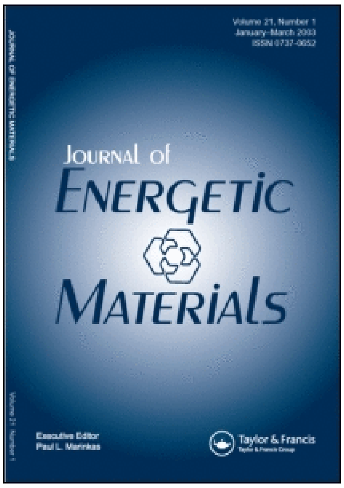

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# Liquid chromatography with photolysis-electrochemical detection for nitro-based high explosives and water gel formulation sensitizers

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# LIQUID CHROMATOGRAPHY WITH PHOTOLYSIS - ELECTROCHEMICAL DETECTION FOR NITRO-BASED HIGH EXPLOSIVES AND WATER GEL FORMULATION SENSITIZERS

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## ABSTRACT

The use of high performance liquid chromatography with photolysis - electrochemical detection (LC-hv-EC) for conventional high explosives has been improved through the use of a knitted open tubular (KOT) photolysis chamber geometry. Improvements in the analytical figures of merit and selectivity of this hybrid analytical technique are a direct result of the improved radial mass transfer of analyte in the KOT reactor, as demonstrated in comparisons with the coiled reactor geometry previously used. Using the KOT photolysis chamber geometry in LC-hv-EC, the limits of detection for aromatic C-nitro compounds, nitramines and nitrate esters are in the range of 120- to 250-pg injected. In addition, an off-line, pre-column chemical derivatization has been developed to convert water gel sensitizer residues to a form which will allow for their determination using LC-hv-EC. In a rapid, single-step process, 2,4-dinitrofluorobenzene (Sanger's reagent) is used to derivatize residues of monomethylamine and monoethanolamine to their 2,4-dinitrophenyl analogues. Under the preliminary conditions reported here, monomethylamine may be quantitatively converted and detected at concentrations between 200-parts per billion and 50-parts per million. Monoethanolamine is detected with about 35% derivatization efficiency at levels between 10- and 200-parts per million. The preliminary results suggest that this methodology may be easily improved to allow for the trace determination of water gel sensitizers in aqueous extracts of post-blast debris.

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# INTRODUCTION

Those involved with the trace determination of explosives in post-blast debris have benefitted greatly from the improvements that have recently been made in gas and liquid chromatographic packings and columns. Capillary gas chromatography (GC) columns allow for facile separation of most nitro-based high explosives without the problem of thermal degradation, while small-particle high performance liquid chromatography (LC) packings enable the rapid separation of many compounds using relatively diminutive columns. Improvements in detector technologies have also provided for more reliable identification and quantitation of explosives. Of course, the selectivity and sensitivity of these chromatographic methods is always subject to improvement, since such improvements ultimately lead to greater clearance rates for bomb-related criminal cases.

In the past few years, the use of reductive electrochemical (EC) detection in LC, and mass spectrometric (MS) and thermal energy analysis (TEA) detection in both LC and GC, have pushed detection limits into the low picogram (pg) range, and have allowed for excellent selectivity of detection for explosives over contaminants in post-blast debris. Unfortunately, MS is very expensive and requires a great deal of operator skill, while TEA is quite expensive, and has shown a relative insensitivity to TNT in the LC mode. Reductive EC detection has not found widespread acceptance for a number of reasons, including the relatively high level of technical sophistication required of the user, and the need to eradicate dissolved oxygen from the mobile phase and samples. For these reasons, an inexpensive detection technique was recently developed which allows for the determination of nitro-compounds with the sensitivity and selectivity inherent in EC, yet without the drawbacks associated with reductive methods. In this approach, a post-column, on-line photolysis unit was used to irradiate the eluent from a reversed phase LC column, and the photolyzed flow stream then entered a thin-layer, amperometric EC detector operated at oxidative potentials. The hybrid technique, called "LC-photolysis-EC" (LC-hv-EC), was initially reported for the determination of explosives at the First International Symposium on the Analysis and Detection of Explosives in Quantico, VA, in 1983.[1] The mechanism of detection in LC-hv-EC, for nitro-compounds, primarily involved photolytic cleavage of nitrite ($NO_2^-$) from the parent compound; this nitrite was then readily detected at oxidative potentials. In this way, explosive compounds which are not inherently electroactive at oxidative potentials could be determined with good sensitivity and excellent selectivity using photolytic-EC detection.

As first constructed, the LC-hv-EC system incorporated a length of Teflon tubing as the photolysis chamber, and this tubing was merely coiled around a medium pressure Hg discharge lamp in order to affect irradiation of the eluent. Using this configuration, limits of detection (LODs) for explosives were found to be between 1- and 4-nanograms (ng) injected (50- to 200-parts per billion [ppb]); these LODs were, at best, 1.5 orders of magnitude higher than those obtained using reductive EC, MS or TEA detection for the same compounds. In addition, the peak shapes in LC-hv-EC were significantly broadened when compared to LC-EC systems than did not have the post-column photolysis unit on-line. This band-broadening led to a loss of resolution of closely adjacent peaks in sample chromatograms, and thus an overall loss in selectivity. Thus, one of the goals of the research described in this manuscript was to improve (minimize) the peak dispersion characteristics of the photolysis chamber, in order to enhance both the selectivity and sensitivity of the method. There have been several reports regarding the use of geometrically configured tubing for mixing and photolysis chambers in post-column reactor systems,[2,3] in which the judicious choice of tubing conformation and internal diameter allowed for a large reduction in the band-broadening of post-column reactors. Therefore, experiments were performed to evaluate the utility of incorporation of such a configured reactor in the LC-hv-EC system.

The second direction of emphasis in our most recent experiments involved the forensic determination of residues of water gel explosive formulations in post-blast situations. Unlike conventional commercial explosives, most water gel formulations are sensitized with nitrostarch, aluminum or alkylammonium nitrates. Thus, in the post-blast debris arising from a water gel-based device, the analyst will not find traces of high explosives, and it may be difficult to make a determination regarding the presence of a commercial product as the main charge in the criminal bombing. However, when a water gel formulation containing alkylammonium nitrate sensitizers, such as monomethylamine nitrate (MMAN) or monoethanolamine nitrate (MEAN), is used, residues of these sensitizers - methylamine (MMA) and ethanolamine (MEA) - should appear in water or methanol extracts of debris.

A TLC approach, incorporating three separate plates and solvent systems for full "identification", has been developed for MEAN and MMAN, but this method gave LODs of 1-microgram (µg), and was time consuming as well.[4] To date, there have been no published reports of the use of LC or GC methods for the determination of these residues. This is not surprising, in light of the fact that aliphatic amines and alkanolamines are not amenable to GC conditions, and can only be chromatographed on reversed phase LC systems when competing bases are added to the mobile phase to occupy adsorptive sites on silica based packings. Also, the pH of the mobile phase must be buffered to rather high values (above pH 8), which generally leads to decreased column lifetime. When one also considers the poor detectability of these analytes using UV absorbance or fluorescence, or electrochemical detection, one quickly fathoms the analytical nightmare that such compounds represent.

Derivatization is often used to convert analytes which have poor chromatographic behavior, or poor detectability, to new forms having improved chromatographic and detection properties. Amines and amino acids are often derivatized using o-phthalaldehyde or dansyl chloride to give derivatives that are excellent chromaphores, and these reactions rely on the nucleophilicity of the amine analytes in substitution reactions. This same nucleophilicity may be used to advantage when amines are reacted with Sanger's reagent (2,4-dinitrofluorobenzene, DNFB),[5] resulting in dinitrophenyl (DNP) derivatives, and these DNP derivatives should then be amenable to the chromatographic and detection approaches commonly used for nitro-based high explosives. With this in mind, DNFB has been evaluated as a pre-column, off-line derivatizing agent for MMA and MEA in water, prior to determination using LC-hv-EC, and the results of this preliminary evaluation are presented in this manuscript.

## MATERIALS

The LC-hv-EC system used in these experiments consisted of three components. Separations of sample mixtures were obtained on an isocratic reversed phase liquid chromatograph composed of a Waters model 590 solvent delivery system with two Waters pulse dampeners (Waters Chromatography Div., Millipore Corp., Bedford, MA) and a LiChromaDamp III pulse dampener (Handy and Harmon Tube Co., Norristown, PA), a Rheodyne model 7010 injector, with 50- or 200-µl sample loops, and 0.2-µm pre-column filter (Rheodyne Corp., Cotati, CA), and a Waters Radial Compression Module with a Radial Pak™ $C_{18}$ (5-µm) 100- x 5-mm cartridge. Irradiation of the eluent was achieved using a Photronix model 816 UV batch irradiator (Photronix Corp., Medway, MA), including a medium pressure Hg lamp (having primary output at 254-nm and minor bands at 314-, 365-, 404- and 435-nm), a voltage regulator, and a quartz sleeve which contained the lamp assembly and allowed for its insertion into a cooling ice-water bath. This 0-5°C cooling bath eliminated problems with vaporization of the methanol content of mobile phases. Teflon (PTFE) tubing having nominal dimensions of 0.5-mm ID and 1.6-mm OD (Rainin Instrument Co., Woburn, MA) was used in the construction of the post-column irradiation chambers studied. It should be emphasized that the transparency of the tubing was quite important in the LC-hv-EC experiment, and some types of Teflon tubing (Cheminert™, for example) did not perform well in the photolysis system. Electrochemical detection was accomplished using dual BAS LC-4B amperometric controllers, a TL-5A dual glassy carbon working electrode cell half, a stainless steel auxiliary cell half and an RE-1 Ag/AgCl reference electrode (all from Bioanalytical Systems, Inc., W. Lafayette, IN). When needed, UV absorbance detection was obtained with a UVIII 254-nm detector (LDC - Milton Roy Corp., Riviera Beach, FL) placed before the photolysis unit in the analytical arrangement. Chromatographic data were recorded on an Omniscribe dual-pen strip chart recorder (Houston Instruments, Inc., Austin, TX), and peak areas were collected using a model 3380A integrator (Hewlett- Packard, Palo Alto, CA). Derivatization of water gel sensitizer residues was accomplished in 5-ml Reacti-Vials (Pierce Chemical Co., Rockford, IL), positioned in a Pierce Reacti-Therm™ heating and stirring apparatus. An Eppendorf pipet with disposable tips (Fisher Scientific, Bedford, MA) was used to remove aliquots of the reaction mixture for dilution before injection onto the chromatographic system. The melting point of the DNP-derivative of MMA was determined using a Thomas Hoover capillary melting point apparatus (Arthur H. Thomas

Co., Philadelphia, PA) while NMR spectra were collected using a Varian T-60 Spectrometer (Varian Associates, Palo Alto, CA).

1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX), 2,4,6,N-tetranitro-N-methylaniline (Tetryl) and 2,4,6-trinitrotoluene (TNT) were obtained from the Bureau of Alcohol, Tobacco and Firearms National Laboratory Center in Rockville, MD, pentaerythritol tetranitrate (PETN) was obtained from Chilcott (San Juan, Puerto Rico) and nitroglycerin (NG) was obtained as the aqueous infusion solution Nitrostat™ (Parke-Davis, Detroit, MI). MMA was obtained from Pfaltz and Bauer (Waterbury, CT) as a 40% aqueous solution, while MEA, N-(2,4-dinitrophenyl)-ethanolamine (the standard DNP derivative of MEA), DNFB and $NaNO_2$ were obtained from Aldrich Chemical Co. (Milwaukee, WI) at 99+% purity. Dimethylformamide (DMF), $NaHCO_3$ and HCl were obtained from J.T. Baker (Phillipsburg, NJ). The NaCl (99.99%) used as the electrolyte in the mobile phase was obtained from Aldrich, and the mobile phase solvents (water and methanol) were obtained from MCB (Cherry Hill, NJ) as the Omnisolv grade.

## EXPERIMENTAL PROCEDURE

In order to study the effects of reactor geometry on the band-broadening characteristics of the photolysis chamber, three 9.144-m (30-ft) lengths of Teflon tubing having different geometries were compared to a 30-cm length of tubing directly connecting the LC column to the EC detector. The first of these long tubes was left in a "straight" configuration (the tube was run across the laboratory and back!), while the second "coil" configuration had the Teflon tubing wrapped about a 2.5-cm diameter cardboard tube. The third configuration, a knitted open tubular ("KOT") arrangement, was prepared by weaving the analytical tubing around a Teflon backbone in such a way as to force the flowing stream to turn at right angles in three dimensions, or transcribe a three dimensional "figure eight" throughout its length. A detailed account of the preparation of the KOT used in these studies will appear elsewhere.[6]

In all of the work described in this manuscript, the mobile phase consisted of 35% to 60% methanol with 0.2M NaCl, filtered through a 0.2-µm filter and vacuum degassed prior to use. The working electrode cell half was polished with alumina prior to the start of each experiment, and the reference electrode was stored in 3M NaCl when not in use. Preliminary study of the relative dispersion characteristics of the three reactor geometries was accomplished by injecting 200-µl of a 1-ppm solution of $NaNO_2$ onto a complete chromatographic system having each of the reactors between the column and the EC detector (in separate trials), as well as the 30-cm connective tubing; electrochemical response was monitored at +0.85V. With such an instrumental configuration, problems of injection irreproducibility were eliminated during travel of the unretained solute through the column. In other words, the same study could be performed in a flow injection analysis (FIA) experiment (without a column on-line), but experience had shown that small changes in injection technique (eg. the speed with which the valve rotor was turned) may be evidenced in resultant chromatograms. Each configuration was tested in four replicate injections; for the first injection, the strip chart recorder ran at 1-cm/min, while for the last three injections the data were collected at 10-cm/min to allow for easy calculation of peak variances.[7] The equation used for these calculations was:

$$M_2 = (W_{0.1})^2 / [1.764(B/A)^2 - 11.15(B/A) + 28] \qquad (1)$$

where $M_2$ is the (second central moment) variance of the peak, $W_{0.1}$ is the peak width at 10% height, A and B are the distances from the peak centroid (at 10% height) to the leading and tailing edges of the peak, respectively, and B/A is the asymmetry factor. When the peak width is measured in volume units, using the information of chart speed and flow rate, the variances calculated will be in squared volume units.

Following this study of the absolute band-broadening characteristics of each of the reactor geometries, the coil and KOT geometries were studied in greater detail. In separate sets of trials, the two reactors were used as photolysis chambers in LC-hv-EC for the separation and detection of a standard explosive mixture (SEM) containing 200-ppb PETN and 100-ppb each RDX, TNT and Tetryl. EC response was monitored at +0.85V, and both peak height and peak area were collected. Resolution differences for the separation of TNT and Tetryl were calculated[8] from the peak height and width data in the resultant chromatograms, using equation 2:

$$R = (t_{r2} - t_{r1}) / 0.5(W_1 + W_2) \qquad (2)$$

In equation 2, R is the (unitless) resolution factor, $t_{r1}$ and $t_{r2}$ are the retention times of the first and second adjacent peaks, respectively, and $W_1$ and $W_2$ are the widths (at 10% height) of the two peaks. Peak areas were collected and used to compare the relative responses for explosives using the two reactor geometries.

With the KOT reactor in place, linearity plots for TNT, Tetryl, RDX, NG and PETN were generated using 200-µl injections of analyte solutions at concentrations of 1-, 10-, 100-, 1000- and 5000-ppb. Limits of detection (LODs) were calculated [9] from EC responses at +1.0V, using equations 3 and 4:

$$\mathrm{LOD} = 3\, s_B / S \quad , \quad s_B = N_{rms} = N_{p\text{-}p} / r \qquad (3,4)$$

where $s_B$ is the standard deviation of the noise, S is the sensitivity (slope of the calibration plot), $N_{rms}$ is the root mean square of the noise, $N_{p\text{-}p}$ is the short term, peak-to-peak baseline 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. By monitoring EC responses in the dual parallel mode at +1.0V and +0.85V, the calibration plots not only allowed for calculation of the LODs for each of the compounds, but also enabled the determination of the linearity of detection and the linearity of dual electrode response ratios (RRs). The overall selectivity of the system was demonstrated through the use of a single-blind study, in which an outside analyst spiked an acetonitrile (ACN) soil extract with explosive at the 200-ppb level. Two different samples of ACN were spiked with a different explosive, and each of these spiked samples was diluted 100X with mobile phase. The diluted samples were then analyzed in triplicate using LC-hv-EC in the dual parallel mode, under both lamp on and lamp off conditions.

In order to allow for calculation of derivatization efficiencies, and to characterize the LC-hv-EC behavior of the DNP-derivatives of MMA and MEA, it was important to have standards of the derivatives on hand. While the DNP-derivative of MEA was commercially available in high purity (99.9+%), a similar standard for MMA was not. Therefore, about 5-g of the DNP-derivative of MMA was prepared using literature procedures.[5] The product was recrytallized three times from ethanol-water, dried over $P_2O_5$, and was then subjected to melting point, NMR (in deuterated DMSO solvent) and LC-UV-hv-EC (tandem UV and photolytic-EC detection) analyses. This DNP-derivative was used as an external standard to characterize the efficiency of the trace derivatization of MMA.

The initial experimental conditions chosen for the derivatization of trace levels of MMA and MEA were adapted from literature reference[5] and previous experiments in our laboratory.[10] As shown in Figure 1, these conditions involved the addition of 2-ml of aqueous sample of the amine, 10-mg $NaHCO_3$, 500-µl DMF and 6-µl of DNFB to a reacti-vial held at 35°C. After a 20-min reaction (with stirring), 4 drops of 6N HCl were added to the reaction mixture and the vial was

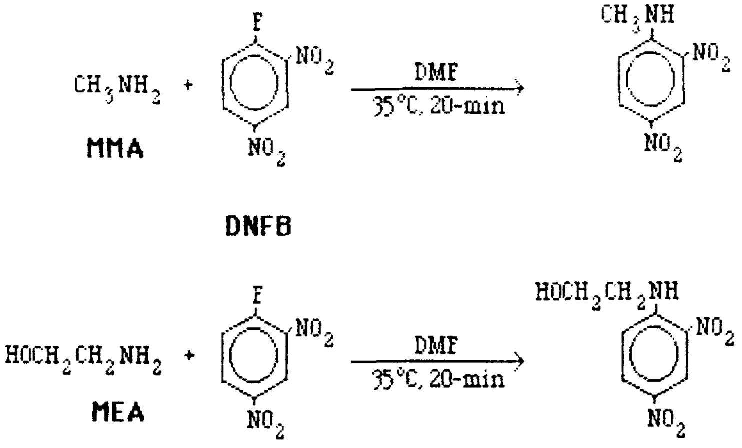

FIGURE 1
**Reaction scheme for the trace derivatization of MMA and MEA with DNFB. Following reaction at 35°C for 20-min, 4 drops of 6N HCl are added.**

tapped for about 30-sec to dislodge bubbles of $CO_2$ adhering to the sides of the vessel. A 10-µl aliquot of this reaction mixture was diluted with 250-µl each of methanol and mobile phase, and 50-µl of the diluted sample was injected in triplicate onto the LC-hv-EC system, operating in the dual parallel mode at +1.0V and +0.85V. For concentrations of the amines in water between 200-ppm and 200-ppb, the linearity of the derivatization procedure was studied through the use of the external standard DNP-derivatives. LODs and RRs were calculated using the equations cited previously for the nitro-based high explosives.

## RESULTS AND DISCUSSION

Whenever one incorporates a post-column chemical step into a chromatographic system for improved detectability of analytes, one must be concerned with axial dispersion of analytical bands in the reactor chosen. There are three common types of post-column reactors: open tubes without segmentation, open tubes with gas or immiscible liquid segmentation, and packed bed reactors. An excellent review of the theory and use of each of these reactor designs, including their peculiar advantages and deficiencies, has recently appeared[11], but it is sufficient to note here that a non-segmented, open tubular reactor is best suited for use as a photochemical reaction chamber, with respect to the particular photolysis unit incorporated in these experiments.

When a concentrated analyte band elutes from the column and enters a straight, open tube, the concentration profile of the band quickly takes on a parabolic appearance (see Figure 2), due to the lack of radial mass transfer in the tube. In this parabolic flow profile, a fluid element in the center of the tube (moving along the axis) travels

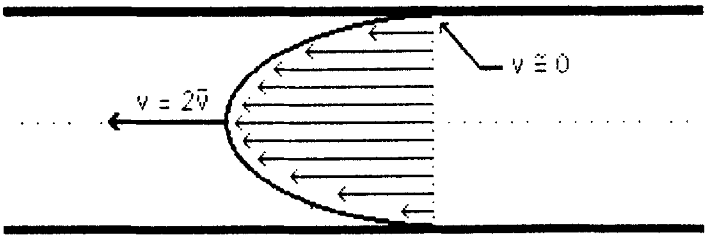

FIGURE 2
**Parabolic flow profile developed under laminar flow conditions in a straight, open tubular reactor.**

at twice the average velocity of the analyte band, while the velocity of fluid elements near the walls approaches zero. If this flow profile is not disrupted, the concentrated analyte zone will undergo band broadening, which leads to a loss of the resolution achieved on the column, and a loss in sensitivity when peak heights are used for quantitation. In theory, the area under a broadened peak will be equal to that for the original peak.

It has been shown that the cross-sections of open tubes may be geometrically deformed (by pinching of metal or glass tubes) in order to disrupt this parabolic flow profile through superimposition of secondary flow.[12-14] The same effect can be produced when Teflon tubing is knitted into a three dimensional "figure eight" geometry,[2,3] even though the cross section of the tubing in the knitted geometry is not deformed. However, the principle behind the usefulness of both of these approaches for reducing band broadening is identical. As shown in Figure 3, when a flow stream is forced to turn through an acute angle, either through the use of geometric deformation or knitting, fluid elements near the inner radius are caused to traverse, by centrifugal action, toward the outer radius of the turning tube. Since liquids are relatively incompressible, fluid elements near the outer radius are forced toward the inner radius, traveling along the wall of the tube. This action sets up circular, secondary flow patterns in the hemispheres about the tube axis, which effectively destroy the parabolic flow profile in the two dimensional space through which the tube is turned. If the flowing stream is then forced to turn in a direction orthogonal to the plane of the first turn, this secondary

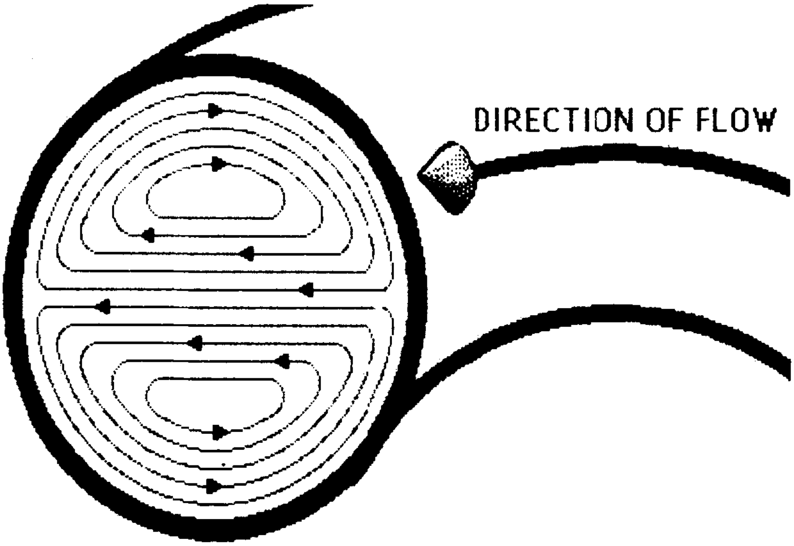

FIGURE 3
Secondary flow generated by bending the tubing through an acute angle. Notice that similar secondary flow profiles are generated on each side of the flow axis.

flow will be imposed in the third dimension. Thus, using a knitted open tube (KOT), one should be able to incorporate a rather long length of tubing as a post-column reactor without incurring prohibitive band broadening.

The 9.144-m (30-ft) length of tubing was chosen for study because this length of 0.5-mm ID tubing has a volume of 1.8-ml, which will deliver residence times of 1.8-min (optimum for explosives) at a flow rate of 1-ml/min. Figure 4 portrays the peak shapes generated by injection of nitrite onto the chromatographic system having either the direct (30-cm) connection, or 30-ft of tubing in one of the geometries studied. The system variances (in units of $\mu l^2$) calculated for each of these situations were 11,200 ±

700 for the direct connection, 158,000 ± 7,000 for the straight configuration, 58,600 ± 500 and 23,300 ± 500 for the coil and KOT geometries, respectively. The normalized variances are shown in Figure 4, above each of the representative peaks. From these results, it is clear that the band-broadening generated in a straight open tube would make such a reactor unusable for all but the shortest of post-column reaction times. Also, at the low flow velocities used in chromatography, simple coiling of the tubing did not readily generate the secondary flow needed to reduce peak dispersion. However, when using the KOT geometry the effective axial dispersion of the peak was only doubled, as compared to the chromatographic system without a post-column reactor, even though a dead volume of nearly 2-ml had been incorporated between the column and the detector. It was evident, therefore, that the use of the KOT reactor should allow for the use of significantly longer residence times for analytes in the photolysis chamber, while retaining chromatographic resolution and minimizing losses in sensitivity.

The true test of the improvement to be realized when converting the photolysis chamber from the coiled geometry to the KOT was in the separation and detection of the standard explosive mixture (SEM). The results of this experiment were striking, in that two colligative improvements were realized through the incorporation of the KOT in place of the coil. As shown in Figure 5, the expected improvement in chromatographic peak shape and retention of resolution was realized. With the KOT, Tetryl and TNT were separated with baseline resolution, while these two peaks overlapped by approximately 30%

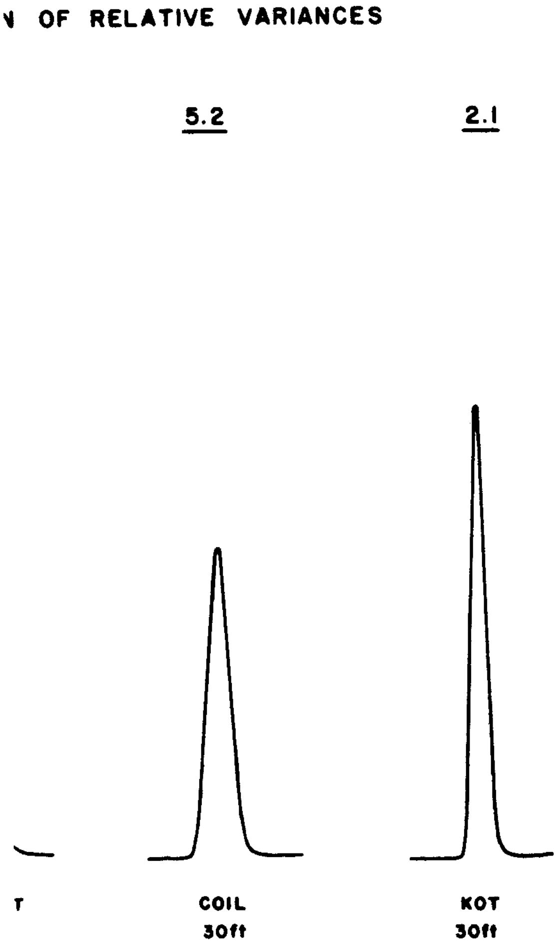

FIGURE 4
peaks generated in the hydrodynamic study of
Relative variances (normalized to the direct
peak. Conditions: RadialPak C-18 (5-µm) 100- x
1.0-ml/min, 200-µl injections, detection at +0.85V.

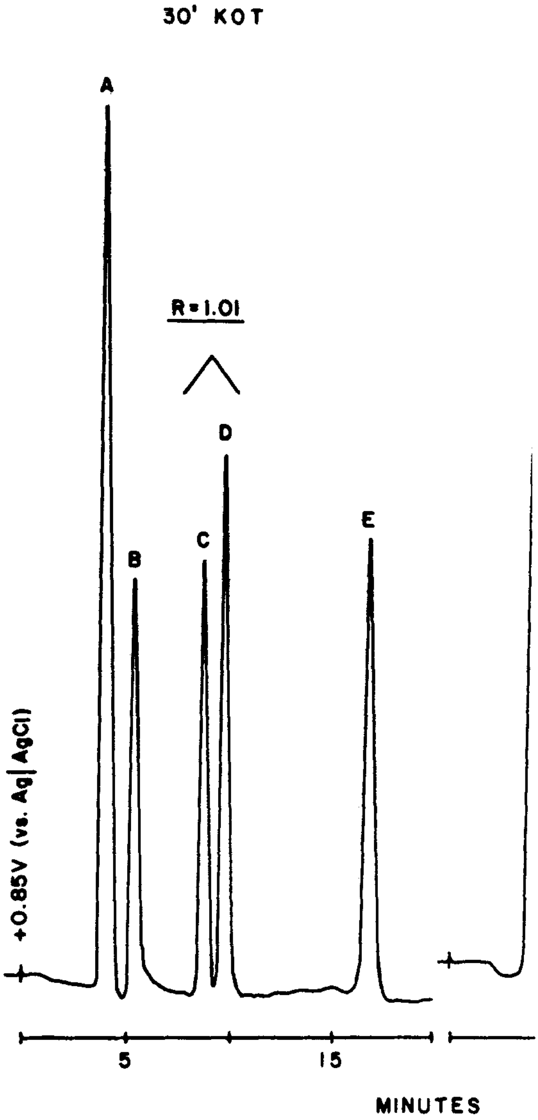

FIGURE 5
Comparison of LC-hv-EC chromatograms generated with
Conditions: Same as Figure 4. Sample: SEM (100-200-ppb PETN).

when the coiled reactor was used. A more interesting result of this study arose in the collection of peak areas during the experiment. It was expected that the peak areas would be roughly similar using the two reactors, since band-broadening should not effect these area measurements. However, for the four analytes, the peak areas in LC-hv-EC with the KOT were (on the average) 2.5 times higher than those generated using the coiled reactor. This result suggests that the conversion of analyte to oxidatively electroactive species is more efficient in the KOT reactor than in the coil. The explanation for this phenomenon probably lies in the improved mass-transfer of analyte within the KOT; since the greatest photon-flux in the irradiator is near the tubing walls closest to the lamp, improved mass-tranfer of analyte in the band from the center and outer walls of the tube towards these areas of higher irradiative flux should result in greater overall conversion. The radial mixing generated by superimposition of secondary flow in the KOT does not occur to nearly the same extent in the coiled reactor, and as a consequence the conversion of analyte is lower.

The hydrodynamic studies of the KOT suggested that the overall sensitivity and selectivity of LC-hv-EC would benefit from substitution of the knitted reactor for the coil. Indeed, the calculated limits of detection for the five high explosives provided in Table 1 were about one order of magnitude better than those obtained in the earlier studies. This table also delineates the dual electrode response ratios (RRs) for each of the explosives; these RRs were calculated over a range of concentrations injected from 1000- to

10-ppb. Within this range, these RRs were linear and reproducible during the day of experimentation, and did not drift by more than a few hundredths on a day-to-day basis, with cleaning of the electrodes and small changes in mobile phase composition. At concentrations lower than 10-ppb, all of the RRs tended toward unity, probably because of non-linearity in the amplification of the small currents generated at +0.85V. However, hv-EC response at +1.0V was linear from about 5-ppm to the LOD for the explosives studied.

TABLE I
Analytical Figures of Merit for High Explosives

| Analyte | RR (+1.0V/+0.85V)[1] | LOD[2] |
|---|---|---|
| RDX | 4.93 ± 0.04 | 0.6-ppb (130-pg) |
| Tetryl | 2.54 ± 0.02 | 0.8-ppb (170-pg) |
| TNT | 2.04 ± 0.07 | 0.6-ppb (120-pg) |
| PETN | 4.65 ± 0.13 | 1.3-ppb (250-pg) |
| NG | 1.88 ± 0.02 | 0.8-ppb (170-pg) |

---

[1] Mean ± Standard Deviation, n=9.

[2] Calculated using $r = 5$, $N_{p-p} = 0.04$-nA, 200-µl injections. Conditions: RadialPak $C_{18}$ (5-µm) 100-x 5-mm, $F = 1.2$-ml/min of 40:60 MeOH:0.2M NaCl.

The single blind study of spiked soil extracts served to demonstrated the excellent selectivity inherent in the LC-hv-EC method. As shown in Figure 6, there are three modes of selectivity operating in the analysis. First, the retention time of the analyte may be used to tentatively assign an identity to an unknown explosive in the sample mixture. Second, the dual electrode response ratio

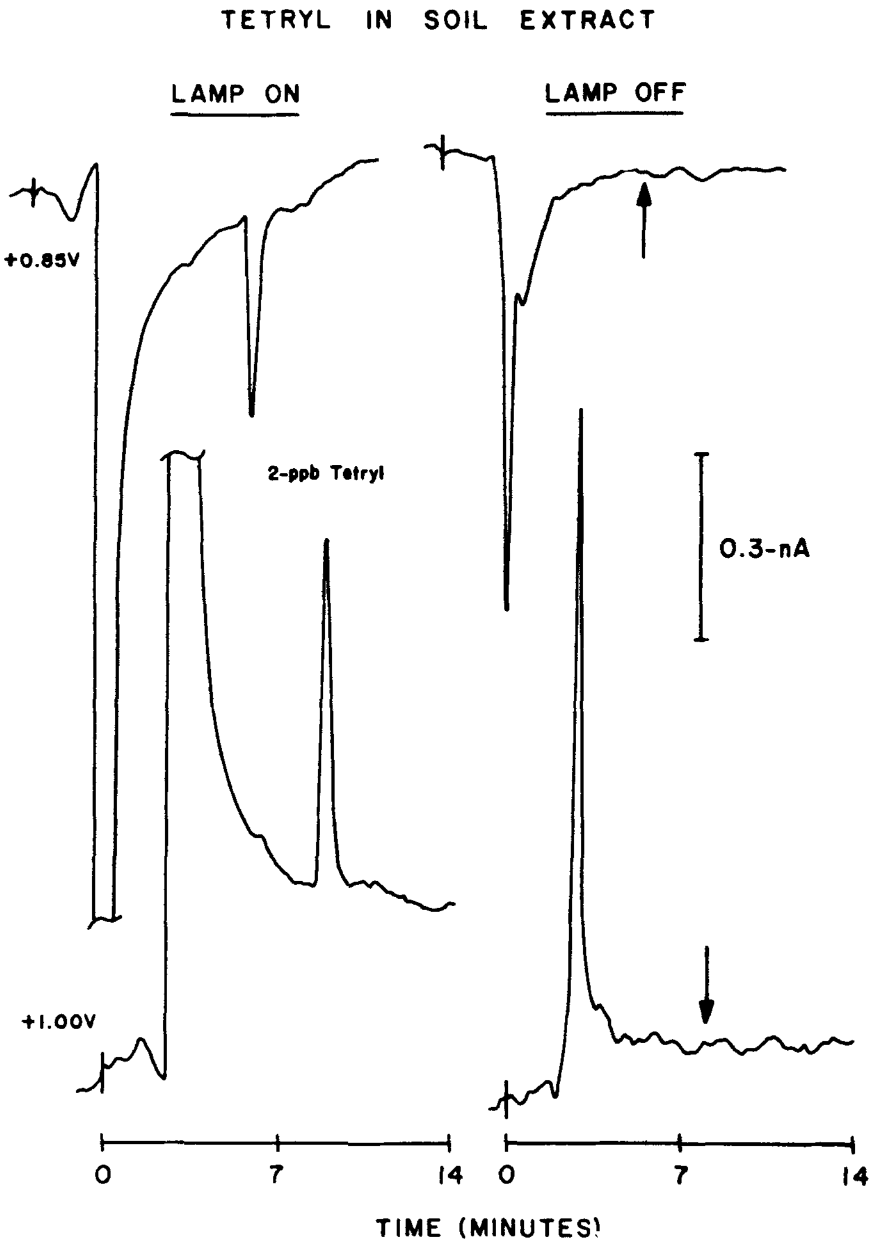

FIGURE 6

LC-hv-EC analysis of spiked soil extract in both lamp on and lamp off mode. Conditions: RadialPak C-18 (5-µm) 100- x 5-mm, 40:60 MeOH:0.2M NaCl, F=1.0-ml/min, 200-µl injections, detection at +1.0V (lower trace) and +0.85V (upper trace). Sample: Extract containing 2-ppb Tetryl.

confirms this initial identification. Finally, a second injection of the sample is made under lamp off conditions, and the presence of an explosive is denoted by a loss of the response initially observed in the lamp on mode, since the explosives do not have inherent oxidative electroactivity. In the single blind study, the presence of Tetryl in one sample, and RDX in the second sample, was accurately determined, even though both were present at a level below 5-ppb.

In preparation for the trace derivatization procedure, DNP-MMA was prepared on a bulk scale. The final product, a bright yellow crystalline solid, gave a sharp melting point at 178-179°C, in good agreement with literature values.[5,15] The NMR spectrum was consistent with the structure of the derivative, and liquid chromatography with both UV and hv-EC detection gave rise to only one peak; there was no trace of DNFB in the LC chromatograms.

The initial conditions chosen for the trace determination of MMA and MEA gave results which were adequate for preliminary evaluation of the method. For the concentration range between 200-ppm and 200-ppb, the derivatization efficiency of MMA was variable. As shown in Figure 7, the MMA was derivatized with an efficiency between 50% and 70% at concentrations greater than 50-ppm, while it was quantitatively converted at levels below 50-ppm. In fact, for the concentration range 50-ppm to 200-ppb, the calibration plot (derivatization followed by detection using LC-hv-EC) for MMA was linear, with a regression equation of $y = 0.695x + 0.021$ (y is current in nA and x is concentration of MMA in ppm), and a correlation coefficient of 0.998. These results suggested that the preliminary

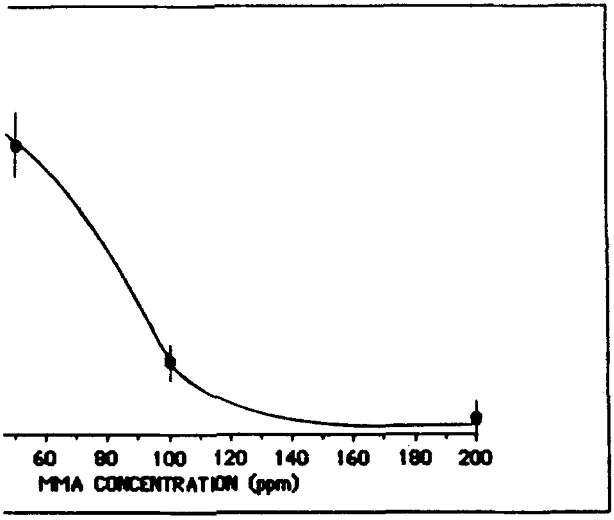

FIGURE 7

ency (%) vs. MMA concentration. Conditions: Derivatization the text. LC-hv-EC used RadialPak C-18 (5-μm) 100- x aCl, F=1.0-ml/min, 50-μl injections, detection at +1.0V.

derivatization conditions would allow for sufficient detectability of MMA in an actual sample down to approximately 10-ppb, if a 200-µl injection volume was used. The LOD could be improved using a preconcentration technique, such as off-line, solid-phase extraction, or by eliminating the sample dilution step in the pre-injection procedure. Eliminating this dilution step would probably require the use of a column switching technique with on-line sample clean-up of the extract, in order to avoid column overload with excess DNFB and solvent effects from DMF. It should also be noted that the lack of linearity in the derivatization efficiency at higher concentrations of MMA is not detrimental from a forensic standpoint, since the presence of MMA in an extract will still be detected. This qualitative identification has the greatest importance during the forensic examination of debris for traces of water gel sensitizer residues, while quantitation often has only secondary importance.

As shown in Figure 8, the LC-hv-EC dual electrode chromatogram for the reaction mixture generated in the derivatization of MMA exhibits all of the selectivity features observed for the conventional nitro-based explosives. The peak at 11-min in the lamp-on chromatogram, corresponding to DNP-MMA, is well resolved from the excess DNFB eluting at 7.5-min, and the peak for the analyte of interest has a characteristic response ratio (1.70 ± 0.05 [n=25]). In addition, the response for the derivative of MMA disappears when the lamp is extinguished, thereby confirming the identity based on retention time and RR.

The results of the application of the initial experimental

# DERIVATIZATION OF MMA FOR LC-hv-EC

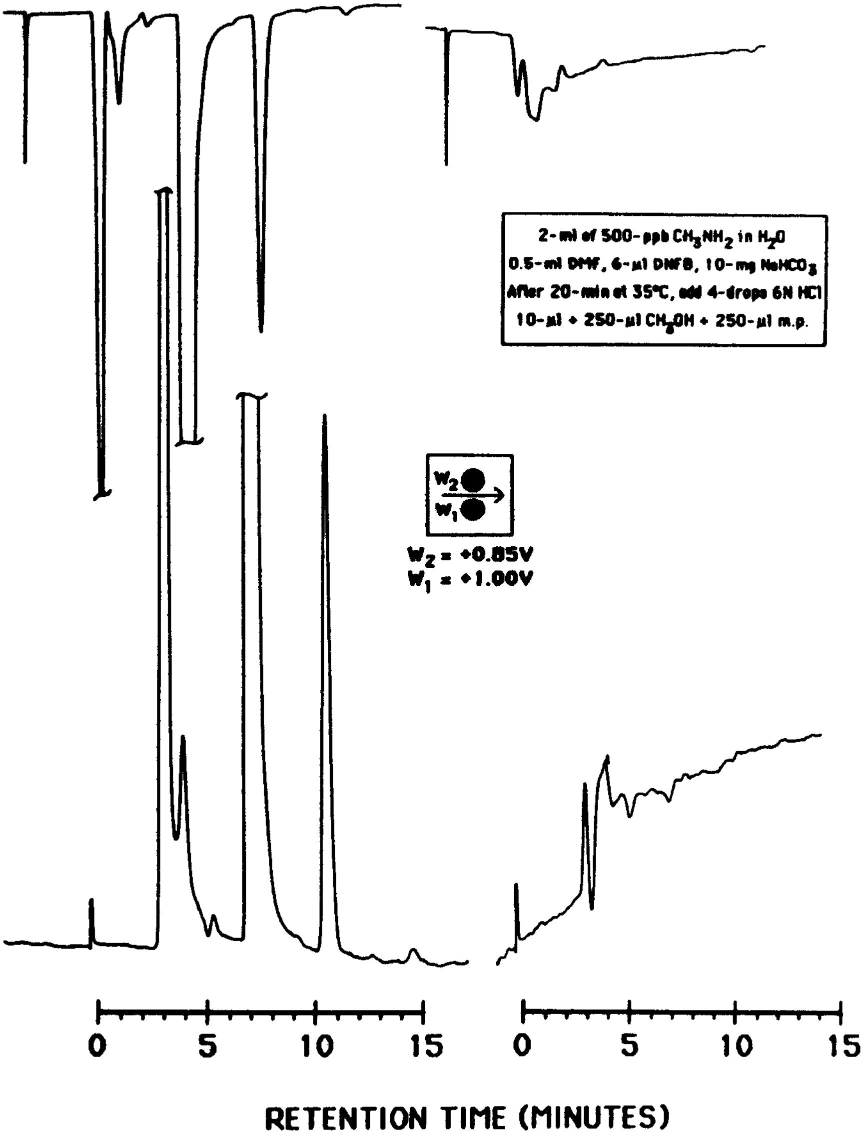

FIGURE 8

LC-hv-EC analysis of reaction mixture from the derivatization of 500-ppb MMA. Left trace in LAMP ON, right trace is LAMP OFF. Conditions: Derivatization conditions are listed on the figure. LC-hv-EC conditions are the same as Figure 7.

conditions for the derivatization of MEA were somewhat different than those for MMA. A plot of derivatization efficiency vs. concentration of MEA was found to be linear over the concentration range of 200- to 10-ppm, with an average efficiency of approximately 35%. The RR for DNP-MEA was 1.99 ± 0.06 [n=15]. It should be possible to improve the derivatization efficiency for MEA using higher reaction temperatures, or longer derivatization times, or both. Such a change should bring the LOD for the determination of MEA into the same range as that for MMA, since the derivatives are quite similar in structure. As for MMA, other modifications could be made to the technique in order to lower the LOD for MEA to the sub-ppb range. Still, as demonstrated in Figure 9, the derivatization-detection procedure used here produced a linear calibration plot for MEA between 200- and 10-ppm, and should be useful for the analysis of aqueous or methanolic extracts of post-blast debris when the extract has been concentrated to a small volume.

## CONCLUSIONS

By exploiting some unique hydrodynamic properties inherent in the incorporation of the KOT in the experimental apparatus, the LODs for nitro-based high explosives have been reduced to sufficiently low levels to allow for trace determinations in all but the most difficult of samples. The selectivity available lends strong credence to the qualitative identification of the explosive, yet at a cost far below those for TEA or MS methods. Added to this set of strengths is the possibility of determining water gel sensitizer residues through the

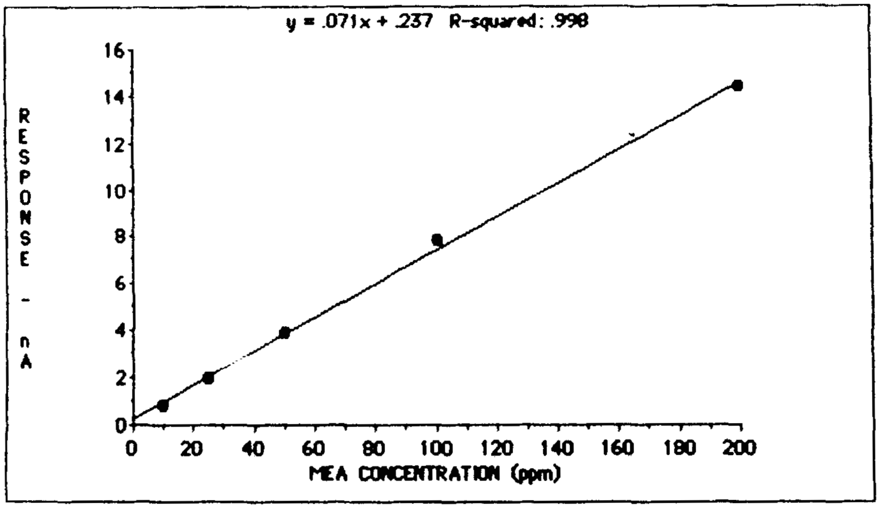

FIGURE 9

Linearity plot for derivatization of MEA with DNFB. The line equation and correlation coefficient (both generated from regression analysis) are shown. Conditions: Same as in Figure 8.

performance of a facile, off-line chemical derivatization. Thus, LC-hv-EC may be utilized as an inexpensive, straightforward method for the confirmation of GC results, or may serve as the primary analytical technique for explosive residue identification in smaller forensic laboratories that cannot afford the more sophisticated, dedicated instruments. The inclusion of detection capabilities for water gel sensitizers will be important in the future, when these explosive formulations gain wider acceptance in the commercial markets and are consequently subject to greater levels of theft and criminal use.

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