595 North Harrison Road
Bellefonte, PA 16823-0048 USA
Telephone 800-247-6628 ● 814-359-3441
Fax 800-447-3044 ● 814-359-3044
email: supelco@sial.com
sigma-aldrich.com/supelco

SUPELCO®

Application Note 51

Highly Characterized Reference Standard: Pyrolysis Gasoline

Pyrolysis gasoline – py gas – is produced by thermal cracking, as a byproduct of ethylene manufacture. An important feed stock for recovering olefins and aromatics, and a source of benzene by hydrodealkylation (benzene concentrations generally range from 30 to 50%), py gas also contains significant levels (>1%) of dicyclopentadiene (DCPD).

Key Words

• pyrolysis gasoline • reference standard • olefins • aromatics

The reference standard described here is a "real world" sample of pyrolysis gasoline, not an artificial mixture of components, and thus it reflects the makeup of typical samples analysts are likely to encounter. Carefully analyzed by GC/FID and GC/MS procedures, this standard is intended for use as both a qualitative and quantitative reference standard. Analysts can use the chromatograms and peak identifications shown here and enclosed with the product as guide maps for evaluating specific py gas samples. We anticipate that this reference standard will be used for evaluating refinery process performance, for identifying sources of contamination, in method development, in PIANO analyses, and in training.

To prepare this standard, we obtain bulk samples of pyrolysis gasoline from a petroleum refinery, add a stabilizer (1,3-phenylenediamine, 75ppm wt/vol), and package the material under nitrogen in amber ampuls. We evaluate packaging homogeneity in our QA department, using randomly selected ampuls from the beginning and end of every packaging run. If the homogeneity evaluations are satisfactory, we send samples to an outside evaluator, Consolidated Sciences Inc. (Pasadena, Texas, USA) for detailed component analysis (Figure A).

The analytical approach taken by Consolidated Sciences provides both quantitative data, based on flame ionization detection, and qualitative information, using a mass spectrometer as the detector (Figure B). Use of an "open split" interface between the column and mass spectrometer mimics FID retention times throughout the analysis and prevents vacuum effects on separations. A preliminary class separation of the saturate and combined aromatic/olefin fractions assures proper mass spectral identification of olefins and naphthenes.

Quantitative data are reported on the basis of area percent (Figure A), as a common ground for all to compare, to preclude controversy over whether liquid or weight percent constitutes proper results and what are proper response factors. Area percent can be measured with reasonable accuracy and precision, while liquid and weight percent determinations depend on response factors and on the use of pure analytical standards, many of which are unavailable.

The temperature programming and linear velocity (pressure) parameters chosen are known to be suitable for a wide range of petroleum stream samples encountered by Consolidated Sciences. The analysis is isobaric, although pressure programming could be used. The head pressure used allows good separation of early eluting components and reasonable linear velocity over a wide temperature range.

DCPD, an important component of py gas, is extremely thermally labile, forming cyclopentadiene at higher injection port temperatures. While conventional practice dictates using an injector temperature of 150°C, the higher temperature we use in analyzing this sample, 200°C, produces better volatilization of higher molecular weight components. If the injector and the injector sleeve are clean, breakdown of DCPD should be minimal at 200°C.

Figure A. Portion of the Analysis Report for Py Gas Reference Standard

Petroleum Refinery Pyrolysis Gasoline (PY Gas)
Cat # 47490-U
Lot # LA40133

Ret. Time	Component	Class	Mol. Wt.	Area %
7.85	Isobutylene + 1-Butene	O	56	0.004
7.89	1,3-Butadiene	O	54	0.011
7.96	n-Butane	P	58	0.002
8.07	trans-2-Butene	O	56	0.005
8.26	cis-2-Butene	O	56	0.011
8.59	1,2-Butadiene	O	54	0.010
8.80	3-Methyl-1-butene	O	70	0.044
9.18	Isopentane	P	72	0.680
9.22	1,4-Pentadiene	O	68	0.164
9.41	Dimethylacetylene	O	54	0.053
9.52	1-Pentene	O	70	0.434
9.70	2-Methyl-1-butene	O	70	0.314

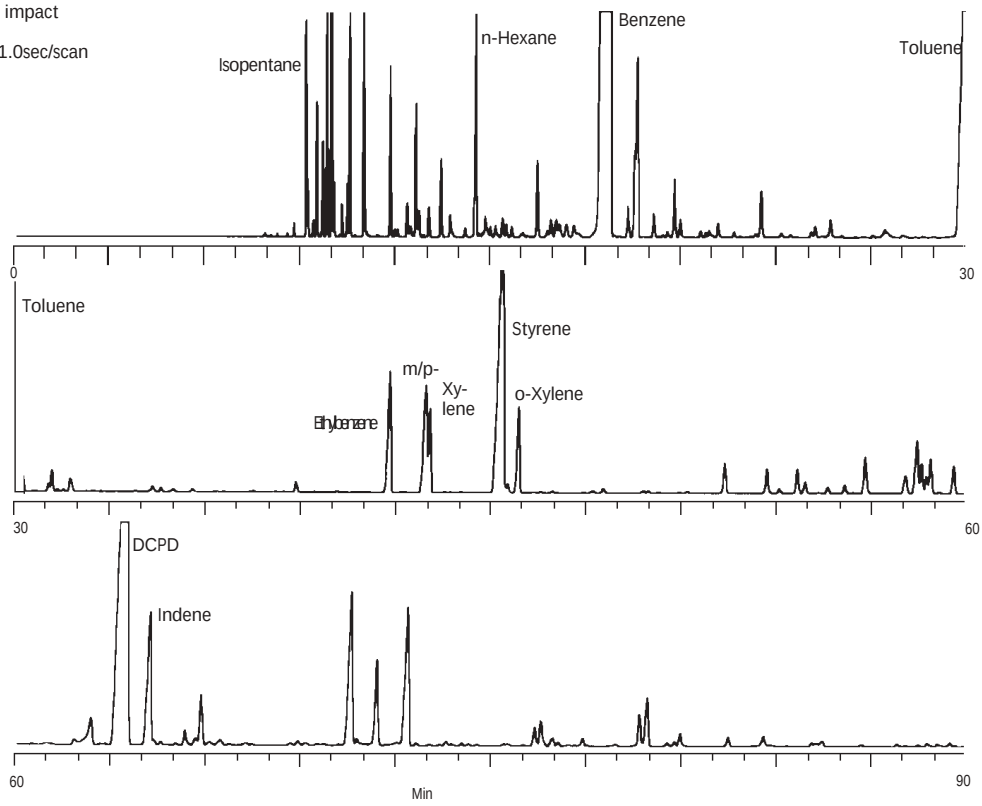
Figure B. Petroleum Refinery Pyrolysis Gasoline (Py Gas)

Capillary GC/FID

Instrument:	Hewlett-Packard 5890, Series II
Column:	**Petrocol™ DH, 100m x 0.25mm ID, 0.5µm film**
Cat. No.:	**24160-U**
Col. Temp.:	35°C (10 min) to 150°C at 1.5°C/min, then to 280°C at 5°C/min, hold 15 min
Carrier:	helium, 48psig (30cm/sec, set at 30°C; $t_{R\ methane}$ = 6.1 min)
Det.:	FID, 275°C
Inj.:	0.1mL, split, 200°C

MS Parameters

Ionization Energy:	70 eV, electron impact
Interface:	open split
Scan:	m/z = 39-200, 1.0sec/scan



794-0314

In the information included with this standard, molecular weights are provided in all cases where they are measurable (Figure A). Along with fragmentation patterns, these values are helpful for identifying less common components. Isomers are identified when possible; total carbon number is given when further identification is not possible. In cases of olefin identification beyond monoolefins, the olefin can be a diolefin, cycloolefin, triolefin, cyclodiolefin, etc.; this distinction becomes difficult by mass spectrometry. However, confidence in the hydrocarbon class assay exceeds 95%. Cases of coelution are dealt with by estimation, based on separate analyses of saturate and combined olefin/aromatic fractions. Olefinic aromatics (styrenes and divinylbenzenes) are counted as aromatics.

If you are monitoring hydrocarbon streams or conducting other analyses involving py gas, this reference standard will become an important tool in your work.

Ordering Information:

Description	Cat. No.
Py Gas Reference Standard	
1mL	**47490-U**
Petrocol™ DH Capillary Column	
100m x 0.25mm ID fused silica, 0.50µm film	**24160-U**

Fused silica columns manufactured under HP US pat. No. 4,293,415.

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