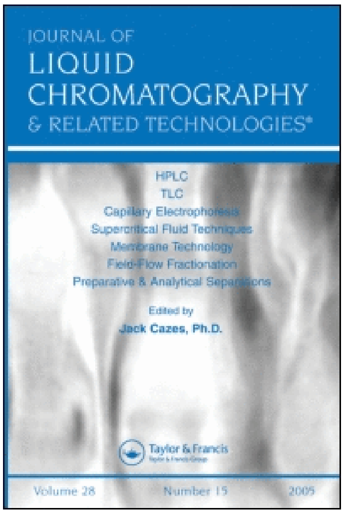

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SEPARATION OF NITRAMINE AND NITROAROMATIC EXPLOSIVES BY CAPILLARY LIQUID CHROMATOGRAPHY

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SEPARATION OF NITRAMINE AND NITROAROMATIC EXPLOSIVES BY CAPILLARY LIQUID CHROMATOGRAPHY

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ABSTRACT

This study outlines the successful separation of nitrated explosives by using high efficiency capillary liquid chromatography. Careful optimization of separation conditions such as mobile phase composition and temperature was performed by using a window diagram, as well as a more global criterion, the chromatographic resolution statistic. These efforts resulted in complete baseline resolution of all 14 components of a standard mixture of explosives, which has not previously been achieved using conventional liquid chromatography. This method was then applied to the determination of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX), and 2,4,6-trinitrotoluene (2,4,6-TNT) in commercial-grade and military-grade explosive samples. As a result, the countries of manufacture of two RDX samples were deduced based on the presence or absence of reaction byproducts.

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INTRODUCTION

Nitroaromatic and nitramine explosives are an important group of compounds in both environmental and forensic science. It has been shown that the soil and ground water of military installations can become contaminated by these compounds and their degradation products at toxic levels.[1-5] In addition, the reliable identification of explosives in post-blast residues is of great importance to criminal investigations.[6-8]

In practice, environmental samples are processed using the U.S. Environmental Protection Agency (EPA) Method 8330.[9,10] In this method, samples are extracted with acetonitrile, pre-concentrated, and then analyzed by using normal- and reversed-phase liquid chromatography (LC) with UV-visible absorbance detection. However, the separation of explosives has remained difficult and commercially available liquid chromatography columns are not capable of resolving all 14 components of the standard test mixture.[9,10] In particular, the isomers 2-amino-4,6-dinitrotoluene (2-am-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4-am-2,6-DNT) co-elute, as do the isomers 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT). Mixed-mode reversed phase/anion exchange LC successfully separated some of the standard explosives, although it was not able to resolve the isomers 2,4-DNT and 2,6-DNT.[11]

Various alternative separation methods have been proposed to achieve higher resolution of explosives mixtures. For example, gas chromatography (GC) has been used to analyze dinitrotoluenes found in nitroglycerine-based explosives[12] and to determine nitrated explosives in ground water.[13] The use of solid-phase microextraction with subsequent GC analysis has also been well explored.[14] Whereas, detectors for GC generally offer better detection limits than LC with UV-visible absorbance detection, they also have a limited linear range and accurate calibration has been problematic.[13] Furthermore, care must be taken in selecting the chromatographic conditions and in deactivating the injection port to avoid loss of explosive solutes by thermal degradation or adsorption.[13]

Supercritical fluid chromatography (SFC) has also been studied as a separation technique for explosives. Although some degree of success was achieved with SFC, it did not provide full resolution of the standard explosives mixture nor was detection sensitivity adequate.[15] More recently, various techniques that take advantage of the high efficiency of a flat electroosmotic flow profile have yielded the best results. In particular, capillary electrochromatography (CEC)[16,17] and micellar electrokinetic capillary chromatography (MEKC)[18,19] have been reported. Of these, only two reports have demonstrated successful resolution of the standard test mixture.[16,18]

In this work, the first successful separation of nitrated explosives and their degradation products by liquid chromatography is described. Through careful optimization of the separation conditions and the use of a highly efficient capillary column, baseline resolution of all 14 components of the standard explosives mixture is achieved. In addition, the performance of this method is demonstrated for the analysis of commercial explosive samples.

EXPERIMENTAL

Materials

Individual standards of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX), nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2-amino-4,6-dinitrotoluene (2-am-4,6-DNT), 4-amino-2,6-dinitrotoluene (4-am-2,6-DNT), 2,4,6-trinitrotoluene (2,4,6-TNT), and methyl-2,4,6-trinitrophenylnitramine (tetryl) are obtained in acetonitrile from Radian International LLC.

Commercial formulations of RDX (M-112-C4 and Demex 100) and 2,4,6-TNT are obtained from the Michigan State Police Laboratory and Michigan State Police Bomb Squad.

High purity, spectroscopic-grade acetonitrile (Baxter Healthcare, Burdick and Jackson Division) and distilled deionized water (Corning Glass Works, Model MP-3A) are used to prepare the mobile phases for liquid chromatography.

Instrumentation

A reciprocating piston pump (Beckman Instruments, Model 114) is used in the constant pressure mode to deliver the mobile phase at a nominal flow rate of 1 µL/min. The samples are introduced by an injection valve (Valco Instruments, Model EC6W) of 1 µL volume, which is split 50:1 before proceeding to the capillary column.

The column is fabricated from fused-silica capillary tubing (Hewlett-Packard, 200 µm i.d., 320 µm o.d., 1.5 m length) that is packed with a 5 µm octadecylsilica material (Shandon, Hypersil C18, 80,000 theoretical plates when using 32.5% acetonitrile/water as mobile phase). The column is maintained at a constant temperature of 28°C in a water bath.

The effluent is directed to a UV-visible absorbance detector (Jasco, Model UVIDEC-100-V) operated at 254 nm.

RESULTS AND DISCUSSION

Separation Optimization

Separations of the 14 component standard mixture of explosives and their degradation products were conducted using various mobile phases, allowing for precise optimization of the separation conditions. The effect of mobile phase composition on the capacity factor of each explosive is shown in Figure 1. Over the range of 30 – 50% acetonitrile/water, the capacity factors are linearly related to mobile phase composition, as shown in Table 1. The y-intercepts of the regression lines represent the predicted retention in pure water and, therefore, reflect the overall polarity of each solute. The magnitude of these intercepts is not surprising based on the structure of the solutes. For example, the addition of a methyl group (e.g., from NB to 2-NT, 1,3-DNB to 2,4-DNT, or 1,3,5-TNB to 2,4,6-TNT) tends to decrease water solubility and, therefore, increase the y-intercept. Conversely, the addition of nitro groups (e.g., from NB to 1,3-DNB to 1,3,5-TNB) tends to increase water solubility and decrease the y-intercept.

The negative slopes of the regression lines imply that all solutes become less retained with increasing concentration of acetonitrile. Some solutes, particularly 2,4,6-TNT and tetryl, experience a larger decrease in retention with increasing concentration of acetonitrile than solutes of similar structure. In contrast, 1,3,5-TNB shows a markedly lower sensitivity to acetonitrile. Another interesting trend is that the slopes for the nitrobenzenes increase as the degree of nitration increases (NB < 1,3-DNB < 1,3,5-TNB), whereas the opposite trend occurs for the nitrotoluenes (2-NT > 2,4-DNT > 2,4,6-TNT). Overall, these different slopes reflect the selectivity of the mobile and stationary phases for these explosives. As will be shown, this selectivity, when combined with the high efficiency of the capillary column, allows for complete resolution of the 14 component mixture.

From the data summarized in Table 1, it is possible to calculate the resolution (R) of adjacent solute pairs using the following equation:[20]

$$R = \left(\frac{\sqrt{N}}{4}\right)\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k}{1+k}\right) \qquad (1)$$

where N is the number of theoretical plates, k is the capacity factor, and α is the selectivity of the solute pair (where $\alpha = k_1 / k_2$ and $k_1 > k_2$).

By graphing the resolution of each solute pair as a function of mobile phase composition, the "window diagram" shown in Figure 2 is obtained.[21,22] In this diagram, mobile phase compositions that produce co-elution are located where the resolution of a solute pair reaches unity and intersects the x axis. In contrast, the mobile phase composition that generates the maximum resolution is located

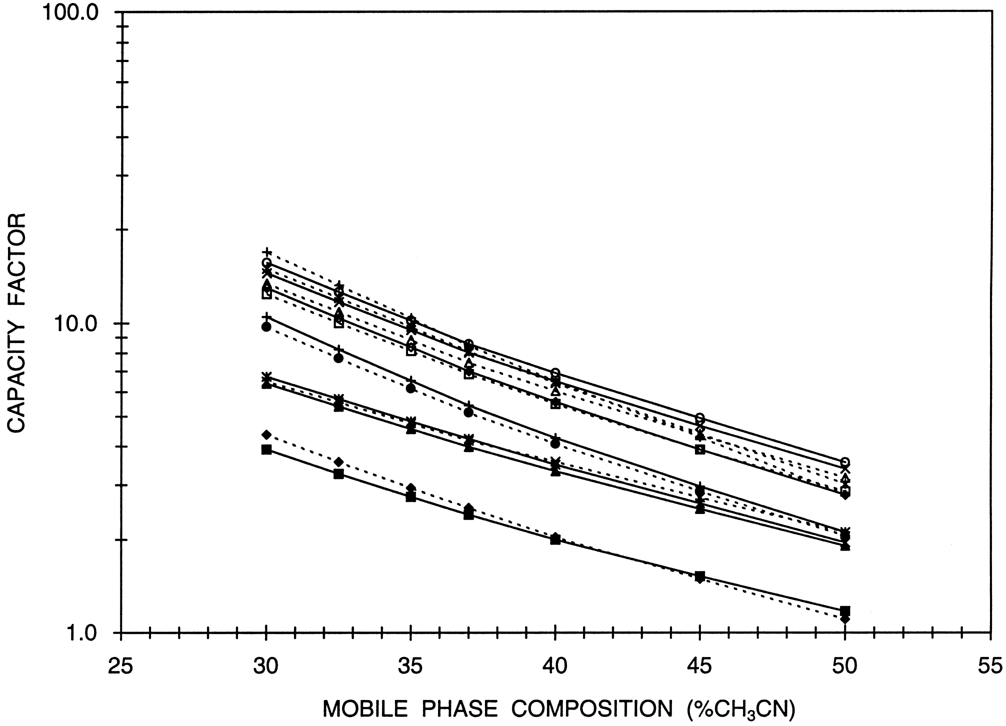

Figure 1. Van Nostrand Reinhold Company Dependence of capacity factor on mobile phase composition. Column: 1.51 m x 200 µm i.d. fused silica capillary, packed with 5 µm Shandon Hypersil C18. Mobile Phase: 30 – 50% acetonitrile/water, 1.0 µL/min, 30 °C. UV-visible absorbance detection: 254 nm, 0.005 ABFS. Solutes: RDX (■, —), HMX (◆, ···), 1,3-DNB (▲, —), 1,3,5-TNB (X, ···), NB (✳, —), 2-am-4,6-DNT (●, ···), 4-am-2,6-DNT (+, —), 2,4-DNT (□, —), 2,6-DNT (◇, —), 2-NT, (△, ···), 4-NT (X, —), 2,4,6-TNT (✳, , ···), 3-NT (○,—), and tetryl (+, ···).

Table 1. Linear Regression of Capacity Factor as a Function of Mobile Phase Composition[a]

Solute	Slope	Intercept	R^2 [b]
RDX	–2.67	1.39	0.995
HMX	–3.05	1.55	0.995
NB	–2.71	1.63	0.999
1,3-DNB	–2.66	1.60	0.997
1,3,5-TNB	–2.46	1.54	0.998
2-NT	–3.19	2.07	0.996
3-NT	–3.26	2.16	0.996
4-NT	–3.20	2.11	0.996
2,4-DNT	–3.26	2.06	0.996
2,6-DNT	–3.40	2.12	0.996
2-am-4,6-DNT	–3.45	2.01	0.994
4-am-2,6-DNT	–3.56	2.08	0.994
2,4,6-TNT	–3.49	2.22	0.999
Tetryl	–3.94	2.40	0.999

[a] Chromatographic conditions as given in Figure 1.

[b] R^2, correlation coefficient.

where the resolution of two limiting pairs intersect to create the tallest apex or “window” in the diagram. Despite the complexity of this figure, it can be seen that the optimal resolution is achieved at 32.5% acetonitrile/water. The critical pairs are predicted to be 1,3-DNB/1,3,5-TNB and 1,3,5-TNB/NB, with resolutions of 1.63 and 1.52, respectively, assuming that a column with 80,000 theoretical plates is utilized for the separation.

A more global measure of separation quality that takes into account the resolution of all solutes, rather than just the critical pairs, can be derived from the first term of the chromatographic resolution statistic (CRS1) of Schlabach and Excoffier:[23]

$$\mathrm{CRS1} = \sum_{i=1}^{n-1} \left[\frac{\left(R_{i,i+1} - R_{opt}\right)^2}{\left(R_{i,i+1} - R_{min}\right)^2 R_{i,i+1}} \right] \qquad (2)$$

where n is the number of solutes, $R_{i,i+1}$ is the resolution of adjacent solute pairs, R_{opt} is the desired resolution, and R_{min} is the minimum acceptable resolution. Based on the form of this equation, CRS1 will reach a minimum value of zero as all $R_{i,i+1}$ approach the desired resolution R_{opt}.

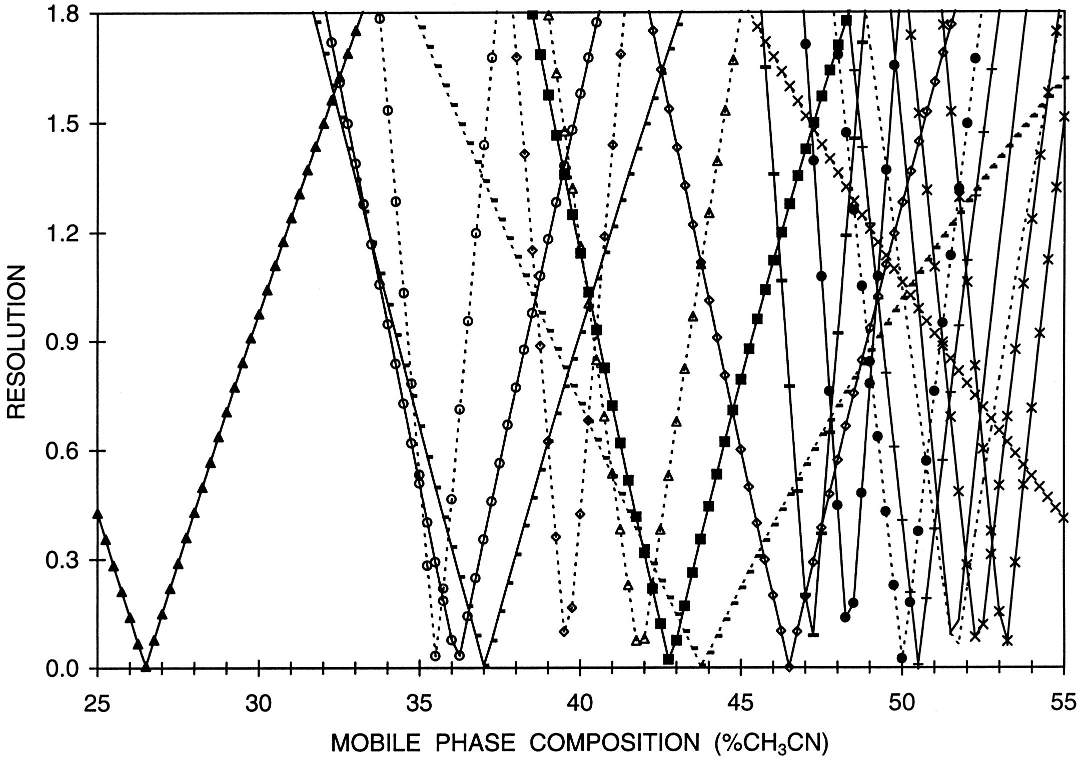

Figure 2. Dependence of the resolution according to Equation (1) on mobile phase composition. Chromatographic conditions as given in Figure 1. Solutes: RDX/HMX (■, —), HMX/1,3-DNB (◆, —), 1,3-DNB/1,3,5-TNB (▲, —), 1,3-DNB/2-am-4,6-DNT (X, —), 1,3-DNB/4-am-2,6-DNT (*, —), 1,3,5-TNB/NB (-, —), 1,3,5-TNB/2-am-4,6-DNT (--, —), 1,3,5-TNB/4-am-2,6-DNT (●, —), NB/2-am-4,6-DNT (+,—), NB/4-am-2,6-DNT (—), NB/2,4-DNT (■, ···), NB/2,4,6-TNT (◆, ···), NB/tetryl (▲, ···), 2-am-4,6-DNT/4-am-2,6-DNT (X, ···), 4-am-2,6-DNT/2,4-DNT (*, ···), 2,4-DNT/2,6-DNT (-, ···), 2,4-DNT/2,4,6-TNT (‾, ···), 2,4-DNT/tetryl (●, ···), 2,6-DNT/2,4,6-TNT (+, ···), 2,6-DNT/tetryl (···), 2-NT/4-NT (□, —), 2-NT/2,4,6-TNT (◇, —), 2-NT/3-NT (△, —), 4-NT/2,4,6-TNT (○,—), 4-NT/3-NT (□, ···), 4-NT/tetryl (◇,···), 2,4,6-TNT/tetryl (△, ···), and 3-NT/tetryl (○, ···).

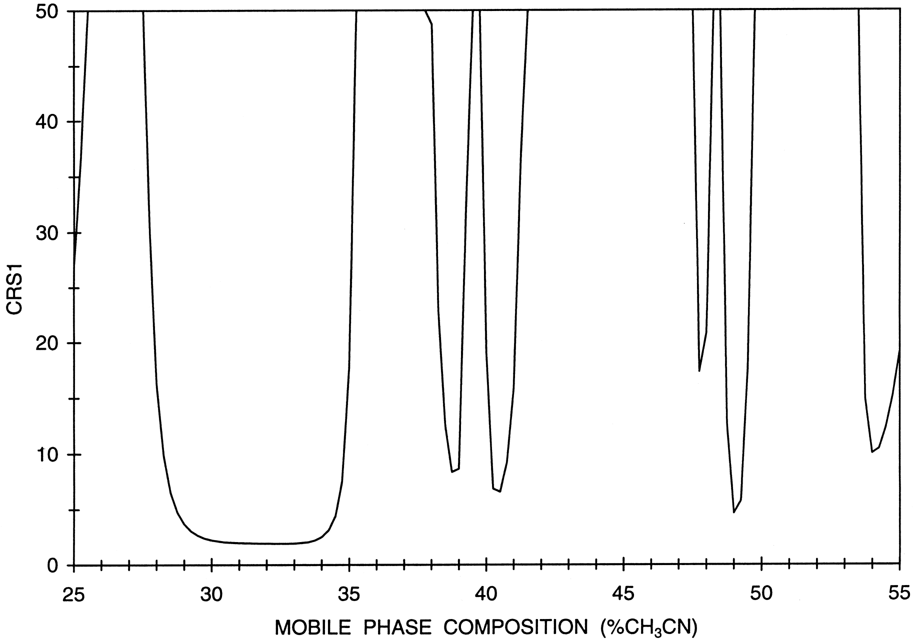

Figure 3. Dependence of CRS1 according to Equation (2) on mobile phase composition. Chromatographic conditions as given in Figure 1.

The CRS1 value for this separation is shown as a function of mobile phase composition in Figure 3 with selected values for R_{opt} of 1.5 and R_{min} of 0.0. The minimum in this graph is observed in the range of 31–33% acetonitrile/water, which represents the region where the best possible resolution is achieved for all components in the mixture. Furthermore, because this optimal region is relatively flat, small variations in mobile phase composition will not adversely affect the quality of the separation. Finally, in agreement with the window diagram in Figure 2, the global minimum is located at 32.5% acetonitrile/water.

In contrast, the U.S. EPA method recommends the use of a conventional LC column and 50% methanol/water as mobile phase. Based on the differing solubility parameters for methanol and acetonitrile,[24] this would correspond to a mobile phase composition of approximately 39% acetonitrile/water. Although there is a local optimum located at this mobile phase composition (see Figures 2 and 3), it does not allow for complete resolution of the mixture. Specifically, the solute pairs 1,3,5-TNB/NB and 4-NT/tetryl are predicted to attain resolutions of only 0.6 when separated on a column with 80,000 theoretical plates.

It is also important to note that a distinct sensitivity to temperature is observed for this separation. As temperature is increased from 30 to 35°C at the same mobile phase composition, the capacity factors of all solutes decrease by an average of −4.7%. However, some of the solutes change as little as −3.1%, whereas others change as much as −8.2%. Accordingly, this leads to a significant change in resolution for certain solute pairs. Most notably, the resolution of 4-NT/2,4,6-TNT decreases from 1.84 to 0.79 and the resolution of 3-NT/tetryl decreases from 3.13 to 1.37 over this temperature range. As a result, column temperature must be carefully controlled and the optimum was determined to be 28°C for a mobile phase composition of 32.5% acetonitrile/water.

The ability of the optimal mobile phase composition and temperature to achieve the best overall separation is confirmed experimentally in Figure 4 using the standard mixture of explosives. In this figure, baseline resolution of all 14 components is successfully demonstrated for the first time using liquid chromatography. As predicted, the solutes that possess the limiting resolution in the mixture are 1,3-DNB/1,3,5-TNB and 1,3,5-TNB/NB, for which the measured resolutions were 2.1 and 1.6, respectively.

Explosives Analysis

The application of this methodology to the analysis of commercially available explosives is shown in Figure 5. The chromatograms obtained from acetonitrile extracts of explosives such as these can be used to identify which energetic compounds are present or to draw conclusions as to the origin of the sample. For example, it is known that the military-grade explosive C4 (M112) and the commercial-grade explosive Demex 100 both use RDX as their primary energetic compound. However, it is interesting to note that a small but detectable level of HMX was seen in the C4 sample (Figure 5A), distinguishing it from the Demex 100 sample (Figure 5B). Currently, the only U.S.-based producer of RDX is the Holsten Army Ammunition Plant in Kingsport, TN. Their synthesis for RDX is known to introduce several percent of HMX into the final product. However, as HMX is also a powerful high explosive, no effort is made to remove it.[25] Therefore, the presence of HMX in the C4 sample confirms that it is domestically produced and intended for military use. In contrast, the Demex sample (which lacks HMX) is not of U.S. origin.

The extract obtained from a commercial sample of TNT yields a single peak at a retention time appropriate for 2,4,6-trinitrotoluene (Figure 5C). There is no evidence of either reductive or oxidative degradation products, which would be more common in an environmentally weathered sample. It is also noteworthy that the peak observed for TNT is highly asymmetric (fronting). One possible cause of this asymmetry is the presence of other TNT isomers that are not fully

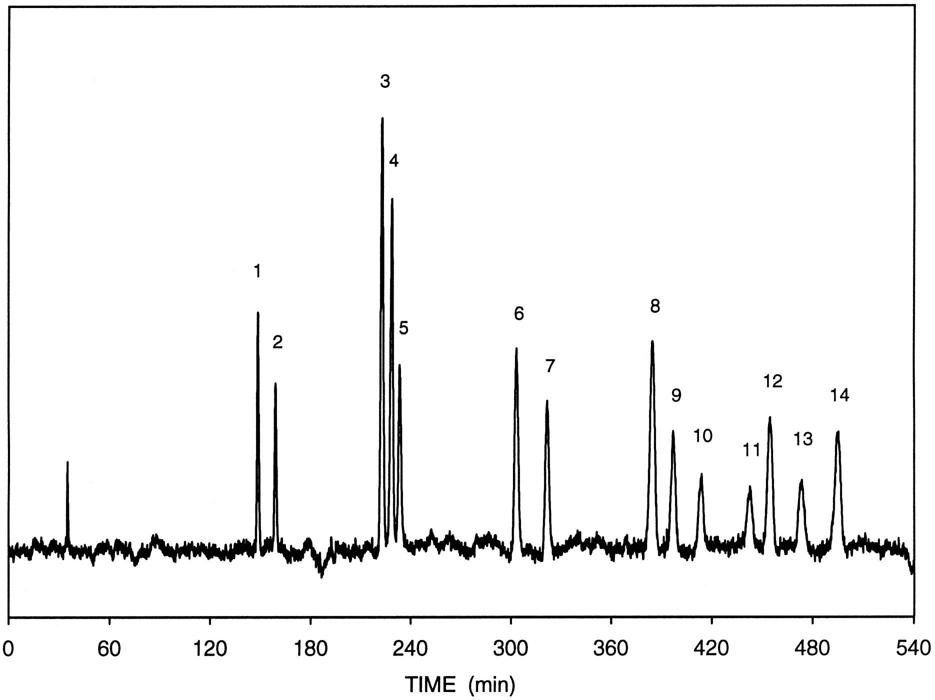

Figure 4. Separation of a standard mixture of explosives and degradation products (EPA 8330). Mobile Phase: 32.5% acetonitrile/water, 1.0 µL/min, 28 °C. Other chromatographic conditions as given in Figure 1. Solutes: (1) RDX, (2) HMX, (3) 1,3-DNB, (4) 1,3,5-TNB, (5) NB, (6) 2-am-4,6-DNT, (7) 4-am-2,6-DNT, (8) 2,4-DNT, (9) 2,6-DNT, (10) 2-NT, (11) 4-NT, (12) 2,4,6-TNT, (13) 3-NT, (14) tetryl.

separated from the 2,4,6-TNT isomer. To examine this possibility, the sample was analyzed by ^{1}H NMR spectroscopy and confirmed to contain only the 2,4,6-TNT isomer. A second explanation is that a nonlinear isotherm may govern the interactions of 2,4,6-TNT with the stationary phase. Ideally, the concentration of solute in the stationary phase is linearly dependent on the concentration of solute in the mobile phase. However, when this is not the case, asymmetric peak shapes result. In particular, the fronting shape of 2,4,6-TNT implies that this solute has a greater tendency for self-association than for association with the octadecylsilica stationary phase. Therefore, as the concentration of the solute increases, there is an increased thermodynamic driving force for additional solute molecules to partition into the phase. This behavior is characteristic of a concave or Brunauer–Emmett–Teller (BET) Type III isotherm.[26-28]

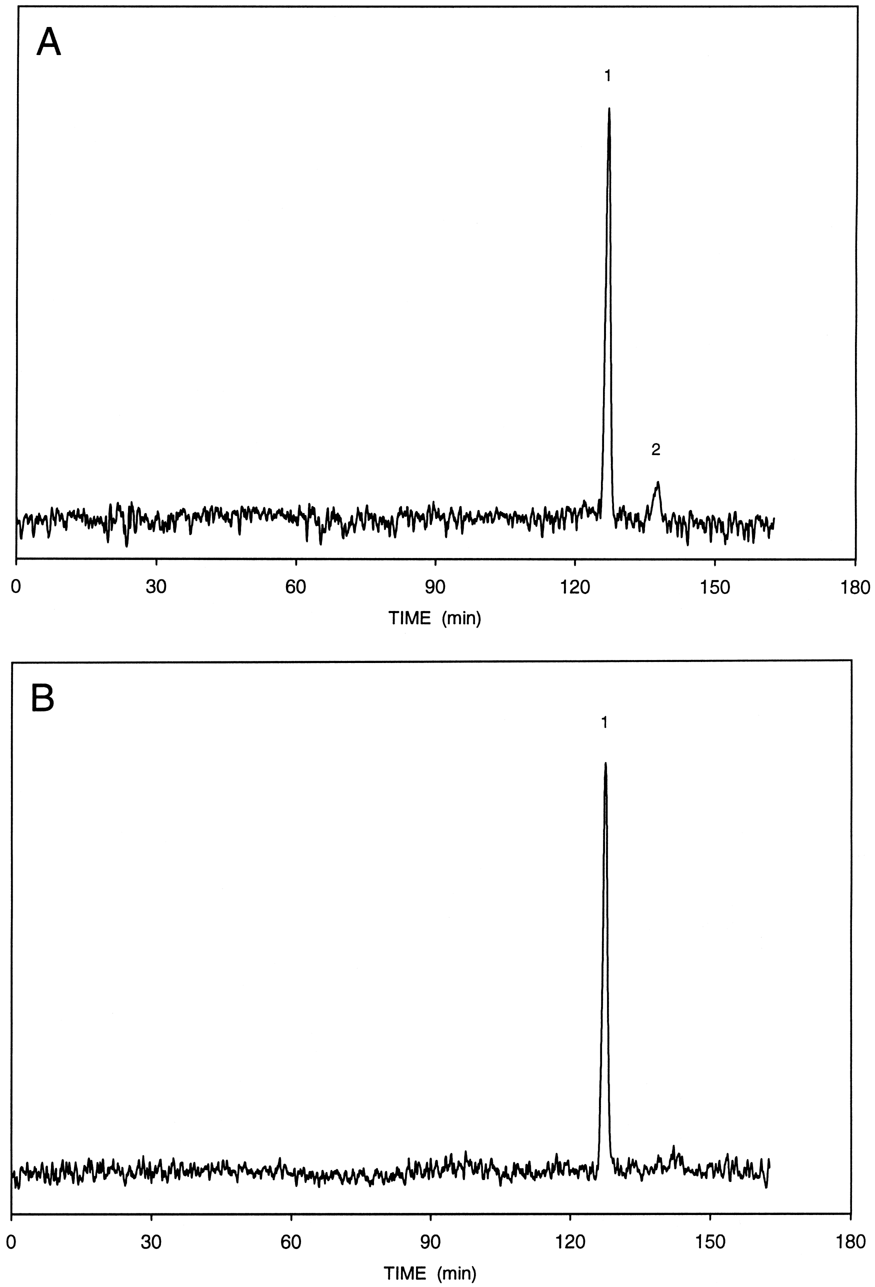

Figure 5. Analysis of commercial explosives samples. Mobile Phase: 32.5% acetonitrile/water, 1.0 μL/min, 28 °C. Other chromatographic conditions as given in Figure 1. A) C4 (M112), Solutes: (1) RDX, (2) HMX; B) Demex 100, Solutes: (1) RDX; and C) 2,4,6-trinitrotoluene, Solutes: (1) 2,4,6-TNT.

(continued)

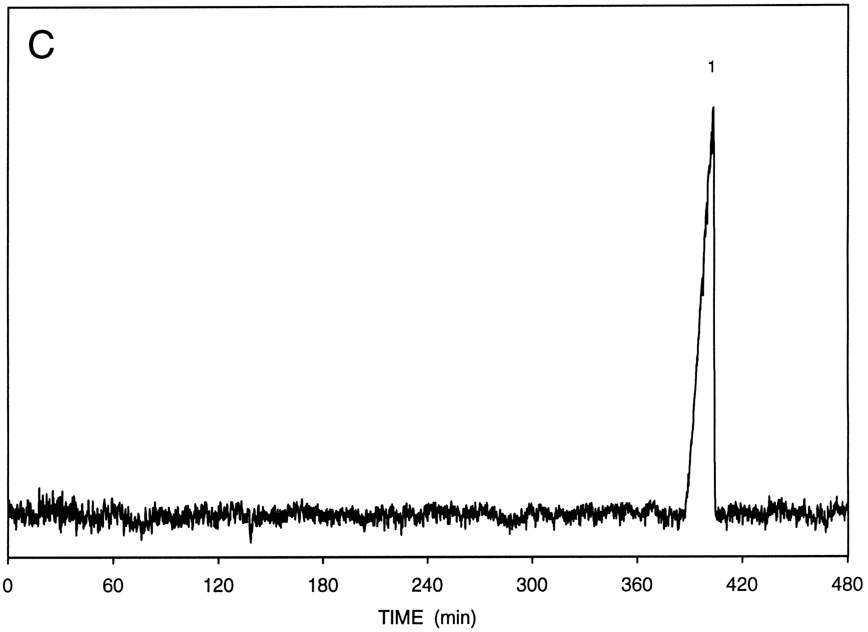

Figure 5. Continued.

To examine this possibility, increasingly dilute samples were injected and the peak asymmetry was measured. On close inspection, even the most dilute explosive samples demonstrate a small persistent degree of asymmetry for 2,4,6-TNT and the closely related explosive tetryl (see Figure 4). Both 2,4,6-TNT and tetryl have strong electron-withdrawing groups linked to an aromatic ring. The aromatic ring is highly electrophilic, whereas the nitro and nitramine groups are good electron donors. Therefore, it seems likely that these solutes would form stable charge-transfer complexes upon self-association. This suggests that a nonlinear isotherm is the most likely cause of the highly asymmetric peak shape for 2,4,6-TNT in Figure 5C.

CONCLUSIONS

Nitrated explosives are of great interest to the environmental and forensic communities, but the methods of separation and detection for these compounds remain underdeveloped. Only after careful optimization of the mobile phase composition, temperature, and the application of a highly efficient capillary column were all 14 components of a standard mixture of explosives fully resolved. This represents the first time that liquid chromatography has successfully been used to separate this mixture, albeit at the sacrifice of analysis time. The optimized method was used to analyze commercial-grade and military-grade samples of RDX and TNT. This approach enabled the composition of the samples to be determined as well as their potential origin.

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