

# Analysis of NTGA’s (Non Traditional Gasoline Additives) in Finished Gasolines according to ASTM D6839 & EN ISO 22854 - ACETON

## REFORMULYZER® M4

-  **Fast Analysis in 42 Minutes**
-  **In compliance with key methods EN ISO 22854 and ASTM D6839**
-  **Aceton performed on M4**

**Keywords:** Reformulyzer, Group-Type Analysis, Gasoline, NTGA’s

### 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 Non Traditional Gasoline Additives (NTGA’s) in Gasoline Blends and Finished Gasolines using the AC Reformulyzer M4. The non-traditional gasoline additive (NTGAs) in this application note is Aceton.

These are organic compounds used as solvents in a wide range of industrial applications. These solvents have recently been detected in gasoline blends and are believed to be linked to several engine performance problems, such as engine start-up and acceleration problems.

|                            | 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   | 32    | 33   | 55    | 40    | 60     | 41       | 15              | 41  |

Table 1: Reformulyzer M4 Analysis Modes vs Product Stream

Gasolines samples spiked with different NTGA's were analyzed using the Reformulyzer M4 in Gasoline mode.

A representative chromatogram with Aceton is shown below and typical report outputs from the analysis is displayed in Table 2.

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.

The chromatograms shows a clear group separation for Paraffins, Naphthenes, Aromatics, Olefins and Aceton.

Response factors for the NTGAs are determined experimentally because of the oxygen content.

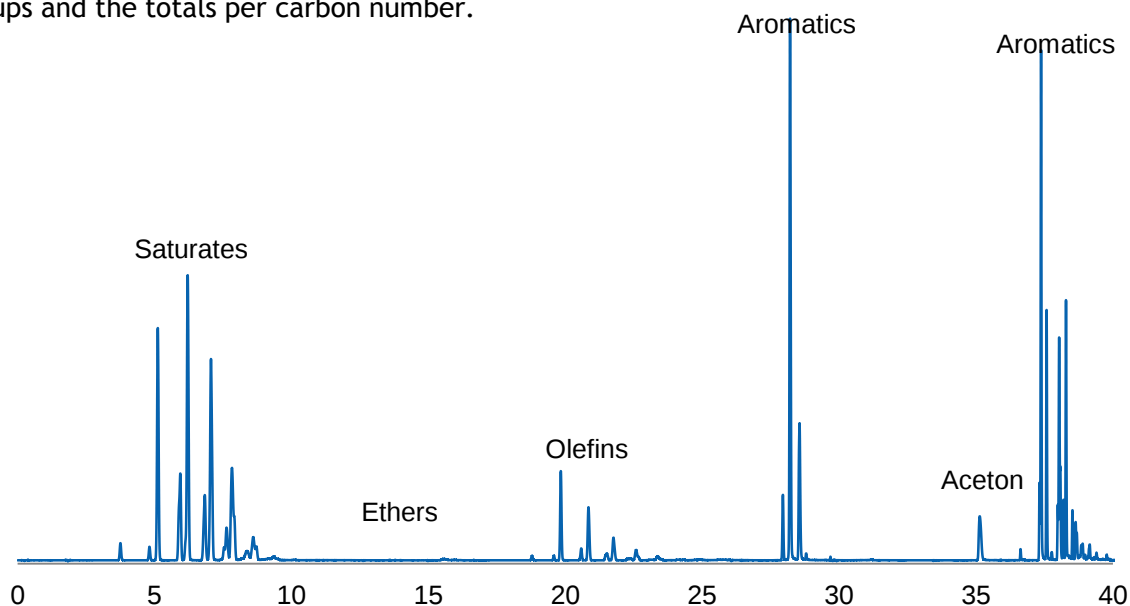


Figure 2: Gasoline spiked with ~ 4 % (m/m) Aceton in Gasoline mode (co-elution with *i*-Propanol)

#### ASTM D 6839 and EN ISO 22854

##### Summary

| Component  | % (w/w) | % (V/V) | % O  |
|------------|---------|---------|------|
| Benzene    | 1.31    | 1.13    | -    |
| Saturates  | 43.52   | 48.55   | -    |
| Olefins    | 7.30    | 8.06    | -    |
| Aromatics  | 44.94   | 39.34   | -    |
| Oxygenates | 4.24    | 4.06    | 1.17 |

##### Oxygenates

| Component         | % (w/w) | % (V/V) | % O  |
|-------------------|---------|---------|------|
| Methanol          | -       | -       | -    |
| Ethanol           | -       | -       | -    |
| Acetone           | 4.24    | 4.06    | 1.17 |
| iso-Propanol      | -       | -       | -    |
| Methyl Acetate    | -       | -       | -    |
| Methylal          | -       | -       | -    |
| n-Propanol        | -       | -       | -    |
| 2-Butanol         | -       | -       | -    |
| Diethylether      | -       | -       | -    |
| iso-Butanol       | -       | -       | -    |
| n-Butanol         | -       | -       | -    |
| tert-Butanol      | -       | -       | -    |
| MTBE              | -       | -       | -    |
| tert-amylalcohol  | -       | -       | -    |
| DIPE              | -       | -       | -    |
| ETBE              | -       | -       | -    |
| sec butyl Acetate | -       | -       | -    |
| TAME              | -       | -       | -    |
| TAE               | -       | -       | -    |

Table 2: Reformulyzer M4 Gasoline method

## 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 42 minutes to produce reliable results in Gasoline mode.

Additionally to the “standard” oxygenates, it is also possible to analyse NTGA’s (Non Traditional Gasoline Additives) in Gasoline mode. Aceton is successfully analyzed using the Reformulyzer M4.

| Specifications           |                                                                                                                                                   |                                                                                                                                                                                                                                                        |
|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Scope / Separation Range | Reformer feed<br>Reformate<br>Straight naphtha<br>FCC naphtha / <u>olefins up to 75%</u><br>Isomerates<br>Alkylate<br>Finished gasoline<br>E10/85 | Paraffins C4-C11<br>Isoparaffins C4-C11<br>Olefins C4-C11<br>Naphthenes C5-C11<br>Aromatics C6-C11<br>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, IP526, EN14517, SH/T 0741                                                                             |                                                                                                                                                                                                                                                        |
| Ordering Information     |                                                                                                                                                   |                                                                                                                                                                                                                                                        |
| CCG35000A                | Reformulyzer M4 110V                                                                                                                              |                                                                                                                                                                                                                                                        |
| CCG35000B                | Reformulyzer M4 200V                                                                                                                              |                                                                                                                                                                                                                                                        |
| CCG35000C                | Reformulyzer M4 230V                                                                                                                              |                                                                                                                                                                                                                                                        |

**Table 3: 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®, DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.