Analysis of Bromo-Chlorobenzenes by Gas Chromatography

GC-Analyse von Brom-Chlor-Benzolen

Analyse des bromo-chlorobenzènes par chromatographie en phase gazeuse

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Summary: Separation and quantitative analysis of all components in a mixture of benzene, chlorobenzene, 1-bromo-4-chlorobenzene, 1-bromo-3-chlorobenzene and 1-bromo-2-chlorobenzene have been achieved by use of a rapid gas chromatographic method. The procedure involves isothermal conditions in a simple laboratory instrument with a 10 foot stainless steel column packed with 8 weight % Bentone-34 modified with 10 weight % DC-200 silicone oil on Chromosorb W. Data obtained include the weight factor, capacity ratio, resolution and retention index for each compound. Analysis time is approximately 14 minutes and component resolutions are greater than 5.


Résumé: La séparation et l'analyse quantitative de tous les constituants d'un mélange de benzzéne, chlorobenzène, 1-bromo-4-chlorobenzène, 1-bromo-3-chlorobenzène et 1-bromo-2-chlorobenzène ont été accomplies grâce à une méthode rapide de chromatographie en phase gazeuse. La chromatographie est faite sous conditions isothermes en employant un instrument simple de laboratoire; cet instrument comprend une colonne en acier inoxydable de 3 mètres de long, remplie de Chromosorb W à 8 % (en poids) de Bentone-34 modifié par 10 % (en poids) d'huile de silicone DC-200. Les données obtenues comprennent, pour chaque composé, le facteur de poids, le facteur de capacité, la résolution et l'indice de rétention. Le temps d'analyse est d'environ 14 minutes et la valeur de la résolution pour chaque couple de pics est supérieure à 5.

Introduction

The five components in a mixture of benzene, monochlorobenzene, 1-bromo-4-chlorobenzene, 1-bromo-3-chlorobenzene and 1-bromo-2-chlorobenzene present a difficult analysis problem even for gas chromatography because of the isomers with similar properties. Attempts to separate substituted benzene isomers [1-6] have pointed to the advantages of using as a stationary phase a mixture of solid Bentone-34 (dimethyldioctadecylammonium bentonite) modified with liquid phases such as silicone oils or dinonyl phthalate. The choice of silicone fluid as a modifying substance is supported by the work of Mortimer, who concluded from x-ray examination that the silicone oil expands the basal spacing of the organoclay from 12.3 Angstroms to 38.5 Angstroms so that the mixed stationary phase exists as a thixotropic gel.

The boiling points of the isomers are very close to each other, making separation difficult, and most of the work done on separation of halogenated benzene compounds has involved either very small sample sizes and long retention times or incomplete separation. However, Karasek [6, 7] has reported a rapid GC technique for separating and quantitatively analyzing both brominated benzene compounds and chlorinated benzene compounds; this technique uses Bentone-34/silicone oil columns and completes analysis in 3-10 minutes with resolutions higher than 3.

The present study involves the use of a column packed with 8 weight % Bentone-34 modified with 10 weight % DC-200 silicone fluid. A simple instrument operated isothermally under conditions of helium carrier flow rate and column temperature that optimize the analysis accomplishes rapid separation and quantitative analysis of all components in a mixture of Bz, C1Bz, 1-Br-4-C1Bz, 1-Br-3-C1Bz and 1-Br-2-C1Bz.

Experimental

Apparatus

The Carle 8000 Gas Chromatograph was used (CARLE Instruments, Inc., Fullerton, California). This instrument can be operated isothermally in the 30-200 °C range.
Table 1 Retention and Weight Factor Data for Compounds Chromatographed on 8 wt. % Bentone-34/10 wt. % DC-200 Silicone Oil Column at 160 °C and 30 ml/min Carrier Flow

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point °C</th>
<th>Weight Factors</th>
<th>Retention Time - sec.</th>
<th>Capacity Ratio*</th>
<th>Resolution**</th>
<th>Retention Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>28.6</td>
<td>1.00</td>
<td>57.2</td>
<td>1.0</td>
<td>7.78</td>
<td>837</td>
</tr>
<tr>
<td>Benzene</td>
<td>80.1</td>
<td>1.06</td>
<td>131.4</td>
<td>3.6</td>
<td>7.15</td>
<td>1077</td>
</tr>
<tr>
<td>MonoC1Bz</td>
<td>132.0</td>
<td>1.06</td>
<td>254.5</td>
<td>7.9</td>
<td>5.48</td>
<td>1227</td>
</tr>
<tr>
<td>1-Br-4-CIBz</td>
<td>196.0</td>
<td>1.46</td>
<td>419.0</td>
<td>13.7</td>
<td>7.03</td>
<td>1326</td>
</tr>
<tr>
<td>1-Br-3-CIBz</td>
<td>196.0</td>
<td>1.46</td>
<td>793.7</td>
<td>26.7</td>
<td>7.03</td>
<td>1451</td>
</tr>
<tr>
<td>1-Br-2-CIBz</td>
<td>204.0</td>
<td>1.62</td>
<td>1327</td>
<td>43.7</td>
<td>7.03</td>
<td>1451</td>
</tr>
</tbody>
</table>

Detector compartments are set at the desired temperature and heat is supplied by a constant input power. Equilibration requires 1-2 hours, after which time there is very little drift even at maximum sensitivity.

The column is 10 foot, 1/8 inch o. d. stainless steel, with a partitioning phase of 8 wt. % Bentone-34 modified with 10 wt. % DC-200 silicone fluid deposited on a solid support of 80/100 mesh Chromosorb W. The column was prepared by Perco Supplies, San Gabriel, California using a methylene chloride solvent.

The detector was a micro thermistor bead thermal conductivity detector.

Analysis Conditions

The column temperature was 160 °C and the detector and inlet temperatures were 170 °C. Other parameters were: sample size, 0.5 microliter; helium flow rate, 30 ml/min; detector output, 1 mV.

Recording and Integration

Peak emergence was recorded with a Sargent model SRG recorder and peak area was measured by the attached DISC integrator.

Standard Solution

Components of the standard solution were weighed, to the nearest hundredth of a milligram, on a Fisher semimicro single pan balance. The resulting weight percentages were calculated to 4 significant figures.

Weight Factors

Samples of the standard solution of all 5 components were analyzed. The peak areas for each component were measured and the resulting weight % for each component was calculated. These weight %’s were then averaged over five runs. The actual weight % for each component, determined by the weighing process, was divided by the corresponding average weight % based on peak areas. The resulting weight factors were set relative to benzene as 1.00.

Procedure

On-column injection of the samples was performed with a 2.5 microliter Hamilton Student syringe (No. 6661 - Cale Instruments, Inc., Fullerton, California). The flow rate was measured with a bubble film flow meter and the temperature with a dial thermometer.

A second mixture of all five components was prepared and weighed and the % composition by weight was calculated. Two GC runs were then performed on this sample, and for each run the % composition was determined according to the following formula:

\[
\% \text{ of } i = \frac{A_i F_i}{\sum_{i=1}^{5} A_i F_i} \times 100\%
\]

where \( A_i \) = peak area for component \( i \)
and \( F_i \) = weight factor for component \( i \)
These % compositions were averaged over the two runs.

Fig. 1

* \( t_k = \frac{(t_i - t_0)}{t_a} \)

** \( R = \frac{2(t_i - t_0)}{(w_i - w_0)} \)