Improving robustness and lowering maintenance on Reformulyzer M4 with next generation Olefin Traps.

- **Improved Olefin Trap Lifetime (>1000 FCC samples)**
- **Linear Range up to 75% Olefins**

Keywords:
Olefin Trap, Reformulyzer M4, EN ISO 22854, ASTM D6839, FCC Naphtha

INTRODUCTION

With the introduction of the 4th generation AC Analytical Controls' (AC) Reformulyzer M4, used for group type analysis of gasolines and its blend streams, many of the key components in the system are completely redesigned for a better performance.

The Olefin Trap, responsible for separating olefins from paraffins and naphthenes, is probably the most critical components in the system.
Up to recently FCC Naphtha samples with higher concentrations of Olefins would be perfectly well handled in the Reformulyzer M3 by special high olefin modes and/or dilution. However, with concentrations sometimes being unknown having to run two samples is undesirable and dilution may even introduce errors or compromise the sample integrity.
Improving lifetime expectancy and lowering dependency on sample type (total olefin concentration) would result in better performance over time, lower maintenance, lower operating cost, and better analytical robustness.

The principal analytical challenge for these olefin traps, a packed chromatographic column with a polar character, is to selectively retain Olefins in gasoline range (up to C11 olefins), while showing little to no retention to Paraffins and Naphtenes (up to C12) at lower temperature, and quantitatively let go of these olefins at elevated temperatures.

This basic separation is one of the foundations of Reformulyzer type methods such as ASTM 6839 and EN ISO 22854. The stability of this separation, like with any gaschromatographic separation, is critical to analytical robustness of the solution, as they will directly affect precision and accuracy for the method

This application note describes the next generation Olefin Traps in the Reformulyzer M4 (see Fig 1), provides example data for this improved trap with typical samples and summarizes the new benefits.

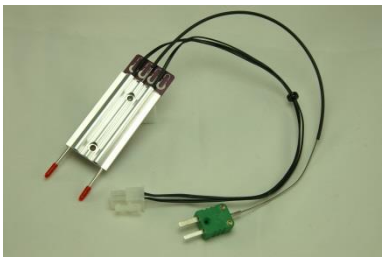

Figure 1: Reformulyzer M4 Olefin Trap

INSTRUMENTAL

The determination of hydrocarbon components in refinery streams containing high concentrations of Olefins is achieved by separation and elution on a series of specifically 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 (in this case PONA) is in Table 2.

Compared to Reformulyzer M3, a number of fundamental changes have been made to the system:

- The system is redesigned using capillary and micro-packed columns, and a S/SL inlet, lowering the actual sample amount by a factor of 20. These changes also mandate lower trap capacities and reduce analysis time significantly.
- The Reformulyzer M4 Olefin Trap material conditioning process was optimized for improved performance and better lifetime.
- The Reformulyzer M4 Olefin Trap is *desorbed in backflush* to inject components onto the 13X column. This major change circumvents irreversible adsorption of heavier components and breakthrough of light end components respectively and improve lifetime.

From (min)	To (min)	Components	Column route
0	13	C4 to C12 N+P	1st Polar column fraction on 13X Column
13	14.5	C6 to C8 A and pN	2nd Polar Column fraction via E/A-trap to Boiling Point Column
14.5	16	Saturates > 200°C	Backflush Boiling Point Column of 2nd Polar Column fraction
16	26	C4 to C12 CO+O	Backflush desorption of Olefin trap on 13X Column
26	28	C8 to C10 A	3rd Polar Column fraction via E/A-trap to Boiling Point Column
28	30	Aromatics > 200°C	Backflush Boiling Point Column of 3rd Polar Column fraction

Table 1: Reformulyzer M4 PONA method

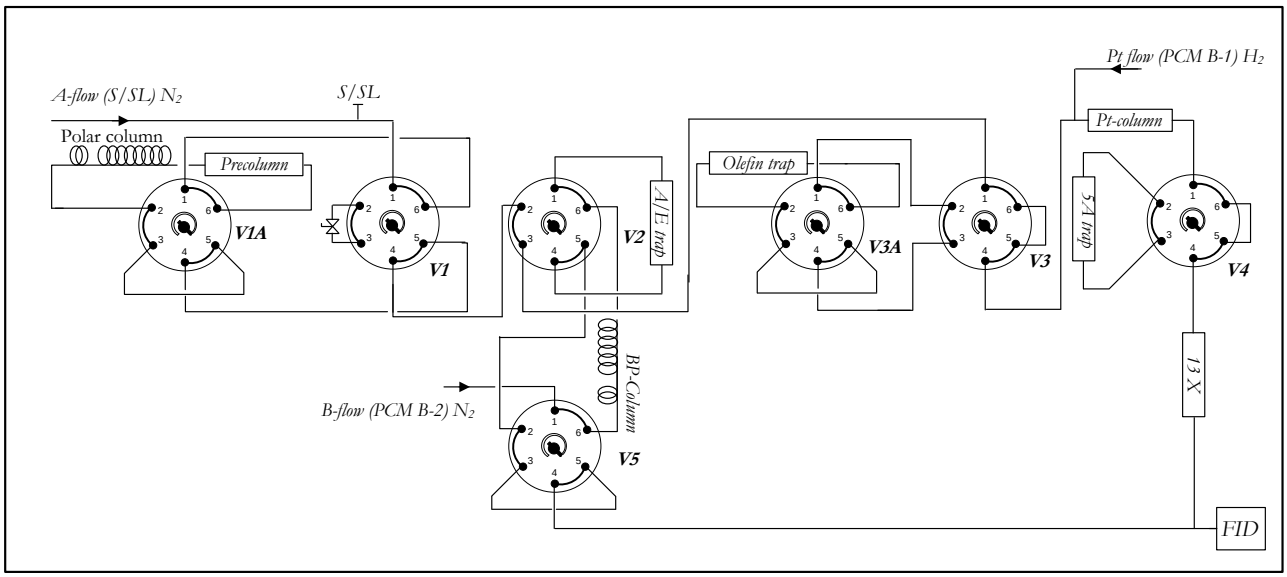

Figure 2: Reformulyzer M4 Flow Diagram

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FCC Naphtha with 48% Olefins

FCC Naphtha Reference Material containing approximately 48% olefins (AC Analytical Controls p/n *00.02.042)* was analyzed repeatedly in PONA mode for a period of over two weeks, totaling >1000 Injections.
Figure 3a shows a representative chromatogram for this analysis and Table 2 summarizes the dataset.

Average values are well within specs and group-totals for Saturates, Olefins and Aromatics are 97-102% recovery to reference value.
Figure 4, shows results for Total Olefins, Cyclic Olefins, C5- and C11 olefins. Clearly Olefin Trap stability proves excellent, even after 1000 runs at 48% Total Olefin level.

Normalized weight percent results

Cnr	Naph.	Paraf.	Arom.	Cycl Ol.	Olef.	Total
4		0.43			1.91	**2.34**
5	0.17	11.26		0.49	14.57	**26.49**
6	2.24	9.64	0.44	1.78	11.37	**25.47**
7	3.50	6.67	2.39	2.27	7.35	**22.18**
8	2.54	4.18	3.64	1.39	4.11	**15.86**
9	1.08	2.08	0.92	0.52	1.77	**6.37**
10	0.12	0.43	0.03	0.09	0.33	**1.00**
11					0.03	**0.03**
12+		0.16	0.04			**0.20**
Poly	0.04					**0.04**
Total	**9.65**	**34.85**	**7.42**	**6.54**	**41.44**	**100.00**
Rsd%	**0.67**	**0.34**	**1.31**	**2.03**	**0.24**	**--**

Table 2: Averaged Results for FCC Naphtha 00.02.042 (n=>1000 injections, result in %w/w)

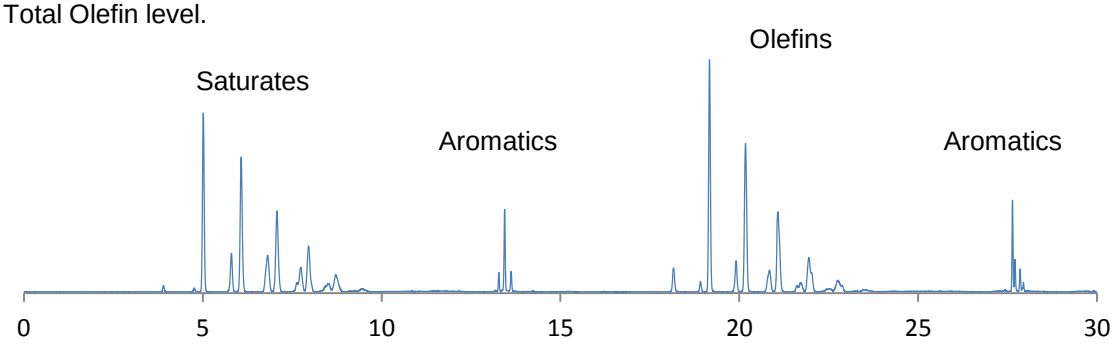

Figure 3: FCC Naphtha CRM (00.02.042) in PONA mode

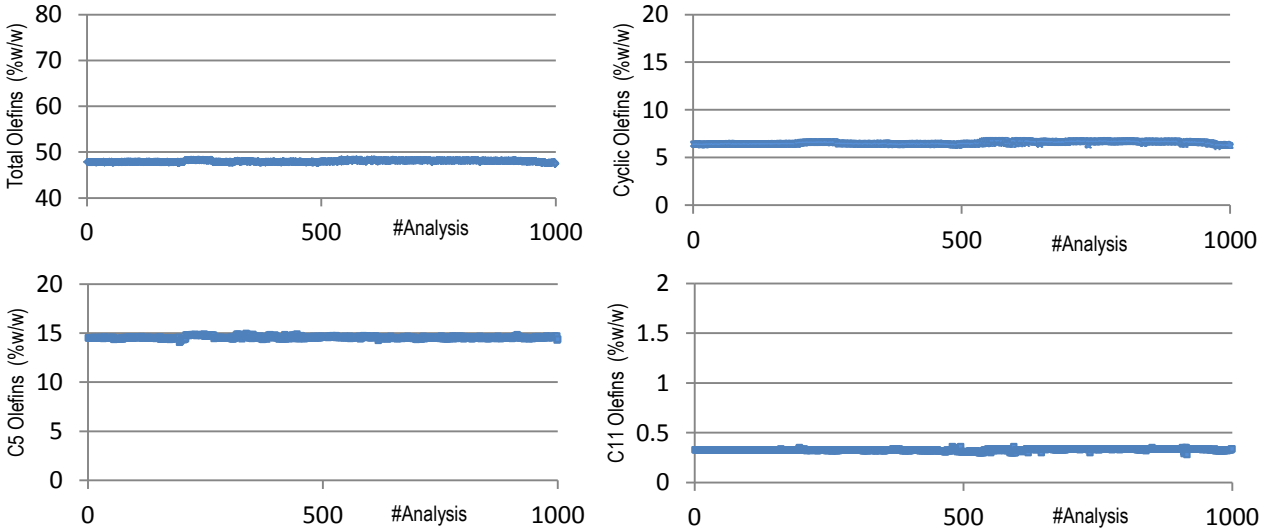

Figure 4: Result various groups as function of # analyses. Sample is 00.02.042

FCC Naphtha with 74% Olefins

FCC Naphtha Reference Material containing (AC p/n *00.02.042)* was diluted 1:1 with a C5 Olefin. The resulting sample mixture theoretically contains approximately 71% Olefins and 3% m/m Cyclic Olefins was analyzed repeatedly in PONA mode, totaling 320 Injections.

Figure 5 shows a typical chromatogram for this analysis and Tables 3 summarizes the dataset.
Average values for Total Olefins in the diluted sample are 74.60% m/m with RSD of only 0.14%, well within precision limit expectations extrapolated from ASTM D6839.
The Olefin Trap demonstrates excellent stability even at these concentrations up to 75%. The difference in result between first and last 20 runs in the series was 0.004% for Total Olefins, confirming this very stable performance.

Normalized weight percent results

Cnr	Naph.	Paraf.	Arom.	Cycl Ol.	Olef.	Total
4		0.23			0.90	**1.92**
5	0.08	5.40		0.24	58.38	**24.02**
6	1.09	4.69	0.21	0.86	5.52	**24.93**
7	1.71	3.26	1.12	1.10	3.58	**23.10**
8	1.25	2.06	1.82	0.66	2.03	**17.41**
9	0.51	1.03	0.45	0.25	0.84	**7.19**
10	0.06	0.21	0.01	0.07	0.17	**1.19**
11						**0.10**
12+		0.16	0.04			**0.12**
Poly						**0.03**
Total	**4.70**	**17.05**	**3.65**	**3.18**	**71.42**	**100.00**
Rsd%	**0.51**	**0.41**	**1.17**	**2.42**	**0.15**	**--**

Table 3: Averaged results for FCC naphtha 00.02.042 with added C5 Olefin. (n=320 injections, results in %w/w)

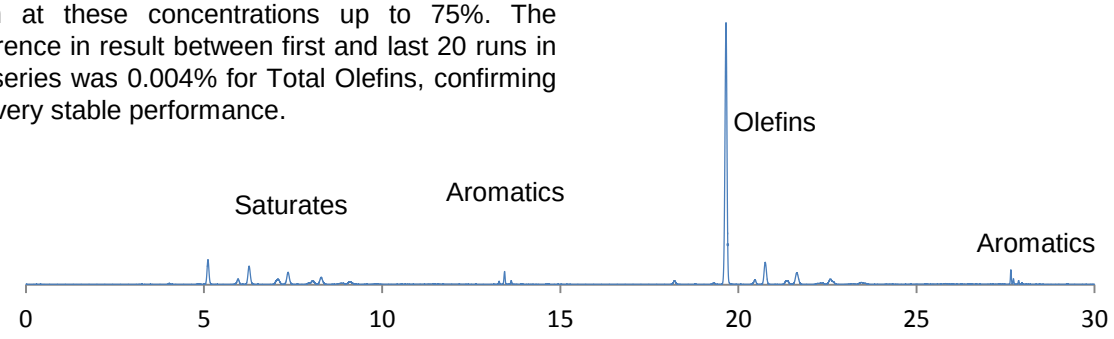

Figure 5: FCC naphtha 00.02.042 with added C5 Olefin in PONA mode

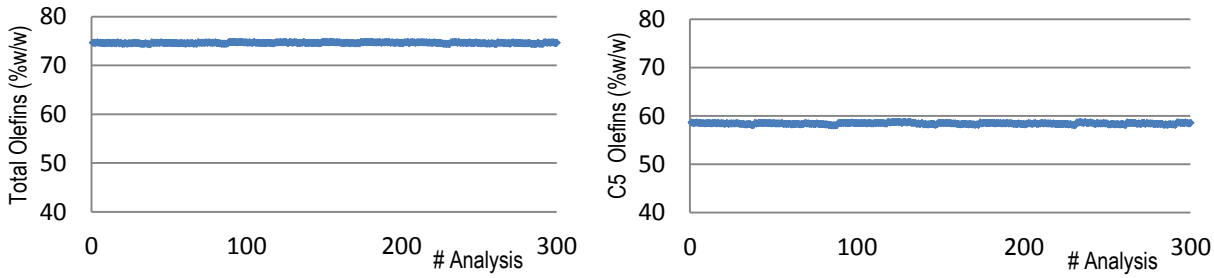

Figure 6: Result Total Olefins & C5 Olefins as function of # analyses. Sample is 00.02.042 FCC Naphtha diluted with C5-Olefin

CONCLUSION

The Reformulyzer M4 provides reports group type data in full accordance with key methods EN ISO 22854 and ASTM D6839. The Reformulyzer M4 Olefin Trap, one of its key components, has been completely redesigned for improved performance and lifetime.
Data in this paper demonstrates that this next generation of Olefin Trap design clearly outperforms traditional trap designs; The improved olefin trap will last significantly longer, run significantly more analyses, and will live up to the challenge of running even FCC samples with olefin concentrations up to 75% without showing any symptoms of deteriorating performance.

The Reformulyzer M4 with its new Olefin Trap Design will:

- Provide for lower maintenance regimes and lower lab downtime.
- Obsolete any sample dilution protocols
- Obsolete special olefin method obsolete.
- Save cost
- Provide more consistent data over longer periods

Specifications		
Scope / Separation Range	Reformer feed Reformate Straight naphtha FCC naphtha / olefins up to **75%** Isomerates Alkylate Finished gasoline E85/E20	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.