



Chemiluminescence detection systems for the analysis of explosives

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Abstract

The objective of this paper is to provide a comprehensive review of explosive detection by chemiluminescence (CL) through a summary of the relevant literature in the last 5 years and a synopsis of current research topics and developments. The literature reviewed is specially addressed for the detection of a group of high explosives, containing nitrogen compounds. Most explosives compounds contain either nitro or nitrate groups which make possible their detection and quantification using detection systems based on chemiluminescent reactions. Practical considerations and experimental requirements are indicated, and the possibilities and limitations are evaluated.

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1. Introduction

There is a continuing need for improved analytical methods to yield better sensitivity in the detection of trace level compounds of forensic interest. In recent years identification and quantification of traces of high explosives has constituted an emerging and important topic of interest due to their relevant role in many areas concerning the security and

Abbreviations: CL, chemiluminescence; DNPM, dinitrosopentamethylenetetramine; 2,4-DNT, 2,4-dinitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; EGND, ethylene glycol dinitrate; FID, flame ionization detector; FNT, 2-fluoro-5-nitrotoluene; GC, gas chromatography; HPLC, high performance liquid chromatography; IR, infrared; Keto-RDX, 1,3,5-trinitro-2-oxo-1,3,5-triazacyclo-hexane; MS, mass spectrometry; MT, musk tibetine; 2-NT, 2-nitrotoluene; 3-NT, 3-nitrotoluene; 4-NT, 4-nitrotoluene; NG, nitroglycerine; PETN, pentaerythryl tetranitrate; RDX, 1,3,5-trinitro-1,3,5-triazacyclo-hexane; SFE, supercritical fluid extraction; SGC, solvating gas chromatography; TEA, thermal energy analyzer; 2,4,6-TNT, 2,4,6-trinitrotoluene; 2-NN, 2-nitronphthalene; TNB, 1,3,5-trinitrobenzene

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health of the population, including environmental and toxicological effects, land mine detection, aviation security or the prevention of terrorist attacks. Recent books and extensive reviews confirm this observation [1–3]. Reid Asbury et al. [4] have pointed out the importance of trace analysis of explosives in two different fields: one, is the threat of an illegal use of these compounds, which has led to major efforts in developing explosive detection systems, and the other is a growing concern about the health risks associated with the release of explosives from military sites and former ammunition plants into the environment.

Governments and industries efforts are addressed into the same direction, to find ways of improving the current technologies as well as the development of new methods which allow speed, selective and sensitive detection, enough to find trace amounts of explosives, commonly in complex matrices.

Explosive detection techniques can be broadly classified into two categories: bulk detection and trace detection. In bulk detection, a macroscopic mass of the explosive material is detected directly, usually by viewing images made by X-ray scanners or similar equipment. In trace detection, the explosive is detected by chemical identification of microscopic residues of explosive compound. These residues can be in either or both of two forms: vapor and particulate [5]. Vapor detectors examine the vapor emanating from the explosives (some explosives have very low vapor pressure so the detection system must be very sensitive) and particulate refers to the amount of microscope residues of explosives that could be present on individuals or material which have been through contamination. Different kinds of methods for explosive analysis include thermal methods, ion mobility spectrometry, gas chromatograph–mass spectrometer, nuclear quadrupole resonance, capillary electrophoresis or X-ray systems, among others. Nevertheless, since explosive residues have to be determined in complex matrices, such as soil or solid surfaces, a separation method prior to the identification is usually necessary. In this sense, chromatographic methods constitute one of the more important tools for this purpose. Kolla [6] has described the potential of several chromatographic techniques (gas chromatography, high performance liquid chromatography and ion chromatography) to the determination of traces of explosives. The author reported that the most important aspect is the combination of the chromatographic techniques with selective detection methods. Gas chromatography (GC) with different detection systems: electron-capture detector [7], mass spectroscopy [8] or chemiluminescence (CL) appeared frequently in the literature in relation to explosive determination.

2. Objectives of this review

The purpose of this paper is to evaluate from the literature reviewed the role of chemiluminescence providing a detection system of choice for explosive analysis, specially for the detection of an ample group of high explosives, those nitrogen-containing compounds. Gas chromatography with chemiluminescence detection presents good selectivity for this topic and has become as mobile and hand-held explosive detector a method of choice in a number of applications such as airport luggage or forensic laboratories. This work has been structured in three parts. The first section is dedicated to established the properties

of chemiluminescence in relation to explosives. The second and the third sections come right into the category of the chemiluminescence as detection system for explosives in environmental monitoring and security.

3. Chemiluminescence and explosives

Chemiluminescence can be defined as the characteristic emission of radiation from a molecule, atom or effective fluorophore, in an excited electronic state, produced in an exothermic chemical reaction. It can take place in the gas, liquid and solid phase. In recent years, CL has become a powerful analytical tool for selective and sensitive detection of chemical species. CL applications in analytical chemistry have numerous advantages such as high sensitivity, a wide linear range, simple and inexpensive instrumentation, and considerable reduction of the background noise. On the other hand, the lack of selectivity (one of the most important disadvantages) is overlooked by coupling CL with separation methods. There are numerous reports supporting the importance of chemiluminescent methods in analytical chemistry, including a great variety of fields such as food [9], biomedical [10], anyway as detection system [11].

Most explosives compounds contain either nitro (NO_2) or nitrate (NO_3) groups, a fact which is exploited by detectors based on chemiluminescence principle, generally coupled to a front-end gas chromatograph [12]. A list of the most widely used nitrogen containing high explosive determined by chemiluminescence is summarized in Table 1. Though some important families of non-nitro-containing explosives, such as, alkyl/acyl peroxides and cyclic peroxides would be excluded [13], an important method for the detection of trace levels of explosives is the thermal energy analyzer (TEA) [14]. TEA coupled to GC was developed at first by Fine and Rounbehler [15]. This detector responds specifically to nitro and nitroso compounds. Briefly, the fundamental operating principle is based upon the chemiluminescent reaction between nitric oxide and ozone. Nitrogen containing components are

Table 1
List of commonly used high explosives analyzed by chemiluminescence (TEA)

| Compound name | Abbreviation | Class | CAS no. | Vapor pressure (high, moderate, low) |
|--------------------------------|--------------|---------------|----------|--------------------------------------|
| Cyclotrimethylene trinitramine | RDX | Nitramine | 121-82-4 | Low |
| 2-Nitrotoluene | 2-NT | Nitroaromatic | 88-72-2 | High |
| 3-Nitrotoluene | 3-NT | Nitroaromatic | 99-08-1 | High |
| 4-Nitrotoluene | 4-NT | Nitroaromatic | 99-99-0 | High |
| 2,4-Dinitrotoluene | 2,4-DNT | Nitroaromatic | 121-14-2 | High |
| 2,6-Dinitrotoluene | 2,6-DNT | Nitroaromatic | 606-20-2 | Very low |
| 2,4,6-Trinitrotoluene | TNT | Nitroaromatic | 118-96-7 | Moderate–low |
| Nitroglycerine | NG | Nitrate ester | 55-63-0 | High |
| Pentaerythryl tetranitrate | PETN | Nitrate ester | 78-11-5 | Low |
| Ethylene glycol dinitrate | EGND | Nitrate ester | 628-96-6 | High |

pyrolyzed at high temperature and nitrogen monoxide formed can be determined using the chemiluminescent reaction between this and ozone, which results in light emission, detected by using a photomultiplier tube. The reaction can be schematized as follow [16]:



4. Detection and determination of explosives with GC–TEA

Chemiluminescence is specially used for trace detection of explosives in combination with chromatographic techniques. Kolla [6] make use of TEA as a chemiluminescence detector for GC. A polymethylphenyl (5%) siloxane (DB-5) is used in order to enhance the selectivity of the column for the nitro compounds. Despite the specify for nitro and nitroso compounds the author reported the necessity of confirmation by another method, since in some samples, in addition to the explosives constituents, many unidentified peaks appear in the chromatogram. GC with mass spectroscopy detection system or a simple column change to a stationary phase of different polarity in the GC–TEA system may render this confirmation possible as reported by the author. Nevertheless, the author has reported that the mass spectrometer is well suited for the determination of nitroaromatics, specially with negative chemical ionization, but problems may arise in the identification of nitrate esters or 1,3,5-trinitro-1,3,5-triazacyclo-hexane (RDX) in complex matrices because the spectra are often not unequivocal if there is co-elution with others substances. In addition, GC–MS is usually use for other analytical problems and the system cannot be modified each time for the trace analysis of explosive. TEA responds specifically to nitro and nitroso compounds and it is introduced as an alternative. Other GC detectors with lower selectivity such as the electron-capture detector can only be used if the matrix is relatively clean.

Since 1989, gas chromatography with selective chemiluminescence detection, TEA, has been adopted by the Forensic Explosives Laboratory (Kent, UK) as its principle technique for explosive trace analysis. A system of contamination prevention procedures (inner and outer) incorporating protective measures was implemented, with progressive improvements, for about 8 years. The sampling process usually used was cotton wool swab sampling for explosive traces. Likewise GC with mass spectrometry (MS) detection for confirmation is commonly used by the authors. Twelve years later, using GC–TEA analysis, the authors have summarized the results from approximately 8 years of tests [17].

These authors usually carry out the identification of an explosive's trace by GC–TEA based upon a comparison of relative retention times with those of explosives in a standard solution analyzed both before and after the sample. A mixture of two retention references markers is co-injected with every sample and standard solution, and retention times are measured relative to these. The markers commonly used by the authors to provide reference peaks in gas chromatographic analyses were 2-fluoro-5-nitrotoluene (FNT) and the fragrance musk tibetine (2,6-dinitro-3,4,5-trimethyl-*tert*-butylbenzene, MT). A solution of both in ethyl acetate solvent. Solutions of common explosives (TEA standard solutions) are used for retention time comparisons. Likewise, three different types of columns are usually used for GC analysis in all the papers reviewed: dimethylsiloxane (type BP1, Scientific Glass Engineering, Ringwood, Australia); 5% diphenyl-dimethylsiloxane (SGE type

BP5) and 7% cyanopropyl-, 7% phenyl-, 1% vinyl-dimethylsiloxane (type CPSIL-19CB, Chrompack, Middelburg, The Netherlands; BP5).

Hiley [18] reports that the GC–TEA systems will detect at worst 50 pg per 0.8 μl injection of the major explosives which corresponds to about 6 ng in a 100 μl sample. Likewise, the same GC–TEA system (and confirmation by GC–MS) has been used by Hiley [19] to evidence the presence of dinitrosopentamethylenetetramine (DNPMT), a compound widely used as a chemical blowing agent in the manufacture of foamed polymers. This produces a strong response in GC–TEA analyses which might incorrectly be taken as indicative of the presence of common explosives such as pentaerythryl tetranitrate (PETN) or cyclotrimethylene trinitramine (RDX). For GC–TEA analysis, a mixed standard solution (TEA standard) containing low concentrations (0.1–0.75 $\text{ng } \mu\text{l}^{-1}$) of the common high explosives, a solution (mixed reference) containing 5 $\text{ng } \mu\text{l}^{-1}$ each of FNT and MT in ethyl acetate solvent and a solution containing approximately 1 $\text{ng } \mu\text{l}^{-1}$ of DNPMT into ethyl acetate were used. The author pointed out that DNPMT produced a strong response in GC–TEA analyses and a similar problem could appear in other instruments using the same nitric oxide/ozone chemiluminescence detection mechanism.

Continuing their investigations, similar conditions for GC–TEA analysis have been reported by Crowson et al. [20] and Warren et al. [21] to determine the background levels of explosive traces in public places (taxis, buses, underground trains, underground stations, passenger aircraft, airport, and, etc.) and to describe a novel method for the simultaneous recovery and extraction of forensic organic and inorganic trace explosive samples, respectively. The detectors were Thermedics TEA model 610 detectors modified to minimize dead volume. The instrument settings were as follow: pyrolysis oven temperature (750 $^{\circ}\text{C}$), interface oven temperature (250 $^{\circ}\text{C}$), reaction chamber pressure reading: 0.5–2 mmHg (70–270 Pa). Thermoelectric cooler temperature reading: –5 to –10 $^{\circ}\text{C}$. The detection limits reported by Warren et al. [21] for GC–TEA analysis of the investigated explosives used in the TEA standard solution (2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), nitroglycerine (NG), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 3,4-dinitrotoluene (3,4-DNT), 2,4,6-trinitrotoluene (2,4,6-TNT), PETN and RDX) were in the range 1–10 ng per 100 μl of sample solution.

TEA has also been used by Francis et al. [22] as a detection method in chromatography combined with supercritical fluid extraction (SFE) to analyze explosives in soil samples. The authors report that the coupling of SFE and GC with a thermal desorption modulator (TDM) interface allows the rapid analysis (10 min) of relatively volatile and thermally stable nitro compounds from solid matrices and it can be used for screening small samples in short periods of times. Use of organic modifiers (15% acetone) was necessary for the extraction of various explosives, without affecting the performance of the system. The explosive standards included: 2,4-DNT, 2-nitronaphthalene (2-NN), 2,6-DNT, 1-nitropyrene (1-NP), 1,3,5-trinitrobenzene (TNB), NG, PETN, TNT and RDX. Two hundred milligrams of soil samples containing 24 ppb of 2,4-dinitrotoluene (results obtained by GC–MS and SCF–MS) were analyzed by this method and gave a 2,4-DNT peak at a signal-to-noise ratio of 27:1. The minimum detectable quantity for the analysis of 2,4-DNT was found to be 2.6 ppb in soil sample.

Solvating gas chromatography (SGC) with chemiluminescence detection (TEA) has been used by Bowerbank et al. [23] for the determination of nitroglycerine (NG) and other

nitrogen-containing explosives including 2,6-dinitrotoluene, 2,4-DNT, 2,4,6-trinitrotoluene, and PETN. Though SGC utilizes packed capillary columns the solvating properties of the mobile phase in SGC allows fast separations under SGC conditions. The transfer line between the SGC column and the TEA pyrolyzer unit consisted of a 50 cm length of large bore (530 μm i.d. \times 700 μm o.d.) fused-silica tubing. The authors compared the SGC–TEA response versus thus obtained using SGC with flame ionization detection (FID). For this purpose a standard NG sample containing 0.40 $\mu\text{g ml}^{-1}$ was introduced, which corresponds to ~ 6 pg on-column after taking into consideration the split ratio (12:1). Both systems used the same column, split line, inlet pressure and temperature. The authors reported that TEA gave a strong NG peak with $S/N \sim 32:1$, while FID failed to detect the compound. The authors reported on the benefit in coupling SGC to the TEA as follow: the carbon dioxide mobile phase does not give rise to added background noise. The limit of detection for the TEA is not increased since it does not contain nitro or nitroso functional groups. Furthermore, it is possible to use certain organic modifiers in the carbon dioxide mobile phase using TEA, but not with FID due to a significant rise in baseline signal.

Several tests including chemiluminescence have been carried out by Östmark et al. [24] for studying the thermal decomposition and thermal stability of 1,3,5-trinitro-2-oxo-1,3,5-triazacyclo-hexane (Keto-RDX), which is very similar to RDX, one of the most commonly used high explosives, differing only in the incorporation of a carbonyl group into the six-membered ring. The analysis of gases evolved during decomposition of both mentioned products showed the presence of NO, made possible by the use of chemiluminescence method based on ozone–NO reaction. The authors reported that the measurements should be regarded as preliminary, not final results since the method was developed for propellants, and was not fully tested on high explosives. The thermal stability, activation energy ($E_a = 140 \text{ kJ mol}^{-1}$), and frequency factor ($K_0 = 9 \times 10^9 \text{ s}^{-1}$) in the temperature interval 90–120 $^\circ\text{C}$ were measured using chemiluminescence. From the CL experiments the authors reported that Keto-RDX is much more thermally unstable than RDX.

5. Chemiluminescence as detection technology in security

The security of civilians against terrorist activities or the need for reducing the number of people killed or disabled by landmines are unfortunately only some of the arguments which underline the need for developing detection technologies to screen explosives. The detection system has to comply with some requirements, so Mauren Rouhi [25] points out that the detection systems in aviation security must be sensitive enough to find small amounts hidden in complex matrices. They also must be specific, able to discriminate between threatening and benign materials, and not generate too many false alarms, and because of the number of baggage pieces that must be screened, they must do the job quickly. Chemiluminescence has been cited in several reports as one of the technologies for this purpose. Gross and Bruschini [26] have mentioned CL as a valid alternative used as explosive vapor sensors in the chemical industry or in airports, though they reported on some disadvantages such as low sensibility, too slow or too large to be use in fields applications.

A patent based on a high speed GC–chemiluminescence detector has been reported [27] as a non-intrusive way of screening people for the presence of clandestinely concealed

explosives, weapons, or drugs for aviation security. A sensitivity as low as parts per trillion is reported. The author included it into the category of trace detection technologies which are based on trace-detection sample air or the material from vapors or particles from clothing or bodies of individuals. The patent included the development of a walk-in, walk-out booth, containing suction vents that horizontally draw in a 'large volume' of air from around a human subject who enters the booth.

GC–CL systems (EGIS II[®] and EGIS III[®] explosive detection system) have been selected by different governments and institutions for explosive trace detection. So, the EGIS trace detector, introduced in 1989 by Thermo Electron Corporation [28] has become the trace detection standard throughout Europe for airport screening of bags and electronic items, likewise it has been deployed to screen British Rail freight and passengers traveling through the Channel Tunnel or selected for FBI to search explosives at the 2002 Olympic Games. Recently, the Germany's Ministry of Interior has chosen the EGIS III[®] system as standard for airport security [29]. The lower detectable limits reported for EGIS II[®] and EGIS III[®] [30] are 300 and 100 pg, respectively.

6. Conclusions

The revised papers in this article illustrate that chemiluminescence detection systems are suitable for explosive detection. The literature found is not very extensive but illustrative enough about CL detectors to play an important role in this area. The papers reviewed shows the preponderance of gas chromatography as a separation technique when combined with CL in the fields of explosives. However, several authors have pointed out the necessity of a second system, usually GC–MS with the aim of confirmation. Due to the nitrogen compound characteristics of most high explosives the CL reaction between ozone and NO is amply used. Some commercial systems are today available and constitute a reality since they are implanted as security systems in different kinds of installations such as airports, forensic laboratories, etc. We suggest that the current literature when reviewed allows us to conclude that chemiluminescence constitute a real alternative for the explosive analysis.

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