



A Honeywell Company

Organic Analysis of Distillate by Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization Detection

UOP Method 990-11

Scope

This method is for organic analysis of distillate or petroleum fractions boiling in the range of 36 – 435°C using comprehensive two-dimensional gas chromatography (GCxGC) coupled with a flame ionization detector (FID). Results, expressed in mass-% can be reported in three different formats: 1) molecular types indexed to n-alkanes; 2) molecular type homologous series by carbon number and 3) user specified resolved compounds or molecular type groups. Individual compounds and molecular type groups are identified by their location, as plotted on a chromatographic two-dimensional image. Olefins, unless specifically identified, are lumped with other molecular types, typically cycloparaffins. Heteroatomic species, when resolved, can be determined; otherwise they are lumped with other aromatic hydrocarbons. The lower limit of detection for a single molecular component is typically below 0.004 mass-% with the specified equipment.

References

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Zoex GC Image Users' Guide, www.gcimage.com

Zoex Technical Note KT030606-1: "What is Loop Modulation?," www.zoex.com

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a two-stage thermal modulator system, "primary" and "secondary" fused silica open tubular capillary GC columns and a flame ionization detector (FID). The modulator serves as an interface between the two GC columns. The primary column is a conventional high resolution capillary GC column coated with a cross-linked methyl silicone stationary phase, which separates molecules based on volatility. The secondary GC column is coated with cross-linked poly (ethylene glycol); it is short and narrow, for fast GC separations based on the molecular property of polarity. The modulator repetitively accumulates, focuses and re-injects "heart-cut" fractions eluting off the primary column onto the secondary column, which is connected to the FID. The outcome is a series of high speed

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 2011 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

chromatograms from the secondary column which are transformed by computer software into a two-dimensional array and displayed as a two-dimensional image, with the x-axis representing the retention time from the primary column and the y-axis representing the retention time from the secondary column. Alternatively the data can be displayed as a 3-dimensional plot containing a third dimension which represents the FID signal intensity. A template is used to identify the boundaries between the different hydrocarbon types and label the separated components. The mass-% composition of the sample is obtained by internal normalization, wherein the peak volumes are normalized to 100 %.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used if equivalent performance can be obtained. The GCxGC-FID instrument items listed below are specifically for the “ZX1-thermal modulator” instrument commercially available from Zoex Corporation.

Analytical balance, readability 0.0001 g

Chromatographic column, primary, 50 m of 0.20 mm ID fused silica capillary, internally coated to a film thickness of 0.5 μm (bonded) with cross-linked methyl silicone, Agilent Technologies, Cat. No. 19091S-001E. Use of this specific column is recommended.

Chromatographic column, secondary, 20 m of 0.10 mm ID fused silica capillary, internally coated to a film thickness of 0.2 μm (bonded) with poly (ethylene glycol), Agilent Technologies, Cat. No. 127-7023. Use of this specific column is recommended. Note: Only a portion of the original column is used. See *Preparation of GCxGC Fused Silica Column Set* in the *Appendix* for specific instructions.

Column holder, for mounting secondary column used specifically in a Zoex two-stage cryo loop modulator, Zoex Corporation, Cat. No. KT-CLM-ZOE02

Comprehensive two-dimensional GC imaging and data processing software, GC-Image V2.1, Zoex Corporation. The precision statement of this method was obtained using data processed by this specific software.

Cryo auto-fill unit, liquid nitrogen level controller with two LSI-48 dual level sensors and liquid nitrogen transfer assembly with installed solenoid valve, Zoex Corporation, Cat. No. KT-DWR-TRG24

Cryo cylinder, 230 LP SB- square base with 22 psi relief valve, container for liquid nitrogen, Chart Inc., Storage System Division, Cat. No. 10648556. This is not needed if there is instrument access to a laboratory supplied liquid nitrogen distribution system.

Data system, electronic, for GC instrument control, data acquisition and data processing. This device must acquire data at a sufficiently fast rate (200 Hz) so that narrow peaks typically resulting from use of a capillary column can be accurately measured. The suggested minimum computer configuration: Microsoft Windows operating system (e.g. Windows XP, Vista or Windows 7), 1000 MHz Intel Pentium 4 (or comparable) CPU (dual-core is preferred), 1 GB RAM (2 GB or more is preferred), 128 MB OpenGL-capable graphics card (256 MB is preferred), and color monitor with 1024x768 (or higher) resolution. Processed GCxGC data may require large disk capacity. It is ideal to have two data systems: one for instrument control and data acquisition and a separate one for data processing. The data acquisition software must allow data to be exported in a format compatible with GC-Image software. Several formats that have been verified to work are

*.ch (Agilent ChemStation IQ Data File Format); ASCII csv (Comma-Separated-Values in text format); and PEG (LECO file format for collected raw FID data).

Excel 2003 or later, software, Microsoft

Fused silica tubing cutter, ceramic wafer, Agilent Technologies, Cat. No. 5181-8836

Gas chromatograph, temperature programmable, capable of constant flow, built for capillary column chromatography, utilizing a split injection system, equipped with a capillary injection port with a deactivated glass liner, and a flame ionization detector, Agilent Technologies, Model 7890A, with additional electronic pressure control

GCxGC two-stage thermal modulation system, consisting of a secondary liquid nitrogen dewar, a vacuum insulated transfer line, a modulator control module, valve assembly (controlled by valve ports 1 through 4 of the Agilent 7890 valve control bank), and a jet assembly, Zoex Corporation, Model No. ZX1; or equivalent.

- This method is written specifically for GCxGC-FID instruments containing two-stage thermal modulators that use liquid nitrogen as a cryo medium. Zoex and LECO both offer Agilent GC instruments configured with this type of modulation system. Other modulation systems such as "consumable free thermal" or "capillary flow" modulators may be limited in scope and have not been evaluated by this method.

Leak detector, gas, Restek, Cat. No. 22451

Refrigerator, flammable-materials storage, Fisher Scientific, Cat. No. 97-938-1

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Sample injector, autosampler or injector capable of introducing a consistent 0.1- μ L volume of sample. The use of an automatic injection device is required to achieve necessary repeatable injection timing. The precision of the method is based on instrumentation that is capable of synchronizing sample injection with initiation of the GCxGC modulator. Agilent Technologies, Model 7683B.

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Autosampler vials, glass, 2-mL volume, 12 x 32 mm, for Agilent autosampler, VWR, Cat. No. HP-5182-0714

Bottle, 120-mL, with fluoropolymer-lined cap, VWR, Cat. No. 16151-286

Caps, for autosampler vials, open hole with septum, screw, 9-mm, with Tef/Sil/Tef liner, VWR, Cat. No. HP-5182-0717

Dichloromethane, ACS reagent, $\geq 99.5\%$ pure, VWR, Cat. No. EM-DX0835-8. CAUTION: Dichloromethane is a known carcinogen. All operations involving its use must be performed in a properly ventilated area, while wearing appropriate personal protective equipment.

Distillate reference material. This should be a wide boiling range material (ideally 36°C - 435°C) containing significant concentrations of n-paraffins, mono-, di-, tri- and 4 plus ring aromatics. It should be of a sufficient quantity for use for multiple quality control analyses over an extended period of time (e.g. year or more). Keep in a tightly sealed glass container stored in a cool dark cabinet when not in use. NIST SRM 1624d is an example of a commercially available material which is suitable for a Distillate Reference Material.

Ferrules, vespel/graphite 85%/15% (short) for 0.10-0.25-mm ID capillary columns for use in connecting secondary column to flame ionization detector, Agilent Technologies, Cat. No. 5181-3323

Gas purifier, air, with 1/8" fittings, to remove moisture from air supply, VICI Mat/Sen, Cat. No. P400-1

Gas purifier, hydrogen, with 1/8" fittings, to remove CO, CO₂, S, oxygen, non-methane hydrocarbons and moisture from carrier gas, VICI Mat/Sen, Cat. No. P200-1

Gas purifier, nitrogen, with 1/8" fittings, to remove CO, CO₂, S, oxygen, non-methane hydrocarbons and moisture from nitrogen supply, VICI Mat/Sen, Cat. No. P300-1

Hydrogen, zero gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Nitrogen, zero gas, 99.95 % minimum purity, total hydrocarbons less than 0.5 ppm as methane. It is recommended to use a "house source" that is supplied moisture free, at 70 psi, preferably from a liquid nitrogen boil off source.

Nitrogen, liquid, for cryogenic thermal modulation. Liquid nitrogen is typically supplied with a larger nitrogen dewar or plumbed laboratory supply.

Pipette bulbs, VWR, Cat. No. 15001-364

Pipets, disposable, short tip, Pasteur, borosilicate glass, 14.6-cm, VWR, Cat. No. 14673-010

Pyrene, sublimed, 99% pure, Sigma-Aldrich, Cat. No. 571245

Syringe, for sample injector, 5-μL, Agilent Technologies, Cat. No. 5181-1273

Septa, ThermoRed 11, 11-mm, low bleed, high temperature, Grace Davison Discovery Sciences, Cat. No. 15132

SilTite metal ferrules, for 0.20-0.25-mm ID capillary columns and use with Agilent Ultimate Union, Agilent Technologies, Cat. No. 5188-5361

Typewriter correction fluid, white, for marking column positions

Zero-dead-volume ultimate union, deactivated, for connecting primary and secondary chromatographic columns, Agilent Ultimate Union Kit contains 1 union, 2 internal nuts, 1 swaging nut and 1 oven wall clip, Agilent Technologies, Cat. No. G3182-61580

Procedure

Preparation of the GCxGC Instrument

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography and the equipment being used. Follow the manufacturer's instructions for installation and set up of the GCxGC instrument. The procedure is written specifically for GCxGC-FID instruments containing two-stage thermal loop modulators that use liquid nitrogen as a cryo medium (see *Apparatus*). If a different instrument is used, modify the procedure as needed. The

instrument should be operated in an environment with reasonable constant temperature (<30°C) and low relative humidity (<50%).

1. Install gas purifiers in the gas supply lines between each gas source (air, nitrogen and hydrogen) and their respective inlets to the gas chromatograph.
 - Column life is significantly reduced if carrier gas purifiers are not used. Purifiers must be replaced periodically according to manufacturer's recommendations.
2. Mount the GCxGC fused silica capillary column set in the gas chromatograph connecting the primary chromatographic column to the injector inlet and the secondary chromatographic column to the detector inlet. Appendices A and B provide specific instructions for column installation of Zoex and LECO instruments, respectively.
3. Commence gas flows to the GC instrument. Check for leaks with a leak detector each time a gas or column connection is made and periodically thereafter. If a leak occurs the column set must be reevaluated and a new fresh connection must be made.
 - CAUTION: Hydrogen carrier gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to check for leaks each time a connection is made and periodically thereafter.
 - A leak will allow oxygen into the column, which can lead to degradation of the stationary phase and reduce GC column performance.
4. Program the recommended operating conditions as given in Table 1.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to that shown in a Typical Chromatogram (Figure 3).

Table 1
Recommended Operation Conditions

Carrier gas	hydrogen
Mode	constant flow
Flow rate	1.5 mL/min
Column head pressure @ 40 °C	170 kPa gauge (25 psig)
Split flow rate	150 mL/min
Split flow ratio	100:1
Injection port temperature	280 °C
Column temperature program	
Initial temperature	40 °C
Initial time	10 min
Programming rate A	1.5 °C/min
Intermediate temperature A	153 °C
Intermediate time A	0 min
Programming rate B	2.0 °C/min
Final temperature	280 °C
Final hold time	11.17 min
Run time	160 min
Hot jet temperature program	
Initial temperature	120 °C
Initial time	10 min
Programming rate	1.5 °C/min
Final temperature	280 °C
Final hold time	70 min
Valve assembly	
Agilent 6890 valve port 1	power for modulation control

Agilent 6890 valve port 2	hot jet
Agilent 6890 valve port 3	cold jet
Agilent 6890 valve port 4	power for control of liquid nitrogen
Detector	flame ionization
Temperature	280 °C
Hydrogen flow rate*	40 mL/min
Air flow rate*	550 mL/min
Makeup gas	nitrogen
Nitrogen flow rate*	25 mL/min
Mode	constant makeup flow
Sampling rate	200 Hz
Sample size	0.1 µL

*Consult the manufacturer's instrument manual for suggested flow rates.

5. Bake out the column set by setting the GC column oven temperature to 280°C. Maintain this temperature until a stable chromatographic baseline has been obtained ($< \pm 1$ pA drift over 10 min).
 - This should take no more than 20 minutes once at temperature. Prolonged heating of the column at this temperature will degrade its performance. The baseline can be monitored by the data acquisition software.
6. Cool the GC primary column oven to a stabilized 40°C.
7. Program the modulator control module parameters as listed in Table 2.
 - For LECO instruments the modulator control settings are programmed in the Chroma-TOF software. A rephase setting is not needed in the Chroma-TOF software.

Table 2
Recommended Modulation Parameters

Duration of modulator hot pulse	300 ms
Modulation period	8 sec
Rephase	negative

8. Start the modulator control module.
 - For LECO instruments, the modulator starts with the commencement of the Chroma-TOF data acquisition (Step 1 of *Sample Analysis*).
9. Turn on the cryo auto-fill unit to start flow of liquid nitrogen to the GCxGC thermal modulation system. Once the secondary liquid nitrogen dewar is filled to the appropriate level and the chromatographic baseline is stabilized ($< \pm 1$ pA drift over 10 min) then sample analysis can begin.
 - Follow the manufacturer's recommended conditions for setting and controlling the liquid nitrogen auto-fill unit.

Tuning the GCxGC Instrument **(Optimizing 2nd dimension GC column length and software volume filter setting)**

1. Prepare a Tune Check Solution (TCS) by weighing 0.1 g pyrene to the nearest 0.001 g in a glass bottle. Dilute with dichloromethane to a final weight of 50 g; cap and mix thoroughly.
2. Analyze the TCS as outlined in the *Procedure - Sample Analysis* section.
3. Identify the pyrene peak by comparing the resulting two-dimensional GCxGC image of the TCS sample analysis with Figure 1.

4. Ensure that the pyrene peak elutes between 7 and 8 seconds on the y-axis and 120 to 130 minutes on the x-axis. If the peak is found outside this boundary, then correct this by doing the following: 1) shorten the secondary column if the peak is found to be wrapped around; and 2) replace or use a longer secondary column if the peak retention time is below 7 seconds on the y-axis. If the pyrene peak is found outside of the x-axis boundary, try adjusting the carrier gas flow rate. Analyze the TCS again to confirm proper elution time of pyrene. Repeat if necessary until the retention time criteria are met.
 - A peak is wrapped around if it is not found to elute on the y-axis within a single modulation period (i.e. 8 seconds). If pyrene is wrapped around it will most likely also have a y-axis retention time displayed less than 7 seconds, often showing up in the second dimension void volume region defined in Figure 3. One way to diagnose if pyrene is wrapped-around is to analyze the TCS sample again under the same chromatographic conditions as before with the exception of using a longer modulation period of 16 seconds. If the pyrene peak retention time in the y-axis increases to beyond 8 seconds, then most likely it was wrapped-around in the original analysis. Wrapped around peaks typically have much wider peak widths (vertical direction). Some examples of wrapped around peaks are illustrated in Figure 3.
5. Prepare a Noise Filter Solution (NFS) by serially diluting the TCS with dichloromethane by weight to a final pyrene concentration of nominally 0.5 mass-ppm in dichloromethane.
 - This is best prepared by serial dilution until the desired concentration is obtained. For example, with a Pasteur pipette, weigh a 0.1 g aliquot of the TCS to the nearest 0.001 g in a separate 120-ml glass bottle. Dilute with additional dichloromethane to a final weight of 40 g; cap and mix thoroughly to create a 5-wt-ppm mixture of pyrene in dichloromethane. With a Pasteur pipette, weigh a 5-g aliquot of the 5-wt-ppm mixture to the nearest 0.001 g in a separate 120-ml glass bottle. Dilute this to a final weight of 50 g in dichloromethane; cap and shake thoroughly to make the NFS (0.5 wt-ppm pyrene in dichloromethane mixture). The exact concentration does not need to be calculated.
6. Analyze the NFS as outlined in the *Procedure - Sample Analysis* section.
7. Use data imaging and processing software to identify, determine, and record the volume of the pyrene peak in the NFS chromatographic analysis. Figure 2 shows a typical two-dimensional GCxGC image of a NFS sample analysis. Use this value to set the threshold for peak detection for subsequent sample analyses. This is typically accomplished by inputting the value into the minimum volume filter of the GCxGC data processing software. If a minimum volume filter is not available then a minimum signal to noise ratio of the pyrene in the NFS can be used instead.
 - In order to detect the pyrene peak, the use of a logarithmic color scale to accentuate the trace components in the chromatographic image is needed. Use a value of 0 for the volume filter when analyzing the NFS.
 - The calculated volume setting will be used to filter out detector signal noise in subsequent sample analyses.

Sample Analysis

1. When the instrument is ready as indicated in Step 9 of *Procedure - Preparation of GCxGC Instrument*, use the autosampler to inject nominally 0.1 μL of sample, immediately starting the data acquisition, column temperature programming sequence, and pulse of modulator controller. The analysis time is 160 minutes. Avoid cross-contamination between samples by rinsing the sample injection syringe several times with sample before injection and rinsing it several times with dichloromethane followed by acetone after sample injection.
 - It is highly preferable to synchronize the start of the analysis such that the data acquisition, column temperature program and modulator pulsing are initiated at precisely the same time.
 - The first materials run when initially setting up this method are the Tune Check Solution and the Noise Filter Solution in order to properly tune the GCxGC-FID instrument (see *Procedure – Tuning the GCxGC Instrument*).

- A distillate reference material is analyzed in order to determine and template chromatographic boundaries for chromatographic peak identification.
 - Prior to and after routine analysis of samples, confirm system suitability by running a distillate reference material (see System Suitability for specific instructions).
2. Upon completion of the sample run, import the data acquisition file into the GCxGC data processing software (i.e. GC-Image) and view a two-dimensional image of the analyzed sample. Indicate an 8 second modulation period when processing the file. Refer to the data processing software for details on processing GCxGC data. This includes correcting the baseline, integrating the peaks, filtering signal noise (using volume value determined in Step 7 of *Procedure – Tuning the GCxGC Instrument*), and displaying the two-dimensional GCxGC image.
 - GC-Image accepts a number of different file formats for importing GCxGC-FID acquisition files such as *.ch from Agilent ChemStation or PEG or ASCII CSV files from LECO Chroma-TOF software.
 - Table 4 provides some suggested parameters for configuring GC-Image software.
 - Use a value of 0 for the volume filter when analyzing the NFS.
 3. Examine the two-dimensional GCxGC image of the analyzed sample and compare it to Figures 4-7 to identify landmark peaks. If there is doubt as to the identity and location of a landmark peak it may be necessary to spike the sample with pure components and analyze it using Steps 1-3 of *Procedure - Sample Analysis* to establish their location. Table 3 provides a list of landmark peak compounds used to aid in navigating the image.
 - The landmark peaks represent core molecules with little or no alkylation that are chromatographically well resolved and readily identified from other sample components. These landmark peaks aid in identifying and establishing chromatographic boundaries for sample quantitative analysis. Identification of the landmark peaks is done by pattern recognition as the retention times can vary between instruments or even in the same instrument over time as the performance of the GC columns deteriorates. Many samples analyzed by this method may not contain all of the landmark peaks.
 - Alternatively, it is useful to identify peaks by analyzing the sample under similar chromatographic conditions on an instrument configured with a Time of Flight – Mass Spectrometer.

Data Processing

1. Construct and save a mesh object template (see bullet below) to identify and label the peaks on the two-dimensional GCxGC image of the distillate reference material. Three different types of templates can be used depending on the desired result reporting format. These are illustrated in Figures 8-12 for mass-% molecular types indexed to n-alkanes; Figures 13-17 for mass-% homologous series of molecular types by carbon number; or Figures 18-22 for mass-% user specified resolved compounds or molecular type groups that have been identified (examples shown are used for quality control and system suitability).
 - A template is a user-defined set of graphical elements, including points, lines and polygons used to establish chromatographic boundaries of separation between analytes in a processed two-dimensional GC image. Templates are used to automate the identification of peaks in subsequent samples. A mesh object template is a specific type of template made of an assembly of polygon panels that contain shared edges and vertices. Each panel of a mesh is drawn to include peaks of the hydrocarbon type group of interest and to exclude the peaks of other hydrocarbon types. The mesh object allows for covering all the relevant regions of the chromatographic image. Shared edges and vertices eliminate gaps between and overlap of different panels ensuring more accurate comprehensive analysis of the entire sample. The type of mesh object template used is dependent on customer needs. The following is a description of the different templates that can be used:
 - a) Indexed to n-Alkanes: In this template n-alkanes are used as an index for the primary column separation which can be directly correlated to boiling point. The secondary column polarity separation determines the hydrocarbon type which is identified by pattern recognition and identity of landmark peaks. This type of template is used primarily when it is difficult to identify the

beginning or ending of individual hydrocarbon type carbon number homologous series. This type of template is recommended when sample results from this method are compared to GCxGC-FID analysis of VGO boiling range fractions.

- b) Homologous Series: In this template, the individual homologous series of each aromatic hydrocarbon type are identified by carbon number. The homologous series are identified by pattern recognition and their relationship to specific landmark peaks. The different homologous series typically arrange themselves in rows with a similar slope on the x-y axis. If the homologous series in a sample are readily identified then this is typically the preferred template to use as the different hydrocarbon types can be identified by molecular formula.
 - c) Specific Molecules or Molecular Types: This is a user-specified template depending on the need to analyze a specific individual peak or molecular type. Use this template when the analytes of interest are well resolved and readily identified. This template is also useful for measuring total aromatic hydrocarbons by ring number. This can be a much simpler template useful for determining initial system suitability or quality control analysis.
 - In GC-Image, each polygon panel is labeled numerically in the order of which it is to appear in the analytical report. The names (i.e. description) of each panel are entered in GC-Image as listed in Tables 5 and 6.
2. Open and display the two-dimensional processed image file of the sample of interest.
 3. Load the appropriate distillate reference material saved mesh object template to the two-dimensional processed image of the sample.
 4. Evaluate the loaded template and modify it as necessary to ensure the accurate identification of the chromatographic peaks. If modification is required, save the modified template file, load, and overwrite it to the image. If no modification is necessary proceed to Step 5.
 - Shifting of the chromatographic boundaries occurs naturally over time due to deterioration of the GC columns or differences in sample analyte concentration or composition. Column deterioration is usually observed as a reduction in y-axis retention time. Conversely, a higher concentration of any analyte can slightly increase its respective y-axis retention time. Mesh object templates allow one to readily move shared vertices or borders between adjacent panels to reestablish the appropriate chromatographic boundaries.
 5. Match and apply the loaded mesh object template to the two-dimensional processed image of the sample.
 6. Save the processed file of different components with their respective integrated volumes. A list of the different analytes for a template indexed to n-alkanes is shown in Table 5. A list of different analytes for a template based on homologous series is shown in Table 6.
 - The Zoex GC-Image software saves the processed file as a blob set table. The blob set table must be configured to contain: name, description and total volume.
 7. Import the saved processed (*.csv) file into Excel to calculate the mass-ppm concentration of the individual components by using Equation 2 from the *Calculations* section of this method.
 - The following is a description of how to use the Excel software to calculate the results:
 - a) Import the *.csv file including: name, description, and volume
 - b) Sort the data by "name", all ascending.
 - c) Determine a total volume by summing the "volume" column.
 - d) Determine the concentration of the individual components by using Equation 2.

Table 3
List of Landmark Peak Compounds

n-paraffins	monoaromatics (contd)	diaromatics
pentane	4-methylindan	naphthalene
hexane	5-methylindan	1-methylnaphthalene
heptane	indene	2-methylnaphthalene
octane	tetralin	biphenyl
nonane	isobutylbenzene	methylbiphenyl
decane	sec-butylbenzene	acenaphthene
undecane	m-cymene	fluorene
dodecane	p-cymene	
tridecane	o-cymene	triaromatics
tetradecane	1,3-diethylbenzene	phenanthrene
pentadecane	1-methyl-3-propylbenzene	anthracene
hexadecane	1,3-dimethyl-5ethylbenzene	fluoranthene
heptadecane	1-methyl-2-propylbenzene	
octadecane	1,4-dimethyl-2-ethylbenzene	4-ring aromatics
nonadecane	1,3-dimethyl-4-ethylbenzene	pyrene
eicosane	1,2-dimethyl-4-ethylbenzene	
heneicosane	1,3-dimethyl-2-ethylbenzene	heteroatoms
docosane	1,3-dimethyl-3-ethylbenzene	dibenzothiophene
tricosane	1,2,4,5-tetramethylbenzene	benzothiophene
tetracosane	1,2,3,5-tetramethylbenzene	dichloromethane
pentacosane	1,2,3,4-tetramethylbenzene	
hexacosane	2-phenyl-3-methylbutane	
heptacosane	3-phenylpentane	
octacosane	isopentylbenzene	
nonacosane	1,2-dimethyl-4-isopropylbenzene	
	1-methyl-2-tert-butylbenzene	
monoaromatics	1,3-dimethyl-5-n-propylbenzene	
benzene	1-methyl-3-n-butylbenzene	
toluene	1-methyl-2,6-diethylbenzene	
ethylbenzene	1,2-dimethyl-4-n-propylbenzene	
m- and p-xylene	1,3,5-trimethyl-2-ethylbenzene	
o-xylene	1,2-dimethyl-3-n-propylbenzene	
cumene	1,2,3-trimethyl-5-ethylbenzene	
n-propylbenzene	1,2,4-trimethyl-3-ethylbenzene	
1,3,5-trimethylbenzene	1,2,3-trimethyl-4-ethylbenzene	
1-methyl-2-ethylbenzene	pentamethylbenzene	
1,2,4-trimethylbenzene	hexamethylbenzene	
1,2,3-trimethylbenzene	styrene	
indane		
1-methylindan		
2-methylindan		

Table 4
Suggested GC-Image Software Configuration Parameters

Color Map	EOSB
Saturation	curve 144, 248
Hue	curve 144, 126
Brightness	curve 144, 5
Color shift	0.5217391
Extrema colors	white and blue
Blob detection	
Blob detection algorithm	two-dimensional
Smoothing	
First column	0.1
Second column	2.0
Blob filter	
Minimum area	15*
Minimum volume	0
Minimum peak	10*
Baseline correction	
Number of deadband pixels	50
Filter window size	3
Distribution	5.0
Stride	0.5
Blob statistics	default values
Blob set table configuration	
Select visible feature	name
Select visible feature	description
Select visible feature	total volume

* set to 0 when minimum volume value is entered

Table 5
Molecular Types Indexed to n-Alkanes

No.	Description
5	n-pentane (BP = 36.1° C)
6	n-hexane (BP = 68.9° C)
7	n-heptane (BP = 98.3° C)
8	n-octane (BP = 126.1° C)
9	n-nonane (BP = 150.6° C)
10	n-decane (BP = 173.9° C)
11	n-undecane (BP = 196.1° C)
12	n-dodecane (BP = 216.1° C)
13	n-tridecane (BP = 235° C)
14	n-tetradecane (BP = 253.9° C)
15	n-pentadecane (BP = 271.1° C)
16	n-hexadecane (BP = 287.2° C)
17	n-heptadecane (BP = 302.2° C)
18	n-octadecane (BP = 316.1° C)
19	n-nonadecane (BP = 329.7° C)
20	n-eicosane (BP = 343.9° C)
21	n-heneicosane (BP = 356.5° C)
22	n-docosane (BP = 368.9° C)
23	n-tricosane (BP = 380.2° C)
24	n-tetracosane (BP = 391.1° C)
25	n-pentacosane (BP = 401.9° C)
26	n-hexacosane (BP = 412.2° C)
27	n-heptacosane (BP = 422.1° C)
28	n-octacosane (BP = 431.1° C)
29	n-nonacosane (BP = 440.8° C)
105	paraffins eluting before n-pentane
106	isoparaffins eluting between nC5 and nC6
107	isoparaffins eluting between nC6 and nC7
108	isoparaffins eluting between nC7 and nC8
109	isoparaffins eluting between nC8 and nC9
110	isoparaffins eluting between nC9 and nC10
111	isoparaffins eluting between nC10 and nC11
112	isoparaffins eluting between nC11 and nC12
113	isoparaffins eluting between nC12 and nC13
114	isoparaffins eluting between nC13 and nC14
115	isoparaffins eluting between nC14 and nC15
116	isoparaffins eluting between nC15 and nC16
117	isoparaffins eluting between nC16 and nC17
118	isoparaffins eluting between nC17 and nC18
119	isoparaffins eluting between nC18 and nC19
120	isoparaffins eluting between nC19 and nC20
121	isoparaffins eluting between nC20 and nC21
122	isoparaffins eluting between nC21 and nC22
123	isoparaffins eluting between nC22 and nC23
124	isoparaffins eluting between nC23 and nC24
125	isoparaffins eluting between nC24 and nC25
126	isoparaffins eluting between nC25 and nC26

Table 5 (Continued)
Molecular Types Indexed to n-Alkanes

<u>No.</u>	<u>Description</u>
127	isoparaffins eluting between nC26 and nC27
128	isoparaffins eluting between nC27 and nC28
129	isoparaffins eluting between nC28 and nC29
207	naphthenes and olefins eluting between nC6 and nC7
208	naphthenes and olefins eluting between nC7 and nC8
209	naphthenes and olefins eluting between nC8 and nC9
210	naphthenes and olefins eluting between nC9 and nC10
211	naphthenes and olefins eluting between nC10 and nC11
212	naphthenes and olefins eluting between nC11 and nC12
213	naphthenes and olefins eluting between nC12 and nC13
214	naphthenes and olefins eluting between nC13 and nC14
215	naphthenes and olefins eluting between nC14 and nC15
215	naphthenes and olefins eluting between nC14 and nC15
216	naphthenes and olefins eluting between nC15 and nC16
216	naphthenes and olefins eluting between nC15 and nC16
217	naphthenes and olefins eluting between nC16 and nC17
218	naphthenes and olefins eluting between nC17 and nC18
219	naphthenes and olefins eluting between nC18 and nC19
220	naphthenes and olefins eluting between nC19 and nC20
221	naphthenes and olefins eluting between nC20 and nC21
222	naphthenes and olefins eluting between nC21 and nC22
223	naphthenes and olefins eluting between nC22 and nC23
224	naphthenes and olefins eluting between nC23 and nC24
225	naphthenes and olefins eluting between nC24 and nC25
226	naphthenes and olefins eluting between nC25 and nC26
227	naphthenes and olefins eluting between nC26 and nC27
228	naphthenes and olefins eluting between nC27 and nC28
229	naphthenes and olefins eluting between nC28 and nC29
307	benzene
308	toluene
309	alkylbenzenes eluting between nC8 and nC9
310	alkylbenzenes eluting between nC9 and nC10
311	alkylbenzenes eluting between nC10 and nC11
312	alkylbenzenes eluting between nC11 and nC12
313	alkylbenzenes eluting between nC12 and nC13
314	alkylbenzenes eluting between nC13 and nC14
315	alkylbenzenes eluting between nC14 and nC15
316	alkylbenzenes eluting between nC15 and nC16
317	alkylbenzenes eluting between nC16 and nC17
318	alkylbenzenes eluting between nC17 and nC18
319	alkylbenzenes eluting between nC18 and nC19
320	alkylbenzenes eluting between nC19 and nC20
321	alkylbenzenes eluting between nC20 and nC21
322	alkylbenzenes eluting between nC21 and nC22

Table 5 (Continued)
Molecular Types Indexed to n-Alkanes

No.	Description
323	alkylbenzenes eluting between nC22 and nC23
411	naphthene substituted monoaromatics eluting between nC10 and nC11
412	naphthene substituted monoaromatics eluting between nC11 and nC12
413	naphthene substituted monoaromatics eluting between nC12 and nC13
414	naphthene substituted monoaromatics eluting between nC13 and nC14
415	naphthene substituted monoaromatics eluting between nC14 and nC15
416	polynaphthenes eluting between nC15 and nC16
417	polynaphthenes eluting between nC16 and nC17
418	polynaphthenes eluting between nC17 and nC18
419	polynaphthenes eluting between nC18 and nC19
420	polynaphthenes eluting between nC19 and nC20
421	polynaphthenes eluting between nC20 and nC21
422	polynaphthenes eluting between nC21 and nC22
423	polynaphthenes eluting between nC22 and nC23
424	polynaphthenes eluting between nC23 and nC24
425	polynaphthenes eluting between nC24 and nC25
426	polynaphthenes eluting between nC25 and nC26
427	polynaphthenes eluting between nC26 and nC27
428	polynaphthenes eluting between nC27 and nC28
429	polynaphthenes eluting between nC28 and nC29
512	naphthalene
513	diaromatics eluting between nC12 and nC13
514	diaromatics eluting between nC13 and nC14
515	diaromatics eluting between nC14 and nC15
516	diaromatics eluting between nC15 and nC16
517	diaromatics eluting between nC16 and nC17
518	diaromatics eluting between nC17 and nC18
519	diaromatics eluting between nC18 and nC19
520	diaromatics eluting between nC19 and nC20
521	diaromatics eluting between nC20 and nC21
522	diaromatics eluting between nC21 and nC22
523	diaromatics eluting between nC22 and nC23
524	diaromatics eluting between nC23 and nC24
525	diaromatics eluting between nC24 and nC25
526	diaromatics eluting between nC25 and nC26
527	diaromatics eluting between nC26 and nC27
528	diaromatics eluting between nC27 and nC28
529	diaromatics eluting between nC28 and nC29
618	triaromatics and aromatics eluting between nC17 and nC18
619	triaromatics and aromatics eluting between nC18 and nC19
620	triaromatics and aromatics eluting between nC19 and nC20
621	triaromatics and aromatics eluting between nC20 and nC21
622	triaromatics and aromatics eluting between nC21 and nC22
623	triaromatics and aromatics eluting between nC22 and nC23

Table 5 (Continued)
Molecular Types Indexed to n-Alkanes

No.	Description
624	triaromatics and aromatics eluting between nC23 and nC24
625	triaromatics and aromatics eluting between nC24 and nC25
626	triaromatics and aromatics eluting between nC25 and nC26
627	triaromatics and aromatics eluting between nC26 and nC27
628	triaromatics and aromatics eluting between nC27 and nC28
629	triaromatics and aromatics eluting between nC28 and nC29
721	4 plus ring aromatics eluting between nC20 and nC21
722	4 plus ring aromatics eluting between nC21 and nC22
723	4 plus ring aromatics eluting between nC22 and nC23
724	4 plus ring aromatics eluting between nC23 and nC24
725	4 plus ring aromatics eluting between nC24 and nC25
726	4 plus ring aromatics eluting between nC25 and nC26
727	4 plus ring aromatics eluting between nC26 and nC27
728	4 plus ring aromatics eluting between nC27 and nC28
729	4 plus ring aromatics eluting between nC28 and nC29
806	polar unknowns eluting between nC5 and nC6
807	polar unknowns eluting between nC6 and nC7
808	polar unknowns eluting between nC7 and nC8
809	polar unknowns eluting between nC8 and nC9
810	polar unknowns eluting between nC9 and nC10
811	polar unknowns eluting between nC10 and nC11
812	polar unknowns eluting between nC11 and nC12
813	polar unknowns eluting between nC12 and nC13
814	polar unknowns eluting between nC13 and nC14
815	polar unknowns eluting between nC14 and nC15
816	polar unknowns eluting between nC15 and nC16
817	polar unknowns eluting between nC16 and nC17
818	polar unknowns eluting between nC17 and nC18
819	polar unknowns eluting between nC18 and nC19
820	polar unknowns eluting between nC19 and nC20
821	polar unknowns eluting between nC20 and nC21
822	polar unknowns eluting between nC21 and nC22
823	polar unknowns eluting between nC22 and nC23
824	polar unknowns eluting between nC23 and nC24
825	polar unknowns eluting between nC24 and nC25
826	polar unknowns eluting between nC25 and nC26
827	polar unknowns eluting between nC26 and nC27
828	polar unknowns eluting between nC27 and nC28
829	polar unknowns eluting between nC28 and nC29
999	other polar unknowns (wrapped)

Table 6
Homologous Series of Molecular Types Reported by Carbon Number

No.	Description	Molecular Formula
5	n-pentane	C_5H_{12}
6	n-hexane	C_6H_{14}
7	n-heptane	C_7H_{16}
8	n-octane	C_8H_{18}
9	n-nonane	C_9H_{20}
10	n-decane	$C_{10}H_{22}$
11	n-undecane	$C_{11}H_{24}$
12	n-dodecane	$C_{12}H_{26}$
13	n-tridecane	$C_{13}H_{28}$
14	n-tetradecane	$C_{14}H_{30}$
15	n-pentadecane	$C_{15}H_{32}$
16	n-hexadecane	$C_{16}H_{34}$
17	n-heptadecane	$C_{17}H_{36}$
18	n-octadecane	$C_{18}H_{38}$
19	n-nonadecane	$C_{19}H_{40}$
20	n-eicosane	$C_{20}H_{42}$
21	n-heneicosane	$C_{21}H_{44}$
22	n-docosane	$C_{22}H_{46}$
23	n-tricosane	$C_{23}H_{48}$
24	n-tetracosane	$C_{24}H_{50}$
25	n-pentacosane	$C_{25}H_{52}$
26	n-hexacosane	$C_{26}H_{54}$
27	n-heptacosane	$C_{27}H_{56}$
28	n-octacosane	$C_{28}H_{58}$
29	n-nonacosane	$C_{29}H_{60}$
105	paraffins eluting before n-pentane	$C_5H_{12}^*$
106	isoparaffins eluting between nC5 and nC6	$C_6H_{14}^*$
107	isoparaffins eluting between nC6 and nC7	$C_7H_{16}^*$
108	isoparaffins eluting between nC7 and nC8	$C_8H_{18}^*$
109	isoparaffins eluting between nC8 and nC9	$C_9H_{20}^*$
110	isoparaffins eluting between nC9 and nC10	$C_{10}H_{22}^*$
111	isoparaffins eluting between nC10 and nC11	$C_{11}H_{24}^*$
112	isoparaffins eluting between nC11 and nC12	$C_{12}H_{26}^*$
113	isoparaffins eluting between nC12 and nC13	$C_{13}H_{28}^*$
114	isoparaffins eluting between nC13 and nC14	$C_{14}H_{30}^*$
115	isoparaffins eluting between nC14 and nC15	$C_{15}H_{32}^*$
116	isoparaffins eluting between nC15 and nC16	$C_{16}H_{34}^*$
117	isoparaffins eluting between nC16 and nC17	$C_{17}H_{36}^*$
118	isoparaffins eluting between nC17 and nC18	$C_{18}H_{38}^*$
119	isoparaffins eluting between nC18 and nC19	$C_{19}H_{40}^*$
120	isoparaffins eluting between nC19 and nC20	$C_{20}H_{42}^*$
121	isoparaffins eluting between nC20 and nC21	$C_{21}H_{44}^*$
122	isoparaffins eluting between nC21 and nC22	$C_{22}H_{46}^*$
123	isoparaffins eluting between nC22 and nC23	$C_{23}H_{48}^*$
124	isoparaffins eluting between nC23 and nC24	$C_{24}H_{50}^*$

- predominant molecular formula

Table 6 (Continued)
Homologous Series of Molecular Types Reported by Carbon Number

No.	Description	Molecular Formula
125	isoparaffins eluting between nC24 and nC25	$C_{25}H_{52}^*$
126	isoparaffins eluting between nC25 and nC26	$C_{26}H_{54}^*$
127	isoparaffins eluting between nC26 and nC27	$C_{27}H_{56}^*$
128	isoparaffins eluting between nC27 and nC28	$C_{28}H_{58}^*$
129	isoparaffins eluting between nC28 and nC29	$C_{29}H_{60}^*$
206	naphthenes and olefins eluting between nC5 and nC6	$C_6H_{12}^*$
207	naphthenes and olefins eluting between nC6 and nC7	$C_7H_{14}^*$
208	naphthenes and olefins eluting between nC7 and nC8	$C_8H_{16}^*$
209	naphthenes and olefins eluting between nC8 and nC9	$C_9H_{18}^*$
210	naphthenes and olefins eluting between nC9 and nC10	$C_{10}H_{20}^*$
211	naphthenes and olefins eluting between nC10 and nC11	$C_{11}H_{22}^*$
212	naphthenes and olefins eluting between nC11 and nC12	$C_{12}H_{24}^*$
213	naphthenes and olefins eluting between nC12 and nC13	$C_{13}H_{26}^*$
214	naphthenes and olefins eluting between nC13 and nC14	$C_{14}H_{28}^*$
215	naphthenes and olefins eluting between nC14 and nC15	$C_{15}H_{30}^*$
216	naphthenes and olefins eluting between nC15 and nC16	$C_{16}H_{32}^*$
217	naphthenes and olefins eluting between nC16 and nC17	$C_{17}H_{34}^*$
218	naphthenes and olefins eluting between nC17 and nC18	$C_{18}H_{36}^*$
219	naphthenes and olefins eluting between nC18 and nC19	$C_{19}H_{38}^*$
220	naphthenes and olefins eluting between nC19 and nC20	$C_{20}H_{40}^*$
221	naphthenes and olefins eluting between nC20 and nC21	$C_{21}H_{42}^*$
222	naphthenes and olefins eluting between nC21 and nC22	$C_{22}H_{44}^*$
223	naphthenes and olefins eluting between nC22 and nC23	$C_{23}H_{46}^*$
224	naphthenes and olefins eluting between nC23 and nC24	$C_{24}H_{48}^*$
225	naphthenes and olefins eluting between nC24 and nC25	$C_{25}H_{50}^*$
226	naphthenes and olefins eluting between nC25 and nC26	$C_{26}H_{52}^*$
227	naphthenes and olefins eluting between nC26 and nC27	$C_{27}H_{54}^*$
228	naphthenes and olefins eluting between nC27 and nC28	$C_{28}H_{56}^*$
229	naphthenes and olefins eluting between nC28 and nC29	$C_{29}H_{58}^*$
300	benzene	C_6H_6
301	toluene	C_7H_8
302	C2-alkylbenzenes	C_8H_{10}
303	C3-alkylbenzenes	C_9H_{12}
304	C4-alkylbenzenes	$C_{10}H_{14}$
305	C5-alkylbenzenes	$C_{11}H_{16}$
306	C6-alkylbenzenes	$C_{12}H_{18}$
307	C7-alkylbenzenes	$C_{13}H_{20}$
308	C8-alkylbenzenes	$C_{14}H_{22}$
309	C9-alkylbenzenes	$C_{15}H_{24}$
310	C10-alkylbenzenes	$C_{16}H_{26}$
311	C11-alkylbenzenes	$C_{17}H_{28}$
312	C12-alkylbenzenes	$C_{18}H_{30}$
313	C13-alkylbenzenes	$C_{19}H_{32}$
314	C14-alkylbenzenes	$C_{20}H_{34}$
315	C15-alkylbenzenes	$C_{21}H_{36}$
316	C16 and higher alkylbenzenes	$C_{22}H_{38}^*$
400	indane	C_9H_{10}

• predominant molecular formula

Table 6 (Continued)
Homologous Series of Molecular Types Reported by Carbon Number

No.	Description	Molecular Formula
401	C1-indans	C ₁₀ H ₁₂
402	tetralin	C ₁₀ H ₁₂
403	C2-indans and C1-tetralins	C ₁₁ H ₁₄
404	C3-indans and C2-tetralins	C ₁₂ H ₁₆
405	C4-indans and C3-tetralins	C ₁₃ H ₁₈
406	C5-indans and C4-tetralins	C ₁₄ H ₂₀
407	other naphthenic substituted monoaromatics and polynaphthenes	?
500	indene	C ₉ H ₈
501	C1-indenes	C ₁₀ H ₁₀
502	C2-indenes	C ₁₁ H ₁₂
503	C3-indenes	C ₁₂ H ₁₄
600	naphthalene	C ₁₀ H ₈
601	C1-naphthalenes	C ₁₁ H ₁₀
602	C2-naphthalenes	C ₁₂ H ₁₂
603	C3-naphthalenes	C ₁₃ H ₁₄
604	C4-naphthalenes	C ₁₄ H ₁₆
605	C5-naphthalenes	C ₁₅ H ₁₈
606	C6-naphthalenes	C ₁₆ H ₂₀
607	C7 and higher naphthalenes	C ₁₇ H ₂₂ ⁺ *
620	benzothiophene	C ₈ H ₆ S
621	C1-benzothiophenes	C ₉ H ₈ S
622	C2-benzothiophenes	C ₁₀ H ₁₀ S
630	biphenyl	C ₁₂ H ₁₀
631	C1-biphenyls	C ₁₃ H ₁₂
640	acenaphthene	C ₁₂ H ₁₀
650	dibenzofuran	C ₁₂ H ₈ O
651	C1-dibenzofurans	C ₁₃ H ₁₀ O
660	fluorene	C ₁₃ H ₁₀
661	C1-fluorenes	C ₁₄ H ₁₂
670	dibenzothiophene	C ₁₂ H ₈ S
671	C1-dibenzothiophenes	C ₁₃ H ₁₀ S
672	C2-dibenzothiophenes	C ₁₄ H ₁₂ S
680	other diaromatics	?
700	anthracene and phenanthrene	C ₁₄ H ₁₀
701	C1-triaromatics	C ₁₅ H ₁₂
702	C2-triaromatics	C ₁₆ H ₁₄
703	C3-triaromatics	C ₁₇ H ₁₆
704	C4-triaromatics	C ₁₈ H ₁₈
705	C5 and higher triaromatics	C ₁₉ H ₂₀ ⁺ *
710	fluoranthene	C ₁₆ H ₁₀
800	pyrene	C ₁₆ H ₁₀
801	C1-4ring aromatics	C ₁₇ H ₁₂
802	C2-4ring aromatics	C ₁₈ H ₁₄
803	C3 and higher 4ring aromatics	C ₁₉ H ₁₆ ⁺ *
901	polar unknowns	?
999	other polar unknowns (wrapped)	?

* predominant molecular formula

Calibration

Relative response factors are required for accurate association of the peak areas of corresponding sample components to mass-% since all hydrocarbon or heteroatomic components do not respond equally in a flame ionization detector. This is particularly true for lower carbon number aromatics such as benzene and toluene which have a higher detector response compared to paraffins. One can correct for the difference in FID response by analyzing distillate reference materials which contain known amounts of the analytes of interest, including n-heptane. It is best when the distillate reference material resembles the samples of interest. Alternatively, one can use theoretical relative response factors as shown in Table 7. These theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. One may also choose for practical reasons to ignore the differences and normalize the results assuming each sample component has an equivalent detector response. The protocol below describes how to determine relative response factors by analyzing a distillate reference material.

1. Analyze three times, as described in Steps 1-3 of *Sample Analysis* and Steps 1-6 of *Data Processing*, a Distillate Reference Material with a known composition similar to the broad spectrum of the samples to be analyzed.
2. Identify the analytes and average the analyte volumes from the triplicate runs.
3. Use the average peak volumes to calculate the relative response factor for each analyte component to three decimal places, using n-heptane as a reference, and Equation 1.

$$F = \frac{AB}{CD} \quad (1)$$

where:

A = concentration of the component or group of components in the calibration blend, mass-%

B = average peak volume of n-heptane

C = concentration of n-heptane, mass-%

D = average peak volume for the component or group of components

F = relative response factor for the component or group of components

- Calculated relative response factors should be similar to the theoretical relative response factors shown in Table 7.

Table 7
Theoretical Relative Response Factors

n-Heptane	1.000
Benzene	0.909
Toluene	0.919
Xylenes	0.927
C₉-Alkylbenzenes	0.933

System Suitability

Prior to and after analysis of a sample set (up to 6 samples), it is highly recommended to confirm proper system chromatographic performance by running a distillate reference material. One material that may be useful for this is the NIST SRM 1624d (0.4% sulfur distillate). Analyze the sample as specified in Steps 1-3 of *Sample Analysis*. Process the sample as specified in Steps 1-7 of *Data Processing*; constructing a template similar to that shown in Figures 18-22. Table 8 provides a list of the System Suitability analytes. Confirm that the sample results are within the established site precision allowable difference of the method (see *Precision*).

- If greater deviations occur, make certain that there are no problems with the equipment, and then make additional runs until the required repeatability is obtained on three consecutive runs.
- GC column performance will gradually thermally degrade, losing activity over time. This typically results in a reduction of retention time of the analytes, particularly in the second dimension. Periodic adjustment of the template has been demonstrated to enable the use of the same columns for up to 6 months without replacement. Typically, it is the secondary GC column that may need to be replaced in order to achieve acceptable values.

Table 8
System Suitability Analytes

Description

n-Decane (n-C₁₀)
n-Pentadecane (n-C₁₅)
n-Eicosane (n-C₂₀)
n-Pentacosane (n-C₂₅)
Indane
Cumene
Tetralin
Naphthalene
1-Methylnaphthalene
2-Methylnaphthalene
Biphenyl
Anthracene & phenanthrene
Dibenzothiophene
Pyrene
Total Saturates
Total Monoaromatics
Total Diaromatics
Total Triaromatics
Total 4+ ring Aromatics

Calculations

Calculations are performed in the Excel software according to the following procedure. Obtain peak volumes for each individual component or group of components and calculate the composition of the sample to the nearest 0.001 mass-% using Equation 2:

$$\text{Component, mass-\%} = 100 \frac{FV}{T} \quad (2)$$

where:

F = previously defined, Equation 1 (otherwise use value 1 for F)

T = sum of the products, **FV**, of all the recorded peaks excluding column bleed artifacts

V = peak volume of individual component or group of components

100 = factor to convert to mass-%

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining impurities in light cycle oil (LCO) by two

analysts, with each analyst performing analyses on multiple days for a total of 18 analyses. The same peak identification template was used by both analysts. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 9. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 9 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 9 with 95% confidence.

Table 9
Repeatability and Site Precision, mass-%

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
n-Decane (n-C ₁₀)	0.016	0.0001	0.001	0.0002	0.001
n-Pentadecane (n-C ₁₅)	0.557	0.0103	0.030	0.0106	0.032
n-Eicosane (n-C ₂₀)	0.409	0.0121	0.035	0.0122	0.037
n-Pentacosane (n-C ₂₅)	0.047	0.0038	0.011	0.0036	0.011
Cumene	0.002	0.0001	0.001	0.0001	0.001
Indane	0.071	0.0003	0.001	0.0004	0.001
Tetralin	0.028	0.0001	0.001	0.0001	0.001
Naphthalene	0.787	0.0020	0.006	0.0019	0.006
1-Methylnaphthalene	1.583	0.0035	0.010	0.0031	0.010
2-Methylnaphthalene	2.983	0.0069	0.020	0.0062	0.020
Biphenyl	0.158	0.0003	0.001	0.0003	0.001
Anthracene & phenanthrene	0.974	0.0006	0.002	0.0009	0.003
Dibenzothiophene	0.093	0.0002	0.001	0.0002	0.001
Pyrene	0.141	0.0004	0.001	0.0004	0.001
Total Saturates	17.146	0.0504	0.148	0.0477	0.150
Total Monoaromatics	15.838	0.0447	0.149	0.0553	0.162
Total Diaromatics	52.548	0.0319	0.094	0.0433	0.123
Total Triaromatics	13.227	0.0135	0.039	0.0332	0.098
Total 4+ Aromatics	1.240	0.0082	0.024	0.0090	0.027

The data in Table 9 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 2-4 hours. The labor requirement is 0.5 to 2.0 hours, depending upon the complexity of the sample.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808, USA (302-633-8000)
www.agilent.com

Chart Industries Inc., Storage System Division, 3505 County Road 42 West, Burnsville, MN 55306, USA (952-758-8275) www.chart-ind.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300) www.fishersci.com

GC Image, LLC., P.O. Box 57403, Lincoln, NE 68505, USA (402-310-4503) www.gcimage.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600) www.discoverysciences.com

Matheson Tri-Gas Products Inc., 166 Keystone Drive, Montgomeryville, PA 18936, USA (215-641-2700) www.mathesontrigas.com

Microsoft, www.microsoft.com

National Institute of Standards and Technology (NIST), Standard Reference Materials Group, 100 Bureau Dr., Gaithersburg, MD 20899, USA (301-975-6776) www.nist.gov

Oakwood Products, Inc., 1741 Old Dunbar Rd., West Columbia, SC 29172, USA (803-739-8800) www.oakwoodchemical.com

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, USA (814-353-1300) www.restekcorp.com

Sigma-Aldrich, P.O. Box 355, Milwaukee, WI 53201, USA (414-273-3850) www.sigma-aldrich.com

VICI Mat/Sen, 26272 Twelve Trees #C, Poulsbo, WA 98370, USA (360-697-9199) www.vici.com

VWR International, Inc., Goshen Corporate Park West, 1310 Goshen Parkway, West Chester, PA 19380, USA (610-431-1700) www.vwr.com

Zoex Corporation, 11665 Fuqua, Suite B 202, Houston, TX 77034, USA (281-484-2828) www.zoex.com

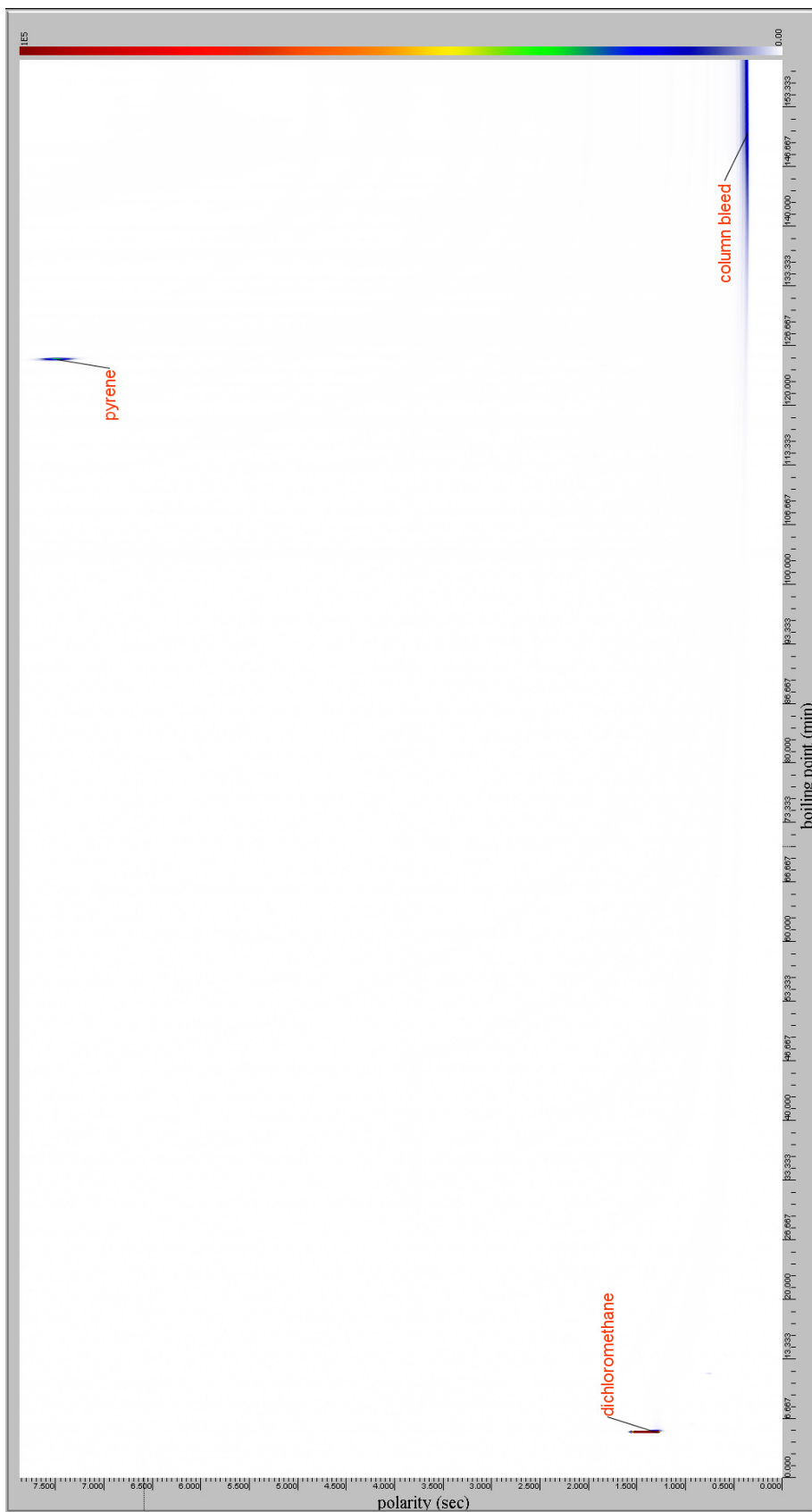


Figure 1
GCxGC two-dimensional image of Tune Check Solution (peak centered between 120 and 130 minutes on the x-axis and 7 and 8 seconds on the y-axis).

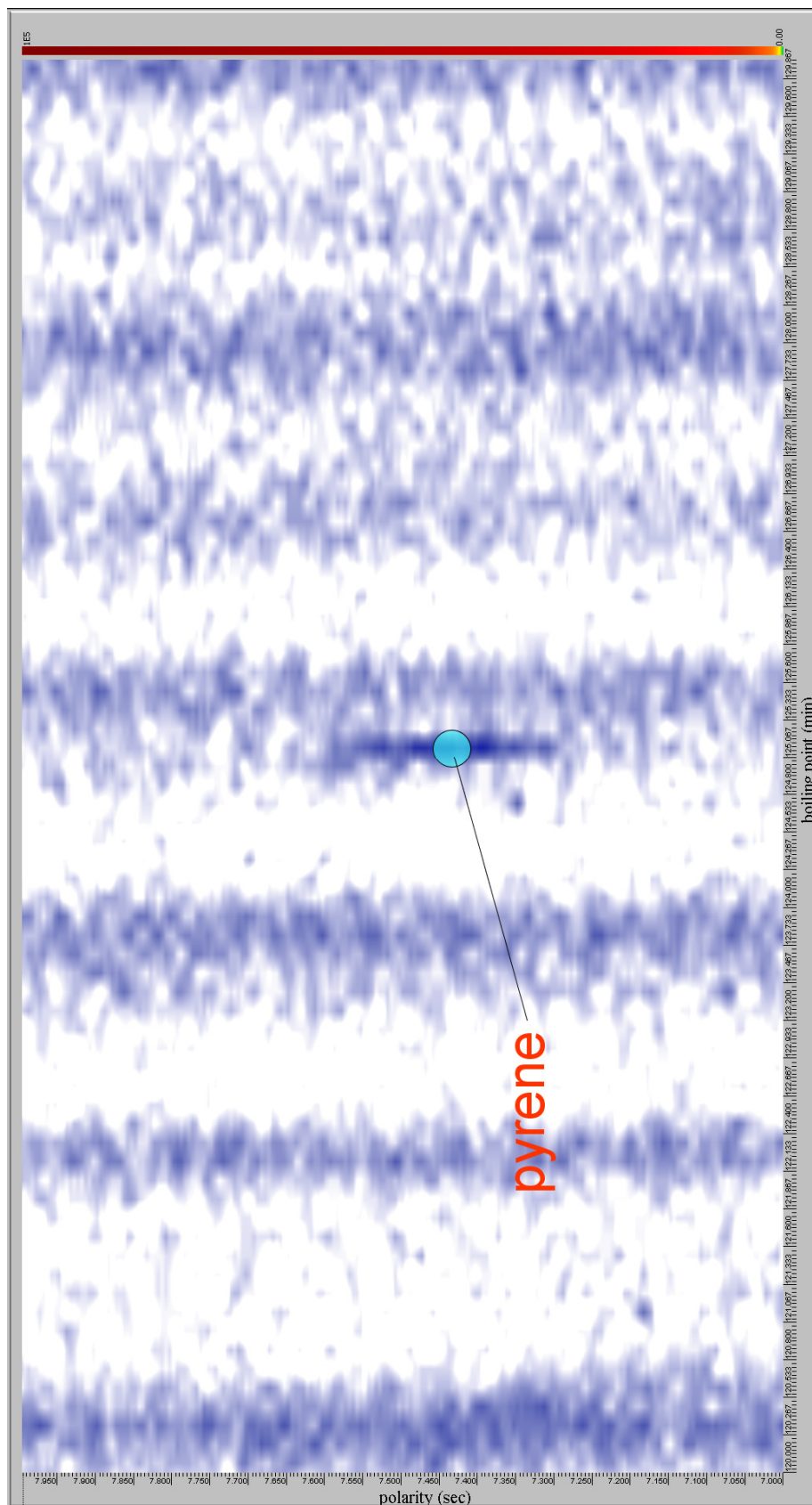


Figure 2
GCxGC two-dimensional image of Noise Filter Solution
(logarithmic color scale used in imaging)

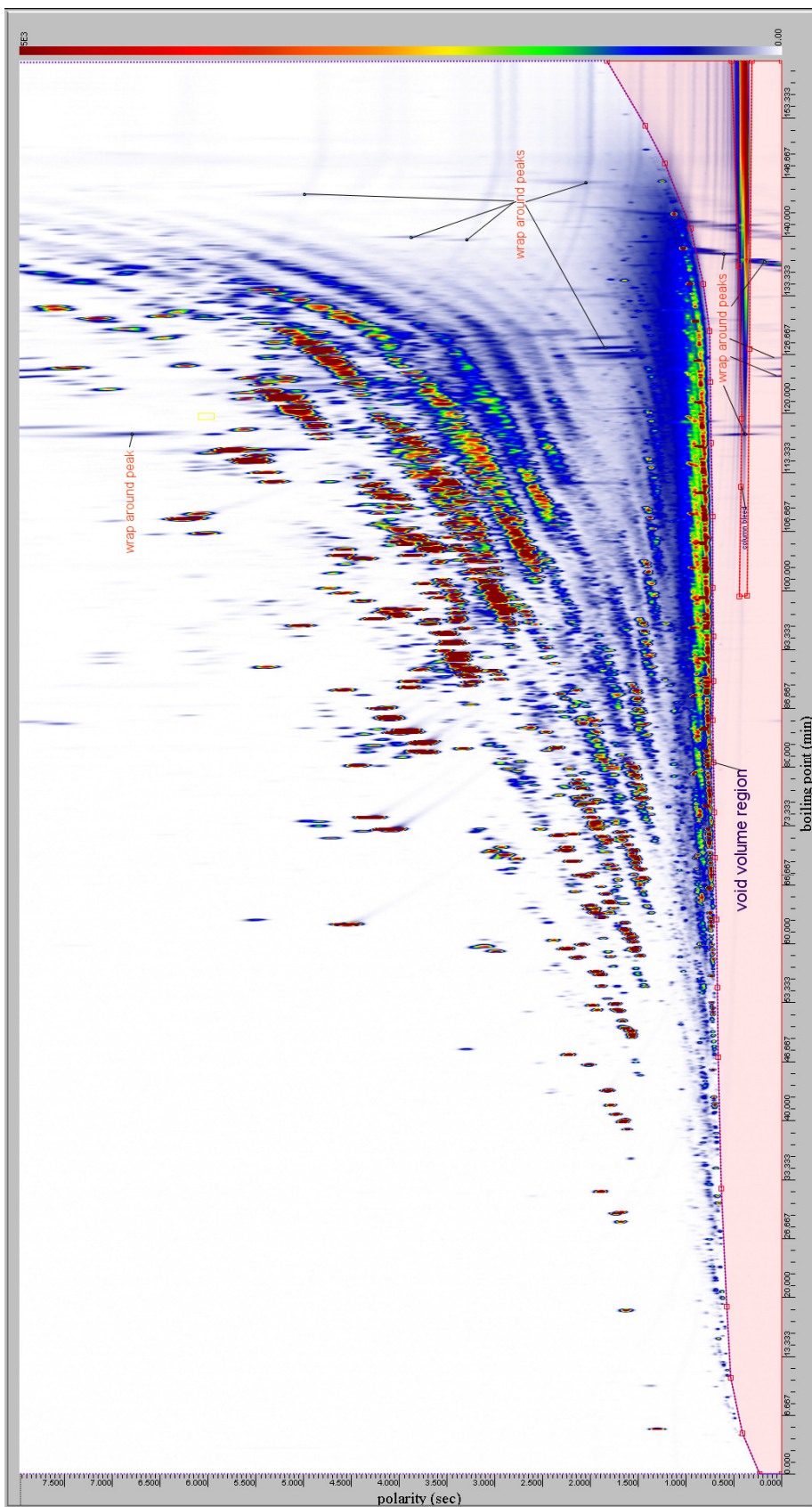


Figure 3
GCxGC two-dimensional image of a light cycle oil indicating secondary column
void volume region and some examples of wrapped around peaks

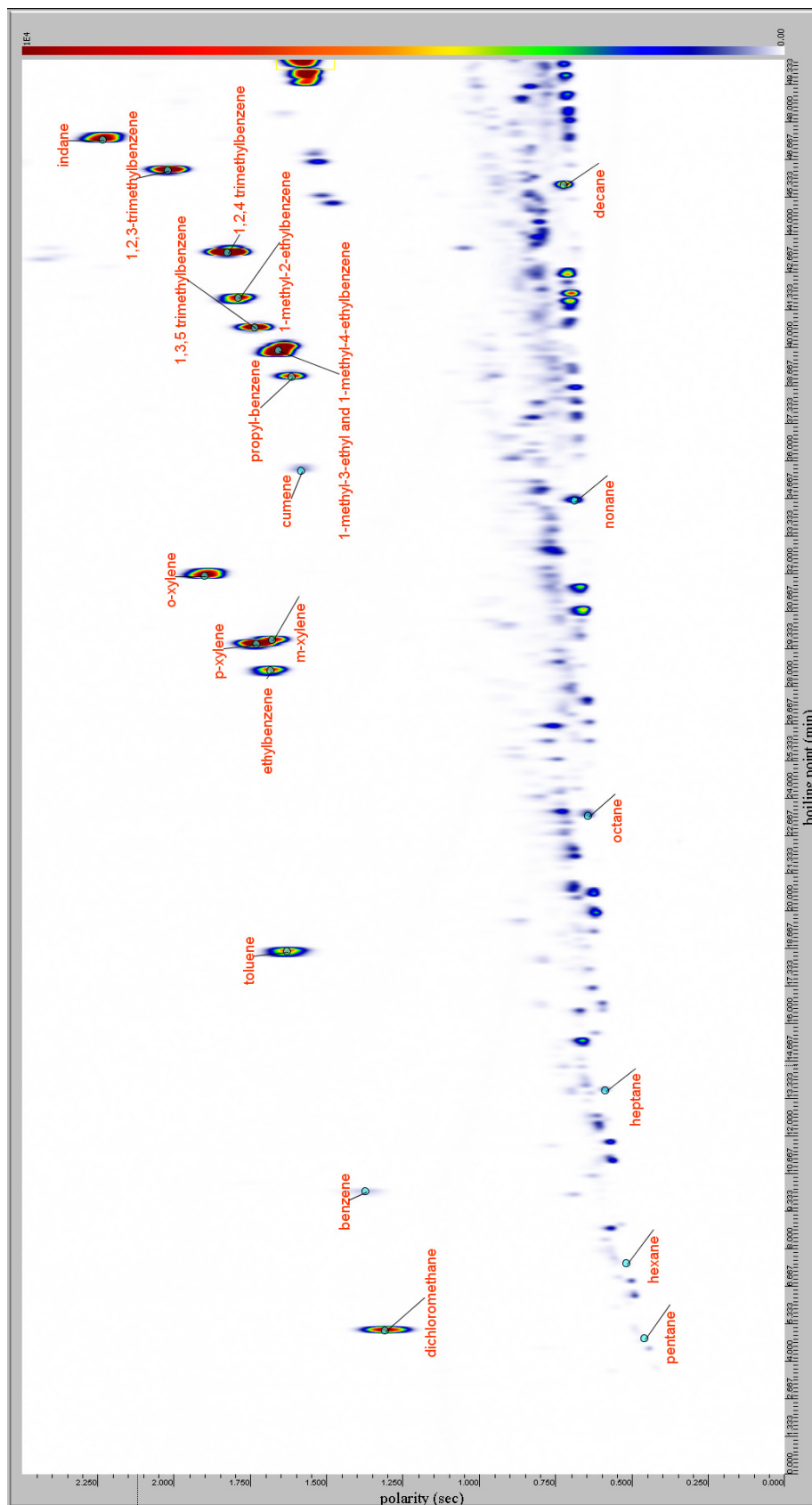


Figure 4
Magnified portion of a GCxGC two-dimensional image identifying
locations of landmark peaks in a Distillate Reference Material
 (The paraffins shown are normal paraffins.)

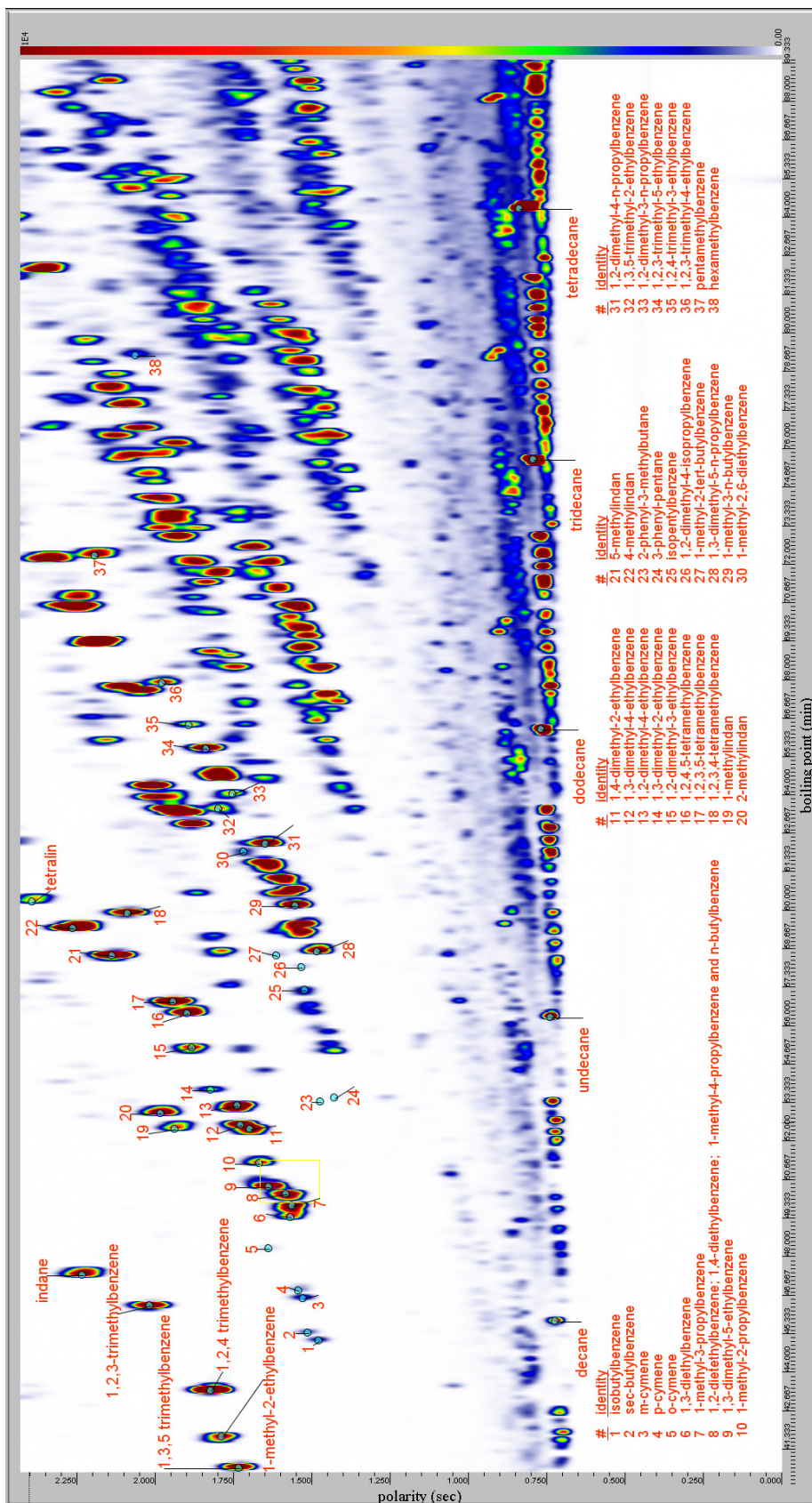


Figure 5
Magnified portion of a GCxGC two-dimensional image identifying locations
of landmark peaks in a Distillate Reference Material

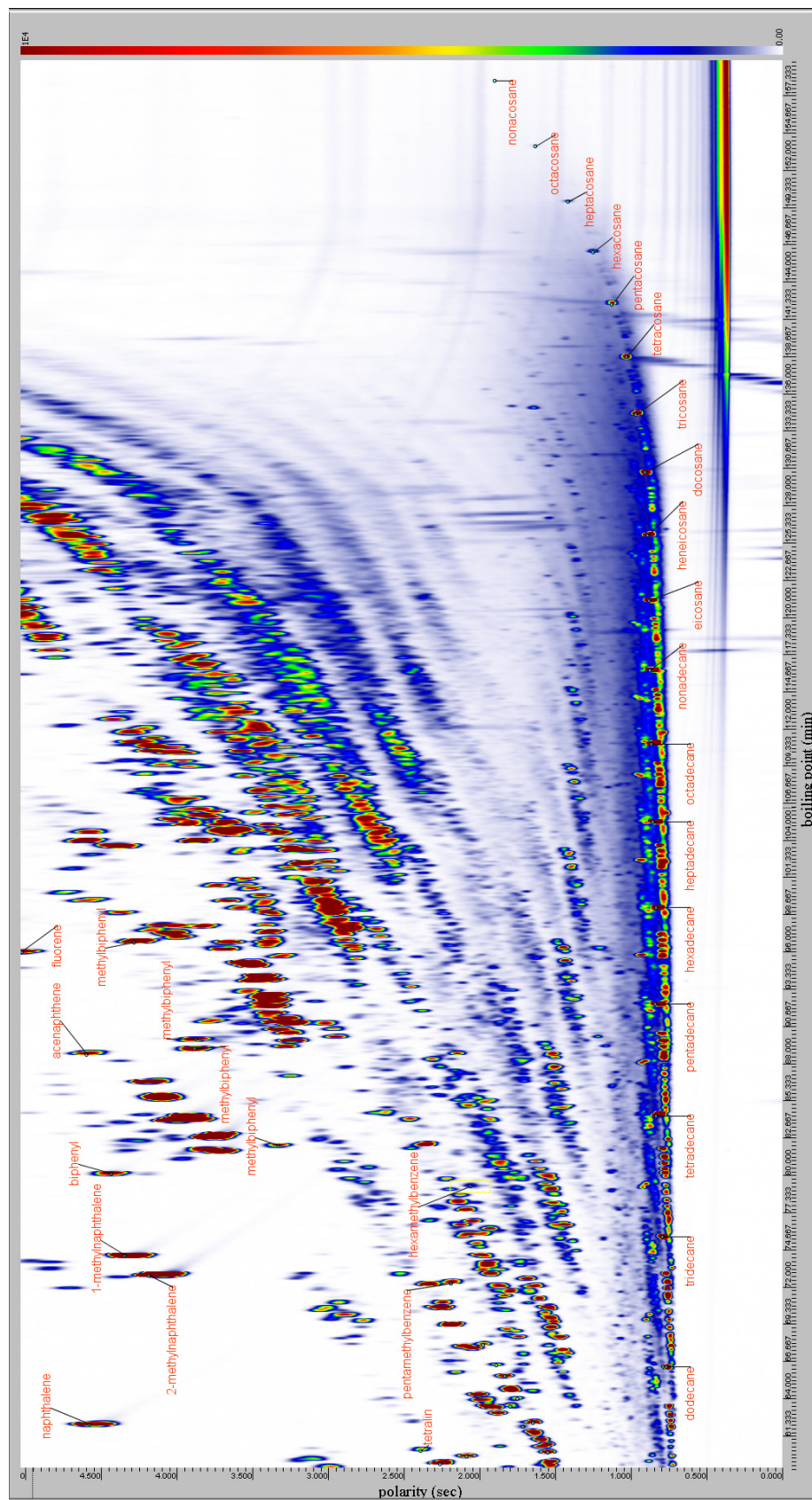


Figure 6
Magnified portion of a GCxGC two-dimensional image identifying locations of landmark peaks in a Distillate Reference Material

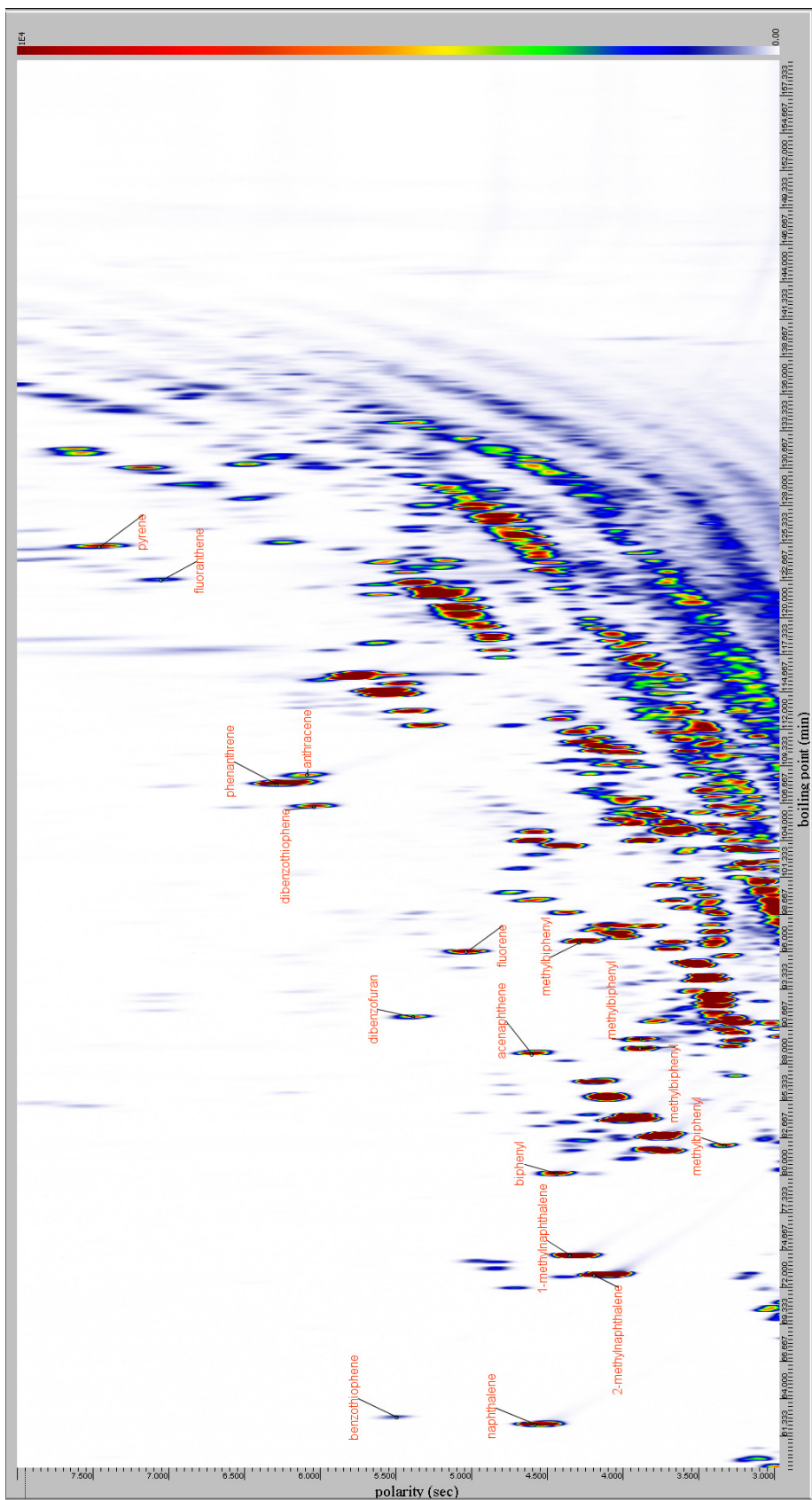


Figure 7
Magnified portion of a GCxGC two-dimensional image identifying
locations of landmark peaks in a Distillate Reference Material

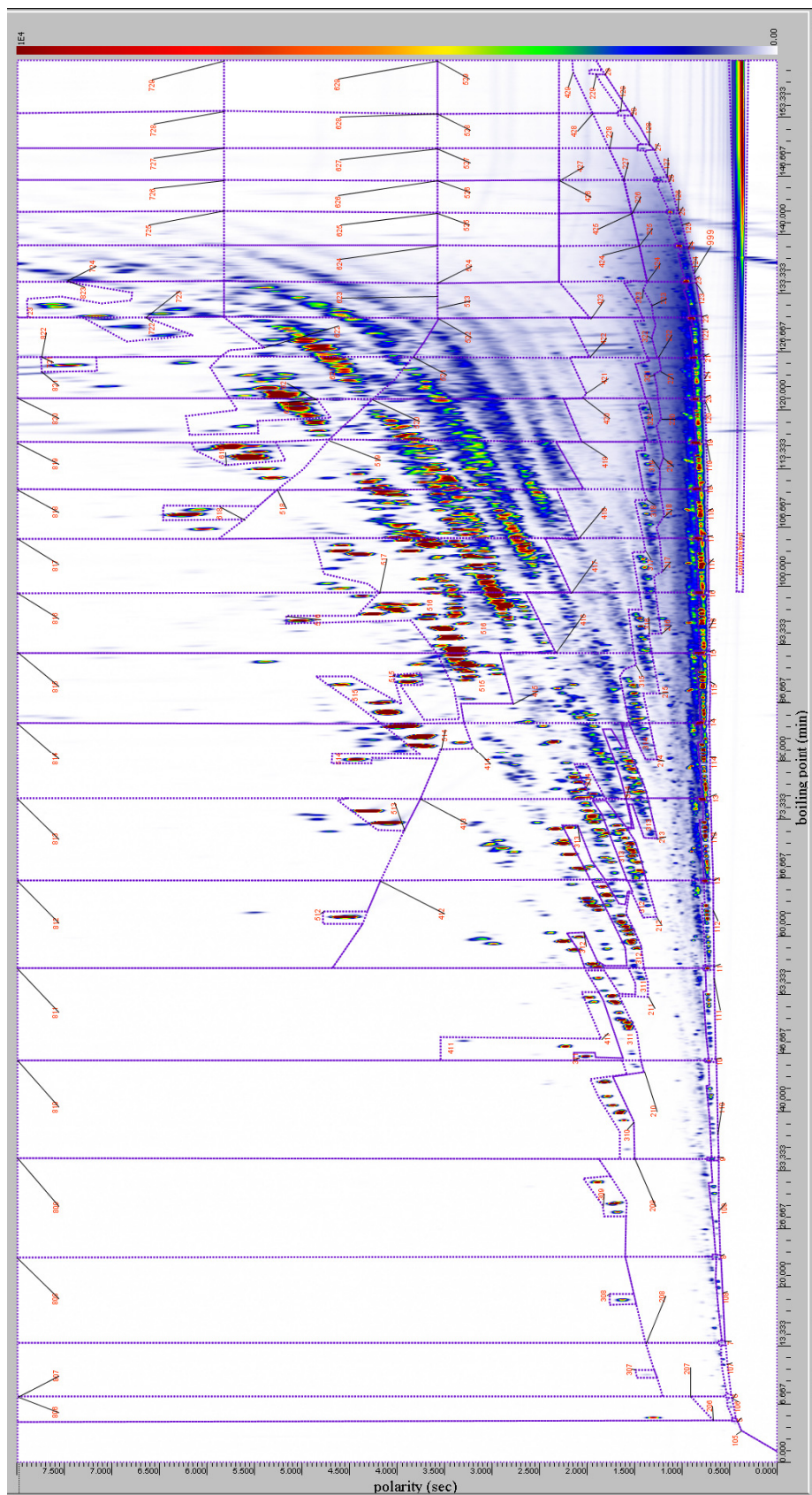


Figure 8
GCxGC two-dimensional templated image of a Distillate Reference
Material with molecular types indexed to n-alkanes

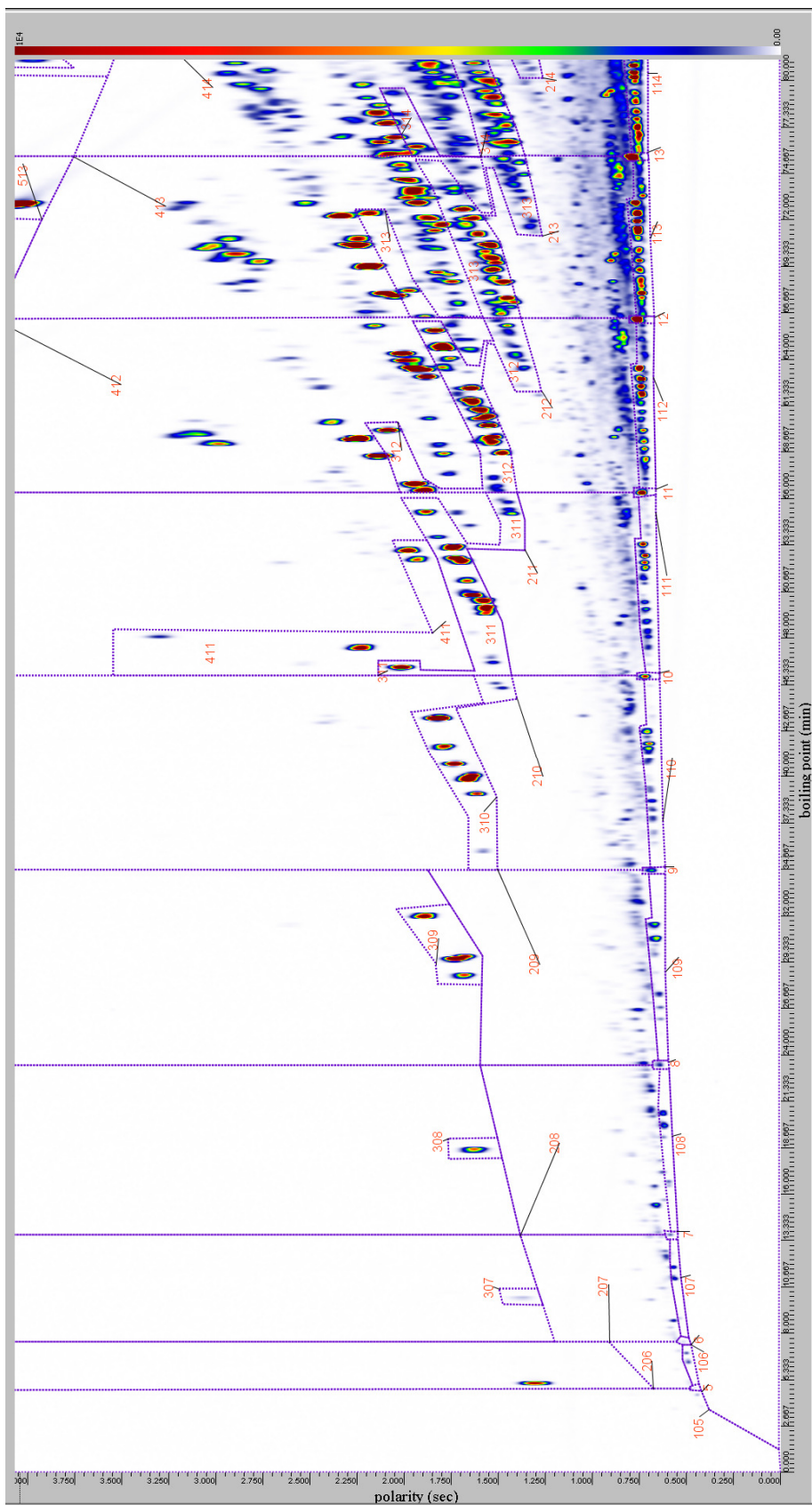


Figure 9
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material with molecular types indexed to n-alkanes

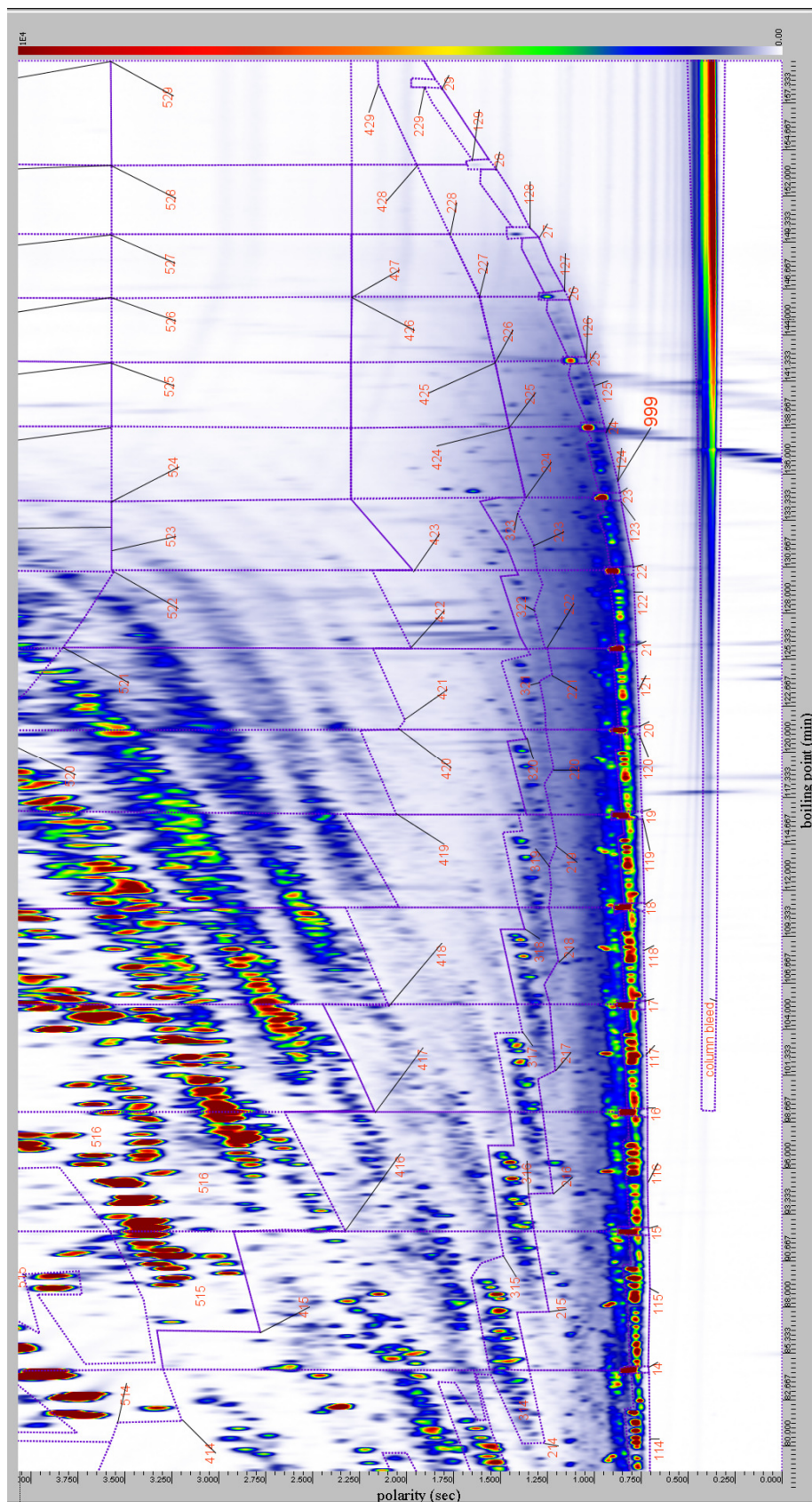


Figure 10
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material with molecular types indexed to n-alkanes

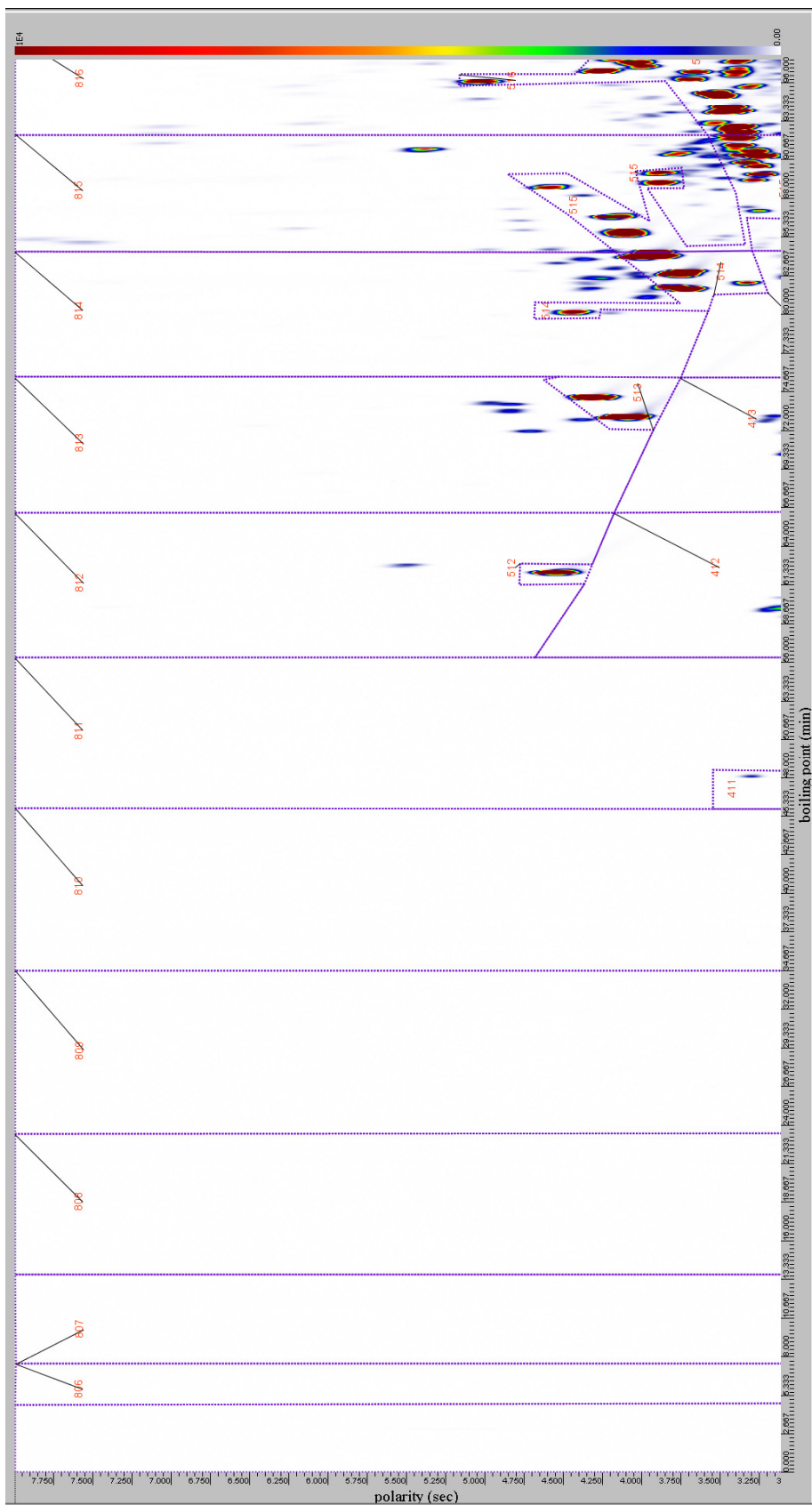
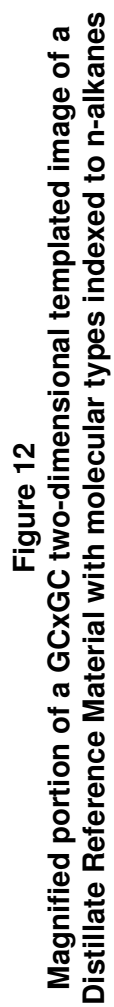
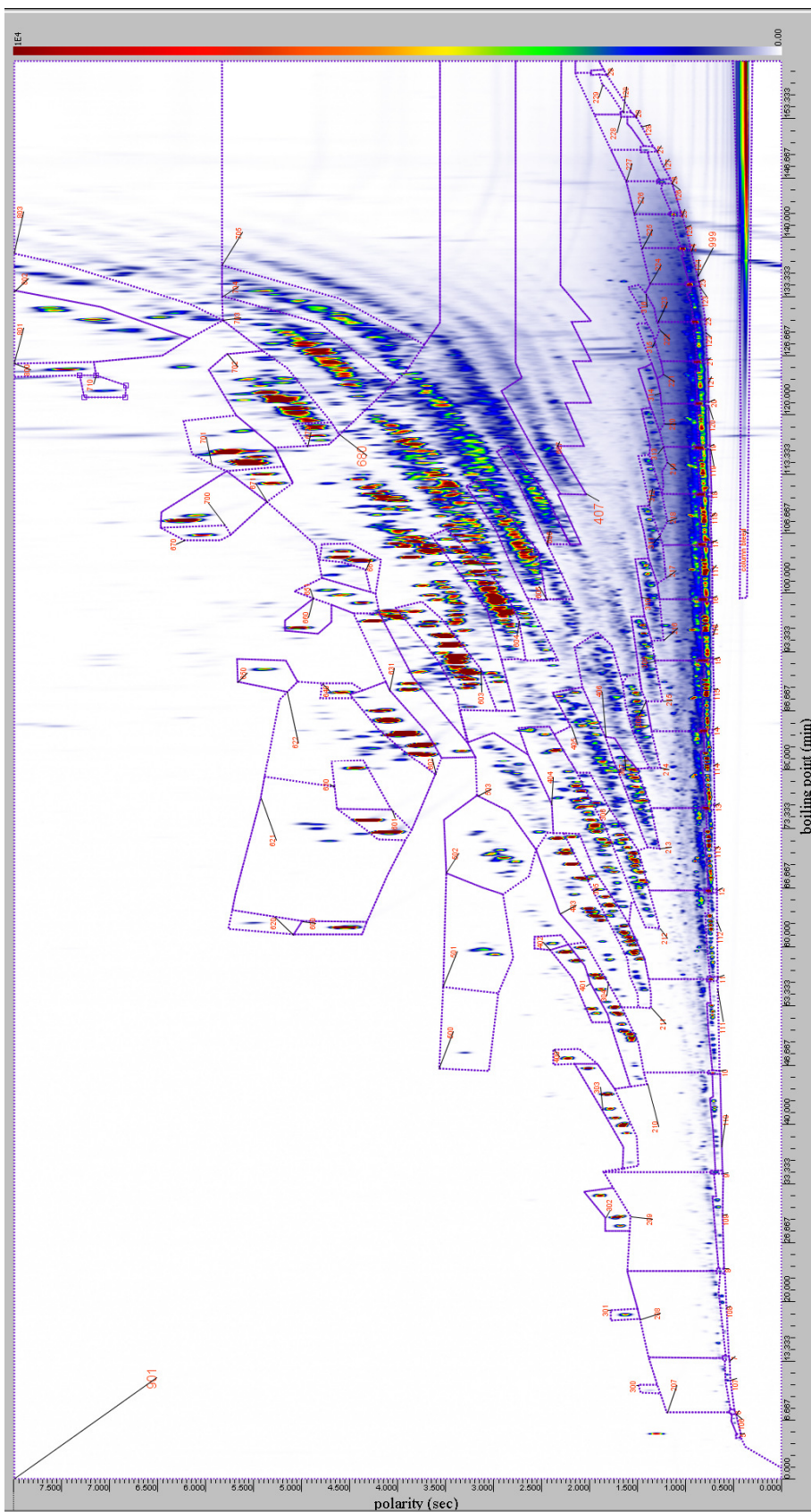


Figure 11
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material with molecular types indexed to n-alkanes





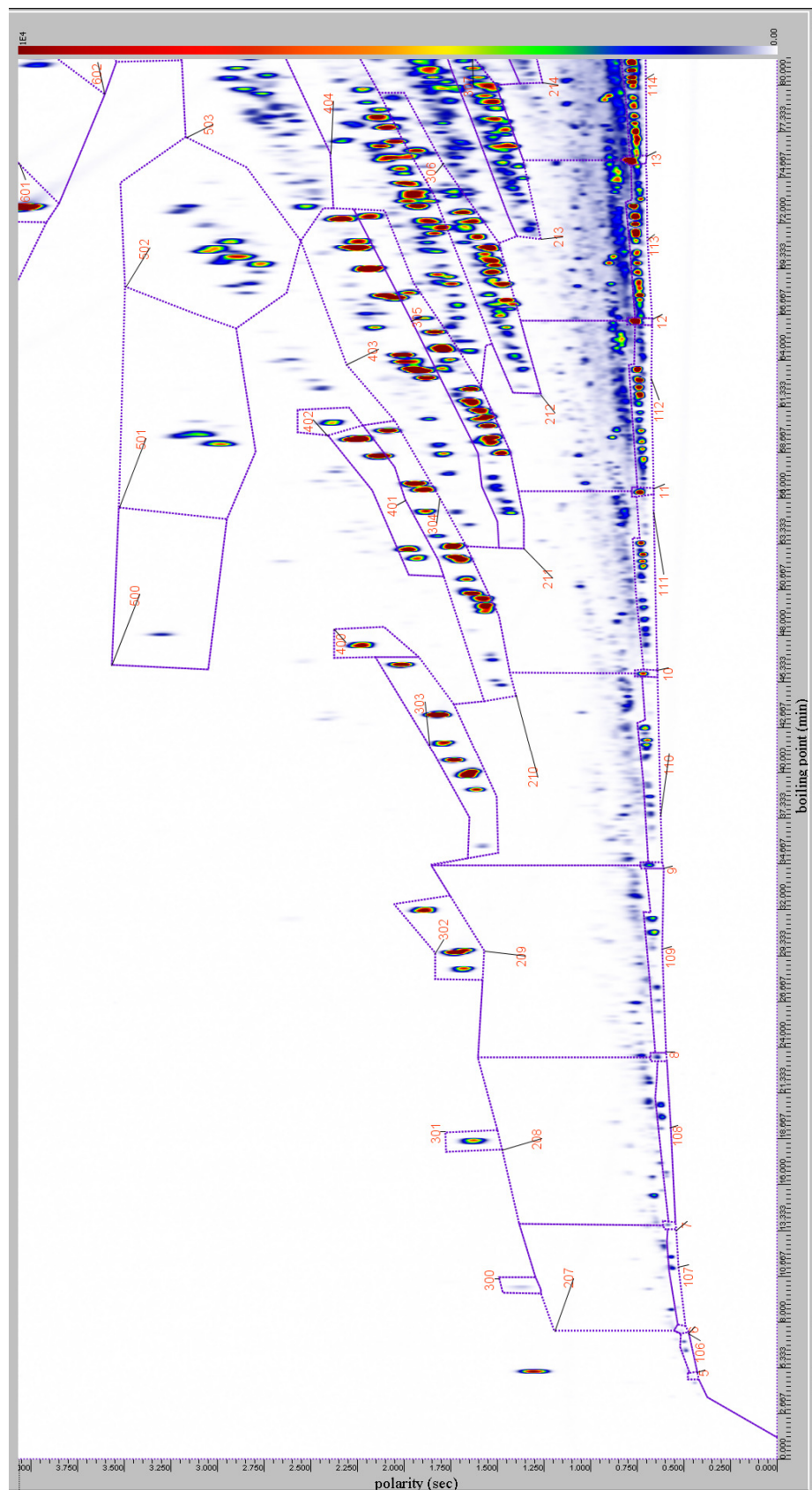


Figure 14
Magnified portion of a GCxGC two-dimensional templated image of a Distillate Reference
Material with homologous series of molecular types identified by carbon number

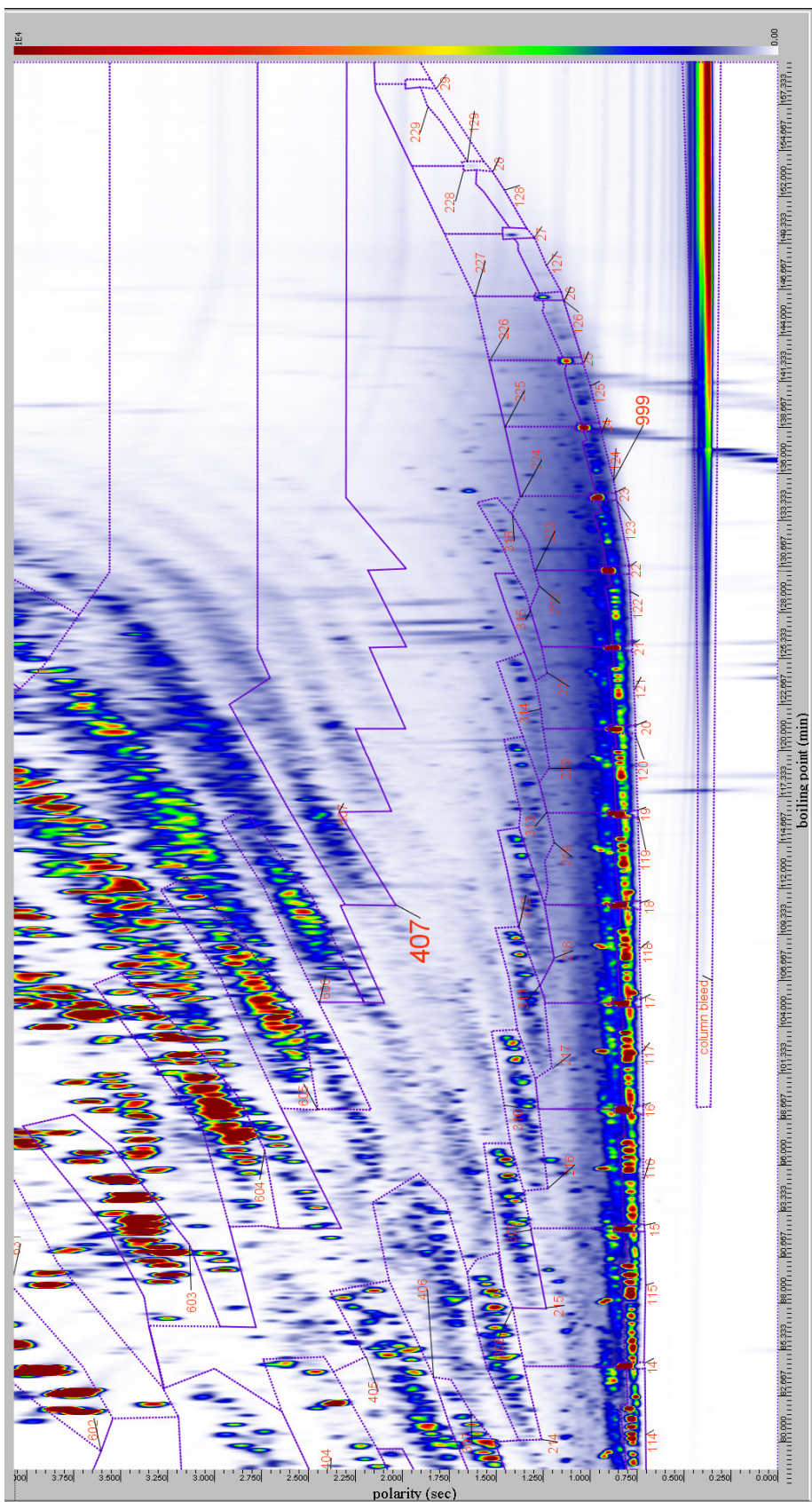


Figure 15
Magnified portion of a GCxGC two-dimensional templated image of a Distillate Reference
Material with homologous series of molecular types identified by carbon number

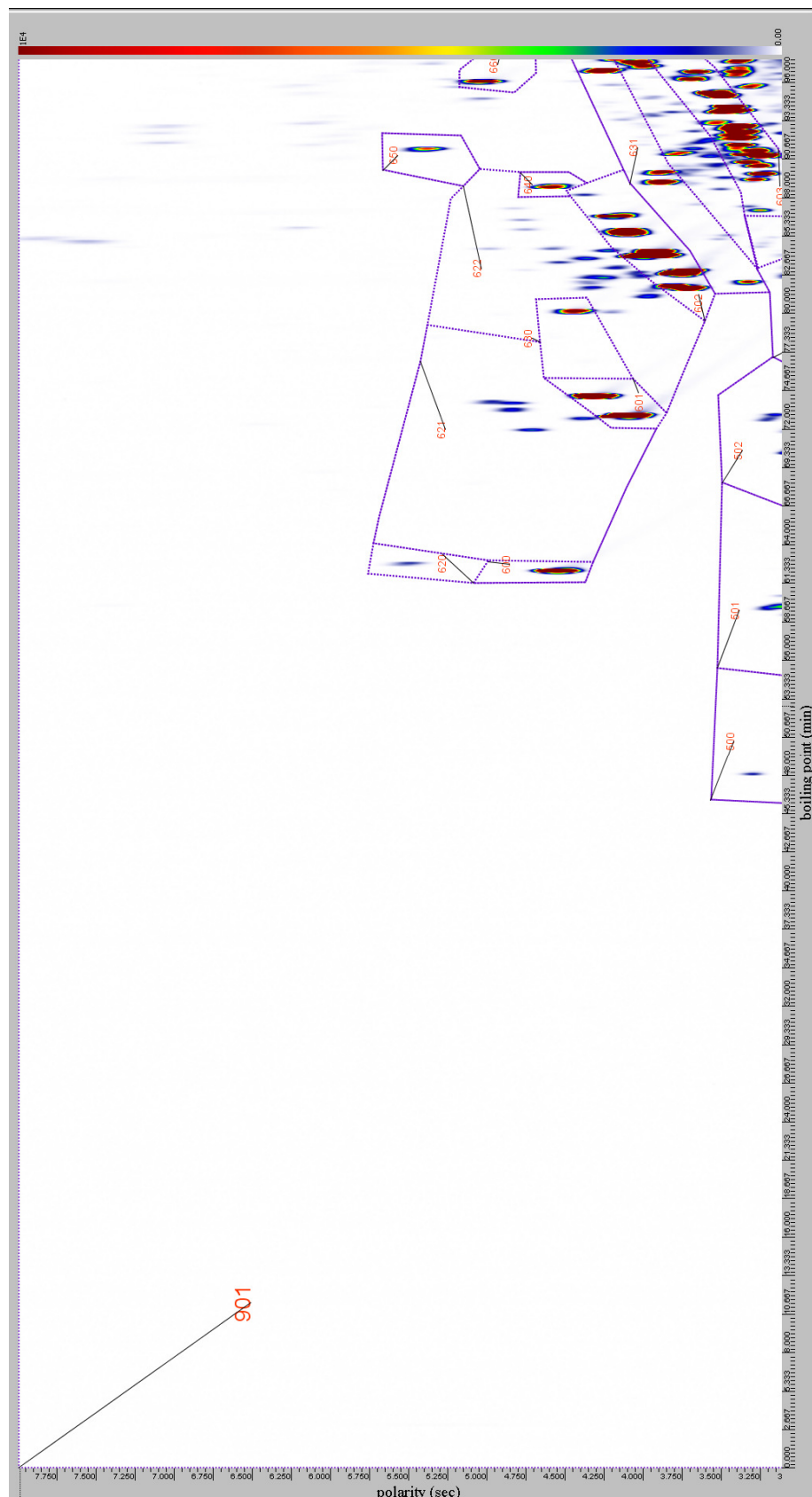


Figure 16
Magnified portion of a GCxGC two-dimensional templated image of a Distillate Reference
Material with homologous series of molecular types identified by carbon number

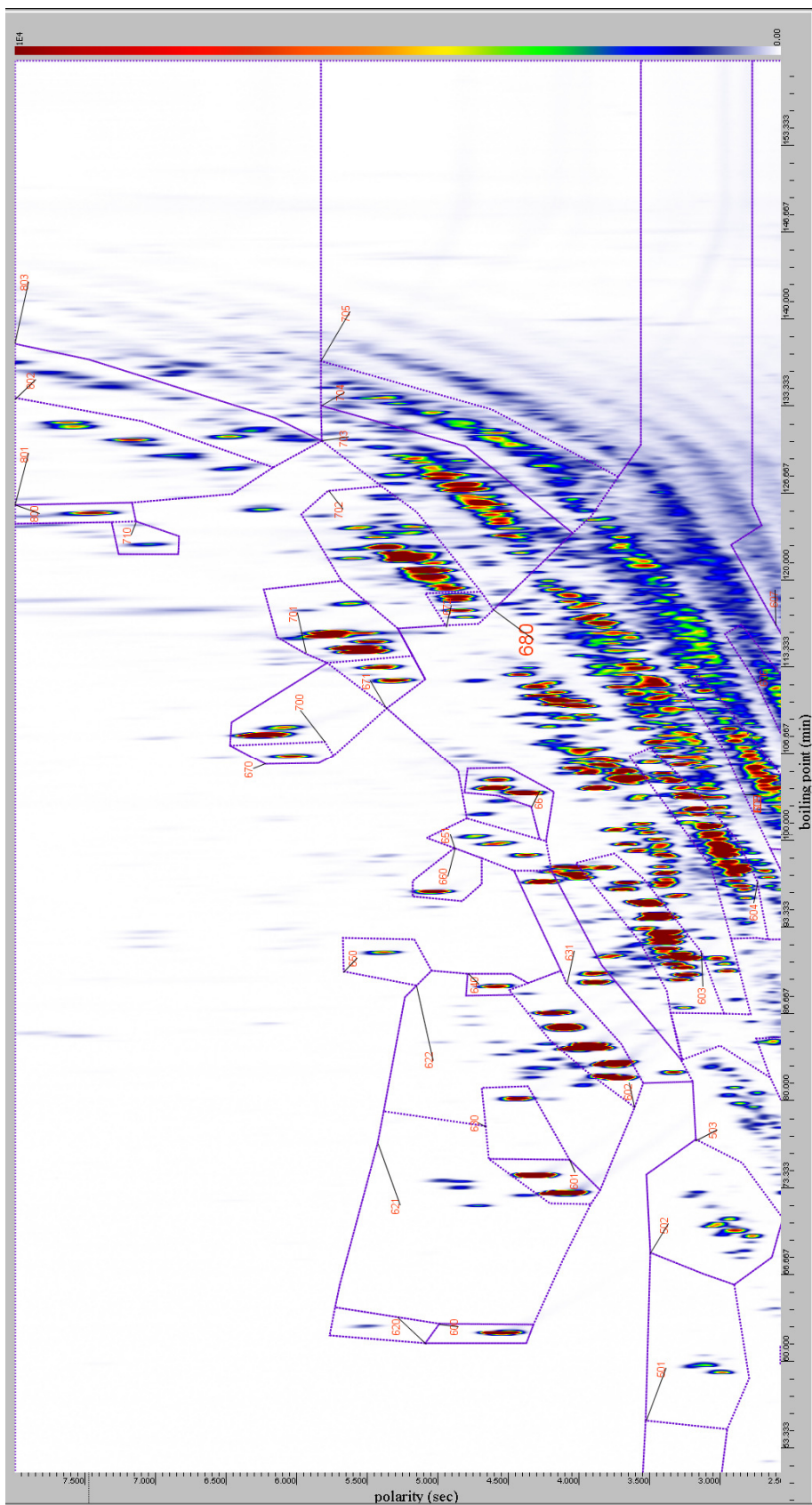


Figure 17
Magnified portion of a GCxGC two-dimensional templated image of a Distillate Reference
Material with homologous series of molecular types identified by carbon number

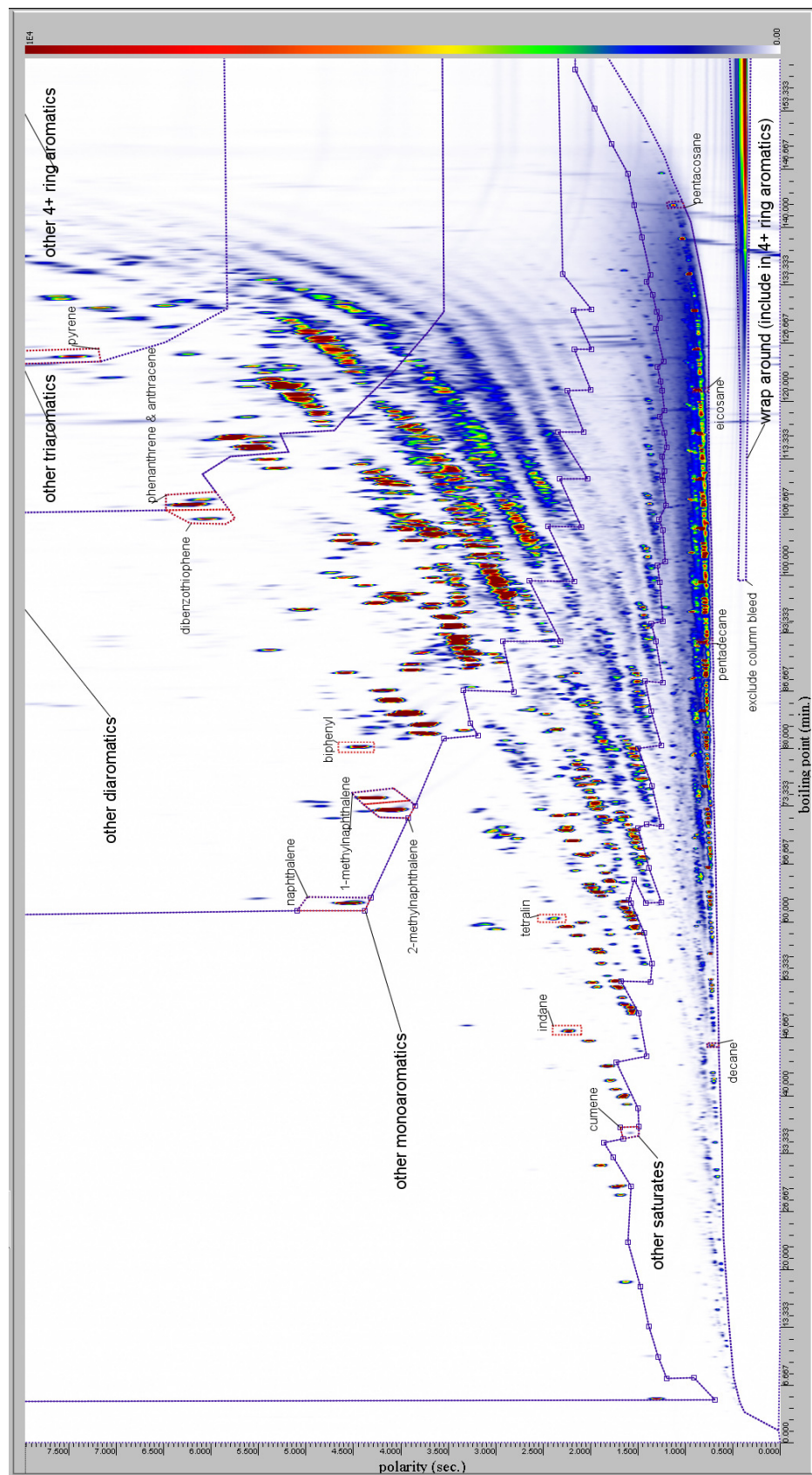


Figure 18
GCxGC two-dimensional templated image of a Distillate Reference Material
for Quality Control or System Suitability

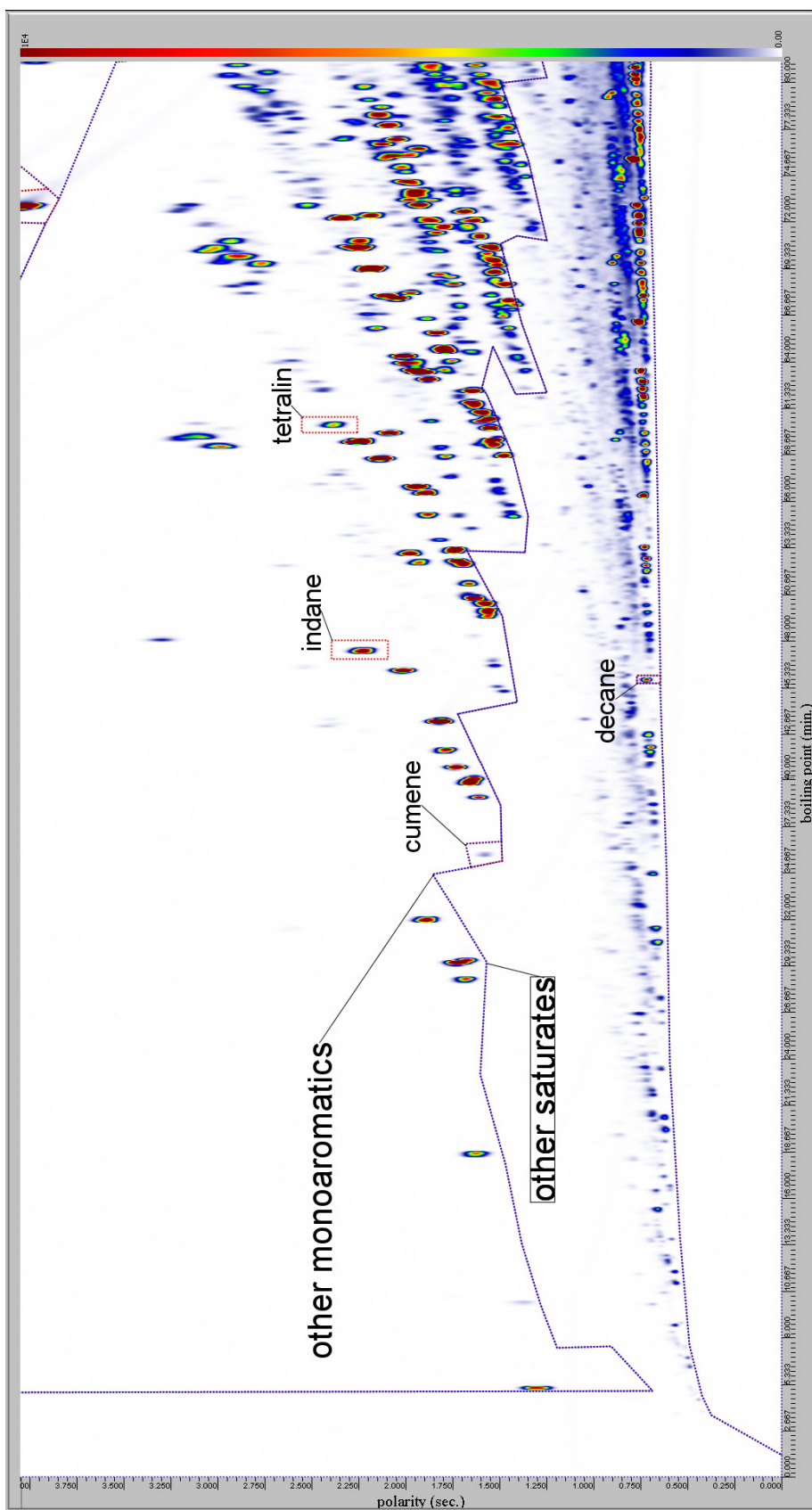


Figure 19
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material for Quality Control or System Suitability

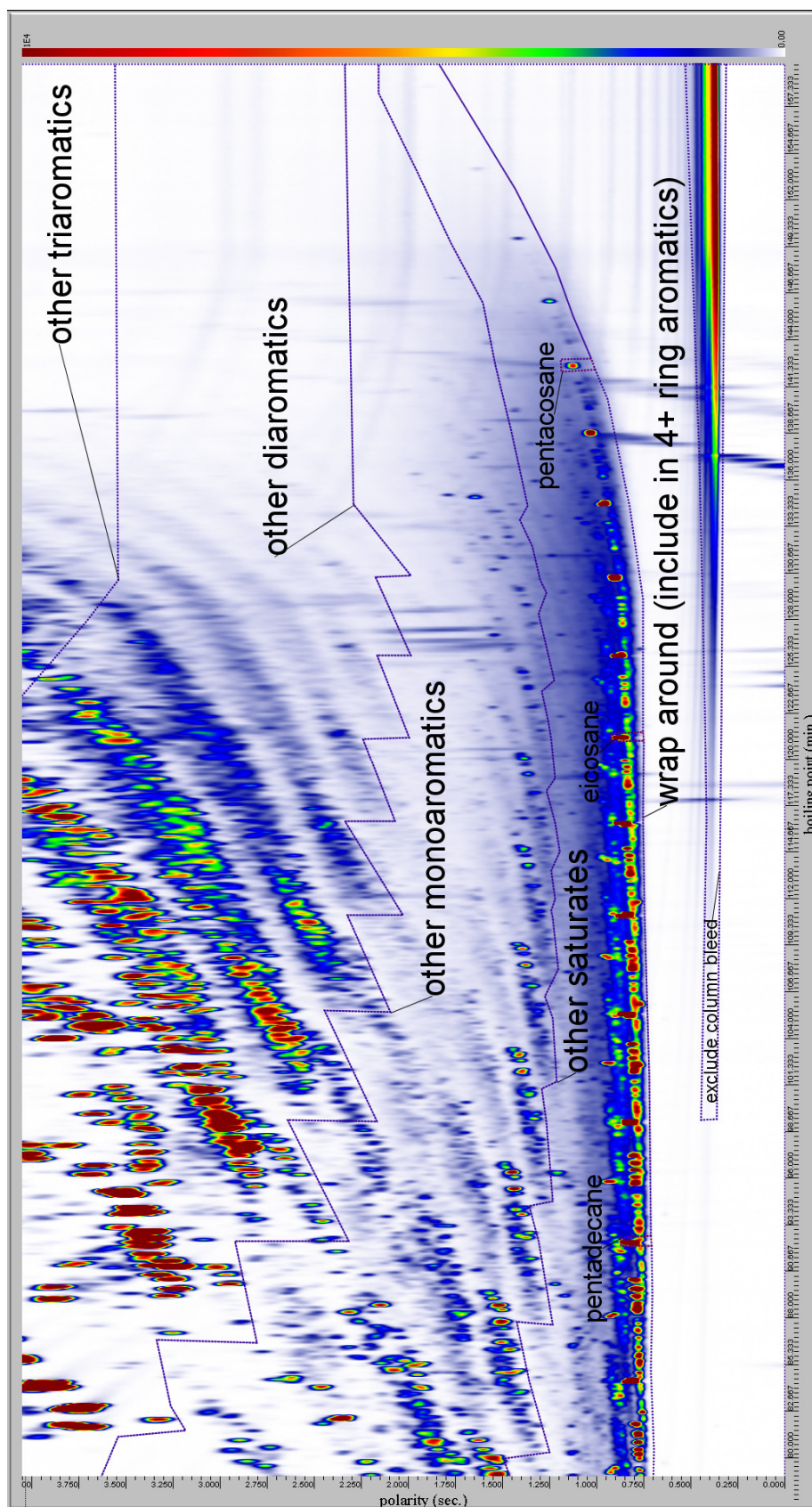


Figure 20
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material for Quality Control or System Suitability

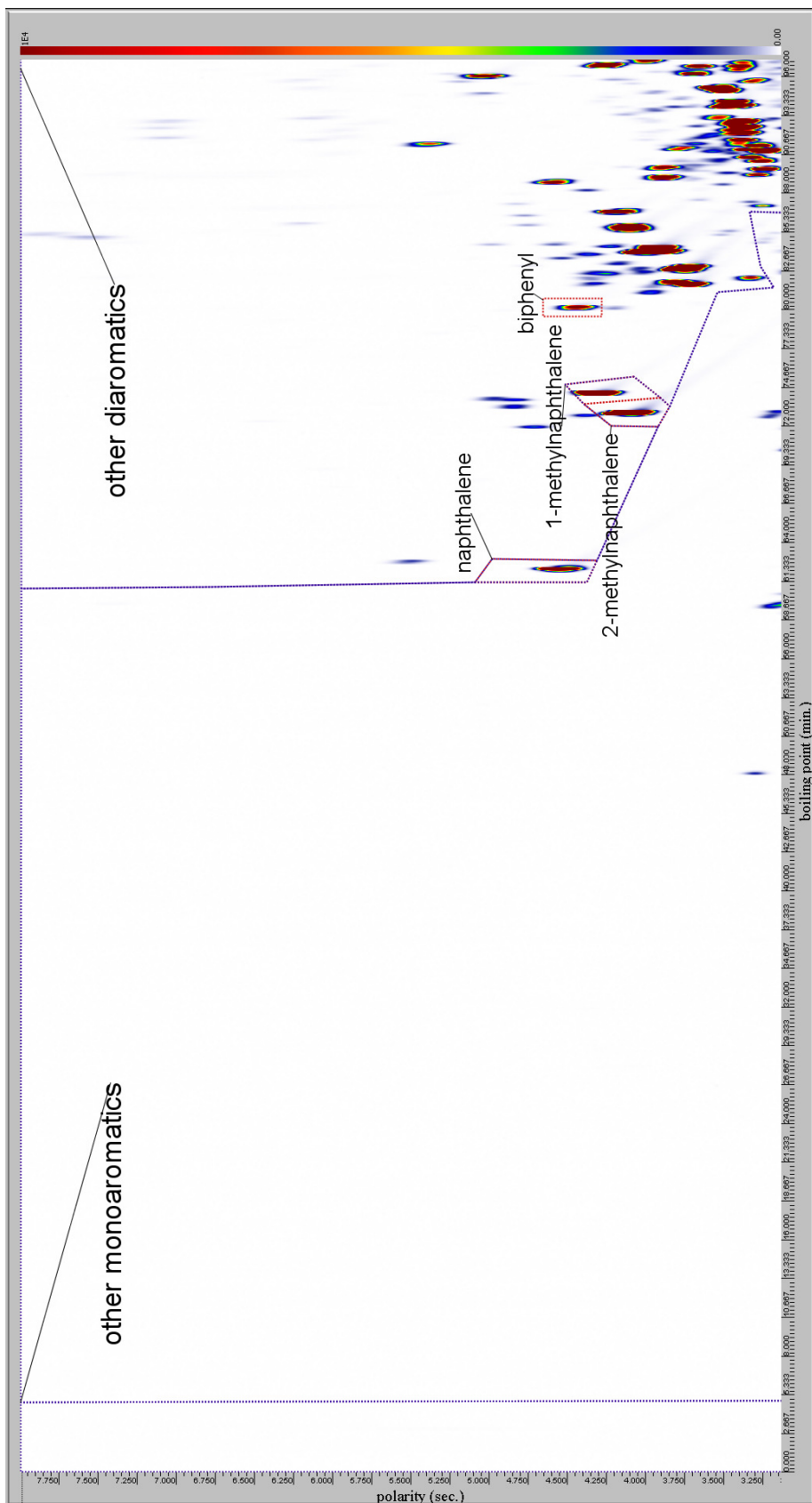


Figure 21
Magnified portion of a GCxGC two-dimensional templated image of a
Distillate Reference Material for Quality Control or System Suitability

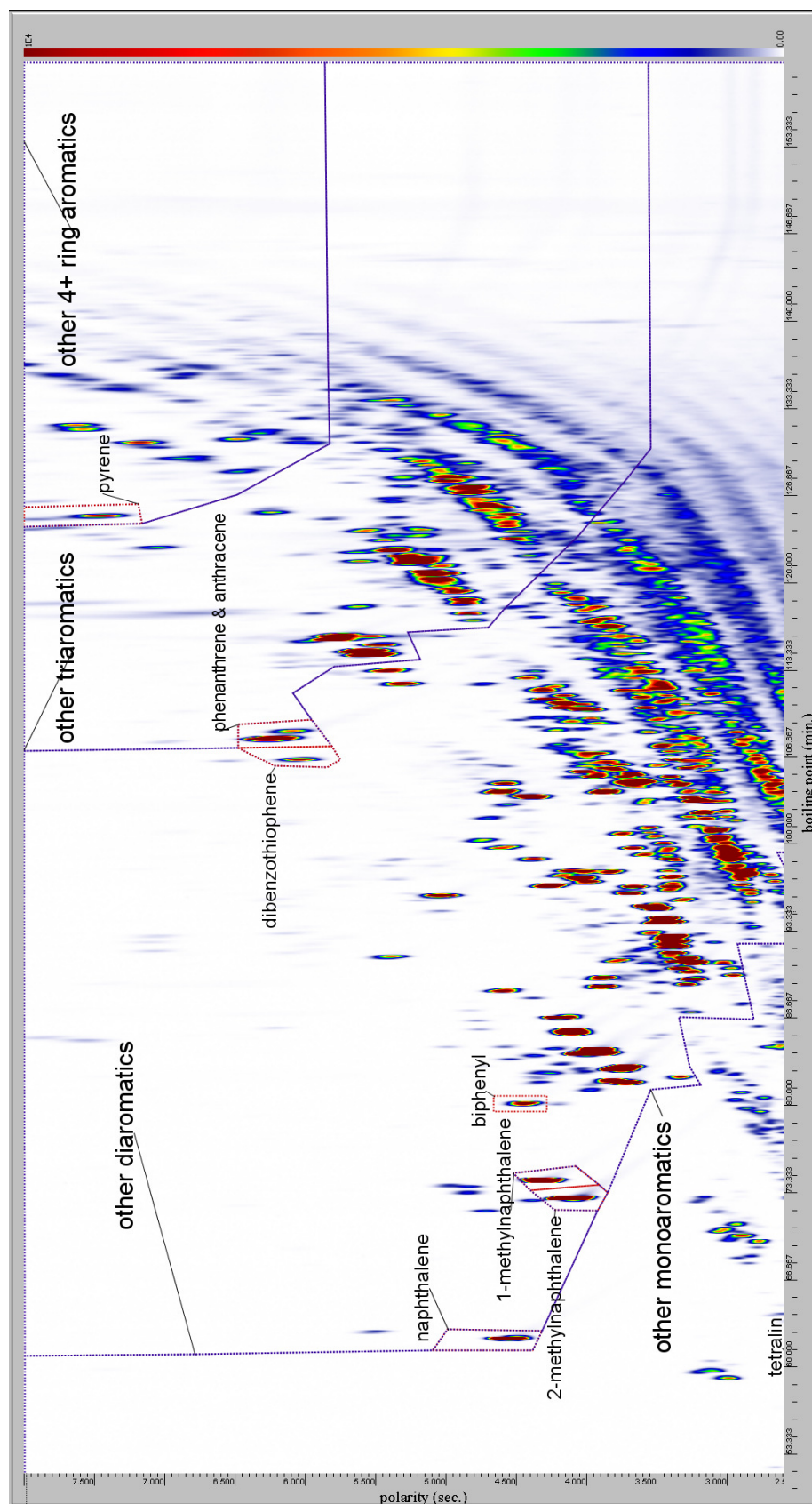


Figure 22
Magnified portion of a GCxGC two-dimensional templated image of a Distillate
Reference Material for Quality Control or System Suitability

Appendix A

Preparation of GCxGC Fused Silica Column Set (Zoex Two-Stage Thermal “Loop Modulator” System)

1. Install the primary column cage onto the GC oven column hanger.
2. On one end of the primary GC column, install a column nut and ferrule. On this same end, cut off a small portion (approximately 1 cm) of the column to ensure that the end is square cut, free of burrs, jagged edges, and/or loose particles of column, stationary phase, and/or material from the sealing ferrule. Install this end into the GC oven injection port. Leave the other column end free until Step 8 of this procedure (*Appendix A*).
 - See Agilent 7890 Operating Manual for proper installation of capillary column into the injection port.
3. Cut a 180-cm length of secondary fused silica column. Select one side as the column inlet.
 - The column length measurements in Steps 3 and 4 of this procedure (*Appendix A*) provide for an additional 1 cm each, at both ends, to make fresh cuts prior to installation.
4. Mark the secondary fused silica column with typewriter correction fluid at two separate points indicating both: 32- and 127-cm lengths from the selected column inlet.
5. Insert the secondary fused silica column into the column holder with the 32-cm marking positioned at the “inlet end” corner edge of the column holder (see Figure A1.)

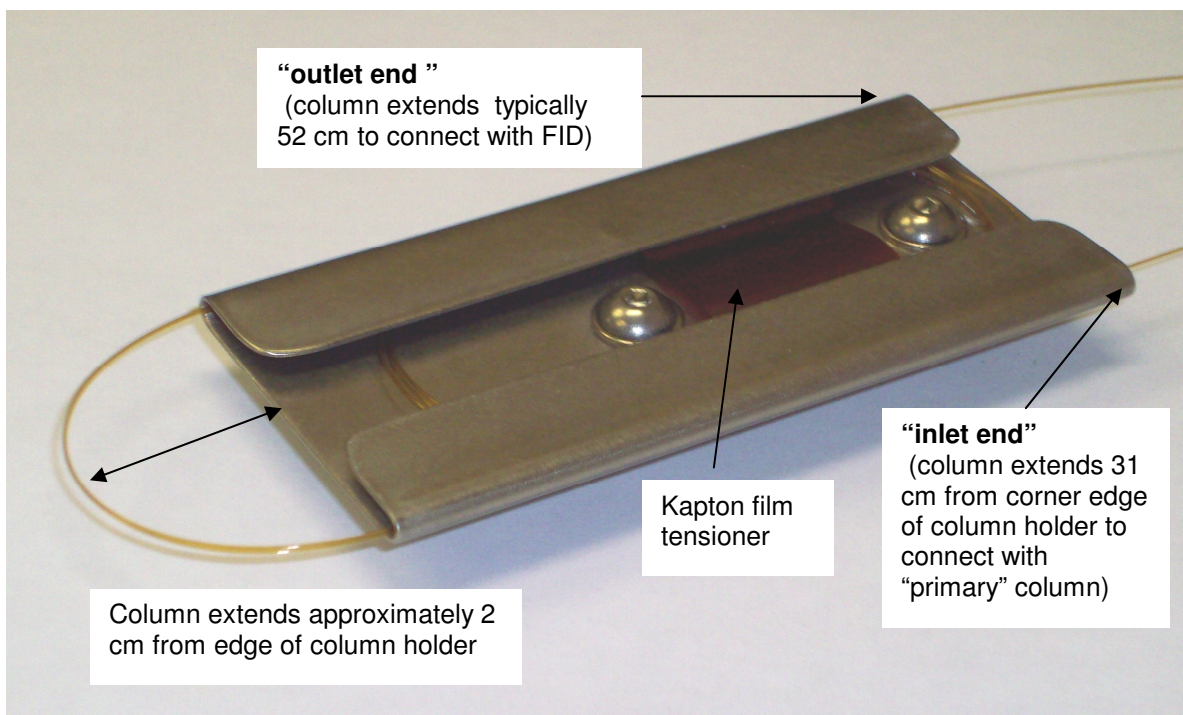


Figure A1. Column Holder (facing bottom)

6. Loop the following 95-cm of column 5 times inside the column holder as shown in Figure A1. The 1st and 5th loop must extend approximately 2 cm outside the column holder as shown. The 127-cm marking should be positioned at the “outlet end”, corner edge of the column holder (opposite of the “inlet end”). Install the Kapton film tensioner and adjust as necessary to keep the column in place.

7. Install the column holder into the modulator assembly.
 - Zoex Technical Note KT030606-1 illustrates the proper alignment of the column holder in the Loop Modulator assembly.
8. Connect the outlet side of the primary fused silica column with a zero-dead-volume ultimate union to the inlet side of the secondary fused silica column, cutting off approximately 1 cm of the end of each column as described in Step 2, above. Ensure that the secondary column is suspended in the column oven in a manner that it does not touch any hot surfaces of the oven.
 - See Agilent Ultimate Union Kit instructions for proper connection of GC columns to the Agilent zero-dead-volume ultimate union.
9. On the outlet side of the secondary GC column, install a column nut and ferrule. On this same end, cut a small portion (approximately 1 cm) to ensure that the column end is square cut, free of burrs, jagged edges, and/or loose particles of column, stationary phase, and/or material from the sealing ferrule. Install this end into the FID inlet.
 - See Agilent 7890 Operating Manual for proper installation of capillary column into the FID.

Appendix B

Preparation of GCxGC Fused Silica Column Set (LECO Two-Stage Thermal Modulator System)

1. Install the primary column cage onto the GC oven column hanger.
2. On one end of the primary GC column, install a column nut and ferrule. On the same end, cut a small portion (approximately 1 cm) to ensure that the column end is square cut, free of burrs, jagged edges, and/or loose particles of column, stationary phase, and/or material from the sealing ferrule. Install this end into the GC oven injection port. Leave the other column end free until Step 13 of this procedure (*Preparation of GCxGC Fused Silica Column Set, LECO Two-Stage Thermal Modulator System*).
 - See Agilent 7890 Operating Manual for proper installation of capillary column into the injection port.
3. Remove the cover on the GC secondary oven by turning the cover counterclockwise.
4. Remove the modulator cover by loosening the thumbscrew of the modulator and pulling the cover straight out from the modulator. Undo the latch that holds the SGE union fitting in the modulator.
 - The latch is a small tab located on the bottom of the modulator which swings out toward the oven door.
5. Cut a 190-cm length of the secondary GC column. Select one end as the outlet end.
 - The column length measurement provides for an additional 1 cm each, at both ends, to make fresh cuts prior to installation. The ends must be cut after pre-installing column nuts and ferrules.
6. Feed the outlet end of the secondary GC column through the SGE union fitting, allowing a short length (approximately 1 cm) of the column to extend through the SGE union fitting. Insert the SGE union fitting into the opening at the bottom of the modulator. Close the latch on the modulator to secure the SGE union fitting.
 - The LECO Chroma-TOF™ Instruction Manual provides figures to aid in the installation of the secondary GC column.
7. Carefully feed the secondary GC column through the modulator and into the secondary oven leaving an 8-cm length of the secondary GC column just outside the inlet to the modulator.
8. Carefully guide approximately 16 cm of the outlet end of the secondary GC column through the outlet of the secondary oven.
9. Carefully wind the remaining middle of the secondary GC column in a counterclockwise motion and place in the secondary oven. If the last full turn is not possible, pull gently on the outlet end of the secondary GC column to remove excess.
10. Replace the cover on the modulator.
11. Replace the cover on the secondary oven but do not over tighten. At the first indication of resistance, stop turning the cover.
12. On the outlet side of the secondary GC column install a column nut and ferrule. On this same end, cut a small portion (approximately 1 cm) to ensure that the column end is square cut, free of burrs, jagged edges, and/or loose particles of column, stationary phase, and/or material from the sealing ferrule. Install this end into the FID inlet.
 - Follow the Manufacturer's recommended instructions for proper connection of the capillary column to the FID.

13. Connect the inlet side of the secondary GC column with a zero-dead-volume ultimate union to the outlet side of the primary GC column, cutting off approximately 1 cm of the end of each column as described in Step 2, above. It is important to make the connection between the primary and secondary GC columns last because this will minimize the twist in the secondary GC column.
 - See Agilent instructions for proper connection of GC columns to the Agilent zero-dead-volume ultimate union.
14. Make certain that no column sections touch the walls of the GC oven, the modulator, or the outside of the secondary oven.

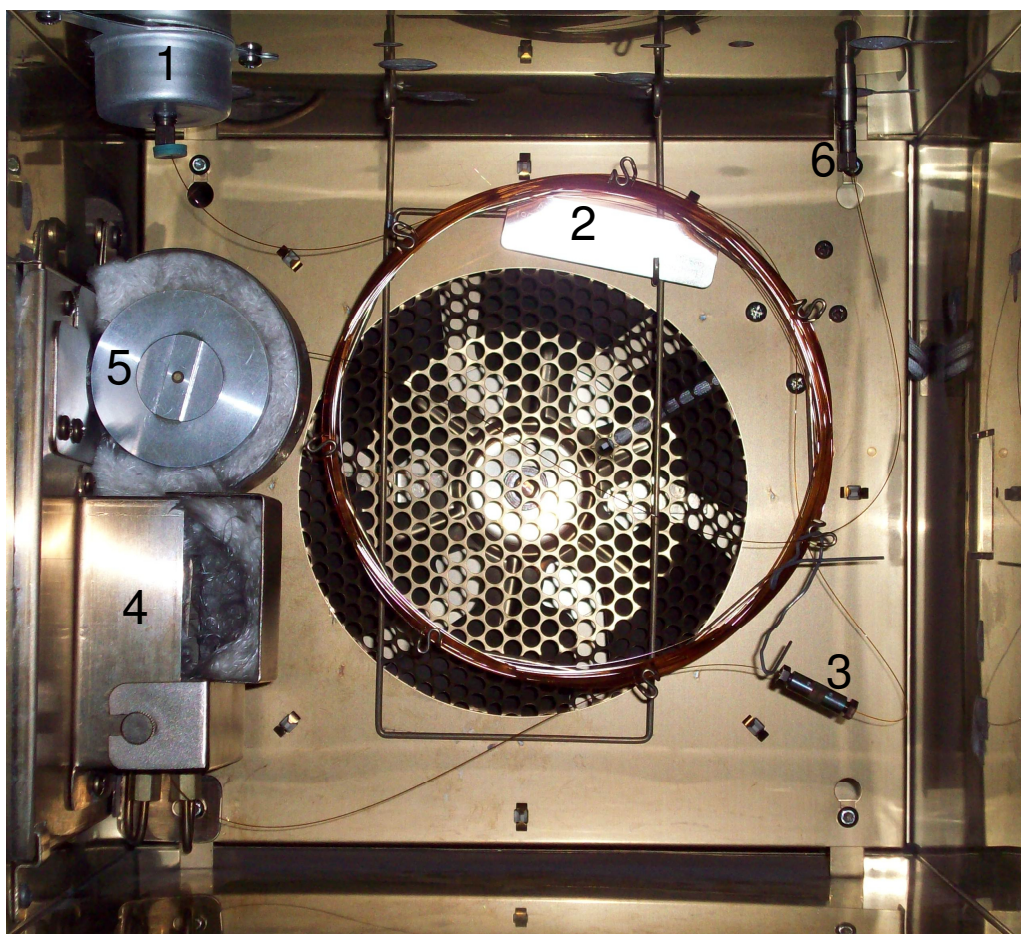


Figure B1
Inside LECO GCxGC-FID SSL GC Oven

Inside of the instrument oven, showing GCxGC components and connections: (1) GC inlet, (2) Primary GC column, (3) Press fit connection between primary and secondary GC columns, (4) Quad-jet modulator, (5) Secondary oven, (6) Detector.