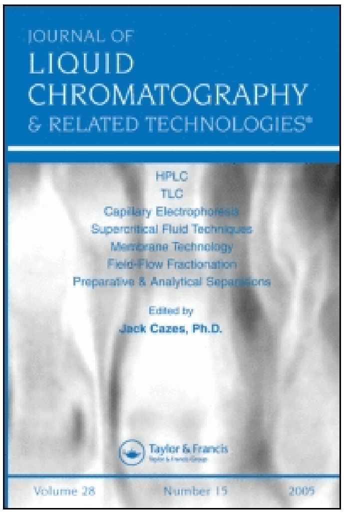

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Analysis of Phthalate Plasticizers for PVC by Liquid Chromatography

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ANALYSIS OF PHTHALATE PLASTICIZERS FOR PVC BY LIQUID CHROMATOGRAPHY

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ABSTRACT

A technique has been developed for the identification of phthalate plasticizer components using high speed liquid chromatography. The plasticizers recovered from post consumer scrap PVC have been analyzed.

INTRODUCTION

Phthalate ester plasticizers are frequently added to poly(vinyl chloride) polymers to enhance processibility and to impart a higher degree of flexibility to the final compound. This is achieved by lowering the glass transition temperature below room temperature. Each phthalate differs in physical properties and can change the characteristics of the polymer in its own particular way. Therefore there is no single phthalate for all PVC resins. However one or a combination of them can be chosen to achieve the desired product.[1]

Different problems arise when the plasticizers are already present in batches of reclaimed polymers. The method of processing such materials requires a knowledge of what additives are already present in the polymers from various sources. It is the purpose of this paper to present the details of a relatively rapid method of analyzing plasticizer mixtures extracted from such scrap materials.

Several phthalate standards were first identified by their separation characteristics on a high speed liquid chromatograph. The knowledge derived from this study was applied to the identification of a series of plasticizer mixtures extracted from PVC reclaimed from post consumer scrap.[2]

Experimental

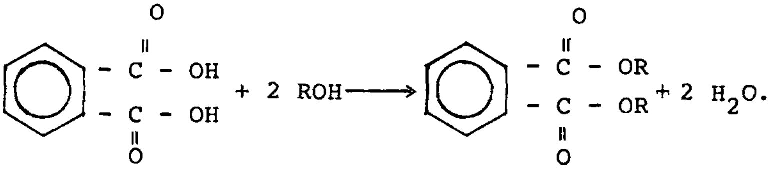
The instrument used in these analyses was the Waters Model ALC202 High Speed Liquid Chromatograph. Installed in this system was a μPORASIL (10μ) packed column whose dimensions are 4mm ID × 30cm. μPORASIL (Waters) is a fully porous silica material designed for difficult analytical separations. The decrease in particle size to ∿10μ produces a packing material of very high efficiency.[3]

The solvent mixture which effected a satisfactory separation was 95 n-hexane/5 ethyl acetate (V/V). The phthalate solutions made with this solvent were carefully filtered through a .45μ(Selas) sintered silver filter. For the micro quantities needed, a septum injector with a Viton septum proved satisfactory. Since the phthalate esters absorb strongly in the UV (254nm), the UV detection system gave more than adequate sensitivity. Concentrations of test solutions were adjusted so that injections of 1-5 μl would give at least half scale deflections at mid-range sensitivity settings. These solutions were on the order of 10^{-2} M.

Solutions of the commonly used phthalate plasticizers were analyzed first. All of the unknown plasticizers recovered from PVC (E. Scalco)[2] were then studied under the same conditions. The flow rate which gave the best separation in a reasonable time was .5cc/min. The pressure drop under these conditions was <200 psi. Individual analyses were completed within 15 minutes.

RESULTS AND DISCUSSION

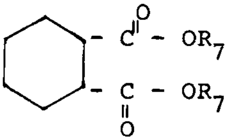
The phthalate esters are formed from the esterification of phthalic acid (or the anhydride) with an alcohol.



Reaction with one alcohol would account for all the single peaked esters: DOP, DINP, DIDP. (See Table I for a list of common plasticizers and their designations).

When more than one alcohol is reacted with the acid (or anhydride) multiple products are formed. An example of this is Santicizer 711 (Monsanto Chem. Co.) which is made from the reaction of phthalic anhydride and mixed alcohols of R=mixed C_7,C_9 and C_{11}. The possible products are:

1-



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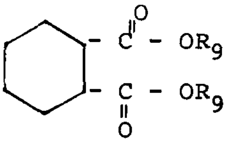

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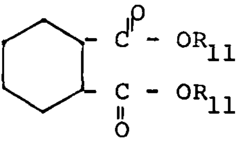

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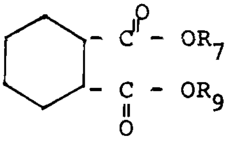

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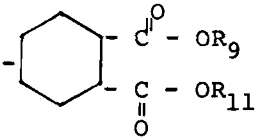

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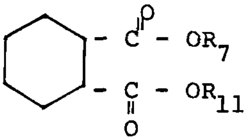
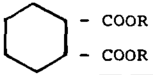
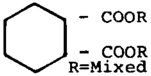
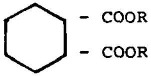
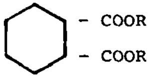
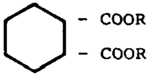
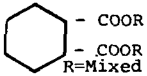
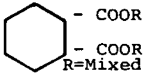
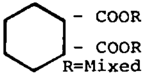


TABLE I

COMMONLY USED PHTHALATE PLASTICIZERS

PHTHALATES	MOLECULAR WEIGHT	STRUCTURE	NO. OF PEAKS
DOP Di(2-ethylhexyl) (Dioctyl Phthalate)	391	 - COOR - COOR R=8	1
DINP Di(Isononyl)	418	 - COOR - COOR R=Mixed C_8,C_9	1+
DIDP Di(Isodecyl)	447	 - COOR - COOR R=10	1
Ditridecyl	531	 - COOR * - COOR R=13	3
DUP Di(Undecyl)	475	 - COOR ** - COOR R=11	5
PX-316(USS Chemicals) 6,10	335-447	 - COOR - COOR R=Mixed C_6,C_8,C_{10}	6
Santicizer 711 (Monsanto) 7,11	363-475	 - COOR - COOR R=Mixed C_7, C_9, C_{11}	6
PX-318 (USS Chemicals) 8,10	391-447	 - COOR - COOR R=Mixed C_8,C_{10}	3

* Probably 2 isomeric forms

** Probably 3 isomeric forms, with 2 overlapping

The chromatogram of 7 11 indeed shows six peaks (Fig. 5B).

Traditionally, the phthalate plasticizers have been identified by gas chromatography (GC).[7] However, with the recent advances in column packings for the liquid chromatograph, using liquid chromatography (LC) may be advantageous. The GC is operated at 275°C, while the entire process of LC is done at room temperature, thus avoiding any possible ester degradation. In addition, the analysis time for each sample elution in LC is approximately half of that for GC.

Other experimentalists[4,5,6] have identified a few of the phthalates by gel permeation chromatography (GPC), with THF as the solvent using small angstrom Styragel[4] and 5μm polystyrene gel particles.[5] Separation by GPC (exclusion chromatography) relies on very small differences in the elution volume of each phthalate. However the final verification is done by other classical techniques.[4,6]

Fig. 1 shows the separation (taking 13 minutes) of dioctyl, dibutyl, diethyl and dimethyl phthalates (DOP, DBP, DEP, DMP), using the experimental procedure described but with flow rate of 2 ml/min. Kato and coworkers[5] published their GPC chromatogram of the same four esters eluted in 10 minutes using their previously described experimental conditions.

Fig. 2 is a chromatogram showing the elution of ditridecyl (Mw 531) and DOP (Mw 391).

Figs. 3 through 6 are the chromatograms of the commonly used commercial phthalates.

Figs. 7 thru 10 are chromatograms of the recovered plasticizers plus two artificial mixtures of known phthalates.

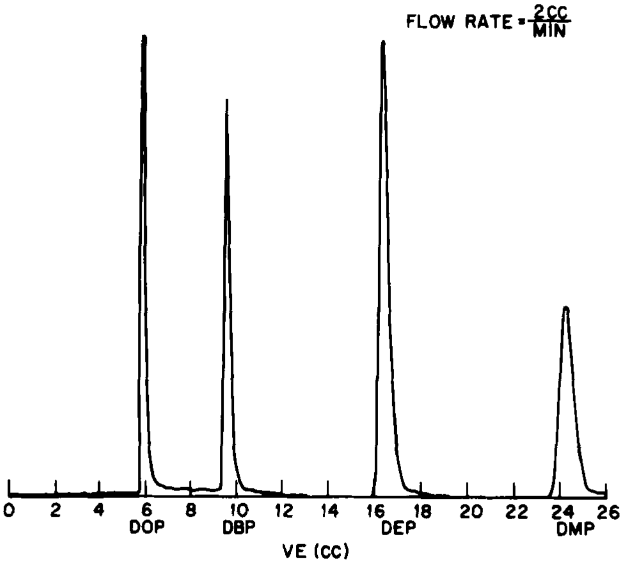


FIGURE 1: Separation of dioctyl, dibutyl, diethyl and dimethyl phthalates; 13 minutes.

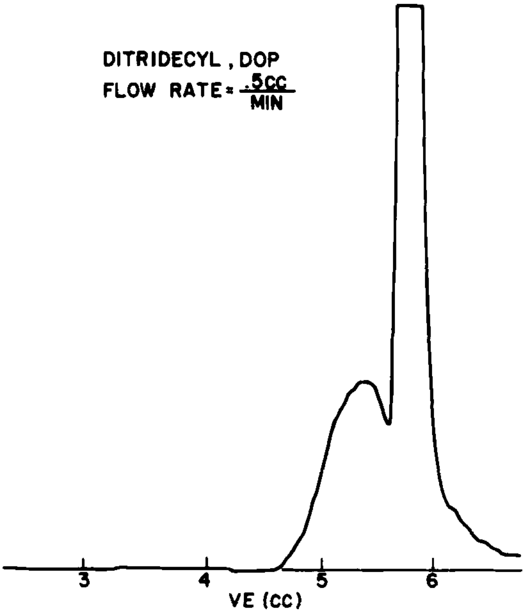


FIGURE 2: Separation of ditridecyl and dioctyl phthalates.

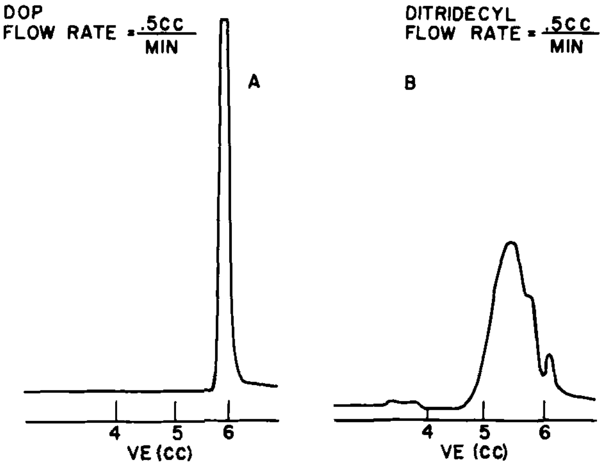


FIGURE 3: Elution of dioctyl and ditridecyl phthalates.

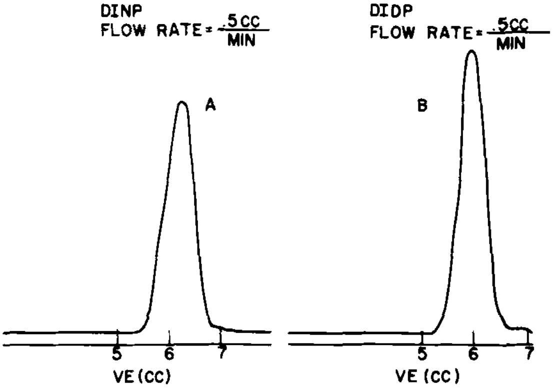


FIGURE 4: Di (isononyl) and di (isodecyl) phthalates.

The chromatographic separations we have achieved may be explained by the combination of two physical effects: (1) liquid/solid (LSC) (adsorption) and (2) exclusion chromatography. Separation by the first mode is carried out using the polar adsorbant silica (μPORASIL) as the stationary phase and the

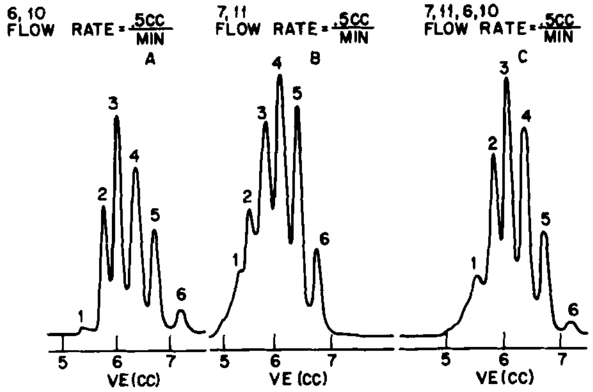


FIGURE 5: Chromatograms of (a) 6,10, (b) 7,11 and (c) a mixture of both.

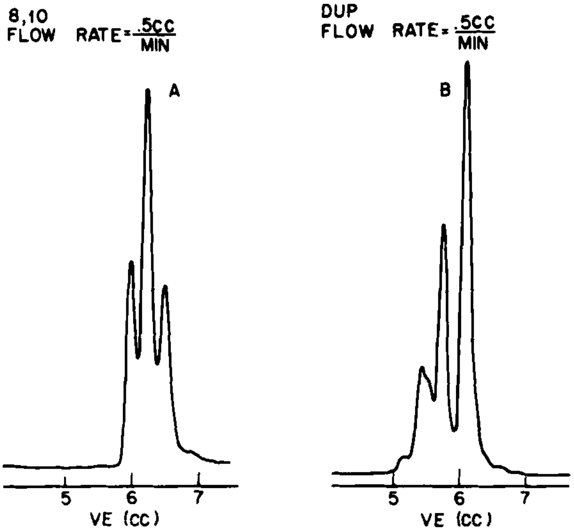


FIGURE 6: Chromatograms of 8,10 and di (undecyl) phthalates.

liquid (hexane/ethyl acetate) as the mobile phase. LSC is appropriate when the components to be resolved are positionally isomeric or otherwise vary in

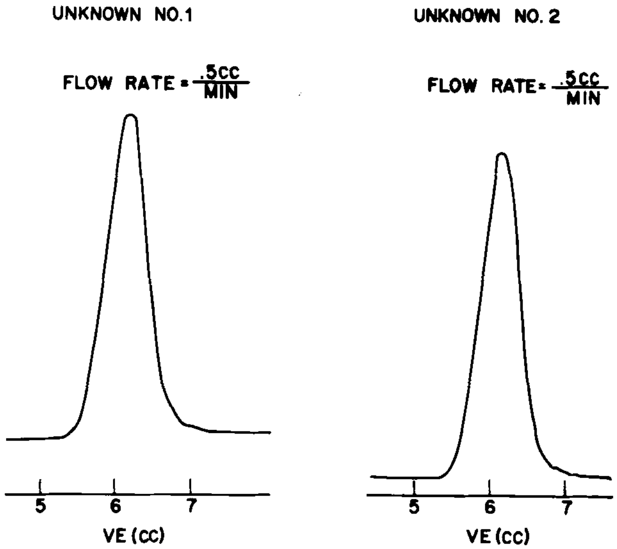


FIGURE 7: Unknown plasticizers 1 and 2.

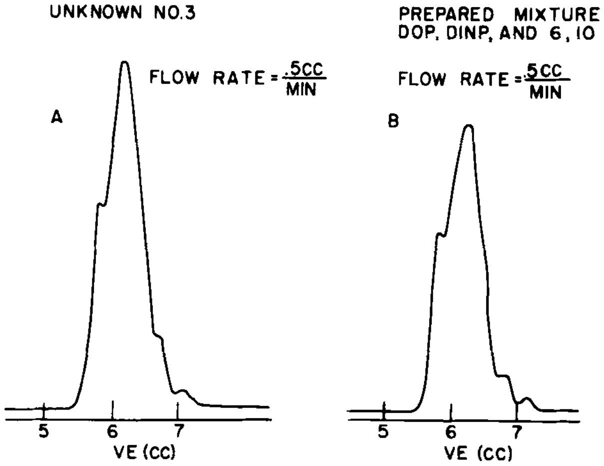


FIGURE 8: Unknown plasticizer 3 and a prepared mixture of DOP, DINP and 6,10 phthalates.

polarity.[8] In addition, adsorption increases as the polarity and number of functional groups increase.[9]

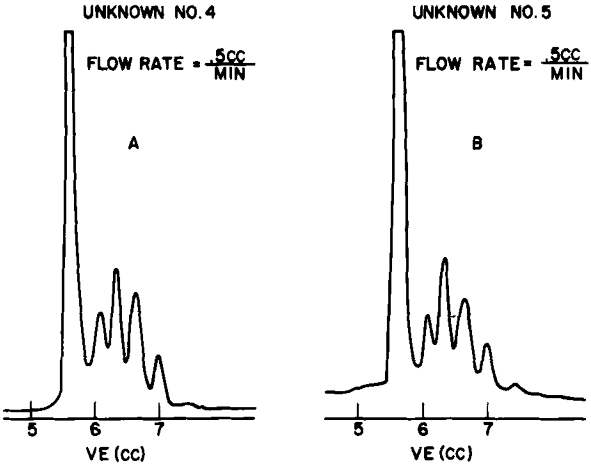


FIGURE 9: Unknown plasticizers 4 and 5.
(a) & (b)

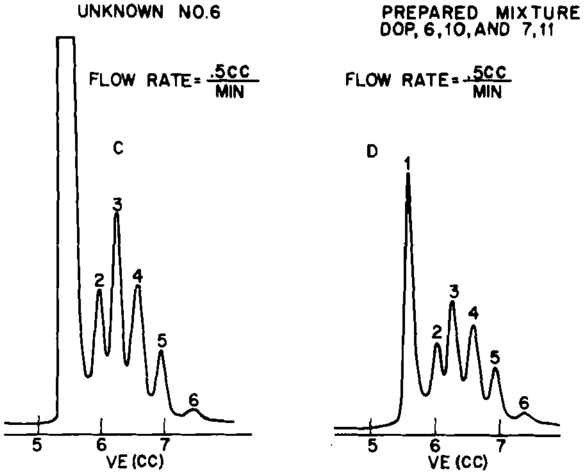


FIGURE 9: Unknown 6 and a prepared mixture of DOP, 6,10 and 7, 11.
(c) & (d)

Other things being equal, the lower molecular weight molecules with the same number of similar functional groups would be more polar; consequently they are more strongly adsorbed and would elute after the higher

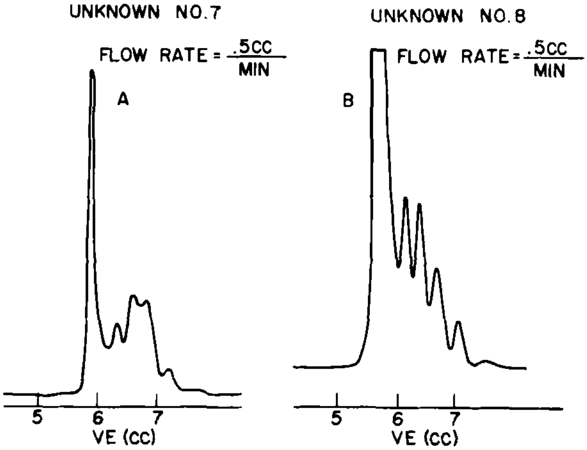


FIGURE 10: Unknown 6 and a prepared mixture of DOP, 6,10 and 7,11.

molecular weight species. DOP, DBP, DEP and DMP (Fig. 1) eluted in the order of the highest molecular weight phthalate first followed sequentially by the next highest one. However, diisononyl (DINP-Mw 418) and diisodecyl (DIDP-MW 447) eluted after DOP (Mw 391). One explanation is that DOP differs from the other two, primarily by its substitution. DOP has two ethyl branches on the second carbon compared to DINP and DIDP which have a methyl branch on the second carbon. DINP and DIDP elute in the order of molecular weight, with the higher molecular weight one first.

The effect of the exclusion process may also contribute to the separation. Since the silica is porous, the plasticizers separate partially by size. The small molecules penetrate deepest and since the large ones cannot enter the pores, they are eluted first.

Table I is a summary of the available standards, their common names, molecular weights, and number of peaks.

Table II is a summary of the unknowns analyzed, giving their origin, method of reclamation and plasticizer identification. This identification was done first by comparing their chromatographic patterns with those of the knowns. The single peaked unknowns were readily identified by this method. The multiple peaked ones were more difficult and required three parts to the identification process. The first narrowed down the possibilities to the phthalates with similar shapes and numbers of peaks. By this method, relying on the matching of elution volumes alone was not necessary. The second identification was done by adding a small amount of the suspected known to the solution of the unknown and following the peak enhancement of the suspected material or the appearance of new peaks. Final confirmation of the composition of mixed phthalates were made by artificially reproducing the chromatogram shapes from prepared mixtures of known plasticizers (Figs. 8B and 9D).

Unknowns 1 (Fig. 7A) and 2 (Fig. 7B) have only 1 peak and using the above technique are identified as DINP. No. 3 (Fig. 8A) is a mixture of DOP, DINP and 6,10. Fig. 8B shows the mixture of the known phthalates. This is to be compared with Fig. 8A.

Sample numbers 4,5 and 6 (Fig. 9A, 9B and 9C) have been determined as mixtures of DOP, 6,10 and 7,11. DOP plus 6,10 gives the proper number of peaks and shapes but with improper peak height ratios. With the addition of 7,11 we see a better match of peak heights, since peaks 6,5,4 of plasticizer 7,11 (Fig. 5B) adds to peaks 5,4 and 3 of plasticizer 6,10 (Fig. 5A). This gives a better approximation to the shape of the unknowns. They are to be compared with Fig. 9D. Samples 7 and 8 (Figs. 10A and 10B) contain DOP, 6,10

TABLE II

PLASTICIZERS EXTRACTED FROM RECLAIMED PVC

Number	Description	Identification
1	Reclaimed through a solution and dissolution process	DINP
2	Same as 1 (earlier batch)	DINP
3	Same as 1	DOP, DINP 6,10
4	Solution process plus ether extraction	DOP, 6,10 and 7,11
5	Same as 4	DOP, 6,10 and 7,11
6	Mechanical liberation process	DOP, 6,10 and 7,11
7	Same as 6	DOP, 6,10 and 7,11 + unknown
8	Same as 6	DOP, 6,10 and 7,11 + unknown

and 7,11 plus an unknown. The ratio of two peak heights of each could not be reproduced, although all the known phthalates were added. These two samples should be verified by other analytical techniques.

CONCLUSIONS

The technique of liquid chromatography, using a μPORASIL Column in the Waters Model ALC202 High Speed Liquid Chromatograph with a solvent mixture of 95 n-hexane/5 ethyl acetate (V/V), was found satisfactory for the separation of the common phthalate plasticizers found in scrap PVC. Identification of these recovered phthalate plasticizers was done by comparison with the knowns. This method is amenable by modification for use as a quantitative technique. It can also be used in conjunction with other physical and chemical techniques to make this method an even more powerful analytical tool.

ACKNOWLEDGMENT

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REFERENCES

1. Monsanto Catalog - "Plasticizers and Resin Modifiers," pg. 1-6, Section 1

2. E. Scalco, R. L. Decker - private communication

3. Waters Associates DS 035

4. M. R. Hallwachs, H. E. Hanson, W. E. Link, N. S. Salomons and C. R. Widder, J. Chromatog. 55(1971) 7-13

5. Y. Kato, S. Kido, H. Watanabe, M. Yanamoto, and T. Hashimoto, J. Applied Polymer Science, Vol. 19(1975), pg. 629-631

6. R. Gladen, Chromatographia 5 (7) (1972) pg. 396

7. P. C. Warren, private communication

8. Waters Associates - "An Introduction to High Speed Liquid Chromatography"

9. L. R. Snyder in "Modern Practice of Liquid Chromatography", edited by J. J. Kirkland, Wiley Interscience, 1971, pg. 205-236