

Technical Note

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Fast Gas Chromatography of Explosive Compounds Using a Pulsed-Discharge Electron Capture Detector*

ABSTRACT: The detection of a mixture of nine explosive compounds, including nitrate esters, nitroaromatics, and a nitramine in less than 140 sec is described. The new method employs a commercially available pulsed-discharge electron capture detector (PDECD) coupled with a microbore capillary gas chromatography (GC) column in a standard GC oven to achieve on-column detection limits between 5 and 72 fg for the nine explosives studied. The PDECD has the benefit that it uses a pulsed plasma to generate the standing electron current instead of a radioactive source. The fast separation time limits on-column degradation of the thermally labile compounds and decreases the peak widths, which results in larger peak intensities and a concomitant improvement in detection limits. The combination of short analysis time and low detection limits make this method a potential candidate for screening large numbers of samples that have been prepared using techniques such as liquid-liquid extraction or solid-phase microextraction.

KEYWORDS: forensic science, forensic chemistry, fast screening, explosives detection, microbore column, fast gas-chromatography, pulsed-discharge electron capture detector, nitroaromatics, nitramine, nitrate esters

This paper describes the combination of a new, nonradioactive electron capture detector (ECD) with a microbore gas chromatography (GC) column to achieve fast separation times and very low detection limits for the analysis of nine common explosives and related compounds. Since the 1960s, standard ECD employing radioactive ³H and ⁶³Ni to generate free electrons have been used for the detection of explosives, either as stand alone units or in combination with GC (1–3). GC-ECDs are standard equipment in forensic laboratories that perform screening methods for explosives residues and are recommended for use in EPA method 8095 for the detection of explosives in water and soil. Despite advances in mass spectrometry (MS) and the advantage of MS for compound identification, ECDs are still actively used in current research projects because of their low detection limits, selectivity, ease of use, and reliability. Continuing the historic success of GC-ECD screening methods, several articles using ECDs for the detection of explosives exploring different sample introduction and preconcentration avenues have been published in recent months (4–8).

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In the 1990s, Wentworth and colleagues (9–11) developed a new type of ECD called the pulsed-discharge electron capture detector (PDECD). The main difference between a conventional ECD and the PDECD is the way in which thermal electrons are produced; the PDECD does not rely on a radioactive β -electron emission source, but instead uses electrical pulses to generate free electrons. Unlike radioactive ECDs, the process of electron generation in the PDECD is facilitated by bleeding a small amount of dopant gas such as CH₄ or Xe to a specific region in the detector. The nature of the gas used has been found to add to the selectivity of the detector toward certain functional groups (12,13). Several publications report the use of the PDECD for halogenated compounds, such as chlorinated pesticides (14,15), and for the detection of peroxyacetyl nitrate (PAN) (16), which is a common air pollutant. Two reviews have also been published on the working principles and general applications of the PDECD (13,17). All known reports show that, at a minimum, PDECDs meet the figures of merit achieved with standard ECDs. In some cases, the PDECD has even proved superior. Although radioactive ECDs have been used extensively for the postcolumn detection of explosives, no reports on the use of the PDECD for the analysis of explosives could be found in the extant literature.

Another important factor in the development of screening methods for the detection of explosives is analysis time. Rapid analysis times and high throughput is particularly important in situations where the analysis of a large number of samples, many of which may contain no analyte of interest, is required. Narrow-bore capillary columns show increased separation efficiency over wider diameter columns by reducing the effect of longitudinal diffusion and minimizing the resistance to mass transfer in the mobile

phase, as predicted by the Golay equation (18) and further studied by Gonnord (19). This improved separation efficiency and concomitant higher linear velocity lead to shorter residence times in the column and result in narrower peaks with larger relative intensities when compared with standard capillary columns (0.25 mm ID) (19). The elution of narrower peaks requires the use of detectors with low dead volumes and fast response times so that peaks are not artificially broadened (20). Because traditional radioactive ECDs require large cell volumes to quench the high-energy electrons from the β -emitter, they are poor candidates for combination with fast GC. However, because the PDECD is non-radioactive, it has a much smaller cell volume and therefore does not artificially broaden eluting peaks.

Separation times using conventional or wide-bore capillary columns reported for mixtures of explosives including nitrate esters, nitroaromatics, and RDX vary between 3.5 and 20 min depending on the application, number of components, instrumental conditions, and type of stationary phase used (3,21–27). Shortening the separation step by utilizing fast GC separations would enable more samples to be analyzed in a set time. An additional positive aspect of using fast GC for the separation of explosive compounds is that the short amount of time the explosives spend at elevated temperatures in the GC oven minimizes the degree of thermal degradation of the fragile explosives. Therefore, a fast analysis time can have the added benefit of minimizing sample losses to thermal degradation.

Methods

Chemicals

Nine individual explosive standards were acquired from Cerilliant Corporation (Round Rock, TX). The compounds were ethylene glycol dinitrate (EGDN), 4-nitrotoluene (4-NT), nitroglycerine (NG), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), and 2,4,6-trinitrophenylmethylnitramine (Tetryl). EGDN was obtained at a concentration of 100 $\mu\text{g}/\text{mL}$ in acetonitrile, while all others were at 1 mg/mL in acetonitrile. A stock solution was first prepared by mixing the nine compounds to an equal concentration of 10 $\mu\text{g}/\text{mL}$ each. This initial mixture was used to prepare working standards in the range of 0.5–500 ng/mL (ppb) using serial dilution with HPLC grade acetone (Fisher Scientific, Fairlawn, NJ). The standards were stored in silanized amber vials (Agilent Technologies, Wilmington, DE) at 4°C in between uses.

Instrumentation

A 6890 Gas Chromatograph (Agilent Technologies) equipped with an autosampler was fitted with the pulsed discharge detector (PDD) model D2 from Valco Instruments Co. Inc. (VICI) (Houston, TX). The PD-D2 detector was used in the electron capture mode with a bias current of 10 nA. Ultra-high purity (UHP) helium (Airgas, Parkersburg, WV) was further purified using a helium gas purifier, model HP2 (VICI), for use as the discharge gas at a flow rate of 26.5 mL/min . A dopant gas consisting of 3% xenon in helium mixture (American Gas Group, Toledo, OH) was introduced at a flow rate of 4 mL/min . Multivariate analysis was used to optimize the column length in the detector (102.5 mm) and the flow rates of the discharge gas, dopant gas and column effluent. The effects of detector temperature were studied independently, as presented in the results and discussion.

Operating Conditions

The injector port was kept at 180°C, detector at 200°C (see “Results”), and all injections were of 1 μL . Two capillary columns were tested in this study although only the results of the microbore column are reported in regards to limits of detection.

Column 1—RTX-5 from Restek Corporation (Bellefonte, PA), 8 m \times 0.25 mm ID \times 0.25 μm stationary phase with a 5:1 split ratio, 2 mL/min He carrier flow rate, and the following temperature program: 70°C initial (1 min), 30°C/min to 230°C final (1 min). Total separation time \sim 5.5 min.

Column 2—DB-5 from Agilent J&W Scientific (Folsom, CA), 5 m \times 0.1 mm ID \times 0.2 μm stationary phase with a split ratio of 25:1, 1.5 mL/min He carrier flow rate, and the following temperature program: 100°C initial (no hold), 60°C/min to 230°C final (1 min). Total separation time $<$ 2.5 min (Folsom, CA).

Results and Discussion

The initial task was to determine the optimal operating conditions of the PDECD for the detection of explosives. The compounds included in this study are expected to capture electrons in a nondissociative manner, as described by



This process is common for conjugated, aromatic, and nitro-containing compounds, as opposed to dissociative electron capture, which is more frequent for halogenated compounds (28). Nondissociative electron capture is known to be more effective at lower detector temperatures because of the larger population of molecules in the vibrational ground state. To test this hypothesis, a study was first performed to investigate the effect of detector temperature on the signal responses for the explosives mixture.

Figure 1 presents the effect of detector temperature on the intensity of the observed signal for three compounds: NG, a nitrate ester; TNT, a nitroaromatic; and RDX a nitramine, which typify the observations of the three classes of explosives in this study. Nitrate esters such as NG and the faster eluting compounds included in this study indeed capture electrons more effectively at lower temperatures and provide a maximum signal response at the lowest temperature studied of 150°C. On the other hand, the explosives with lower volatility, such as TNT, show a maximum signal response at a temperature around 200°C with inferior signal responses at higher or lower temperatures. The lower response of

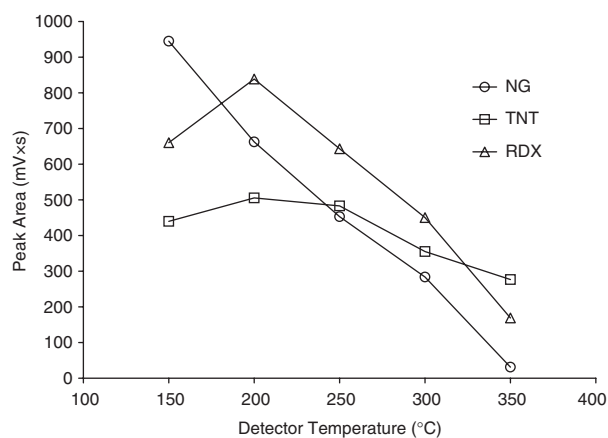


FIG. 1—Influence of detector temperature on signal intensity for different explosives. Data obtained using column 1 with conditions described in text using 1 μL injection of a 100 ng/mL standard mixture solution ($n = 3$).

the later-eluting compounds at 150°C can be explained by the possibility of condensation on the sapphire insulator inside the detector. Partial condensation/sublimation of the lower-volatility explosives causes the residence time in the detector to increase. This reduction in the instantaneous gas-phase concentration of the analytes causes peak broadening/tailing and therefore reduces the measured peak intensities. The curves observed for the less volatile explosives such as TNT and RDX almost certainly represent a nondissociative capture mechanism, but a certain threshold temperature must be reached in order to overcome the condensation/sublimation point of these compounds. A detector temperature of less than 150°C would presumably further improve the electron capturing abilities of the highly volatile and fragile compounds EGDN and NG, but would be detrimental to most of the other compounds in the mixture because of peak broadening effects. A compromised detector temperature of 200°C was therefore adapted as the optimal value for the detection of the entire set of compounds included in this study.

Figure 2 shows a typical chromatogram obtained for the separation of a mixture of the nine compounds included in this study and reveals that a complete separation is achieved in less than 2 min and 15 sec. The efficiency of the separation, despite the short column (5 m), allows the elution time of each compound to provide an adequate method of identification for each explosive. For application as a screening method, a time window of 1 sec (1.5 sec for Tetryl) representing three standard deviations of the retention time ($n = 30$) could be set around each peak to trigger an alarm in the case of a possible positive result. If one wanted to analyze relatively uncomplicated samples, an even shorter column with concomitant faster elution times could be used. The low capacity offered by the narrow bore column easily leads to swamping of the first eluting peaks (EGDN, 4-NT) by the solvent peak as well as broadening of the later eluting peaks when used in splitless mode. Therefore, split injection was used to eliminate the problem of solvent overloading. Split injection is usually not the preferred choice of injection when used for quantification purposes, but, as a screening procedure, still permits trace analysis at levels that do not require additional preconcentration steps beyond normal. The high oven ramping rate used (60°C/min) also helped in mobilizing the analytes through the column in the shortest possible time, thereby minimizing longitudinal diffusion and thermal degradation of the explosives on the column.

The main reasons for using an ECD for the analysis of explosives are threefold: (1) low detection limits; (2) selectivity of electron-capturing compounds over nonelectron-capturing back-

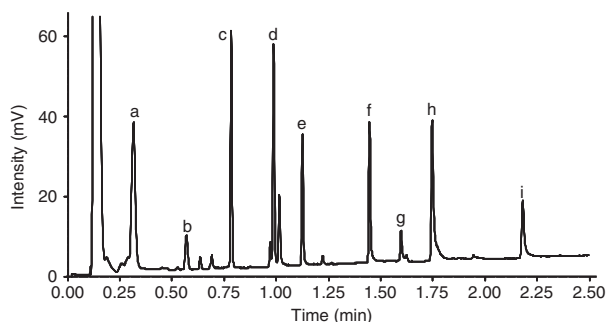


FIG. 2—Typical chromatogram of a standard run on column 2 with the conditions described in the text (25 ng/mL, 1 pg on-column). The peaks correspond to the following in order: (a) ethylene glycol dinitrate; (b) 4-nitrotoluene; (c) nitroglycerine; (d) 2,6-dinitrotoluene; (e) 2,4-dinitrotoluene; (f) trinitrotoluene; (g) pentaerythritol tetranitrate; (h) cyclotrimethylenetrinitramine; and (i) 2,4,6-trinitrophenylmethyltrinitramine.

ground species; (3) low cost and relative ease of use compared to more elaborate detectors such as mass spectrometers. Table 1 shows the detection limits, linear ranges, and least-squares regression analysis values obtained using the fast GC-PDECD method. The results compare favorably with the values presented by Douse (3) with at least an order of magnitude improvement in detection limits. The limits of detection (LOD) values are reported as three times the signal-to-noise (S/N) ratio and the linear range begins at the limit of quantification (LOQ) established at 10 times S/N. The amounts “on-column” reported take into account the split ratio of 25:1 applied in the injection port. LODs in the low femtogram range obtained with this fast GC-PDECD method are thought to be among the lowest reported. Yip (29) reported detection limits as low as 10 fg for a method optimized for EGDN and NG. In methods developed and applied to real samples such as water or soil extracts, limits of detection are usually a few orders of magnitude larger, primarily due to the increase in noise caused by interfering species. However, using a μ ECD (Agilent Technologies), Walsh (25) reported detection limits for explosives in soil matrices in the femtogram to low picogram levels on-column after extraction. These values are also included in Table 1. Bishop (26) also reported similar values from soil and water samples. The application of fast GC-PDECD to aqueous or soil samples has not been performed at this time.

With the exception of PETN and EGDN, linear ranges for the nine explosives studied span at least two orders of magnitude in concentration. Linear regression values of R^2 are in excess of 0.98 for all the explosives studied. The PDECD is known to saturate and behave in a nonlinear fashion at high concentrations, and this application is no exception. The saturation of the detector at high instantaneous concentrations is not considered to be too detrimental to its success as a screening method. In fact, conventional ECDs display similar behavior and they have performed quite satisfactorily as screening detectors until now.

It is important to mention that all the compounds, especially PETN, are sensitive to degradation in the injector port. Therefore, it was necessary to maintain a clean injector port and a clean, deactivated liner to obtain the lowest possible detection limits. Cyclotetramethylenetetranitramine (HMX) was originally included in this work, but was eventually abandoned because it is much less volatile than the other explosives used in this study. A higher injector port temperature is required to volatilize HMX, but such a modification was greatly detrimental to the signal intensities of EGDN, NG, and PETN, which are all prone to thermal degradation. In principle, a temperature-programmable injector port could be used to allow HMX to volatilize in the injector port after the other compounds have left the injector port, hence eliminating the problem of thermal degradation of the other components. This adaptation could improve the survival probability and chromatographic performance of the different compounds, but has not been demonstrated at this time.

The results presented here clearly demonstrate that the PDECD is a suitable detector for combination with fast GC. The main improvements described are the combination of the PDECD with a microbore column and the reduction of the analysis time to less than 2.5 min for the mixtures of nine explosives compounds studied. The detection limits for explosive compounds by ECD is strongly dependent on many factors including the injection port and detector temperatures, which tend to affect the survival and chromatographic performance more than the electron-capturing response in the detector. A potential advantage yet to be examined for the PDECD is that the distribution of kinetic energy of the electrons in the source can be controlled to some extent by

TABLE 1—Figures of merit and comparative values for the analysis explosives.

Compounds	Literature Values (pg on-column)		Limits of Detection (pg on-column) [†]	Linear Range (pg on-column)	R ² (n = 3)
	Douse (3)	Walsh (25)*			
EGDN	1	—	0.036 [‡]	0.120–4.00	0.9913
NG	5	2.6	0.006	0.020–4.00	0.9851
PETN	30	3.2	0.072	0.240–4.00	0.9977 [§]
4-NT	—	2.0	0.019	0.064–4.00	0.9971
2,6-DNT	—	0.138	0.006 [‡]	0.020–4.00	0.9891
2,4-DNT	10	0.138	0.006	0.020–4.00	0.9854
TNT	5	0.090	0.005	0.016–4.00	0.9858
Tetryl	40	4.0	0.018	0.060–6.00	0.9931
RDX	10	0.680	0.009	0.030–4.00	0.9972

*Values calculated from the method detection limit given and the experimental protocol.

[†]Determined as the smallest value producing a peak height equal to $3 \times S/N$.

[‡]Both peaks were shoulders on impurity peaks, which increased the detection limits.

[§]The linear regression was not forced to zero.

EGDN, ethylene glycol dinitrate; NG, nitroglycerine; PETN, pentaerythritol tetranitrate; 4-NT, 4-nitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; 2,4-DNT, 2,4-dinitrotoluene; TNT, trinitrotoluene; Tetryl, 2,4,6-trinitrophenylmethyl nitramine; RDX, cyclotrimethylenetrinitramine.

changing the nature of the dopant gas. This capability might allow improved selectivity of nitro-containing compounds over halogenated compounds, which could eliminate some of the interferences in the study of real life samples. The sensitivity of the detector for the explosives might also be improved in a similar manner.

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