

## Capillary supercritical fluid chromatography of explosives

### Investigations on the interactions between the analytes, the mobile phase and the stationary phase

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#### ABSTRACT

The independent effects of pressure and temperature in supercritical fluid chromatography on the capacity ratio on chromatographic resolution of some polar organic model compounds were investigated. Increasing the pressure isothermally leads to a steady decrease in retention and resolution. With changing temperature, a maximum in the capacity ratio as well as the resolution was observed. These observations may be related to a combination of gas chromatographic (GC) and liquid chromatographic (LC) theories of solute interactions with the mobile and stationary phases. However, pure GC- or LC-like behavior was not observed either below or above the critical point of the mobile phase. Capacity ratios for various explosives, propellants and related compounds were determined on capillary open tubular columns coated with either a non-polar methyl- or a polar cyanopropyl phenyl-substituted siloxane stationary phase. The mobile phase for all studies was carbon dioxide. On the polar column, many of the solutes exhibited a good correlation between their bulk dipole moment and chromatographic retention. Deviations from this correlation could be explained by means of the physical or steric properties of these solutes. The elution order of the compounds on the non-polar column was similar to the order achieved using GC rather than LC.

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#### INTRODUCTION

Due to the complex interactions present in supercritical fluid chromatography (SFC), there is still no straightforward explanation of the phenomena occurring. However, many authors have performed theoretical and experimental investigations to study the effects of pressure, temperature and density of the fluid on the chromatographic behavior of test compounds [1–18]. In most cases the test solutes were a homologous series of alkanes, phthalates or polycyclic aromatic hydrocarbons.

Our intention was to compare the findings of previous authors with our results obtained on a set of more polar species. In our selection of polar test compounds,

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a polar stationary phase and a non-polar mobile phase, we tried to achieve a better understanding of the solute-stationary phase interactions.

#### EXPERIMENTAL<sup>a</sup>

A Model 501 capillary supercritical fluid chromatograph (Lee Scientific, Salt Lake City, UT, U.S.A.) was used, which was equipped with a split injector and both UV and flame ionization detectors. A bonded methylpolysiloxane column (SB methyl-100, 5 m × 100 μm I.D., 0.25 μm film thickness, Lee Scientific) and a bonded 50% cyanopropyl-phenylpolysiloxane column (DB 225, 10 m × 50 μm I.D., 0.05 μm film thickness, J & W Scientific, Folsom, CA, U.S.A.) were used for the studies described.

Nitroglycerine, nitrocellulose, 2,4,6,N-tetranitro-N-methylaniline (tetryl) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) were obtained from the U.S. Army Explosives Repository (Dover, NJ, U.S.A.). Ethylene glycol dinitrate, diethylene glycol dinitrate, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and pentaerythritol tetranitrate (PETN) were received from the Bureau of Alcohol, Tobacco & Firearms (Rockville, MD, U.S.A.). SFC-grade carbon dioxide and additional reference chemicals were obtained in the highest purity available from commercial sources.

#### RESULTS AND DISCUSSION

##### *Interaction with the mobile phase*

First, we investigated the effects of pressure and temperature on the capacity ratio as well as the chromatographic resolution of a set of test compounds, the three isomeric of mononitrotoluene (NT). The first inflection of the baseline from the UV detector response was generally taken as the chromatographic void volume for retention measurements. Chromatographic resolution ( $R_s$ ) was calculated as follows:

$$R_s = 1.177 [t_{s(2)} - t_{s(1)}] / [b_{0.5(2)} + b_{0.5(1)}]$$

where  $t_s$  is the retention time and  $b_{0.5}$  is the peak width at half height of the compounds under consideration. The instrument was used in the pressure control mode and was equipped with a cyanopropyl phenylpolysiloxane column. The column was maintained at a constant temperature while a range of different pressures was applied. Increasing the column pressure led to a steady decrease in capacity ratio ( $k'$ ) (Fig. 1). Similar behavior using different separation systems has been reported by other authors [1-7]. At even higher pressures (*e.g.*, greater than 250 atm),  $k'$  is reported to increase [8].

The fluid density increases with increasing pressure as does the solubility of the analytes in the mobile phase. Therefore, the decrease in  $k'$  of the analytes can be explained by the increase in their solubility with increasing pressure. The minimum observed in the  $k'$  versus pressure plot arises from intermolecular repulsion forces in the

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<sup>a</sup> Certain commercial equipment, instruments or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

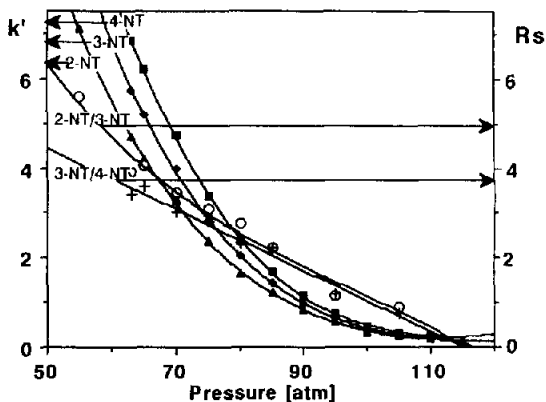


Fig. 1. Effect of pressure in SFC on the capacity ratio and the chromatographic resolution of the three nitrotoluenes. Column: DB 225 (10 m × 50 μm I.D., 0.05 μm film thickness), at 60°C. ■ = 4-NT; ◆ = 3-NT; ▲ = 2-NT; ○ = 2-NT/3-NT; + = 3-NT/4-NT.

bulk fluid. These forces appear with increasing density or pressure [9], thus decreasing the solubility of the solutes. This minimum also coincides with a maximum in a solubility–pressure plot [19,20]. In this context, “solvent strength” of the fluid, rather than solubility of a test compound, might be the appropriate term to use. Others have applied thermodynamic models to predict the dependence of  $k'$  on the pressure yielding results that were in good agreement with the experimental data [1,2,4,5,9–12].

Chromatographic resolution of the three compounds decreased steadily as the pressure increased (see Fig. 1). This observation is similar to the results reported by others [3,7]. Evidently, at low densities the diffusion coefficients in the mobile phase were high, which led to high effective plate numbers and thus to high  $R_s$  [3]. It should be emphasized that, as the system turned from the subcritical to the supercritical state (at 73 atm), no discontinuity in either the plots of  $k'$  or  $R_s$  versus pressure was observed, as reported by others [12].

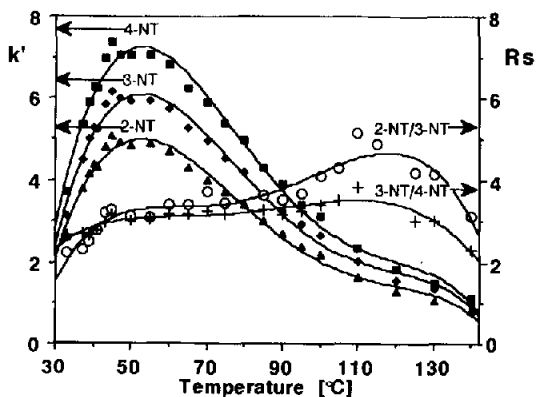


Fig. 2. Effect of temperature in SFC on the capacity ratio and the chromatographic resolution of the three nitrotoluenes. Column as in Fig. 1; 63 atm.; symbols as in Fig. 1.

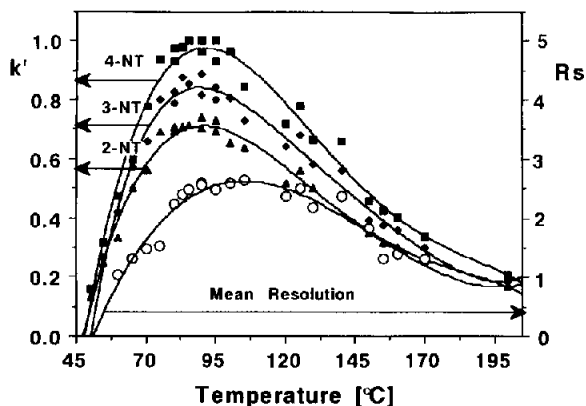


Fig. 3. Effect of temperature in SFC on the capacity ratio and the chromatographic resolution of the three nitrotoluenes. Column as in Fig. 1; 100 atm; ■, ◆ and ▲ as in Fig. 1; ○ = mean resolution.

Next, the density was changed under isobaric conditions by varying the temperature. In contrast to the isothermal change of the density, maxima were present for both the capacity ratio as well as the chromatographic resolution (Figs. 2 and 3). In the case of subcritical pressure (63 atm, Fig. 2), the maxima for the capacity ratios were observed at a lower pressure than the maxima in the chromatographic resolution. Under supercritical conditions, however (100 atm, Fig. 3), the maxima of the two different kinds of chromatographic variables almost coincide. The mean resolution was calculated as the mean of the chromatographic resolution of 2-NT/3-NT and 3-NT/4-NT, respectively, at the respective temperature.

Maxima of both capacity ratio and chromatographic resolution, as determined in the isobaric experiments (Figs. 2 and 3), appeared at three different densities. These same densities were encountered in the isothermal experiments (Fig. 1), where no maxima were observed. Therefore, the appearance of such maxima cannot be due to changes in density alone. Several authors, who also observed such maxima in capacity factors (*e.g.*, [3,6,10–18]), interpreted this effect as a superposition of both volatilization and solvation of the compounds. Increasing temperature decreases density and therefore increases retention. At even higher temperature, the volatility of the components becomes more important, leading to a gas chromatographic (GC)-like decrease in retention with increasing temperature.

Although the maxima in plots of capacity ratios *versus* temperature have been described by other authors for a broad range of phase systems as well as analytes, it has not been emphasized that, with homologous series of isomers, the maxima occur at the same temperature for all components. In other words, the onset of the "GC behavior" evidently is not influenced by the nature of the analyte. Because the series investigated covered a broad range of boiling points, the appearance of the descending section of the plot cannot be attributed solely to volatilization of the test components at elevated temperatures. Other, less straightforward retention mechanisms are likely to occur.

With more strongly retained compounds than the nitrotoluenes (such as polycyclic aromatic hydrocarbons), additional minima in the capacity ratio [3,4,7,16,17] and the chromatographic resolution [3,16,17] have been reported. This

correlates with the maxima occurring when solubility of a test compound in a fluid is plotted *versus* temperature [19,20]. Because these minima in the  $k'$ -temperature and  $R_s$ -temperature plots were observed when the temperature was lowered further, they might be related to the effect of the density on  $k'$ , as are the minima observed in the  $k'$  *versus* pressure plots [8]. This would be in contrast to the maxima that occurred only in the case of isobaric changes in density.

Determination of the extrema of  $k'$  at several different pressures showed that at higher pressure both minima and maxima were shifted towards a higher temperature (lower density) and became less pronounced, as has also been reported by others [3,12-18]. The same holds true for the solubility-temperature plots [19]. Although the positions of the extrema are linked to the density of the mobile phase, there is generally no absolute value of the density where those extrema appear. For example, there is an absence of maxima in the plots of capacity factor *versus* pressure shown in Fig. 1. Components with stronger retention and higher boiling points also show stronger extrema than their less-retained, lower-boiling isomers or homologues (Figs. 2 and 3, [13-18]). Those observations summarized above may be generalized in the following manner: the more intense the analyte-stationary phase interactions (reflected in relatively long retention times), the more sensitive is their chromatographic behavior to changes both in pressure and temperature. It is interesting that neither the choice of the phase system used for the separation, nor the nature of the test compounds has any impact on those general findings. This could be concluded from our data as well as those cited earlier.

Although some of the phenomena have been treated theoretically on a thermodynamic basis [1-5,9-12,16], there is still a need for an explanation of the complex effects observed and described above.

#### *Interaction with the stationary phase*

To investigate the interactions between the analytes and the stationary phase, the retention behavior of a large set of compounds, namely a variety of explosives, propellants and related compounds, was determined on two columns with phases of totally different selectivity. The non-polar methyl column should display a separation following partition phenomena, whereas the cyanopropyl-phenyl column is expected to show evidence of polar interactions. For the two different columns, the capacity ratios of the compounds investigated are listed in Table I.

Whereas the elution order of the dinitrotoluenes on the polar DB 225 column is similar to that observed in reversed-phase liquid chromatography (LC) [21], RDX is much less retained in the LC system. The elution order of various explosives in our SFC separations is very different from that observed in other reversed-phase LC separations [22-25].

There are apparently more similarities between GC and SFC [26-28]; *e.g.*, the elution order of the different mono- and dinitrotoluenes is the same in GC (irrespective of the column used) as in SFC on the methyl column. This observation suggests that, in the case of this non-polar column, a partition-type retention mechanism is effective.

There are only a few publications on SFC of explosives [29-35]. Nevertheless, the elution order of the limited number of compounds investigated by those authors agrees well with our results.

We next focused on investigating a likely retention mechanism for the

TABLE I

CAPACITY RATIOS OF ALL EXPLOSIVES, PROPELLANTS AND RELATED COMPOUNDS CONSIDERED IN THE PRESENT STUDY

Compound	SB Methyl-100 (60°C, 83 atm, 11 min. 3 atm/min, 95 atm)	DB 225 (85°C, 100 atm, 11 min. 3 atm/min, 180 atm)
2-Nitrotoluene (2-NT)	0.62	0.32
3-Nitrotoluene (3-NT)	0.70	0.38
4-Nitrotoluene (4-NT)	0.77	0.52
2,6-Dinitrotoluene (2,6-DNT)	1.48	1.38
2,3-Dinitrotoluene (2,3-DNT)	1.98	3.08
2,4-Dinitrotoluene (2,4-DNT)	2.06	2.17
3,4-Dinitrotoluene (3,4-DNT)	2.36	4.19
2,4,6-Trinitrotoluene (TNT)	2.52	4.71
Picric acid (PA)	3.76	n.c. <sup>a</sup>
Tetryl	5.20	11.00
1-Nitronaphthalene (1-NN)	2.67	2.06
1,5-Dinitronaphthalene (1,5-DNN)	4.41	5.67
1,3-Dinitronaphthalene (1,3-DNN)	4.93	6.23
2,7-Dinitronaphthalene (2,7-DNN)	6.13	7.59
1,8-Dinitronaphthalene (1,8-DNN)	7.39	10.90
Ethylene glycol dinitrate (EGDN)	n.r. <sup>b</sup>	0.46
Diethylene glycol dinitrate (DEGDN)	n.r.	1.25
Nitroglycerine (NG)	1.53	2.48
Diphenylamine (DPA)	3.35	2.20
PETN	3.36	6.98
N-Nitroso diphenylamine (NNDPA)	3.61	2.16
Dibutylphthalate (DBP)	4.52	1.46
RDX	4.57	13.30
Diethyldiphenylurea (DEDPU)	4.83	1.40
2-Nitrodiphenylamine (2-NDPA)	5.77	4.40
HMX	n.e.	n.e.
Nitroquinoline (NQ)	n.e.	n.e.

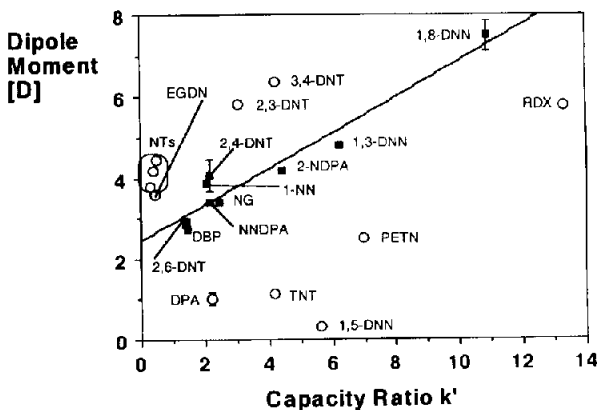
<sup>a</sup> n.c. = Not eluted under the conditions applied.<sup>b</sup> n.r. = Not retained under the conditions applied.

Fig. 4. Dipole moment versus capacity ratio in SFC for various explosives. Column: DB-225 (10 m  $\times$  50  $\mu$ m I.D., 0.05  $\mu$ m film thickness); see Table I for conditions. ■ Indicates data used for generation of correlation line. Error bars represent standard deviation of the mean of dipole moment data found in the literature.

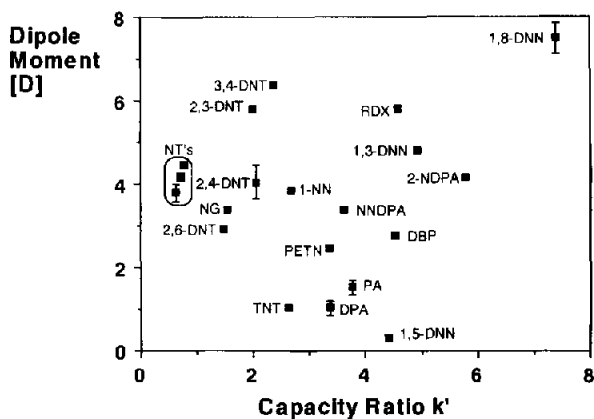


Fig. 5. Dipole moment *versus* capacity ratio in SFC for various explosives. Column: SB Methyl-100 (5 m  $\times$  100  $\mu$ m I.D., 0.25  $\mu$ m film thickness); see Table I for conditions.

compounds on the polar DB 225 column, *i.e.*, the effect of dipole moment. Fig. 4 shows the elution order of the analytes on the DB 225 column plotted *versus* their dipole moment. For those compounds not appearing in the graph, data on their dipole moment were not available. About half of the points are on a straight line (obtained by linear correlation calculations) correlating polarity of the compound and retention on the polar column.

Some compounds showed weaker retention than expected considering their dipole moment, thus falling above the line. Those compounds were either more volatile species (nitrotoluenes, ethyleneglycol dinitrate) or there was some steric hindrance of the polar substituents (as in 2,3-dinitrotoluene and 3,4-dinitrotoluene), which influenced the retention. The other group of compounds that did not follow the simple correlation between dipole moment and retention exhibited stronger retention than predicted. In other words, their bulk dipole moment was lower than expected based on retention. Most members of this group contained highly polar groups, but in highly symmetrical positions, leading to a low bulk dipole moment, (*e.g.*, 2,4,6-trinitrotoluene, 1,5-dinitronaphthalene, PETN and RDX). Diphenylamine is a very polarizable compound, and therefore was more strongly retained than would be expected based on its low dipole moment. Consequently, the retention of the compounds in SFC on the DB 225 column may be generally understood as a polar interaction between sterically free polar sections of the analyte molecule and the cyanopropyl-phenyl stationary phase.

A similar plot of the elution order *versus* the dipole for the methyl column is shown in Fig. 5. No obvious correlation is observed, which suggests that the retention mechanism is not based on a polar interaction of the compounds with the stationary phase.

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## REFERENCES

- 1 P. J. Schoenmakers, *J. Chromatogr.*, 315 (1984) 1.
- 2 C. R. Yonker and R. W. Gale, *J. Phys. Chem.*, 91 (1987) 3333.
- 3 E. Klesper, *Fresenius Z. Anal. Chem.*, 330 (1988) 200.
- 4 C. R. Yonker, R. W. Wright, S. L. Fryc and R. D. Smith, *ACS Symp. Ser.*, 329 (1987) 172.
- 5 C. R. Yonker and R. D. Smith, *J. Chromatogr.*, 459 (1988) 183.
- 6 I. K. Barker, J. K. Kithinji, K. D. Bartle, A. A. Clifford, M. W. Raynor, G. F. Shilstone and P. A. Halford-Maw, *Analyst (London)*, 114 (1989) 41.
- 7 D. Leyendecker, D. Leyendecker, F. P. Schmitz and E. Klesper, *J. Chromatogr.*, 371 (1986) 93.
- 8 R. G. Christensen, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 824.
- 9 D. E. Martire and R. E. Boehm, *J. Phys. Chem.*, 91 (1987) 2433.
- 10 C. R. Yonker and R. D. Smith, in B. A. Charpentier and M. M. Sevenants (Editors), *Supercritical Fluid Extraction and Chromatography*, American Chemical Society, Washington, DC, 1988, p. 161.
- 11 C. R. Yonker, B. W. Wright, R. C. Petersen and R. D. Smith, *J. Phys. Chem.*, 89 (1985) 5526.
- 12 T. A. Berger, *J. Chromatogr.*, 478 (1989) 311.
- 13 T. Takeuchi, Y. Hashimoto and D. Ishii, *J. Chromatogr.*, 402 (1987) 328.
- 14 T. L. Chester and D. P. Innis, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 561.
- 15 P. J. Schoenmakers and L. G. M. Uunk, in J. C. Giddings, E. Grushka, P. R. Brown (Editors), *Advances in Chromatography*, Vol. 30, 1989, p. 1.
- 16 D. Leyendecker, D. Leyendecker, F. P. Schmitz and E. Klesper, *J. Liq. Chromatogr.*, 10 (1987) 1917.
- 17 F. P. Schmitz, D. Leyendecker and E. Klesper, *Ber. Bunsenges. Phys. Chem.*, 88 (1984) 912.
- 18 T. Takeuchi, K. Ohta and D. Ishii, *Chromatographia*, 25 (1988) 125.
- 19 M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction. Principles and Practice*, Butterworth, Stoneham, MA, 1986.
- 20 E. Stahl, K. W. Quirin, A. Glatz, D. Gerard and G. Rau, *Ber. Bunsenges. Phys. Chem.*, 88 (1984) 900.
- 21 E. P. Meier, L. G. Taft, A. F. Graffeo and T. B. Stanford, *4th Int. Conf. Sens. Environ. Pollut., New Orleans, November, 1977*, Paper 132.
- 22 K. Bralin, P. T. Kissinger, R. C. Briner and C. S. Bruntlett, *Anal. Chim. Acta*, 130 (1981) 295.
- 23 M. P. Maskarinec, D. L. Manning, R. W. Harvey, W. H. Griest and B. A. Tomkins, *J. Chromatogr.*, 302 (1984) 51.
- 24 A. H. Lyter, *J. Forens. Sci.*, 28 (1983) 446.
- 25 J. B. F. Lloyd, *J. Chromatogr.*, 261 (1983) 391.
- 26 T. Tamiri and S. Zitrin, *J. Energ. Mater.*, 4 (1986) 215.
- 27 I. S. Krull, M. Swartz, K. H. Xie and J. N. Driscoll, *Proc. Int. Symp. Anal. Detect. Explos.*, Fed. Bur. Invest., Washington, DC, 1988, p. 107.
- 28 J. M. F. Douse, *J. Chromatogr.*, 328 (1985) 155.
- 29 F. Belkin, R. W. Bishop and M. V. Sheely, *J. Chromatogr. Sci.*, 23 (1985) 532.
- 30 J. M. F. Douse, *J. Chromatogr.*, 445 (1988) 244.
- 31 K. Grolimund, in M. L. Lee and K. E. Markides (Editors), *SFC-Applications*, Brigham Young University Press, Provo, UT, 1988, p. 175.
- 32 E. C. Huang, in M. L. Lee and K. E. Markides (Editors), *SFC-Applications*, Brigham Young University Press, Provo, UT, 1988, p. 177.
- 33 P. Sandra, in M. L. Lee and K. E. Markides (Editors), *SFC-Applications*, Brigham Young University Press, Provo, UT, 1988, p. 176.
- 34 M. Ashraf-Khorassani and L. T. Taylor, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 12 (1989) 40.
- 35 W. H. Griest, C. Guzman and M. Dekker, *J. Chromatogr.*, 467 (1989) 423.