APPLICATION NOTE

Analysis of Paraffins, Naphthenes and Aromatics (PNA) in Hydrocarbon Streams using Reformulyzer® M4

- **Fast Analysis in 25 minutes**
- **In compliance with key methods EN ISO 22854 and ASTM D6839**

Keywords:
Reformulyzer , Group-Type Analysis, PNA

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 paraffins, naphthenes and aromatics (PNA) in hydrocarbon products 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, E10										X
Analysis Time	**25**	**30**	**30**	**30**	**55**	**40**	**60**	**39**	**15**	**39**

Table 1: Reformulyzer M4 Analysis Modes vs Product Streams

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INSTRUMENTAL

The determination of different hydrocarbon types 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. Further separation of the Paraffins and Naphthenes on the 13X Column results in a carbon number distribution.

By using multiple valves and columns the Aromatics and PolyNapthenes are analyzed on a Boiling Point Column in two different Aromatic fractions. 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 25 minutes.

From (min)	To (min)	Components	Column route
0	14	C1 to C12 N+P	1st Polar column fraction on 13X
14	16.5	C6 to C8 A and pN	2nd Polar Column fraction via E/A-trap to Boiling Point Column
16.5	18	Saturates > 200°C	Backflush Boiling Point Column of 2nd Polar Column fraction
18	22.5	C8 to C10 A	3rd Polar Column fraction via E/A-trap to Boiling Point Column
22.5	25	Aromatics >200°C	Backflush Boiling Point Column of 3rd Polar Column fraction

Table 2: Reformulyzer M4 PNA method

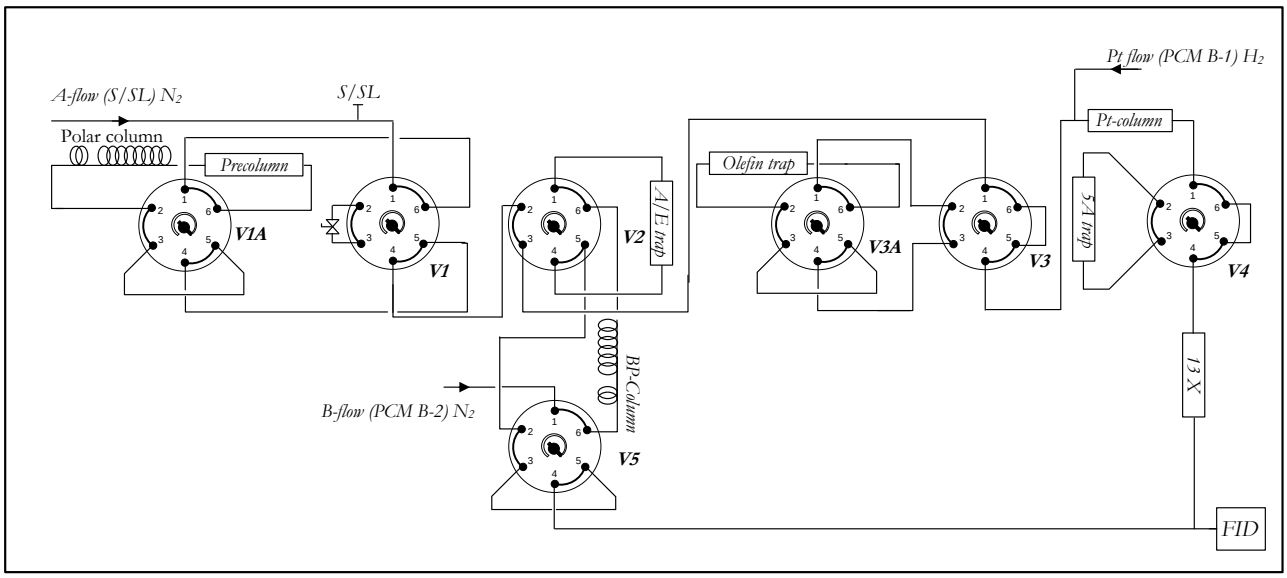

Figure 1: Reformulyzer M4 Flow Diagram

Gravimetric Blends and a Reformer Feed Certified Reference Materials (CRM) were analyzed using the Reformulyzer M4 in PNA 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 Paraffins, Naphthenes 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.

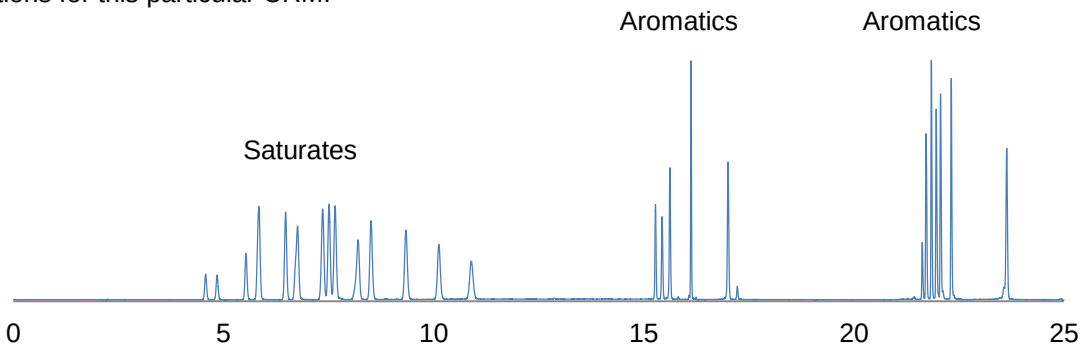

Figure 2: Reference Sample Gravimetric Blend (50.16.512) in PNA

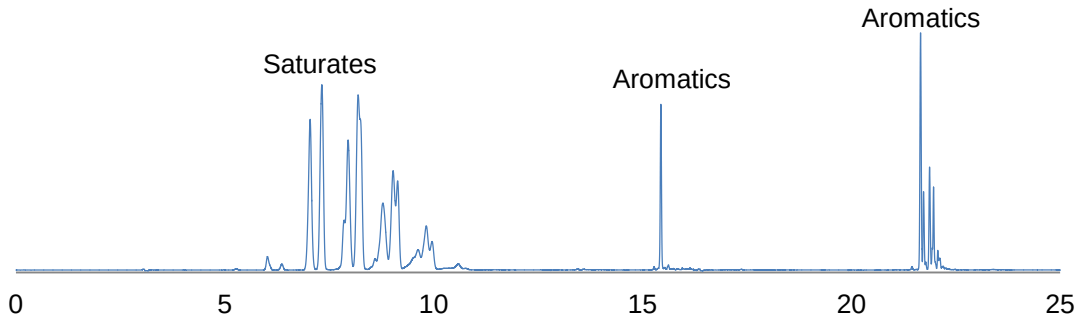

Figure 3: Reformer Feed CRM (00.02.040) in PNA mode

Normalized weight percent results

Cnr	Parafins	Arom.	Naphtenes	Total
4				
5	0.06			**0.06**
6	0.32	0.06	0.77	**1.15**
7	12.11	3.80	9.51	**25.42**
8	17.48	7.69	11.45	**36.62**
9	12.72	5.21	7.95	**25.88**
10	6.13	0.30	3.02	**9.45**
12	0.12		0.94	**1.06**
12+	0.10	0.11		**0.21**
Poly			0.14	**0.14**
Total	**49.04**	**17.17**	**33.78**	**100.00**

Table 3: Reporting Reformer Feed Weight%

Normalized volume percent results

Cnr	Parafins	Arom.	Naphtenes	Total
4				
5	0.08			**0.08**
6	0.37	0.05	0.77	**1.19**
7	13.34	3.31	9.47	**26.12**
8	18.73	6.7	11.13	**36.56**
9	13.26	4.5	7.61	**25.37**
10	6.34	0.26	2.82	**9.42**
12	0.12		0.85	**0.97**
12+	0.09	0.09		**0.18**
Poly			0.12	**0.12**
Total	**52.33**	**14.91**	**32.77**	**100.00**

Table 4: Reporting Reformer Feed 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 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 25 minutes to produce reliable results in PNA 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		
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.