Talanta 161 (2016) 219–227

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Progressing the analysis of Improvised Explosive Devices: Comparative study for trace detection of explosive residues in handprints by Raman spectroscopy and liquid chromatography

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ARTICLE INFO

Article history:
Received 12 February 2016
Received in revised form
19 May 2016
Accepted 21 May 2016
Available online 2 August 2016

Keywords:
Improvised Explosive Devices (IEDs)
Handprints
Black powder
Dynamite
Raman spectroscopy
Liquid chromatography

ABSTRACT

Concerning the dreadful global threat of terrorist attacks, the detection of explosive residues in biological traces and marks is a current need in both forensics and homeland security. This study examines the potential of Raman microscopy in comparison to liquid chromatography (ion chromatography (IC) and reversed-phase high performance liquid chromatography (RP-HPLC)) to detect, identify and quantify residues in human handmarks of explosives and energetic salts commonly used to manufacture Improvised Explosive Devices (IEDs) including dynamite, ammonium nitrate, single- and double-smokeless gunpowders and black powder. Dynamite, ammonium nitrate and black powder were detected through the identification of the energetic salts by Raman spectroscopy, their respective anions by IC, and organic components by RP-HPLC. Smokeless gunpowders were not detected, either by Raman spectroscopy or the two liquid chromatography techniques. Several aspects of handprint collection, sample treatment and a critical comparison of the identification of compounds by both techniques are discussed. Raman microscopy and liquid chromatography were shown to be complementary to one another offering more comprehensive information for trace explosives analysis.

1. Introduction

Terrorist events have increased in frequency during the last two decades and represent an on-going and extremely harmful global threat [1–7]. Terrorist attacks often involve the use of explosives; compounds which have a great destructive power even in small quantities. Currently, there is a growing trend towards using home-made devices called Improvised Explosive Devices (IEDs) [1–7]. Dreadfully, IEDs have been widely used in recent years in different terrorist attacks including those in Madrid (2004), London (2005), Norway (2011), Boston (2013), Santiago de Chile (2014), Paris (2015), Nigeria, Ankara, Brussels and Pakistan (2016) in addition to war zones as Afghanistan, Syria and Iraq where IEDs are constantly used. IEDs are manually manufactured explosive devices, which consist of a variety of elements arranged in a specific way to produce an explosion. Since their destructive effectiveness lies in being unnoticed, IEDs often have varied design and appearance. Thereby, IEDs often evade being neutralized before an explosive attack. IEDs have become an ideal weapon used by terrorists for several reasons, including their low cost, ease of manufacture and subsequent use and difficulty to be detected [1–7]. Therefore, their detection must be tackled as a matter of urgency to avoid such atrocities and guarantee the security of citizens.

Although IEDs can be manufactured from a large variety of explosive materials including military, commercial, or home-made explosives, they usually contain explosive mixtures based on inorganic energetic oxidants including nitrate, chlorate or perchlorate salts [3,7–9]. In fact, these explosive mixtures are used to manufacture commercial explosives such as dynamites, black powders and other propellants whose purchase is widely available [3]. In addition, the manufacture of home-made mixtures combining any of these oxidant salts (ammonium nitrate, potassium nitrate, potassium chlorate, potassium perchlorate, etc.) with any fuel (petrol, diesel, sugar, charcoal, flour, etc.) is quite simple [3]. In

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http://dx.doi.org/10.1016/j.talanta.2016.05.057
0039-9140/

addition, they are even more freely available than commercial explosives. Ammonium nitrate is used as a fertilizer, but in combination with certain fuels may produce explosive compounds such as dynamite, ammonium nitrate/fuel oil (ANFO) and other nitrate-based explosives [3]. Potassium nitrate, besides also being used as a fertilizer, is a component of black powder widely used to manufacture firecrackers, fireworks and any other pyrotechnic devices. In addition, firecrackers and fireworks usually include potassium chlorate, perchlorate and other nitrate salts such as barium or strontium nitrates to get different colours and effects [9].

Liquid chromatography, in particular ion chromatography (IC), has been usually employed to identify and quantify energetic salts mainly through the analysis of their characteristic anions (nitrates, chlorates and perchlorates) [10–15]. Complementarily, reversed-phase liquid chromatography (RP-HPLC) is useful for the analysis of organic non-ionic explosives [16,17]. Until now, only a few preliminary studies have proved their suitability to determine residues in human fingermarks [18,19]. The detection and identification of explosives in human fingermarks is a comprehensive approach that tackles the challenging task of locating the evidence (illicit substance) as well as potentially identifying a suspect (human fingerprint). The challenge of detecting explosives on fingerprints has been explored using different analytical techniques, being mass spectrometry [20,21], IR [22–30] and Raman spectroscopy [31–34] those most used up to date. The high sensitivity of mass spectrometry and the speed and non-destructiveness of IR and Raman spectroscopy are highly seductive features. With regards to explosives detection on fingerprints by Raman spectroscopy [31–34], it is important to highlight that the explosives investigated included hexogen (RDX) [31–33], octogen (HMX) [31–33], penthrite (PETN) [31–33], 2,4-dinitrotoluene (2,4-DNT) [34], ammonium nitrate [31–33], potassium nitrate [34] and urea nitrate [34]. In addition, Raman imaging mode was used in those studies and solely the fingerprint area was scanned revealing the presence of explosive residues. Nevertheless, scanning large areas is usually time-consuming, being most effective, in certain cases, the analysis of few selected explosive particles by point measures. Raman microscopy is highly useful to this aim, allowing the rapid detection of microscopic residues. In this study, residues of smokeless gunpowder, black powder and dynamite on human handprints, have been analysed due to the high forensic interest of these explosives. In addition, the whole human handprint, instead of a unique fingerprint, was considered with the aim of studying the distribution of the explosive residues adsorbed on the hand and subsequently left on the handprint.

The aim of this work is to study and compare Raman microscopy and liquid chromatography, using both IC and RP-HPLC, for the analysis of explosives residues in handprints.

2. Materials and methods

2.1. Materials and chemicals

2.1.1. Explosive samples

Smokeless gunpowder, dynamite and ammonium nitrate samples were kindly provided by the Criminalistic Service of *Guardia Civil*. Two different smokeless gunpowders were used. According to the information included in the official label [35], a single-base gunpowder sample, which was composed by 94% of nitrocellulose and a double-base gunpowder sample containing 85% of nitrocellulose and 10% of dinitrotoluene (DNT) were included in this study. Dynamite was composed by ethylene glycol dinitrate (EGDN), ammonium nitrate, nitrocellulose, dynamite dye, sawdust, calcium carbonate ($CaCO_3$), guar gum and plasticizers, with ammonium nitrate and EGDN declared as its major components [36]. A black powder sample was extracted from a commercial firecracker available in the Spanish market. Black powder is technically defined as a mixture of sulphur, charcoal and potassium nitrate. However, the charge of the pyrotechnic device was composed by sulphur, charcoal and potassium perchlorate. Consequently, and strictly speaking, a black powder substitute product where the potassium nitrate has been replaced by potassium perchlorate, was analysed in this study.

2.1.2. Reagents

All reagents were of analytical or reagent grade. For Raman spectroscopy, potassium perchlorate, potassium nitrate, potassium chlorate, sodium nitrate and sodium chlorate were purchased from Sigma-Aldrich (St. Louis, MO, USA).

For IC, chloride, nitrite, nitrate, (BDH Chemicals Ltd., Poole, UK), chlorate, perchlorate, cyanate (Sigma-Aldrich, Gillingham, Dorset, UK) were prepared from their sodium salts; sulphate was prepared from its copper salt (BDH Chemicals Ltd., Poole, UK). Acetate (BDH Chemicals Ltd., Poole, UK) and thiocyanate were prepared from their ammonium salts. Formate was prepared from an ammonium solution (Sigma-Aldrich, Gillingham, Dorset, UK). Lactate, oxalate (BDH Chemicals Ltd., Poole, UK), phthalate, and benzoate (Sigma-Aldrich, Gillingham, Dorset, UK) were prepared from their acids. All stock solutions were prepared to a concentration of 1000 mg/L and working standards were prepared daily from these using ultrapure water. Eluents were prepared using a 50% v/v NaOH solution in ultrapure water (Sigma-Aldrich, Gillingham, Dorset, UK) for anion-exchange chromatography. For RP-HPLC, EGDN, DNT and nitroglycerin (NG) were purchased from Kinesis (St Neots, Cambridgeshire, UK). All stock solutions were prepared to a concentration of 100 mg/L and working standards were prepared daily from these using ultrapure water. Mobile phases were prepared using ammonium acetate and methanol (Fisher Scientific, Loughborough, Leicestershire, UK).

All eluents, stocks, standards and samples solutions were prepared using ultrapure water (18.2 MΩ cm) delivered from a Millipore Synergy UV ultra-purification system (Millipore, Bedford, MA, USA). Stock standards were kept in the dark at 5 °C and were re-prepared fortnightly.

2.2. Sample preparation and handprint collection

Smokeless gunpowder, dynamite and ammonium nitrate materials were handled without any prior preparation or treatment by seven volunteers (five women and two men). However, black powder had to be extracted from a commercial firecracker. For this, first the fuse was pulled out and then the cartridge was opened with laboratory scissors in such a way that the pyrotechnic charge was collected for handling.

2.2.1. Procedure for Raman spectroscopy

Prior to the explosive handling, and in order to study whether sweat or common exogenous components can influence the Raman spectra of handprints, the seven volunteers washed their hands in ultrapure water and left to air dry for 15 min with the aim of regenerating the sweat as proposed by Gilchrist et al. [18]. During this time, participants were not allowed to handle anything to minimise external contamination. Handprints from both hands were then deposited using a light pressure on the adhesive side of a clear self-adhesive vinyl book cover film of 22 × 38 cm size. For sample conservation and protection, films were covered with another piece of film of the same size. Additionally (and with the aim of testing the influence of common dirt), the handprints (right and left) of two participants who had not washed their hands for at least 3 h and had performed normal daily tasks were also