GLOBAL™ ANALYSER SOLUTIONS G·A·S

APPLICATION NOTE 213WA1409D

ProQ-PIONA Analyser

Single column GCMS method

INTRODUCTION

GCMS based methods are widely used nowadays in petrochemical laboratories. Examples are ASTM D-5769 (Aromatics in gasoline by GCMS) and IP 585/10 (FAME in aviation fuel by GCMS).

The ProQ-PIONA-GCMS analyser from G·A·S offers complete analysis of Paraffins, Iso-paraffins, Olefins Naphthenes, Aromatics and Oxygenates in gasoline-range materials. The instrument analyses large numbers of gasoline samples like spark ignition fuels, providing fast, precise hydrocarbon characterisation for each carbon number up to C12. The GCMS method offers a number of advantages over the commonly used multidimensional method, like only 35 minutes analysis time and individual component reporting. Since a single high resolution capillary column is used, the system guarantees high uptime and low maintenance. The method shows excellent conformity with the multidimensional PIONA analyser.

ProQ-PIONA-GCMS is the method for detailed group type analysis of gasoline and petroleum naphtha containing hydrocarbons with boiling points between -161 °C (methane) and 216 °C (dodecane). The gasoline compounds are divided into 94 subgroups. In addition the method includes six oxygenates: methanol, ethanol, t-butanol, t-butylmethylether, t-butylether, t-amylmethylether; others can be added by the user.

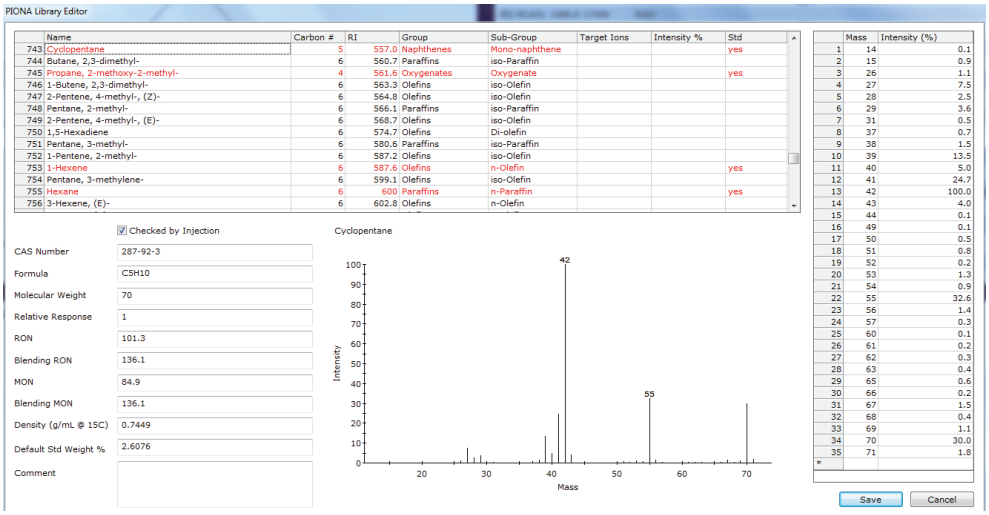

Figure 1. PIONA library with 1100 components, which can be expanded by the user.

The main features of ProQ-PIONA software are:

▲ MS library containing 1100 mass spectra of different compounds present in gasoline/ naphtha. See figure 1. The user can expand the library with additional components.

▲ RI (Retention Index) database of 400 compounds for correct isomer identification.

▲ Automated peak identification and quantitation.

▲ Automated reporting of the main PIONA groups.

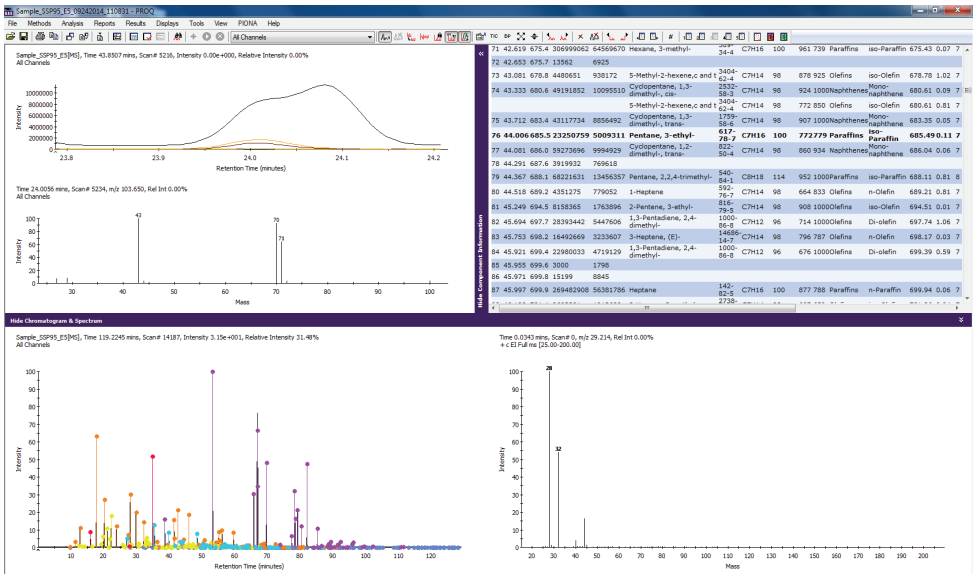

Figure 2. ProQ PIONA software workflow with peak deconvolution and peak identification

ProQ-PIONA-GCMS uses a single high resolution column, and has therefore a resemblance with DHA (Detailed Hydrocarbon Analyser). Compared to DHA-FID, resolution and identification are enormously enhanced thanks to mass spectrometer detection. Deconvolution algorithms play an important role, see figure 2 (upper left window): unresolved GC peaks are separated by their masses. The lower left window shows the total chromatogram; each O-PIONA component group has a different colour.

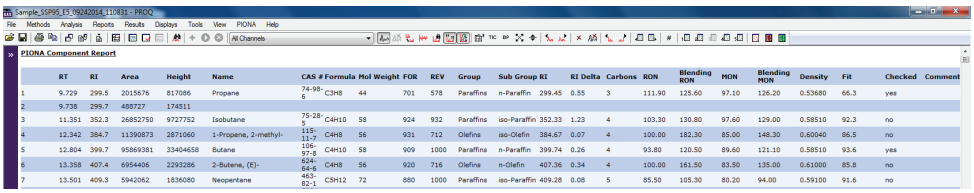

Figure 3. PIONA component report

Besides group type information, all individual components are reported as well. Figure 3 shows detailed information per component, like peak area, library fit, RON/MON values, and others.

Results and chromatograms

Figure 4 shows the TIC chromatogram of a commercial gasoline blend, with 35 minutes analysis time. The system is calibrated by injecting a 38 component mixture (figure 5) containing components from each PIONA component group. Each group has its specific calibration curve, see figure 6 (upper left window).

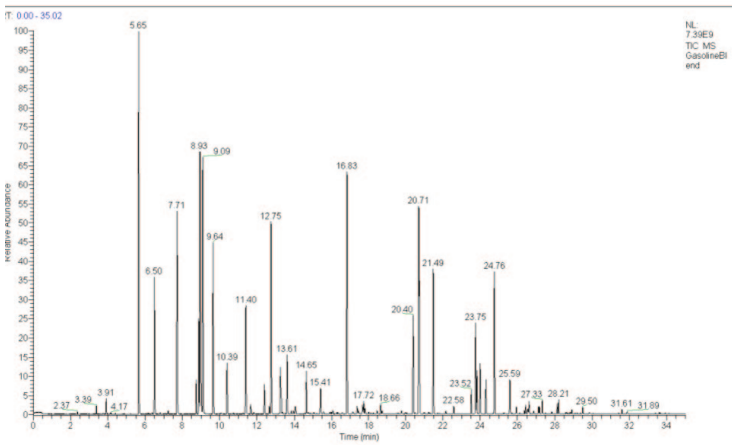

Figure 4. TIC chromatogram Gasoline blend. 35 min. analysis time

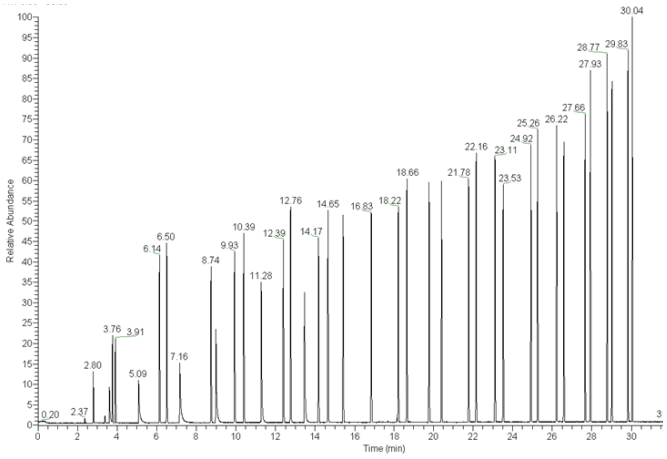

Figure 5. 38 component calibration standard

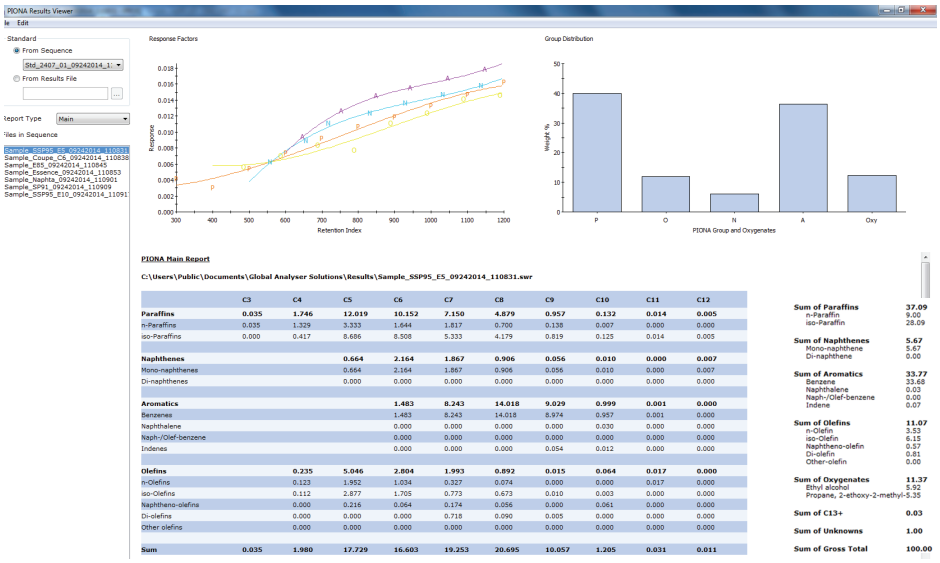

Figure 6. PIONA main report with calibration curves

Besides the calibration curve for each component group, figure 5 shows the main report with:

- ▲ Amount of each group per carbon number, in weight% or volume%
- ▲ Summary of O-PIONA groups
- ▲ Graphical O-PIONA group presentation

ProQ-PIONA software also reports:

- ▲ RON (Research Octane Number) and MON (Motor Octane Number)
- ▲ Density
- ▲ All Individual components

Comparison with PIONA multi-dimensional method

The ProQ-PIONA-GCMS single column method was extensively compared with the commonly used multidimensional method. This analyser uses multiple valves, several columns and selective component traps. Figure 8 and 9 show the result of Round Robin tests. The compliance between both methods is excellent. The GCMS method offers clear advantages over the multidimensional method:

- ▲ The analysis time is only 35 minutes (with 0.18mm ID capillary column)
- ▲ The ProQ-PIONA analyser only uses a single column, saving effort in setting up and maintaining the instrument.
- ▲ The multidimensional analyser offers only group-type information, while the GCMS method reports individual components as well. This additional information is often required in case of samples like Pye gas and Reformates.
- ▲ The multidimensional instrument cannot analyse samples with high olefin content (30-40%) because of limited trap capacity. The ProQ-PIONA method handles these samples very well since each component is analysed separately.
- ▲ The GCMS instrument can be used for all kind of applications, such as Fame in Jet Fuel.

results in weight%	reformulyzer	SI-PIONA GCMS
Benzene	1,56	1,534
C6-Naphtens	8,32	8,244
C7-Naphtens	13,11	12,820
C7-Paraffins	12,74	12,458
C8-Aromatics	4,57	4,993
C8-Naphtens	10,11	9,245
C8-Paraffins	10,41	10,86
C9-Aromatics	2,05	2,257
C9-Paraffins	8,10	8,308
Toluene	4,67	4,647
Total Aromatics	13,17	13,411
Total Naphtens	38,41	38,896
Total Paraffins	48,42	47,328

Figure 7. Comparison with multi-dimensional PIONA method

Figure 7 shows the comparison with the multidimensional method for C6-C9 group results.

sample	fraction	results GCMS- PIONA (vol%)	mean Reformulyzer (vol%)	Z-score
1	Total Aromatics	41,3	41,33	0,0
	Total Olefins	1,80	2,1	-1,4
2	Total Aromatics	37,8	39,04	-1,1
	Total Olefins	8,00	7,38	0,5
3	Total Aromatics	29,6	30,34	-1,0
	Total Olefins	6,80	6,15	0,7

Figure 8. Comparison with multi-dimensional PIONA method

In figure 8 the comparison for total aromatics and total olefines can be found for 3 different samples. The 'result GCMS-PIONA' column is the result obtained by INTERTEK OCA, using PIONA-GCMS method, while 'mean Reformulyzer' shows the mean value of all participating laboratories in this Round Robin test, using the multidimensional instrument. Z-score <2 implies good compliance.

Results obtained from: INTERTEK OCA Rotterdam B.V.

Benefits

- ◊ Single column analyser delivers full PIONA analysis
- ◊ Only 35 minutes analysis time
- ◊ Very stable performance, high uptime
- ◊ Low costs in comparison with multi-dimensional method
- ◊ Easy method setup, low maintenance
- ◊ Results of individual components
- ◊ Can handle high olefin content
- ◊ Excellent compliance with complex multidimensional method
- ◊ GCMS can be used for other applications as well (such as FAME in Jet Fuel A1)

Specifications

Application:	Full PIONA analysis of several hydrocarbon samples like naphtha and spark ignition fuels
Configuration:	One channel instrument based on single column separation and MS detection
Injector:	Split-Splitless injector
Column:	100m * 0.25mm id, 0.5u apolar phase, or 40m * 0.18mm id, 0.5u apolar phase
Detection:	Thermo ISQ quadropole mass spectrometer
Software:	Dedicated ProQ-PIONA software, with databases of 1100 MS spectra, and 400 component Retention Indices. Automated peak identification, quantitation and reporting. Automatic deconvolution (resolving co-eluting peaks)
Analysis Time:	100 minutes (100m column); 35 minutes (40m column)

For more information:

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