

TRACE C₄-C₉ SATURATES IN HIGH PURITY AROMATICS BY GC

UOP Method 976-02

SCOPE

This gas chromatographic method is for determining individual and composite trace non-aromatic hydrocarbon impurities in olefin-free aromatic mixtures. C₈ and lower boiling paraffins and naphthenes are determined individually and then summed by carbon number and carbon type. C₉ non-aromatics are reported as a composite. The method is not quantitative for C₃ and lower molecular weight hydrocarbons due to their volatility. The range of quantitation for each component is 1 to 2000 mass-ppm. The range of quantitation for each composite depends upon the number of components in the composite.

An alternative method providing similar information is UOP Method 868, Trace Saturates in High Purity Aromatics by GC. It uses a two-column system to report paraffins and naphthenes by carbon number through C10.

OUTLINE OF METHOD

The sample is injected into a gas chromatograph equipped with a flame ionization detector and a fused silica capillary column, internally coated with cross-linked methyl silicone. The mass-ppm concentration of the impurities in aromatic mixtures is obtained on an absolute basis by the external standard method of quantitation, wherein the peak areas for the impurity components are compared to the peak area for a known amount of 2,2,4-trimethylpentane in the calibration blend.

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).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The 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.

APPARATUS

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

Balance, readability 0.1-mg

Chromatographic column, PONA, 50 m of 0.21-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked methyl silicone, Agilent Technologies, Cat. No. 19091S-001

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 1 mass-ppm 2,2,4-trimethylpentane when operated under the recommended conditions, Agilent, Model 6890

Gas purifier, hydrogen purifier, Mat/Sen, Cat. No. P200-1

Integrator, or data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured.

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sample injector, any syringe or injector capable of introducing a 1- μ L volume of sample. An automatic injection device is recommended, Agilent Technologies, Model 7683.

Syringe, 10- μ L, for sample injector, Agilent Technologies, Cat. No. 5181-1267

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

Hydrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Pipet, Pasteur, disposable, 146-mm, Fisher Scientific, Cat. No. 13-678-20A

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 13-678-9A

2,2,4-Trimethylpentane, 99.9% minimum purity, Acros Organics, Cat. No. 29572-0010

Xylenes, reagent, Acros Organics, Cat. No. 42268-5000

Vial, 14.8-mL, with screw cap, Fisher Scientific, Cat. No. 03-339-21J

PROCEDURE

Preparation of Apparatus

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life may be significantly reduced if a gas purifier is not used.
2. Install the fused silica capillary column in the gas chromatograph.
 - 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.
3. Establish the recommended operating conditions as given in Table 1.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Column head pressure	137 kPa gauge (20 psig)
Equivalent flow @ 32°C	1 mL/min
Equivalent linear velocity	32.5 cm/sec
Split Flow	100 mL/min
Injection port temperature	250°C
Column temperature program	
Initial temperature	32°C
Initial time	6 min
Programming rate A	5°C/min
Final temperature A	52°C
Holding time A	14 min
Programming rate B	20°C/min
Final temperature B	250°C
Final time	10 min
Detector	
Detector temperature	300°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	275 mL/min
Makeup nitrogen flow rate*	30 mL/min
Sample size	1 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 (Figs. 1 and 2).

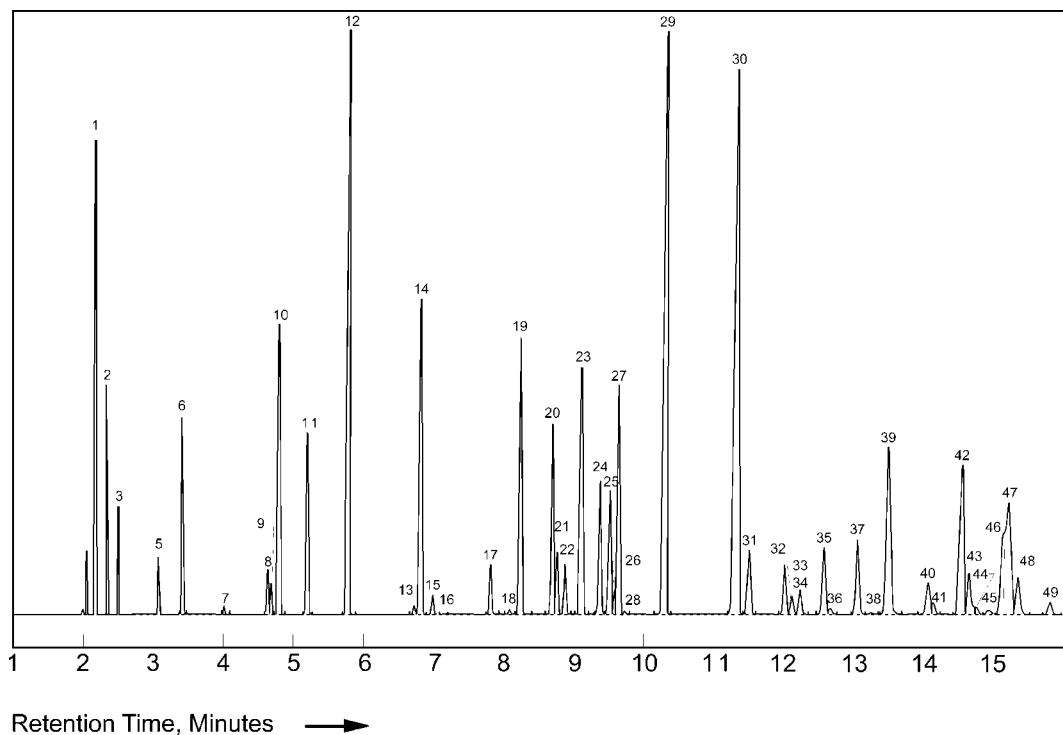


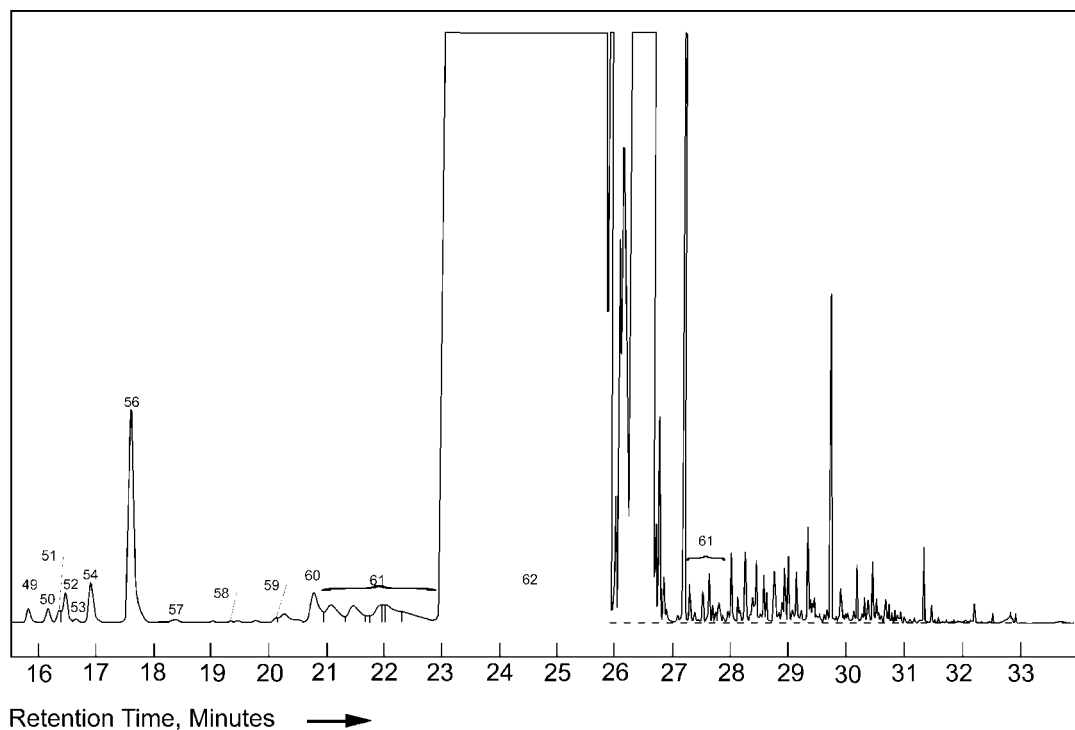
Figure 1

Typical Chromatogram, Part 1

4. Program the column oven to 250°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 32°C.

Chromatographic Technique

1. Inject 1.0 μL of sample and immediately start the gas chromatograph and integrator.
2. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatograms, Parts 1 and 2 (Figs. 1 and 2) and Retention Times of Identified Components (Table 2). Sum the impurity peak areas into groups by carbon number and type: paraffin or naphthene.
3. Determine the density of the sample by ASTM Test Method D 4052, or other suitable technique.

**Figure 2**

Typical Chromatogram, Part 2

Calibration

1. Analyze the xylenes as described under Chromatographic Technique and confirm that there are no impurity peaks in the 2,2,4-trimethylpentane region (Peak No. 28).
 - If there is any interference, obtain the xylenes from another source. If an impurity eluting at the retention time of 2,2,4-trimethylpentane cannot be eliminated, analyze the xylenes every time a calibration blend is analyzed and subtract the area of the impurity from the area of the 2,2,4-trimethylpentane in the calibration blend.
2. Prepare a calibration blend as described in ASTM Test Method D 4307.
3. Tare a vial to the nearest 0.1 mg. Add approximately 10 g of xylene and record the weight.
 - The xylene is deposited in the center of the vial with a Pasteur pipet so that the liquid does not contact the neck.
4. Add approximately 0.1 g of 2,2,4-trimethylpentane using a Pasteur pipet and quickly reweigh to the nearest 0.1 mg. This solution will correspond to an approximate concentration of 1 mass-% of 2,2,4-trimethylpentane in xylenes.

- The external standard is added to the vial while on the balance pan and deposited into the center of the liquid, not on the side of the vial.
5. Cap the vial and mix well by inverting the vial several times. Label this solution as Standard Solution A.
 6. Tare another vial to the nearest 0.1 mg. Add approximately 10 g of xylene and record the weight.
 - The xylene is deposited in the center of the vial with a Pasteur pipet so that the liquid does not contact the neck.
 7. Add approximately 0.1 g of Standard Solution A. Record the weight to the nearest 0.1 mg. This solution will correspond to an approximate concentration of 100 mass-ppm of 2,2,4-trimethylpentane in xylenes.
 - Standard Solution A is added to the vial while on the balance pan and deposited into the center of the liquid, not on the side of the vial.
 8. Cap the vial and mix well by inverting the vial several times. Label this solution as Calibration Blend.
 - This solution is stable for one month.
 9. Calculate the concentration of the Calibration Blend using Eq. 1:

$$C = \frac{10^6 XY}{(X + Z)(Y + W)} \quad (1)$$

where:

C = concentration of 2,2,4-trimethylpentane in Calibration Blend, mass-ppm

W = the weight of mixed xylenes in Calibration Blend

X = the weight of 2,2,4-trimethylpentane in Standard Solution A

Y = the weight of Standard Solution A in Calibration Blend

Z = the weight of mixed xylenes in Standard Solution A

10⁶ = factor to convert to mass-ppm

10. Analyze the Calibration Blend in triplicate daily as described under *Chromatographic Technique* when samples are analyzed.
11. Identify the 2,2,4-trimethylpentane peak and average the peak area from the triplicate runs.
 - Peak areas from each of the triplicate runs should not deviate from the average by more than 2% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

Table 2
Retention Times of Identified Components

Typical Retention	Peak		
<u>Time, Min</u>	<u>No.</u>	<u>Component Identification</u>	<u>Group</u>
2.04		Ethane site	C ₂ Paraffin
2.15	1	Propane	C ₃ Paraffin
2.33	2	Isobutane	C ₄ Paraffin
2.48	3	<i>n</i> -Butane	C ₄ Paraffins
2.75	4	2,2-Dimethylpropane	C ₅ Paraffins
3.06	5	Isopentane	C ₅ Paraffins
3.38	6	<i>n</i> -Pentane	C ₅ Paraffins
3.97	7	2,2-Dimethylbutane	C ₆ Paraffins
4.60	8	Cyclopentane	C ₅ Naphthene
4.64	9	2,3-Dimethylbutane	C ₆ Paraffins
4.75	10	2-Methylpentane	C ₆ Paraffins
5.16	11	3-Methylpentane	C ₆ Paraffins
5.74	12	<i>n</i> -Hexane	C ₆ Paraffins
6.70	13	2,2-Dimethylpentane	C ₇ Paraffins
6.78	14	Methylcyclopentane	C ₆ Naphthenes
6.97	15	2,4-Dimethylpentane	C ₇ Paraffins
7.18	16	2,2,3-Trimethylbutane	C ₇ Paraffins
7.79	17	Benzene	
8.07	18	3,3-Dimethylpentane	C ₇ Paraffins
8.22	19	Cyclohexane	C ₆ Naphthenes
8.68	20	2-Methylhexane	C ₇ Paraffins
8.75	21	2,3-Dimethylpentane	C ₇ Paraffins
8.86	22	1,1-Dimethylcyclopentane	C ₇ Naphthenes
9.09	23	3-Methylhexane	C ₇ Paraffins
9.37	24	1- <i>cis</i> -3-Dimethylcyclopentane	C ₇ Naphthenes
9.51	25	1- <i>trans</i> -3-Dimethylcyclopentane	C ₇ Naphthenes
9.58	26	3-Ethylpentane	C ₇ Paraffins
9.64	27	1- <i>trans</i> -2-Dimethylcyclopentane	C ₇ Naphthenes
9.72	28	2,2,4-Trimethylpentane	C ₈ Paraffins
10.28	29	<i>n</i> -Heptane	C ₇ Paraffins
11.30	30	Methylcyclohexane + 1- <i>cis</i> -2-Dimethylcyclopentane	C ₇ Naphthenes C ₇ Naphthenes
11.49	31	1,1,3-Trimethylcyclopentane + 2,2-Dimethylhexane	C ₈ Naphthenes * C ₈ Paraffins *
12.00	32	Ethylcyclopentane	C ₇ Naphthenes
12.10	33	2,5-Dimethylhexane	C ₈ Paraffins
12.22	34	2,2,3-Trimethylpentane + 2,4-Dimethylhexane	C ₈ Paraffins C ₈ Paraffins
12.56	35	1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	C ₈ Naphthenes
12.66	36	3,3-Dimethylhexane	C ₈ Paraffins

Typical Retention	Peak		
<u>Time, Min</u>	<u>No.</u>	<u>Component Identification</u>	<u>Group</u>
13.04	37	1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	C ₈ Naphthenes
13.25	38	2,3,4-Trimethylpentane	C ₈ Paraffins
13.48	39	2,3,3-Trimethylpentane + Toluene	C ₈ Paraffins *
14.06	40	2,3-Dimethylhexane+ 1,1,2-Trimethylcyclopentane	C ₈ Paraffins * C ₈ Naphthenes *
14.13	41	2-Methyl-3-ethylpentane	C ₈ Paraffins
14.53	42	2-Methylheptane	C ₈ Paraffins
14.65	43	4-Methylheptane	C ₈ Paraffins
14.75	44	3,4-Dimethylhexane + 3-Methyl-3-ethylpentane	C ₈ Paraffins C ₈ Paraffins
14.94	45	1- <i>cis</i> -2- <i>trans</i> -4-Trimethylcyclopentane+ 1- <i>cis</i> -2- <i>cis</i> -4-Trimethylcyclopentane	C ₈ Naphthenes C ₈ Naphthenes
15.15	46	3-Methylheptane	C ₈ Paraffins
15.21	47	3-Ethylhexane + 1- <i>cis</i> -3-Dimethylcyclohexane + 1- <i>cis</i> -2- <i>trans</i> -3-Trimethylcyclopentane	C ₈ Paraffins * C ₈ Naphthenes * C ₈ Naphthenes *
15.37	48	1- <i>trans</i> -4-Dimethylcyclohexane	C ₈ Naphthenes
15.83	49	1,1-Dimethylcyclohexane	C ₈ Naphthenes
16.17	50	1-Methyl- <i>trans</i> -3-ethylcyclopentane	C ₈ Naphthenes
16.37	51	1-Methyl- <i>cis</i> -3-ethylcyclopentane	C ₈ Naphthenes
16.47	52	1-Methyl- <i>trans</i> -2-ethylcyclopentane	C ₈ Naphthenes
16.66	53	1-Methyl-1-ethylcyclopentane	C ₈ Naphthenes
16.92	54	1- <i>trans</i> -2-Dimethylcyclohexane	C ₈ Naphthenes
17.42	55	1- <i>cis</i> -2- <i>cis</i> -3-Trimethylcyclopentane	C ₈ Naphthenes
17.61	56	<i>n</i> -Octane + 1- <i>cis</i> -4-Dimethylcyclohexane + 1- <i>trans</i> -3-Dimethylcyclohexane	C ₈ Paraffins * C ₈ Naphthenes * C ₈ Naphthenes *
18.38	57	Isopropylcyclopentane	C ₈ Naphthenes
19.34	58	1-Methyl- <i>cis</i> -2-ethylcyclopentane	C ₈ Naphthenes
20.15	59	1- <i>cis</i> -2-Dimethylcyclohexane	C ₈ Naphthenes
20.78	60	<i>n</i> -Propylcyclopentane + Ethylcyclohexane	C ₈ Naphthenes C ₈ Naphthenes
	61	C ₉ Non-Aromatics	**
	62	Xylenes	

* Some co-eluting peaks contain components belonging to different groups. Select the most appropriate group for those peaks, based upon sample characteristics.

** The C₉ Non Aromatic group was defined in the chromatogram by analyzing known C₉ compounds (Fig 1 and 2).

12. Determine the response factor relative to the mass-ppm concentration of 2,2,4-trimethylpentane in the Calibration Blend using Eq. 2.

$$M = \frac{C}{A} \quad (2)$$

where:

A = average peak area of 2,2,4-trimethylpentane from chromatogram (Fig. 2)

C = concentration of 2,2,4-trimethylpentane in Calibration Blend, mass-ppm

M = response factor

CALCULATIONS

Calculate the concentration of each impurity or group of impurities in the sample to the nearest mass-ppm using the following equation:

$$\text{Impurity or grouped impurities, mass-ppm} = \frac{BMS}{D} \quad (3)$$

where:

B = peak area of a specific impurity or group of impurities

D = density of sample

M = response factor

S = density of Calibration Blend

- The flame ionization detector responds equally on a mass basis to all measured impurities.

REPORT

Report the following impurity groups to the nearest mass-ppm:

C₄ Paraffins	C₅ Naphthene
C₅ Paraffins	C₆ Naphthenes
C₆ Paraffins	C₇ Naphthenes
C₇ Paraffins	C₈ Naphthenes
C₈ Paraffins	C₉ Non-Aromatics

If desired, individual impurities may also be reported to the nearest mass-ppm.

PRECISION

Precision statements were determined using UOP Method 999. An autoinjector was used for sample injection.

ASTM and UOP Repeatability

A nested design was carried out for determining components in two high purity aromatic samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day for sample A and three tests each day for Sample B. The total number of tests for each constituent was 20. The precision data are summarized in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference with 95% confidence.

The data in Table 3 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 3
ASTM and UOP Repeatability, mass-ppm

Sample/ Component	Mean Conc.	ASTM Repeatability		UOP Repeatability	
		Within- <u>Day esd</u>	Allowable <u>Difference</u>	Within- <u>Lab esd</u>	Allowable <u>Difference</u>
<u>Sample A</u>					
C ₄ Paraffins	160	2.2	9	3.7	15
C ₅ Paraffins	13.5	0.50	2.0	0.56	2.2
C ₅ Naphthenes	2.0	0	0	0	0
C ₆ Paraffins	1.3	0.50	2.0	0.43	1.7
C ₆ Naphthenes	1.1	0.35	1.4	0.35	1.4
C ₈ Paraffins	1.4	0.61	2.4	0.50	2.0
C ₈ Naphthenes	12	1.5	6	2.2	9
<u>Sample B</u>					
C ₄ Paraffins	3600	130	400	180	700
C ₅ Paraffins	2310	31	100	62	240
C ₅ Naphthenes	299	5.1	17	7.2	26
C ₉ Non-Aromatics	48	1.8	6	2.7	10

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.6 hours. The labor requirement is 0.8 hours.

REFERENCES

UOP Method 868, "Trace Saturates in High Purity Aromatics by GC"

UOP Method 999, "Precision Statements in UOP Methods"

ASTM Methods D 4052 and D 4307, www.astm.org

SUGGESTED SUPPLIERS

Acros Organics, 500 American Rd., Morris Plain, NJ 07950 (973-889-6300) www.fishersci.com

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com

Matheson Gas Products Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
www.mathesontrigas.com

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