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## HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF NITROAROMATIC COMPOUNDS ON AN N-PROPYLANILINE BONDED STATIONARY PHASE

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### SUMMARY

N-Propylanilinetrिमethoxysilane was reacted with 10  $\mu\text{m}$  silica and the resulting bonded stationary phase was assessed for the liquid chromatographic separation of nitro and polynitroaromatic solutes, comparisons being made with octadecylsilyl- (ODS), phenyl- and arylether-bonded phases. The elution order was non-nitro, mono-, di- and trinitroaromatics in both reversed- and normal-phase modes. Enthalpies of transfer from the mobile to the stationary phase were determined for selected solutes, the values being more negative than for the aryl ether and ODS phases. The column was used for the analysis of munition standards and compositions.

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### INTRODUCTION

Selectivity can be enhanced in a chromatographic process by taking advantage of specific interactions between solutes and the stationary phase; such interactions should be rapid and reversible. Charge-transfer complexation is such a selective interaction; this occurs when an electron-rich "donor" molecule such as phenol approaches an electron-deficient "acceptor" species such as nitrobenzene. The equilibrium distances separating donor and acceptor, *ca.* 3  $\text{\AA}$ , are greater than those for covalent bonds but are much less than in Van der Waals interactions<sup>1</sup>. In general, charge-transfer complexes in solution have enthalpies of formation between 0.5 and 4.5 kcal/mole, the rates of complexation being rapid and reactions reversible<sup>2</sup>.

Among early investigators of chemically bonded charge-transfer phases, Lochmüller and Amoss<sup>3</sup> bonded a tetranitrofluorenimino acceptor to silica; this phase gave selective chromatographic separations of donor compounds such as polycyclic aromatic hydrocarbons. Nondek and Málek<sup>4</sup> studied dinitrophenyl-bonded silica as an acceptor stationary phase for polycyclic aromatic hydrocarbons (PAHs) and concluded that charge-transfer interactions were responsible for the separations and large

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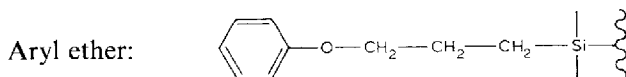
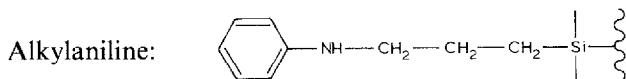
capacity factors. One of the first donor-bonded HPLC stationary phases was developed by Mourey and Siggia<sup>5</sup>, who noted that a donor aryl ether-bonded silica was selective for nitroaromatics; in the reversed-phase mode the elution order non-nitro followed by mono-, di- and trinitroaromatics was observed. Holstein and Hemetsberger published a two-part review<sup>6,7</sup> on LC separation through the formation of donor-acceptor complexes. They discussed the effects of the chemical structure of donors and acceptors and of temperature and mobile phase composition on retention. Recent studies have also focused on reversed-phase separations on aromatic bonded phases, including nitronaphthalene resolution<sup>8</sup>, and normal-phase<sup>9</sup> and reversed-phase<sup>10</sup> separations on pyrene- and anthracene-bonded phases.

This investigation involved the preparation, evaluation and application of an N-propylaniline chemically bonded HPLC phase. The aim was to compare it with aryl ether-<sup>5</sup> and octadecylsilyl-bonded phases (ODS) with respect to separations and thermodynamic considerations. The aniline-bonded phase was also evaluated for the high-performance liquid chromatographic (HPLC) separation of nitroaromatic explosives that have been found to be mutagenic and/or carcinogenic in laboratory animals<sup>11</sup>. There is a need for the determination of compounds such as pentaerythritol tetranitrate (PETN), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and trinitrotoluene (TNT)<sup>12</sup>, for which some HPLC studies have been reported<sup>13</sup>. In addition, there is a need for the determination of hazardous nitropolycyclic hydrocarbons in the atmosphere.

## EXPERIMENTAL

### *Bonded phase preparation*

Silica gel (10  $\mu\text{m}$ ) (Alltech, Chicago, IL, U.S.A.) was refluxed with 6 *M* hydrochloric acid for 2 h, filtered and washed with copious amounts of distilled, deionized water. The silica was dried under vacuum at 160°C for 12 h and was then placed in a closed vessel at a constant relative humidity of 11% to aid the reaction of the silanol groups of the silica with the methoxy groups of the silane reagent. A 5-g amount of the conditioned silica was placed in a 250-ml round-bottomed flask containing 25 ml of dry toluene. To this slurry were added 6 ml of N-phenylaminopropyltrimethoxysilane (Petrarch Systems, Bristol, PA, U.S.A.) in 25 ml of dry toluene. After a 24-h reflux, the modified silica was filtered, washed with toluene, acetone, water and again with acetone, then dried at 60°C under vacuum for 12 h. It was then placed in a flask containing 10 ml of chlorotrimethylsilane in 25 ml of toluene and refluxed for 2 h; the modified silica was filtered and washed as before. Elemental nitrogen analysis showed a loading of 10% (w/w). The aryl ether phase was prepared according to the procedure of Mourey and Siggia<sup>5</sup>. The structures of the two phases are shown below.



*Column packing procedure*

To pack a 25 cm × 0.5 cm O.D. column, 2.5 g of the bonded-phase silica were dried for 1 h at 60°C and was then slurried in 15 ml of isopropanol. The slurry was introduced into the column and packed downwards for 1 h at 6000 p.s.i. using a constant-pressure Haskel DST 122 pump and isopropanol as the packing solvent.

*Chromatography*

The ODS column was obtained from IBM Instruments (Danbury, CT, U.S.A.). The efficiencies of the packed columns were approximately 10 000–12 000 plates per meter. All flow-rates were 1 ml/min. For elution order studies the column temperature was 30°C. The UV detector wavelength was 254 nm.

*Temperature studies*

Temperatures of 30, 40, and 50°C were investigated in the thermodynamic study. The column was allowed to equilibrate thermally for 1 h at a flow-rate of 0.5 ml/min.

*Reagents and instrumentation*

The liquid chromatography system was a Perkin-Elmer (Norwalk, CT, U.S.A.) LC system equipped with two Series 2 pumps, an LC-100 column oven, an LC-75

TABLE I

## ELUTION ORDER ON AN N-PROPYLANILINE COLUMN

Mobile phase: methanol–water (52:48). Temperature: 30°C.

| <i>Compound</i>            | <i>Capacity factor, k'</i> | <i>Compound</i>           | <i>Capacity factor, k'</i> |
|----------------------------|----------------------------|---------------------------|----------------------------|
| Aniline                    | 0.20                       | 2,6-Dibromophenol         | 1.09                       |
| Phenol                     | 0.24                       | Nitrobenzene              | 1.14                       |
| Acetanilide                | 0.34                       | <i>p</i> -Chloroaniline   | 1.16                       |
| <i>p</i> -Chlorophenol     | 0.52                       | 2,4-Dichloroaniline       | 1.28                       |
| <i>m</i> -Nitrophenol      | 0.53                       | 2,5-Dichloroaniline       | 1.40                       |
| <i>p</i> -Bromophenol      | 0.62                       | 2,4,6-Trichlorophenol     | 1.49                       |
| <i>p</i> -Nitrophenol      | 0.63                       | 1,4-Dinitrobenzene        | 1.54                       |
| <i>o</i> -Nitroacetanilide | 0.64                       | 1,3-Dinitrobenzene        | 1.67                       |
| <i>m</i> -Nitroaniline     | 0.65                       | 2,4-Dinitroacetanilide    | 1.80                       |
| <i>p</i> -Nitroaniline     | 0.70                       | 2,4-Dinitroaniline        | 2.02                       |
| 2,6-Dimethylphenol         | 0.74                       | 2,5-Dinitrophenol         | 3.08                       |
| 2,6-Dichlorophenol         | 0.75                       | 2,4,6-Trinitrobenzene     | 4.30                       |
| Benzene                    | 0.77                       | 2,4,6-Trinitroaniline     | 5.90                       |
| 2,5-Dichlorophenol         | 0.76                       | 2,3,5,6-Tetrachlorophenol | 6.22                       |
| <i>p</i> -Nitroacetanilide | 0.85                       | Pentachlorophenol         | 15.88                      |
| <i>m</i> -Nitroacetanilide | 0.92                       | 2,4-Dinitrophenol*        | 16.8                       |
| 2,4-Dichlorophenol         | 0.93                       | 2,4,6-Trinitrophenol**    | 24.0                       |
| 2,4,6-Trimethylphenol      | 0.96                       |                           |                            |

\* After 32 min gradient to 84% methanol.

\*\* After 50 min gradient to 90% methanol.

TABLE II  
COMPARISON OF ELUTION ORDERS ON FOUR BONDED PHASES

| <i>Aniline</i>             | <i>k'</i> | <i>Aryl ether</i>          | <i>k'</i> | <i>ODS</i>                 | <i>k'</i> | <i>Phenyl</i>              | <i>k'</i> |
|----------------------------|-----------|----------------------------|-----------|----------------------------|-----------|----------------------------|-----------|
| Aniline                    | 0.20      | Aniline                    | 1.17      | Aniline                    | 1.71      | Acetanilide                | 0.06      |
| Phenol                     | 0.34      | Phenol                     | 1.19      | Phenol                     | 2.26      | <i>p</i> -Nitrophenol      | 1.24      |
| Acetanilide                | 0.53      | Acetanilide                | 1.49      | <i>p</i> -Nitroaniline     | 2.50      | <i>o</i> -Nitroacetanilide | 1.25      |
| <i>m</i> -Nitrophenol      | 0.63      | <i>p</i> -Nitroaniline     | 1.98      | Acetanilide                | 2.57      | Benzene                    | 1.28      |
| <i>p</i> -Nitrophenol      | 0.64      | <i>p</i> -Nitrophenol      | 2.19      | 1,3,5-Trinitrobenzene      | 3.13      | <i>m</i> -Nitrophenol      | 1.51      |
| <i>o</i> -Nitroacetanilide | 0.70      | <i>m</i> -Nitrophenol      | 2.19      | <i>p</i> -Nitrophenol      | 3.86      | 1,3,5-Trinitrobenzene      | 1.77      |
| <i>p</i> -Nitroaniline     | 0.77      | <i>o</i> -Nitroacetanilide | 2.33      | 2,6-Dinitrophenol          | 4.13      | 2,5-Dinitrophenol          | 1.94      |
| <i>m</i> -Nitroacetaniline | 0.85      | <i>m</i> -Nitroacetanilide | 2.91      | <i>m</i> -Nitrophenol      | 4.29      | 2,4-Dinitrophenol          | 1.94      |
| <i>m</i> -Nitroacetanilide | 0.92      | Benzene                    | 2.98      | <i>m</i> -Dinitrobenzene   | 4.58      | Aniline                    | 2.09      |
| Nitrobenzene               | 1.14      | <i>p</i> -Nitroacetanilide | 3.24      | <i>o</i> -Nitroacetanilide | 4.78      | <i>p</i> -Nitroaniline     | 2.11      |
| <i>p</i> -Dinitrobenzene   | 1.54      | 2,6-Dinitroacetanilide     | 3.28      | <i>m</i> -Nitroacetanilide | 4.78      | 2,6-Dinitrophenol          | 2.25      |
| <i>m</i> -Dinitrobenzene   | 1.67      | Nitrobenzene               | 3.76      | 2,4-Dinitrophenol          | 4.78      | Phenol                     | 2.40      |
| 2,4-Dinitrobenzene         | 1.80      | 2,5-Dinitrophenol          | 3.85      | 2,5-Dinitrophenol          | 5.17      | <i>m</i> -Dinitrobenzene   | 2.43      |
| 2,4-Dinitroaniline         | 2.02      | 2,4-Dinitrophenol          | 4.22      | <i>p</i> -Dinitrobenzene   | 5.54      | 2,4,6-Trinitroaniline      | 3.27      |
| 2,5-Dinitrophenol          | 3.08      | <i>p</i> -Dinitrobenzene   | 4.40      | 2,4,6-Trinitroaniline      | 5.64      | <i>p</i> -Dinitrobenzene   | 3.29      |
| 1,3,5-Trinitrobenzene      | 4.30      | <i>m</i> -Dinitroaniline   | 4.88      | <i>p</i> -Nitroacetanilide | 5.81      | Nitrobenzene               | 3.48      |
| 2,4,6-Trinitroaniline      | 5.90      | 2,4-Dinitroaniline         | 5.11      | 2,4-Dinitroacetanilide     | 5.84      | 2,4-Dinitroaniline         | 3.89      |
| 2,4-Dinitrophenol          | 16.80     | 2,4-Dinitroacetanilide     | 5.84      | Nitrobenzene               | 6.95      | <i>m</i> -Nitroacetanilide | 4.23      |
| 2,4,6-Trinitrophenol       | 24.00     | 1,3,5-Trinitrobenzene      | 6.94      | 2,4-Dinitroaniline         | 7.30      | <i>p</i> -Nitroacetanilide | 4.24      |
|                            |           | 2,4,6-Trinitroaniline      | 9.60      | Benzene                    | 8.18      | 2,4-Dinitroacetanilide     | 4.60      |

| <i>Column*</i> | <i>Mobile phase</i>    | <i>Temperature</i> |
|----------------|------------------------|--------------------|
| Aniline        | Methanol-water (52:48) | 30°C               |
| Aryl ether     | Methanol-water (45:55) | Ambient            |
| ODS            | Methanol-water (35:65) | Ambient            |
| Phenyl         | Methanol-water (6:94)  | Ambient            |

\* For more information on the aryl ether, ODS and phenyl retention studies, see ref. 5.

spectrophotometric detector and a Rheodyne 7105 syringe injector with a 10- $\mu$ l loop. Methanol was of HPLC grade. Water was distilled, deionized and passed through a bed of activated carbon. All solvents were filtered through 0.45- $\mu$ m filters. The nitroaromatics were obtained from Fisher Scientific (Pittsburgh, PA, U.S.A.) and Aldrich (Milwaukee, WI, U.S.A.) and the munition standards and compositions were obtained from Ensign-Bickford (Simsbury, CT, U.S.A.).

## RESULTS AND DISCUSSION

The properties of the N-propylaniline-bonded phase were characterized in both the reversed- and normal-phase modes.

### *Reversed-phase mode*

Methanol-water mobile phases gave an elution order of non-nitro, mono-, di- and trinitroaromatics. In Table I are listed the capacity factors of the solutes in order of elution from the aniline-bonded phase; this was similar to that on the aryl ether-bonded phase studied by Mourey and Siggia<sup>5</sup>. This order was not found for either the ODS- or phenyl-bonded phases studied by Mourey and Siggia<sup>5</sup>; no systematic order of retention time was obtained with respect to the number of nitro groups on the aromatic ring. Elution orders for the four bonded phases are given in Table II. The similar elution order for nitroaromatics on the alkyaniline and aryl ether phases is understandable, as both have a high electron density in the aromatic ring; this can interact selectively with electron-deficient ring systems such as nitroaromatic compounds, resulting in charge-transfer complexation. In contrast, non-nitro aromatic compounds such as aniline, phenol, acetanilide and benzene have identical elution orders on the alkyaniline, aryl ether and ODS stationary phases.

Examples of reversed-phase separations of nitroaromatics on the alkyaniline phase are shown in Figs. 1-3.

A separation of nitro-substituted acetanilides is shown in Fig. 1. The *o*-, *p*-

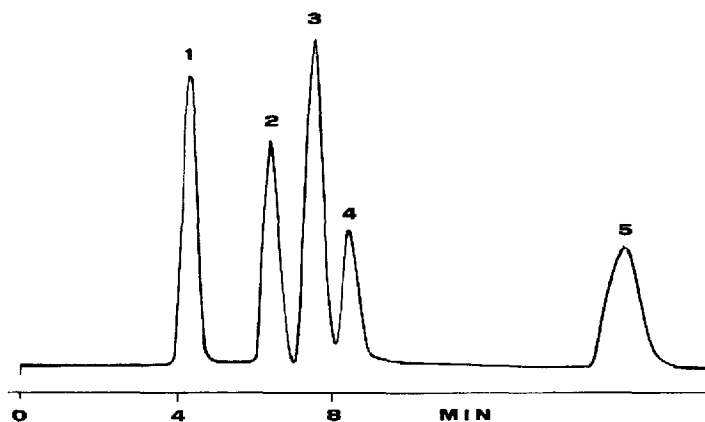


Fig. 1. Separation of acetanilides using the N-propylaniline-bonded stationary phase. Mobile phase, methanol-water (45:55). Flow-rate, 1 ml/min. 1 = Acetanilide; 2 = *o*-nitroacetanilide; 3 = *p*-nitroacetanilide; 4 = *m*-nitroacetanilide; 5 = 2,4-dinitroacetanilide.

and *m*-nitroacetanilide isomers are resolved in that sequence, in contrast to the order *o*-, *m*-, *p*- observed on the aryl ether and ODS phases.

Fig. 2 depicts a separation of nitroanilines, showing increasing retention with more extensive nitro group substitution. Even with a relatively high concentration of methanol (88%) in the mobile phase, the trinitroaromatics are readily separated from the other nitro and non-nitroaromatics, and there is also resolution of similar trinitroaromatics. Such resolutions is seen in Fig. 3, where trinitrobenzene and trinitrotoluene are partially separated even with rapid elution. This permits the rapid determination of trinitroaromatics with less interference from the matrix than ODS, with which the trinitroaromatics typically elute earlier among other non-nitro compounds.

### Normal-phase mode

The alkyylaniline-bonded phase was also evaluated in the normal-phase mode with dichloromethane-hexane as a mobile phase (Fig. 4). The elution order of nitrobenzenes was similar to that in the reversed-phase mode, non-nitroaromatics followed by mono-, di- and trinitrobenzene. The capacity factors for the nitrobenzene series are listed in Table III. Their sequence is different to that more typically seen, where the elution order is reversed on changing from the reversed-phase to the normal-phase mode. This behavior also suggests a selective interaction attributable to charge-transfer processes, which gives separation in a different fashion from silica and ODS.

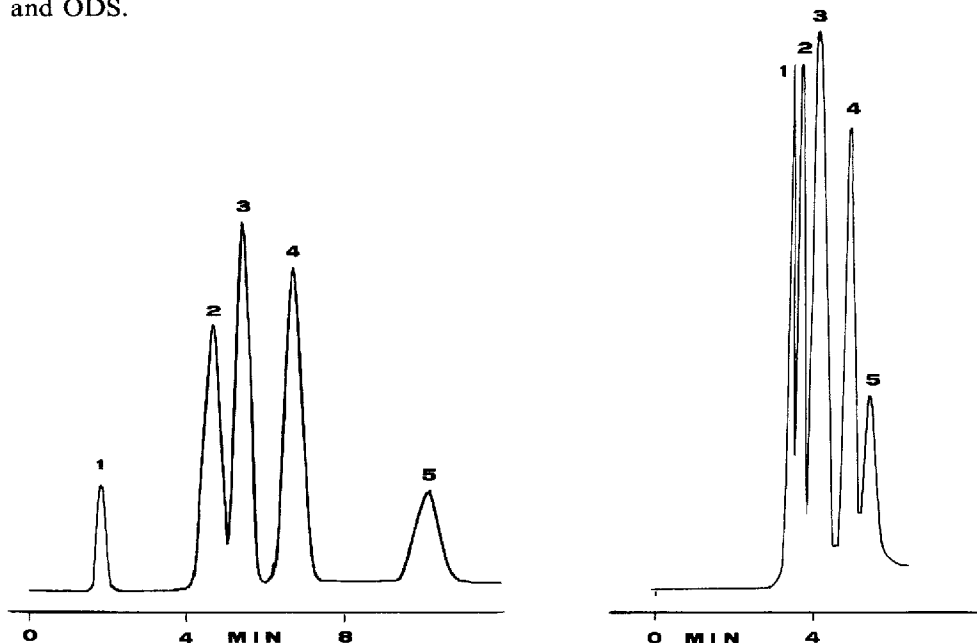


Fig. 2. Separation of anilines on the N-propylaniline-bonded phase. Mobile phase, methanol-water (50:50). 1 = Aniline; 2 = *m*-nitroaniline; 3 = *p*-nitroaniline; 4 = 2,4-dinitroaniline; 5 = 2,4,6-trinitroaniline.

Fig. 3. Separation of aromatics on the N-propylaniline-bonded phase using methanol-water (88:12) as the mobile phase. 1 = Benzene; 2 = nitrobenzene; 3 = *m*-dinitrobenzene; 4 = trinitrobenzene; 5 = trinitrotoluene.

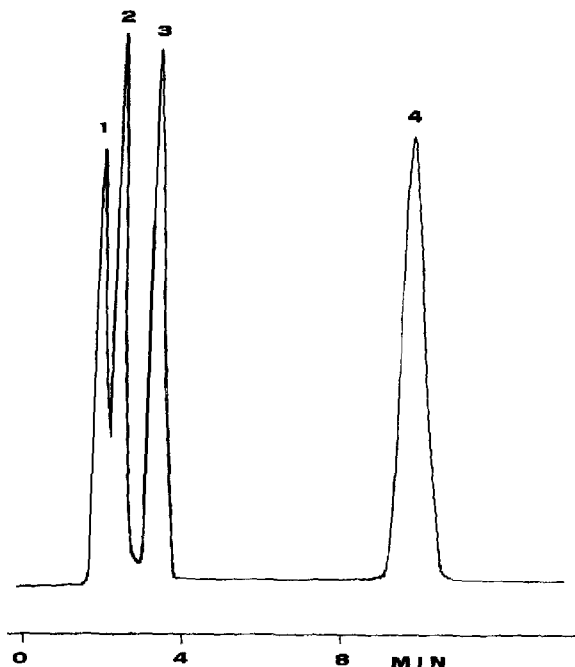


Fig. 4. Separation of aromatics using dichloromethane-*n*-heptane (25:75) as the mobile phase. 1 = Benzene; 2 = nitrobenzene; 3 = *m*-dinitrobenzene; 4 = trinitrobenzene.

#### *Studies of retention mechanism*

To explore the mechanism of retention of the nitroaromatics on the aniline-bonded phase, a number of diagnostic methods were employed. Examination of the reversed-phase elution order for the non-nitroaromatic compounds aniline, phenol, acetanilide and benzene shows it to be similar to that on alkyaniline, aryl ether and octadecylsilyl stationary phases. This suggests that a reversed-phase partition mechanism is in effect for all of these phases. There is also a linear relationship between the natural logarithm of the capacity factor and the concentration of the organic modifier (methanol) in the mobile phase at the three temperatures investigated. This phenomenon has been found in other reversed-phase systems<sup>14</sup>. A linear relationship is also found between the natural logarithm of the capacity factor and the number of nitro groups attached to the aromatic ring, analogous to the relationship on ODS of the capacity factor and the carbon number of solutes within a homologous series<sup>15</sup>. This is a further indication that charge-transfer interactions are involved in the retention mechanism; the electron ring density of an acceptor decreases with increase in the number of electron withdrawing groups on the ring; hence the charge-transfer complex strengthens, yielding an increase in the capacity factor<sup>16</sup>.

To explore further the retention mechanism, temperature dependence studies were conducted for the following solutes with ODS, aryl ether and alkyaniline stationary phases: *N*-methylaniline, benzene, toluene, *p*-dinitrobenzene and trinitrobenzene. In all instances the capacity factors decreased with increasing temperature. Linear Van 't Hoff plots were obtained for all the solutes on each column, indicating that the enthalpies and the mechanism of retention remained constant over the temperature range studied<sup>17</sup>. The slopes of these plots were used to calculate the enthalpy

TABLE III  
CAPACITY FACTORS IN THE NORMAL-PHASE MODE

Mobile phase: dichloromethane-*n*-heptane (25:75). Column: N-propylaniline-bonded phase.

| <i>Compound</i>          | <i>k'</i> |
|--------------------------|-----------|
| Benzene                  | 0.00      |
| Nitrobenzene             | 0.08      |
| <i>p</i> -Dinitrobenzene | 0.45      |
| <i>m</i> -Dinitrobenzene | 0.56      |
| 1,3,5-Trinitrobenzene    | 3.10      |

of transfer from the mobile phase to the stationary phase; values are given in Table IV. Comparison of the enthalpy data for the aniline and aryl ether columns with that for the ODS column must be treated with caution, but some conclusions can be drawn. The silica base and bonded substrate loading of the commercial ODS column undoubtedly differ from those of the prepared phases, affecting the capacity factors and enthalpies of transfer. In all instances the enthalpies of transfer were more favored (more negative) as the capacity factor increased. The enthalpies were greater for the aniline-bonded phase than for the aryl ether and ODS phases, that of 1,3,5-trinitrobenzene being particularly large. This observation parallels that found in solution studies in which aniline exhibited a higher enthalpy of complexation with trinitrobenzene than did anisole<sup>18</sup>. This suggests that a knowledge of solution chemistry may be used to tailor a bonded phase for a particular separation. The enthalpy of transfer is higher on the aniline column than for the aryl ether or ODS phases<sup>17-19</sup>.

The similar elution sequences for aromatic nitro compounds in both normal- and reverse-phase modes is noteworthy. For the reversed-phase mode, it may be concluded from the elution sequences, the relationship between the logarithm of the capacity factor and the number of nitro groups in the aromatic ring and the high enthalpy of transfer from the mobile phase to the stationary phase that the mechanism of retention involves two processes: first, a distribution of the solutes between the mobile phase and the aniline bonded phase, the former repelling the less polar solutes from the mobile phase into the stationary phase (a solvophobic effect); second, once the solutes are close to the bonded phase, charge-transfer interactions prevail, especially for strong electron-acceptor solutes such as trinitrobenzene.

TABLE IV  
ENTHALPIES OF TRANSFER FROM MOBILE TO STATIONARY PHASE (kcal/mole)

| <i>Solute</i>            | <i>Bonded phase</i> |                   |            |
|--------------------------|---------------------|-------------------|------------|
|                          | <i>Aniline</i>      | <i>Aryl ether</i> | <i>ODS</i> |
| N-Methylaniline          | -4                  | -2                | -3         |
| <i>p</i> -Dinitrobenzene | -5                  | -3                | -4         |
| Benzene                  | -4                  | -3                | -3         |
| Toluene                  | -5                  | -4                | -          |
| 1,3,5-Trinitrobenzene    | -6                  | -4                | -3         |



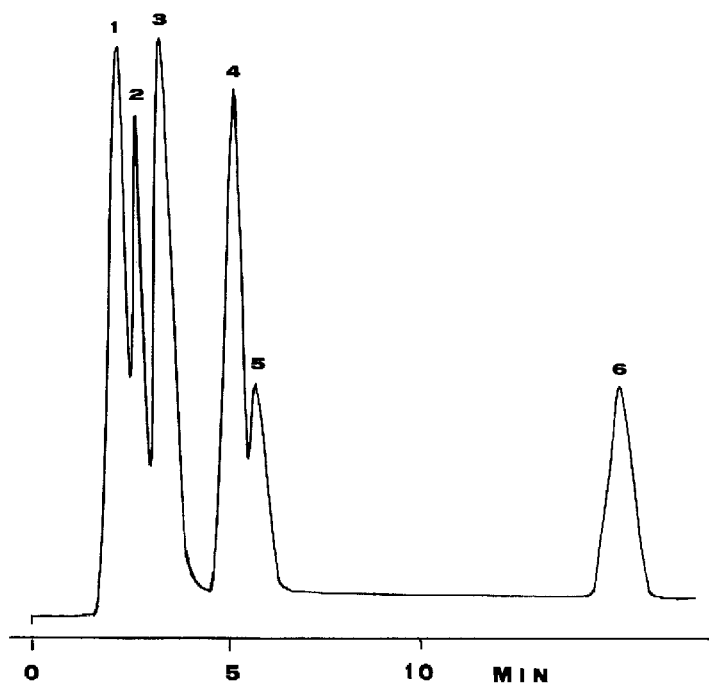


Fig. 5. Chromatography of a synthetic mixture with methanol-water (80:20) as the mobile phase. 1 = Phenol, aniline, benzene, methylphenol, chlorophenol and chloroaniline; 2 = nitrobenzene; 3 = *m*-dinitrobenzene; 4 = trinitrobenzene; 5 = trinitrotoluene; 6 = trinitrophenol. Peak 3 shows detector saturation.

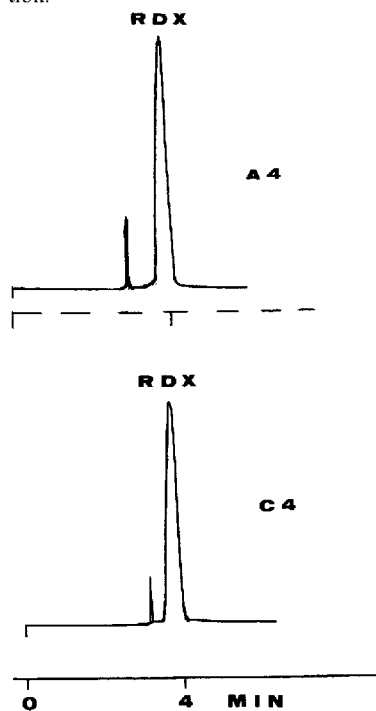


Fig. 6. Analysis of RDX in compositions A-4 and C-4 using dichloromethane-*n*-heptane (50:50) as the mobile phase. The attenuation of the void volume peak is 1024 and that of the RDX is 32.

### *Separation of nitroaromatic munitions materials*

An application of the selectivity of the alkylaniline phases for polynitroaromatics in the normal- and reversed-phase modes was in the analysis of the explosive materials PETN, HMX, RDX and TNT. Using reversed-phase conditions, the non-aromatic nitro compounds (HMX, RDX, PETN) co-eluted. The nitroaromatics, however, were well separated both from each other and from non-aromatic nitro compounds. Under normal-phase conditions this column separated polynitroaromatics from other nitro and non-nitroaromatics (Fig. 5). It also separated aromatic and non-aromatic nitro compounds, TNT, HMX, RDX and PETN being resolved.

Compositions A-4 and C-4 were also analysed after solubilization for 1 h in methanol in an ultrasonicator. Composition A-4 contains RDX and a wax desensitizer and its uses are in shape charges and armor-piercing projectiles. Composition C-4 contains RDX, polyisobutene, binder, dye additive, lead chromate and lamp black, and its use is as a plastic demolition explosive. Fig. 6 shows chromatograms for these samples. It is clear that TNT may also be quantitated in either the reversed- or normal-phase mode. This bonded phase merits evaluation in the explosives industry for monitoring synthetic batches and possibly also for waste-water management analysis.

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