

Separating Isotopic Molecules Using SPB™ Capillary GC Columns

Improved retention times for isotopic molecules are now observed with the introduction of high efficiency capillary columns. This article describes a study comparing three SPB-series columns and their ability to perform isotopic separations quickly and accurately.

Key Words:

- isotopic molecules • aliphatic molecules
- isomers • gas chromatography

Gas chromatography (GC) is a convenient and accurate method for separating isotopically labeled (deuterium) molecules for studying the role of kinetic isotope effects in reaction mechanisms. However, GC analyses for this application typically are conducted at relatively low temperature. As a result, long retention times have been observed, limiting the use of GC in isotopic separations.

The introduction of high efficiency GC columns in recent years has improved analyses of isotopically labeled molecules (1). Conceivably, GC could be applied to economically separate larger amounts of material.

In a comparison study, we used three columns — SPB-5 (60m length), SPB-35 (60m), and SPB-50 (30m) — to determine their capability to separate isotopically labeled molecules. Table 1 shows the time and temperature needed to achieve complete,

baseline separation of nine isotopic pairs. All pairs were separated completely on the SPB-5 column except ethylbenzene ring- d_5/d_0 , which exhibited an overlap between the two peaks. However, all of the compounds could be determined quantitatively within the range of the experimental error (1-2%). The SPB-35 column exhibited a less effective separation of benzene- d_6/d_0 and toluene-methyl- d_3/d_0 . The other pairs, however, had larger separation factors because of the relatively longer retention times.

Since the SPB-50 column used in the study is a shorter length, comparison with the other two columns is difficult. However, methylcyclohexane- d_{14}/d_0 , octane- d_{18}/d_0 , and ethylbenzene- d_{10}/d_0 were separated completely in four minutes or less.

Representative chromatograms of toluene- d_5/d_0 , octane- d_{18}/d_0 , and ethylbenzene- d_{10}/d_0 separations using all three SPB columns are shown in Figure A. The heavier (more deuterated) isomer always elutes first in a phenomenon known as the inverse isotope effect. The vapor pressure isotope effect is the major contributor to the inverse isotope effect on GC.

In studying the mechanism for the dehydrocyclization of alkanes using a Pt/SiO₂ catalyst, we used octane- d_{18}/d_0 and/or methylcyclohexane- d_{14}/d_0 as the feed to define the extent of deuterium/hydrogen exchange and the kinetic isotope effects (2). In this reaction, the major products are benzene, toluene, o-xylene, and ethylbenzene. Unreacted starting reagents and other compounds are also contained in the reactor effluent. The amount of each component, including deuterated components, have been determined quantitatively by using GC methods. Figure B shows a standard mixture of possible components from these reactions obtained on an SPB-5 column. From our experience, the GC method gives a more accurate analysis of the deuterium contents than some other methods, such as deuterium NMR and infrared.

For a mixture containing both aliphatic and aromatic pairs of isotopic molecules, the SPB-5 column appears to offer the best separation. For a mixture containing only aliphatic molecules, SPB-35 and SPB-50 columns are the best choice because of reduced elution time.

Table 1. Conditions Needed for Complete Separation of Isotopically Labeled Molecule Pairs

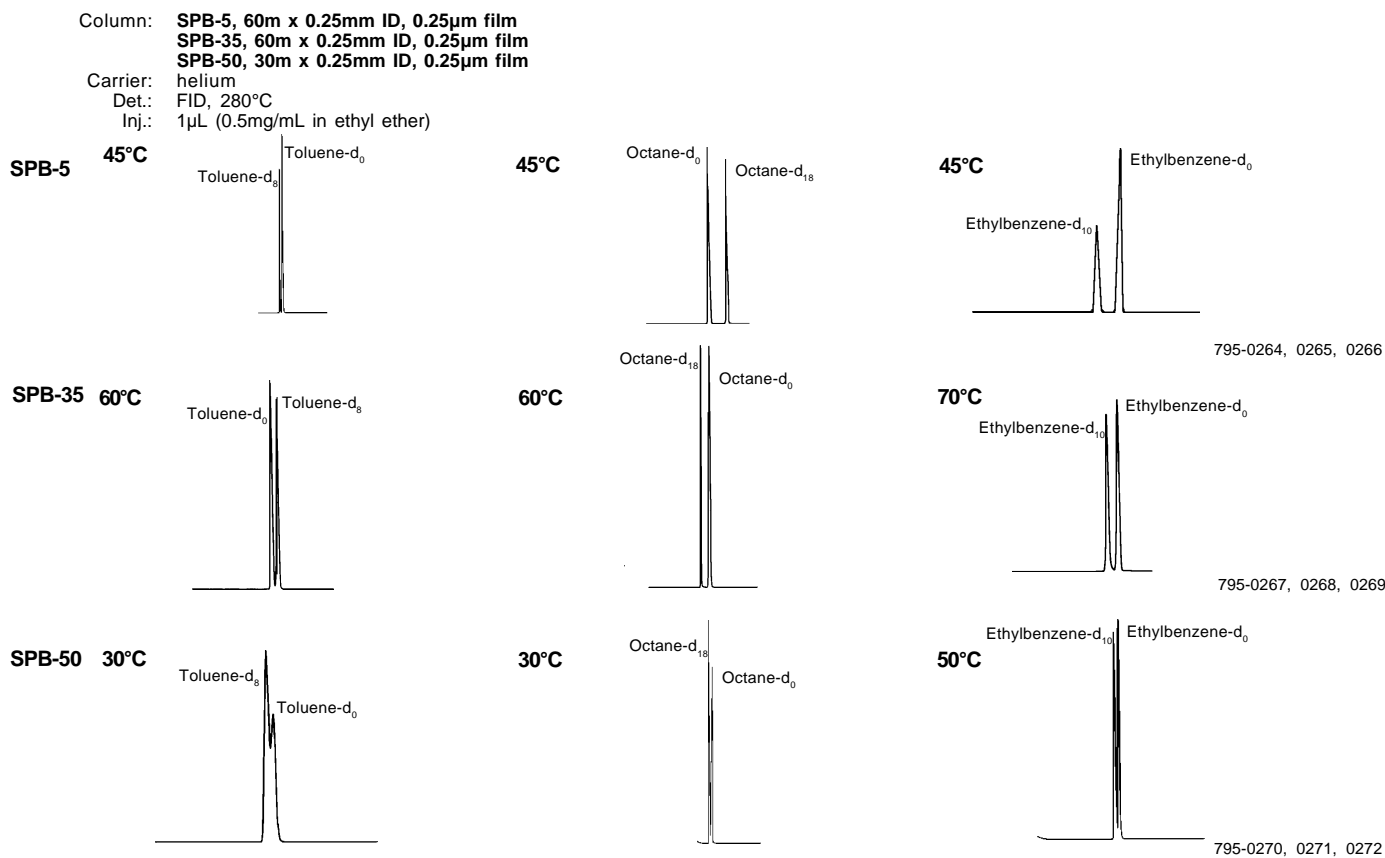
Isotopic Pair	SPB-5		SPB-35		SPB-50	
	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)
Benzene- d_6/d_0	25	6	30	14*	**	**
Toluene-methyl- d_3/d_0	30	11	50	16*	**	**
Toluene- d_5/d_0	60	7	70	9	30	4*
Methylcyclohexane- d_{14}/d_0	60	6	60	7	40	2
Octane- d_{18}/d_0	80	6	90	5	30	3
Ethylbenzene-ring- d_5/d_0	35	23*	50	33*	**	**
Ethylbenzene-ethyl- d_5/d_0	60	10	80	12	30	9*
Ethylbenzene- d_{10}/d_0	80	7	80	12	50	4
Naphthalene- d_8/d_0	110	12	140	17	80	16

*An overlap exists between the two peaks.

**The two compounds were not separated.

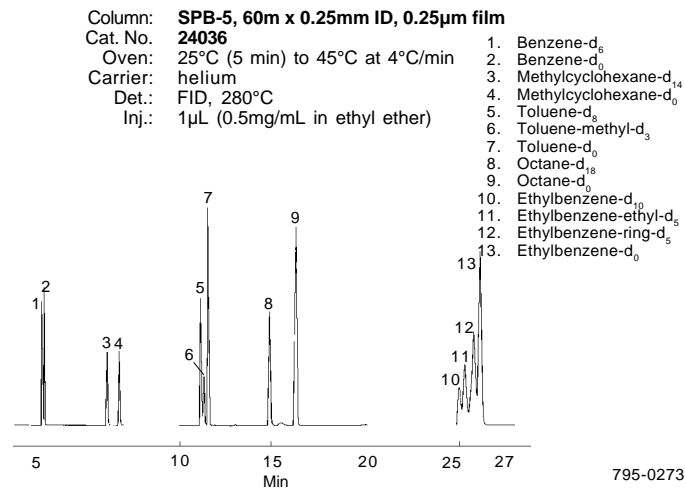
Data provided by Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511 USA.

Figure A. Comparative Separation of Isomers on Three Capillary Columns



Chromatograms provided by Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511 USA.

Figure B. Standard Mixture of Dehydrocyclization of Alkanes



Chromatogram provided by Buchang Shi, Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511 USA.

Ordering Information:

Fused Silica Capillary Columns

SPB-5, 60m x 0.25mm ID, 0.25µm film	24036
SPB-35, 60m x 0.25mm ID, 0.25µm film	24093
SPB-50, 30m x 0.25mm ID, 0.25µm film	24181

References

1. Shi, B. and H. Davis, *J. Chromatogr.*, **654**, 319 (1993).
2. Shi, B. and H. Davis, *J. Catal.*, **147**, 38 (1994).

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

SPB is a trademark of Supelco, Inc.

Contact our Technical Service Department
 (phone 800-359-3041 or 814-359-3041, FAX 814-359-5468)
 for expert answers to your questions.

Note 75

For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website (www.sigma-aldrich.com), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.

ARGENTINA · Sigma-Aldrich de Argentina, S.A. · Buenos Aires 1119 **AUSTRALIA** · Sigma-Aldrich Pty. Ltd. · Castle Hill NSW 2154 **AUSTRIA** · Sigma-Aldrich Handelsgesellschaft GmbH · A-1110 Wien
BELGIUM · Sigma-Aldrich N.V./S.A. · B-2880 Bornem **BRAZIL** · Sigma-Aldrich Quimica Brasil Ltda. · 01239-010 São Paulo, SP **CANADA** · Sigma-Aldrich Canada, Ltd. · 2149 Winston Park Dr., Oakville, ON L6H 6J8
CZECH REPUBLIC · Sigma-Aldrich s.r.o. · 186 00 Praha 8 **DENMARK** · Sigma-Aldrich Denmark A/S · DK-2665 Vallensbaek Strand **FINLAND** · Sigma-Aldrich Finland/YA-Kemia Oy · FIN-00700 Helsinki
FRANCE · Sigma-Aldrich Chimie · 38297 Saint-Quentin-Fallavier Cedex **GERMANY** · Sigma-Aldrich Chemie GmbH · D-82041 Deisenhofen **GREECE** · Sigma-Aldrich (o.m.) Ltd. · Ilioupoli 16346, Athens
HUNGARY · Sigma-Aldrich Kft. · H-1067 Budapest **INDIA** · Sigma-Aldrich Co. · Bangalore 560 048 **IRELAND** · Sigma-Aldrich Ireland Ltd. · Dublin 24 **ISRAEL** · Sigma Israel Chemicals Ltd. · Rehovot 76100
ITALY · Sigma-Aldrich s.r.l. · 20151 Milano **JAPAN** · Sigma-Aldrich Japan K.K. · Chuo-ku, Tokyo 103 **KOREA** · Sigma-Aldrich Korea · Seoul **MALAYSIA** · Sigma-Aldrich (M) Sdn. Bhd. · Selangor
MEXICO · Sigma-Aldrich Quimica S.A. de C.V. · 50200 Toluca **NETHERLANDS** · Sigma-Aldrich Chemie BV · 3330 AA Zwijndrecht **NORWAY** · Sigma-Aldrich Norway · Torshov · N-0401 Oslo
POLAND · Sigma-Aldrich Sp. z o.o. · 61-663 Poznań **PORTUGAL** · Sigma-Aldrich Quimica, S.A. · Sintra 2710 **RUSSIA** · Sigma-Aldrich Russia · Moscow 103062 **SINGAPORE** · Sigma-Aldrich Pte. Ltd.
SOUTH AFRICA · Sigma-Aldrich (pty) Ltd. · Jet Park 1459 **SPAIN** · Sigma-Aldrich Quimica, S.A. · 28100 Alcobendas, Madrid **SWEDEN** · Sigma-Aldrich Sweden AB · 135 70 Stockholm
SWITZERLAND · Supelco · CH-9471 Buchs **UNITED KINGDOM** · Sigma-Aldrich Company Ltd. · Poole, Dorset BH12 4QH
UNITED STATES · Supelco · Supelco Park · Bellefonte, PA 16823-0048 · Phone 800-247-6628 or 814-359-3441 · Fax 800-447-3044 or 814-359-3044 · email: supelco@sial.com

H

Supelco is a member of the Sigma-Aldrich family. Supelco products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for a particular use. Additional terms and conditions may apply. Please see the reverse side of the invoice or packing slip.