SHIMADZU

SSI-Pittcon12-GC-001

Combining Methods CAN/CGSB-3.0 and ASTM D-5580 in a Single GC platform

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Introduction

To improve productivity and lower the capital cost, a single gas chromatograph has been configured to perform two standard methods: CAN/CGSB-3.0 and ASTM D-5580.

Detailed hydrocarbon (DHA) analysis of automotive gasoline has become a routine gas chromatographic method. The Canadian standard CAN/CGSB-3.0 requires cryogenic temperature programing to provide better separation of early-eluting components than conventional non-cryogenic DHA measurements. Determination of aromatics in the presence of methanol and ethanol is also an important requirement for bio-ethanol; method ASTM D-5580 is the standard method for this analysis.

In this work, the two applications have been successfully integrated into one GC. The methods of three tests – one for CAN/CGSB-3.0 and two for ASTM D-5580, can be switched smoothly with minimum effort. Automated software control provides separation of hydrocarbons in groups and reporting of the results for method CAN/CGSB-3.0. Repeatability (%RSD) of ASTM D-5580 was less than 1.2% for analysis No. 1, and less than 1.8% for analysis No. 2.

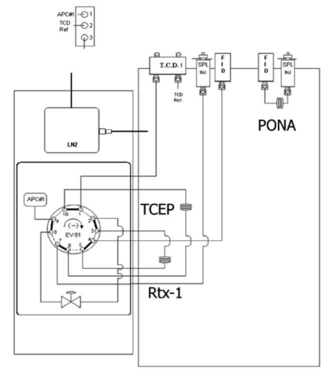
This configuration is not limited to motor gasoline analysis though; it can be applied to other finished products such as blend alcohol and other new green energy products.

Instrumentation

GC-2010Plus

- Columns:
  - 20% TCEP, 0.558m X 0.75mm
  - Rtx-1 30m X 0.53mm X 5µm
- LN_2 Cryo-cooling
- Injection Volume: 1 µL

- Valve box Temp: 80 °C
- APC1 Pressure: 210.0KPa
- GCSolution ver. 2.41
- PONASolution ver. 2.60



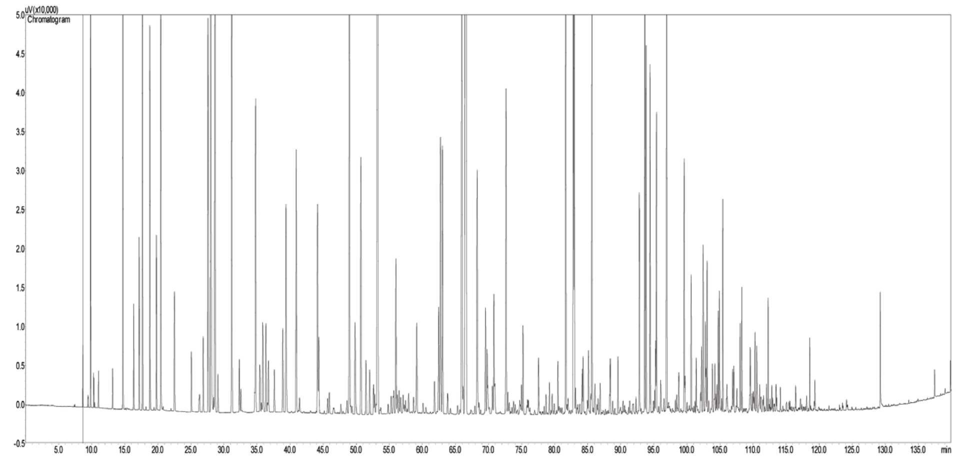
Canadian PONA Method CAN/CGSB-3.0

- Objective
  Separation of hydrocarbons into types
  - **P**araffins, **O**lefins, **N**aphthene, **A**romatics
  - Separation of each type according to carbon number
- Method
  Single capillary column separation of all components, followed by grouping with a post-run program - PONA Solution

Canadian PONA Experimental

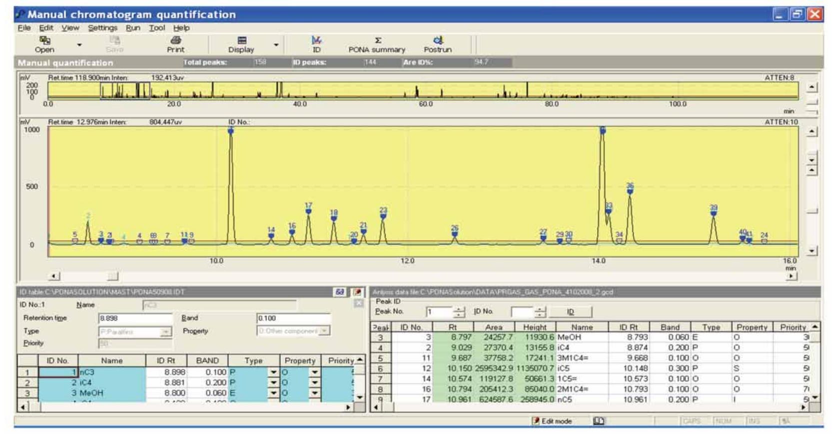
- Column: Rtx-1 PONA 100mX0.25mmX0.5µm
- Sample: Premium Gas
- Carrier Gas: He, Linear velocity: 25.6cm/sec
- Split ratio: 270, Gas Saver: On (split ratio 270 to 5 after 5min)
- Injector temperature: SPL 275˚C
- Oven Temperature: 0˚C hold 15min, 1˚C/min to 50˚C, 2˚C/min to 130˚C, 4˚C/min to 270˚C
- Detector: FID 300 ˚C
- Injection volume: 0.5 µL

Chromatogram



0.5 µL injection of premium gas

Manual Chromatogram Quantification



All components are identified and classified

Canadian PONA Report

Sample name	Premium Gas
Sample ID	Premium Gas
Operater	Admin
ID table	CanadianPONA
Comments	Premium Gas
Sampling date	2/21/2012
Analysis date	4/6/2011
Identified peaks	[323/367]
Total area	19776176

Hydrocarbon Type	% by Mass	% by Mole	% by Volume
Paraffins	3.81	3.80	4.46
Isoparaffins	39.31	39.49	42.53
Olefins	11.37	11.66	12.14
Naphthenes	4.97	5.09	4.79
Aromatics	29.53	31.95	25.11
Oxygenates	11.02	8.01	10.99

Density(15deg)	0.75	g/cm3
Average molecular weight	99.34	
Reseach Octane Number	89.79	
Vapor pressure (37.78deg)	41.56	kPa

Peak Name	Hydrocarbon Type	Retention Time	% by Mass	% by Mole	% by Volume
Isobutane	P	8.66	0.09	0.091	0.121
1-Butene	X	9.44	0.019	0.018	0.023
Isobutene	O	9.48	0.013	0.013	0.016
n-Butane	A	9.83	0.88	0.889	1.132
trans-2-Butene	X	10.3	0.054	0.053	0.064
cis-2-Butene	O	11.02	0.062	0.06	0.072
3-Methyl-1-butene	O	13.15	0.087	0.085	0.1
Isopentane	O	14.71	5.616	5.636	6.72
1-Pentene	P	16.34	0.262	0.256	0.295
2-Methyl-1-butene	O	17.17	0.451	0.44	0.5
n-Pentane	P	17.68	1.337	1.342	1.585
trans-2-Pentene	P	18.78	1.042	1.017	1.161
cis-2-Pentene	O	19.79	0.495	0.483	0.544
2-Methyl-2-butene	N	20.44	1.267	1.236	1.379
"2,2-Dimethylbutane"	O	22.51	0.406	0.405	0.461
Cyclopentene	O	25.07	0.205	0.195	0.186
4-Methyl-1-pentene	O	26.24	0.038	0.038	0.042
3-Methyl-1-pentene	O	26.32	0.069	0.067	0.074
Cyclopentane	P	26.85	0.254	0.248	0.247
"2,3-Dimethylbutane"	O	27.58	1.397	1.395	1.561
Methyl-tert-butylether	O	27.98	7.979	10.963	10.937
"2,3-Dimethyl-1-butene"	P	28.45	0.031	0.03	0.033
2-Methylpentane	P	28.63	2.516	2.513	2.846
trans-4-Methyl-2-pentene	P	29.08	0.133	0.13	0.144
3-Methylpentane	X	31.17	1.546	1.543	1.719
2-Methyl-1-pentene	A	32.33	0.194	0.19	0.206
1-Hexene	X	32.55	0.087	0.085	0.094

ASTM D5580-02

Scope:
Determination of benzene, toluene, ethylbenzene, xylenes, C9 and heavier aromatics, and total aromatics

Sample:
Finished motor gasoline

Two Step Analysis

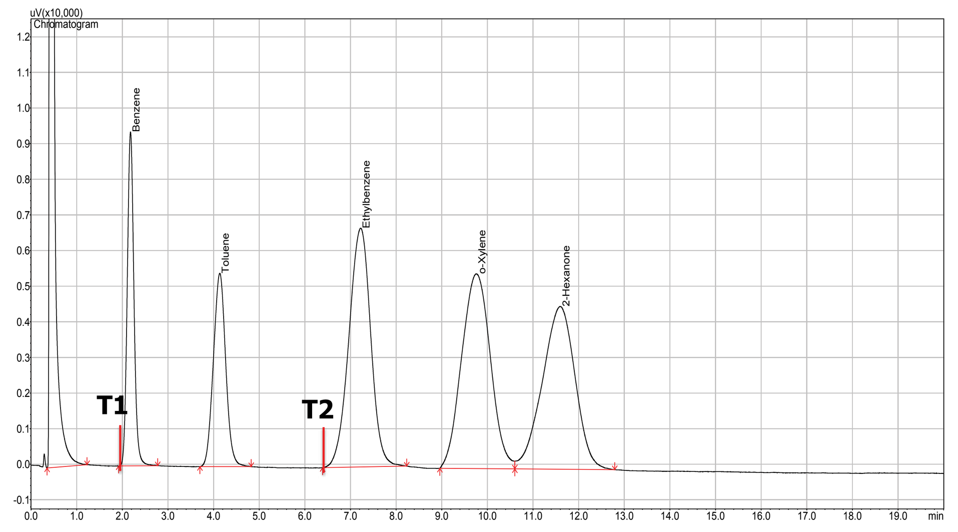
No.1
Determination of benzene and toluene, with 2-Hexanone as internal standard; backflush C8+ aromatics and hydrocarbons

No.2
Determination of ethylbenzene, xylenes, and C9+ aromatics, with 2-Hexanone as internal standard

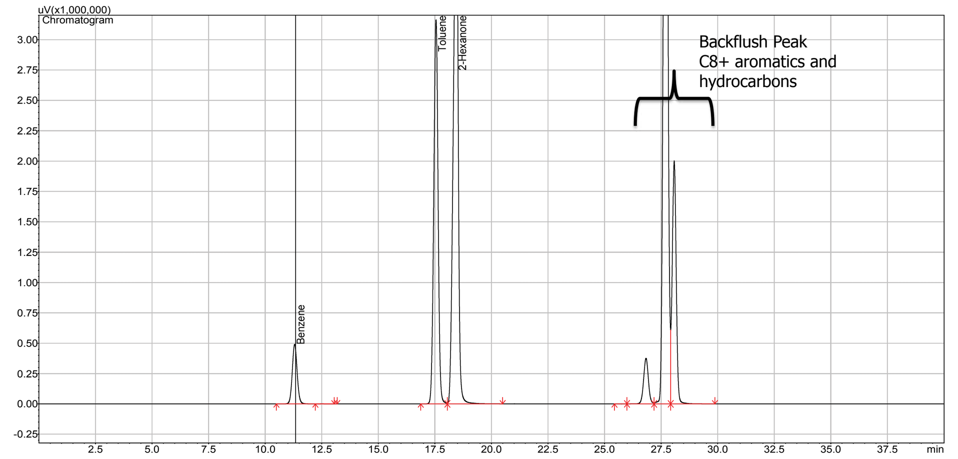
ASTM D-5580 Experimental

- INJ Temp: 200 °C, Carrier Gas: He, Flow Control Mode: Pressure, INJ Pressure: 160KPa, TCEP Column Flow: 10 mL/min, Rtx-1 column flow: 10 mL/min, Split vent flow: 100 mL/min, Purge Flow: 1mL/min, Split Ratio: 11:1
- Valve Box Temp: 80.0 °C
- Oven1 Temp: 40.0 °C hold 6 min, 2 °C /min to 80 °C, 3 °C/min to 115 °C hold 2.33 min
- FID Temp: 250 °C, Makeup Gas: He, Makeup Flow: 20.0mL/min, H2 Flow: 40.0mL/min, Air Flow: 400.0mL/min.
- TCD Temp: 200 °C, Makeup Gas: He, Makeup Flow: 8 mL/min, Current: 60 mA
- T1: 1.8 min, T2: 6.2 min, T3: 21.0 min, T4: 30.0 min

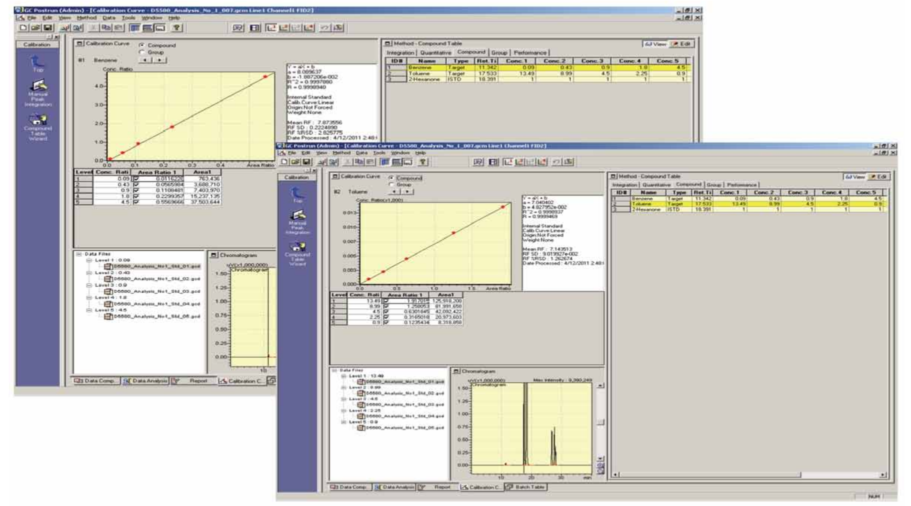
TCD Chromatogram



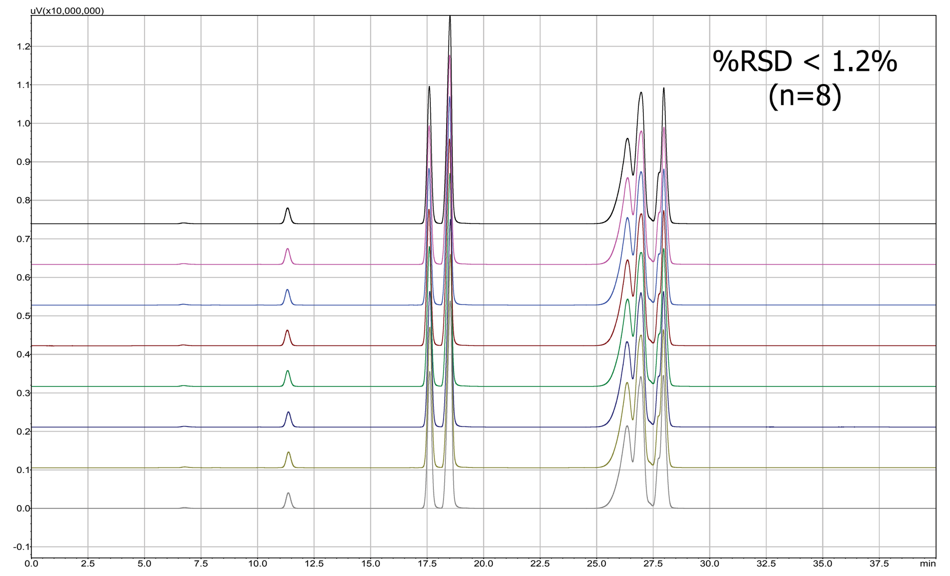
Analysis No.1



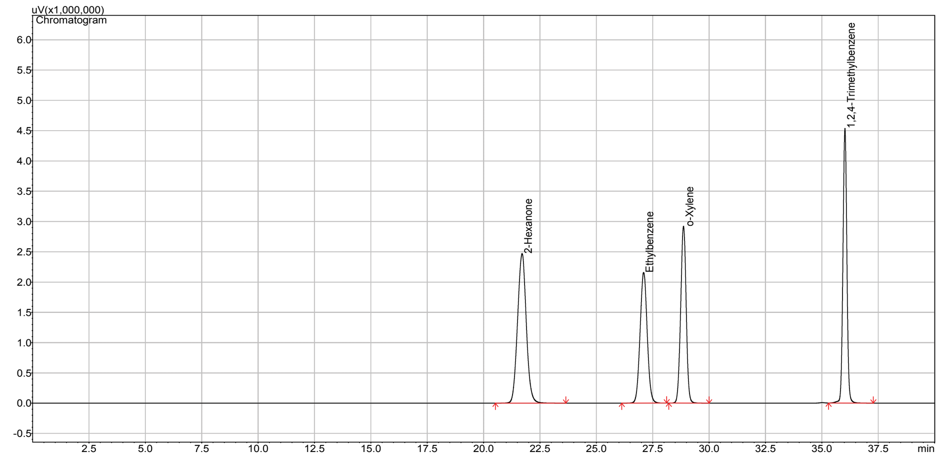
Calibration Curves: Benzene & Toluene



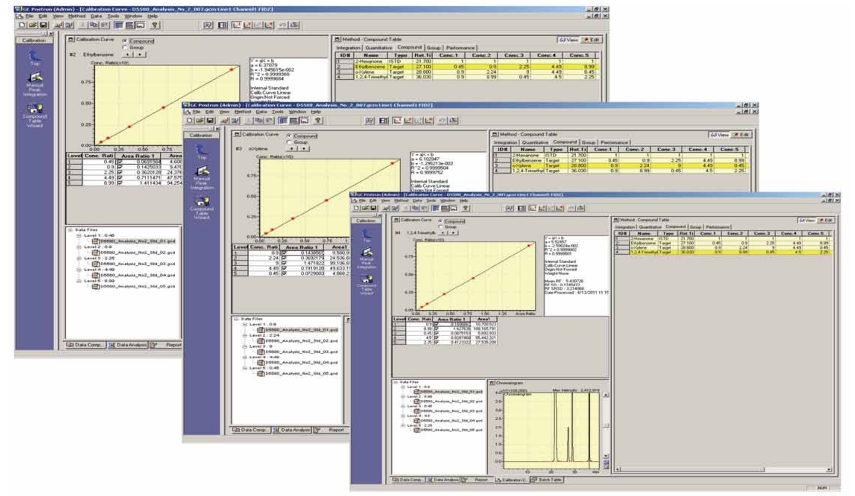
Premium Gas Analysis No.1



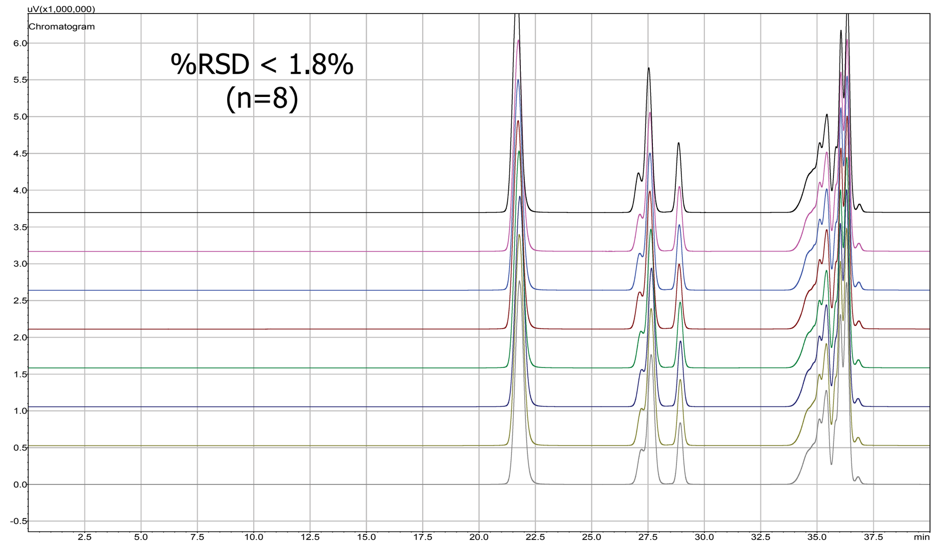
Analysis No.2



Calibration Curves Ethylbenzene, o-Xylene, and 1,2,4-Trimethylbenzene



Premium Gas Analysis No.2



Conclusions

- Mechanical valve-based multidimensional GC-2010 Plus has successfully achieved ASTM D5580 requirements.
- Excellent retention time stability allows for the ease of determining backflush times.
- Excellent qualitative and quantitative results.
- In addition to ASTM D-5580 method, a separate analytical line has been incorporated to be able to run Canadian PONA analysis on the same GC, which has lowered instrumentation cost and improved productivity.

Acknowledgements

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