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New, Highly-Characterized Reference Standards: Reformate, Heavy Naphtha, Pyrolysis Gasoline

D. Henderson, S.B. Cole

Until now, the only reference materials available to petroleum analysts were synthetic mixes which did not adequately reflect the complexity of true petroleum streams. Our new reference standards are authentic, highly characterized process stream samples that accurately reflect the composition of typical reformates, heavy naphthas, and pyrolysis gasolines. Carefully analyzed by GC/FID and GC/MS procedures, these new standards are both qualitative and quantitative reference materials for evaluating refinery process performance, identifying contamination, method development, PIANO analyses, and training. Chromatograms and peak identifications enclosed with the products are useful guides. Molecular weights are provided whenever measurable and isomers are identified when possible. Total carbon number is given when further identification is not possible.

Modern petroleum refinery processes yield products of complex aromatic, olefinic, and saturate content which require detailed chromatographic study. Until now, the only reference materials available to petroleum analysts were those laboriously characterized by the analyst or commercially offered synthetic mixes which did not adequately reflect the complexity of true petroleum streams. Because of this Supelco, in conjunction with a well-known petroleum analysis laboratory, now introduces a line of authentic, fully characterized petroleum reference standards.

Our new reference standards are "real world" samples, taken from process streams. They accurately reflect the composition of typical reformates, heavy straight run (high boiling) naphthas, and pyrolysis gasolines analysts are likely to encounter. Carefully analyzed by GC/FID and GC/MS procedures, these new standards are intended for use as both qualitative and quantitative reference materials.

Analysts can use the chromatograms and peak identifications enclosed with the products as guides to evaluating their own specific materials. We recommend these reference standards for evaluating refinery process performance, identifying sources of contamination, method development, PIANO analyses, and training.

To prepare these standards, we obtain bulk samples of reformate, heavy straight run naphtha, and pyrolysis gasoline from a petroleum refinery (we add 75ppm of a stabilizer, 1,3-phenylenediamine, to the pyrolysis gasoline) 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. A small portion of a typical analysis is shown in Figure A.

The detailed analysis provides both quantitative data, based on flame ionization detection, and qualitative information, using mass spectrometry. 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. All three standards are initially subjected to a detailed hydrocarbon analysis, using one of our 100-meter Petrocol™ DH capillary columns and a flame ionization detector. For the reformate and pyrolysis gasoline standards, a preliminary class separation of the saturate and combined aromatic/olefin fractions ensures proper mass spectral identification of olefins and naphthenes.

Figure A. Initial Portion of the Analysis Report for Reformate Reference Standard

Reformate Reference Standard Cat # 47489 Lot # LA40361				
Ret. Time	Component	Class	Mol. Wt.	Area %
7.62	Isobutane	P	58	0.010
7.95	n-Butane	P	58	0.110
8.11	2,2-Dimethylpropane	P	72	0.002
8.25	cis-2-Butene	O	56	0.001
8.78	3-Methyl-1-butene	O	70	0.004
9.16	Isopentane	P	72	1.570
9.50	1-Pentene	O	70	0.003
9.68	2-Methyl-1-butene	O	70	0.010
9.81	n-Pentane	P	72	0.960
10.03	trans-2-Pentene	O	70	0.009

Samples used for the naphtha reference standard are further characterized. They are separated into aromatic and saturate fractions, using silica gel column chromatography. Each fraction is analyzed, using a column designed for detailed hydrocarbon analysis, then the data are recombined mathematically, based on analysis of key aromatic components. Loss of lighter components during the silica gel separation is corrected for by using the data generated from the original sample. Thus, we provide three chromatograms with this standard: one for the original sample, one for the aromatic fraction, and one for the saturate fraction.

Quantitative data are reported on the basis of area percent (Figure A), as a common ground for comparisons, 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. While conventional practice dictates using an injector temperature of 150°C, the 200°C injector temperature we use in analyzing this sample produces better volatilization of higher molecular weight components. Dicyclopentadiene (DCPD), an important component of pyrolysis gasoline, is extremely thermally labile, forming cyclopentadiene at higher injection port temperatures. If the injector and the injector sleeve are clean, DCPD breakdown is minimal at 200°C. The isobaric head pressure used allows good separation of early eluting components and reasonable linear velocity over a wide temperature range. If necessary, pressure programming can be used.

In the comprehensive data packet included with these standards, we provide molecular weights where they are measurable (Figure A). Along with fragmentation patterns, these values are helpful for identifying less common components. Isomers are identified when possible, and total carbon number is given when further identification is not possible. Cases of coelution are dealt with by estimation, based on mass spectral signal strength or, for the pyrolysis gasoline standard, on separate analyses of saturate and combined olefin/aromatic fractions. In the naphtha standard, some paraffin/naphthene coelutions are known to occur. Mass spectra and corresponding signal strengths for ions in these two hydrocarbon classes are used to estimate the degree of coelution. The error in this estimate is less than 10%. Distinction among diolefins, cycloolefins, triolefins, cyclodiolefins, etc. in the pyrolysis gasoline standard is difficult by mass spectrometry. However, error in the class identification is less than 5%. Olefinic aromatics (styrenes and divinylbenzenes) are counted as aromatics.

If you are monitoring hydrocarbon streams or conducting other analyses involving reformates, naphthas, or pyrolysis gasoline, we feel these new reference standards will become important tools in your work.

New Reference Standards for Important Petroleum Products

Reformate

Catalytic conversion at temperatures of 850°-1000°F converts – reforms – low-octane naphthas into high-octane products for gasoline and aviation fuel blending and aromatic concentrates. The predominant reaction during reforming is the dehydrogenation of naphthenes (cycloparaffins) to the corresponding aromatics. For example, cyclohexane reforms to benzene, and methyl-cyclohexane reforms to toluene. Research Octane Numbers can be increased from the low 40s to over 100 through reforming.

Naphtha (Heavy Straight Run)

A straight run naphtha, commonly known as “gasoline,” is produced from crude oil by distillation, typically in the temperature range of 60°-320°F. Light straight run naphtha is the distillate fraction collected at 60°-170°F; heavy straight run naphtha typically is collected at 170°-320°F. Heavy straight run naphtha is a hydrotreating or reforming base (feed) stock. Straight run naphthas usually have low octane numbers.

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).

Ordering Information:

Reformate Reference Standard, 1mL	47489
Heavy Naphtha Reference Standard, 1mL	47488
Pyrolysis Gasoline Reference Standard, 1mL	47490-U
Petrocol DH Capillary Column 100m x 0.25mm ID fused silica, 0.50µm film	24160-U

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