



A Honeywell Company

Total Cycloparaffins and Total Aromatics in Synthetic Paraffinic Kerosene Fuels by Comprehensive Two-Dimensional GC with Flame Ionization Detection

UOP Method 965-10

Scope

This method is for determining total cycloparaffins (naphthenes) and total aromatics in synthetic paraffinic kerosene fuels (SPK) or petroleum distillates in the boiling range of 69°C to 350°C using comprehensive two-dimensional gas chromatography (GCxGC) coupled with a flame ionization detector (FID). Molecular type groups are identified by their location, as plotted on a chromatographic contour plot image. The precision of this test method has been established for SPK fuels containing from 1.6 to 32.3 mass-% naphthenic hydrocarbons and 0.03 to 1.9 mass-% aromatic hydrocarbons. Alkenes and compounds containing sulfur, nitrogen, and oxygen are possible interferences.

References

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 capillary GC columns and a flame ionization detector (FID). The modulator serves as an interface between the two GC columns. The first "primary" column is a conventional high resolution capillary GC column coated with cross-linked methyl silicone stationary phase, which separates molecules based on volatility. The "secondary" GC column is coated with cross-linked polyethylene 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

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chromatograms from the “secondary” column which are transformed by computer software into a two-dimensional array, with one dimension representing the retention time from the “primary” column and other 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.

Autofill unit, liquid nitrogen level controller with 2 LSI-1 dual level sensors and liquid nitrogen transfer assembly with installed solenoid valve, Zoex Corporation, Cat. No. KT-DWR-AMI24

Balance, readable to 0.1-mg

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. 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, Zoex Corporation, Cat. No. KT-CLM-ZOE02

Comprehensive two-dimensional GC imaging and data processing software, GC Image, Cat. No. R.2.0. The precision statement of this method was obtained using data processed by this specific software.

Computer, suggested minimum hardware configuration: 1000MHz Intel Pentium 4 (or comparable) CPU, 512MB RAM (2GB or more RAM is preferred), 32MB graphics card (128MB is preferred), and color monitor with 1024x768 (or higher) resolution. Processed GCxGC data may require large disk capacity.

Cryo cylinder, 230 LP SB, container for liquid nitrogen, square base, with 22 psi relief valve, Chart Industries, Inc. Storage System Division, Cat. No. 10648556

Data system, electronic, for GC instrument control and data acquisition (i.e. recording detector response as a *.ch file). 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. Agilent Technologies, ChemStation.

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 thermal loop modulation system, consisting of a 5-L “secondary” liquid nitrogen dewar, a 30 inch 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

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

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, syringe or injector capable of introducing a consistent 0.5- μ L volume of sample. An automatic injection device is highly recommended, although injection can be accomplished with manual injection with a syringe. 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

Bottles, glass, narrow mouth, round, supplied with fluoropolymer resin-lined caps, 120-ml, VWR, Cat. No. 16151-060

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

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

Naphthalene, scintillation grade, $\geq 99\%$ pure, Sigma-Aldrich, Cat. No. 184500

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

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

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

Syringe, for sample injector, 5- μ L, 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

Synthetic paraffinic kerosene (SPK) reference material. This is a material similar in composition to samples to be analyzed, in sufficient quantity for use for multiple quality control analyses over an extended period of time (e.g. year or more). It should be kept in a tightly sealed glass container and stored in a cool dark cabinet when not in use. Petroleum derived kerosene can also be used if similar in composition to samples to be analyzed. This material may need to be spiked with additional pure cycloparaffins or aromatic compounds to obtain a material similar in composition to the samples to be analyzed. The final composition of the SPK or petroleum derived kerosene reference material shall contain a minimum concentration of cycloparaffins (>1 mass-%) and aromatics (>0.25 mass-%).

Typewriter correction fluid, white, for marking column positions

Zero-dead-volume internal 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

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. This procedure is written for the analyzer listed in *Apparatus*. If a different instrument is used, modify the procedure as needed.

Chromatographic Technique

Follow factory instructions for installation and set up of GCxGC Instrument. The instrument should be operated in an environment with a reasonably constant temperature (<30°C) and humidity.

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 gas purifiers are not used. Purifiers should be replaced periodically in accordance with manufacturer's recommendations.
2. Mount the GCxGC fused silica capillary column set in the gas chromatograph connecting the "primary" column to the injector inlet and the "secondary" column to the detector inlet. Install the column holder into the modulator assembly. Be sure to cut fresh ends to each column after inserting compression screw and ferrule before connecting columns to the inlet of the injector and the detector.
 - See the **Appendix** for specific instructions on the preparation of a GCxGC fused silica column set for a Zoex Two-Stage Thermal Loop Modulator System.
 - Zoex Technical Note KT030606-1 illustrates the proper alignment of the column holder in the modulator assembly.

3. Commence hydrogen carrier gas flow to the GC. Check for leaks with a leak detector each time a column connection is made and periodically thereafter.
 - CAUTION: Hydrogen carrier gas leakage into the confined volume of the GC column oven can cause a violent explosion.
4. Program the recommended operating conditions as given in Table 1.

Table 1
Recommended Operation Conditions

Carrier gas	hydrogen
Column head pressure @ 100 °C	169 kPa gauge (24.54 psig)
Mode	constant flow
Equivalent linear velocity	43 cm/sec
Split flow rate	449 mL/min
Split flow ratio	100:1
Injection port temperature	260 °C
Column temperature program	
Initial temperature	40 °C
Initial time	5 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	250 °C
Final hold time	1.17 min
Run time	130 min
Hot jet temperature program	
Initial temperature	120 °C
Initial time	5 min
Programming rate A	1.5 °C/min
Intermediate temperature A	233 °C
Programming rate B	2.0 °C/min
Final temperature	250 °C
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	260 °C
Hydrogen flow rate*	40 mL/min
Air flow rate*	450 mL/min
Makeup gas	nitrogen
Makeup gas flow rate	35 mL/min
Mode	constant makeup flow
Sampling rate	200 Hz
Sample size	0.5 µL

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

- Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatograms (Figures 2-4).
5. Set the column oven temperature initially to 250°C. Maintain this temperature until a stable baseline has been obtained at the required detector sensitivity.
 6. Cool the column oven to a stabilized 40°C.
 7. Set the modulator control module parameters as listed in Table 2.

Table 2
Modulator Parameters

Duration of modulator hot jet pulse	300 ms
Modulation period	6000 ms
Rephase	negative

8. Start the modulator control module.
9. Turn on the autofill unit to start flow of liquid nitrogen to the GCxGC loop modulation system. Once the secondary liquid nitrogen dewar is filled to the appropriate level one can begin sample analysis.
 - Follow the manufacturer's recommended conditions for setting and controlling the liquid nitrogen autofill unit.

Tuning the GCxGC Instrument

(Optimizing 2nd dimension GC column length and software volume filter setting)

1. Prepare a solution of 0.5 mass-ppm naphthalene in dichloromethane.
 - This is best prepared by serial dilution until the desired concentration is obtained. For example, weigh 0.1 gram of naphthalene to the nearest 0.001g in a 120-ml glass bottle. Dilute with dichloromethane to a final weight of 50 g; cap and mix thoroughly to create a 0.2 wt-% mixture of naphthalene in dichloromethane. With a Pasteur pipette, weigh a 0.1 g aliquot of the mixture 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 naphthalene 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 to make the 0.5 wt-ppm naphthalene in dichloromethane mixture.
2. Analyze the 0.5 mass-ppm naphthalene solution as outlined in *Sample Analysis*.
3. Identify the naphthalene peak by comparing the resulting chromatographic contour plot of the naphthalene sample analysis with Figure 1.
4. The naphthalene peak must elute between 5.5 and 6 seconds on the y-axis. If the peak is found outside this boundary, then correct by the following: 1) the secondary column must be shortened if the peak is found in the wrap around aromatics region (see Figure 2); 2) the secondary column must be replaced with a longer one if the peak is below 5.5 seconds.
5. Integrate and obtain the volume of the naphthalene peak to use for input into the volume filter setting in the GCxGC data processing software.
 - This volume setting will be used to filter out detector signal noise.

Sample Analysis

1. Inject nominally 0.5 µL of sample and immediately start the data acquisition, column temperature programming sequence and hot jet pulse directed by the modulator controller. The sample analysis run time is 130 minutes.

- Prior to and after analysis of samples, confirm proper FID performance by running a SPK reference material (see System Suitability). Also as indicated above in Tuning the GCxGC Instrument, analyze the 0.5 wt-ppm naphthalene in dichloromethane mixture to confirm the 2nd dimension GC column length and to determine a volume filter setting for data processing.
 - It is highly preferable to use a data system (e.g. Chemstation) to automate the start of analysis such that the data acquisition, column temperature program and modulator pulsing can be synchronized and initiated at precisely the same time.
2. Upon completion of the analysis, import the acquired data file (e.g. *.ch) of the analysis into the GCxGC data processing software.
 - *.ch is the Agilent Chemstation data file format.
 3. Select and process the data acquisition file and view a contour plot image of the analyzed sample. A 6 sec modulation period must be indicated while processing the file.
 - Use the GC Image Users Guide for details on how to use the software. This includes: correcting the baseline, integrating the peaks and processing the contour plot image. Suggested software parameters for color map, blob detection, blob filter, baseline correction and blob statistics and template matching are listed in Table 3.
 - Note: GC Image software defines the 3-dimensional chromatographic interpolated peaks as "blobs".

Table 3
GC Image Software Parameters

Color Map:	EOSB
Blob Detection	
Smoothing	
First column	0
Second column	2.0
Blob filter	
Minimum area	0
Volume filter	see <i>Tuning the GCxGC Instrument</i>, Step 5
Minimum peak	8.0
Baseline Correction	
Number of deadband pixels	50
Filter window size	3
Distribution	14.0
Stride	0.5
Blob Statistics	default values
Template matching	default values

4. Identify the separated sample components by comparing the chromatographic contour plot image obtained to typical images shown in Figures 2-5. A list of the different group molecular types is found in Table 4.
 - Some samples may contain more polar aromatic components or heterocyclic compounds that may be found in the "wrap-around" labeled region (see Figure 2) of the template. If so, identify such separated components as aromatics.

5. Construct and save a template to identify and label the molecular group types separated on the contour plot image. Make sure to exclude sample analysis artifacts such as column bleed (see Figure 5) or other excessive detector noise.

- The template can be used to automate the identification of molecular group types in the analysis of subsequent samples.

Table 4
Identified Group Molecular Types

<u>No.</u>	<u>Component</u>
1	Paraffins
2	Cycloparaffins
3	Aromatics

6. Obtain the volumes of the different sample components by integration of the data file.
 - This is done in GC Image by loading the constructed template; matching and applying it to the image.
7. Save the processed file of different molecular group types with their respective integrated volumes.
 - The GC Image software saves the processed file as a blob set table.
 - In alternative software, one must at least save the group name, 1st dimension retention time, 2nd dimension retention time and volume for each respectively identified peak in a *.csv file.
8. Calculate and report the concentration of the different molecular group types by using Equation 1 in *Calculations*.
 - In GC Image this is accomplished automatically by creating a summary report from the processed image file.
 - Alternatively, a saved processed *.csv file can be imported into Microsoft Excel to calculate the concentration of the different molecular group types as follows:
 - a) Import the *.csv file including: group name, 1st dimension retention time, 2nd dimension retention time and volume.
 - b) Sort the data first by “group name”, second by “1st dimension retention time”, and third by “2nd dimension retention time”, all ascending. The existence of a header row must be indicated.
 - c) Search the volume column for any components not present in the GC image and set their value to 0.
 - d) Create a pivot table with columns of “group name” and “volume.”
 - e) Copy the two columns of the pivot table and paste in 2 separate columns to the right in the spreadsheet.
 - f) Determine a total volume by summing the “volume” column.
 - g) Determine the concentration of the individual components by using Equation 1.

Note, the initial template of the identified sample group component locations should be created on an SPK reference material (see *System Suitability*). GC columns will gradually thermally degrade, losing activity over time. This typically results in a reduction of retention time of the analytes usually most noticeable in the second dimension. The SPK reference material should be run periodically to determine how to adjust the template. The adjusted template should provide the same results for the SPK reference material within the repeatability of the method (see *Precision*). The GC columns, particularly the secondary chromatographic column, may need to be replaced occasionally in order to achieve acceptable values.

System Suitability, Analysis of SPK Reference Material

1. Prior to and after analysis of new samples, it is highly recommended to confirm proper system chromatographic performance by running a SPK reference material as outlined in Sample Analysis in *Procedure*. Confirm that the results for the SPK reference material are within the established repeatability of the method (see *Precision*).
2. If the precision is not met in step 1, replace the columns or troubleshoot the instrument as necessary to achieve proper performance.

Calculations

Obtain peak volumes for each hydrocarbon group of components and calculate the composition of the sample to the nearest 0.01 mass-% using Equation 1:

$$C_i = \frac{100 A}{B} \quad (1)$$

where:

A = peak volume of each hydrocarbon type group of components

- If a response other than column bleed is detected in the wrap around aromatics region, include that in the total aromatics volume.

B = sum of peak volumes of all the recorded peaks, excluding column bleed artifacts

C_i = concentration of hydrocarbon type group of components, mass-%

i = paraffins, cycloparaffins or aromatics

100 = factor to convert to percent

Report each group of components to the nearest 0.01 mass-%.

Calculate the volume-% for cycloparaffin and aromatic components to the nearest 0.01 vol-% by using Equation 2:

$$D_i = C_i \times E_i \quad (2)$$

where:

C_i = concentration of hydrocarbon type group of components, mass-%

E_i = conversion factor to convert mass-% to vol-%

D_i = concentration of hydrocarbon type group of component, vol-%

where:

$$E_{\text{cycloparaffins}}^* = 0.93$$

$$E_{\text{aromatics}}^* = 0.86$$

*values derived from average densities of paraffins, cycloparaffins and aromatics in the carbon number range of SPK

Report each group of components to the nearest 0.01 vol-%.

Precision

Precision statements were determined using UOP Method 999, using data processed by GC Image R.2.0. Some apparent scatter in the data at similar concentrations is due to different sample types and the limited quantity of sample available for testing. Some samples used in the precision study were doped with several pure aromatic and naphthenic compounds to obtain the higher concentrations listed in the *Scope*.

Repeatability and Site Precision

A nested design was carried out for determining aromatics and cycloparaffins in five samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on each sample each day. The total number of tests was 40. The precision data for estimated standard deviation and allowable difference are summarized in Table 5. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 5 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table 5
Repeatability and Site Precision, Aromatics and Cycloparaffins, 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>
Aromatics	0.03	0.0003	0.01	0.0004	0.01
Aromatics	0.07	0.0005	0.01	0.002	0.01
Aromatics	0.71	0.002	0.01	0.003	0.01
Aromatics	1.43	0.003	0.01	0.004	0.02
Aromatics	1.92	0.025	0.10	0.037	0.17
Cycloparaffins	1.61	0.021	0.08	0.072	0.44
Cycloparaffins	11.15	0.027	0.10	0.064	0.29
Cycloparaffins	24.05	0.232	1.04	0.306	1.20
Cycloparaffins	29.91	0.157	0.69	0.176	0.71
Cycloparaffins	32.36	0.399	1.57	0.501	2.25

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 approximately 3 hours. The labor requirement for an initial sample is approximately 1.0 hour with each additional sample in a batch requiring approximately 0.5 hour.

Suggested Suppliers

Agilent Technologies, Inc., 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

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

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

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

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

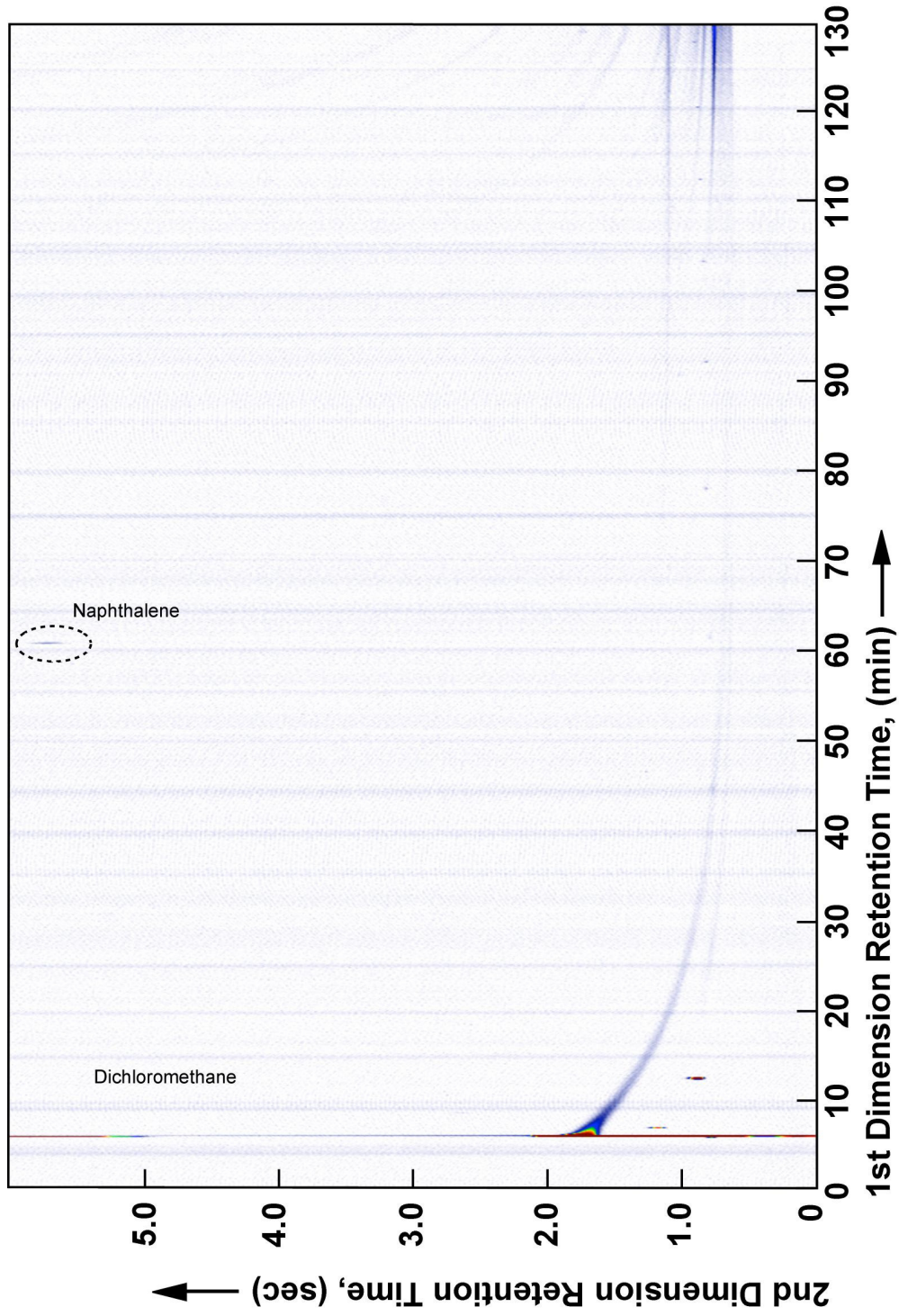


Figure 1

Contour plot image showing 0.5 mass-ppm naphthalene

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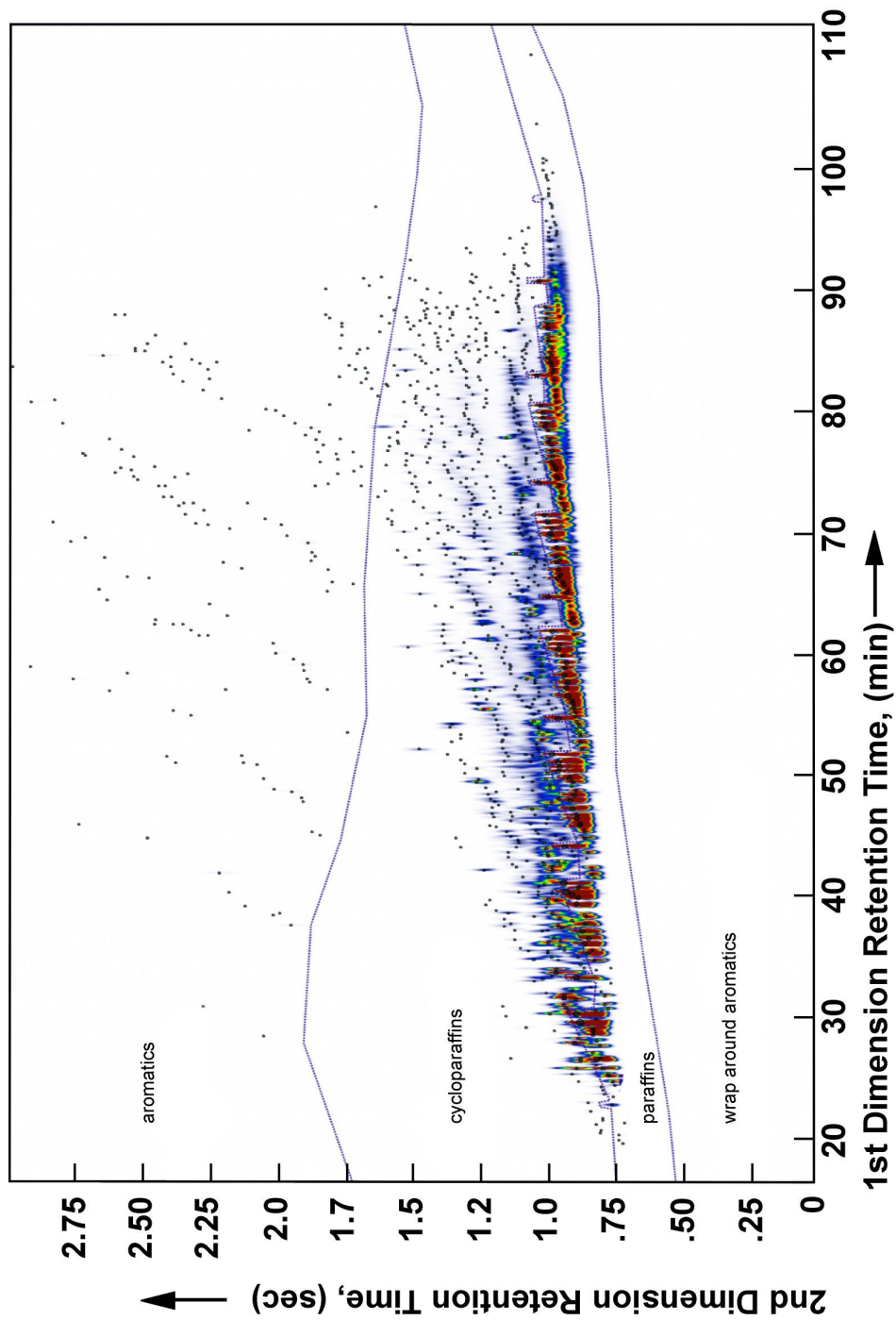


Figure 2

Contour plot of SPK sample with template indicating location of cycloparaffins and aromatics. The bubbles represent the apexes of the detected peaks

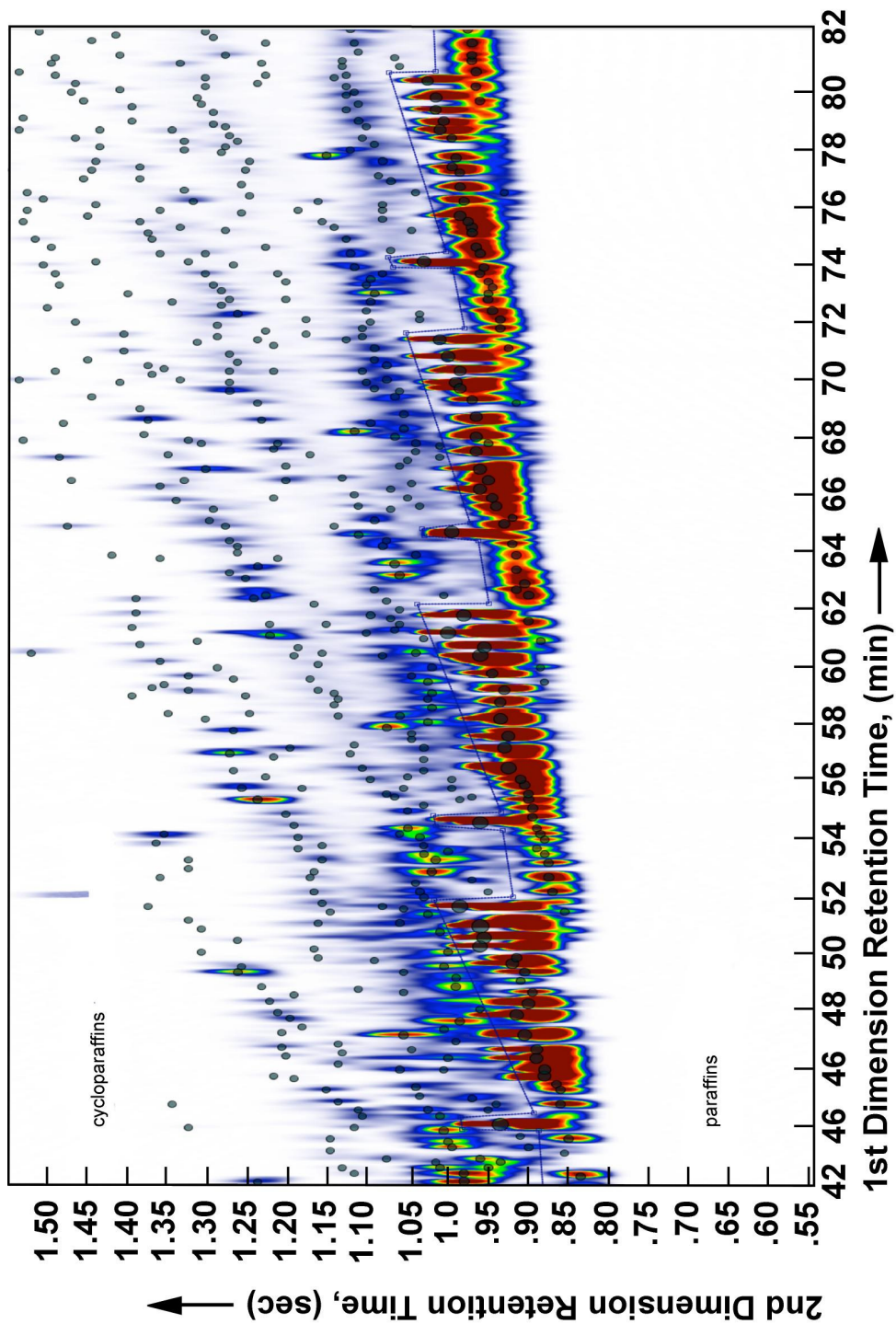


Figure 3
Enlargement of paraffin/cycloparaffin boundary
indicating saw tooth pattern of template

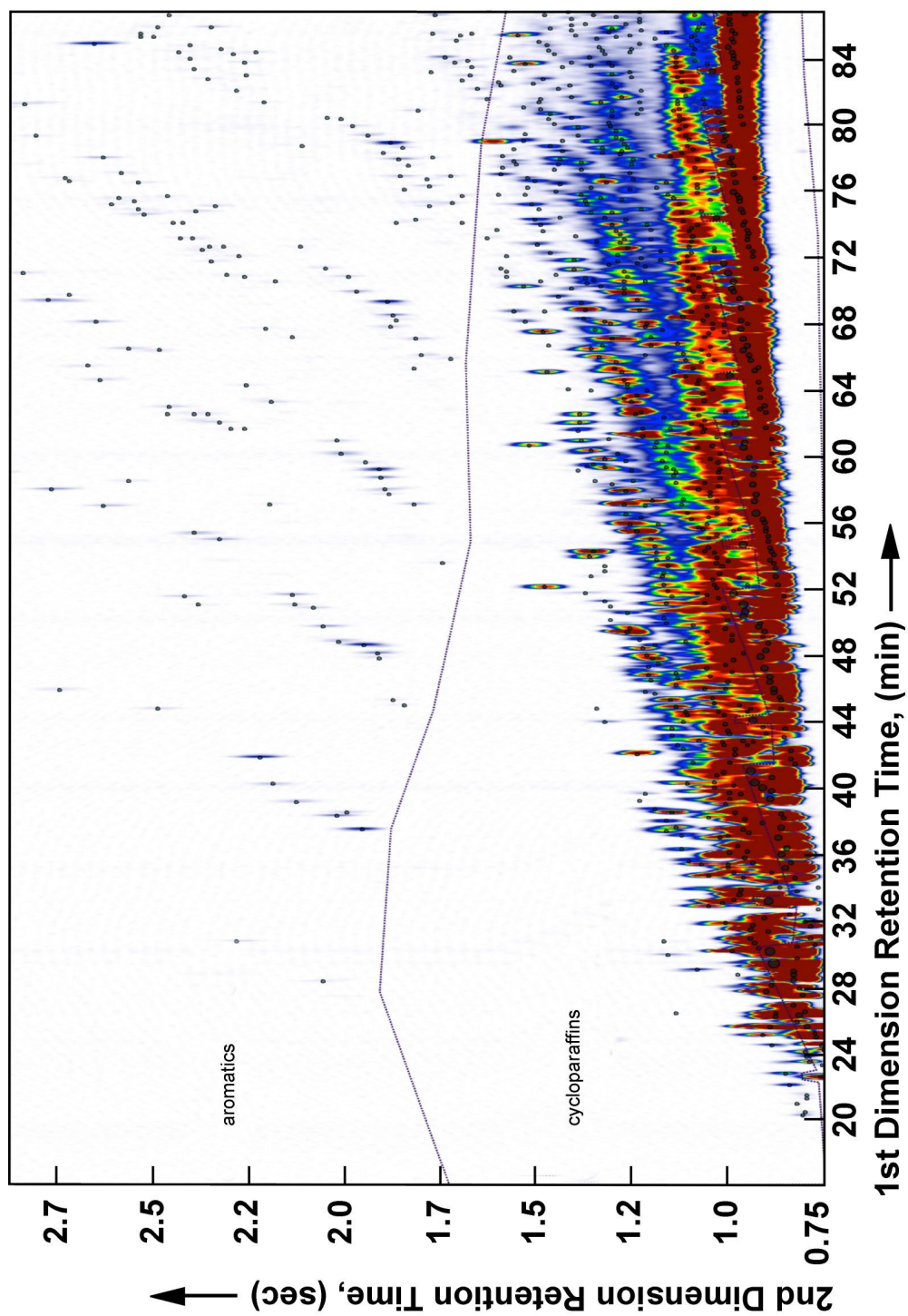


Figure 4
Enlargement of cycloparaffin/aromatic boundary

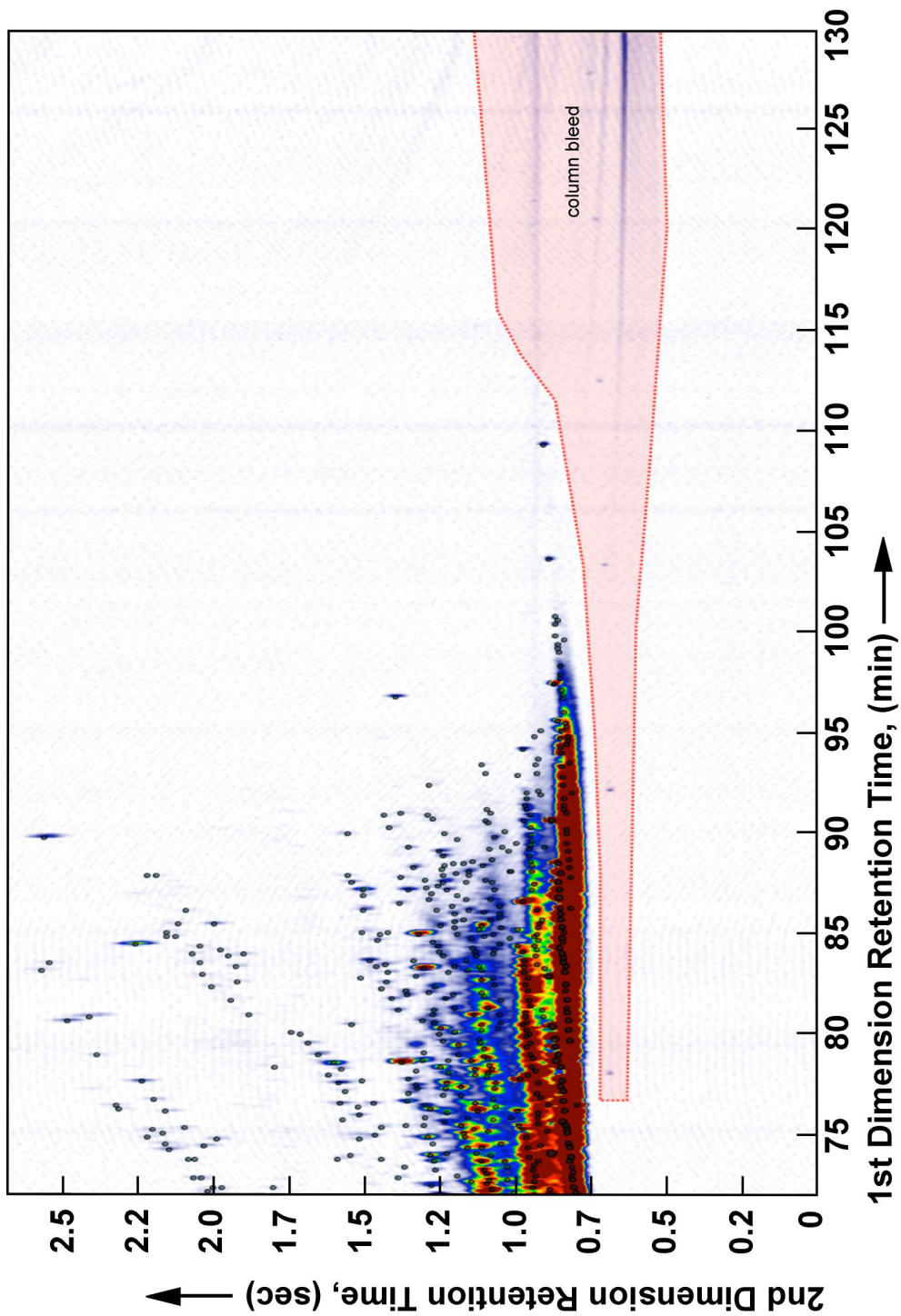


Figure 5

Contour plot image indicating column bleed which should be excluded from detector response

Appendix

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

1. Cut a 2 m length of “secondary” fused silica column. Select one side as the column inlet.
 - It is important that column ends be fresh, free of burrs, jagged edges, and/or loose particles of column, stationary phase, and/or material from a sealing ferrule. The ends must be cut fresh after pre-installing column nuts and ferrules. The column length measurements in steps 1 and 2 of this procedure provide for an additional 1 cm each, at both ends, to make fresh cuts prior to installation.
2. Mark the “secondary” fused silica column with typewriter correction fluid at two separate points indicating both: 32 and 127 cm length from the selected column inlet.
3. 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.)

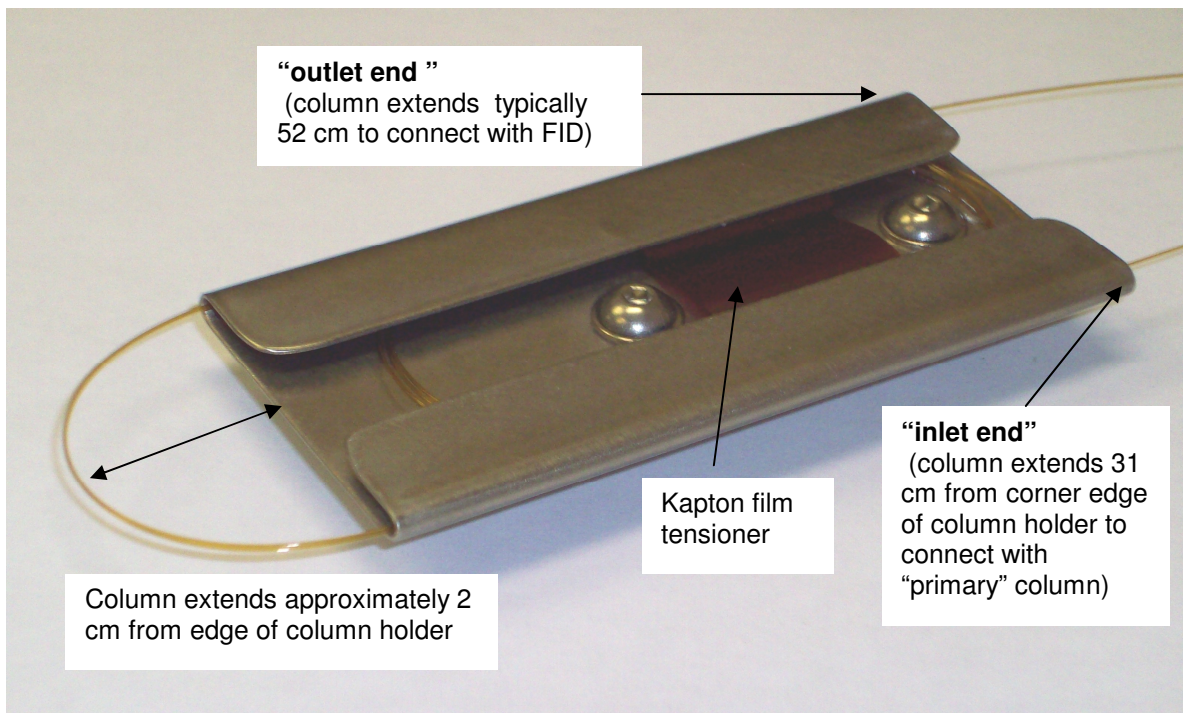


Figure A1. Column Holder (facing bottom)

4. Loop the following 95-cm of column 5 times inside the column holder as shown in Figure 1. 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 to the “inlet end”). Adjust the Kapton film tensioner as necessary to keep the column in place.
5. Connect the outlet side of the “primary” fused silica column with a zero-dead-volume internal union to the inlet side of the “secondary” fused silica column. Make a fresh cut and remove 1

cm of the inlet side of the “primary” column before connecting to the zero-dead-volume internal union.

6. Make a fresh cut and remove 1 cm of the inlet side of the “secondary” column before connecting it to the zero-dead-volume internal union. Install column in GC oven as described in the body of the method under *Chromatographic Technique*.