Merlin MicroScience, Inc.

Tech Notes

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Hydrocarbon Type Analysis of Kerosenes and Diesels

The determination of Hydrocarbon Types in Diesels (middle distillates) and Kerosenes (jet fuel) is becoming of more and more importance with respect to many processes as well as environmental modeling. Compositional analyses of materials in the middle distillate/diesel range has traditionally been performed on samples using a combination of elution chromatography ASTM D-2549 [1] , and mass spectrometric analysis of each fraction ASTM D-2425 [2].

ASTM D-2549 provides for the elution of only two fractions, aromatic and non-aromatic species and their quantitation gravimetrically. This technique is hampered by several problems. The elution chromatography or Bauxite-Silica Gel (BSG) separation limits the boiling range of the sample to 400 to 650 ^{o}F. Samples of lower initial boiling points are subject to losses in the elution chromatography step because the elution solvents must be thermally removed prior to analysis. This limitation precludes the use of the mass spec method for jet fuel/kerosene which would otherwise be quite viable. Additionally, the BSG separation process is tedious, labor intensive and lacks the precision of other methods. After collection and quantitation of the two fractions a mass spectrometer analysis is performed on each fraction. The results of the two separate mass spectral analyses are then mathematically recombined as in the following example:

Non-aromatic Fraction

Hydrocarbon Type	Wt.%	Gravimetric Weight of	Resulting
Paraffins	45.0		29.66
Naphthenes	25.0		16.48
Dinaphthenes	17.0	X 65.9%	11.20
Trinaphthenes	7.0		4.61
Alkylbenzenes	6.0		3.95

Aromatic Fraction

Hydrocarbon Type	Wt.%	Gravimetric Weight of	Resulting
Paraffins	5.0		1.71
Naphthenes	7.0		2.39
Alkylbenzenes	42.0		14.32
Indanes/Tetralins	35.0		11.94
Naphthalenes	5.0	X 34.1%	1.71
Acenaphthenes	3.0		1.02
Acenaphthylenes	2.0		0.68
Tricyclics	1.0		0.34

Re-combined Results

Hydrocarbon Type	Combined fraction	Resulting
Paraffins	1.71 + 29.66	31.4
Naphthenes	2.39 + 16.48	18.9
Dinaphthenes		11.2
Trinaphthenes		4.61
Alkylbenzenes	3.95 + 14.32	18.28
Indanes/Tetralins		11.94
Naphthalenes		1.71
Acenaphthenes		1.02
Acenaphthylenes		0.68
Tricyclics		0.34

As yet, conventional gas chromatographic columns do not have the ability to resolve kerosene and diesels by type or by individual components. In recent years various HPLC and SFC methods have been developed to speciate the various classes according to ring number, saturates, etc. However, they cannot provide the same speciation which is often desired and provided by the mass spectrometric type analyses. These methods also tend to be time consuming and are subject to both the new hardware problems of SFC and the traditional hardware problems of HPLC (i.e. pumps, detectors, columns, solvents, valving).

The Merlin Batch Inlet and Merlin Analytical Tools Software is particularly suited to analyze the fractions obtained using ASTM D-2549 by the traditional ASTM D-2425 methodology. In addition to this method we have developed software which will provide similar results as D-2425 without the preparatory chromatographic separation. Use of this software allows us to extend hydrocarbon type analysis to kerosene range material obtaining results with throughput times of less than 4 minutes!

Table 1

	HP-309		**HP-310**		**HP-311**		**SRM-2724**	
Method	**Modified Wt.%**	**D-2425 Wt.%**	**Modified Wt.%**	**D-2425 Wt.%**	**Modified Wt.%**	**D-2425 Wt.%**	**Modified Wt.%**	**D-2425 Wt.%**
Paraffins	30.07	32.65	28.78	28.40	33.83	36.25	41.22	41.19
Cycloparaffins	18.68	19.55	15.13	11.85	23.89	27.12	13.73	14.10
Dicycloparaffins	18.02	15.59	11.52	12.41	21.82	17.52	9.29	9.19
Tricycloparaffins	4.42	4.65	4.06	4.55	3.49	3.30	2.59	2.56
Alkylbenzenes	9.67	8.94	14.35	15.11	5.02	5.69	11.12	11.15
Indanes/Tetralins	8.04	7.72	11.56	11.14	4.74	4.90	11.02	10.91
Indenes	2.53	2.59	3.77	3.28	0.99	1.50	2.44	2.41
Naphthalene	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Naphthalenes	3.17	3.92	4.50	5.90	2.06	1.88	3.39	3.35
Acenaphthenes	2.60	2.44	3.48	4.29	2.35	1.07	3.51	3.47
Acenaphthylenes	2.05	1.30	1.78	1.98	1.68	0.53	1.19	1.18
Tricyclic Aromatics	0.75	0.67	1.07	1.09	0.12	0.24	0.50	0.49
	100.00	100.02	100.00	100.00	100.00	100.00	100.00	100.00

Table 2

	Method	**Modified Wt.%**	**D-2425 Wt.%**	**SFC Wt.%**	**Other MS Wt.%**
HP-3	Total Aromatics	22.72	-	18.40	19.81
	1-Ring	16.75	-	17.20	-
	2-Ring *	5.97	-	1.20	-
HP-309	Total Aromatics	28.81	27.58	28.10	28.20
	1-Ring	20.24	19.25	20.90	-
	2-Ring *	8.57	8.33	7.20	-
HP-310	Total Aromatics	40.51	42.79	38.60	38.60
	1-Ring	29.68	29.53	27.50	-
	2-Ring *	10.83	13.26	11.10	-
HP-311	Total Aromatics	16.97	15.81	14.80	-
	1-Ring	10.75	12.09	11.20	-
	2-Ring *	6.22	3.72	3.60	-
HP-JET	Total Aromatics	26.87	-	23.60	NA
	1-Ring	20.67	-	19.00	-
	2-Ring *	6.20	-	4.60	-
SRM-2724	Total Aromatics	33.17	32.96	32.98	-
	1-Ring	24.58	24.47	24.03	-
	2-Ring *	8.59	8.49	8.95	-

* Does not include I/T,

The Merlin “modified” method is based upon similar calculations as those presented in D-2425, however by removing those ions from the matrix elements which contribute to most of the interferences represented by the overlapping hydrocarbon types between aromatic and non-aromatic fractions, we can eliminate the need to evaluate each fraction separately. The loss of contribution of these ions from the calculations is compensated by re-weighting those types with new sensitivity coefficients in the method. These coefficients are derived by using a representative standard reference material which has been analyzed using the conventional ASTM D-2425 method. This standardization is generally required only one time. While this methodology is qualified, empirical data suggest that it represents a very close approximation to those generated using conventional BSG separations and recombination of spectral data.

Table 1 describes the results of this modified D-2425 methodology with that of the standard D-2425 method. These results compare very favorably and deviate only when the total aromatics are very low. This is as might be expected due to the ions in common with cycloparaffins and acenaphthenes/acenaphthylenes. This interference is usually not significant and can be controlled by user defined sensitivity coefficients. Turnaround time using this method is 4 to 5 minutes. This modified D-2425 method was also compared among several samples with data generated from SFC analyses and Mass Spectrometer analyses performed by a third party as shown in Table 2.

As mentioned earlier, one of the advantages of the modified method Merlin has developed is the ability to perform hydrocarbon type analyses on samples that are otherwise too low in boiling point for conventional D-2425. As an example, a wide boiling range kerosene sample was studied using the standard D-2425 method and the modified Merlin method. Approximately 20% of the sample had boiling point below 400°F. Simulated distillation results for this material are listed in Table 3.

The problem of loss was avoided using the less conventional ASTM D-1319 which is used primarily for naphtha samples as a preparative method for the aromatic and non-aromatic fraction. Comparison of the two methods is given in Table 4. The modified method was based on a calibration of a diesel sample 4 months prior without any further calibration since that time!

Table 3
Simulated Distillation

% Overhead	Feed °F
IBP	279
5	319
10	360
20	401
30	424
40	438
50	453
60	467
70	484
80	505
90	540
95	568
EP	624

It should be noted that some of the differences are due to errors in the original method development which was based on hypothetical materials and that in actual practice the Merlin method allows for the user tuning of the response coefficients which may very slightly from one instrument to another.

Table 4

	Modified D-2425 Feed Wt.%	Conventional D-2425 Feed Wt.%
Paraffins	15.03	18.40
Naphthenes	16.72	19.34
Dinaphthenes	15.59	15.89
Trinaphthenes	4.11	3.67
Alkylbenzenes	22.19	20.03
Indanes/Tetralins	23.83	21.28
Naphthalenes	1.02	0.47
Acenaphthenes	0.80	0.39
Acenaphthylenes	0.54	0.11
Tricyclics	0.17	
Total Aromatics	48.55	42.71

In field trials the Merlin Modified D-2425 method has been in use for several months analyzing process samples for process quality assurance. During this period a tuning procedure has been developed to provide consistency from one instrument to another. One of the keys to any batch analysis is the reproducibility or precision of the mass spectrometer. The Hewlett-Packard MSD has certainly been up to this task. In addition to the practice of running daily control samples against our tune file on an instrument in service for five months, we decided to use the same tune criteria on a new MSD and compare the results on the same control sample. This data described in Table 5 and is based solely on raw data without further adjustments. We believe this data testifies to the ability of the instrumentation to obtain excellent results with minimal adjustment.

Table 5

Method	**Modified D-2425**	**Modified D-2425**
Instrument	**5972 MSD**	**5971 MSD**
Date	**9/3/96**	**9/21/96**
Sample	**Control**	**Control**
	Wt. %	**Wt. %**
Paraffins	18.24	15.65
Naphthenes	20.29	20.14
Dinaphthenes	34.96	34.37
Trinaphthenes	11.28	12.34
Alkylbenzenes	5.03	5.92
Indanes/Tetralins	7.11	7.99
Naphthalenes	0.38	0.38
Acenaphthenes	0.58	0.61
Acenaphthylenes	0.75	0.99
Tricyclics	1.39	1.62

The Merlin Inlet system can be used to do the conventional D-2425 analysis utilizing the BSG separation to determine type analysis on diesels, however it has the ultimate flexibility which allows the methods to be tailored to the stream being monitored. The on-board software allows the user to supply a reference sample to provide the weighting factors necessary to generate results based on prior or more detailed separation. This allows rapid sample analysis of a stream with sufficient accuracy and precision to track process changes effectively.

[1] ASTM D-2549 Separation of Representative Aromatics and Non-aromatics Fractions of High Boiling Oils by Elution Chromatography
[2] ASTM D-2425 Hydrocarbon Types in Middle Distillates by Mass Spectrometry