SUPPLEMENTARY INFORMATION - EXPLOSIVE COLORIMETRIC DISCRIMINATION USING A SMARTPHONE, PAPER DEVICE AND CHEMOMETRICAL APPROACH

1. MATERIALS AND METHODS

1.1 Safety note

Explosive compounds were used in this study. It is important to highlight that extra care must be taken when handling these types of materials, as they may undergo spontaneous combustion; hence, no more than 50 mg should be handled at a time. The explosives can be susceptible to heat; shock and friction, hence in addition to the amount of explosive manipulated, one must beware of the variations of temperature and possible impacts on the explosive.

1.2 Chemicals

All solid reagents were of analytical grade and were used without further purification. Acetonitrile, acetone, citric acid, hydrochloride acid, hydrogen peroxide, methanol, potassium chloride, potassium ferricyanide, potassium iodide, and sodium hydroxide were purchased from Merck (Darmstadt, Germany). 4-Amino-2-nitrophenol (4A2NP), aniline, creatinine, and ferric chloride were purchased from Sigma-Aldrich (Steihheim, Germany). Picric acid (PA) was purchased from Reagen (Rio de Janeiro, Brazil). Nitrobenzene (NB) was purchased from Carlo Erba (Milano, Italy). Hexamethylenetetramine was purchased from Acros Organics (Geel, Belgium). All explosives solutions were prepared by dissolving the solid explosives in acetonitrile:methanol (1:1). The other solutions were prepared by dissolving the reagents in deionized water obtained using a water purification system (Direct-Q® 5 Ultrapure Water Systems, Millipore, MA, USA).

The reagents chosen to react with the explosives were: KI 20 mmol L^{-1} in a 1 mol L^{-1} hydrochloride acid solution, creatinine 100 mmol L^{-1} in a 0.1 mol L^{-1} NaOH solution and ACS reagent grade aniline ($\geq$ 99.5 %).

1.3 Syntheses of peroxide explosives

Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) were synthesized from hydrogen peroxide/acetone/hydrochloride acid and hydrogen peroxide/hexamethylenetetramine/citric acid, respectively, as previously reported [1, 2]. The identity of the products was confirmed using NMR (Figs. S5 and S6).

1.4 Colorimetric sensor

For the colorimetric tests, an Apple iPhone 4S was used as a colorimetric detector. Each array was photographed using the built-in camera of the smartphone, and the red, green, and blue (RGB) components of each spot of interest were analyzed using an iOS application developed for that purpose. The application was built in Apple Xcode 4.3.2 using the Apple iOS 5 Software Development Kit (SDK; Apple Inc., Cupertino, CA, USA). The RGB values for each spot and the standard deviation for each component were measured using a specific Application Program Interface (API) that converted each pixel of the image into 24-bit (8 bits per component) data. This information was then processed inside the application, and the mean values of the components were displayed as a percentage of the RGB. In addition, the program allowed the user to take a photograph of the spot test through a graphical user interface (GUI), choose the area to be analyzed, and save the results.

1.5 Smartphone support

As the RGB values determined were strongly dependent on the light conditions during image acquisition, a closed chamber providing a fixed focal distance and homogeneous lighting was built using black poly(methyl methacrylate). The structure was designed using CorelDraw X6 software (Corel Corporation, Ottawa, Canada) and was cut using a gravograph laser cutter machine (Gravograph, La Chapelle St Luc, France). The light was produced by four white LEDs passed through a series of transparent sand-blasted poly(methyl methacrylate) sheets to optimize the distribution of light over the sample. The support schematics with the dimensions and photographs of the support with the smartphone are shown in Figs. S1 and S7. The support was designed in such a way that the iPhone could be firmly attached to it, forming a portable, self-sustainable colorimetric analysis unit that could be employed regardless of outside light conditions, providing enhanced mobility to the operator.

Electronic Supplementary Material (ESI) for Analytical Methods

1.6 Quantitative performance of the paper device

In order to evaluate the quantitative performance of the paper device, we used an approach based on the colorimetric response of the spots expressed using the Euclidian distance (ED) versus the concentration [3] of each explosive, which could be expressed by the equation 1:

$$ED = ((\Delta R)^2_{KI} + (\Delta G)^2_{KI} + (\Delta B)^2_{KI} + (\Delta R)^2_{creatinine} + (\Delta G)^2_{creatinine} + (\Delta B)^2_{creatinine} + (\Delta R)^2_{aniline} + (\Delta G)^2_{aniline} + (\Delta B)^2_{aniline})^{0.5}$$

1.7 Prussian blue deposited onto a glassy carbon surface to evaluate residual hydrogen peroxide in the organic peroxides explosives

Prussian blue film was deposited as reported by R.A.A. Munoz et al. [4]. A glassy carbon electrode, Ag/AgCl electrode, and platinum wire were used as the working, reference, and counter electrodes, respectively. A portable electrochemical potentiostat from PalmSens BV (Houten, Netherlands) was used to perform electrochemical measurements.

2. SUPPLEMENTARY FIGURES

Figure S1: Photographs of different angles of the smartphone support with the smartphone.

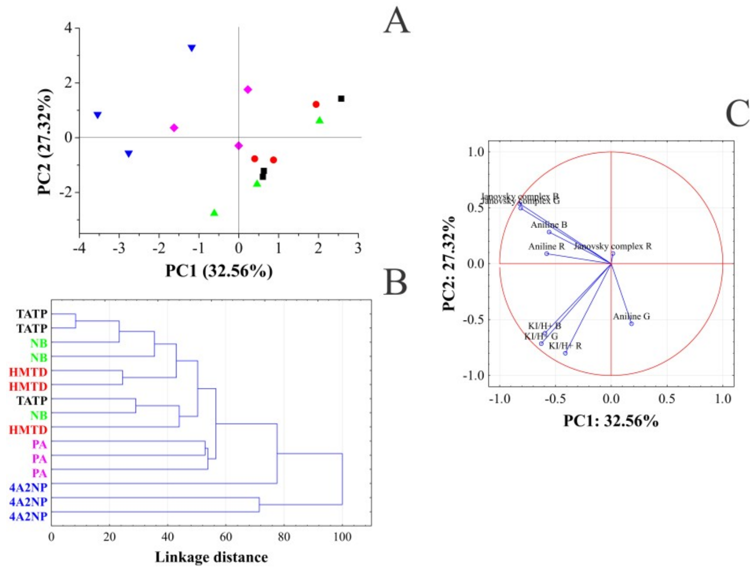

Figure S2: After 0 min of reaction time: (A) PCA scores plot, (B) dendogram of 15 samples, and (C) loadings plot of colorimetric signals for the five different explosive samples with three different reagents. Legend of the PCA graph: ■ – TATP; ● – HMTD; ▲ – Nitrobenzene (NB); ▼ – 4-amino-2-nitrophenol (4A2NP); ♦ - Picric acid (PA).

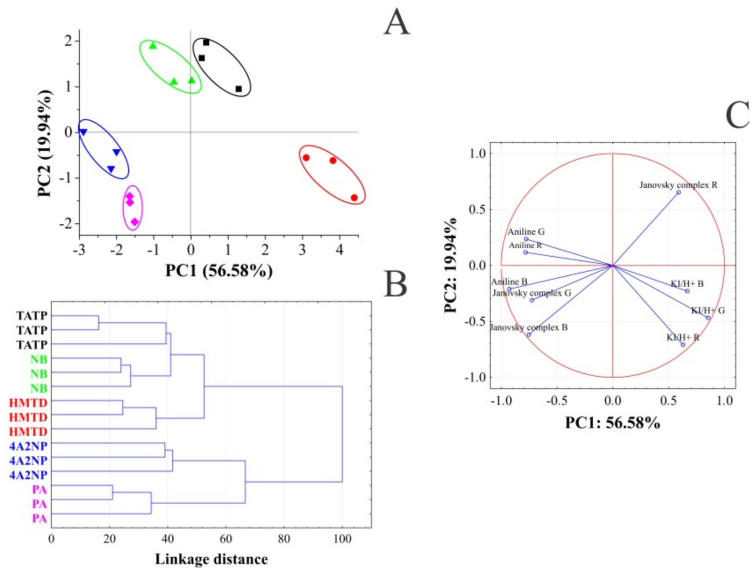

Figure S3: After 10 min of reaction time: (A) PCA scores plot, (B) dendogram of 15 samples, and (C) loadings plot of colorimetric signals for the five different explosive samples with three different reagents. Legend of the PCA graph: ■ – TATP; ● – HMTD; ▲ – Nitrobenzene (NB); ▼ – 4-amino-2-nitrophenol (4A2NP); ♦ - Picric acid (PA).

Electronic Supplementary Material (ESI) for Analytical Methods

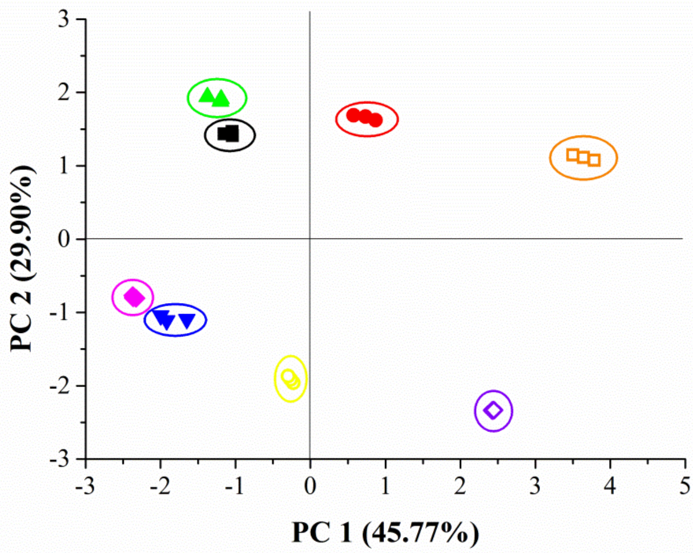

Figure S4: PCA score plots for the five different explosives, the mixture of the peroxide explosives, the mixture of the nitro explosives and all explosives together samples with three different reagents. Legend of the PCA graph: ■ – TATP; ● – HMTD; ▲ – Nitrobenzene (NB); ▼ – 4-amino-2- nitrophenol (4A2NP); ♦ - Picric acid (PA), ◇ – Nitro explosives (NB + 4A2NP + PA); □ – Peroxy explosives (TATP + HMTD); ◊ - All explosives (NB + 4A2NP + PA + TATP + HMTD).

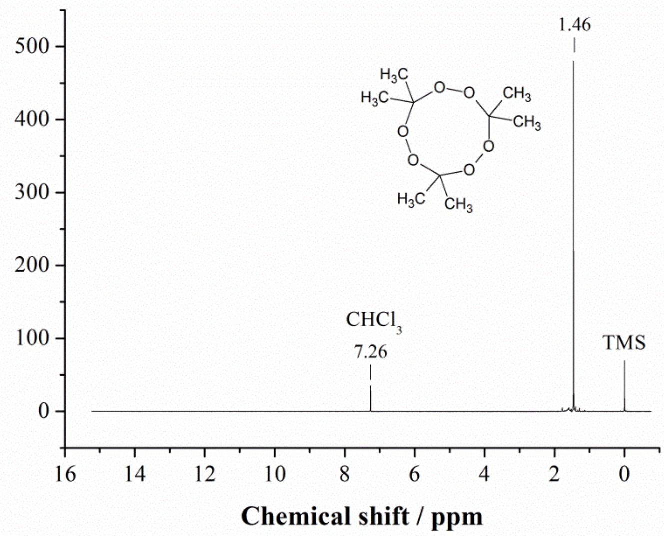

Figure S5: NMR spectra of synthesized TATP.

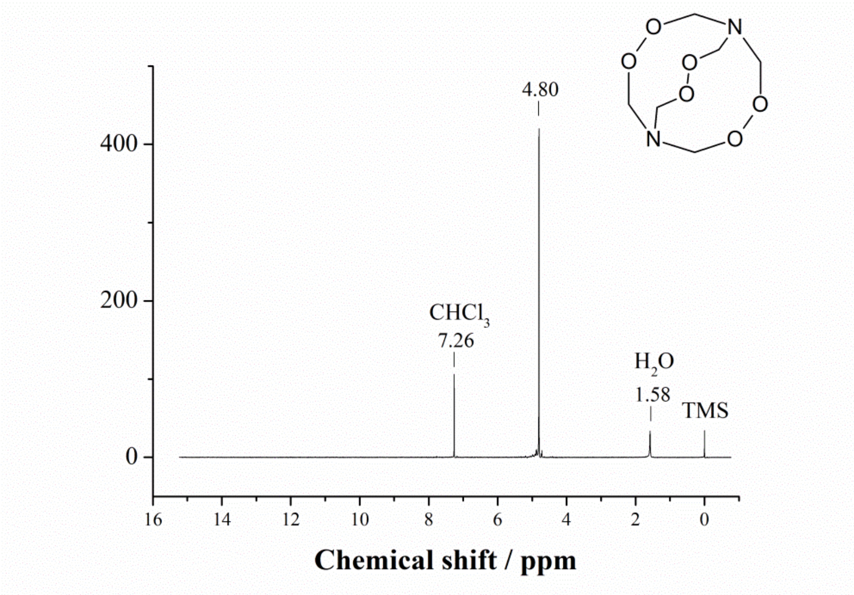

Figure S6: NMR spectra of synthesized HMTD.

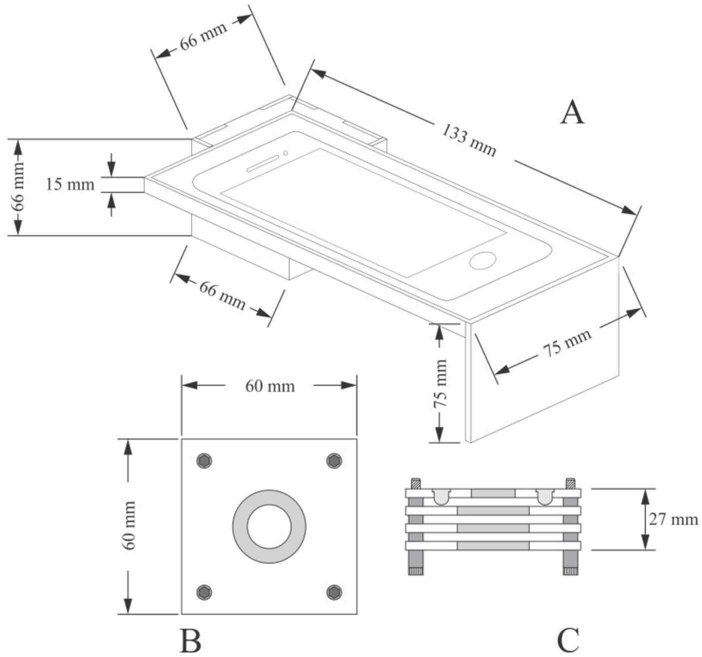

Figure S7: iPhone support (A) with light system; (B) bottom and (C) side views.

3. SUPPLEMENTARY TABLES

Table S1: RGB values and relative standard deviations obtained with the developed colorimetric sensor from blue, red and green squares.

	Blue square			Red square			Green square		
	R	G	B	R	G	B	R	G	B
Average	80.6	28.9	246.51	253.89	125.9	130.5	69.9	187.7	110.5
RSD (%)	0.4	0.3	0.04	0.03	0.7	1.0	0.6	0.2	0.3

Table S2: Electronic eye, nose and tongue used for explosive discrimination

Device	Explosives	Reference
Electronic tongue	RDX, TNT, PETN, Tetryl, HMX, SemtexH, Comp. B, Comp.C-3, Pentolite and Tetrytol.	5
Electronic tongue	TNT, nitrobenzene, nitrotoluene, dinitrotoluene	6
Electronic nose	Review (book)	7
Electronic nose	RDX, TNT, PTEN	8
Electronic nose	Review	9
Electronic nose	RDX, TNT, 2,6 – DNT, 2,4 - DNT	10
Electronic nose	Review (book)	11

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