

INFLUENCE OF SUPPORT MODIFICANTS ON SUBSTRATE SELECTIVITY IN GAS CHROMATOGRAPHY

KARL J. BOMBAUGH

Research and Development Division, Spencer Chemical Company, Merriam, Kan. (U.S.A.)

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INTRODUCTION

The importance of selectivity in gas chromatography is well known. POLLARD AND HARDY¹ in 1956 demonstrated the effect of selectivity in the separation of halohydrocarbons, and in 1957 TENNY² compared substrates of widely differing selectivities ranging from hydrocarbon oils to β,β' -oxydipropionitrile.

By proper use of substrate selectivity, difficult separations can be made using short columns which otherwise would require much longer columns. Selectivity is most useful with mixtures of compounds which enable one to take advantage of differences in polarity between closely boiling materials. Unfortunately, tailing is most severe with highly polar materials which are partially adsorbed by the solid support. This limits the range of substrates that may be used to separate polar materials. To reduce tailing, solid support modificants have come into use. JAMES AND MARTIN³ used stearic acid. JOHNS⁴ used both oleic acid and base amines. More recently METCALFE⁵ used 2 % phosphoric acid to enable direct separation of carboxylic acids, and SMITH AND RADFORD⁶ used various amounts of sodium hydroxide to enhance separations of diamines. These latter modificants may do more than suppress tailing; as binary or ternary mixtures with other substrates they may function as entirely new substrates.

EXPERIMENTAL

Apparatus and materials

The instrument used in this work was a dual column thermal detector instrument constructed in this laboratory. Columns were prepared from $\frac{1}{4}$ in. copper tubing coiled after packing. The solid support used was White Chromesorb (Johns Manville Products Corporation). Liquid phases were Silicone Oil 550 (Dow Corning), Polyethylene Glycol 20 M (Union Carbide Corporation) and Lac 296 (Cambridge Industries Company, Inc.). The chemicals used in the separations were Eastman Organic Chemicals Products. Liquid samples were injected with a Hamilton Microliter syringe equipped with a Chaney Adapter.

Influence of phosphoric acid on Lac 296

The influence of 2 % phosphoric acid on the selectivity of Lac 296 is illustrated in Fig. 1. The only difference in the two columns which produced these chromatograms

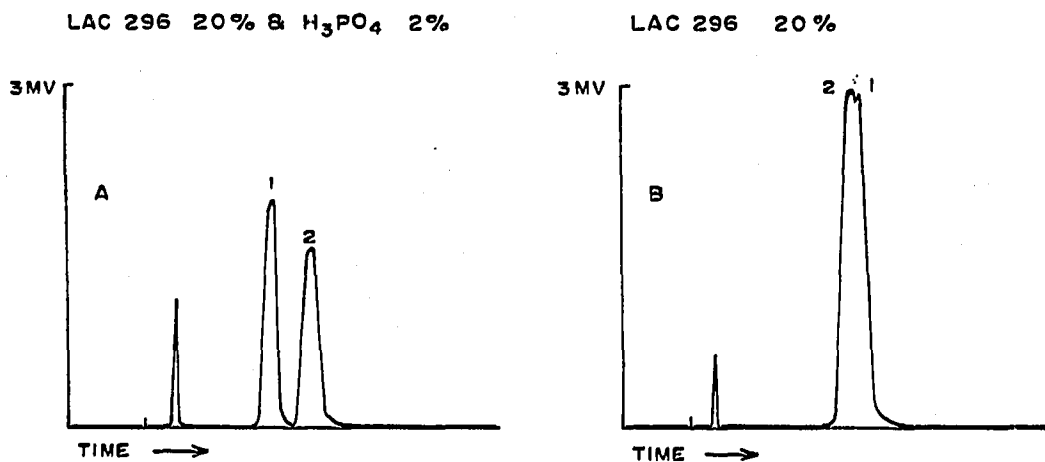


Fig. 1. Influence of H_3PO_4 on the selectivity of Lac 296. Operating conditions: flow: 55 ml/min He; temperature: 70° ; column length: 2 m. (1) *tert.*-butyl acetate; (2) *tert.*-butyl alcohol.

was the presence of 2% phosphoric acid on the one which produced the separation represented as curve A. Not only does the acid-containing column make a complete separation of *tert.*-butyl alcohol and *tert.*-butyl acetate, but it reverses the order of elution from the Lac 296 column. This column also separated methacrolein, water, and methacrylic acid. Not only did it produce well-shaped peaks for the methacrylic acid, but it resolved methacrolein and water. Without phosphoric acid, water and methacrolein were not resolved. Carbowax 20 M functioned in the same way. Without acid, it did not resolve water and methacrolein. With acid, it did.

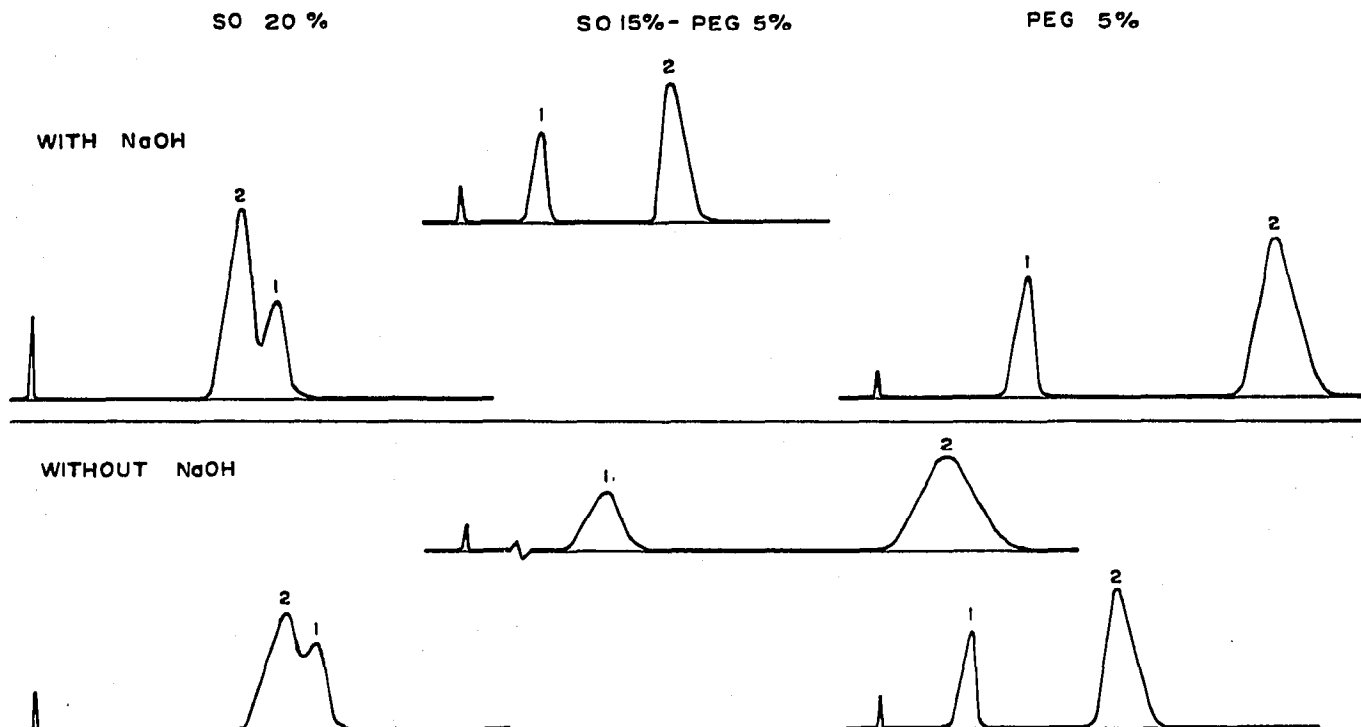


Fig. 2. Influence of 2% NaOH on substrates. Operating conditions: flow rate: 50 ml/min; temperature: 150° ; column length: 0.72 m. (1) *m*-Chloronitrobenzene; (2) *m*-Chloroaniline.

Influence of strong base on silicone oil and polyethylene glycol

During an investigation to provide a rapid, accurate method to follow the reduction of chloronitrobenzene to *m*-chloroaniline it was discovered that the addition of 2% NaOH to a packing loaded with a 15 to 5% mixture of Silicon Oil (SO 550) and Polyethylene Glycol (PEG 20M) produced substrate properties which could not be deduced from the effect of NaOH on the individual substrates. The effect is shown in Fig. 2. The columns were operated under virtually identical conditions. The top chromatograms in each case were from columns containing 2% sodium hydroxide. The presence of NaOH markedly hastened the elution of both components from the mixed column yet retarded their elution from the PEG 20M.

The effect of NaOH on SO 550-PEG 20M mixtures at several different proportions was investigated. The results are shown in Table I. Ten columns of equal length were

TABLE I
SEPARATION DATA FOR *m*-CHLOROANILINE AND *m*-CHLORONITROBENZENE

	20% Silicone		15% Silicone- 5% PEG		10% Silicone- 20% PEG		20% PEG		5% PEG	
	No NaOH	2% NaOH	No NaOH	2% NaOH	No NaOH	2% NaOH	No NaOH	2% NaOH	No NaOH	2% NaOH
<i>150°</i>										
Separation factor	—1.12	—1.15	1.83	2.59	2.16	2.76	2.86	3.12	2.59	2.54
Plates*	148	236	570	272	460	400	350	491	248	341
Resolution	0.42	0.71	4.95	6.55	6.22	8.78	8.73	11.8	6.25	7.10
Analysis time	16	13	60	19	53	70	103	162	17	30
Retention time <i>m</i> -chloronitrobenzene**	14.5	11.6	29.3	5.9	21.3	21.7	31.5	42.2	5.3	9.8
<i>190°</i>										
Separation factor			1.45	2.03	1.81	2.16	2.37	2.53	2.06	1.81
Plates*			410	236	342	260	340	409	286	360
Resolution			2.22	3.95	3.75	4.68	6.30	7.61	3.29	3.86
Analysis time			20	5	15	12	27	44	5	15
Retention time <i>m</i> -chloronitrobenzene**			11.8	1.7	6.9	4.3	9.6	15.4	1.7	7.1

* Based on the *m*-chloroaniline peak.

** Corrected to 50 ml/min.

loaded as shown; all helium flow rates were between 40 and 55 ml per minute. The investigation showed that NaOH increased the retention and improved the resolution⁷ of the PEG 20M at either the 5% or the 20% load. It decreased retention and increased resolution of the silicone column. But, the effect in the 15 SO-5 PEG-2 NaOH mixed column was most striking. With NaOH in the mixture the resolution is improved by 1/3 and the analysis time reduced to 1/3 of that without NaOH present. A comparison of the optimized mixed phase column with an equivalent length single-phase column is shown in Fig. 3.

It was observed that the separation characteristic of the 15 SO-5 PEG-2 NaOH mixed column approximated that of the 5% PEG single phase column. Therefore, the quantitative performance of these columns was investigated to evaluate the influence of NaOH on the adsorption isotherms. The calibration curves in Fig. 4 show

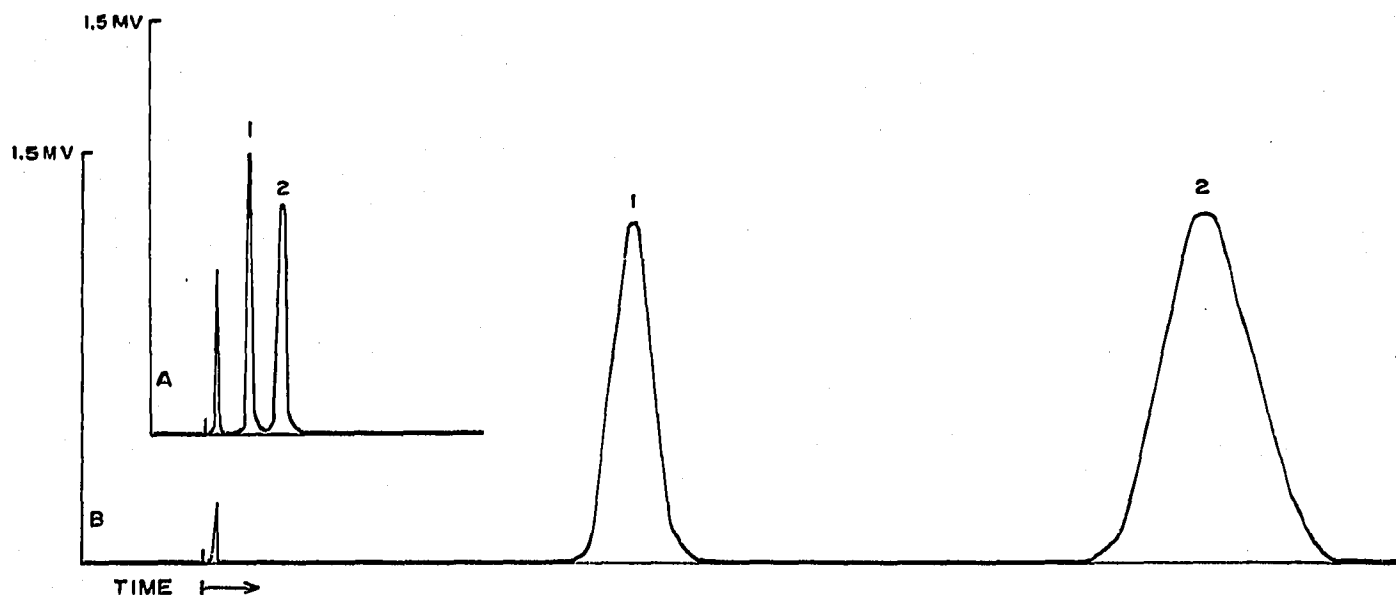


Fig. 3. Comparison of a single-phase column with an optimized mixed-phase column. Operating conditions: (A) column: 15% SO-5% PEG-2% NaOH; length: 0.77 m; temperature: 190°; flow: 97 ml/min He; (B) column: 20% PEG; length 0.77 m; temperature: 190°; flow: 39 ml/min He. Component identity same as in Fig. 2.

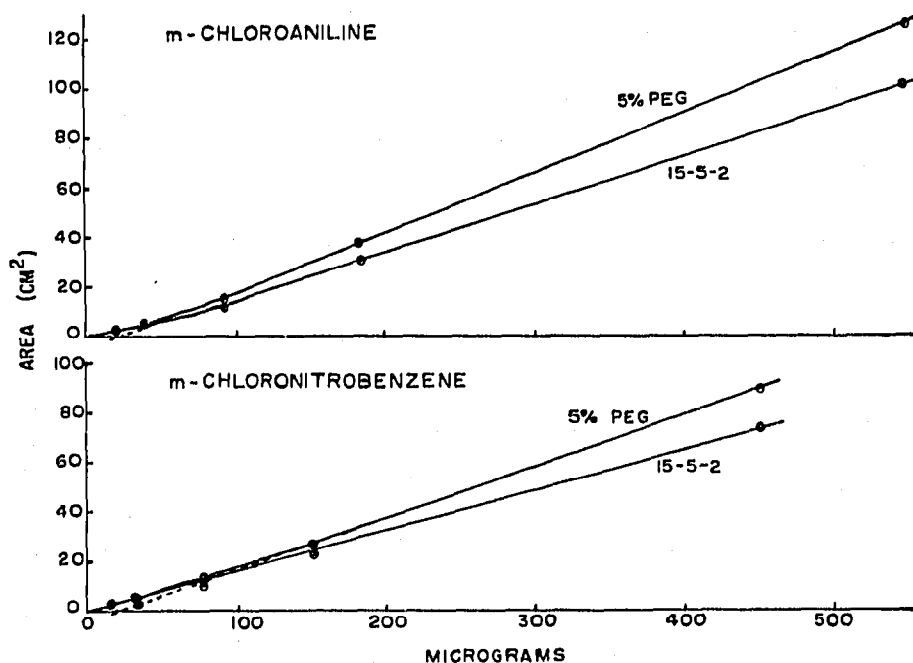


Fig. 4. Calibration curves comparing a 5% PEG column with a 15% SO-5% PEG-2% NaOH column. Operating conditions: same as Fig. 2. Top graph has a 24 μg intercept with either column. Bottom graph has a 20 μg intercept with the 5% PEG column only.

that the mixed column containing NaOH provided a linear calibration curve with a zero intercept with *m*-chloronitrobenzene while the 5% PEG 20M column shows a slight curvature at low *m*-chloronitrobenzene levels, or an extrapolated intercept of 20 μg . Neither column produced a linear curve for *m*-chloroaniline. Both lines extrapolated through an intercept at 24 μg . This indicated that the 2% NaOH did not suppress the low level *m*-chloroaniline adsorption beyond that afforded by the 5% PEG.

Either column would be satisfactory for quantitative analysis of the *m*-chloronitrobenzene-*m*-chloroaniline mixture with an adequate component load. However, at low load, such as with traces of *m*-chloronitrobenzene, the mixed column would be preferred. An additional advantage afforded by the mixed column is that it can serve in a dual capacity, as both a selective column for the *m*-chloroaniline-*m*-chloronitrobenzene mixture, and as a primarily silicone column for a wide variety of hydrocarbon mixtures.

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SUMMARY

It has been shown that solid support modificants as phosphoric acid and sodium hydroxide may do more than suppress peak tailing. They may alter substrate properties significantly. As binary or ternary mixtures with other substrates, they may provide a new dimension to substrate selectivity. Benefits may be achieved through the ability to alter substrate selectivity and through reduced analysis time.

REFERENCES

- ¹ F. H. POLLARD AND C. J. HARDY, in D. H. DESTY, *Vapour Phase Chromatography*, Academic Press, New York, 1956, p. 115.
- ² H. M. TENNY, *Anal. Chem.*, 30 (1958) 2.
- ³ A. T. JAMES AND A. J. P. MARTIN, *J. Biol. Chem.*, 50 (1952) 679.
- ⁴ T. JOHNS in V. J. COATES, H. J. NOEBELS AND I. S. FAGERSON, *Gas Chromatography*, Academic Press, New York, 1958, p. 31.
- ⁵ L. D. METCALFE, *Nature*, 188 (1960) 142.
- ⁶ E. D. SMITH AND R. D. RADFORD, *Anal. Chem.*, 33 (1961) 1160.
- ⁷ W. L. JONES AND R. KIESELBACH, *Anal. Chem.*, 30 (1958) 1590.