

GAS CHROMATOGRAPHIC DATA COMPILATION

Supplement 1

ASTM AMD 25A S-1

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Introduction

Since James and Martin [1]¹ reported their initial separations by gas chromatography in 1952, an increasing number of retention data and conditions for separations have been published for a wide variety of materials. In 1961, a system for compiling published data as well as privately generated data was developed by the Gas Chromatography Subcommittee of the Tennessee Eastman Company Analytical Committee[2]. Data were coded in a standard form and were stored in IBM cards; when desired, the retention data could be retrieved directly from the cards or from listings of the accumulated data, which could be produced periodically.

In 1962, ASTM Committee E-19 on Gas Chromatography adopted the system developed at the Tennessee Eastman Company. The system was named the Tennessee Eastman-ASTM System. Data compiled by J. S. Lewis and his co-workers were published in 1963 as *Compilation of Gas Chromatographic Data, ASTM STP 343*, which designation was later changed to *DS 25*.

Task Group 2 of Subcommittee I on Definitions, Nomenclature, and Standard Data, ASTM Committee E-19, was formed to evaluate the original system, to find methods for the accumulation of data from published and unpublished sources, and to keep the data in the system as current as possible. Toward these ends, several changes were made to include retention indexes as well as "unorthodox data" and to facilitate data retrieval; gas chromatographers world wide were invited to donate unpublished retention data to the system; and a program was instigated in which abstractors were hired by ASTM to compile data from published sources. All data (23,000 items) accumulated in the system through 1965 were published by ASTM as *DS 25A* in July 1967. The designation was later changed to *AMD 25A*.

The published data abstraction project was started in 1965 at the Rochester Institute of Technology under the direction of William Hayles and has continued

under his direction. A second data abstraction project was started at the University of Waterloo, Waterloo, Ontario, Canada, under the direction of F. W. Karasek in June 1969. Additional projects at other universities are being contemplated.

Data accumulated in the system in January 1969 totaled 43,000 items. Since this quantity of data would make a cumbersome and rather expensive volume, it was decided to publish data added to the system since 1965 as a supplement to *AMD 25A*. In addition, all data accumulated through January 1969 will be published directly on microfilm using the Kodak KOM-90 microfilmer and will be available on magnetic tape for computer retrieval.

At the annual meeting of ASTM Committee E-19 in 1968, Subcommittee VI was formed to replace Task Group 2, Subcommittee I, take over its responsibilities, and expand its activities. The organization of Subcommittee VI lists six task groups:

- Task Group 1 on Direction, Policy, Format, and Layout
- Task Group 2 on Abstracting Data from Published Sources
- Task Group 3 on Compiling of Unpublished and Published Copyrighted Data
- Task Group 4 on Assembly and Care of Supplementary Tables
- Task Group 5 on Correction of Errors
- Task Group 6 on Liquid Chromatographic Data

Individuals willing to serve on one of these task groups are encouraged to do so by notifying either the membership secretary, O. L. Hollis, The Dow Chemical Co., Freeport, Texas 77541, or Subcommittee VI chairman, O. E. Schupp, III, Eastman Kodak Company, Rochester, New York 14650.

We invite chromatographers throughout the world to contribute their unpublished gas chromatographic retention data. Interested persons should contact Task Group 3 chairman, R. A. Hively, Goodyear Tire and Rubber Co., Akron, Ohio 44316.

¹ Italic numbers in brackets refer to the list of references on page 9.

Description of the Compilation

The object of this compilation is to provide the gas chromatographic conditions used for the separation of a wide variety of compounds and to facilitate the ten-

tative identification of materials producing peaks on chromatograms. Our ultimate aim is to have reference to all published articles that give conditions for the

separation of compounds. This book contains tabulations of gas chromatographic data printed from magnetic tape in a format which provides convenient means for rapid retrieval. Most of the data were obtained from the literature, although some are unpublished data contributed by laboratories, as noted in Supplementary Table 1. The use of commercial names or trademarks to designate some materials is for the convenience of compilers and users of this system and does not imply that they are recommended or preferred for any applications.

This supplement, plus *AMD 25A*, contains the retention data accumulated. The supplement differs from the first edition in that (1) the volume of data has about quadrupled, (2) the retention data include the retention index and capacity ratio, (3) a new format is used to facilitate data retrieval, and (4) reference is made to chromatographic data for specific compounds which are in a nonstandard or unorthodox retention form. Unorthodox retention data include references to a journal where only the chromatogram is given, where nonlinear temperature programming is used, or where retention data are not in a form suitable for coding into the system.

In addition, the retention data have been examined by a computer using a program developed at Eastman Kodak Company[3]. This program is designed to do four things: (1) determine if the correct value of the gas holdup was used in calculating the relative retentions when three or more *n*-alkanes are included in the data reported; (2) recalculate, if necessary, the reported relative retentions using a gas holdup correction factor when four or more *n*-alkanes are present; (3) calculate retention indexes; and (4) calculate retentions relative to the nearest *n*-alkane whenever sufficient data are present. Data found to be incorrect are discarded when they cannot be corrected. Every precaution has been taken in the computer program to ensure that the high quality of the data is retained.

Data are coded into the system on two types of punched cards. The name-formula card (NFC) contains the compound name in standard punched card alphabet, the molecular formula, and a cross-reference serial number. The cross-reference serial number identifies a compound for which gas chromatographic data are coded and is the same for a given compound even though the compound may be named in various ways. For instance, anthanthrene and dibenzo [def, mno] chrysene would both have the same serial number (471784) since they are two names for the same compound.

The compounds have been arranged in molecular formula sequence and assigned numbers according to that order. The molecular formula sequence is deter-

mined, first, by the number of carbon atoms, starting with the lowest number and proceeding to the higher numbers, second, by the number of hydrogen atoms, and thereafter, in alphabetical order by the number of atoms of each additional element. The elements included in the NFC are bromine, chlorine, fluorine, iodine, nitrogen, oxygen, sulfur, and silicon; since the publication of *AMD 25A*, boron, deuterium, and phosphorus have been added to the system. Thus C_6H_{10} appears before C_6H_{12} and has a smaller serial number. Similarly, $C_6H_{12}Br$ has a lower serial number than $C_6H_{12}Cl$. A survey of the listing of NFC in the Compound Data List and the sequence of serial numbers and molecular formulas is essential to a complete understanding of the system.

The data-bibliography card (DBC) contains data which describe the gas chromatographic column used, retention data, bibliographic reference, and cross-reference serial number. The data that describe the column include liquid phase or active solid (L.P), solid support (SS), column temperature in deg C (T), concentration of liquid phase (GLP), and reciprocal of the slope of the semilogarithmic plot of net retention volume versus carbon number for *n*-alkanes (1/B). The retention data coded include reference material (REF), relative retention, specific retention volume, or capacity ratio (REL-RET), and retention index (I). The bibliographic reference includes codes for the journal, volume, year, and page of published articles and company and laboratory codes for unpublished data.

Data-name cards (DNC) were added to the system after the publication of *STP 343* and contained some of the data from the DBC and the name of the compound from the NFC. The DNC was reproduced from both the DBC and the NFC. These cards were not made for unorthodox data entries. When the data were stored on magnetic tape, the use of DNC was discontinued.

Once the decks of cards have been produced, they can be reproduced, sorted, and rearranged with conventional equipment for handling punched cards. Previous lists of data were prepared directly from the punched card decks; however, as noted previously, this supplement was prepared directly from magnetic tape. The cards are used to update the master decks which form the input to the computer. All sorting and data handling are carried out on magnetic tape.

Changes in the Tennessee Eastman-ASTM System

This supplement, *AMD 25A Supplement 1*, is expected to be used closely with the original compila-

tion, *AMD 254*; therefore, it is important that the user understand changes that have been made in the system and differences between the two volumes. All data listed in the latter which have been corrected or changed are relisted in the supplement. The changes in the system have been made to supply more information to the user or to reduce the number of codes assigned to liquid phases, solid supports, and active solids.

Active Solid/Solid Support/Liquid Phase Codes

Active solid and solid support codes for materials not used to date (or perhaps used only once) have been deleted from the system. Codes for specific grades of a material have been deleted and one general code assigned. Footnotes are assigned to indicate the specific grade used. Active solids are coded under liquid phase codes, columns 2 and 3, rather than solid support codes, columns 4 and 5. Materials used as liquid phases, solid support or active solid for the first time will be assigned a code of 999 or 99 and a footnote designating the material. Mixed liquid phases are not given separate liquid phase codes but are given a single mixed liquid phase code, and the predominant material is coded under liquid phase. A liquid phase coated over an active solid is treated as a mixed liquid phase.

Footnotes

Footnotes are used to denote new or special conditions so that additional codes need not be assigned. A footnote, code A, B, etc., is coded in column 38 of the DBC. This code is printed between the SS and REF columns under F in the Stationary Phase and Compound Data Lists. The footnotes are found in Supplementary Table 13, under the AS/LP code and the bibliography for the data item. Footnotes are used also for unorthodox data to indicate other experimental conditions which were used (only one compound entry per article is coded into the system).

Mixed Liquid Phase Codes

Mixed liquid phases are treated as follows. The active material or principal liquid phase is coded under liquid phase. A code, A, B, etc., is keypunched in column 37 of the DBC. The composition of the mixed liquid phase is found in Supplementary Table 14 by looking up the AS/LP code and the bibliography. Multiple mixed liquid phases for a given bibliography are denoted by the mixed liquid phase code A, B, C, etc. As shown in Supplementary Table 14, the first, third, and fifth columns are codes for the liquid phases, active solids used and the second,

fourth, and sixth columns are for the proportions of each. The type of mixed liquid phase, that is, mixed liquid, mixed bed, or series column, is indicated next, followed by the bibliography. Columns containing less than 5 percent of a tailing reducer are not considered mixed liquid phases.

Supplementary Tables

Supplementary Table 1 contains acknowledgments to those who have donated to the system, abstracted data into the system, and handled data in the system.

Supplementary Table 2 contains the codes for the active solids and liquid phases arranged in numerical order. These codes appear as LP in the Stationary Phase and Compound Data Lists. A two-digit number indicates that the stationary phase was an active solid. Supplementary Table 3 is divided into part A for active solids in alphabetical order and part B for liquid phases in alphabetical order.

The codes for the solid supports are listed in sequence by the code number in Supplementary Table 4. These codes appear under the headings SS in the Stationary Phase and Compound Data Lists. Identical or essentially identical solid support materials often are sold under different commercial names. For simplicity and ease in using the system, similar materials always are given a common code designation, for example, eight commercial materials are listed under SS code 50.

The solid supports and codes are listed in alphabetical order in Supplementary Table 5.

Supplementary Table 6 is a list of the codes for the reference materials, also arranged in numerical order. Codes for the reference material appear under the heading REF in the Stationary Phase and Compound Data Lists. The reference compounds are assigned an arbitrary adjusted retention time of 1.00. For code numbers up to and including 40, the number coded under REF refers to the corresponding number of carbon atoms in the *n*-alkane used as the reference compound. When a V is listed under REF, the data coded under REL-RET are for the specific retention volume. A K under REF indicates that the capacity ratio is listed under REL-RET. The reference materials and codes are listed in alphabetical order in Supplementary Table 7.

When the original retention data are recalculated by the abstractor as they are coded into the system, this is noted by a description code. Supplementary Table 8 is a list of these codes. They appear under the heading A in the Stationary Phase and Compound Data Lists.

Supplementary Table 9 lists the codes for indicating the unorthodox form in which the unorthodox data were published. These codes appear in the Compound Data List under the heading U.

Supplementary Table 10 lists the codes for indicating operations performed by the computer for upgrading the data. These codes appear in the Compound Data List under the heading C.

Supplementary Table 11 contains a list of standard four-letter abbreviations for journal titles (CODEN) [4] used in the system. The CODEN assignments appear under the heading JRNL in the Compound Data List. The code BOOK is under the JRNL heading, indicating that the data were taken from a book. The particular book has a four-letter code under VOL in the Compound Data List. The titles and authors of the various books are given under the CODEN BOOK in Supplementary Table 11.

Supplementary Table 12 gives the temperature-retention relationships for those liquid phases for which data are included in the system to allow their calculation. The Antoine equation has been written

$$B = I + \frac{S}{(T+C)} \dots \dots \dots (1)$$

where B is the logarithm of the relative retention of two successive n -alkanes, $B = \log(r_{z+1,z})$, I is a constant, S is the slope showing the temperature dependence, T is the absolute temperature, and C is a correction factor sometimes required to make the relationship linear. The values reported in Supplementary Table 12 may be used to calculate B values at any temperature. Since the relationships were calculated using data from several sources, there may be some error in the calculated B values.

Supplementary Tables 13 and 14 list the footnotes and mixed liquid phases reported in the Stationary Phase and Compound Data Lists. The use of these tables is discussed in the previous section.

Stationary Phase Data List

The Stationary Phase Data List is a tabulation of the gas chromatographic data that have been processed by the computer arranged in the following sequence: liquid phase (LP), column temperature in deg C (T), reference material (REF), and retention data (REL-RET).

The heading at the top of each page in the Stationary Phase and Compound Data Lists refers to the data coded in that particular column. Reading from left to right, under LP are the codes for the liquid phase or active solid used which are identified in Supplementary Table 2. Also, the first entry for each

new liquid phase is the name or names of the liquid phase. For example, the first entry in Stationary Phase Data List for LP 150 is the name squalane. Thus, squalane is the liquid phase for all the data coded under LP 150. Under liquid phase code 163, the first two entries are Apiezon Grease L and Perkin-Elmer Column Q. Thus, liquid phase code 163 is for Apiezon Grease L, which sometimes is referred to in the literature as Perkin-Elmer Column Q.

If a code is present under the heading M, the liquid phase is mixed. The mixture used is found in Supplementary Table 14 by looking under the LP code, the M code, and finally the bibliography.

Under the heading SS are the codes for the solid supports used, which are identified in Supplementary Table 4. A code under the heading F indicates that additional information may be found in Supplementary Table 13 for footnotes by looking under the LP code, the F code, and the bibliography in that table.

Under REF are the codes for the various reference materials used, which are identified in Supplementary Table 6. For numbers up to and including 40, the number listed refers to the corresponding number of carbon atoms in the n -alkane used as the reference compound.

The retention data are listed under the heading REL-RET. When a V is listed in the column headed REF, the specific retention volume is coded under the heading REL-RET. When a K is coded in the column headed REF, the capacity ratio is listed under the heading REL-RET.

The data under the heading T are the column temperatures in deg C.

Under the heading A is listed a description code identified in Supplementary Table 8, which is used by the abstractor when original retention data are recalculated as they are coded into the system.

The data under heading I are the retention indexes. The retention index is the preferred retention parameter [5,6]. It is defined relative to the retention of n -alkanes and represents the hypothetical (whole number plus interpolated decimal fraction) n -alkane which would have an identical retention multiplied by 100. Retention index and net retention volume are related as follows:

$$I_x = 100 \left(z + \frac{\log V_{Nx} - \log V_{Nz}}{\log V_{N(z+1)} - \log V_{Nz}} \right) \dots \dots (2)$$

When flow rate is constant, relative retentions can be substituted for net retention volumes.

$$I_x = 100 \left(z + \frac{\log r_{x,z}}{\log r_{(z+1),z}} \right) \dots \dots \dots (3)$$

$$I_x = 100 \left(z + \frac{\log r_{x,z}}{B} \right) \dots \dots \dots (4)$$

where:

V_N = net retention volume,

x = a compound with a retention between that of the first and second n -alkane standards,

z = number of carbon atoms in the first n -alkane standard,

$r_{x,z}$ = relative retention of compound x with respect to the first n -alkane standard,

$(z+1)$ = number of carbon atoms in the second n -alkane standard,

I_x = isothermal retention index of compound x ,

I_{PT} = linear programmed temperature gas chromatography (PTGC) retention index,

V_{Nx} = net retention volume of x ,

V_{Nz} = net retention volume of the first n -alkane standard,

$V_{N(z+1)}$ = net retention volume of second n -alkane standard,

$r_{(z+1),z}$ = relative retention of the second n -alkane with respect to the first, and

B = slope of semilogarithmic plot of net retention volume versus n -alkane carbon number. It should be based on n -alkane retentions that are about a decade apart.

Equation 2 can be extended to linear PTGC by rewriting it thus

$$I_{PT} \cong 100 \left(z + \frac{V_{Nx} - V_{Nz}}{V_{N(z+1)} - V_{Nz}} \right) \dots \dots (5)$$

In linear PTGC, any one retention parameter (volume, time, chart distance, or temperature, with or without correction for gas holdup) can be substituted for V_N .

Equations 2 and 3 are preferred for calculating I_x for storage in the system, since n -alkanes with retentions that bracket the retention of the compound for which I_x is to be calculated are used. Equation 4 is used for correlation of data over a wide range of retentions and for extrapolation of data outside the range for which experimental measurements are available for the n -alkanes.

The other headings in the Stationary Phase Data List refer to the compound name and the molecular formula. The molecular formula is given so that the same data can be located in the Compound Data List. The molecular formula of 2-butanone is C_4H_8O . By looking in the Compound Data List under C_4H_8O and the compound name, one can locate other information coded into the system. The bibliography also is coded for reference.

Compound Data List

The Compound Data List is a tabulation from magnetic tape of the merged NFC and DBC in molecular formula order. Each NFC for a given compound is listed and is followed by all the DBC for that compound in the same order as in the Stationary Phase Data List. Unorthodox data entries also are included in the Compound Data List. The headings at the top of each page refer to the data in the DBC rather than to the name and formula of the compound. The list contains all the data except the compound names that are listed in the Stationary Phase Data List, plus additional data.

The code under the heading U is identified in Supplementary Table 9 and indicates the unorthodox form in which the data were published. As a rule, very few or no retention data are given where a code is listed under the heading U. The main reason for listing unorthodox data is so that the user can obtain a bibliographic reference for the chromatography of that material.

The data under GLP show the concentration of the liquid phase used. The number coded is the parts LP to 100 parts SS by weight.

Data under O-RM and OLD-RR are the data that originally were coded into the system. These data were transferred to the present list by the computer during the operation coded under volumn heading C.

The Compound Data List also contains the code for unpublished data which have been donated to the system. Under the heading N/P for such data, an N refers to data from a notebook and a P refers to data from a procedure or company report. As a rule, no information other than that coded on the DBC is available when an N or P is listed under the heading N/P; however, the company donating the data is identified by codes under the heading CO and LAB. These codes are listed in Supplementary Table 1.

Uses of Data in System

The data accumulated in the Tennessee Eastman-ASTM System can be used in several ways; for example,

- (1) to determine conditions for separations that have been reported for specific compounds,
- (2) to tentatively identify materials producing unknown peaks on a chromatogram, or
- (3) to select a column for the best separation of two or more known compounds.

Other uses of the system undoubtedly will be obvious to persons engaged in gas chromatographic

GAS CHROMATOGRAPHIC DATA TABULATED ON BASIS OF MOLECULAR FORMULA

| C16 H24 | N2 O4 | PHTHALAMIDE, N,N,NPR,NPR-TETRAETHYL | 4461505 |
|------------|-------------|-------------------------------------|-----------------|
| 265 1 107 | 1.130 175 | N | 61 A RA 4461505 |
| 265 1 107 | 1.130 190 | N | 61 A RA 4461505 |
| 265 1 107 | 1.150 210 | N | 61 A RA 4461505 |
| C16 H24 | N4 O4 | DECANAL, 2,4-DNP | 4461555 |
| 225 51 115 | 6.550 250 T | 11.0 ANCH 36 2256 64 | 4461555 |
| C16 H24 | O10 | L-TALITOL PENTAACETATE, 6-DEOXY- | 4464305 |
| 619 41 70 | .710 213 | CJCH 39 1895 61 | 4464305 |
| 620 1 70 | .710 213 | CJCH 39 1895 61 | 4464305 |
| 621 41 70 | .700 213 | CJCH 39 1895 61 | 4464305 |

FIG. 1 — Portion of Compound Data List.

work. Subcommittee VI, Committee E-19 on Chromatography, hopes to maintain an up-to-date file of gas chromatographic data; the editors would welcome any additions or corrections to these data. A brief description of the three uses mentioned is given to illustrate the utility of the system.

Search for Specific Compounds

Probably the greatest use of the system in *AMD 25A* is to determine whether or not data have been reported for a particular compound or class of compounds. Figure 1 is reprinted from *AMD 25A* and is a portion of the Compound Data List. Suppose a chromatographer is interested in the feasibility of separating 2,4-dinitrophenylhydrazone derivatives of ketones and aldehydes. To begin, he might wish to see if anyone has reported work on decanal or decanone. The molecular formula for these materials is $C_{10}H_{18}N_4O_4$. By searching the Compound Data List for this molecular formula, one finds the 2,4-dinitrophenylhydrazone derivative of decanal listed as Serial No. 446155 in Fig. 1. Reference is given to its separation under I.P. code 225 at 250 C in ANCH 36 2256 (1964). By referring to the Stationary Phase Data List, for liquid phase code 225 at a column temperature of 250 C (not shown here), one finds that thirty-seven 2,4-dinitrophenylhydrazone derivatives have been chromatographed. Other pertinent information on the separation of this class of compounds might be obtained by referring to the article listed under the bibliography reference — ANCH 36 2256 (1964) — which is easily found since ANCH is the CODEN for *Analytical Chemistry*.

Identification of Unknown Peaks

The homologous series of *n*-alkanes are recommended as reference materials. If all data were relative to *n*-alkanes, comparison of data from different laboratories could be made easily.

The retention index system of designating retention data is a normalized logarithmic function of retentions relative to *n*-alkanes in which the *n*-alkanes are arbitrarily assigned indexes of 100 times their number of carbon atoms, that is, *n*-nonane has an index $I_x = 900$.

The use of retention indexes has advantages over the use of relative retentions for qualitative identification. For example, the retention indexes of successive members of any homologous series will differ by 100 plus or minus a small number; thus, a calibration for the whole series might be possible using only three or four members of the series. Note that in Fig. 2 the retention indexes for acetone and 2-butanone differ by 100, as do those for 2-butanone and 2-pentanone. Thus, by extrapolation of this 100-unit separation per carbon number fact, an unknown peak on an Apiezon Grease L column with a retention index between 1138 and 1147 might be tentatively identified as 2-decanone.

The greatest utility of the Stationary Phase Data List probably lies in the tentative identification of unknown materials producing peaks on a chromatogram. Figure 2 is a portion of the Stationary Phase Data List using Apiezon Grease L (code 163) as the liquid phase. Most of the data shown in Fig. 2 are for a column temperature of 70 C. Suppose a solvent mixture is run on an Apiezon Grease L column operating at 70 C and an unknown peak is observed at a retention index of 617. The material producing this unknown peak would be tentatively identified as one of the materials listed in Table 1 or a mixture of two or more of these compounds. A more positive identification might be possible if the unknown component is run on a column with characteristics different from those of Apiezon Grease L, such as a high molecular weight poly (ethylene glycol). Emulphor O is such a compound. Assume the unknown component had a retention index of 974 ± 5 on Emulphor O, the only material common to both liquid phases at the

GAS CHROMATOGRAPHIC DATA TABULATED ON BASIS OF LIQUID PHASE

| TENNESSEE EASTMAN-ASTM SYSTEM | | | | | | SER NO | |
|-------------------------------|----|-----|---------|----|-------|-------------------------------|---------|
| LP | SS | REF | REL-RET | T | A | | |
| GLP | | | | | | COMPOUND NAME | |
| | | | | | | | |
| 163 | 2 | 7 | .88 | 50 | 687. | PENTANE, 2,2,4-TRIMETHYL- | 267700S |
| 163 | 50 | 57 | .676 | 50 | | BENZENE, ETHYL- | 239800S |
| 163 | 50 | 57 | 1.000 | 50 | 5.25 | D-XYLENE | 239900S |
| 163 | 50 | 57 | 1.150 | 50 | 5.25 | STYRENE | 229300S |
| 163 | 50 | 57 | 1.320 | 50 | 5.25 | ACETYLENE, PHENYL | 224700S |
| 163 | 50 | 57 | 1.450 | 50 | 5.25 | BENZENE, N-PROPYL- | 283500S |
| 163 | 51 | 4 | .47 | 70 | 315.0 | METHANOL | 6200S |
| 163 | 51 | 4 | .60 | 70 | 343.0 | ACETALDEHYDE | 16500S |
| 163 | 51 | 4 | .76 | 70 | 370.0 | FORMATE, METHYL- | 16700S |
| 163 | 51 | 4 | 1.00 | 70 | 400.0 | ETHYL ALCOHOL | 19300S |
| 163 | 51 | 4 | 1.30 | 70 | 429.0 | METHANE, BROMO- | 5200S |
| 163 | 51 | 4 | 1.33 | 70 | 432.0 | ETHANE, CHLORO | 17400S |
| 163 | 51 | 4 | 1.42 | 70 | 439.0 | ACETONITRILE | 14300S |
| 163 | 51 | 4 | 1.42 | 70 | 439.0 | ACETONE | 36500S |
| 163 | 51 | 4 | 1.53 | 70 | 447.0 | ACETONE | 36500S |
| 163 | 51 | 5 | 1.53 | 70 | 547.0 | 2-BUTANONE | 72100S |
| 163 | 51 | 5 | 1.55 | 70 | 549.0 | 2-BUTANONE | 72100S |
| 163 | 51 | 6 | .84 | 70 | 581.0 | 1-PROPANOL, 2-METHYL- | 80600S |
| 163 | 51 | 6 | .86 | 70 | 583.0 | NITROETHANE | 18400S |
| 163 | 51 | 6 | .86 | 70 | 583.0 | PROPANE, 2-BROMO- | 38200S |
| 163 | 51 | 6 | .87 | 70 | 585.0 | FORMIC ACID, TERT-BUTYL ESTER | 106702S |
| 163 | 51 | 6 | .89 | 70 | 587.0 | 1-HEXENE | 154500S |
| 163 | 51 | 6 | .97 | 70 | 596.0 | ACETIC ACID, ISOPROPYL ESTER | 106300S |
| 163 | 51 | 6 | .99 | 70 | 599.0 | SEC-BUTYL CHLORIDE | 76200S |
| 163 | 51 | 6 | 1.03 | 70 | 603.0 | ISOBUTYL CHLORIDE | 76100S |
| 163 | 51 | 6 | 1.05 | 70 | 605.0 | 2-BUTANONE, 3-METHYL- | 104200S |
| 163 | 51 | 6 | 1.12 | 70 | 613.0 | CHLOROFORM | 4000S |
| 163 | 51 | 6 | 1.15 | 70 | 616.0 | ISOBUTYRIC ACID, METHYL ESTER | 105400S |
| 163 | 51 | 6 | 1.18 | 70 | 618.0 | FURAN, TETRAHYDRO | 72900S |
| 163 | 51 | 6 | 1.18 | 70 | 618.0 | 1-BUTANOL | 80400S |
| 163 | 51 | 6 | 1.19 | 70 | 619.0 | PROPANE, 2-BROMO-2-METHYL- | 75900S |
| 163 | 51 | 6 | 1.27 | 70 | 627.0 | PROPANE, 1-BROMO- | 38300S |
| 163 | 51 | 6 | 1.33 | 70 | 632.0 | FORMIC ACID, SEC-BUTYL ESTER | 106701S |
| 163 | 51 | 6 | 1.37 | 70 | 635.0 | CYCLOPENTANE, METHYL- | 156300S |
| 163 | 51 | 6 | 1.41 | 70 | 638.0 | 2-PENTANONE | 104800S |
| 163 | 51 | 6 | 1.42 | 70 | 639.0 | FORMIC ACID, ISOBUTYL ESTER | 106700S |
| 163 | 51 | 6 | 1.43 | 70 | 640.0 | ACETIC ACID, TERT-BUTYL ESTER | 160950S |
| 163 | 51 | 6 | 1.45 | 70 | 641.0 | N-BUTYL CHLORIDE | 76000S |
| 163 | 51 | 6 | 1.53 | 70 | 647.0 | DIETHYL KETONE | 104300S |

FIG. 2 - Portion of Stationary Phase Data List for Apiezon Grease L (LP 163).

indicated retention indexes is 1-butanol, and it would be identified as the material producing the unknown peak. Table 1 also shows the retention indexes found on the Emulphor O column for the materials listed

under Apiezon Grease L. Even though a mixture of these compounds would not be separated on the Apiezon Grease L column, the compounds would easily be separated on the Emulphor O column. The materials

TABLE 1 - Tentative identification of unknown peak on Apiezon Grease L and Emulphor O columns.

| Apiezon Grease L, 70 C | | Emulphor O, 130 C | |
|------------------------|-------------------------|-------------------|-------------------------|
| Index | Material | Index | Material |
| 613 | Chloroform | 970 | N-butyronitrile |
| 616 | Methyl isobutyrate | 970 | sec-butyl propionate |
| 618 | Tetrahydrofuran | 971 | n-butyl acetate |
| 618 | 1-butanol | 971 | tert-butyl butyrate |
| 619 | 2-bromo-2-methylpropane | 973 | 1-butanol |
| | | 974 | Propyl isobutyrate |
| | | 975 | Isoamyl formate |
| | | 976 | 1-methylcycloheptene |
| | | 979 | 2-hexanone |
| | | 879 | Chloroform |
| | | 825 | Methyl isobutyrate |
| | | 800 | Tetrahydrofuran |
| | | 756 | 2-bromo-2-methylpropane |

found in the Stationary Phase Data List for Emulphor O over this range of retention indexes also are given in the table.

Column Selection for Separating Binary Mixtures

As shown in Table 1, tetrahydrofuran and 1-butanol both have a retention index of 618 on the Apiezon Grease L column. Consider finding a column which will separate these materials. The Emulphor O column will accomplish this, but are there other columns which will give a better separation? Using the Compound Data List of *AMD 254*, one would find that there were 162 entries for 1-butanol and 17 entries for tetrahydrofuran. By meticulously searching through the Compound Data List for these materials, 13 common liquid phases and column temperatures could be found. If retention data were available on these 13 matches found and if these data were relative retentions to a common reference material, then the approximate number of theoretical plates, n , required for separation could be calculated as follows:

$$n = 4 R^2 \left(\frac{r + 1}{r - 1} \right)^2$$

where r is the retention of one solute relative to the other and R is the resolution. A manual search of the Compound Data List such as this would require less time than repeated experimental evaluation of sev-

eral columns; however, when considering many columns and combinations of temperature, this search would still be quite time consuming. A computer program has been written at Tennessee Eastman Company to calculate the number of theoretical plates required for a base line separation with a resolution of 2 for any two solutes using the DBC from the Tennessee Eastman-ASTM System as input into the computer.² Codes for the liquid phases, reference material, relative retention, temperature, reciprocal slope, and serial number for all the cards of one of the solutes are stored in the computer. Then, each card of the second solute is compared to the DBC of the first solute. When a common liquid phase and temperature are found for both solutes, a check is made to see if the retention data are relative to the same reference material. If so, then the approximate number of theoretical plates required for separation is calculated. If the retention data are relative to different reference materials and the reference materials happen to be n -alkanes, then the retention data are calculated relative to the same reference material using the reciprocal slope value calculated and stored in the system. The number of theoretical plates required for separating the two solutes is calculated and printed out by the computer along with the column temperature

² A FORTRAN program list can be obtained from J. S. Lewis, Research Laboratories, Tennessee Eastman Kodak Company, Kingsport, Tenn. 37662.

TABLE 2—Portion of computer output for plates required to separate 1-butanol (080400) and tetrahydrofuran (072900).

| LP | TEMP | REF | REL-RET | 1/B | PLATES | SER. NOS. |
|--|------|-----|---------|--------|--------|-----------|
| 160 | 100 | 6 | 1.020 | 3.0497 | 1032. | 72900. |
| 160 | 100 | 6 | 1.310 | 3.0497 | 1032. | 80400. |
| UNABLE TO SEPARATE PEAKS WITH 163 COLUMNS AT 70 DEGREES C. RELATIVE RETENTIONS FOR ALL SERIAL NOS. 72900. AND 80400. ARE EQUAL. | | | | | | |
| 163 | 130 | 6 | 1.230 | 3.4536 | 2283. | 72900. |
| 163 | 130 | 6 | 1.040 | 3.4536 | 2283. | 80400. |
| 163 | 130 | 6 | 1.230 | 3.4536 | 6084. | 72900. |
| 163 | 130 | 6 | 1.110 | 3.4536 | 6084. | 80400. |
| 200 | 80 | 8 | 0.710 | 2.9497 | | 72900. |
| 200 | 80 | 7 | 1.550 | 2.9497 | 105. | 72900. |
| 200 | 80 | 7 | 0.680 | 2.9497 | 105. | 80400. |
| 200 | 213 | 5 | 1.100 | 6.1908 | | 72900. |
| 200 | 213 | 6 | 0.758 | 6.1908 | 846. | 72900. |
| 200 | 213 | 6 | 1.000 | 6.1908 | 846. | 80400. |
| 263 | 100 | 7 | 3.222 | 0.0000 | 36. | 72900. |
| 263 | 100 | 7 | 15.703 | 0.0000 | 36. | 80400. |

and the code for the liquid phase, as in Table 2. For a base line separation of $R = 2.0$, the separation of 1-butanol and tetrahydrofuran using Apiczon Grease I. (code 163) as the liquid phase at 70°C would not be possible, since the relative retentions for these materials are equal. Using the liquid phase with a code of 263 (Carbowax 300) one would need only 36 plates for the separation of these materials. This is a simple problem, requiring a column less than 1 ft long.

The data in the Compound Data List can be used to determine whether or not combination liquid phases can be used to achieve desired separations, provided that the capacity ratio k of the compounds can be determined. The technique has been described in detail by Hildebrand and Reilley [7]. Capacity ratios can be calculated for all data for which k is given for one member, that is,

$$k_i = \frac{t'_{R,i}}{t_M} = r_{i,s} \times k_s \dots \dots \dots (6)$$

where t'_R is the adjusted retention time, t_M is the gas holdup time, $r_{i,s}$ is the retention of the component i relative to the reference material s , and k_i and k_s are the capacity ratios of i and s . Once the capacity ratios are known for the desired compounds, a graph is constructed as follows. Two y axes are drawn on graph paper 100 x units apart. One y axis is for 100 percent liquid phase A (0 percent B), and the other y axis is for 100 percent liquid phase B. The x axis is for the fractional combination, m , in terms of the second liquid phase B. A fractional combination of 0.60, therefore, would be a column containing 60 percent liquid phase B and 40 percent liquid phase A. The y axes are for plotting the capacity ratios of the compounds on the pure liquid phases. Straight tie lines are then drawn between the capacity ratios of each of the compounds. These lines give the capacity ratio of each compound at intermediate fractional combinations of the two liquid phases. The m value at which all the tie lines are farthest apart is the fractional combination of liquid phases in which the best separation of the components is to be found.

Since the chromatographs used in obtaining the data for the two liquid phases probably will not be identical, the m values will be, in all probability, only good approximations. To obtain the best value, one should conduct the experiment on his own equipment. The value in using the data in the system is simply that, if a separation worked with data in the system, it is sure to work in the laboratory. If a separation could not be achieved on paper, it cannot be achieved in the laboratory, and the time that would be required to try an experiment is saved.

Lewis et al [8] reported the use of data in the system to calculate the approximate m value needed to separate a mixture of hexane, acetone, ethyl alcohol, and ethyl acetate on Silicone DC-200 and Carbowax 20M. The calculated 60 percent Carbowax 20M and 40 percent Silicone DC-200 gave the desired separation.

References

- [1] James, A. T. and Martin, A. J. P., *Analyst*, ANALA, Vol. 77, 1952, p. 915.
- [2] Lewis, J. S., McCloud, G. T., and Schirmer, W., Jr., *Journal of Chromatography*, JOCRA, Vol. 5, 1961, p. 541.
- [3] Schupp, O. E., III, "Recalculation of Published Gas Chromatographic Retention Data," presented at the 18th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 9 March 1967.
- [4] Kuentzel, L. E., Ed., *CODEN for Periodical Titles*, ASTM DS 23A, 2nd ed., American Society for Testing and Materials, 1966.
- [5] Kovats, E., *Helvetica Chimica Acta*, HCACA, Vol. 41, 1958, p. 1915.
- [6] Kovats, E., *Helvetica Chimica Acta*, HCACA, Vol. 42, 1959, p. 2709.
- [7] Hildebrand, G. P. and Reilley, C. N., *Analytical Chemistry*, ANCHA, Vol. 36, 1964, p. 47.
- [8] Lewis, J. S., Schupp, O. E., III, Simmons, M. W., and Patton, H. W., "Column Selection Using the Tennessee Eastman-ASTM System for Storage and Retrieval of Gas Chromatographic Data," presented at the 18th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 9 March 1967.
- [9] Lewis, J. S., Patton, H. W., and Kaye, W. I., *Analytical Chemistry*, ANCHA, Vol. 28, 1956, p. 1370.

SUPPLEMENTARY TABLE 1

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