Merlin MicroScience, Inc.

Tech Notes

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A Batch Inlet System for Rapid PNA Analysis by Mass Spectrometry

Knowing the hydrocarbon composition of gasoline process streams, blending stocks, and finished motor fuels is useful in following the effect of changes in plant operating conditions, diagnosing process upsets, blending finished products and in evaluating the relationship between composition and performance properties. The mass spectrometer preceded the gas chromatograph as an analytical tool by nearly fifty years. Prior to the hyphenated technique of GC/MS the most common method of sample introduction into the mass spectrometer has been the batch inlet. Because of economic considerations and perhaps technical and cultural resistance to the continued use of the mass spectrometer, gas chromatography using the flame ionization detector supplanted the use of the batch inlet mass spectrometer particularly for hydrocarbon type analysis of gasoline.

Recently, the mass spectrometer has become cheaper, more reliable and easier to use than in the past. The separation, identification and classification of hundreds of individual components, a time consuming and tedious process. Despite advances in chromatographic stability and the use of computer software to automate this process, this type of characterization still takes considerable time. For this reason Merlin is reintroducing a batch inlet specifically designed for the Hewlett-Packard MSD (mass selective detector. Where applicable, the singular advantage of using this introduction is the speed of analysis. Analytical turnaround can be less than five minutes.

Samples are analyzed based on the summation of characteristic mass fragments to determine the range of hydrocarbon types in the mixture. The average number of carbon atoms of the sample is estimated from spectral data. Calculations are made from calibration data which are dependent upon the average carbon number of the sample. In addition to typical Paraffin, Naphthene and Aromatic (PNA) distributions, this method can be applied to many simple mixtures. These analyses can be performed using response factors applied to the ions or masses of interest in a mixture -- for example the amount of toluene (m/z 92) in Benzene (m/z 78). Things are rarely this simple, but more complex mixtures can be resolved by mathematically determining contributions by matrix inversion and multiplication.

Example

Five components--Toluene, Ethylbenzene, Methylcyclohexane, Benzene, and Octane are analyzed as pure components and then as an equal volume mixture in order to establish response factors. The initial array is set up as follows:

	Toluene	Ethylbenzene	MCH	Benzene	Octane
92	0.7948	0.0782	0.0037	0.0000	0.0000
91	1.0000	1.0000	0.0037	0.0000	0.0000
83	0.0050	0.0050	1.0000	0.0000	0.0113
78	0.0026	0.0818	0.0000	1.0000	0.0000
43	0.0194	0.0309	0.0900	0.0064	1.0000

The inverse is then taken and multiplied by peaks of interest in standard spectra yielding:

$$\begin{matrix} 92 & = \\ 91 & = \\ 83 & = \\ 78 & = \\ 43 & = \end{matrix} \begin{vmatrix} 235 \\ 600 \\ 150 \\ 362 \\ 230 \end{vmatrix} \cdot \begin{vmatrix} 1.3955 & -0.1091 & -0.0048 & 0.0000 & 0.0001 \\ -1.3955 & 1.1091 & 0.0011 & 0.0000 & 0.0000 \\ -0.0002 & -0.0046 & 1.0010 & 0.0001 & -0.0113 \\ 0.1105 & -0.0904 & -0.0001 & 1.0000 & 0.0000 \\ 0.0154 & -0.0312 & -0.0900 & -0.0064 & 1.0010 \end{vmatrix}$$

Ion	Compound	Corr. peak Ht.	Response factor
92	Toluene	261.8	1.00
91	Ethylbenzene	337.7	1.29
83	Methylcyclohexane	144.8	0.55
78	Benzene	333.7	1.27
43	Octane	199.3	0.76

We can now calculate the spectra of an unknown mixture multiplying by the inverse

$$\begin{matrix} 92 & = \\ 91 & = \\ 83 & = \\ 78 & = \\ 43 & = \end{matrix} \begin{vmatrix} 285 \\ 610 \\ 128 \\ 165 \\ 370 \end{vmatrix} \cdot \begin{vmatrix} 1.3955 & -0.1091 & -0.0048 & 0.0000 & 0.0001 \\ -1.3955 & 1.1091 & 0.0011 & 0.0000 & 0.0000 \\ -0.0002 & -0.0046 & 1.0010 & 0.0001 & -0.0113 \\ 0.1105 & -0.0904 & -0.0001 & 1.0000 & 0.0000 \\ 0.0154 & -0.0312 & -0.0900 & -0.0064 & 1.0010 \end{vmatrix}$$

and dividing by response factors we get:

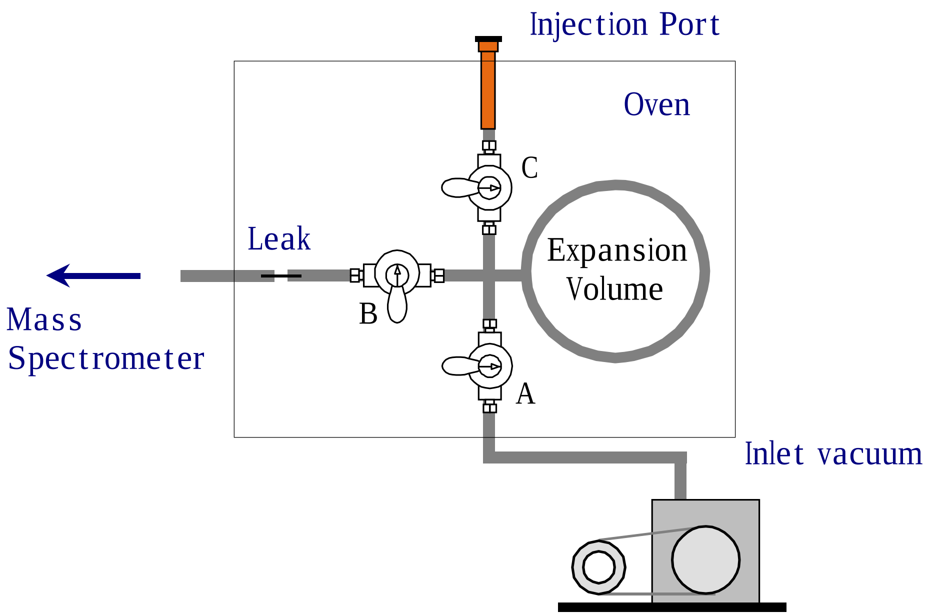
							L. V. %	
							Found	Actual
Toluene	92	=	330.6/1.00	=	330.6	=	24.9	25.0
Ethylbenzene	91	=	278.9/1.29	=	216.3	=	16.3	16.7
Methylcyclohexane	83	=	121.1/0.55	=	218.9	=	16.5	16.7
Benzene	78	=	141.3/1.27	=	110.9	=	8.4	8.3
Octane	43	=	343.2/0.76	=	450.7	=	34.0	33.3
Total					1327.4			

This is the principle used in many ASTM Mass Spectrometer procedures specifically *D-2789 - Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry*. Although this method is specific to gasoline with less than 3 volume percent olefin content, methods involving mathematical comparison of a saturate fraction collected from a preparative FIA separation with the total sample allow the characterization of even highly olefinic samples. The use of a batch inlet with the mass spectrometer is an ideal method of monitoring many processes very close to real time, but in a laboratory environment. With an autosampler, more than 200 samples could be processed in a 24 hour period.

We have found the batch inlet useful in pre-screening samples for oxygenates and aromatics in gasoline where more lengthy mandated methods are required but not necessarily timely. It is useful in screening any unknown for determination of gross composition. And it is well suited for quatitation of highly aqueous organic solutions.

Merlin MicroScience, Inc. has develooped a batch inlet system which incorporates the Hewlett-Packard MSD. Fully automated analysis can be achieved with software provided which does all the necessary mathematical manipulations on the spectra collected

The principle of the batch inlet is simple and is illustrated in the schematic below. Prior to injection valves A and B are closed and sample introduced through injection port. After a short equilibration period valve C is closed and valve B is opened. A small leak between the batch inlet and the mass spectrometer facilitates the ‘steady state’ introduction of sample into the spectrometer. Spectra is recorded across a range from mass 35 to 165. After completion of the short collection period, all valves are opened--rapidly removing the sample via the auxiliary pump. This process is repeated for each sample.



As a test of efficacy the mass spectrometer was tuned with the mixture specified in ASTM D-2789 using the Merlin Batch Inlet. After this initial tuning two samples were analyzed over several weeks without further calibration. Listed below are results of analyses performed on a reformate according to method D-2789.

ASTM D-2789 Mass Spectrometer

Date	10/27	10/21	10/28	10/31	11/1	11/7	11/9	11/10	AVG.	STD. DEV.
Type	L.V. %									
Paraffins	28.91	29.67	29.75	28.45	30.03	30.22	29.89	29.06	***29.50***	***0.55***
Naphthenes	2.20	2.14	2.58	2.26	2.52	2.51	2.56	2.58	***2.42***	***0.16***
Aromatics	68.89	68.19	67.67	69.29	67.45	67.27	67.55	68.36	***68.08***	***0.64***

Independent analysis of the above sample resulted in an Aromatics concentration of **66.72 L.V.%** by capillary gas chromatography. Analysis by capillary gas chromatography required approximately **2 hours** while the same analysis on the Merlin Batch Inlet analysis takes **4 minutes!**

A straight run naphtha was also run over this time period. Average results of those analyses are compared to capillary gc analysis below.

Straight Run Naphtha

Type, L.V. %	ASTM D-2789	Capillary GC
Paraffins	54.33	54.20
Naphthenes	35.20	34.95
Aromatics	10.47	10.71
Unknowns	-----	0.14
Analysis Time	**4 Minutes**	**2 Hours**

The Merlin Batch Inlet offers the following features:

- Full Integration with Hewlett-Packard MSD hardware
- Full Integration with Hewlett-Packard MSD software
- Compatibility with Hewlett-Packard and Leap Autosamplers
- No GC -- Eliminates need for carrier gases and GC pneumatics
- No GC column--Analysis time under 5 minutes
- On-board ASTM D-2789 Software for low olefin naphthas
- Integrated software for olefinic naphthas

Applications Include:

- PONA Analysis of naphthas and gasoline
- Oxygenate determination in naphthas and gasoline
- Hydrocarbon (PNA) types in Kerosene and Light Middle Distillates
- QA/QC of Organic and Aqueous mixtures

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