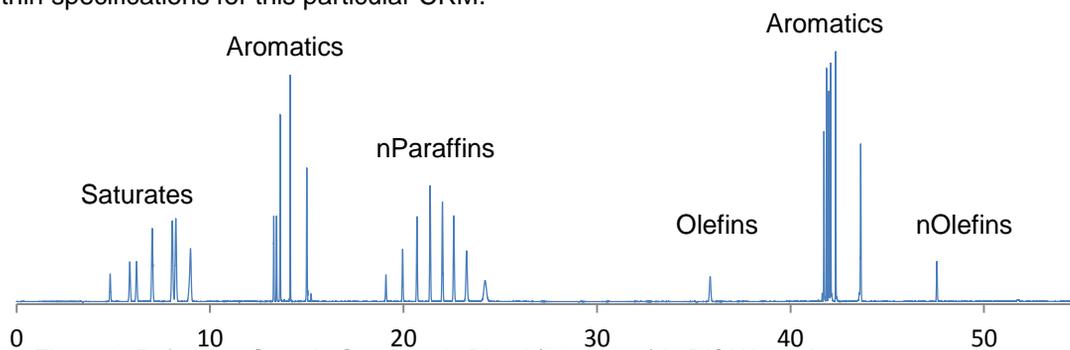


Figure 1: Reformulyzer M4 Flow Diagram

Gravimetric Blends and a Reformate Certified Reference Materials (CRM) were analyzed using the Reformalyzer M4 in PIONA mode.

Representative chromatograms are shown below and typical report outputs from the analysis for the CRM are in Tables 3 and 4. Chromatograms show clear group separations for Iso- and nParaffins, Naphthenes, Iso- and n-Olefins and Aromatics, and %Weight and %Volume by carbon numbers are well within specifications for this particular CRM.

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.



### Normalized weight percent results

Cnr	Naph.	i-Par.	n-Par.	Cycl Ol.	i-Olef.	n-Olef.	Arom.	Total
4		0.01						0.01
5	0.08	5.84	3.25		0.04			9.21
6	0.30	4.77	1.87	0.01	0.06	0.02	1.66	8.69
7	0.67	7.76	2.08	0.04	0.16	0.03	19.23	29.97
8	0.33	3.04	0.58	0.03	0.06	0.01	28.17	32.22
9	0.07	0.51	0.09		0.01	0.02	16.37	17.07
10			0.07			0.02	1.99	2.08
11					0.01	0.10		0.11
12+							0.65	0.65
Poly								0.00
<b>Total</b>	<b>68.07</b>	<b>0.08</b>	<b>0.34</b>	<b>21.93</b>	<b>0.34</b>	<b>0.20</b>	<b>68.07</b>	<b>100.00</b>

Table 3: Reporting Reformate Weight%

### Normalized volume percent results

Cnr	Naph.	i-Par.	n-Par.	Cycl Ol.	i-Olef.	n-Olef.	Arom.	Total
4		0.02						0.02
5	0.08	7.43	4.11		0.05			11.67
6	0.32	5.75	2.24	0.01	0.07	0.03	1.49	9.91
7	0.70	8.98	2.41	0.04	0.18	0.03	17.59	29.93
8	0.34	3.42	0.66	0.03	0.07	0.01	25.75	30.28
9	0.07	0.55	0.10		0.01	0.02	14.86	15.61
10			0.07			0.03	1.77	1.87
11					0.01	0.11		0.12
12+							0.59	0.59
Poly								0.00
<b>Total</b>	<b>1.51</b>	<b>26.15</b>	<b>1.51</b>	<b>0.08</b>	<b>0.39</b>	<b>0.23</b>	<b>62.08</b>	<b>100.00</b>

Table 4: Reporting Reformate 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, iso- and n-paraffins, iso- and n-olefins and aromatics 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 55 minutes to produce reliable results in PIONA mode.

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		
Accordinging 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.