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The Trace Analysis for Explosives and Related Compounds Via High Performance Liquid Chromatography-Photolysis-Electrochemical Detection

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ABSTRACT: Organic nitro compounds, such as explosives, are amenable to high performance liquid chromatographic (HPLC) analysis with a variety of appropriate, selective or general, detectors. Although such compounds have been studied recently by electrochemical detection (EC) in the reductive mode, virtually nothing has been reported on the application of oxidative EC for such compounds. Since the parent compounds themselves cannot be electrochemically oxidized, nitrite (NO_2^-) released post-column, on-line, in real time, by photolysis of the HPLC effluent, can very readily be detected at trace levels by oxidative EC methods and techniques. A wide variety of organic nitrate esters (R-O- NO_2), N-nitro (N- NO_2) nitramine derivatives, as well as aliphatic/aromatic C-nitro (C- NO_2) compounds, can all be analyzed at trace levels by this HPLC-photolysis-EC (HPLC-hv-EC) approach. A large number of explosives and certain drugs have been studied by these approaches. The basic high performance liquid chromatography-photolysis-electrochemical detection (HPLC-hv-EC) system has been optimized with regard to minimum detection limits (MDLs), linearity of responses as a function of concentration/amounts injected, specific HPLC separations and mobile phases compatible with hv-EC derivatization-detection, dual detector EC response ratios for individual analytes, and other suitable analytical parameters of importance and interest. Some applications of this method to real world samples of explosive debris are also described.

KEYWORDS: criminalistics, explosives, chromatographic analysis, high performance liquid chromatography, on-line photolysis-derivatization, electrochemical detection, organic nitro compounds

Nomenclature

HPLC High performance liquid chromatography
hv Photolysis/photohydrolysis/photochemical derivatization

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EC	Electrochemical detection
UV	Ultraviolet
HOH	Water
MeOH	Methanol
MDL	Minimum detection limits
ppm	Parts per million
ppb	Parts per billion
NO ₂ ⁻	Nitrite ion
<i>N</i> -NO	<i>N</i> -nitroso compound
mL/min	Millilitres/minute
GC	Gas chromatography
TEA	Thermal energy analyzer
MS	Mass spectrometry
ECD	Electron capture detector
LCEC	Liquid chromatography/electrochemistry
TNT	2,4,6-Trinitrotoluene
DNT	Dinitrotoluene
NG	Nitroglycerin
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane
TETRYL	2,4,6, <i>N</i> -tetranitro- <i>N</i> -methylaniline
NO ₃ ⁻	Nitrate ion
FIA	Flow injection analysis

Introduction

Most commonly used explosives contain the nitro (NO₂) group somewhere within their structures, usually bonded directly to either carbon, nitrogen, or oxygen (C-NO₂, N-NO₂, O-NO₂). Indeed, most explosives contain more than one nitro group per molecule of the compound. Although much of the early work on the analysis of explosive materials utilized gas chromatography (GC) with a wide variety of suitable and often selective/sensitive detectors, within the past decade or so most of the emphasis has shifted towards the use of high performance liquid chromatography (HPLC) [1-8]. A number of selective and general type detectors for HPLC have been shown to be suitable for the trace analysis of complex mixtures of explosives, including: ultraviolet-visible (UV-VIS), electron capture detection (ECD), mass spectrometry (MS), thermal energy analysis (TEA), and reductive electrochemical detection (EC). However, there remain certain quite significant disadvantages inherent within each of these detection approaches. UV-VIS is often not selective enough for explosives alone, and it is not generally sufficiently sensitive either. ECD is no longer commercially available, and it is not easily compatible with reversed phase HPLC solvents. MS can be used as an LC detector, but it tends to be very expensive, difficult to operate routinely, and requires sophisticated operator training or experience or both. TEA is somewhat selective for organic nitro type compounds, but it will respond to other classes, it is not at all compatible with aqueous based reversed phase HPLC separations, and it is very expensive for a routine HPLC detector.

Reductive EC has been used by very few workers thus far. It can, at times, present serious operational problems, especially at trace levels, where oxygen in the sample and mobile phase can interfere with the analyte of interest. It is clear today that reductive LCEC is becoming more popular as a method of trace analysis, and thus it may yet become a method of choice for explosives. Still, at the present time, oxidative liquid chromatography-electrochemistry (LCEC) is the more widely used and preferred mode of electrochemical detection in HPLC [9-12]. Nitro compounds, such as explosives, are not directly amenable to oxidative LCEC approaches, since they are already in their highest oxidation state. However, there was sufficient evidence in the literature to indicate the possibility of using oxidative LCEC for inorganic nitrite (NO₂⁻)

perhaps generated on-line, post-column, in real time, from suitable precursor organic nitro compounds [13-19].

Oxidative LCEC has long been used for the trace determination of inorganic nitrite, using ion chromatography, ion exchange HPLC, or paired-ion HPLC [20-22].⁶ There was little question that nitrite was indeed amenable to oxidative LCEC approaches, with working potentials of +1.2 V or below. The dual electrode EC detection was another approach that could eventually be utilized for explosives. The success of this new approach relied on the release of inorganic nitrite from suitable organic nitro derivatives, perhaps by a photohydrolysis/photolysis type reaction after the HPLC separation and before the oxidative EC detection step(s). Most of the reports on photohydrolysis reactions in HPLC have involved the formation of nitrite from *N*-nitroso compounds, followed by analysis by a Griess Test or alternative HPLC detection method [15-19]. The photoconductivity detector for HPLC marketed by Tracor Corporation (Austin, TX) involves photolysis/photohydrolysis reactions on various organic compounds, including *N*-nitroso or organohalogenes, followed by detection of the inorganic anions by an on-line conductivity detector [23-24]. In almost all of this work virtually nothing has been reported emphasizing organic nitro compounds. There has been a suggestion of this in the work of Snider and Johnson, that organic nitro compounds were often seen as interferents [15]. All of the available literature seemed to suggest that HPLC-photolysis-EC (HPLC-hv-EC) might well serve as a practical approach to the trace analysis of a variety of explosives and other organic nitro compounds. These methods could also be adapted to other classes of organic compounds, wherein these can release an inorganic anion by photolysis that could then be detected by analogous EC approaches.

Although our initial interest in the use of HPLC-hv-EC was directed to the trace analysis of explosives, it became apparent that these basic methods could readily be used for a wide variety of other organic nitro compounds. We therefore describe here our results for a variety of commonly used explosives, including: 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), and 2,4,6, *N*-tetranitro-*N*-methylaniline (TFTRYL). In addition, we have applied HPLC-hv-EC to aliphatic nitrate esters (R-O-NO₂) such as *n*-propyl nitrate and isopropyl nitrate, as well as to a particular coronary vasodilator, isosorbide dinitrate (ISDN). Finally, we have tried to apply these methods to other aromatic nitro derivatives, such as mono-nitrotoluene isomers, dinitrotoluene isomers, and certain nitro derivatives of polycyclic aromatic hydrocarbons (nitro-PAHs). We have also attempted to define what inorganic anions might interfere in these analyses and which present no problems as interferents. These results suggest that there will be several other classes of organic compounds that will be amenable to HPLC-hv-EC approaches. Improved analyte identification is possible by the use of appropriate dual electrode EC approaches, where these are feasible for the particular inorganic or organic anion generated by the photolysis/photohydrolysis reaction [10-12]. In addition, these results are shown to provide a flow injection analysis method, FIA-hv-EC, in the absence of an initial HPLC separation, using just hv-EC, that can be practical for quality control or screening purposes.

Experimental Procedure

Reagents, Chemicals, and Explosives

Standards of various explosives were obtained from the Bureau of Alcohol, Tobacco, and Firearms (U.S. Treasury Department) Forensic Laboratory, Rockville, MD. Some of these explosives were obtained from the FBI Academy, Forensic Research and Training Center, Quantico, VA. Two samples of post-blast debris extracts were also obtained from the ATF laboratory as acetonitrile solutions. These samples had been analyzed by thin-layer chromatographic (TLC) methods and found to contain nitroglycerin (NG). The NG standard was a

⁶K. Bratin, unpublished results, 1983.

sample of Parke-Davis Nitrostat-IV, lot AK725, 8-mg/mL infusion solution. Other organic nitro standards were obtained from commercial sources, such as: Aldrich Chemical Co. (Milwaukee, WI), Pfaltz & Bauer Co. (Stamford, CT), or Fisher Scientific Co. (Medford, MA). Inorganic salts were obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ), Fisher Scientific Co., Aldrich Chemical Co., and others. The HPLC solvents were obtained from Waters Associates, Inc. (Milford, MA) or MCB Chemicals Co. (Cincinnati, OH), the latter as their Omnisolv®-brand of HPLC grade solvents.

Instrumentation and Equipment

Figure 1 illustrates the HPLC-hv-EC instrumentation used in all of these studies and the arrangement of the various parts. The HPLC portion utilized a Rheodyne Model 7125 syringe loading injection valve (Rheodyne Corp., Cotati, CA), a Laboratory Data Control (LDC) Constametric II solvent delivery system (Laboratory Data Control, Riviera Beach, FL), a LiChromaDamp II pulse dampener (Alltech Associates, Inc., Deerfield, IL), a Bioanalytical Systems pulse dampening column (Bioanalytical Systems, Inc., West Lafayette, IN), a Photronix Model 816 HPLC batch irradiator (Photronix Corp., Medway, MA), a BAS Model LC-4A single electrode amperometric controller or a BAS Model LC-4B dual electrode amperometric system for LCEC, a BAS glassy carbon single/dual working electrode with a silver/silver chloride reference electrode, and a Linear Instruments Model 585 dual pen strip chart recorder (Linear Instruments, Inc., Reno, NV). All HPLC injections were made with a 25- μ L flat-tipped Hamilton HPLC syringe (Hamilton Corp., Reno, NV). HPLC mobile phases were de-gassed and filtered before use with a 0.45- μ m solvent filtration kit (Millipore Corp., Bedford, MA). Samples for HPLC injection were filtered with a sample filtration kit using a 0.45- μ m filter (Millipore Corp.). The irradiation finger was maintained at a constant temperature of about 0 to 5°C with a constant temperature water bath (Forma Scientific, Model 2095, VWR Scientific Co., Boston, MA). Irradiation of the HPLC effluents took place inside a 3- to 3.65-m (10- to 12-ft), 1.6-mm (1/16-in.) outer diameter, 0.76-mm (0.03-in.) inner diameter Teflon® fluorinated ethylene-propylene (FEP) tubing, Catalog no. HGC-024 (Rainin Instruments Co., Woburn, MA). Swagelok stainless steel fittings and ferrules were used for all of the HPLC-hv-EC connections, except where the EC detector cells required their own connection fittings (Cambridge Valve & Fittings Co., Billerica, MA). The dual electrode HPLC-hv-EC unit used HPLC-hv-EC equipment similar to that described above for the single electrode unit, replacing the single electrode amperometric controller with the dual electrode/controller system from BAS. In the reductive EC mode, the HPLC mobile phase was first de-gassed under nitrogen using an approach described elsewhere [6, 11]. The use of a Teflon irradiation line before the EC detector in the reductive mode did not preclude the ability to perform trace explosives analyses at moderate working potentials, as below. The HPLC columns utilized in these studies were obtained from a variety of commercial sources: a Biophase C₁₈, 10 μ m,

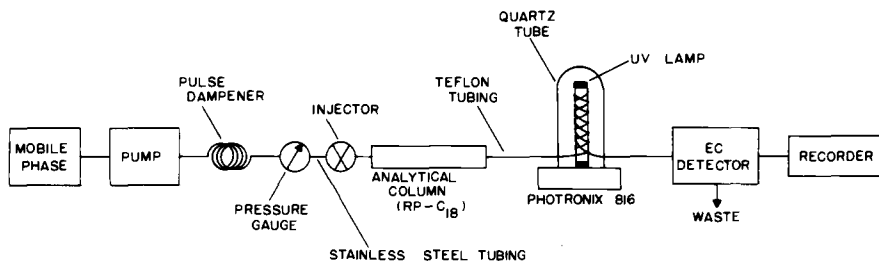


FIG. 1—Schematic diagram of the HPLC-hv-EC instrumentation.

25-cm by 4.6-mm inner diameter (Bioanalytical Systems, Inc.), a Perkin-Elmer Fast-LC C₁₈, 3 μ m, 10-cm by 4.6-mm inner diameter (Perkin-Elmer Corp., Norwalk, CT), a Waters μ Bondapak C₁₈, 10 μ m, 25-cm by 4.6-mm inner diameter (Waters Associates), and various in-house slurry packed C₈ or C₁₈ reversed phase columns.

Methods and System Optimization

The cyclic voltammograms (CVs) were obtained on a Bioanalytical Systems Model CV-1B unit, using a supporting electrolyte of 50/50 MeOH/0.1M sodium chloride, with a scan rate of 150mV/s, with a silver/silver chloride reference electrode and a glassy carbon working electrode. The CVs were obtained by plotting applied working potentials versus current generated in the conventional manner. Linear hydrodynamic voltammograms (LHVs) were obtained using FIA-hv-EC approaches, varying the applied potential and measuring the current generated with the same amount of analyte injected into the flowing stream each time. LHVs were obtained on the same FIA-hv-EC instrumentation used for all FIA studies or HPLC-hv-EC interfacing. The final LHVs were obtained by simply plotting applied working potential against current generated, in the conventional manner.

The FIA-hv-EC and HPLC-hv-EC systems had to be optimized before their use, and this was crucial for the photochemical part of the system. This was accomplished by varying the internal diameter of the Teflon tubing and its total length around the irradiator finger. By measuring EC peak heights as a function of either the inner diameter or total length, it was possible to determine the optimum tubing parameters that would provide maximum nitrite generation with minimum concomitant nitrite destruction. The final optimal tubing parameters have been indicated above (Instrumentation and Equipment). An external standard of sodium nitrite was used, with the lamp off, as a control. The optimal flow rate was also determined by flow injection methods (FIA-hv-EC), without the HPLC column on-line. These experiments determined the ideal flow rates and residence times for the final HPLC-hv-EC system. The FIA-hv-EC system had to be optimized with regard to salt concentration and overall compatibility with both photolysis and EC detector conditions. A number of inorganic salts were studied, but only sodium chloride (NaCl) appeared to be totally inert to the photolysis and EC conditions, and to be free of impurities that might interfere. The pH also had to be optimized for FIA-hv-EC approaches by using maximum nitrite generated from the same standards.

Results and Discussion

These HPLC-hv-EC or flow injection analysis, FIA-hv-EC methods, depend on the photolytic or photohydrolytic generation of an inorganic or organic anion from an appropriate organic precursor. These needs are quite similar to those for photoconductivity detection in HPLC [23,24]. It is also possible that certain inorganic anions, electrochemically active in the absence of photolysis, might be converted by photolysis to electrochemically active ions. In FIA-hv-EC there may be a problem of interferences arising in the analysis from one or more inorganic anions already present in the sample. To determine such possible interferents, we obtained a series of cyclic voltammograms (CVs) for four typical inorganic anions of interest as possible interferents or photolysis products derived from suitable organic precursors (Fig. 2). Of the four anions, it is clear that nitrate (NO₃⁻) is not oxidized at the potentials of interest. Nitrite (NO₂⁻), iodide (I⁻), and bromide (Br⁻) all have very different optimal oxidation potentials for maximum current generation in either CV or EC detection. Thus, it should be possible to differentiate between an organic nitrate ester, an aromatic C-nitro derivative, an organic alkyl nitrite, an organoiodine compound, or an organobromine substance leading to the corresponding anions by photochemical derivatization (that is, NO₃⁻/NO₂, NO₂⁻, NO/NO₂⁻, I⁻, or Br⁻). However, an organic nitrate ester could conceivably lead to both nitrite and nitrate, while an aryl nitro or an alkyl C-nitro compound might only lead to inorganic nitrite on

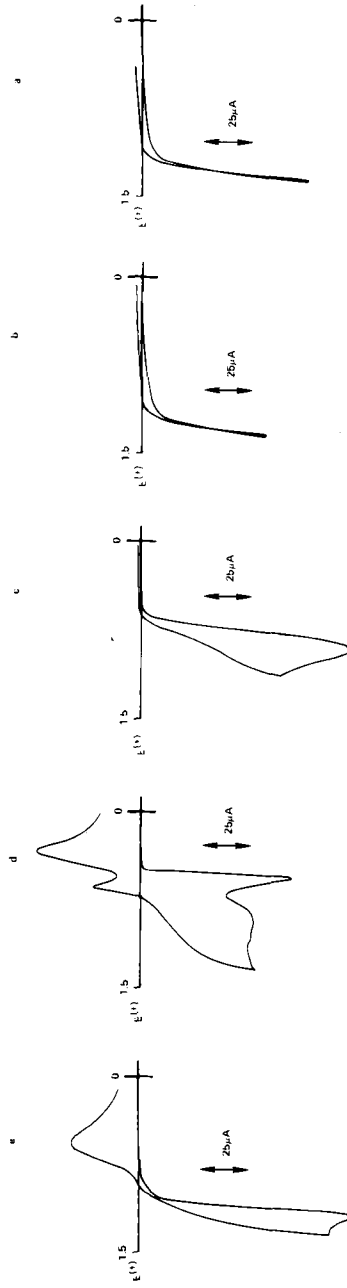


FIG. 2—Cyclic voltammograms (CVs) of various inorganic anions: (a) supporting electrolyte of MeOH/0.1M NaCl (50/50, v/v); (b) 0.0065M KNO_3 ; (c) 0.0048M $NaNO_2$; (d) 0.0026M KI; and (e) 0.0035M KBr.

irradiation. It is also possible that the initially formed nitrate or nitrite species could further react with oxygen in the aqueous sample solution or HPLC mobile phase, leading to further EC active species. It is further possible that other electroactive species, besides nitrate/nitrite, could be formed from certain organic nitro compounds on photolysis. The formation of varying mixtures of electroactive species, dependent on the original nitro compound photolyzed, would then lead to different dual detector EC responses as a function of the working potentials employed. Our results thus far support the already established fact that photolysis of organic nitrate esters leads to inorganic nitrite formation, and that this can then be readily detected by oxidative EC methods [25]. Since inorganic nitrite is of most interest as the major photolysis product of organic nitrate esters, we obtained a separate linear hydrodynamic voltammogram (LHV) using flow injection analysis, which indicated usable oxidative potentials for EC detection of about +0.8 to +1.0 V. Thus, for most of the studies that follow, especially in HPLC-hv-EC work we have emphasized oxidative potentials around +1.0 V, with either a single or dual electrode system.

Table 1 summarizes a number of inorganic and organic anions and their determined oxidative EC responses at +0.8 and +1.0 V, with and without the irradiation lamp operative. These results suggest that there are relatively few inorganic and organic anions that produce

TABLE 1—Summary of possible inorganic anion responses in HPLC-hv-EC using hv-EC.^a

Anion Studied	EC Active With Lamp Off ^b		EC Active With Lamp On ^b	
	+0.8 V	+1.0 V	+0.8 V	+1.0 V
Cl ⁻	no	no	no	no
ClO ₃ ⁻	no	no	no	no
ClO ₄ ⁻	no	no	no	no
Br ⁻	no	no	no	no
F ⁻	no	no	no	no
I ⁻	yes	yes	yes	yes
IO ₃ ⁻	no	no	yes	yes
IO ₄ ⁻	no	no	yes	yes
HCO ₃ ⁻	no	no	yes	yes
NO ₂ ⁻	yes	yes	yes	yes
NO ₃ ⁻	no	no	yes	yes
SO ₃ ²⁻	yes	yes	no	no
SO ₄ ²⁻	no	no	no	no
HSO ₃ ⁻	yes	yes	yes	yes
S ⁻²	yes	yes	yes	yes
Benzoate	no	no	yes	yes
Acetate	no	no	no	no
CNS ⁻	no	yes	yes	yes
CN ⁻	yes	yes	yes	no
H ₂ PO ₄ ⁻	no	no	yes	yes
HPO ₄ ⁻	no	no	yes	yes
HPO ₂ ⁻	no	no	no	no
CrO ₄ ⁻²	no	no	no	yes
Cr ₂ O ₇ ⁻²	no	no	no	yes
H ₂ AsO ₄ ⁻	no	no	no	no

^aThese analyses of possible anion responses via dual electrode EC in hv-EC approaches were done using flow injection methods, with no HPLC column yet in-line. Dual electrode glassy carbon cell used here.

^bThe words yes or no refer to the presence of absence of an EC response for each anion indicated at the working potentials indicated above.

the same qualitative results as inorganic nitrite under such conditions. In view of the available CVs for various inorganic anions, for example, Fig. 2, it might be concluded that dual detector response ratioing in FIA-hv-EC or HPLC-hv-EC could provide almost unequivocal identification for inorganic anions generated by photolysis of very specific precursors. These initial speculations have now been confirmed by the results indicated below.

Qualitative EC Oxidative Responses

Knowing the optimum potentials for oxidative EC detection of the expected anions to be derived from explosives or other nitro compounds by FIA-hv-EC, it was necessary to demonstrate that such analytes would indeed respond in FIA under these irradiation conditions. It was necessary to show that there would be no response for such compounds with the lamp off (Table 2). Of interest is the observation that inorganic nitrate does not show any response at these oxidative potentials with the lamp off, as expected, but that after irradiation, it does show a very good EC response at these oxidative potentials. This suggests that there may be some photoreduction of the nitrate to nitrite or other electrophore occurring, and that it is the final species that is being detected. It would appear, therefore, that FIA-hv-EC might provide a rapid, reliable, specific, and sensitive method of direct analysis for these and other explosives and organic nitro compounds. This would include nitro derivatives of polycyclic aromatic hydrocarbons, such as 9-nitroanthracene (Table 2). Such compounds are of current interest as possible environmental pollutants, since they have demonstrated animal carcinogenic and mutagenic properties. Such analyses might only be feasible where the sample matrix is relatively simple, and where there would be very few, if any, anionic interferents present that could produce similar dual electrode responses. In a separate study, we have investigated the dual electrode response ratios at fixed concentrations injected for two different oxidative potentials for various explosives and nitro derivatives (Table 3). These results suggest that each explosive, drug, nitroaromatic, or nitro-PAH may have its own unique dual detector response ratio. Such a characteristic could be used to confirm its presence in a simple sample matrix by FIA-hv-EC, or in more complex sample matrices, using HPLC-hv-EC. That is, where an explosive is thought to be present in a post-blast extract, its presence could be confirmed using the dual

TABLE 2—Dual electrode EC responses for various compounds via flow injection analysis-photolysis-electrochemical detection (FIA-hv-EC).^a

Compound Studied	Compound EC Active With Lamp Off		Compound EC Active With Lamp On	
	+0.8 V	+1.0 V	+0.8 V	+1.0 V
TNT	no	no	yes	yes
RDX	no	no	yes	yes
TETRYL	no	no	yes	yes
NG	no	no	yes	yes
ISDN	no	no	yes	yes
iso-propylnitrate	no	no	yes	yes
n-propylnitrate	no	no	yes	yes
9-nitroanthracene	no	no	yes	yes
o-nitrotoluene	no	no	yes	yes
Dinitrobenzene	no	no	yes	yes
Dinitrotoluene	no	no	yes	yes
Sodium nitrate	no	no	yes	yes
Sodium nitrite	yes	yes	yes	yes

^aThese determinations were performed with no HPLC column on-line, using just FIA-hv-EC.

TABLE 3—Dual electrode response ratios at fixed concentrations injected for two different oxidative potentials, +1.0 V/+0.8 V, for various explosives and nitro derivatives.^a

Compound Studied	Dual Electrode Response Ratios ^b
NG	4.69 ± 0.24
TETRYL	2.04 ± 0.15
TNT	2.26 ± 0.18
RDX	2.94 ± 0.22
ISDN	1.66 ± 0.26

^aThese detector response ratios were determined by flow injection analysis-hv-EC. All FIA-hv-EC analyses were performed within the same working day.

^bNumbers represent the average of four to five different concentrations of each compound injected under identical conditions ± standard deviations (average ± S.D.).

detector response ratio. This method has been applied to a real world explosion debris extract, as below.

Calibration Plots and Minimum Detection Limits for Various Explosives

We have obtained a number of calibration plots for various explosives and organic nitrate esters by FIA-hv-EC methods including: *n*-propylnitrate, iso-propylnitrate, 9-nitroanthracene, inorganic nitrite, RDX, NG, TETRYL, and isosorbide dinitrate (ISDN). These studies used a single working electrode potential of +1.0 V, and each calibration plot was linear from the low nanogram level to a few hundred nanograms injected. It is possible that these calibration curves will be linear beyond these two orders of magnitude. The correlation coefficients for such plots were all in excess of 0.999.

The minimum detection limits (MDLs) are summarized in Table 4. These determinations of MDLs were made using injection volumes of 20 μ L, and thus it would be expected that improved MDLs could be obtained by using larger (100- to 200- μ L) injection volumes. It may prove possible to lower these reported MDLs five- to ten-fold by such approaches. Even the

TABLE 4—Minimum detection limits via HPLC-hv-EC.^a

Compound Name	Minimum Detection Limit (MDL) ^b
RDX	500 pg = 25 ppb
TETRYL	500 pg = 25 ppb
TNT	500 pg = 25 ppb
NG	4.0 ng = 200 ppb
ISDN	2.5 ng = 125 ppb
NaNO ₂	1.56 ng = 78 ppb

^aHPLC-hv-EC conditions used a C-18 RP column, 3 μ m, 10-cm by 4.6-mm inner diameter, with mobile phase of 50/50 MeOH/0.1M NaCl, 0.6 mL/min flow rate, +0.8 V oxidative EC detection.

^bInjections were made in 20- μ L volumes, MDL given in terms of mass of analyte injected and concentration, ppb = parts per billion, ppm = parts per million, and so forth.

now demonstrated MDLs using HPLC-hv-EC are useful for post-blast extract samples. It is possible that MDLs could also be improved by reducing the total void volume in the current HPLC-hv-EC system, so that peak shapes and peak heights would be improved. All of the detection limits were determined using peak height measurements with a final signal/noise ratio of 3:1.

Single Electrode EC Detection via HPLC-hv-EC for Explosives and Drugs

We have used both single and dual electrode detection for various mixtures of standards, but because the dual approach provides more qualitative and quantitative information on a single injection, it has been emphasized. Figure 3 illustrates the single electrode oxidative determination of RDX, TETRYL, and TNT, first with the lamp on in HPLC-hv-EC (a), and then with the lamp off (b). Figure 3c indicates the single electrode response for a mixture of NG and ISDN. Detection of these and other explosives or nitro derivatives is entirely dependent on the irradiation step for the generation of the EC detectible species. Although +1.0 V is the optimal oxidative potential for detection of these analytes, it is clear that a large variety of other oxidative and perhaps reductive working potentials could also be used in HPLC-hv-EC work. That is, inorganic nitrite as an irradiation product of explosives can be detected oxidatively, but others have shown that underivatized explosives can also be detected reductively [6,11]. It should be possible to utilize both oxidative and reductive dual electrode detection for these explosives, with and without the irradiation lamp on in HPLC-hv-EC or FIA-hv-EC approaches. Thus, although single electrode detection is useful and practical for real world samples, dual electrode detection in LCEC or HPLC-hv-EC or FIA-hv-EC can provide significant qualitative and quantitative advantages, as seen below [11,12].

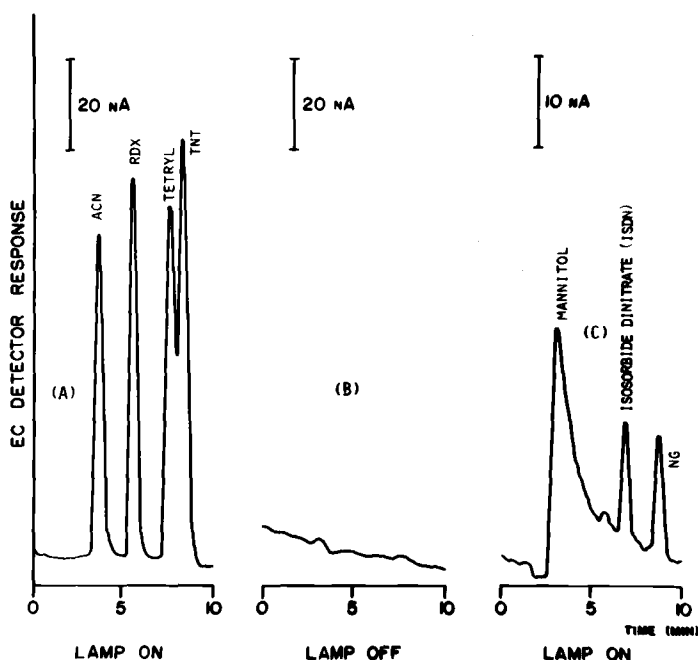


FIG. 3—HPLC-hv-EC single electrode chromatograms for RDX, TNT, and TETRYL using RP C-8, 10 μ m, 25-cm by 4.6-mm inner diameter column with 50/50 MeOH/0.1M NaCl mobile phase at 1.4 mL/min flow rate. Glassy carbon electrode at +1.0 V. (a) hv lamp on; (b) hv lamp off; and (c) hv lamp on with NG and ISDN standards.

Dual Electrode Detection in HPLC-hv-EC for Explosives and Drugs

Figure 4 illustrates a typical dual electrode, oxidative/oxidative HPLC-hv-EC set of chromatograms for a mixture of RDX, TETRYL, and TNT. Detection here used dual EC methods in the parallel mode, with a glassy carbon working electrode operated at +1.0 and +0.9 V. Alternative oxidative/oxidative, oxidative/reductive, or reductive/reductive potentials are possible, as above with the single working electrode situation. With the lamp off, only the reductive electrode would detect underivatized explosives, but with the lamp on, both oxidative and reductive electrodes would produce signals. The oxidative electrode would respond to photolytically generated nitrite, while the reductive electrode would respond, by and large, to underivatized, starting explosive. These generalizations are only true for the parallel (adjacent) orientation of the dual electrodes, different EC responses might be observed with the series (upstream-downstream) arrangement of electrodes [11].

Figure 5 illustrates the use of dual electrode detection in HPLC-hv-EC, but using one electrode in the oxidative mode at +1.0 V, and the other in the reductive mode at -0.55 V. Again, detection is in the parallel mode of operation, which provides the optimal amount of qualitative and quantitative information by ratioing the detector responses at various working potentials. Mannitol is present in this sample of ISDN because our source was a commercial formulation that contained both ISDN and mannitol.

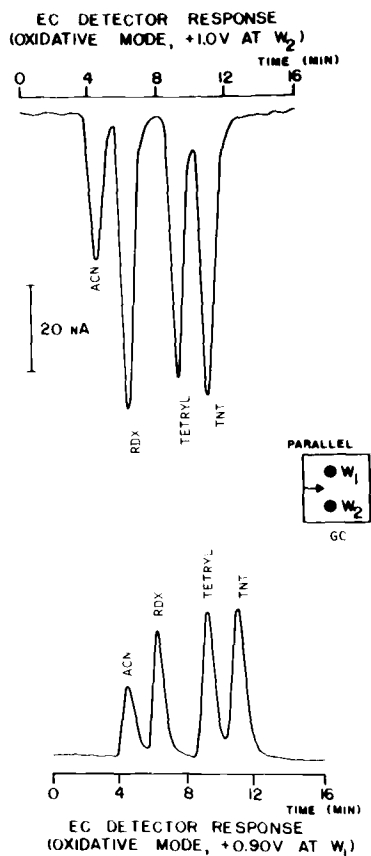


FIG. 4—HPLC-hv-EC dual electrode chromatograms of RDX, TETRYL, and TNT, using C-18, RP 3 μm , 10-cm by 4.6-mm inner diameter column with 50/50 MeOH/0.1 M NaCl at 0.6 mL/min flow rate. Dual electrodes operated in the oxidative/oxidative modes using glassy carbon surfaces.

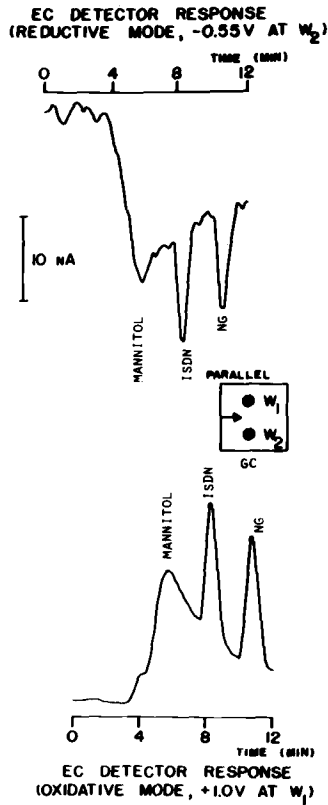


FIG. 5—HPLC-hv-EC dual electrode chromatograms for NG and ISDN using C-18 RP 3- μ m column, 10-cm by 4.6-mm inner diameter with 50/50 MeOH/0.1 M NaCl, 0.6 mL/min flow rate. Dual electrodes operated in oxidative/reductive modes with glassy carbon surfaces.

Dual Electrode HPLC-hv-EC Detection of Post-Blast Explosion Debris

Figure 6 is a set of HPLC-hv-EC dual electrode chromatograms for a sample from a pipe bomb explosion under a private car. The post-blast debris was extracted with acetonitrile (ACN). This solution was then concentrated, and analyzed first by TLC within the labs of the Bureau of Alcohol, Tobacco, and Firearms. This TLC analysis indicated the presence of NG, and this was verified using HPLC-hv-EC. Although this sample contained crankcase oil together with the NG, the NG was satisfactorily separated by HPLC, and it could be clearly identified with the irradiation lamp turned on. With the lamp off, only the interferences are seen, presumably motor oil and derivatives. With the lamp on, NG is clearly evident at the correct retention time. Additional confirmatory evidence could be obtained by comparing the dual electrode response ratios at various working potentials with the ratios obtained for authentic NG analyzed under the same set of HPLC-hv-EC conditions. When this was done here, these two sets of detector response ratios were found to be identical within experimental error. Thus, these methods of trace analysis for explosives and related organic nitro compounds provide a very high degree of analyte specificity for individual explosives present in real world samples.

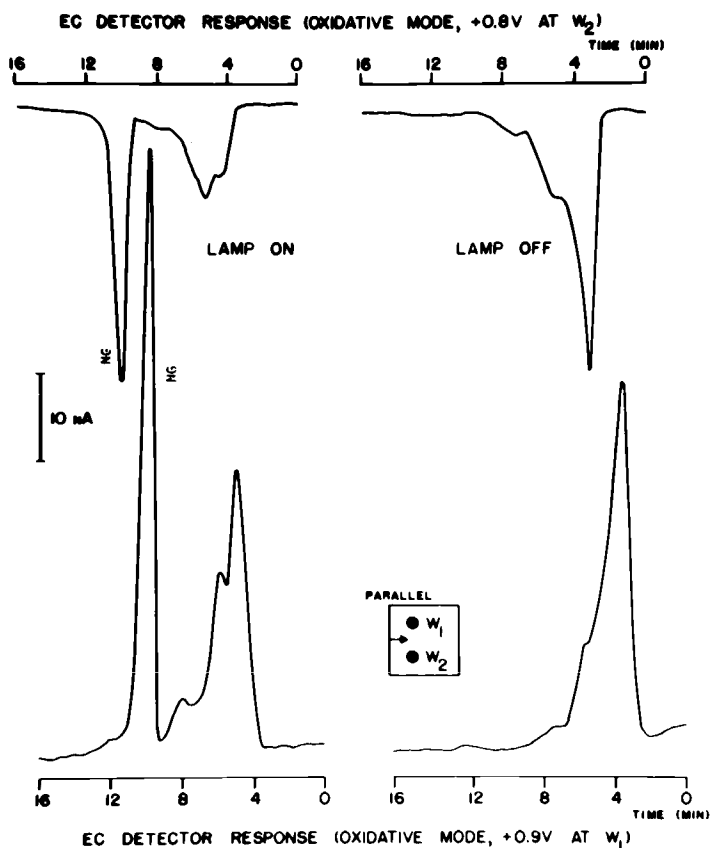


FIG. 6—HPLC-hv-EC dual electrode chromatograms for post-blast debris extracts, using a RP C-18 column, 3 μ m, 10-cm by 4.6-mm inner diameter with mobile phase of 50/50 MeOH/0.1 M NaCl at 0.6 mL/min flow rate. Glassy carbon dual electrodes operated in oxidative/oxidative modes at +0.8 and +0.9 V, with lamp on and lamp off.

Conclusions

We have developed and applied a new approach for the trace analysis of organic nitro compounds. These HPLC-hv-EC methods have been applied to a number of standard explosives and other organic nitro compounds, using both single and dual electrode detection. We have demonstrated the dual electrode responses for these compounds as a function of working potentials applied, by plotting amounts injected versus peak heights thus generated. The selectivity of these methods far exceeds that possible by single electrode HPLC-hv-EC methods. It has further been shown that these newer approaches can be readily applied to materials such as: explosives, drugs, nitrate ester compounds, nitro aromatics, nitro-PAHs, and similar nitro derivatives (O-nitro, C-nitro, or N-nitro). Calibration plots and linearities of EC response for various nitro compounds have also been described, together with already established minimum detection limits via single electrode HPLC-hv-EC methods. It is suggested that FIA-hv-EC and HPLC-hv-EC analytical approaches should find wide applicability in a number of areas of trace organic or inorganic analysis. Such extensions of this work are in progress.

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