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Thermal signature measurements for ammonium nitrate/fuel mixtures by laser heating

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ABSTRACT

Measurements were carried out to obtain thermal signatures of several ammonium nitrate/fuel (ANF) mixtures, using a laser-heating technique referred to as the laser-driven thermal reactor (LDTR). The mixtures were ammonium nitrate (AN)/kerosene, AN/ethylene glycol, AN/paraffin wax, AN/petroleum jelly, AN/confectioner's sugar, AN/cellulose (tissue paper), nitromethane/cellulose, nitrobenzene/cellulose, AN/cellulose/nitromethane, AN/cellulose/nitrobenzene. These mixtures were also compared with AN/nitromethane and AN/diesel fuel oil, obtained from an earlier investigation. Thermograms for the mixtures, as well as individual constituents, were compared to better understand how sample thermal signature changes with mixture composition. This is the first step in development of a thermal-signature database, to be used along with other signature databases, to improve identification of energetic substances of unknown composition. The results indicated that each individual thermal signature was associated unambiguously with a particular mixture composition. The signature features of a particular mixture were shaped by the individual constituent signatures. It was also uncovered that the baseline signature was modified after an experiment due to coating of unreacted residue on the substrate surface and a change in the reactor sphere oxide layer. Thus, care was required to pre-oxidize the sphere prior to an experiment. A minimum sample mass (which was dependent on composition) was required to detect the signature characteristics. Increased laser power served to magnify signal strength while preserving the signature features. For the mixtures examined, the thermal response of each ANF mixture was found to be different, which was based on the mixture composition and the thermal behavior of each mixture constituent.

1. Background

Forensic identification of homemade explosive materials is essential for determining the composition and origin of the explosive mixtures and their precursors, and formulation procedures. Such information can then be used to develop strategies to disrupt or discourage the manufacturing of these materials, and provide protocols for their safe disposal. Homemade explosives are difficult to detect, and used increasingly by extremists and terrorists due to the widespread availability and easy accessibility of the precursors [1]. Currently, hundreds of compounds are classified as precursors [2,3]. The improvised nature of the mixture chemical composition and formulation/synthesis procedures presents a formidable challenge for forensic processing and analysis. Most common mixtures are prepared by physically mixing an oxidizer with a fuel, however in more recent years, improvised formulations have been developed through chemical reaction synthesis to combine both the oxidizer and fuel into complex molecules. In a recent FBI investigation [4], a variety of fuels were identified as significant materials to warrant further characterization of their explosive/detonation properties (e.g., detonation velocity, pressure/impulse, critical radius, etc.). Standard procedures were also developed for preparing these materials.

The explosive properties of ammonium nitrate (AN)/fuel mixtures have been investigated extensively. In a series of articles, Miyake et al. (e.g., [5,6]) investigated the detonation properties of AN/activated carbon mixtures at stoichiometric composition for different physical parameters (i.e., mixing ratio and charge diameter). They found that the detonation velocity at the peak pressure was far below the theoretically predicted value and thus confirmed its non-ideal detonation behavior (i.e., detonation reaction kinetics are relatively slow, resulting in a long detonation

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Nomenclature

A	sample geometric cross-sectional area [m^2]
$c_p(T)$	specific heat capacity [$J\,g^{-1}\,K^{-1}$]
(dT/dt)	sample temperature–time derivatives [$K\,s^{-1}$]
$F(T, T_o)$	heat transfer term [W]
I_l	intensity of the laser beam that heats the sample [$W\,m^{-2}$]
k	coverage factor
$m(t)$	sample total initial mass [g]
n	number of samples
$q(T)$	specific heat release rate due to chemical reaction [$W\,g^{-1}$]
Q	total specific heat release (or absorption) [$kJ\,g^{-1}$]
s	standard deviation
t	time [s]
T	temperature [K]
T_o	baseline sample temperature [K]
u_c	combined uncertainty

Greek symbols

$\beta(T)$	absorptivity
λ	laser wavelength [m]
ΔH	change in enthalpy [$kJ\,g^{-1}$]
Δm	mass of the reactive portion of the sample, mass loss [g]
$\tau(T)$	temperature-dependent relaxation time [s]

Subscripts

1, 2	two different laser fluences
sas	sample and substrate
so	substrate only

zone and dependency on different physical parameters). Hurley et al. [7] studied the explosion characteristics of AN with different alternative solid fuels (i.e., sugar and coal dust). Grain size of the AN and solid fuel was found to be a critical parameter. The solid fuel detonation velocity was also found to be lower than that for fuel oil. Buczkowski [8] presents calculated values for the heat of explosion (total thermal energy release) for isolated AN, as well as for AN/fuel (ANF) mixtures, which are compared with those for standard high explosives such as trinitrotoluene (TNT) and hexogen. The addition of fuel to isolated AN was found to increase considerably the heat of explosion, while inert substances tend to absorb and reduce the released thermal energy [9]. Their calculated result for isolated AN was 1.712 $kJ\,g^{-1}$, which compared well with the total energy release measured by Nazarian and Presser [10] of $2.10 \pm 0.22\,kJ\,g^{-1}$. The measured thermal decomposition temperature for both studies was estimated to be 503 K. It is noted that AN mixtures with wooden dust, coal, and mineral oil are characterized by a more than twofold increase in the heat of explosion (i.e., 3.803 $kJ\,g^{-1}$, 3.860 $kJ\,g^{-1}$, and 4.018 $kJ\,g^{-1}$, respectively), as compared to isolated AN. These values are only lower than the value for TNT by 10% to 20% (i.e., 4.584 $kJ\,g^{-1}$), whereas, the AN/aluminum mixture value (i.e., 6.744 $kJ\,g^{-1}$) is significantly higher than that of TNT. Also, the thermal decomposition temperature was found to decrease with the additive fuels, as compared to the isolated AN.

1.1. Need for improving confidence in identifying mixture composition

A variety of commercially available analytical techniques are used in forensics analyses to identify the composition of improvised mixtures to some level of uncertainty [11]; often the compound signature may not be in the instrument database, forcing the software to make a "best" choice [12]. These techniques provide thermal, mass, and optical-spectral signatures from the unknown composition for comparison to signatures in database libraries [13]. In addition, signatures from secondary sources (e.g., residues from either materials used in the preparation or products of reaction) potentially can provide additional information for identification purposes. To improve the confidence level for identifying a particular mixture and its precursors, and meet forensic-analysis standards, new methodologies and database tools are required to statistically combine signatures from a variety of analytical instruments for chemical identification under different environmental conditions. Statistically combined signatures obtained from different independent measurement techniques (as opposed to reporting these signatures separately), can potentially improve the confidence level for identification and reduce the forensic processing time. A statistical/probability methodology is needed to combine (fuse) accessible signature data sets [14], which specifies confidence levels associated with the proper identification of a selected chemical. A variety of different mathematical approaches exist (e.g., Bayesian statistics [15], Dempster-Shafer theory [16,17], and Rule-Based Data Fusion [18] methods), which may be used to address this issue of statistical data fusion. Ultimately, the thermal, mass, and spectral signatures can be correlated to pre-identified precursors, and used to establish a database with improved confidence levels. Thus, measuring thermal, mass, and spectral signatures of a precursor or residue of unknown composition could then be matched with signatures of known composition from a variety of databases, with improved confidence levels through the use of statistical data fusion, to identify the unknown substance with higher certainty. To this end, this investigation addresses one aspect of this overall strategy, which is to provide thermal signatures from calorimetry measurements.

1.2. Issues associated with commercially available calorimetry techniques

Typically, calorimetry techniques are used to estimate the thermal energy release from materials. Commercially available calorimetry techniques include differential scanning calorimetry, differential thermal analysis, thermogravemetric analysis, and a family of variant arrangements. These systems are widely used in a variety of different applications, however, one must be aware of the reported systemic operating issues (affecting sensitivity and resolution [19]), as well as some more significant limitations. For example, these techniques are associated with relatively low heating rates (limited to 10 K/min to 20 K/min), which can result in integration of the detailed thermal behavior, as fuel volatile components decompose and vaporize prior to reaching the sample preselected steady-state temperature [20]. The sample composition then may not be representative of the expected thermal behavior. Thus, higher heating rates are required to attain higher temperatures before the occurrence of significant substance decomposition and chemical reactions. Also, the instrument measurement depends on sample size and heating rate. If the sample mass is too small, or the heating rate too high (as with micro-differential scanning calorimetry [21]), then the sample is consumed before completion of the thermal cycle and precise thermogram details are not recorded with actual sample. The data obtained with these instruments may underestimate the explosive potential of an energetic material under certain conditions [20,22]. In addition, multiphase mixtures and nonhomogeneous solutions [19,23] are unsuitable for instrument analysis due to endothermic vaporization of volatile components (preferential vaporization) and leakage from the pan [23]. Other reported effects [24] include sensitivities due to mass contact area, geometry and shape as it