Talanta 160 (2016) 15–20

Contents lists available at ScienceDirect

Talanta

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

Locating bomb factories by detecting hydrogen peroxide

Francesco Saverio Romolo [a,b,*], Samantha Connell [a], Carlotta Ferrari [a], Guillaume Suarez [c], Jean-Jacques Sauvain [c], Nancy B. Hopf [c]

[a] Institut de Police Scientifique (IPS), Université de Lausanne, 1004 Dorigny, Lausanne, Switzerland
[b] Legal Medicine Section, Department SAIMLAL, Sapienza Università di Roma, Viale Regina Elena, 336, Rome, Italy
[c] Institute for Work and Health (IST), 1066 Epalinges, Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 19 February 2016
Received in revised form
8 June 2016
Accepted 14 June 2016
Available online 18 June 2016

Keywords:
Precursor
Improvised Explosive (IE)
Improvised Explosive Devices (IED)
Home Made Explosive (HME)
Security
Hydrogen peroxide
Luminol

ABSTRACT

The analytical capability to detect hydrogen peroxide vapour can play a key role in localizing a site where a H_2O_2 based Improvised Explosive (IE) is manufactured. In security activities it is very important to obtain information in a short time. For this reason, an analytical method to be used in security activity needs portable devices. The authors have developed the first analytical method based on a portable luminometer, specifically designed and validated to locate IE manufacturing sites using quantitative on-site vapour analysis for H_2O_2. The method was tested both indoor and outdoor. The results demonstrate that the detection of H_2O_2 vapours could allow police forces to locate the site, while terrorists are preparing an attack. The collected data are also very important in developing new sensors, able to give an early alarm if located at a proper distance from a site where an H_2O_2 based IE is prepared.

1. Introduction

The study of precursors used to produce explosives is a forensic field of increasing importance. These precursors allowed homemade preparation of improvised explosives (IEs) used in several recent bombings [1–4], possibly including the recent terrorist attacks in Paris [5]. The European Parliament and the Council adopted the Regulation (EU) No. 98/2013 on the marketing and use of explosives precursors on 15 January 2014 [6]. According to this regulation, seven precursors shall not be available to the general public anymore in concentrations greater than their limit values listed in Table 1. Despite the importance of the subject, few articles can be found in the scientific literature when searching with the keywords “explosive” and “precursor”.

Chung et al. developed a methodology to prioritise potential precursor chemicals in order to assess the urgency of controls based on commodity chemicals being controlled under Korean regulations [7]. Considering analytical papers, standoff deep Raman allowed remote detection of concealed explosive precursors such as nitromethane and ammonium nitrate [8]. Ali et al. detected ammonium nitrate, hexamethylenetetramine and pentaerythritol on clothing by Raman microscopy, after spotting particles with optical microscopy [9]. Nazarian and Presser used a laser-driven thermal reactor to obtain the thermal/chemical signatures of nitromethane and ammonium nitrate [10]. Finally Lazarowski and Dorman studied the capability of trained detection dogs to correctly signal the presence of one or more explosive mixtures containing potassium chlorate [11]. In addition, some authors have evaluated an isotopic analysis application to study a possible association between precursors used as starting material and explosive products obtained [12–15].

The scientific literature search was later focused on hydrogen peroxide (H_2O_2). This explosive precursor is of particular importance after its involvement in the foiled plot to blow up several aircrafts during their flights from London-Heathrow Airport. In this case, H_2O_2 was used to prepare homemade liquid explosives [16]. This kind of explosive, capable of detonating [17], was extensively studied in UK during the investigation and the criminal trial [18,19]. Hydrogen peroxide (aq) has been detected through containers or packaging using Raman spectroscopy [20,21]. Ramirez-Cedeno et al. reported analyses of H_2O_2 concealed in mixtures with alcoholic beverages, such as whiskey, rum, and tequila via Raman [22]. Petterson et al. demonstrated the standoff detection capability of Raman with 5% H_2O_2 solutions in water through coloured glasses and PET at 30 m [23]. Stewart et al. proposed a handheld Raman spectrometer to determine H_2O_2 concentrations in liquids found at suspected IE manufacturing

* Corresponding author at: Legal Medicine Section, Department SAIMLAL, Sapienza Università di Roma, Viale Regina Elena, 336, Rome, Italy.

http://dx.doi.org/10.1016/j.talanta.2016.06.033
0039-9140/

Table 1
Substances available to the public at concentrations equal or lower than the limit value according to Regulation (EU) No. 98/2013 of the European Parliament and of the Council on the marketing and use of explosives precursors (Annex 1) [6].

	ANNEX I Regulated Substance	Limit Value (w/w)
1	Hydrogen Peroxide	12%
2	Nitromethane	30%
3	Nitric acid	3%
4	Potassium Chlorate	40%
5	Potassium Perchlorate	40%
6	Sodium Chlorate	40%
7	Sodium Perchlorate	40%

sites [24].

An online analyser was developed and used by Francois et al. in the field to measure atmospheric H_2O_2 obtaining values down to 3.5×10^{-1} μg m^{-3} (177 pptv) [25]. Cotton swabs used for sample collection of hydrogen peroxide post-blast have been analysed using reversed-phase high-performance liquid chromatography with either fluorescence detection (HPLC–FD) or electrochemical detection (HPLC–ECD) [26,27].

With the new H_2O_2 limit concentration for the products available to the general population (12%), criminals intending to use H_2O_2 to produce IE are forced to carry out a concentration process, as was done in 2005 in a flat in New Southgate, London. Terrorists allegedly used 443 litres of a commercial product containing 18% hydrogen peroxide and concentrated the H_2O_2 in heated pans in the kitchen to prepare the IE. Heating such liquids is expected to disperse significant H_2O_2 vapours into the surrounding air continuously throughout the production phase of the IE [28]. The detection of such vapours could allow police forces to locate sites, where the on-going manufacturing of a H_2O_2 based IE is suspected. This approach for protecting citizens from bombings is expected to be more effective than simply patrolling a possible target, because the production time of IE is much longer than the time needed to transport an improvised explosive device (IED) close to the target from the manufacturing site [29]. To our knowledge, no method has been specifically designed and validated to locate IE manufacturing sites using quantitative on-site vapour analysis for H_2O_2. The aims of the research described in this paper were to develop a sampling and on-site detection method allowing low levels of H_2O_2 vapour to be measured for security reasons. This method was further tested at a military test site, where H_2O_2 vapours were emitted from a bomb factory kitchen.

2. Materials and methods

2.1. Safety note

A literature and media review was completed to become familiar with the typical procedures used to concentrate commercially available H_2O_2, which is a dangerous material. The handling of this substance in general and the activity described in this article in particular may only be carried out by authorised and highly qualified personnel, using appropriate safety measures (reinforced goggles and gloves, splinter-proof vessels, protective shield, etc.). Moreover, in Italy "It is forbidden to manufacture, to hold at home or elsewhere, to transport or to sell … explosives that have not been recognised and classified by the Minister of the Interior" [30], such as a mixture containing H_2O_2.

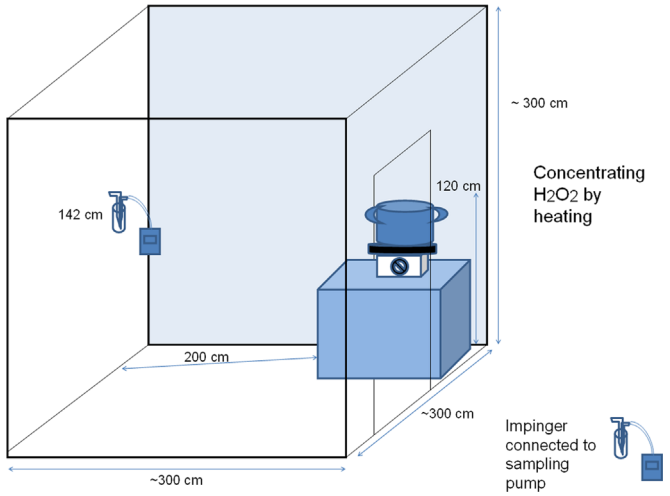

Fig. 1. Drawing depicting exposure chamber experimental set-up at IST.

2.2. Materials

Hydrogen peroxide (12%) was purchased from a general store and H_2O_2 (30%) from Sigma Aldrich (5L, ref. 16911–5L-F, St. Louis, MO, USA). A 12 L stainless steel casserole (24 cm diameter) was also bought from a general store. A hot plate with a magnetic stirrer (Bibby, HC1202), a glass laboratory thermometer, and an oscillating fan operating statically (Sanyo) were used. A weather station was used to determine wind direction in field experiments (IROX model PRO-X2, ref. #IR4.1769.30).

2.3. Approach

To estimate H_2O_2 vapour emissions during concentration steps via heating, two approaches were used; a controlled laboratory experiment and a mock test. Three tests were performed in a controlled environment [31] at the Institute for Work and Health (IST) (Lausanne, Switzerland). Hydrogen peroxide sampling at different distances from the source were carried out inside a closed and ventilated exposure chamber (10 m^3) (Fig. 1). The capability of the developed method to detect H_2O_2 vapours in field conditions was tested at the Armasuisse, Science & Technology Competence Center in Thun, Switzerland, where an IE manufacturing site was created and used as a model. The drawing in Fig. S1 of the supplementary material section shows the experimental set-up on-site with the positions of the IE manufacturing site and the sampling units located along the direction of the wind.

2.4. Air sampling

Air samples were collected using a personal air sampling pump (SKC AirChek 500 or SKC AirChek 224 PCXR4; Eighty Four, PA, USA), connector tubing (Tygon®), and glass impingers (SKC Fritted Midget Impinger, Glass, 25 mL, with Standard Nozzle) containing water (15 mL from Milli-Q Q-POD, Switzerland, 18.2 MΩ cm, < 4 ng/g total organic carbon, filtrated through 0.22 μm filter) operated at a flow rate of 1 l per minute (Lpm) (Fig. 2).

2.5. Chemiluminescent method development

2.5.1. Bench-top analysis

Chemiluminescence methods were sensitive to H_2O_2 and appeared convenient for the envisioned application. The method described here corresponds to the combination of two published