



ELSEVIER

Contents lists available at ScienceDirect

Talanta

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

Analysis of pre-ignited improvised incendiary devices using portable Raman



Carlos Martín-Alberca¹, María López-López¹, Carmen García-Ruiz^{*}

Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University Institute of Research in Police Sciences (IUICP), University of Alcalá, Ctra. Madrid-Barcelona km. 33.600, Alcalá de Henares, 28871 Madrid, Spain

ARTICLE INFO

Article history:

Received 3 February 2015

Received in revised form

18 June 2015

Accepted 26 June 2015

Available online 2 July 2015

Keywords:

Molotov cocktail

Containers

Ignitable liquid

Improvised incendiary device

Raman spectroscopy

ABSTRACT

In this work, the use of a portable Raman spectrometer is evaluated for the non-invasive analysis of two types of pre-ignited improvised incendiary devices (IIDs), the classic Molotov cocktails and the chemical ignition Molotov cocktails (CIMCs). The most common ignitable liquids (ILs) used to make classic Molotov cocktails (gasoline, diesel fuel, kerosene and ethanol) were measured in seven different clear and colored glass bottles to evaluate if the container features could hamper the Raman measurements. The results showed that the portable Raman spectrometer can be employed to detect ILs in glass bottles without disturbances. Chemical changes on the ILs are produced when they are mixed with acid; therefore, to evaluate the use of the portable Raman spectrometer for the analysis of CIMCs required an investigation of how time and movement influence the measurements. Thus, two different IL–sulfuric acid mixtures commonly used to make CIMCs (gasoline–sulfuric acid and diesel fuel–sulfuric acid) were measured over time under static and motion conditions. In spite of the intense fluorescence encountered in both CIMCs, it was possible to identify the acid and the gasoline for the first hours of the reaction both in the static and motion experiments. Concerning the diesel fuel present in the CIMC, it underwent instantaneous chemical changes under both measurement conditions, showing high fluorescence that impeded its identification. In view of the results achieved, the portable Raman spectrometer can be a useful instrument for the rapid, non-invasive and safe analysis of pre-ignited IIDs.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The improvised incendiary devices (IIDs) are a group of homemade devices adapted to cause physical harm to persons, environment, or property by means of fire [1–4]. These devices are easy to make with readily available and cheap compounds. In most cases, IIDs consist of one or more ignitable liquids (ILs) (*i.e.*, gasoline, diesel fuel, ethanol or kerosene), a container and an ignition source. The most popular IID is the classic Molotov cocktail [5], which consist of a glass bottle filled with IL and a wick that is lighted just before being hurled. An advanced and more dangerous version of this device is the chemical ignition Molotov cocktail (CIMC) [6–8]. CIMCs are usually closed glass bottles containing gasoline or diesel fuel and concentrated sulfuric acid [5,7]. Taped to the bottle, a chlorate salt is wrapped in a folded sheet of paper.

When the bottle breaks after been thrown at a target, the contact between chlorate salt and sulfuric acid produces a strong exothermic reaction that ignites the IL.

The IIDs samples submitted to the forensic laboratories can be pre-ignited samples (*i.e.*, failed or seized devices) or post-ignited samples (*i.e.*, fire debris or container fragments). Their analysis may provide useful information contributing to the forensic investigation. Nowadays, gas chromatography–mass spectrometry (GC–MS) is the technique commonly used to analyze these samples at the laboratory [9]. Recently, capillary electrophoresis (CE) with a diode array detector was used to detect anions in post-ignited remains of CIMCs [6,7]. The anions detected provide guidance about the initial composition of the CIMC ignition system. However, there is a lack of specific methods to confirm the presence of ILs and/or strong acids in pre-ignited IIDs, both in the laboratory and on the field, in order to manage the hazards and their associated safety measures. For example, the current methodologies to confirm the presence of sulfuric acid in CIMCs (*i.e.*, litmus paper or a pH-meter) involve the bottle aperture/manipulation exposing the analyst to the acid and hazardous gases (*i.e.*, the reaction between sulfuric acid and some ILs generates hydrogen sulfide) [7,10]. Therefore, it would be very useful for

^{*} Correspondence to: Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Multipurpose Building of Chemistry, University of Alcalá, Ctra. Madrid-Barcelona km 33.600, Alcalá de Henares, 28871 Madrid, Spain.

E-mail address: carmen.gruiz@uah.es (C. García-Ruiz).

URL: <http://www.inquifor.com> (C. García-Ruiz).

¹ Both authors contributed equally to this work.

laboratory technicians and for the first attendees of law enforcement agencies to have fast and non-invasive techniques that can be directly used to identify the above mentioned compounds through transparent containers.

Raman spectroscopy complies with these requirements. Raman spectroscopy was employed to analyze several ILs used in IIDs [11–16]. Quality indicators as well as the physicochemical properties of gasoline [11,12], diesel fuel [13] or kerosene [14] were determined using Raman spectroscopy either alone or in combination with Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR) or statistical techniques. Other proposed applications of the combined use of Raman spectroscopy with chemometrics are the identification of adulterated gasoline with kerosene [15], methyl *tert*-butyl ether (MTBE) and benzene [11], or to measure the ethanol proportion in ethanol–gasoline mixtures [16]. However, the use of Raman spectroscopy to analyze pre-ignited IIDs was not evaluated to date.

This article aims to evaluate the use of a portable Raman spectrometer for the non-invasive analysis of pre-ignited classic Molotov cocktails and CIMCs. Field portable Raman spectrometers are rugged, handheld, lightweight tools that allow users without extensive chemistry training to perform rapid raw material verification. In fact, these systems have been used to analyze samples of forensic interest such as gasoline, explosives or abuse drugs [11,17,18]. However, various factors may influence the results such as the focalization of the laser beam, the daylight and artificial light sources (*i.e.*, neon light), and the color and thickness of the container [19]. In fact, the color of the glass represents a challenge due to the fluorescence originated from some surface materials [20]. Additionally, it should be considered that chemical modifications are produced over time in the gasoline and diesel fuel due the presence of sulfuric acid [8]. Therefore, in this work, compounds present in IIDs were measured in different glass bottles to assess if the container features hamper the Raman measurements. Additionally, two different types of CIMCs were analyzed over time under static and motion conditions to investigate how time and movement influence the measurements.

2. Materials and methods

2.1. Reagents and containers

Gasoline 98 and 95 Research Octane Number (RON), and diesel fuel were acquired in a local petrol station (Alcalá de Henares, Madrid, Spain). Charcoal starter (trading name: *barbecue liquid*) made of kerosene 100% (v/v) was obtained in a supermarket (Alcalá de Henares, Madrid, Spain). Ethanol 96% (v/v) was purchased from Panreac (Barcelona, Spain), sulfuric acid of analytical grade 95–98% (m/v) was acquired from Labkem (Mataró, Barcelona, Spain), and potassium chlorate and sodium chlorate were purchased from Sigma-Aldrich (St. Quentin, Fallavier, France).

Seven clear and colored glass bottles were used as containers for Molotov cocktails and CIMCs devices. The type, color and wall thicknesses of the bottles are summarized in Table 1. The wall thickness of the bottle was measured with a hand-held caliper.

2.2. Instrumentation

Raman spectra were acquired using a portable CBEX Raman spectrometer (size $9.14 \times 7.11 \times 3.81 \text{ cm}^3$ and 0.333 kg weight) from Bonsai Advanced Technologies (Alcobendas, Madrid, Spain) equipped with a 785 nm laser. The laser power was 100 mW (70 mW at sample) and the measurement range was $400\text{--}2300 \text{ cm}^{-1}$.

Table 1
Types of bottles used.

Bottle type	Glass color	Wall thicknesses (mm)
Tonic water	Clear	20
Mineral water	Clear	30
Sparkling wine	Dark blue	22
Beer	Brown	15
Beer	Dark brown	22
Cough medicine	Amber	28
Beer	Green	15

2.3. Sample preparation and data acquisition

The reference spectra of gasoline 98 and 95 RON, diesel fuel, kerosene, ethanol, chlorate salts, and sulfuric acid were collected in quartz cuvettes that were held in close contact against the Raman spectrometer. Then, the ILs and the sulfuric acid were poured in the seven glass bottles and the Raman spectra were measured through the glass, placing the Raman spectrometer as close as possible to the wall bottle. Acquisition times between 0.6 and 3 s and 8 scans were selected. The measurements were taken under illumination (daylight and artificial light) and darkness conditions.

A mixture of 400 mL gasoline 98 RON and 200 mL sulfuric acid and a mixture of 400 mL diesel fuel and 200 mL sulfuric acid were prepared in duplicate in clear glass bottles (mineral water bottles). Clear bottles were selected in order to easily visualize changes in the physical appearance of the mixture. A total of 5 measurement points at different heights were set (see Fig. 1). The first two points were set on the lower third of the bottle where the sulfuric acid was present. The first point of measurement was taken near the bottom of the bottle and the second one some centimeters above. The other three points of measurement were set on the two-thirds of the upper part of the bottle, where there was IL. The third point of measurement was set near the sulfuric acid, and the fourth and the fifth points of measurement some centimeters above, being the fifth point of measurement the nearest to the bottleneck. For the static experiments, two of the bottles remained motionless until the end of the experiment. They were measured for approximately 10.5 days (each 5 min for the first 8 h and each 8 h for the next 245 h). The second pair of bottles remained under

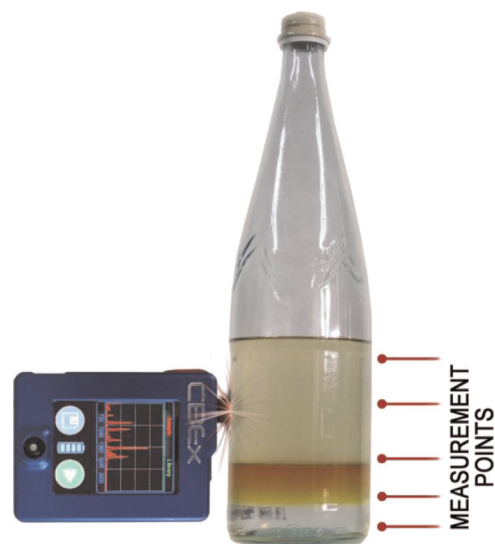


Fig. 1. Scheme of the five points (red arrows) set for the measurement of the CIMCs devices. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/7678780>

Download Persian Version:

<https://daneshyari.com/article/7678780>

[Daneshyari.com](https://daneshyari.com)