Fast testing for explosive properties of mg-scale samples by thermal activation and classification by physical and chemical properties

Stephan Maurer *, Ramona Makarow, Johannes Warmer, Peter Kaul

University of Applied Sciences Bonn-Rhein-Sieg, Institute of Safety and Security Research ISF, Grantham-Allee 20, 53757 Sankt Augustin, Germany

ABSTRACT

To test explosive properties of substances, the strong exothermal reaction of an explosive after ignition can be used. Monitoring the emitted visible or infrared radiation by photodiodes and the change in pressure by a transducer in a closed system offers a low cost and mobile explosive identification device. The explosives investigated were hexamethylene triperoxide diamine, pentaerythritol tetranitrate, ammonium gelignite, ammonium nitrate fuel oil, cyclotrimethylene trinitramine, cyclotetramethylene tetranitramine, black powder, nitrocellulose, trinitrophenylmethylnitramine, gun propellant, triacetone triperoxide and trinitrotoluene. It has been shown, that the fast thermal activation of single-digit mg samples yields reproducible results for primary explosives, propellants, and trinitrotoluene. An analysis of the volatile reaction products with commercial semi-conductor gas sensors enables a differentiation between nitrate- and peroxide-based explosives and non-explosives.

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1. Introduction

Improvised explosive devices (IED) are threats in conflict areas all over the world. Both protection of people and material counter-IED efforts are essential. Therefore, security and military forces require the means to classify unknown substance findings as either explosives or non-explosives. Key requirements on identification devices are easy usability, reliability, cost-effectiveness, and mobility. Several analytical methods and applications have been proposed or are currently used to detect explosives, such as ion mobility spectroscopy [1–3], liquid or gas chromatography coupled mass spectrometry [4,5], Raman and infrared spectroscopy [7–9], fluorescent polymers [10,11], gas sensors [12,13], and explosive-sniffing dogs [14,15]. A micro-calorimetric approach was reported by Zuck et al. [16], monitoring the change in temperature of µm-sized particles on a thin film heater by a thermopile sensor.

This paper presents a proof of concept to determine explosives based on their tendency to react quickly, strongly, and measurably exothermic after absorbing the activation energy required. The decomposition of explosives results in measurable thermal change and emission of light. A pressure increase is caused by the formation of low-molecular reaction products and rise in temperature. The analysis of specific gaseous reaction products, combined with pressure transducers and photodiodes response, gives further, detailed information on the respective substance classes. In contrast to analytical methods mentioned above, this approach does not identify the chemical itself, but its reactivity, and therefore shall detect even heretofore unknown explosives or products of explosive preparation.

To meet the requirement of a mobile and cost-effective sensing device, common electronic components and miniaturized heaters with low power consumption were used. Photodiodes were chosen to observe the emitted radiation, pressure transducers measure the blast, and semiconductor gas sensors were used to identify various gaseous components. The activation energy required was provided by use of resistance heaters. In order to avoid stress to the measuring device and protecting the operator, the sample amount was limited to the lower mg-range, thus lowering the expected energy uptake by the heater. With regard to the field of application, single-use heaters were preferred, to prevent contamination by previous samples.

Various explosives, explosive precursors and non-explosives were investigated, and results of sensor signals were compared. Finally, reproducibility of explosives detection was determined.
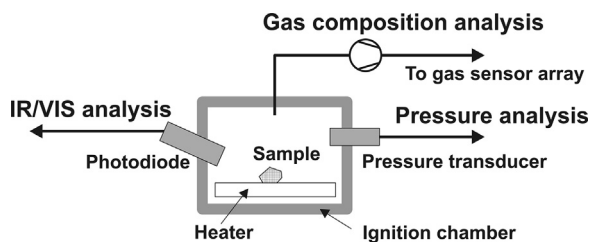

Fig. 1. Schematic view of explosive identification concept. The sample is placed on the heater inside the heating chamber. Heating up results in sensor signal response, followed by signal analysis. In this work the measurement of emission/pressure and the determination of gas composition were conducted separately.

Fig. 2. Schematic sectional view of the photodiode ignition chamber.

2. Materials and methods

A schematic view of the proposed concept is shown in Fig. 1. The sample is placed on top of a heater inside an ignition chamber. Strong and fast heating leads to decomposition of the sample. Photodiodes and pressure sensors monitor the reaction. Subsequently, a gas sensor array responds to the respective gaseous reaction products. It was presumed that non-explosives, in contrast to explosives, do not emit significant spectral signals nor increase the pressure rapidly; thus this measurement constitutes a fast and easy method to distinguish between explosives and non-explosives. The proposed concept of explosive detection required investigation on UV/IR emission, pressure changes and gas-phase composition. It was decided to use separate experimental setups for emission/pressure investigations and gas sensing respectively. The combination of both setups shall be part of future works.

Decomposition by thermal activation needs an energy input (provided in this case by the heater). To avoid melting or sublimation and yet to induce an (exothermal) reaction, a maximized heat impulse is applied. The maximum heater temperature needs to exceed the decomposition temperature of known explosives (Table 1). The heating rate was maximized in respect to the maximum heater temperature and heater stability. Energy loss due to the thermic capacity of the heater itself is to be avoided.

2.1. Chemicals

Unless otherwise stated, all chemicals were purchased from Merck (Darmstadt, Germany) in reagent grade ≥98% and used without further purification.

2.1.1. Test agents

The explosives used were hexamethylene triperoxide diamine (HMTD), pentaerythritol tetranitrate (PETN), ammonium gelignite, Hanal® – an ammonium nitrate fuel oil (ANFO) explosive -, cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), black powder, nitrocellulose, trinitrophenylmethylnitramine (Tetryl), gun propellant, and trinitrotoluene (TNT), all provided by the German Armed Forces. TNT was additionally purified by recrystallization in 65% nitric acid (twice). Triacetone triperoxide (TATP) was synthesized according to Matyas and Pachmann [17]. Ammonium nitrate (AN) and
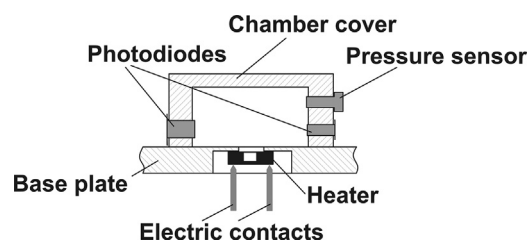
hexamethylenetetramine (urotropine) were investigated because of their possible use as precursors for homemade explosives preparation. As non-explosive but common substances, which on first glance might be mistaken for an explosive, ATA scrubbing agent (Henkel, Germany), wheat flour, saccharose and starch were used.

2.2. Heater characteristics

The surface temperature vs. heating voltage characteristic of both types of heaters was measured with a KGA 740 high speed infrared pyrometer (KLEIBER infrared, D), with a measuring range from 160 °C to 1000 °C, a macro optic with a measuring field-diameter of 1.0 mm, and a response time of 6 μs. Pyrometer signal output, from 0 to 10 V, was linear over the measuring range. Heating voltage was provided by a voltage-controlled power supply (Voltcraft, VSP 2653HE) and switched by a digital control relay to ensure the heating time.

2.3. Photodiode and pressure measurement setup

The ignition chamber had an inner diameter of 16 mm and a height of 18 mm (Fig. 2). Two photodiodes were placed circularly at 6 mm above the heater both to minimize heater radiation influences and to get a maximized emission signal out of the sample's possible deflagration or explosion. A pressure transducer was mounted, and the chamber was gas-tightly sealed. For control and data acquisition, a customized LabView program was developed.

The micro-structured heaters (Type A) shown in Fig. 3(a) and (b) were produced by CAESAR (Center of Advanced European Studies and Research, Germany). Two different types of cavities were etched into a SiO_2-substrate to allow variation of the test agents' amount. One type measured 1.0 mm × 1.0 mm, the other 0.5 mm × 0.5 mm. The depth of the cavity was always 0.4 mm. The overall dimensions of the heaters were 3.4 mm × 3.4 mm × 0.5 mm.

A nickel heating structure, manufactured with a squared and rounded track, was placed on the bottom side of the heater. This variation was made to find out whether or not the track shape influences the heating characteristics. The nominal resistance of the heating track at 25 °C was 15 Ω.

Fig. 3(c) shows the base plate of the ignition chamber (without cover), with the sample being applied by tweezers. After replacing the chamber cover, the device was ready for use.

Emissions inside the ignition chamber were measured with two different photodiodes. One diode was a silicon detector with UV

Table 1
Melting and boiling points of some explosives [18,19].

Explosive	Melting point (°C)	Boiling point (°C)
Trinitrotoluene (TNT)	80.2	240 (explodes)
Pentaerythritol tetranitrate (PETN)	141.3	190 (decomposes)
Cyclotrimethylene-trinitramine (RDX)	204.1	Decomposes
Cyclotetramethylene-tetranitramine (HMX)	276–280	Decomposes
Trinitrophenylmethylnitramine (Tetryl)	129.5	187 (decomposes)
Hexamethylene triperoxide diamine (HMTD)	150 (decomposes)	–