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"SELECTIVITY" OF HIGH-TEMPERATURE LIQUID PHASES FOR GAS CHROMATOGRAPHY

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SUMMARY

Most of the high-temperature gas chromatographic columns, under their normal operating conditions, will not separate the test compounds usually employed to measure "selectivity". Therefore, we are proposing a new set of higher boiling test compounds to be utilized for measurement and comparison of the "selectivity" of high-temperature liquid phases.

INTRODUCTION

The liquid phase is an essential and very important part of every gas-liquid chromatography (GLC) column. Column efficiency, the elution order of sample components, peak shapes and background "noise" level depend upon the physical and chemical properties of the liquid phase.

Over the years, in order to improve chromatographic column performance, the number of liquid phases has increased from the few early compounds and polymers to several hundred which have been utilized and reported in the literature. As more difficult separations were attempted, and as operating temperatures were raised, chromatographers tried many new liquids, and, indeed, synthesized new polymers to achieve satisfactory results. This vast increase in the number of phases has created difficulty for suppliers, who have been requested to stock these many materials, and for theoreticians who have attempted to correlate and report the "selectivity" parameters of all these phases. There have been suggestions that the number of liquid phases be restricted, or limited, to a few materials which are widely used, and whose "selectivity" parameters are well known. The pros and cons, and the practical results of adopting this suggestion will be debated for some time. Although the authors have definite opinions on this topic, this suggestion will not be discussed here. Instead, we shall examine and discuss the systems of measuring liquid phase "selectivity." In particular, we shall propose a new set of test compounds to be employed in measuring the "selectivity" of liquid phases that are utilized at temperatures above 200°. We feel that this is a necessary extension of the systems of Kováts¹, Rohrschneider², and McReynolds³.

Kováts index

Wehrli and Kováts¹ proposed a retention index system where the number for a normal paraffin is $n00$. (n = Number of carbon atoms in the compound.) Then, the retention time, or index, of other compounds is expressed relative to that of normal paraffins. If the relative retention of derivatives of saturated hydrocarbons containing unsaturation, halogen atoms, or oxygen atoms is measured, the retention index values may be used to characterize a given liquid phase.

Rohrschneider constants

Rohrschneider² developed a system for the measurement of "selectivity" and classification of liquid phases based upon the measurement of retention times for benzene, ethanol, methyl ethyl ketone, nitromethane, and pyridine.

McReynolds constants

In 1970, McReynolds³ extended the work of Kováts and Rohrschneider by adding five additional compounds for "selectivity" measurement to those utilized by Rohrschneider. Further, he presented complete data for retention indices of about 200 liquid phases. These data were obtained at 120°.

High-temperature gas-liquid chromatography

During the past few years, a number of new liquid phases have been proposed for use at high-temperature (250–400°). Most of these are polymers prepared specially for these applications.

GLC separations at 250–400° are now used for separation, identification, and measurement of many organics including hydrocarbons, chlorinated compounds, lipid derivatives, pesticides, drugs, pollutants, etc.

In some cases, in order to achieve maximum thermal and chemical stability, it became necessary to employ polymers with relatively high melting points. For example, the polyphenyl ether sulfones melt at about 100° but do not yield efficient columns at 100°. Thus, their proper use is in the temperature range of about 175–400°. Obviously, in order to measure the "selectivity" of such phases, it is necessary to use a set of compounds which can be separated at these elevated temperatures.

If we were to extend the work of Rohrschneider or McReynolds by using higher-molecular-weight mono-substituted derivatives, we would be able to perform the separations at 175–400°. However, the "polarity" or "selectivity" of higher-molecular-weight mono-substituted compounds would be considerably less than that of the compounds proposed originally. Therefore, we decided to select compounds where the ratio of "polar" groups to hydrocarbon groups is similar to that of the compounds utilized by Rohrschneider and McReynolds.

In order to conform more closely to modern column technology, and to the newer high-temperature procedures, a few changes in column construction and operation were adopted for our measurements of "selectivity." First, a change was made to 1/8-in. columns packed with 100–120 mesh support. Then, the liquid phase loading was set at 10% rather than the 20% formerly employed. Many high-temperature preparations are performed with 2–5% loadings, and, it was felt that 10% would be adequate to overcome the adsorption effects of the support at these elevated temperatures. Further, it is often difficult to load 20% packings into 1/8-in. columns.

EXPERIMENTAL

Equipment

A Barber-Coleman Series 5000 gas chromatograph equipped with a hydrogen flame ionization detector was used in this study.

Reagents

The support material, 100–120 mesh Gas-Chrom Q, as well as the liquid phases (OV-275, Poly-S 179, and SE-30) were obtained from Applied Science Labs. (State College, Pa., U.S.A.).

Solvents used in preparing the column packings, *i.e.*, acetone and chloroform, were procured from Matheson, Coleman and Bell (East Rutherford, N.J., U.S.A.). Carbon disulfide used for dissolving the sample compounds was obtained from the same source.

Column preparation

The metal columns used in this study were prepared from Type 304 stainless steel, 0.125 in. O.D. \times 0.062 in. I.D., from Handy and Harmon (Norristown, Pa., U.S.A.). All columns were 2 m in length.

SE-30 and Poly-S 179 were coated onto the support from chloroform solution. Acetone was used for the OV-275. All packings were prepared with a 10% loading of liquid phase. The columns were conditioned by programming from ambient temperature to 250° at 0.5°/min. The final temperature was held until the baselines had stabilized.

RESULTS

Retention times in mm, chart speed 12.7 mm/min, at 250°, corrected for the retention time of methane, were determined on SE-30, Poly-S 179, and OV-275 columns for the compounds we propose for high-temperature "selectivity" measurements. These results are presented in Table I.

As a further comparison, retention times for the first five compounds proposed by McReynolds were determined at 120° for the SE-30 and OV-275 columns. These results are presented in Table II. All columns were operated with helium at 20 p.s.i.

TABLE I
CORRECTED RETENTION TIMES (mm) AT 250°

Liquid phase	<i>n</i> -Decane	Naphthalene	Dipyridyl	Benzil
SE-30	3.5	9.0	15.5	37.5
Poly-S 179	1.5	16.5	44.5	139.0
OV-275	0	5.0	22.5	57.0

TABLE II
CORRECTED RETENTION TIMES (mm) AT 120°

Liquid phase	<i>n</i> -Hexane	Benzene	Pyridine	2-Pentanone	<i>n</i> -Butanol	1-Nitropropane
SE-30	2.0	4.0	7.0	4.5	4.0	7.0
Poly-S 179	Phase is not usable at 120°					
OV-275	1.0	4.5	17.5	6.5	9.5	25.0

At 250°, the retention times for dipyrldyl and for benzil are appreciably greater on Poly-S and on OV-275. The hydrocarbons are eluted more rapidly on OV-275 than on SE-30, but naphthalene is retarded, most on Poly-S 179.

DISCUSSION

The systems of Kováts, Rohrschneider, and McReynolds are based upon measurement of retention times for the volatile organic compounds listed earlier. In order to extend these systems, so that they would be useful for liquid phases that are used at 200–400°, we looked for, and selected, certain compounds of higher molecular weight. In addition to those listed, namely, naphthalene, dipyrldyl, and benzil, we attempted to utilize a dihydroxynaphthalene and a dinitronaphthalene. With our metal system, these compounds were not eluted in reasonable time. Further, we expect to use a diol compound (C₁₀), but this material was not available at the time this report had to be submitted.

REFERENCES

- 1 A. Wehrli and E. Kováts, *Helv. Chim. Acta*, 42 (1959) 2709.
- 2 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
- 3 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.