Chemical Group Analysis Using Smart Templates with Comprehensive Two-Dimensional Gas Chromatography with Mass Spectrometry (GCxGC-MS)

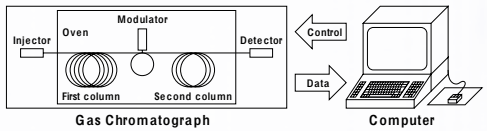
Stephen E. Reichenbach,[1] Qingping Tao,[2] Edward B. Ledford, Jr.,[3] Stella B. Cabanban,[4] Hung A. Pham,[4] Wayne E. Rathbun,[4] Haiyan Wang[4]
[1]University of Nebraska – Lincoln; [2]GC Image, LLC; [3]Zoex Corporation; [4]UOP LLC, a Honeywell company

Challenge

Group-type analysis of petroleum.

Methods

Smart Templates™ with CLIC™ rules for comprehensive two-dimensional gas chromatography with mass spectrometry.



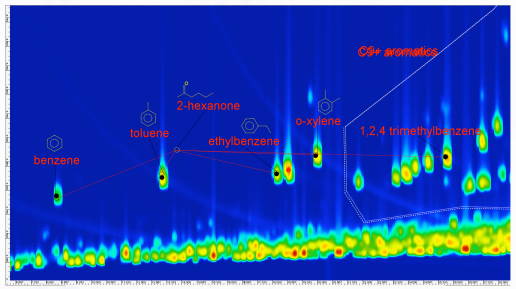
GCxGC-MS

Comprehensive two-dimensional gas chromatography (GCxGC) cycles a thermal modulator (from Zoex Corporation) to progressively trap analytes from the first column and then release them into the second column. The fast separation in the second column completes during each modulation cycle. The mass spectrometer operates at high speed to generate multiple spectra across each peak in each modulation cycle. The sequential data from the mass spectrometer is re-ordered as a two-dimensional array in which each successive second-column separation is presented as a bottom-to-top column of data points in the two-dimensional array.

Smart Templates

Smart Templates™ describe the 2D retention-time pattern of expected peaks and utilize rules pertaining to the retention-times and mass spectra in order to match analyte peaks.

Multi-type templates also include other objects such as geometric shapes, text labels, and chemical structure diagrams.



Template-Matching Example

This example illustrates a 2D chromatogram from a diesel sample. The overlay shows the matching between a template created from the retention-time pattern of peaks observed in a gasoline sample (shown with open circles) to peaks detected in the diesel sample (indicated by filled circles). The matching is imperfect, because different columns were used, but is sufficient to accurately identify analyte peaks.

CLIC Rules for Identification

Retention-time based matching can be improved by mass spectral rules. CLIC™ is a language for expressing rules for identifying analyte peaks.

For example, the CLIC rule for a rule *"Peaks for m/z 96 and 106 are among the three largest"* to identify xylene isomers is:

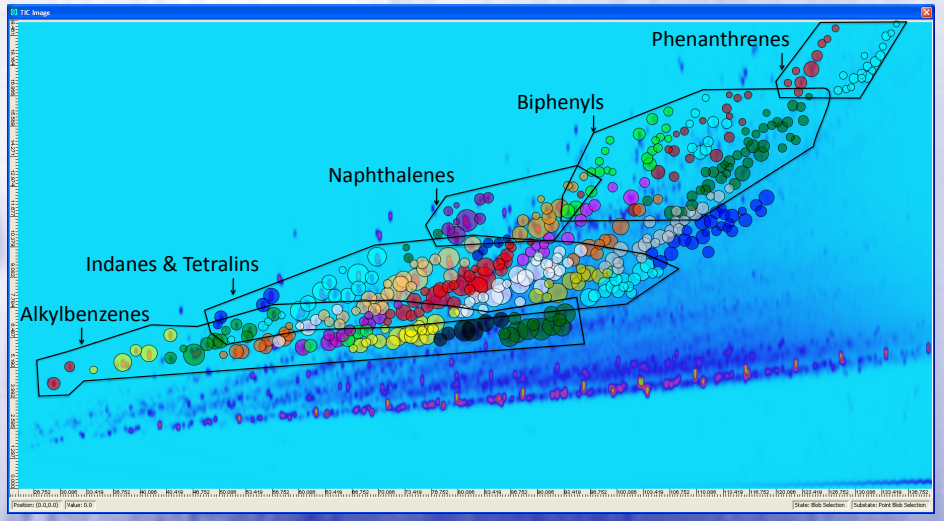
(Ordinal(96) < 4) & (Ordinal (106) < 4)

Group-Type Analysis

The goal of group-type analysis is an aggregated quantification of analytes by chemical structure and carbon number. Group-type analysis provides a highly useful characterization of petroleum samples.

CLIC Rules Group-Type Analysis

This report describes initial results for group-type analysis of diesel using GCxGC-MS and Smart Templates with CLIC rules for group-type identification. The research began with the interactive creation of 31 CLIC rules to select groups of peaks with similar mass spectra and clustered in the retention-time plane. The large figure (at the top of the following page) illustrates the 31 clusters with 430 peaks, with each selected peak indicated by a filled circle colored by cluster.



Group Identifications and Confirmations

Group identifications and confirmations were performed by expert analysis of NIST MS Search results. Larger molecules were not identified well by NIST MS Search, preventing confirmation even where peak groupings likely were correct. Some CLIC-selected groups for large molecules also could not be identified conclusively by NIST MS Search.

Results for several groups with subgroups by carbon number are given below. An important attribute of the group identifications with CLIC rules is that group membership for peaks can be distinguished even where groups overlap in the retention-time plane.

CLIC rules can be combined with peak templates to confirm group membership for peak identification. CLIC rules also can be associated with polygons to identify the set of all peaks satisfying the rule (regardless of whether the peak is in the template of expected peaks).

Alkylbenzenes

Ten CLIC rules identified alkylbenzene groups, e.g., for B:C7, "Ordinal(176) < 5". Some groups were identified by two CLIC rules.

Group	Color	Confirmed
B:C2		2/2
B:C3		5/5
B:C4		11/11
B:C5		15/15
B:C6		16/16
B:C7		19/20
B:C8		1/6
B:C9		2/12

Indanes and Tetralins

Seven CLIC rules identified indane and tetralin groups, e.g., for I:C2/T:C1, "Ordinal(131) < 5 & Ordinal(146) <5". The rules did not distinguish between the indanes and tetralins.

Group	Color	Confirmed
I:C1I		4/4
I:C2/T:C1		14/15
I:C3/T:C2		21/25
I:C4/T:C3		25/27
I:C5/T:C4		14/27
I:C6/T:C7		1/12
I:C7/T:C8		0/17

Naphthalenes, Biphenyls, Phenanthrenes

Seven CLIC rules identified naphthalenes, biphenyls, and phenanthrenes, e.g., for N:C3, "Ordinal(155) < 3 & Ordinal(172) < 3" .

Group	Color	Confirmed
N:C2		9/9
N:C3		11/12
BP:C2		17/21
BP:C3		1/12
BP:C4		0/17
P:C2		7/9
P:C3		17/17

Ongoing and Future Research

The CLIC rules are being tested with other samples, other systems, and other column configurations.

The CLIC rules are being refined for greater selectivity and extended additional groups.

The CLIC rules are being structured hierarchically to group super-groups and sub-groups (e.g., as illustrated to the right).

Confirmations other than NIST MS Search are being investigated.

The CLIC rules are being enhanced to utilize high mass-resolution spectra.

Group	Color	Group	Color
B:C8H10		B:C15H20	
B:C9H12		B:C15H22	
B:C10H14		B:C15H24	
B:C11H14		B:C16H24	
B:C11H16		N:C11H10	
B:C12H18		N:C12H12	
B:C13H16		N:C13H14	
B:C13H18		N:C14H16	
B:C13H20		BP:C13H12	
B:C14H18		BP:C14H14	
B:C14H20		BP:C15H16	
B:C14H22