



APPLICATION NOTE 213WA0907C

SI-PIONA analyser

Single column GC-MS method

Introduction

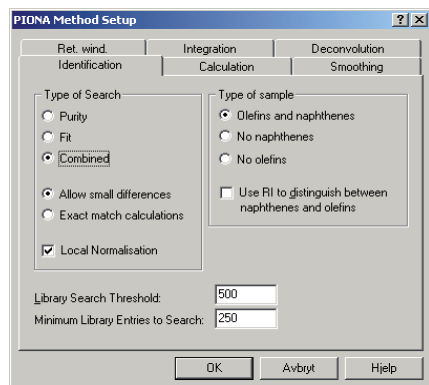
The SI-PIONA GC-MS analyser offers complete analysis of Paraffins, Iso-paraffins, Olefins Naphthenes, Aromatics and Oxygenates in gasoline-range materials. The instrument analyses large numbers of gasoline samples like spark ignition fuels, providing fast, precise hydrocarbon characterisation for each carbon number up to C12. The GC-MS method offers a number of advantages over the common multidimensional method, like 35 minutes analysis time and individual component reporting.



Trace 1300 gaschromatograph with ISQ mass spectrometer and AS1310 autosampler .

The Trace 1300 GC offers unique InstantConnect injector/detector module technology for optimal flexibility and serviceability.

Method



SI-PIONA is a method for detailed group type analysis of gasoline and petroleum naphtha containing hydrocarbons with boiling points between -42 °C (propane) and 216 °C (dodecane). The gasoline compounds are divided into 94 subgroups. In addition to these hydrocarbon groups, the method includes six oxygenates: methanol, ethanol, t-butanol, t-buthylmethylether, t-butylether, t-amylmethylether.

The SI-PIONA GC-MS analyser is based on GC/MS data, using a single high resolution capillary column. The method shows excellent conformity with the multidimensional PIONA analyser.

The main elements of SI-PIONA are:

1. A MS library containing approximately 1100 mass spectra of the different compounds present in gasoline/naphtha.
2. ARI (Retention Index) database of approximately 400 compounds for correct isomer identification.
3. Software for automated peak identification and quantitation.
4. Software for reporting the main PIONA groups.

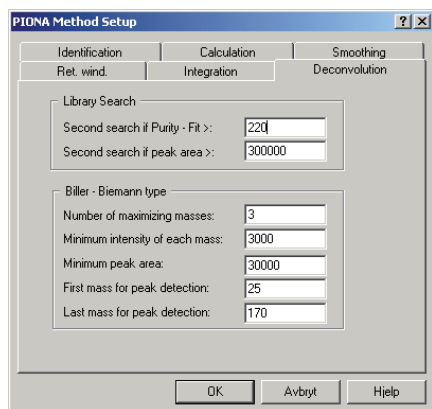
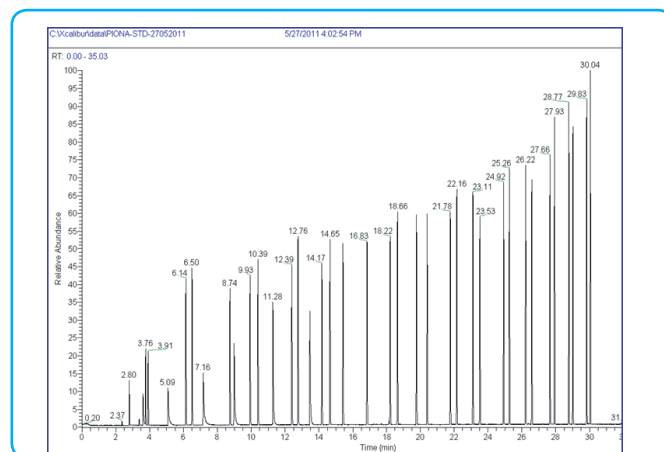
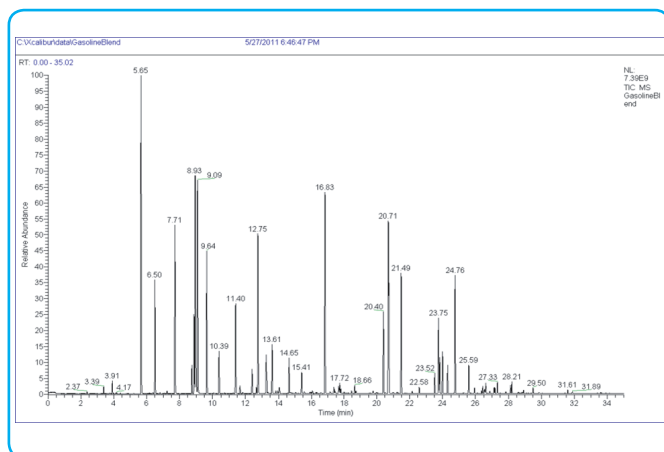


Figure 1 and 2: method setup parameters

Results and chromatograms



Chromatogram 2: calibration, runtime 35 min.

SI-PIONA analysis report of C:\CALIBUR\DATA\193883.S1 in weight-%.

Description:

	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Paraffins	0.000	3.378	25.546	19.868	13.000	9.115	5.326	1.313	0.023	0.000
n-Paraffins		2831	11917	8.304	5.312	3.192	1.620	0.191	0.011	
iso-Paraffins		0.447	13.629	11.564	7.689	5.923	3.706	1.122	0.012	
Naphthenes	0.664	4.097	5.686	3.378	1.875	0.109	0.000	0.000	0.000	0.000
Mono-naphthenes	0.664	4.097	5.686	3.378	1.810	0.109				
Di-naphthenes					0.065					
Aromatics			1.740	2.361	1.791	0.506	0.051	0.000	0.000	0.000
Benzenes			1.740	2.361	1.791	0.506	0.051			
Naphthalene										
Naph-Olef-benzenes:										
Olefins	0.000	0.000	0.000	0.000	0.042	0.084	0.040	0.000	0.000	0.000
n-Olefins					0.062					
iso-Olefins						0.016				
Naphtheno-olefins					0.042	0.005	0.032			
Di-olefins							0.008			
Other olefins										
Sum	0.00	3.37	26.21	25.70	21.04	14.32	7.790	1.51	0.02	0.00
Sum of Paraffins :	77.57									
n-Paraffins	33.48									
iso-Paraffins	44.09									
Sum of Naphthenes	15.81									
Mono-naphthenes	15.74									
Di-naphthenes	0.07									
Sum of Aromatics:	6.45									
Benzenes	6.45									
Naphthalene	0.00									
Naph-Olef-benzenes:	0.10									
Indenes	0.00									
Sum of Olefins	0.17									
n-Olefins	0.06									
iso-Olefins	0.02									
Naphtheno-olefins	0.08									
Di-olefins	0.01									
Other olefins	0.00									
Sum of Oxygenates	0.00									
Sum of C13+	0.00									
Sum of Unknowns	0.00									
Sum of Gross Total	100.00									

Analysis report

The shown chromatograms represent the calibration mixture and a sample. Besides the listed main report, a detailed report is available as well, showing the following information for each individual component:

- Scan number at peak apex
- Retention Index (RI)
- Compound name
- Area
- Amount
- Fit (calculated fit value from library search)
- Fit (match with library spectrum)

RON (Research Octane Number) and MON (Motor Octane Number) are reported as well.

Comparison with PIONA multi-dimensional method

The SI-PIONA GC-MS single column method was extensively compared with the commonly used multidimensional method. This analyser uses multiple valves, several columns and selective component traps. Tables 1 and 2 show the result of Round Robin tests. The compliance between both methods is excellent. The GC-MS method offers clear advantages over the multidimensional method:

- The analysis time is only 35 minutes (with 0.18mm ID capillary column)
- The SI-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 GC-MS method reports the 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 the limited capacity of the trap. The SI-PIONA method can handle these samples since each component is analysed separately. In case of detector overload by a single component, the value of this component is entered in the software, and the results are recalculated automatically.
- The GC-MS instrument can be used for all kinds 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

Table 1 : comparison with multi-dimensional PIONA method

Table 1 shows the comparison with the multidimensional method for C6-C9 group results.

sample	fraction	results GC-MS 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

Table 2 : comparison with multi-dimensional PIONA method

In table 2 the comparison for total aromatics and total olefines can be found for 3 different samples. The 'result GC-MS PIONA' column is the result obtained by INTERTEK OCA, using the SI-PIONA 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
- GC-MS 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 GC/MS detection
Injector:	Split
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 SI-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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