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Improved Determination of Nitrotoluenes Using Liquid Chromatography with Photolytically Assisted Thermal Energy Analysis (LC-PAT)

ABSTRACT: A post-column, on-line, photolysis unit is incorporated in a normal phase, high-performance liquid chromatography (LC) system to improve the thermal energy analyzer (TEA) detectability of mono-, di- and tri-nitrotoluenes. The construction of this photolytically assisted TEA (PAT) detection approach includes the use of an ultraviolet lamp and a knitted open tubular (KOT) reaction chamber of Teflon®. The mechanism for improved detection using PAT is explored, using batch irradiations followed by LC-TEA and gas chromatography/mass spectrometry, and is postulated to involve photochemically induced isomerization leading to homolytic cleavage of the $C-NO_2$ bond, followed by hydrogen abstraction. After optimization of photolytic residence time and cooling bath temperature, PAT allows for an improvement in the TEA detectability of trinitrotoluene and dinitrotoluene by factors of 30 and 16, respectively. Mononitrotoluene, which is not responsive under conventional TEA conditions, may be detected with good sensitivity using LC-PAT. The use of LC-PAT does not interfere with the determination of other nitro-based high explosives which exhibit adequate responses under conventional LC-TEA conditions.

KEYWORDS: forensic science, explosives, chromatographic analysis, thermal analysis, explosives analysis, liquid chromatography-thermal energy analyzer, on-line photolysis, trinitrotoluene, nitrotoluenes, post-column reaction detection

During the forensic science examination of materials collected from the scene of a bombing, one of the most important determinations to be made by the analyst is the identity of the explosive material involved. Following extraction of blast debris, identification of explosives is generally obtained using thin-layer chromatography (TLC), gas chromatography (GC) or high-performance liquid chromatography (LC). These chromatographic approaches cannot be expected, in all cases, to resolve completely the explosives in an extract from coextracted matrix materials. Therefore, the selectivity of detection has become an important consideration when designing the analytical apparatus to be used for compound identification. In addition, traces of explosives are commonly present in debris at very low levels, so sensitivity

is important as well. Currently, there are several detection options available which fulfill these requirements.

Following GC separation, high explosives containing the nitro functionality in their structures may be detected with good sensitivity and adequate selectivity using electron capture detection (GC-ECD) [1]. LC-ECD has also been reported for the determination of explosives [2], but the routine application of this approach has not been forthcoming since the initial descriptions. LC with reductive electrochemical (EC) detection (LCEC) has been incorporated as a selective, sensitive approach for nitro compounds [3], but this method has several operational difficulties that have precluded its wide acceptance among forensic science practitioners. One newer technique uses post-column, photolytic derivatization of nitro compounds to form nitrite, which is then determined using oxidative EC detection [4]. This oxidative LC-photolysis-EC method requires less operator attention than reductive LCEC approaches, yet retains the sensitivity and selectivity of EC detection. Negative ion mass spectrometry (MS) detection in GC [5] and LC [6] offers excellent sensitivity (using single ion monitoring) and selectivity (under less sensitive, scanning conditions), but the operator attention required and the cost of such instrumentation are beyond the means of many forensic science laboratories.

In recent years, there has been an important addition to the detector arsenal of the forensic bomb analyst: the thermal energy analyzer (TEA). The TEA detector is a gas-phase, chemiluminescence device which has been demonstrated to provide excellent sensitivity and selectivity for nitroso- and nitro-compounds. Although TEA instrumentation has previously been described in depth [7,8], a brief summary of the operational mechanism of this detector will facilitate understanding of the new approach discussed in this paper. In GC-TEA, the effluent from the column is directed through an interface into a heated chamber at reduced pressure, where catalytic pyrolysis of a nitro compound yields NO_2. This NO_2 is readily converted to nitrosyl radical ($NO \cdot$) under the same catalytic conditions [9]. The pyrolyzed effluent then flows through a cryogenic trap; most contaminants are condensed in the trap, but nitrosyl radicals survive and are swept into a reaction chamber. When ozone (O_3) is mixed with $NO \cdot$, electronically excited nitrogen dioxide (NO_2^*) is formed. This excited species then undergoes radiative decay to the ground state, emitting wavelengths of light within a rather broad range between 600 and 1600 nm. However, as a result of the response characteristics of the photomultiplier (PMT) used, only the light between 600 and 800 nm is detected, thereby making this device quite selective for analytes which can be pyrolyzed to form NO or NO_2 (nitroso- and nitro-compounds, respectively). The sensitivity of the detector stems from the high quantum efficiency of the chemiluminescent reaction, and from the low background noise (dark current of the PMT) incurred.

In GC-TEA, it is possible to alter the temperature of the pyrolysis chamber to gain selectivity for nitroso-compounds over the response for nitro-compounds. In other words, in the "nitroso mode," the pyrolyzer is held at 550°C. LaFleur and Mills [7] have shown that nitroaromatics are not readily detected using a pyrolyzer temperature of 500°C; rather, these compounds require temperatures of 800°C or greater for molar (or near molar) response [7,9]. Unfortunately, when LC-TEA is performed, the use of pyrolysis chamber temperatures greater than 550°C gives rise to substantial baseline noise, which severely limits the detector's sensitivity and selectivity. Thus, LC-TEA is always performed in the "nitroso mode." While nitramines (compounds containing $N-NO_2$ bonds) and nitrate esters (containing the $-O-NO_2$ moiety) are amenable to LC-TEA under the influence of the lower pyrolysis temperatures [10], nitro-aromatics (containing $C-NO_2$ bonds) cannot be detected with even adequate sensitivity. These differences are understandable, since the $C-N$ bond energy (292 kJ/mol) in $C-NO_2$ compounds is significantly higher than the $O-N$ (175 kJ/mol) and $N-N$ (159 kJ/mol) bond energies for nitrate esters and nitramines, respectively [11].

Several of the larger laboratories involved with explosives investigations, including the

ATF National Laboratory Center, have incorporated GC-TEA for the identification of explosives in post-blast debris extracts and swabbings [12,13], wherein identities based on GC-TEA are confirmed using LC-TEA. This approach takes advantage of the complementary modes of separation inherent in GC and LC, lending credence to the identification and allowing for certainty in the report. The obvious downfall of this method involves the confirmation of the nitro-toluenes, including trinitrotoluene (TNT), the dinitrotoluenes (DNT), and mononitrotoluene (MNT) isomers.

Reports in the literature suggested that ultraviolet (UV) irradiation could be used to facilitate TEA detection of C-nitro compounds. The incorporation of photolytic derivatization for nitro-compounds, before oxidative EC detection [4], was based on the generation of nitrite (NO_2^-) from the parent explosives. In addition, it was clear that nitrite (or nitrate, formed from nitrate esters) could be pyrolyzed to form nitrosyl radical [13], which would then be suitable for detection in the TEA approach. In fact, Spicer et al. have utilized pyrolysis and chemiluminescence for the determination of nitrate in atmospheric particulate matter [14]. Thus, we chose to attempt an on-line, post-column UV irradiation to improve the LC-TEA detectability of nitrotoluenes. One important aspect of this LC-photolytically-assisted TEA (LC-PAT) approach involved the use of a knitted open tubular (KOT) photochemical reactor design. This KOT significantly reduced the band broadening which results whenever long lengths of tubing, having large dead volumes, are used to construct post-column reaction chambers. Without this inclusion in the experimental design, the sensitivity gained using PAT would be canceled by the loss in resolution caused by band diffusion.

Experimental Procedure

Materials

Equipment used in the construction of the LC-PAT system included the components used in the conventional LC-TEA apparatus: two 6000A solvent delivery systems, a model 660 solvent programmer, and a U6K back-flush injector (all Waters Chromatography Division, Millipore Corp., Milford, MA), a normal phase, 3-μm CN analytical column, 7.5 cm by 4.6 mm, and an "LC-CN" guard column (both Supelco, Inc., Bellefonte, PA), and a TEA Model 510 detector (Thermo Electron Corp., Waltham, MA) operated in the nitroso mode (pyrolyzer temperature at 550°C), with a cryogenic methanol bath held at −80°C using a Flexicool refrigeration probe (FTS Systems, Stone Ridge, NY). Detector response was monitored on an Omniscribe strip chart recorder (Houston Instruments, Austin, TX). The irradiation apparatus used for LC-PAT and batch photolysis studies was a Photronix model 816 UV batch irradiator (Photronix Corp., Medway, MA), composed of a low pressure mercury discharge lamp (approximately 10W) having principle output at 253.7 nm (and minor bands at 313, 365, 404, and 435 nm), and a voltage regulator. Photolysis of the eluate from the column took place in a knitted open tubular (KOT) reactor composed of Teflon® tubing, 1.6 mm outside diameter by 0.8 mm inside diameter by 11.9 m (39 ft) long, having a volume of 6 mL (Fig. 1).

The optimum geometry for a KOT involves the continuous turning of the tubing at 90° angles in three dimensions [15]. The KOT used in these studies was of our own design and was produced by weaving the reactor tubing around another length of the Teflon tubing, which acted as a backbone. The finished KOT reactor was wrapped around the UV lamp, and the entire assembly was placed inside a reflective, thermally transmitting flask. This flask was covered with foil to shield the operator from the UV irradiation and was then situated in a Hotpack model 603340 refrigerated circulating bath (Hotpack Corp., Philadelphia, PA). A vacuum source was used to pull air around the lamp, to remove ozone, and to cool the reactor. Gas chromatograph/mass spectrometer studies regarding the mechanism of detection were performed using a Finnigan 1020 (OWA) in the electron impact mode with
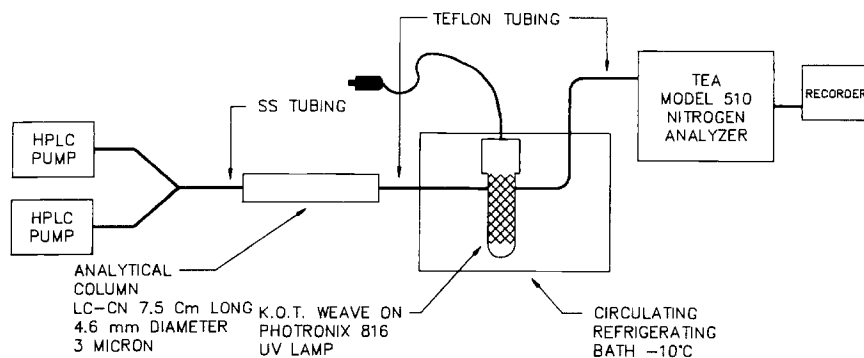
FIG. 1—*Block diagram of LC-PAT apparatus.*

a 15-m DB-5 fused silica capillary column (J &W Scientific, Inc., Rancho Cordova, CA). The explosive standards were obtained from known explosives, while 2,4-dinitrotoluene (DNT) and 4-nitrotoluene (MNT) were obtained from Aldrich Chemical Company (St. Louis, MO). Stock and working solutions of these compounds were prepared in dichloro methane (DCM), and were frozen after preparation. DCM and isooctane used in the mobile phase were obtained from Burdick and Jackson Laboratories, Inc. (Muskegon, MI).

Procedure

To evaluate the chances for success of the proposed LC-PAT approach, a scouting experiment was performed in which a 1-part-per-thousand (1-ppth, 1-mg/mL) solution of TNT in DCM was subjected to batch irradiations for a controlled period of time. These batch irradiations were performed for 1 to 5 min, at 1-min increments, with the sample solution contained in a piece of Teflon tubing (100-μL volume) that had been wrapped around the UV lamp (Fig. 2). The photolyzed solution was collected in chilled vials and was subjected to flow injection analysis (FIA)-TEA, to study any changes in the bulk detectability of the TNT
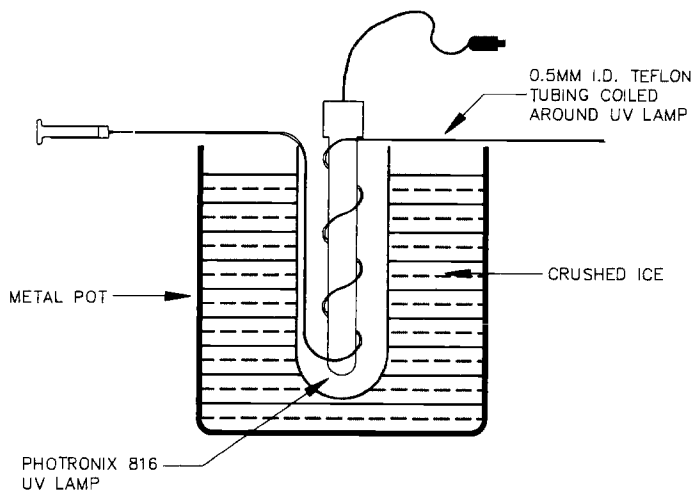

FIG. 2—*Apparatus used for scouting experiment batch-mode irradiation.*

solution following irradiation. The responses for these photolyzed solutions were compared with that for 1-ppth TNT which had not been subjected to photolysis. Following this initial study, the experiment was repeated, except that the photolyzed solutions were injected onto an LC-TEA system. In this way, the loss of TNT and the formation of any nitrated photo-products could be studied with respect to irradiation time. To confirm the identities of the products of the photochemical reaction of TNT, GC/MS was performed on the irradiated solutions as well.

The success of these early studies led to the incorporation of the flow-through KOT reactor for post-column, continuous, UV irradiation of the LC eluent before TEA detection. During operation, the lamp utilized for the photolysis generates heat sufficient to vaporize the eluate (DCM:isooctane mixtures). On the other hand, since higher temperatures might lead to accelerated photolysis, a cursory study of the effect of cooling bath temperature was performed. First, the lamp was air-cooled using a vacuum source in the base of the containment vessel to draw room air around the lamp, and the signal for TNT and baseline noise characteristics were observed. The containment vessel was then placed in a cooling bath held first at 0°C, and then at −10°C, and the experiment was repeated. These three temperature conditions allowed for a qualitative evaluation of the effect of temperature on the LC-PAT method and for optimization of this operating parameter.

To study the effect of irradiation time on the response for TNT, we repeatedly injected a 10-ppm (10-μg/mL) solution of the explosive in DCM while varying the irradiation time. Triplicate injections of the 10-ppm TNT solution onto the LC-PAT system were made for each time evaluated. The chromatographic flow rate was held constant at 1 mL/min. TNT responses at irradiation times from 0 to 6 min were studied. Irradiation times were controlled by switching the lamp "off" after the proper UV exposure time.

Following the optimization of residence time, injections of equimolar (44-μM) solutions of 4-mononitrotoluene (MNT), 2,4-dinitrotoluene (DNT), and TNT in DCM were injected onto the LC-PAT system under both lamp on (6-min photolysis time) and lamp off conditions. This experiment was designed to aid in delineating the mechanism of improvement in response for TNT under PAT conditions and to quantitate the improvement in TEA response for these nitrotoluenes. In addition, injections of a standard explosive mixture (SEM) containing 10 ppm each of TNT, nitroglycerin (NG), pentaerythritol tetranitrate (PETN), and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) in DCM were performed under both lamp-on and lamp-off conditions to study the influence of the 6-min irradiation on the responses for nitramine (RDX) and nitrate ester (NG, PETN) compounds. Finally, a calibration plot was constructed for TNT by injecting four concentrations of the explosive in triplicate between 0.1 ppm and 100 ppm. From this calibration plot, the limit of detection (LOD) for TNT was calculated, using the method of Foley and Dorsey [16]: LOD $= 3s_b/S$, where s_b is the standard deviation of the noise and S is the sensitivity (slope of the calibration plot). The value of s_b is equivalent to the root mean square of the noise (N_{rms}), which is given by the relationship $s_b = N_{rms} = N_{p-p}/r$, where N_{p-p} is the short term, peak-to-peak noise, and r is a unitless parameter which is dependent on the type of noise involved. When the noise is random and exhibits a Gaussian distribution, $r = 5$.

Results and Discussion

The photochemistry of aliphatic and aromatic nitro compounds has been analyzed in some depth. TNT has been the subject of a large number of photochemical experiments, wherein its properties upon electronic excitation have been studied. At 254 nm, the predominant absorption process involves a Pi,Pi* transition to an excited singlet state [17,18], although the initial absorption has been postulated to involve a higher level excited singlet species, which then either rapidly decays to the lowest excited singlet or may undergo intersystem crossing to the ground triplet state [19]. The higher excited singlet species and the

ground state triplet are n,Pi* states in which excitation is localized on the nitro groups. This localization of energy distorts these groups in relation to their electronic character in the ground state molecule, and when TNT is in its lowest excited singlet state, there is intramolecular electronic charge transfer from the aromatic ring to the nitro group [20]. This results in an increase in the negative charge density for the nitro group oxygens, as well as a decrease in the positive charge density on the nitrogen atom [17]. The effect of this electronic charge transfer is that the nitro group summarily becomes more electron-withdrawing in character.

Irradiation of TNT is postulated to lead, through a photochemically induced isomerization, to an "aci-quinoid" form or its conjugate base (Fig. 3), which has only transient existence [18,21,22]. Continued photolysis of TNT can allow for the formation of nitroso products [23,24] or may result in homolysis of the C—N bond, coupled with hydrogen abstraction, to form nitrogen dioxide and the protonated residue of TNT (now DNT or MNT) [4,25]. The formation of nitroso products or the bond cleavage would make TNT more responsive under LC-TEA conditions, since the pyrolyzing temperature (550°C) would be sufficient for the formation of NO· from such photoproducts.

In the initial batch photolysis of TNT, followed by FIA-TEA, responses for the solutions irradiated from 0 to 5 min rose linearly with photolysis time (correlation coefficient, r^2 = 0.909, Fig. 4) This confirmed the thesis that photolysis could be used to enhance the detectability of TNT in LC-TEA. Evidence for the loss of NO_2 from TNT was found during the performance of the batch irradiation, followed by LC-TEA. As shown in Fig. 5, increasing irradiation led to a loss of TNT, with the concommitant rise in response for compounds having retention times corresponding to those for standards of MNT and DNT injected under identical conditions. The identity of the second photoproduct was found to be a mixture of 2,4 and 2,6-dinitrotoluene by GC/MS analysis of the photolyzed solutions. Charge migration following C—N bond homolysis would be unlikely [24], and the expected products of the photolysis are probably 4-nitrotoluene and 2,4-dinitrotoluene. Of course, the improved detectability of TNT in LC-PAT is primarily due to the release of NO_2.

The study of the effect of cooling bath temperature on the TEA response for TNT under on-line photolysis conditions, although limited in scope, allowed for qualitative evaluation of
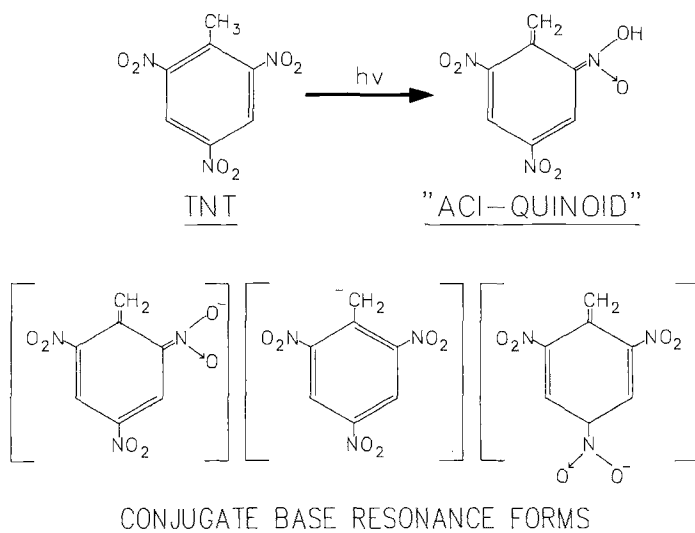

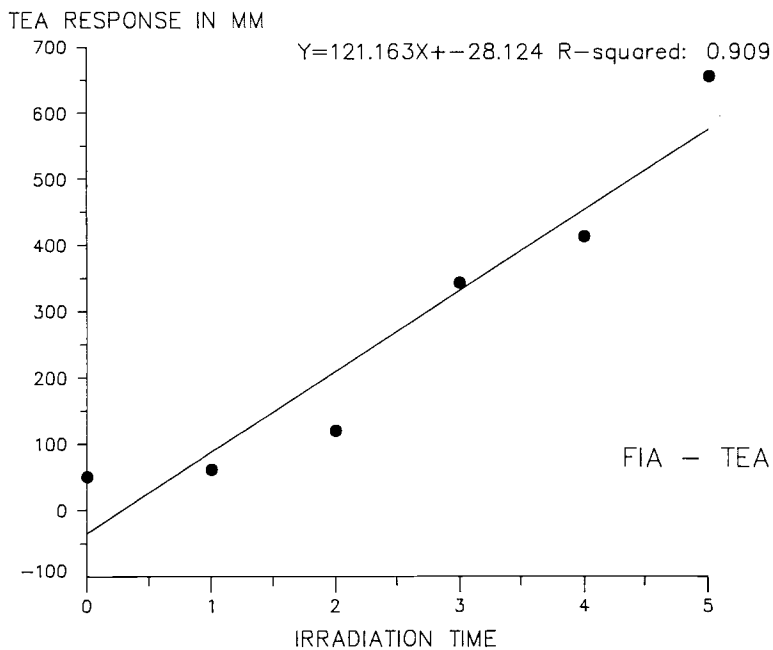FIG. 3—*Photochemical isomerization of TNT to "aci-quinoid" form, and its conjugate base, with resonance structures.*

TEA RESPONSE IN MM

Y=121.163X+−28.124 R−squared: 0.909

FIA − TEA

IRRADIATION TIME

FIG. 4—*Irradiated TNT response using flow injection analysis (FIA-TEA). Irradiation times (0 to 5 min) plotted versus TEA response in millimetres.*
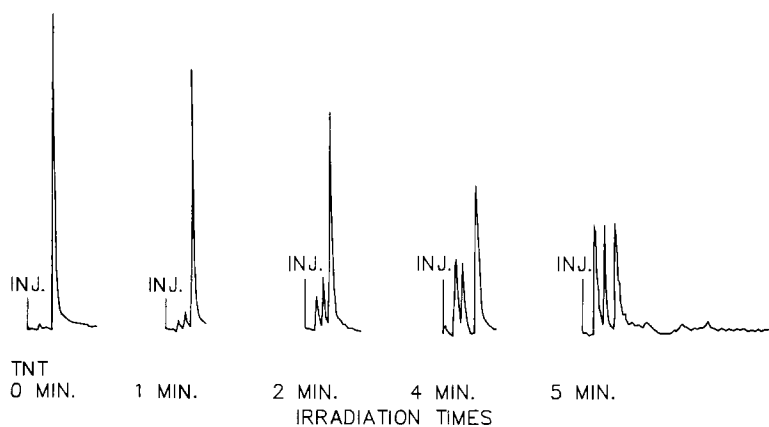
INJ.   INJ.   INJ.   INJ.   INJ.

TNT
0 MIN.   1 MIN.   2 MIN.   4 MIN.   5 MIN.

IRRADIATION TIMES

FIG. 5—*Chromatograms obtained from the LC-TEA analysis of aliquots from batch irradiations of 1-ppth TNT in DCM. Times noted indicate the length of irradiation. Experimental conditions are noted in the text.*

an optimum condition. When simple air cooling was employed, bubbles were continuously formed in the irradiation chamber (KOT) as a result of vaporization of mobile phase components. Since the TEA interface is under vacuum, once the mobile phase was sufficiently volatilized, the expanding gases and liquid droplets were rapidly swept from the KOT into the TEA. This led to an overall reduction in the time that the eluate was actually irradiated, thus generating—not surprisingly—decreased responses for TNT. When the irradiation assembly was immersed in a cooling bath at 0°C, small bubbles were still formed in the eluate flowing through the KOT, but responses were much larger than had been evidenced under air-cooled conditions. Finally, when the bath was held at −10°C, no vaporization of eluate was apparent, and the response for TNT was the largest of any of the cooling temperatures studied. Thus, this cooling bath temperature was incorporated during operation of the LC-PAT in the remaining studies.

FIA-TEA temporal studies of the batch photolysis of TNT were sufficient for evaluation of the efficacy of PAT. In theory, however, these studies were not entirely applicable to the situation where photolysis occurs in a flowing stream, especially within a KOT reactor where mass transfer of solution to areas of greatest photon flux (near the walls of the tubing, closest to the lamp) is homogeneous for all fluid elements. In the conversion study (response versus irradiation time) of LC-PAT for TNT, it was determined that response rose linearly with time ($r^2 = 0.984$), and the equation from the regression was $Y = 11.2S - 9.9$, where S is the peak height (mm) normalized to " ×32" attenuation (Fig. 6). There did not appear to be a plateau in PAT response within the time domain studied, so the greatest sensitivity would be obtained at longer irradiation times. Thus, a KOT which would deliver a 6-min photolysis time at a flow rate of 1 mL/min was incorporated into the system for the remaining characterization studies.

By injecting equal volumes of equimolar solutions of MNT, DNT, and TNT, it was possible to study the "normalized" responsiveness of LC-PAT for these C-nitro compounds. As shown in Fig. 7, a plot of the response versus the number of nitro groups is not linear; rather, response for TNT is less than one would expect on the basis of two things: the presence of three nitro moieties in its structure and the responses for DNT and MNT. This attenuation
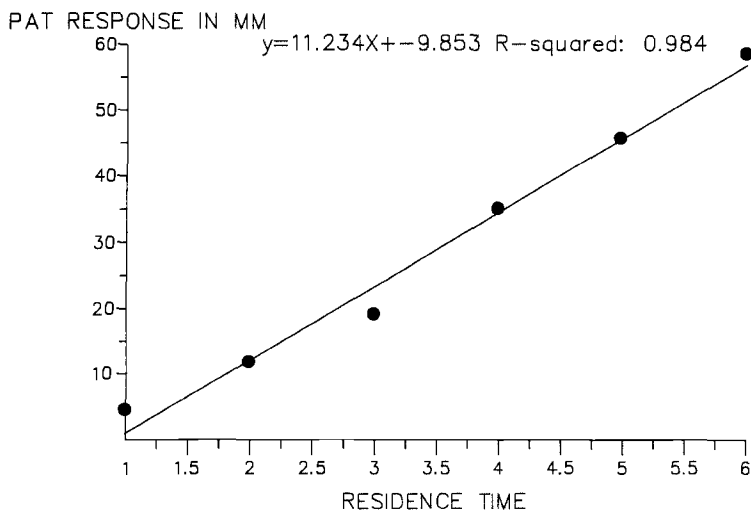
PAT RESPONSE IN MM

y=11.234X+−9.853 R−squared: 0.984

FIG. 6—*Plot of LC-PAT conversion study. Residence time (0 to 6 min) in KOT is plotted versus TEA response in millimetres.*
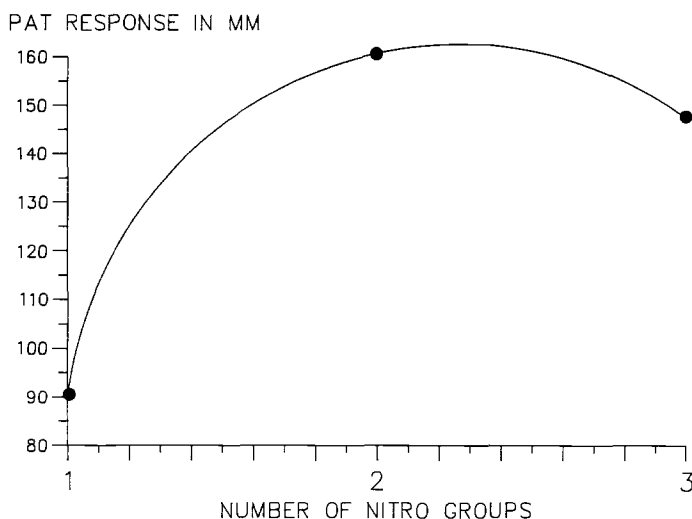
PAT RESPONSE IN MM

FIG. 7—*Plot of LC-PAT response as a function of the number of NO_2 substituents on the molecule. (MNT = one nitro group; DNT = two nitro groups; TNT = three nitro groups).*

in response for TNT is probably an artifact of the use of a 6-min irradiation time in that the conversion study suggested that at greater photolysis times one could expect greater response. The choice of a 6-min irradiation time was not arbitrary; the length of tubing needed to produce a KOT having a 6-mL volume leads to a final reactor that covers the UV lamp with a single layer of "wrapping." Incorporation of a different (longer) lamp and a longer KOT, or a slower flow rate with the present length, would provide longer photolysis time, greater conversion efficiency, and improved sensitivity for TNT. A lamp with higher energy output at the lambda max for TNT would also improve conversion. In the present design, LC-PAT increased the responses for TNT and DNT (440 picomoles (pM), 1 and 0.8 μg, injected) by factors of 30 and 16, respectively, over their corresponding responses when the photolysis unit was not operating. MNT could not be detected at this level (440 pM, 60 ng injected) when the lamp was extinguished. However, under LC-PAT conditions, it was clear that MNT could be detected into the sub-nanogram range. After generation of a calibration plot, regression of the data revealed that PAT response was linear over three orders of magnitude (100 to 0.1 ppm). This could be described by the equation $R = 19.6X + 1.66$, where R is response in millimetres at $\times 32$ attenuation and X is concentration in parts per million. The limit of detection for TNT under LC-PAT was calculated to be 50 ppb (500 picograms) in a 10-μL injection. The LOD for all of these compounds could be improved, if necessary, through the use of larger injection volumes.

To study the effect of photolysis on the TEA response for nitramines and nitrate esters, a standard explosive mixture (SEM), containing 10 ppm each of four explosives commonly identified in post-blast residues, was injected onto the LC-PAT system under both lamp-on and lamp-off conditions. In the resultant chromatograms (Fig. 8), there were obvious differences in response for all of the compounds. As expected, the response for TNT was significantly enhanced when the lamp was on, whereas the responses for NG and PETN (nitrate esters) were actually attenuated in relation to lamp-off conditions. RDX (a nitramine) exhibited a slight increase in response with the lamp-on. These differences in responses do not necessarily detract from the utility of LC-PAT. Rather, they may be used to confirm the identity of the explosive in an extract if further experimentation reveals that these changes
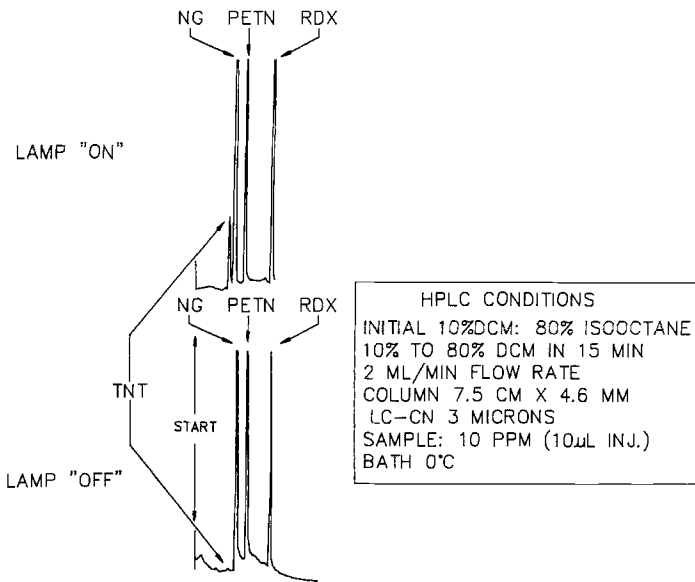
FIG. 8—*LC-PAT chromatograms for SEM under lamp-on and lamp-off conditions. Conditions: each explosive 10 ppm in DCM, 10 μL injected, 15-min linear gradient from 10 to 80% DCM in isooctane with flow = 2 mL/min.*

are characteristic of the species being detected. This confirmation approach has been incorporated in similar studies, where post-column photolysis was used to enhance oxidative electrochemical response following LC separation [26].

Conclusions

LC-TEA is an important method for the identification and confirmation of the presence of a nitro-based explosive in post-blast residues and swabbings. Through the use of LC-PAT, the presence of TNT can now be determined with good sensitivity. The experimental setup is straightforward, requiring only inexpensive additional equipment, and does not detract from the normal operation of the TEA. LC-PAT has already been used to confirm successfully the presence of TNT in several bomb cases, and has allowed for greater certainty in the examination results. If required, the sensitivity of the new method could be further improved by making several small changes in the instrumentation used.

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