

Development of a miniature calorimeter for identification and detection of explosives and other energetic compounds

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Abstract

The development of versatile systems capable of providing rapid, portable, and inexpensive detection of explosives and energetic compounds are critically needed to offer enhanced levels of protection against current and future threats to homeland security, as well as satisfying a wide range of applications in the fields of forensic analysis, emergency response, and industrial hazards analysis. Calorimetric techniques have been largely overlooked in efforts to develop advanced chemical analysis technology, largely because of limitations associated with the physical size of the instruments and the relatively long timescales (>30 min) required to obtain a result. This miniaturized calorimeter circumvents these limitations, thereby creating a first-of-its-kind system allowing thermal analysis to be performed in a portable format that can be configured for use in a variety of field operations with a significantly reduced response time (~2 min). Unlike current explosives detectors, this system is based on calorimetric techniques that are inherently capable of providing direct measurements of energy release potential and therefore do not depend on prior knowledge of familiar compounds.

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1. Introduction

Thermal analysis or calorimetry is a widely used technique for obtaining both qualitative and quantitative information about thermal transitions associated with a particular material or process. Because all chemical reactions and most physical changes are associated with intake or release of heat, a quantification of thermal energy provides a simple and universal method for characterizing materials and processes. Thermal analysis has been effectively employed in forensic and customs applications and for the analysis of pharmaceuticals, asphalts, oils, and waxes [1–4]. Despite these advantages, there is an ongoing need for next-generation calorimetric devices to provide advanced sensing capabilities for use in chemical process-safety, homeland security, and military applications. The ability to perform chemical fingerprinting on the basis of thermal characterization data

will provide new capabilities that will be broadly applicable in both current benchtop scale and future microscale calorimetric systems. When dealing with explosives, the nanocalorimetry system will allow a rapid characterization to be performed so that an appropriate level of initial response can be deployed while subsequent detailed analyses are performed to confirm the fingerprint result, as shown in Fig. 1.

After sample collection and concentration, the miniaturized calorimeter and data analysis capabilities will be used to provide a rapid chemical fingerprint of the compounds in question. If signatures consistent with explosive materials are identified, an initial level of response can be quickly deployed while subsequent detailed analyses (e.g., GC/FTIR, GC/MS) are performed to confirm the fingerprint result.

1.1. Overview of current explosives detection technologies [5–7]

Explosives detection technology includes bulk detectors that use X-rays or nuclear-based technologies to detect materials in containers, trace detectors for vapors and small amounts

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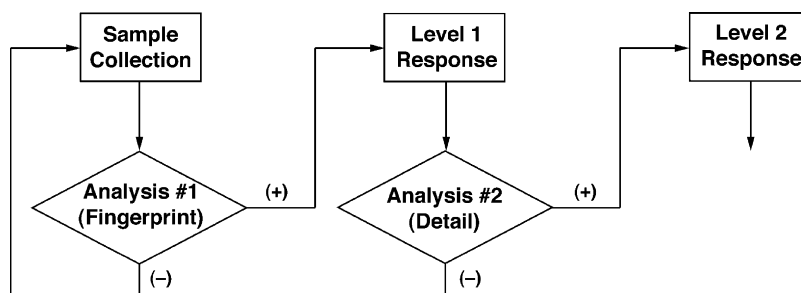


Fig. 1. Overview of the explosive/energetic material fingerprinting system.

of condensed materials, and composite detector systems that include more than one technology. Current explosive trace detectors include the following:

- *Gas chromatography (GC)/electron-capture detector (ECD)* detects compounds with high electron affinity, including nitroexplosives, carbonyls, alkyl halides, and organometals. Because it also detects some common non-explosive substances such as oxygen and fertilizers, ECD is often fitted with an front-end gas chromatography (GC) to achieve a higher probability of explosive material identification.
- *GC/chemiluminescence (CL)*, also known as *GC/thermal energy analyzer (TEA)*, uses an infrared detector for nitro (NO_2) or nitrate (NO_3) groups that are contained in many explosive compounds and fertilizers. Therefore, CL is also combined with a front-end GC for acceptable selectivity.
- *GC/ion mobility spectrometry (IMS)* ionizes sample molecules by a weak radioactive source with the reactant gas to create reactant ions such as Br^- , Cl^- , NO_3^- , or NO_2^- . The product ions formed are transported by an electric field toward a detector. Identification of specific explosives is based on times for ions to reach the detector. IMS detectors can identify some of the most common explosives, but the resolution can be insufficient in certain cases involving sample mixtures. For such sample mixtures, a front-end GC is used to separate the species and increase the resolution [8].
- *Field ion spectrometry (FIS)*, also known as *transverse field compensation ion mobility spectrometry*, is similar to IMS, requires a radioactive source, and involves quantifying ions carried in a gas at atmospheric pressure but attains an acceptable selectivity without a GC.
- *GC/surface acoustic wave (SAW)* employs shifts in the resonant frequency of a piezoelectric crystal based on mass and properties of materials condensed on the crystal. To separate explosives from potential interferents, it must be coupled with a front-end GC.
- *Thermo-Redox* is a nitro group-specific detector. Thus, it cannot distinguish explosives from potential interferents containing nitro groups.

1.2. Motivation for developing a miniaturized calorimeter to detect explosives

Almost all the early explosive detection techniques focus on identifying common nitrogen-based commercial and mili-

tary explosives (e.g., organic nitrates, organonitro, and nitrogenous compounds). However, as the procurement of traditional explosives becomes difficult with increasingly stricter regulations and security, terrorists have been seeking to utilize “non-traditional explosives” or “transparent explosives” to circumvent nitro/nitrate detectors. For example, ANFO, black powder, TATP, perchlorates, and chlorates are common transparent explosives used in various terrorist situations. In addition, there are a number of energetic materials that can be potentially utilized as explosives. For example, hydrogen peroxide and hydroxylamine are two common inorganic chemicals capable of undergoing detonations at elevated concentrations [9]. These compounds can easily be carried in an ordinary water bottle, and an exothermic reaction leading to explosion can be initiated using readily available metal powder.

Traditional explosives generally contain the atoms carbon (C), hydrogen (H), nitrogen (N), and oxygen (O), and usually incorporate sufficient oxygen to serve as an oxidizer during the chemical reaction leading to explosion. “Composite” explosives can also be created in which oxidizers and fuel are not part of the same molecule by mixing common oxidizers (chlorates, peroxides, perchlorates) and fuels (petroleum, turpentine, heavier hydrocarbons). A few of the oxidizers and fuels that can be used to produce composite explosives are listed in Table 1 [10].

Non-nitro/nitrate explosives are extremely difficult to identify using most of the current employed explosive detection techniques. The explosion potential of such systems can, however, be gauged from their thermal analysis curves. The determination of explosive tendency of a composition is based on the energy content obtained from thermal analysis. The rate of energy release information, which can be obtained from the aspect ratio of the thermal analysis trace, is useful for characterizing energetic behavior and categorizing the material [11]. Because the determination of explosive behavior from a thermal analysis is based on the amount and the rate of energy released, it is possible to characterize pure chemicals and mixtures. Calorimetric techniques have been used to characterize a variety of substances. Unfortunately, due to limitations associated with size, cost, and throughput, no currently existing calorimeters are suitable for field deployment to detect explosives.

The samples of explosives trace detectors may include a plurality of particles, which can be collected from the ambient environment. A recent study shows that explosives can still be detected using tabletop differential scanning calorimeters (DSC), which implies that there is no issue of false negative

Table 1
Oxidizers and fuels capable of forming explosives [10]

Oxidizer		Fuel		
Functional group	Examples			
Perchlorates	KClO ₄	Nitrobenzene	Petroleum	Halogenated hydrocarbons
Chlorates	KClO ₃	Nitrotoluene	Turpentine	Halogens
Hypochlorite	Ca(OCl) ₂	Nitronaphthalene	Naptha	Powdered metals
Nitrates	KNO ₃	Nitrocellulose	Castor Oil	Carbon disulfide
Chromates	PbCrO ₄	Picric Acid	Sugar	Phosphorus
Dichromates	K ₂ Cr ₂ O ₇		Glycerin	Sulfur
Iodates	KIO ₃		Acetylene	
Permanganates	KMnO ₄		Wax	
Metal oxides	BaO ₂		Sawdust	
Peroxides	Na ₂ O ₂			

when a device fails to alarm in the presence of explosives [12]. The explosives, however, might not be identifiable if the sample is contaminated with other particles, as the shapes of the thermograms would change as the concentrations of the samples changes. Nevertheless, the nanocalorimeter is designed to be a versatile detection or screening system for all condensed phase energetic materials or explosives. If the sample contains other particles that are not resolved by the calorimeter trace, a more detailed analysis can be performed if necessary, to identify the specific type of explosive. All of these current technologies rely on specific identification of explosive material and therefore depend on knowledge of type of explosives. The nanocalorimetry system, however, is based on calorimetric techniques that are inherently capable of providing direct measurements of energy release potential and thus does not depend on prior knowledge of familiar compounds. Consequently, the nanocalorimeter device will be able to characterize thermally any type of energy releasing compounds. In addition, due to their low cost, it will be cost effective to use the devices both as stand-alone detectors and to supplement other detection technology in order to achieve a higher level of characterization and categorization accuracy.

2. Calorimeter design and fabrication

Although thermal analysis is an established technique for material characterization and miniaturized calorimeter systems have been reported in the literature [13–15], none of them are suitable for field measurements. The basic design of the calorimetry cell consists of (i) a thermal control module incorporating arrays of micro-fabricated heaters and temperature sensors, as well as necessary electronic interconnections, and (ii) a sample encapsulation module incorporating etched enclosures designed to accommodate either solid or liquid samples. These two components are fabricated separately and assembled to form the completed calorimetric cell, as shown in Fig. 2.

The device consists of separate thermal control and sample encapsulation components, which are assembled to form the complete device. The sample enclosure configuration depicted here is suitable for use with liquid samples. At this size scale, over 200 devices can be fabricated on a single 6-in. diameter wafer.

A number of thermal isolation strategies are available involving etching the substrate from the backside of the wafer to create a barrier between the reference and sample locations in order to minimize lateral heat flow. A simplified approach to provide an enhanced degree of thermal isolation involves a dicing saw to machine trenches in the backside of the wafer. Preliminary 3D heat transfer simulations performed using the COMSOL Multiphysics software (formally FEMLAB) indicate that greatly enhanced thermal isolation can be achieved using these strategies relative to an unmodified wafer. Also, a series of additional simulation studies were performed to explore an optimal design to achieve sufficient thermal isolation for expected applications.

In addition to silicon, transparent substrates can be used for fabrication of the thermal control components in order to provide the unique capability to achieve simultaneous optical and thermal characterization of the sample. The heater and temperature sensor array can be fabricated on the surface of glass or z-cut quartz wafers using essentially the same processes described for silicon substrates. To allow maximum light transmission

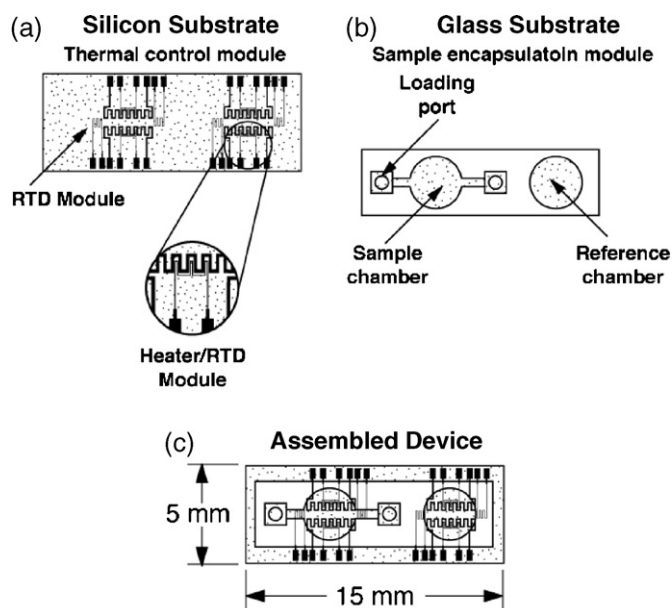


Fig. 2. Schematic illustration of the proposed micro-fabricated calorimetry cell.

through the substrate, the thermal control elements can either be positioned around the perimeter of the sample chamber, or be fabricated using polysilicon or indium tin oxide (ITO) thin films that allow light transmission with minimal attenuation. The use of glass or quartz substrates is also potentially advantageous from the standpoint of providing reduced thermal conductivity, thereby offering improved thermal isolation between the sample and reference cells. Such devices have the potential to provide simultaneous optical, X-ray, spectroscopic (e.g., FTIR), or light scattering measurements during the course of a calorimetric experiment so that an enhanced degree of material characterization and fingerprinting can be achieved. It is possible that a sufficient level of thermal isolation may not be achievable in certain specialized reaction systems. Even if this is the case, our device design can still be used by separating the sample and reference chamber portions of the device into two physically distinct dies.

The heaters and RTDs are located directly beneath the sample in order to provide a highly accurate reading of the temperature inside the sample and reference chambers. We also perform coordinated experiments and simulations to determine the performance of heating and sensing elements fabricated using different metals (e.g., Pt, Al, Au, Ti, Cr). Temperature control is achieved using resistive heaters patterned on the thermal control module. Because the resistance of the heaters is known, the electrical output current can be monitored to determine the power supplied to the heater. Similarly, temperature is measured by monitoring the change in resistance of similar elements as a function of temperature. For platinum heating elements, resistances in the vicinity of 2 k Ω provide temperature sensitivity to within 0.2 °C depends on precision of voltage drop measurements. A four-lead arrangement is used to isolate the resistance change in the vicinity of the sample from that associated with the connector leads. The readings of several temperature sensors can be used to account for spatial inhomogeneities in the temperature field.

The sample enclosure design and loading process largely depend on the type of sample to be studied. For liquid samples, the enclosure consists of a fluidic channel intersecting a chamber centered over the heaters and temperature control circuitry. Access holes are machined into the glass substrate, allowing individual samples to be loaded using a syringe. An externally pumped fluidic manifold can be constructed to allow automated loading and unloading for processing of multiple samples. After loading the sample into the channel, the access ports are sealed using epoxy, through the application of mechanical pressure to cover the holes or through the use of sealing valves in a fluidic manifold. Solid samples can be inserted directly into an etched chamber, after which the chamber is covered and sealed. Additional mechanical pressure can be applied using a loading fixture to maintain sample confinement during the run.

A key question is the extent to which the calorimetric cell can be scaled down. The potential loss of sensitivity due to a reduced sample quantity must be balanced by allowance for a sufficient number of devices to be fabricated on a single wafer in order to realize the enormous cost benefits from photolithographic fabrication techniques. Because these micromachined

calorimetry cells occupy a small surface footprint, they can be closely spaced to maximize the number of devices produced on a wafer. This level of cost savings also is expected to allow disposable single-use calorimetry cells, thereby reducing complexities and potential contamination issues associated with unloading and reloading multiple samples.

3. Data acquisition and analysis

The control algorithm and associated data acquisition system for the nanocalorimeter employs a simplified proportional control circuit whereby the same heating power (P_{avg}) is supplied to both sample and reference chips, in order to change their mean temperature according to a preset scanning rate. When a reaction (or any thermal event) occurs in the sample, a temperature difference is created between the two chambers. This temperature differential is fed to a proportional controller that compensates for the reaction heat flow rate by increasing or decreasing the heating power by an increment ΔP . The compensating heating power is proportional to the measured temperature difference ($\Delta T = T_S - T_R$) according to the relationship $\Delta P = K_1 \Delta T$, where K_1 is a constant. A heat flow rate, $\varphi = K_2 \Delta T$, is then assigned to the measured temperature difference, where K_2 is determined by calibration.

The control algorithm was implemented via a modular distributed I/O system (FieldPoint; National Instruments) and controlled by a Windows-based PC. The FieldPoint unit consists of a terminal base incorporating analog voltage outputs with a range of zero to five volts as well as a resistance temperature detector (RTD) module. This unit enables the device to impose a user controlled constant heat rate on the sample. The PC connected to the distributed I/O system can independently address and control the various voltage outputs of the modules using LabVIEW Express™ 7 software. The modular design of the LabVIEW-based platform will allow the development and testing of a variety of operation and analysis modes to suit the needs of a range of samples and applications. This system is also highly amenable to portable operation using a laptop computer or personal digital assistant (PDA) to perform instrument control and data acquisitions outside the laboratory environment.

Calibration of the temperature sensors was performed by placing each device in an oven and monitoring the RTD resistance at a series of temperatures. A fit to these data provided a calibration curve for the temperature response, which was linear within the range of interest for these applications. On-chip temperature control was achieved by resistive heating in response to a potential applied to the heater elements using feedback control from the RTD sensors. The LabVIEW system was used to monitor and control the thermal output, as well as measure the changes in power applied to the heaters in order to identify thermal transitions.

To test the concept of the simplified nanocalorimeter design, the thermal transition associated with the boiling point of acetone ($T_{bp} = 56.2$ °C) was studied. A 350 nL volume of acetone was loaded into the sample channel of the prototype device shown in Fig. 2c, after which access holes were sealed with

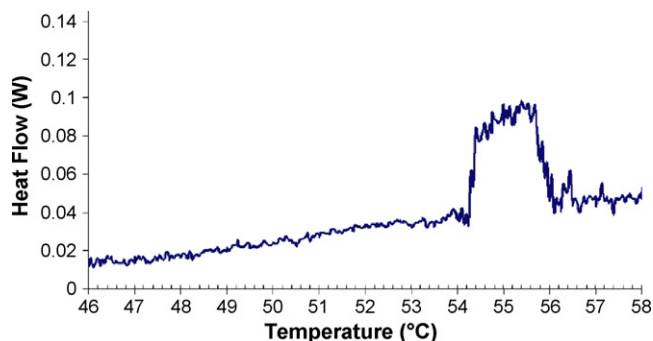


Fig. 3. Thermal analysis data from the nanocalorimeter prototype. Plot of heat flow as a function of temperature during a 1 °C/min heating scan of a 350 nL acetone sample using the prototype nanocalorimeter device shown in Fig. 2c. The observed curve centered near 55.2 °C is roughly consistent with literature values for the boiling point (56.2 °C).

epoxy to fully encapsulate the sample. The nanocalorimeter chip was then heated at a rate of 1 °C/min while the power supplied to the heaters was monitored. Using this protocol, a peak was observed consistent with the liquid–vapor transition, as shown in Fig. 3).

The measured phase transition temperature for acetone is about 1 °C lower than the literature value because of thermal lag from the sample to the RTDs and high surface to volume ratio of the sample chamber. Calibrations can be performed in applications where more accurate temperatures are required for phase transitions or other measured phenomena due to thermal lag.

3.1. Redesign and improvements

The preliminary results obtained in the prototype device illustrated proof of concept for calorimetry, and we now plan to design and fabricate reactors to be used as nanocalorimeters. Key improvements incorporated in the nanocalorimeter design, shown in Fig. 4, include: a 98% reduction in overall thermal mass, simplified single-mask layout, improved temperature sensing circuit, and improved thermal isolation. The dramatic reduction in device thermal mass is beneficial both in terms of increased sensitivity owing to the greatly reduced heat capacity of the chip itself, and in terms of significantly faster heating rates requiring less power so that scans can be performed in a few minutes. Moreover, because the proposed device is used to study thermal transitions associated with energetic compounds, the overall sensitivity requirements are expected to be easily achievable. The fact that the thermal transition associated with

Table 2
Typical calorimetric calibration standards [16]

Material (transition)	T_{trans} (°C)	ΔH_{trans} (J/g)
Gallium (s → l)	29.8	79.9
Benzoic acid (s → l)	123	148
Indium (s → l)	156.6	28.6
Tin (s → l)	231.9	60.4

acetone boiling was measurable using the relatively crude prototype virtually assures that the more sensitive redesigned device will detect the much stronger thermal signatures corresponding to the materials of interest (e.g., explosives).

4. Operation

A calorimetric experiment captures thermal transitions (phase change, reactions) that occur within the system. Because most of the explosive test systems of interest are expected to be solids, the thermal events expected within a calorimetric run are: phase transition from one solid state to the other (e.g., α -phase → γ -phase), melting or sublimation, and thermal decomposition. These transitions can be exothermic or endothermic as indicated by a positive or negative deflection in the measured power. The accuracy and sensitivity of the calorimetry system will be measured through the use of well-characterized calibration standards, as shown in Table 2 [16].

The onset temperatures, reaction enthalpies, and other reaction parameters will be measured in the nanocalorimeter with sample sizes of $\sim 1 \mu\text{g}$ and compared with the same parameters measured in an automatic pressure tracking adiabatic calorimeter (APTAC) or an accelerated rate calorimeter (ARC[®]) that use a larger sample size of ~ 2 –50 g. A library of representative reference chemical systems, shown in Table 3, will then be tested to benchmark the performance of the nanocalorimeter relative to other conventional hardware. Further refinements to the device design and control algorithm will compensate for systematic deviations and optimize performance.

4.1. Pressure inside the sample cell

Explosives are energetic compounds that can decompose or react rapidly with the production of a large volume of gas. If a decomposition reaction occurs, non-condensable gases such as nitrogen are usually formed. The volume of those non-condensable gases can be 100–1000 times of the original sample volume depending on the reaction conditions. With the

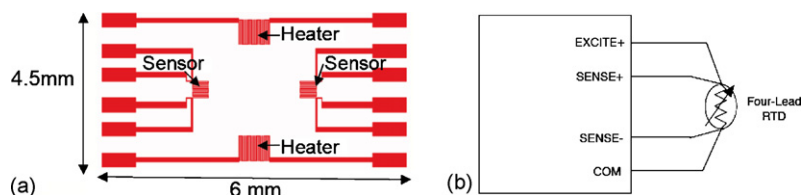
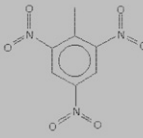
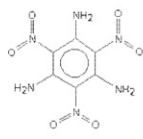
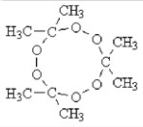
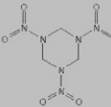


Fig. 4. Key elements of the redesigned nanocalorimeter chip, (a) heater and temperature sensor layout. The sample chamber will be centered on the chip, with temperature control elements located at the perimeter. (b) Circuit schematic of four-lead RTD arrangement.

Table 3
Common explosives

Explosive	Chemical Formula
Ethylene glycol dinitrate (EGDN)	$(\text{CH}_2\text{ONO}_2)_2$
Nitroglycerine (NG)	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{HCONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$
Trinitrotoluene (TNT)	
Ammonium Nitrate (AN)	NH_4NO_3
Urea Nitrate (UN)	$\text{NH}_2(\text{CO})\text{NH}_2 \cdot \text{NO}_3^-$
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	
Pentaerythritol tetranitrate (PETN)	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{O}_2\text{NOCH}_2\text{CCH}_2\text{ONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$
Triacetone Triperoxide (TATP)	
Cyclonite, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	

increasing vapor volume, the pressure inside the sample cell will also increase significantly. The working pressure of Pyrex[®] borosilicate glass can be up to 800 psi depending on its diameter and wall thickness (i.e., about 50 times the atmospheric pressure). Thus, there is a possibility that the nanocalorimeter cell may fail during tests of rapid decomposition or combustion reactions of explosives. Nevertheless, the nanocalorimeter chip is designed to be disposable with a relatively low cost. In addition, with nanogram amounts of samples, consequences of rapid runaway reactions will be minimized.

5. Conclusions

The hand-held nanocalorimeter will serve as a new generation of identification and detection tools for explosive and energetic compounds with high efficiency, reduced cost, and simplicity with ease of use. Initial work has led to successful fabrication of a chip capable of sampling nano-sized solid or liquid compounds. Control algorithms incorporating the DSC principle have also been written using LabVIEW. Future work will focus on modifying the chip design and control algorithm to improve accuracy and sensitivity, and developing trace analysis software to link it to a database of explosive information.

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