Available online at www.sciencedirect.com
ScienceDirect
Journal of Chromatography A, 1154 (2007) 174–181
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Use of porous graphitic carbon for the analysis of nitrate ester, nitramine and nitroaromatic explosives and by-products by liquid chromatography–atmospheric pressure chemical ionisation-mass spectrometry

Romain Tachon [a], Valérie Pichon [b,*], Martine Barbe Le Borgne [a], Jean-Jacques Minet [a]

[a] *Laboratoire Central de la Préfecture de Police, 39 bis rue de Dantzig, 75015 Paris, France*
[b] *Laboratoire Environnement et Chimie Analytique (UMR CNRS 7121), École Supérieure de Physique et Chimie Industrielles, 10 rue Vauquelin, 75231 Paris, France*

Received 17 October 2006; received in revised form 16 March 2007; accepted 19 March 2007
Available online 21 March 2007

Abstract

A new LC/MS method was developed for the analysis of sixteen different analytes including the most common organic explosives encountered in forensic investigations. The separation was achieved using a porous graphitic carbon (PGC) column with a binary gradient elution. Molecular modeling suggested a possible interpretation for the elution order of explosive compounds on PGC. The introduction of ammonium formate in the mobile phase resulted in the formation of characteristic adduct ions thus enhancing the mass spectrometric detection of nitrate ester and nitramine compounds. Atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) were compared in terms of sensitivity. The final LC/APCI-MS method allowed easy identification of investigated compounds with limits of detection ranging from 0.04 to 1.06 ng/μl. The analysis of simulated forensic samples confirmed the performance of the method.

Keywords: Explosives; Nitrate esters; Nitramines; Nitroaromatics; LC/MS; APCI; ESI; Porous graphitic carbon

1. Introduction

In recent years, increased terrorist activity has generated a need for analytical methods that can accurately identify explosives. The analysis of postblast residues is essential for the confirmation of the type of bomb used in terrorist attacks. But this task can be particularly challenging when the explosive materials left on the bombing site are present at trace level in various and complex matrices. Therefore, both selective and sensitive analytical methods are required. Gas chromatography with either mass spectrometry or electron capture detection is a well established technique for the analysis of explosive compounds but suffers from a lack of sensitivity for the more thermally labile molecules which decompose in either the heated injector or column [1–3]. The combination of the separation power of liquid chromatography (LC) with the identification capability of mass spectrometry (MS) has resulted in a powerful analytical system, which is ideally suited for the analysis of organic explosives. Hence, LC/MS has been preferred to other techniques.

Organic explosives belong to various chemical classes, including nitrate esters, nitramines and nitroaromatics, and have very different physical properties, which make their analysis by a single method difficult. In several studies [4–14] they have been detected by electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mass spectrometry. However, these studies were limited to specific compounds and there is still a demand for methods that can provide simultaneous analysis of several classes of explosives. Negative ion mode is most adapted to the detection of explosive compounds with electron-withdrawing nitro groups. Commonly, nitroaromatic compounds are detected as molecular ions by APCI mass spectrometry [4,5] whereas nitramine and nitrate ester compounds are detected as adduct ions by ESI mass spectrometry [5–10]. The introduction of particular additives in the mobile phase

* Corresponding author. Tel.: +33 1 40 79 47 72; fax: +33 1 40 79 47 76.
E-mail address: valerie.pichon@espci.fr (V. Pichon).

0021-9673/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2007.03.059

presents the advantage to promote the formation of characteristic adduct ions, which improves sensitivity and allow unambiguous identification of the explosive compounds [9,10].

In addition to its nature, it is important to know the origin of an explosive. Various amounts of by-products can be found in an explosive, depending on the way it was manufactured. Isomers of nitroaromatic compounds, which are typical resulting by-products, cannot be easily analyzed on classical supports like C18 bonded silica because of their similar behavior on this type of stationary phase [4,15,16]. Tandem mass spectrometry may help in identifying different isomers of nitroaromatic compounds [14] but cannot always success to determine their ratios. That is why, they should be properly separated before MS detection. A way to solve this problem is the use of porous graphitic carbon (PGC). This medium is composed of flat sheets of hexagonally arranged carbon atoms leading to unique characteristics [17]. PGC is stable through the entire pH range and is not affected by aggressive mobile phase. Its singular retentive properties provide solution for several problematic separations observed on classical reversed phase column [18–21]. Retention on PGC is governed by two types of mechanism: adsorption on the flat graphite surface depending on the shape of the molecule and charge induced interaction between the polar groups of the molecule and the polarizable graphite surface. This unique mechanism of interaction allow retention of very polar compounds and discrimination of geometric isomers. Recently, some authors reported the use of PGC for the separation of nitroaromatic compounds [22,23]. The simultaneous analysis of nitrate ester, nitramine and nitroaromatic compounds by LC/MS has also been described [24] but PGC is used with rather complicated chromatographic conditions and sensitivity needs to be improved for nitrate ester compounds.

The present study describes the development of a simple method for the forensic analysis of most common explosive compounds and by-products among nitrate esters, nitramines and nitroaromatics. It consists in LC separation using PGC followed by MS detection with negative ion adduct formation. Ionization was studied when using ESI and APCI interfaces. Selectivity and sensitivity were evaluated and simulated samples were analyzed to confirm the performances of the method.

2. Experimental

2.1. Reagents and standards

Acetonitrile, methanol and isopropanol were HPLC grade solvents purchased from VWR (Fontenay Sous Bois, France). Water was purified with a Milli-Q system from Millipore (Bedford, MA, USA). Ammonium formate 97% was purchased from Avocado (La Tour Du Pin, France). Liquid nitrogen and helium were ultrapure grade gases supplied by Air Liquide (Nanterre, France).

Three groups of explosives were investigated: (1) *nitrate ester compounds*: nitroglycerine (NG), pentaerythritol tetranitrate (PETN); (2) *nitramine compounds*: 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), (3) *nitroaromatic compounds*: 2,4,6,*N*-tetranitro-*N*-methylaniline (Tetryl), 2,4,6-trinitrotoluene (TNT), 2,3-dinitrotoluene (2,3-DNT), 2,4-dinitrotoluene (2,4-DNT), 2,5-dinitrotoluene (2,5-DNT), 2,6-dinitrotoluene (2,6-DNT), 3,4-dinitrotoluene (3,4-DNT), 3,5-dinitrotoluene (3,5-DNT), 1,3,5-trinitrobenzene (TNB), 1,2-dinitrobenzene (1,2-DNB), 1,3-dinitrobenzene (1,3-DNB), 1,4-dinitrobenzene (1,4-DNB). All standards were purchased from Restek (Evry, France) except 2,5-DNT, 3,4-DNT and 3,5-DNT from LGC Promochem (Molsheim, France) and 2,3-DNT, 1,2-DNB and 1,4-DNB from Sigma–Aldrich (Saint Quentin Fallavier, France). A stock solution at 1000 ng/μl was prepared by dissolving solid compounds in acetonitrile. Standard mixtures at concentration levels ranging from 0.2 to 20 ng/μl were prepared by diluting the stock solutions with acetonitrile. All solutions were stored at 4 °C. Because of their potential carcinogenicity and mutagenicity, nitramine and nitroaromatic compounds are hazardous to human health and should be handled with care.

2.2. Molecular modeling

Molecular modeling of investigated compounds was performed using the Hyperchem 6.01 software package from Hypercube (Gainesville, FL, USA). The lowest energy conformation was evaluated using consecutively molecular mechanics (AMBER) and semi-empirical (AM1) optimization. Electronic distribution was then calculated for nitroaromatic compounds.

2.3. Simulated samples preparation

Simulated samples were prepared in the laboratory by extracting commercial motor oil with methanol. About 20 ml of commercial motor oil was added to a 100 ml flask along with 50 ml of methanol. The mixture was stirred overnight. After the stirrer was turned off, the phases were allowed to separate. The methanol phase was removed and spiked with investigated compounds at 10 ng/μl concentration level.

2.4. Instrumental conditions

The LC system was composed of a Surveyor LC pump and autosampler from Thermo Electron (San Jose, CA, USA). A C18 Supelcosil ABZ+ column (150 mm × 2.1 mm I.D., 5 μm) from Sigma–Aldrich was used during method development but the separation of all the analytes, except 2,6-DNT and 3,4-DNT, was achieved with a binary gradient on a PGC Hypercarb column (100 mm × 2.1 mm I.D., 5 μm) from Thermo Electron. Solvent A was a mixture of ammonium formate solution and acetonitrile (70:30, v/v) and solvent B a mixture of acetonitrile and isopropanol (40:60, v/v). The concentration of the ammonium formate solution was 1 mM. The binary gradient conditions used on the PGC column were as follows: the percentage of solvent B was raised linearly from 10 to 12% over 2 min, then to 60% over 12 min and finally to 90% over 30 min. The mobile phase was then returned to its original composition over 1 min and the column was equilibrated for 15 min. Mobile phase flow rate was set at 200 μl/min, column temperature at 70 °C and injection volume at 10 μl.