DEVELOPMENT OF AN ADVANCED NANOCALORIMETRY SYSTEM FOR

RAPID MATERIAL CHARACTERIZATIONS

A Dissertation

by

YEN-SHAN LIU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2006

Major Subject: Chemical Engineering

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Approved by:

Co-Chairs of Committee,	M. Sam Mannan
	Victor M. Ugaz
Committee Members,	Simon W. North
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ABSTRACT

Development of an Advanced Nanocalorimetry System for Rapid Material

Characterizations. (December 2006)

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Co-Chairs of Advisory Committee: Dr. M. Sam Mannan

Dr. Victor M. Ugaz

The development of a versatile system capable of providing rapid, portable, and inexpensive detection of explosives and energetic compounds is needed critically to offer an enhanced level of protection against current and future threats to homeland security, as well as to satisfy a wide range of applications in the fields of forensic analysis, emergency response, and industrial hazards analysis. The hand-held nanocalorimeter will serve as a first-of-its-kind screening tools for explosive and energetic compounds directly in the settings where they are needed with high efficiency, reduced cost, and simplicity with ease of use. 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.

The microfabricated calorimetry instrument consists of (i) a *thermal control modul*e incorporating arrays of microfabricated heaters and temperature sensors, as well as any necessary electronic interconnections, and (ii) a *sample encapsulation module* incorporating etched enclosures designed to accommodate either solid or liquid samples.

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. Device performance of the original and redesigned chips were tested by studying the thermal transitions associated with the boiling points of acetone and pentane. With the redesigned chip, the heat loss issue was reduced: the measured input heat was reduced from 32 times of the required energy to 5 times of the required energy. Future work will focus on modifying the chip design and control algorithm to improve accuracy and sensitivity, developing a trace analysis software to link it to a database of explosive information, and adapting different fabrication procedures for high temperature operation and large scale production.

DEDICATION

To my parents, brother, aunts, and grandparents for all their love and support.

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Finally, I am thankful for the support from the members of Mary Kay O'Connor Process Safety Center, especially Dr. William J. Rogers, who helped me with my research and technical work throughout my graduate study.

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CHAPTER I

INTRODUCTION OF THE PROJECT

1.1   Background

1.1.1   Thermal Analysis Techniques

Thermal analysis or calorimetry is a widely used technique for obtaining both qualitative and quantitative information about the thermal transitions associated with a particular material or process. Since all chemical reactions and most physical changes are associated with intake or release of heat, such a quantification of thermal energy provides a simple and universal method for characterizing materials or processes. There are a variety of commercial calorimeters and they are classified based on their measuring algorithm, mode of operation and construction. For example, Differential Scanning Calorimeter (DSC), Thermogravimetric Analysis (TGA), and Adiabatic Calorimeters (Bershtein et al., 1994; Wunderlich, 2005). By its very nature calorimetry facilitates determination of thermal properties such as heat capacity, enthalpies and other thermodynamic material characterization, quality control, and generation of physicochemical data, and Table 1 summarizes the applications of miniaturized calorimetry systems in various fields.

In addition, thermal analysis has been effectively employed in forensic and customs applications and for the analysis of pharmaceuticals, asphalts, oils, and waxes. Law enforcement agencies use DSC to trace the type of tires of offending vehicles

This dissertation follows the style of the *Journal of Loss Prevention in the Process Industries*.

Table 1.   Impact areas benefiting from miniaturized calorimetric technology

Application Area	Projected Uses of Instrumentation	Impact Areas
Fundamental studies	▪ Thermal transitions in micro/nano-scale samples (e.g., nanoparticles) ▪ Surface effects on chemical reactions in micro/nano-scale geometries	▪ Chemistry ▪ Chemical engineering
High-throughput screening	▪ Instrumentation for rapid characterization of thermal transitions in material libraries ▪ Simultaneous optical and thermal characterization	▪ Rational design of materials with tailored chemical properties ▪ Pharmaceuticals, drug discovery
Portable, low power instrumentation	▪ Routine calorimetric characterization ▪ Sensors to detect hazardous compounds via fingerprinting	▪ Fundamental research ▪ Homeland security ▪ Process safety

involved in traffic accidents (Lombardi, 1985). Furthermore, thermal analysis techniques have been used to help investigators solve a mobile home fire case by determining that the cause was explosion rather than external force (Riga, 1998). The U.S. Customs Service has even established several DSC methodologies to verify the countries of origin of imported nuts and cheese products (Dyszel, 1996). DSC has also proven to be an effective tool for detection and identification of illicit drugs (Chen et al., 2001).

1.1.2   Current DSC Technology

The differential scanning calorimeter (DSC) is a widely used technique on account

of its smaller sample size requirements (1-10 mg) and relatively rapid scanning rates (up to 20 $^{\circ}$C/min). During DSC analysis, a sample is heated under controlled conditions such that the difference between the power flow to the sample and a reference cell can be measured and correlated with the rate of energy change in the sample. Both the shape and location of features in the heat flow curve are useful for material characterization. Two predominant DSC system designs are currently in use, as shown in Figure 1 (Hatakeyama & Quinn, 1999; Höhne et al., 2003).
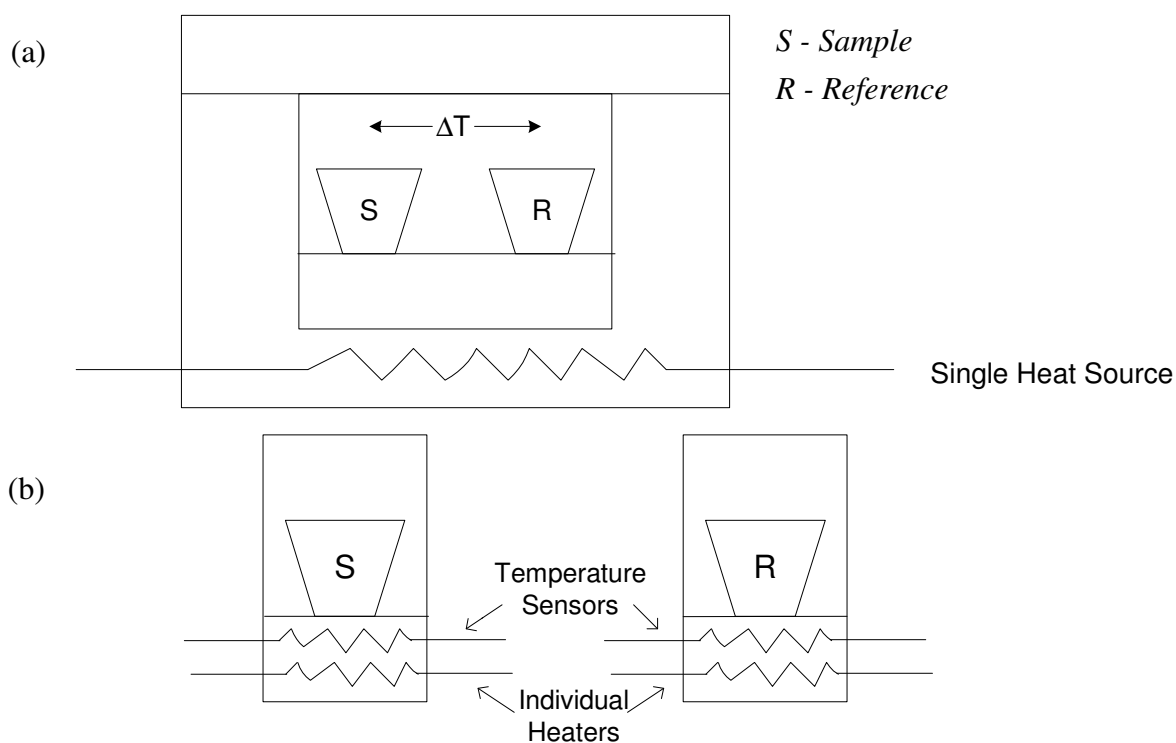
Figure 1. Illustration of DSC operational modes. Heat flux and (b) power-compensation DSC

(a)   In *heat-flux DSC*, the sample and reference are connected by a low-resistance heat flow path (e.g. a metal disc) and the assembly is enclosed in a single furnace.   The temperature difference between sample (S) and reference (R) is recorded and can be related to enthalpy change in the sample using calibration experiments.

(b)   In *power-compensation DSC*, the temperatures of the sample and reference are controlled independently using separate but identical heaters. The temperatures of the sample and reference are kept identical by varying the power input to the two heaters, and the energy required to do this provides a measure of enthalpy or heat capacity changes in the sample relative to the reference.

The instrumentation in our research plan operates under the *power-compensation mode*.

1.1.3   Motivation for Developing a Miniaturized Calorimeter

One drawback of conventional macroscale DSC technology is the large thermal mass of the calorimetric cell itself and its associated hardware. Consequently, the required energy input may be large compared with the energy associated with the thermal transitions to be measured.   This can pose problems in cases where only minute sample quantities are available for testing. The ability to perform calorimetric analyses over much faster time scales using reduced sample amounts is critical to meeting future needs. The advantages of miniaturizing this technology include reduced costs (including hardware and reagents), faster screening (suitability for high-throughput operation), portability, and ease of use.

The ability to perform thermal analysis in an inexpensive and portable format also has the potential to greatly expand the use of these techniques in the areas of quality

control and on-line measurement of chemical processes (Cheng et al., 2000) . Stricter customs procedures are currently being implemented in an effort to improve national security. These efforts, however, require the development of new and effective screening tools to identify trace amounts of energetic and hazardous materials in a rapid and cost effective manner. These miniaturized systems must incorporate a very small thermal mass and be able to use reagent quantities in the nanogram/nanoliter range. In order for these systems to operate effectively, rapid and uniform heating and cooling must be achieved while maintaining a high level of temperature homogeneity.

Recent developments in the area of nanoscale analysis of energetic materials (Carrillo, 2003) have motivated the development of calorimetric instrumentation for testing of nano-scale samples (ng, nL). These miniaturized systems are also inherently safer because the reactor size is very small, so hazardous materials cannot cause serious explosions or generate excessive heat. Lightweight lab-on-a-chip devices will allow detection of chemicals to be completed on site in seconds rather than hours. This feature will assist process engineers, armed forces, police officers, and other authorities during emergency response (Ratner & Ratner, 2004). 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 Figure 2.
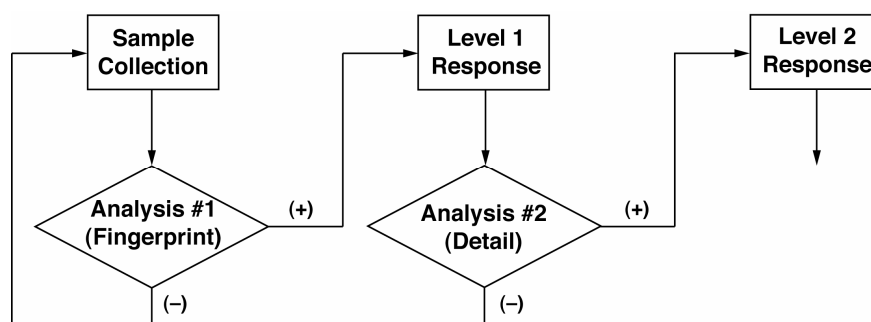
Figure 2. Overview of the explosive/energetic material fingerprinting system. After sample collection and concentration, the miniaturized calorimeter and data analysis capabilities will be used to provide a rapid chemical fingerprint of the compounds in question. If signatures consistent with explosive materials are identified, an initial level of response can be quickly deployed while subsequent detailed analyses (e.g., GC/FTIR, GC/mass spectroscopy) are performed to confirm the fingerprint result.

Although miniaturized calorimeter systems have been reported in the literature (Gevorgian, 1994; Mathonat et al., 1998; Nakagawa, 2000; Olson et al., 2000; Parlouer, 2000; Olson et al., 2003), none of them report the accuracy and precision of a conventional DSC. This research project can meet the ongoing need for next-generation nanoscale calorimetric devices for use in chemical process-safety, homeland security, and military applications.

CHAPTER II

APPLICATIONS OF THE NANOCALORIMETER

2.1   Trace Explosives Detection

2.1.1   Importance of Trace Explosives Detection

Since 1969, explosives have killed about 2,000 people on planes. Aviation security measure changed when major events occurred such as the 9/11 attacks in 2001 and the U.K. foiled plane-bombing plot in 2006.   After the U.K. bomb plot in August 2006, the strictest security measures in years have been implemented at airports. Many items are no longer permitted as carry-on items on planes, including iPods, cellular phones, laptops, and even books and magazines (Ripley, 2006). In addition, European ministers released 350,000 euros ($450,000) for urgent research into technology for detecting liquid explosives (EUbusiness, 2006). Besides air travel, mass transit also suffers from explosive attacks. Both of the London bombings in 2005 and Mumbai train bombing in 2006 have alerted government officials the need of improving explosives detection for public transportation. Common explosives detection methods may not perform well in mass transit. For example, canine detection suffers from several limitations as discussed in Section 2.1.2.1.

2.1.2   Types of Explosives Detection Methods

Explosives detection methods are classified in to two main categories: bulk explosives detection and trace explosives detection.

- Bulk explosives detection: Detection of explosives concealed in bulk quantities

can be achieved by remotely senses physical or chemical properties of explosives using either imagine or the nuclear properties of explosives, including x-ray backscatter imaging, gamma rays, millimeter wave energy analysis, terahertz imaging, electromagnetic imaging, neutron-based technologies such as thermal neutron analysis (TNA), fast neutron analysis, pulsed fast neutron analysis (PFNA), and pulsed fast thermal neutron analysis. A common drawback of most drawback systems is that they sometimes alerts false positive alarms by misidentify non-treat materials as explosives

- <u>Trace explosives detection</u>: Detecting residues of explosives or a tiny amount of explosives is usually based on the physical transport of vapor or particulates of explosives for direct chemical identification. Examples of common trace detection methods are usually separated in to two categories such as biosensors and chemical sensors. An ideal trace system would be capable of inexpensively detecting a specific threat substance and distinguishing it from a complex background on a time scale appropriate for terminating the threat and mitigating the impact on people, property and flight operations. Unfortunately, there is no trace detection system that is widely deployable and able to identify all threat substances in real time. In addition, trace detection systems sometimes results in false negatives due to various reasons such as low vapor pressure, inadequate sample collection, contaminated samples (Yinon, 1999; NRC, 2004).

2.1.2.1 Biosensors

Despite the recent surge in the publication of novel instrumental sensors for

explosives detection, canines are still widely regarded as one of the most effective real-time field method of explosives detection. Detector dogs are usually German shepherds, Belgium Malinois, or Labrador retrivers. With the most sensitive vapor detector among all the bio- and chemical sensors, sniffer dogs can recognize around 19,000 known smells associated with explosives such as nitrate compounds and acid salts, as well as chlorates and peroxides, acids. However, trained dogs do not perform well in mass transit due to several factors: boredom, distraction, unfamiliar signals, and inattention from handlers. Sniffer dogs work best in quiet places hat have been cleared of people other than their handlers, and need frequent rest such as every 30 minutes out of every couple of hours; otherwise, their performance can fall off quickly. In addition, direct contact between dogs and airline passengers raises liability concerns, especially when sniffer dogs are hungry or tired. Detector dogs may miss potential hidden explosives in small areas where are inaccessible to them (Gazit & Terkel, 2003; Schaffer, 2006). To reduce or eliminate the variability of this natural system, electronic dog's noses are created by a combination of chemical sensors, readout devices, and neural network processing schemes. However, it is still a long way to go for this type of electronic devices to be field operational.

Due to the drawbacks of sniffer dogs and reliability issues of electronic noses, researchers have turned their attention to other chemical specific biological systems such as wasps and rodents as novel trace detectors. Both of them do not have as sensitive vapor detectors as dogs; however, their training sessions take much shorter time and thus much cost-effective. For example, training a bee for a new explosive can take as quickly as five

minutes. Sniffer rats, on the other hand, require more training time. A selected breed of African rats, Cricetomys gambianus, are employed as explosives detectors in Mozambique. Rats can adapt to different environments easily. However, sniffer rats may pose a health concern of spreading local diseases. Additional field trails are still required to validate the reliability of sniffer rats for trace explosives detection. Given those limitations, it is recommended to combine several detection methods to ensure public safety, which include chemical sensors.

2.1.2.2 Chemical Sensors

Current explosive trace detectors include the following:

- GC/ECD (electron-capture detector) detects compounds with high electron affinity, including nitro explosives, carbonyls, alkyl halides, and organometals. Because it also detects some common nonexplosive substances such as oxygen and fertilizers, ECD is often fitted with a front-end gas chromatography (GC) to achieve a higher probability of explosive material identification.

- GC/CL (chemiluminescence), also known as GC/TEA (thermal energy analyzer), 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/IMS (ion mobility spectrometry) 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 (Ewing, Atkinson et al. 2001).

- FIS (field ion spectrometry), 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/SAW (surface acoustic wave) 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 (Rhykerd et al., 1999; Yinon, 1999; Thiesan et al., 2005).

2.1.3 Advantage of Thermal Analysis for Trace Explosives Detection

2.1.3.1 "Transparent" Explosives

A large variety of energetic materials are used as explosives such as organic nitrates and organonitro compounds, ketone and acyl peroxides, inorganic chlorates, perchlorates, nitrates, fulminates, and acetylides. Early detection technologies focus on organic nitrates, organonitro, nitrogenous compounds because all commercial and military explosives are those 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, triacetone triperoxide (TATP), perchlorates, and chlorates are common "transparent" explosives used in various terrorist situations. A common highly unstable liquid explosive and "transparent" explosive is TATP, which has been employed by Middle East terrorists in suicide bombings, e.g. London bombings in 2005. When the peroxide bond of TATP breaks, a series of decomposition reaction will occur and release a significant amount of heat and pressure. TATP has 88% of the power of TNT and is comprised of peroxide, acetone, and sulfuric acid. Thus, a TATP bomb can be made of common materials for about $50. 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 (Cisneros et al., 2004). 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.

2.1.3.2 "Composite" Explosives

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 are another types of novel explosives that 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 2
(Oxley, 1995).

Table 2. Oxidizers and fuels capable of forming explosives (Oxley, 1995)

Oxidizer		Fuel		
Functional group	*Examples*			
Perchlorates	$KClO_4$	Nitrobenzene	Petroleum	Halogenated hydrocarbons
Chlorates	$KClO_3$	Nitrotoluene	Turpentine	Halogens
Hypochlorite	$Ca(OCl)_2$	Nitronapthalene	Naptha	Powdered metals
Nitrates	KNO_3	Nitrocellulose	Castor Oil	Carbon disulfide
Chromates	$PbCrO_4$	Picric Acid	Sugar	Phosphorus
Dichromates	$K_2Cr_2O_7$		Glycerin	Sulfur
Iodates	KIO_3		Acetylene	
Permanganates	$KMnO_4$		Wax	
Metal oxides	BaO_2		Sawdust	
Peroxides	Na_2O_2			

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 (Saraf et al., 2003). 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 the 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 nanocalorimeter can serve as a "transparent" explosive detection device for a screening purpose by measuring a direct energy release from the compounds without prior knowledge of explosives in its analysis database. If the sample is contaminated with other particles, after a potential explosive is found, a more detailed analysis can be done if necessary in order to identify the specific type of the explosive.

2.1.4 Cost Evaluation of Trace Explosives Detection

In addition to the initial capital cost for the trace explosives detection system, other recurring or ongoing costs such as the operation, consumables, maintenance, and quality assurance costs should also be considered. An economic analysis of the common trace detection systems including the nanocalorimeter were carried out. The present values of those detection systems are summarized in Table 3 using the following formula:

Present Value = Capital Cost + Recurring Costs * (*P/A, i, n*)

– Salvage Value * (*P/F, i, n*)

Where P = a present sum of money

i = interest rate per interest period

n = number of interest periods

F = a future sum of money

Table 3. Present values of trace explosives detection technologies

(IAB, 2006; Shea & Morgan, 2006)

	Year 0	Year 1-10		Year 10	
	Capital Cost*	Operating Cost	Maintenance Cost**	Salvage Cost	Present Value
Nanocalorimeter	$2,000	$6,825	$500	$200	$55,800
GC/IMS	$30,000	$5,000	$10,000	$1,500	$139,562
GC/ECD	$20,000	$5,000	$5,000	$800	$93,153
GC/CL	$20,000	$5,000	$15,000	$5,000	$164,408
GC/SAW	$25,000	$5,000	$800	$1,000	$67,129
FIS	$30,000	$5,000	$1,000	$1,000	$73,601
Thermo-Redox	$15,000	$5,000	$800	$600	$57,352

Assumptions :   An interest rate of 6% is used to calculate present worth.

The operating cost of the nanocalorimeter is estimated with 5 chips/day and $1/chip.

As shown in Table 3, the present worth of our calorimeter is about $55.8K, while the present worths of the rest are approximately $139.6K, $93.2K, $164.4K, $67.1K, $73.6K, and $53.4K. Thus, the calorimeter is competitive economically among the trace explosives detection systems.

2.1.5 Potential Markets for Trace Explosives Detection

Threats posed to a country's critical infrastructure are constantly changing. With Homeland Security efforts changes domestically, there continues to be a significant need for innovative methods for detecting explosives. Detection technology has many applications from protecting the ports and borders, to airports and other mass transit systems, to crime scenes and hostile military areas. The nanocalorimeter can address the needs of the U.S. defense and related government agencies. The emergency responders and crime-fighters can use the nanocalorimeter for identifying explosive potential of a compound or mixture. Similar analysis can be utilized by the army for on-site screening of unknown chemicals. The estimated explosives detection market includes airports ($4 - $5 billion in the U.S. and $50 billion worldwide), border cargo (~ $1 billion), sea cargo ($2 - $4 billion), and vehicle screening according to Transportation Security Administration (TSA). It is apparent that the detection technology area in the Homeland Security industry continues to be a growing market. Besides explosives detection, the nanocalorimetry system will be an effective screening tool for process control and process safety, especially for small and medium-sized companies in the chemical processing industry (CPI) because those companies may not have a material screening tool in their risk assessment programs. Therefore, the nanocalorimeter market for process control and

process safety is also promising.

2.2   Process Control and Process Safety

One of the applications of calorimetry is to understand reactive hazards arising in chemical manufacturing. Chemical reactivity can be viewed as a double-edged sword for the chemical industry. On the one hand, it allows materials to undergo desired reactions to form products under moderate temperature and pressure. On the other hand, reactive hazard exists when changes in chemical structure have the potential to generate heat, energy and gaseous byproducts that cannot be safely absorbed by the immediate surroundings. If the rate of energy release is rapid enough and not adequately controlled, it may also lead to uncontrolled catastrophic incidents caused by polymerization, decomposition, oxidation-reduction (redox), acid-base reactions, or reactions with water.

Most large companies have reactive-hazard management programs to assess potential reactive hazards during storage, transport and processing of reactants, intermediates and products. The recommended procedure for evaluating and quantifying reactive hazards, shown in Figure 3, is slow and resource-intensive, and in-house tests are expensive and not practical. Screening of chemicals for reactive hazards represents a key first step in identifying reactive hazards. The use of appropriate screening tools can assure higher levels of process safety and reduce the high costs of detailed hazard assessment.

In addition, the decomposition behavior of energetic compounds is critically important for the safe handling, use, storage, and transportation of materials. Reactive chemical incidents involving runaway reactions represent a significant hazard and have contributed to a large number of fatalities, injuries, and property losses. Accurate
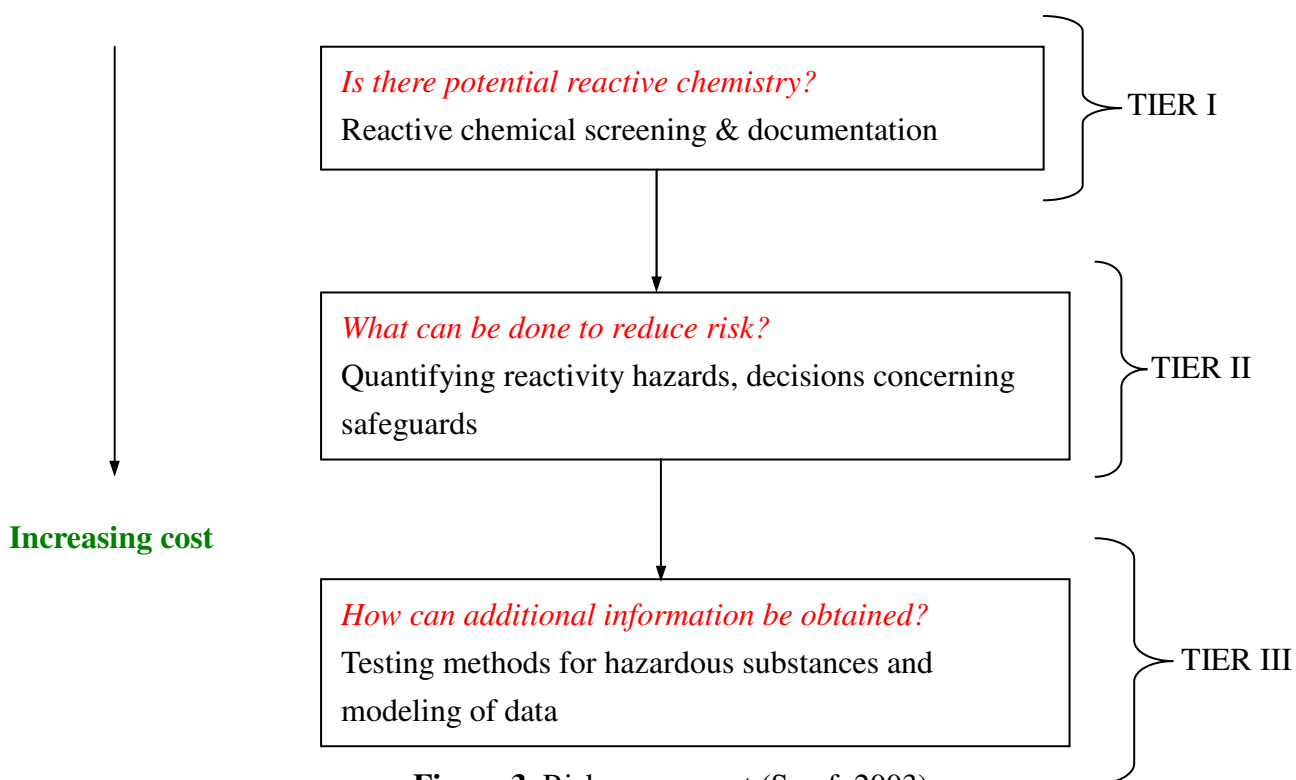
Figure 3. Risk assessment (Saraf, 2003).

measurement of the decomposition characteristics, however, is expensive, time consuming, requires high expertise, and poses numerous hazards for large scale testing. To classify energetic chemicals for transportation, the U.N. Recommendations specify tests for detonation, deflagration, and heating under confinement. These tests, however, are relatively large scale and very time consuming. One of the growing applications of calorimetry is to understand thermal hazards arising in chemical manufacturing processes in response to regulatory concerns raised by the U.N. and U.S. Chemical Safety and Hazard Investigation Board (CSB, 2002). DSC tests using small sample sizes (~1mg) are often employed for decomposition characterization of new chemicals because of the

lower costs and lower hazards of small sample sizes. Instrumentation capable of performing rapid testing using smaller reagent quantities is needed to reduce testing costs and to allow more samples to be tests.

Besides instrumentation tests, the following screening methods have been proposed to identify potentially reactive chemical hazards and avoid the expense of conducting numerous detailed hazard assessments (Liu et al., 2006):

- New Jersey's Toxic Catastrophe Prevention Act (TCPA), a state regulation that focuses on a substance's functional groups to identify reactive hazards (Bureau of Chemical Release Information and Prevention, 2004)

- The National Oceanic and Atmospheric Administration's (NOAA) Chemical Reactivity Worksheet, which has a large database of incompatible materials (NOAA, 2006)

- "*Bretherick's Handbook of Reactive Hazards,*" which provides detailed information on reactive chemicals, including incident records (Bretherick & Urben, 1999)

- Material Safety Data Sheets (MSDS), which can indicate such potential hazards as combustible liquid, explosive, flammable, organic peroxide, oxidizer, pyrophoric, unstable (reactive) or water-reactive.

Both of the NOAA Chemical Reactivity Worksheet and *Bretherick's Handbook of Reactive Hazards* focus on the incompatibility information of chemicals. There are many recent incidents due to chemical incompatibility or chemical contaminants in the streams, including two recent runaway reaction incidents involving hydroxylamine that in each

case destroyed the plant and caused multiple fatalities, as shown in Table 4. HA decomposition is very sensitive to contamination with Fe^{+2} or Fe^{+3}. The possible cause of these two incidents is HA decomposition initiated by the contamination with Fe^{+2} or Fe^{+3}. The nanocalorimeter can serve as an onsite screening tool for contamination in the streams, which can be critical for process safety and quality control for small- and mid-sized companies due to lack of effective screening tools.

Table 4. Two recent hydroxylamine (HA) incidents

Company	Date	Location	Consequences
Concept Sciences, Inc.	February 19, 1999	Pennsylvania	5 people killed;13 injured; 45,000-ft2 structure destroyed
Nissin Chemical	June 16, 2000	Japan	4 people killed; 25 injured; Plant destroyed

2.3   Other Applications

2.3.1. Forensic Analysis

Forensic scientists continue to search for new ways to find chemical residues on clothing, fingernail, hair, and skin samples. Such residues may provide a link between a suspect and a chemical weapon or agent. Advances in technologies for detecting and distinguishing trace evidence are finding their way to police precincts and forensic labs. The forensic analysts can utilize the nanocalorimeter to pre-screen the compounds at the investigation site for speeding up evidence collection and easing analysis.

2.3.2. Characterization of Nanoparticles

Recent advances in the synthesis of nanoscale materials present unique challenges for analysis and characterization of nanoparticles. According to the National Science Foundation (NSF), the nanotechnology-related products and services will become a $1 trillion industry worldwide by the year 2015 (Rittner & D'Aquino, 2003). The world market for nanoparticles has already reached $555.6 million and is rising at a 12.8%/yr, projected to exceed $900 million in 2005 (Roco, 2001). In order to advance scientific discovery and fundamental research in the area of nanoscale materials, a new generation of instrumentation must be developed with the capability to characterize sample quantities in the nanogram/nanoliter range with a greatly enhanced level of sensitivity. The miniaturized calorimetery system has the potential to provide enhanced sensing capabilities in an inexpensive portable format, so that measurements can be made directly in the settings where they are needed.

2.3.3 High Throughput Screening

During process or product development in the pharmaceutical industry it is critical to generate material properties using the smallest possible amount of sample. The sample size is extremely important in development process since drugs are synthesized in small quantities and are expensive, and very little of it is available for testing. Thermal analysis of minute samples will greatly impact the development of high-throughput materials screening technologies to aid in the rational design of materials with tailored chemical and biochemical properties. The molecular thermodynamics of drug candidates can be analyzed by the nanocalorimetry system.

CHAPTER III

FALSE ALARMS

3.1   Minimum False Negative Alarm Issue

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 when a device fails to alarm in the presence of explosives (Bannister et al., 2004). 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.

3.2   False Positive for a Screening Tool

Another performance factor of trace explosives detection technology is false negative: a detector reading suggesting the presence of an explosive or explosive device when explosives are not present. For common trace explosives detection technologies, personal items in the carry-on luggage such as hand creams, aftershave, heart pills, dry-cleaning and fertilizers can trigger false positive alarms. Similarly, the nanocalorimeter system may produce false positive results if the thermal signature of the

sample is mistaken as other compounds'. For the nanocalorimeter device, however, the false positive issue is not a serious issue because the nanocalorimeter device is primarily used as a versatile screening tool. Subsequent testings can further verify the identity of the substances. In addition, due to the low cost of the calorimeter cells, it will be cost effective to use the nanocalorimeter device both as a stand-alone detector and to supplement other detection technologies in order to achieve a higher level of characterization and categorization accuracy.

CHAPTER IV

CURRENTLY AVAILABLE SMALL-SCALED CALORIMETER AND CHIPS

4.1   Comparison of Small-scaled Calorimeters

Although thermal analysis is an established technique for material characterization

and several commercial small-scaled calorimeter systems are available (Table 5), none of

them is portable for field measurements. Furthermore, those small-scaled calorimeters are

not only expensive, but also with large minimum working sample volumes in either milli-

or micro-scale. The maximum heating rates are not suitable for the rapid screening

purpose, except TA Q1000 DSC.

Table 5. Comparison of smalled-scaled calorimeters

	TA Q1000 DSC (TA Instruments)	**Nano-DSC III** (Setaram Inc.)	**SuperCRC**^{TM} (OmniCal Inc.)
Cost of equipment	~ $110,000	~ $70,000	~ $50,000
Min. sample volume	1 mg	10 µg	2 ml
Temperature range	-180 ~ 770°C	-10 ~ 160°C	-100 ~ 200°C
Scanning rate	0.1 ~ 200 °C/min	1°C/min	1 ~ 2°C/min

4.2   Comparison of Calorimeter Chips

Several miniaturized calorimeter chips have been reported in the literature

(Gevorgian, 1994; Mathonat, 1998; Nakagawa, 2000; Olson et al., 2000; Parlouer, 2000;

Olson et al., 2003), however, each of them suffers from limitations that make them

difficult to deploy outside a laboratory environment, as shown in Table 6. For example, microfabricated calorimeters have been demonstrated for use in thin film characterization studies, however the thin film samples often delaminate from the surface and lose contact with the thermal control elements due to thermal stresses at elevated temperatures. A second design based on a thermopile array (Xensor Corp.) has also been used for thermal characterization of polymer and biological samples at temperatures up to 200 °C, however the distribution of thermopile elements on the chip surface introduces a position dependent response that can lead to incorrect measurements. Also, sample deposition cannot be performed outside the lab for onsite screening. In addition, the cost of the TDSC chip is too expensive to be disposable for screening highly energetic materials.

The nanocalorimeter devices can avoid these problems by employing a simplified cell design in which all elements possess temperature stability. In addition, this cell design can be constructed using a single mask photolithography process to greatly reduce the time and costs associated with fabrication. Miniaturization of the calorimetric cell also allows hundreds of devices to be produced on a single 6-inch silicon wafer, thereby reducing the per-device cost to a level below $1. Consequently, individual calorimetric devices can be considered disposable in order to eliminate problems associated with cross contamination and fouling due to repeated use of the same cell

4.3   Cost Analysis of Naocalorimeter System and Chips

Because these micromachined calorimetry chips occupy a small surface footprint, they can be closely spaced to maximize the number of devices produced on a wafer.

Table 6. Comparison of calorimeter chips

Company	Model	Sample Size (ng)	Max. Operating Temp.(°C)	Sensitivity	Sampling Technique	Major Applications	Cost / cell (US $)
Xensor	LCM 2506	ng	100	50 – 80 mV/K	deposition	Enzyme & catalytic reactions	150+
Xensor	LCM 2524	ng	100	50 – 80 mV/K	deposition	Enzyme & catalytic reactions	150+
IPHT	MKS 76	NA	NA	NA	NA	Bio-analysis	NA
	ETH	NA	NA	NA	NA	Bio-analysis	NA
	XI-71	NA	200	NA	NA	NA	NA
	PTB-TK	NA	200	NA	NA	NA	NA
UIUC	Thin-film	µg	700	0.01 mJ/cm^2	deposition	Polymer characterization	NA
This work	TAMU	10 - 50 nL	500	4 µW	injection	Fast on-site screening	< 1

This is an important consideration in order to realize the enormous cost savings available through mass production via photolithography. For example, for the proposed devices incorporating a footprint of 27 mm^2, nearly 300 nanocalorimeters could be arrayed on a 10 cm wafer, and over 650 could be arrayed on a 15 cm wafer. Based on a fairly conservative fabrication cost of $200 per wafer, this yields hardware costs of 66 and 30 cents per device for 10 and 15 cm wafers sizes, respectively. This level of cost savings will make it feasible to produce disposable single-use calorimetry chips, thereby eliminating complexities and contamination issues associated with unloading and reloading samples in the same device. The total cost of the complete system (hardware and software) is projected to be less than $2,000.

4.4   Advantages of the Nanocalorimeter

The total analysis of the nanocalorimeter is about two minutes because the DSC scanning rate is inversely proportional to the sample size, as shown in Table 7. Besides the rapid analysis time of the nanocalorimeter, the nanocalorimeter is also inherently safer because with nanogram samples, the consequences of a runaway reaction will be minimized.

Table 7. Estimated DSC scanning rate based on sample size (Wunderlich, 2004)

Sample size	Maximum scanning rate (order of magnitude)
1g	1 K/min
1mg	100 K/min
1mg	100 K/s
1ng	10,000 K/s

CHAPTER V

CALORIMETER DESIGN AND FABRICATION

## 5.1   Printed Circuit Board (PCB)

Printed circuit boards are designed in-house to accommodate any custom device layout requirements. The PCB fabrication involves the following steps: Prepare the circuit layout using graphic design software and then print the circuit artwork on an overhead transparency. Cut the copper-clad PC boards to the designed size, peel off the protective coating from the board, avoid touching the photo-sensitive surfaces, expose the transparencies and boards under the UV lamp, develop the boards, etch the boards by placing the PC boards with their artwork side up in a hot bath of etchant, and lift off photoresisit, as shown in Figure 4.

5.2   Nanocalorimeter Cell

The nanocalorimetry cell incorporates a modular design consisting of (i) a *thermal control module* incorporating arrays of microfabricated 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 were fabricated separately and assembled to form the complete calorimetric cell, as shown in Figure 5. This modular fabrication approach provides an enhanced level of flexibility by allowing the same thermal control module design to be used for testing a variety of samples through selection of an appropriate encapsulation module.
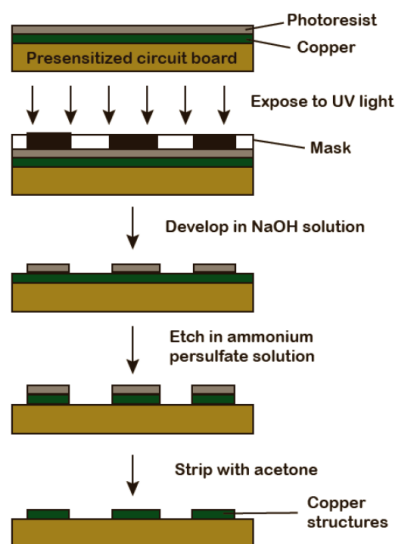
Figure 4. Process flow diagram of fabricating PC boards.
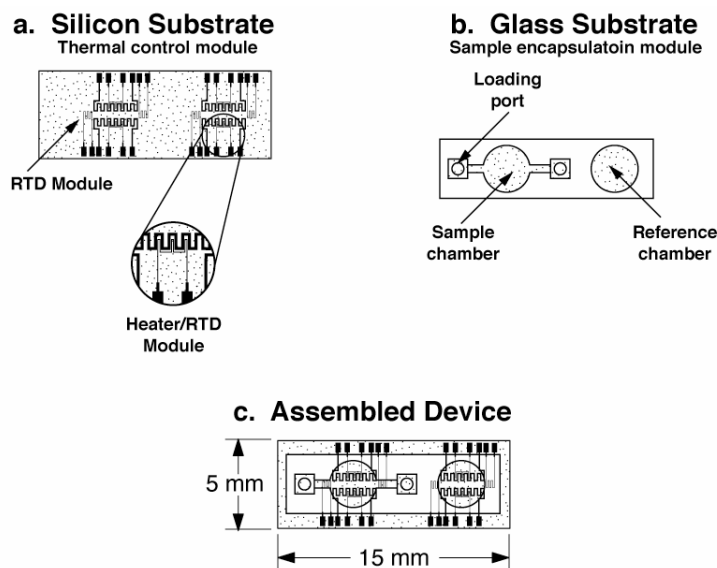
Figure 5. Illustration of the proposed microfabricated calorimetry cell.
The device consists of separate thermal control and sample encapsulation components, which are assembled to form the complete device. The sample enclosure configuration depicted here is suitable for use with liquid samples. At this size scale, over 200 devices could be fabricated on a single 6-inch diameter wafer.

5.2.1 Thermal Control Module

The basic fabrication process for the thermal control components (Figure 5a) begins with deposition of a thermal oxide layer (2,000 Å) on the surface of a standard p-type (100) silicon wafer (500 μm thick, 15 cm dia.) to provide electrical insulation from the substrate. The wafer is then spin-coated with a positive photoresist (e.g. Shipley #1827) and patterned with the heater and resistance temperature detector (RTD) arrays. After the pattern is developed, metal layers of 500 Å titanium followed by 1,000 Å platinum are deposited by electron beam evaporation. The photoresist and overlying metal is lifted-off using acetone, leaving only the heater and RTD array. Next, a 1–2 μm thick passivation layer is deposited to electrically insulate the heaters and RTDs from the sample to be studied. A number of passivation layer choices exist, including silicon oxide, silicon nitride, or polycrystalline silicon. The choice passivation layer depends on factors including the desired service temperature range, ease of deposition process, and ease of subsequent etching to establish electrical contact with the metal layer below. For example, both silicon dioxide and polysilicon can be deposited using conventional silane-based chemical vapor deposition processes at relatively low temperatures (400 – 600 °C).

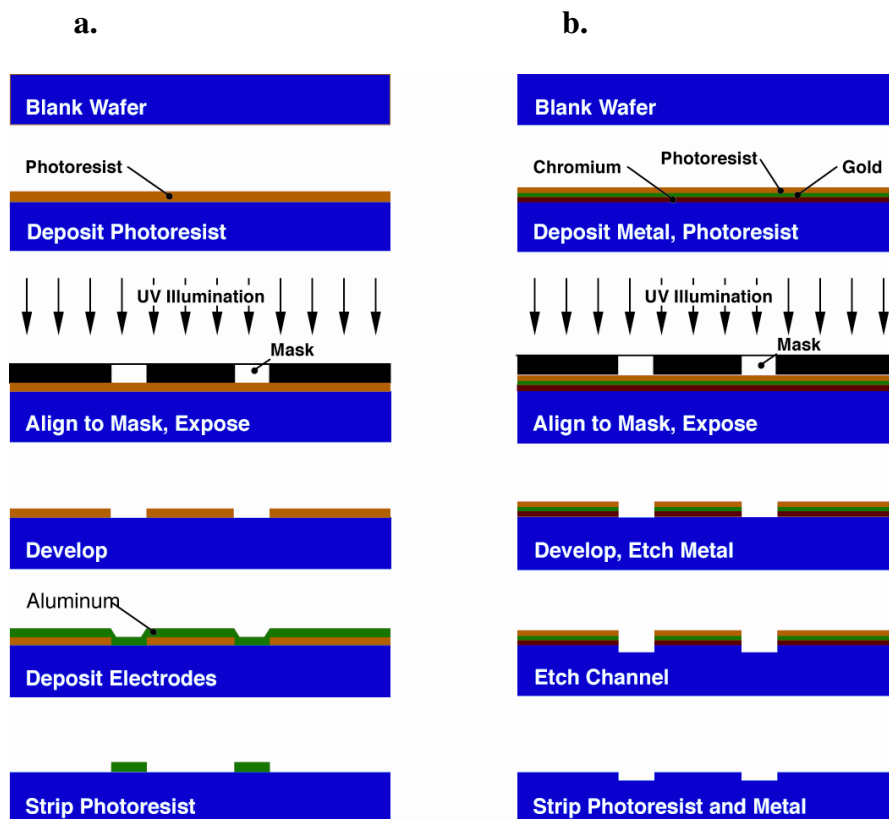A second lithography step is then performed to pattern the heater and RTD electrical contact pads, and the developed photoresist is hard baked for 30 minutes at 110 °C. An etching process is then performed to expose the underlying metal at the locations where electrical contacts are to be made. For silicon oxide, this process involves immersing the wafers in a solution of buffered hydrofluoric acid (7.2% HF /

36% Ammonium Fluoride, etch rate ~ 0.3 μm/min). If polycrystalline silicon is used as the passivation layer, etching can be performed using a 44g/100mL aqueous KOH solution at room temperature in order to allow the photoresist layer to serve as a mask. Because the choice of passivation layer plays a key role in our calorimetric device design, we will perform a detailed study of various passivation approaches (material, film thickness, deposition process, etching process conditions) in order to identify those that provide an optimal combination of processing ease and device performance. The ellipsometry equipment requested in the budget will be used to measure passivation layer film thicknesses to aid in this characterization process.   It is likely that different passivation approaches will be required depending on the samples and service temperature ranges of interest (30 – 400 ^{o}C), and the results of these characterization studies will allow rational selection of the optimum fabrication conditions.

5.2.2   Sample Encapsulation Module

Fabrication of the sample encapsulation component primarily involves an etching process to create a suitable enclosure.   First, metal layers of 600 Å chromium followed by 4000 Å gold are deposited on the surface of a borofloat glass wafer (500 μm thick, 15 cm dia.), which has been thermally annealed by heating to the vicinity of 600 °C for one hour to provide a smooth etched sidewall profile (Fan and Harrison 1994).   The wafer is then spin-coated with photoresist, patterned with the channel network, and developed. The metal layers are etched in gold etchant and chromium etchant respectively, leaving glass exposed in the locations where the channels are to be etched.   Channel etching is performed by immersing the wafers in a solution of 49% hydrofluoric acid, yielding an

etch rate of ~ 7 µm/min.   Finally, the photoresist is lifted-off, and the remaining metal layers are removed using their corresponding etchants.   Using this process, we will be able to fabricate sample chambers to satisfy a variety of volume requirements, and to accommodate both liquid and solid samples.   The use of a glass substrate for the sample encapsulation component provides the benefit of being able to visually observe the sample during loading and operation of the device, while the relatively low thermal conductivity reduces heat loss from the sample to the ambient environment. The process flow diagrams of fabricating the thermal control module and sample encapsulation module are shown in Figure 6.

a.   **b.**

Blank Wafer	Blank Wafer
Photoresist	Chromium Photoresist Gold
Deposit Photoresist	Deposit Metal, Photoresist
UV Illumination	UV Illumination
Mask	Mask
Align to Mask, Expose	Align to Mask, Expose
Develop	Develop, Etch Metal
Aluminum	
Deposit Electrodes	Etch Channel
Strip Photoresist	Strip Photoresist and Metal

Figure 6. Process flow used for fabrication of calorimetric devices.

(a) Fabrication of thermal control module, and (b) fabrication of sample encapsulation module.

5.2.3   Assemblage of Nanocalorimeter Cell

Each substrate wafer contains a number of dies, from which individual devices were cut or "diced."   Final assembly involved drilling access holes in the glass wafer (e.g., using an electrochemical spark discharge apparatus).   The glass structures were then bonded to the silicon substrate using a UV-cured adhesive (e.g., SK-9; Summers Optical). Electrical connections were made by wire bonding the assembled devices to printed circuit boards designed to interface with a standard 25 pin card edge connector format. A

prototype of the miniaturized reactor is shown in Figure 7. Electrical connections were made by wire bonding the assembled devices to printed circuit boards designed to interface with a standard 25 pin card edge connector format.
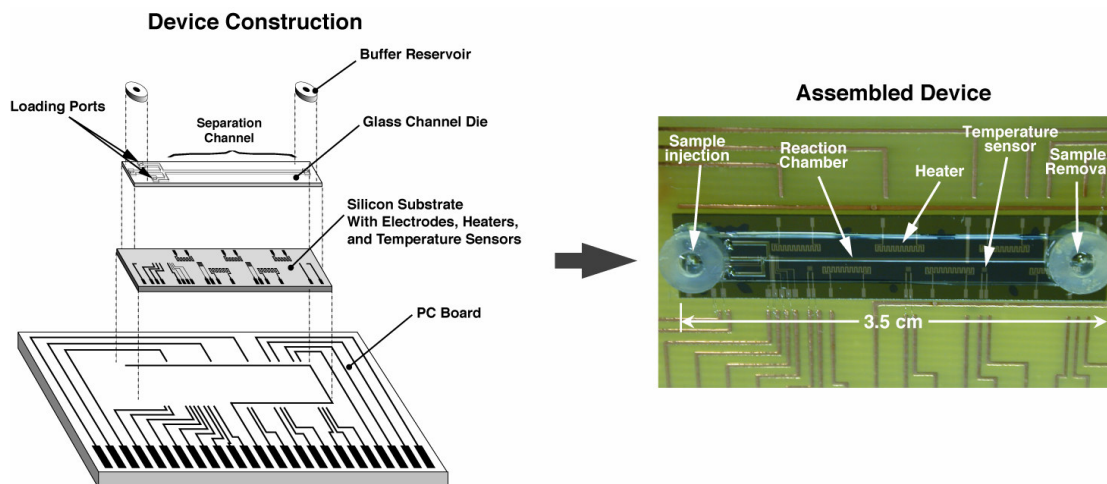
Figure 7.   Prototype of a miniaturized reactor.

The device incorporates an etched glass reaction chamber bonded to a silicon substrate incorporating an array of heaters and temperature sensors.   Electrical components are addressed via a standard 25 pin card edge connector.

The ability to achieve a sufficient level of thermal isolation between the sample and reference chambers is an important issue, since any residual heat flow between these locations will reduce the sensitivity of the instrument. Previous micro-scale calorimeter devices have focused on measuring thermal transitions associated with thin films no more than a few microns thick deposited directly on the wafer surface (Denlinger et al., 1994; Olson et al., 2003; Cavicchi et al., 2004).   The instruments developed here will

be used to study larger quantities of materials, thereby reducing the sensitivity requirements of our devices. 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 (Figure 6a). This can be done using conventional anisotropic silicon wet etching processes (e.g. KOH, EDP, TMAH). The etched patterns on the back side of the wafer will be aligned to the circuitry patterned on the front side using the back-side alignment capability of our mask aligner. The etch depth can be controlled using either a timed etching process, or by heavily doping the front side of the wafer with boron using either an ion implantation or a high temperature diffusion process (e.g. to concentration levels $> 10^{19}$ cm^{-3}) to create a concentration selective etch stop.

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 investigated a variety of heater and temperature sensor layouts to determine which designs offer a balance between ease of fabrication, power requirements suitable for use in a portable format, and overall device performance. For example, if heaters and temperature sensors can be placed around the perimeter of the sample cavity rather than directly underneath, the intermediate passivation layer will not be needed and the entire fabrication process can be competed using a single photolithography step. Coordinated simulations were also performed to determine the performance of heating and sensing elements fabricated using different metals (e.g. Pt, Al, Au, Ti, Cr).

5.2.4   Temperature Control

Temperature control is achieved using resistive heaters patterned on the thermal control module. Since the resistance of the heaters is known, the electrical output current can be monitored to determine the power supplied to the heater. Similarly, temperatures will be 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 kΩ provide temperature sensitivity to within 0.2 °C. A conventional 4-lead arrangement will be 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.

A key question to address is the extent to which the calorimetric cell can be scaled down. The potential loss of sensitivity due to the use of a reduced sample quantity must be balanced by allowing a sufficient number of devices to be fabricated on a single wafer in order to realize the enormous cost benefits available through the use of photolithographic fabrication techniques. In addition, the ability to produce many different designs on a single photolithographic mask will allow us to study the influence of many different design parameters and easily compare the performance of various designs fabricated over a wide range of size scales.

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, as shown in Figure 8.   Preliminary 3-D 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.
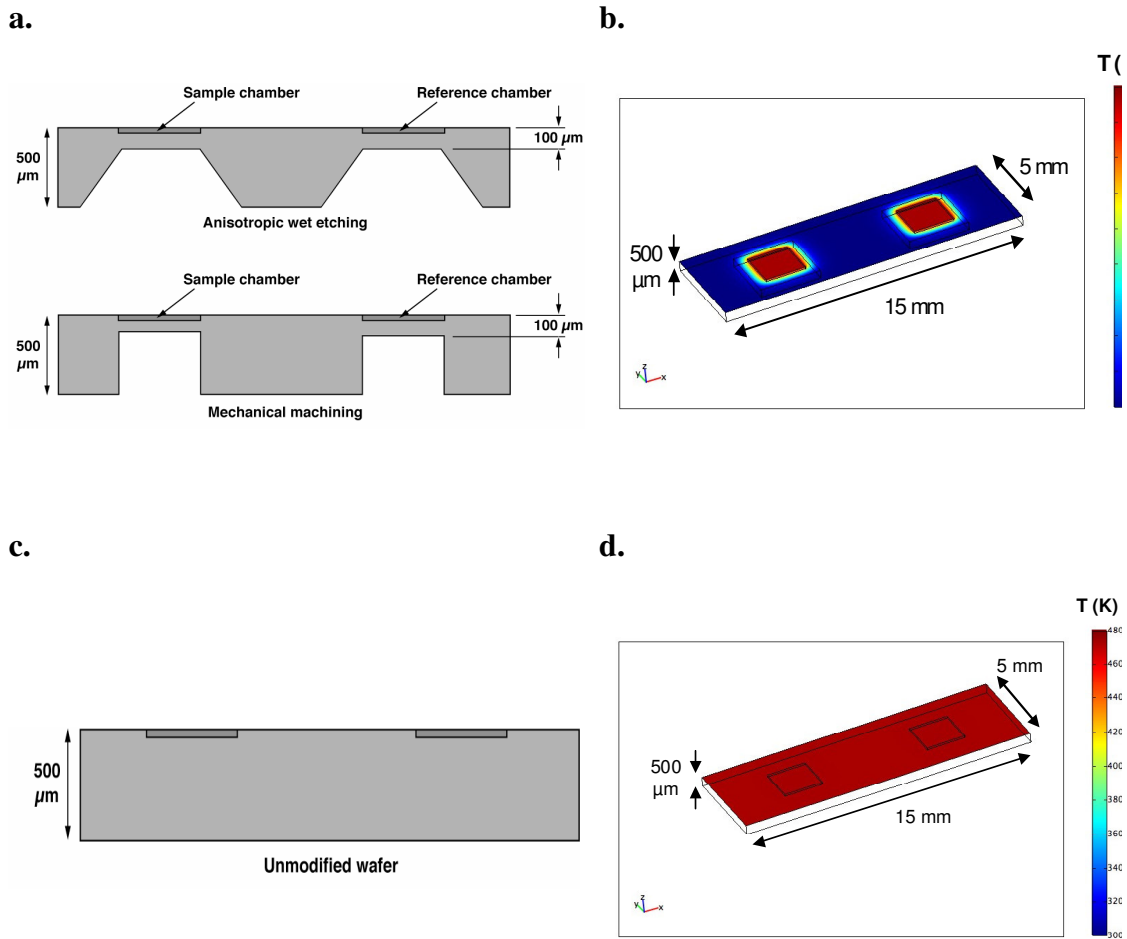
Figure 8. Strategies to reduce lateral heat flow between the sample and reference chambers.

(a) Cross-sectional view depicting removal of material from the backside of the wafer by anisotropic wet etching and mechanical machining processes. (b) 3-D simulation showing thermal isolation between isothermal regions on the surface of a silicon calorimeter device with the same dimensions as depicted in Figure 4. The heated regions are maintained at 200°C, and a convective heat flow boundary condition is imposed on all surfaces except the bottom which is maintained at 27°C. (c) and (d) Cross sectional view and heat flow simulation of a device under the same conditions as (b), except that no material has been removed from the backside of the structure (i.e. unmodified wafer). Without backside etching, the entire device surface is heated to a uniform temperature.

CHAPTER VI

SAMPLING STRATEGY

6.1   Sample Collection

Two effective techniques for sampling condensed substances from the environment for the nanocalorimeter are described below:

- Collect solid and liquid samples using a portable vacuum that is integrated to the nanocalorimter with microfilters for reversed air cleaning.

- Swipe surfaces for particles from a surface by wiping with cotton swabs; then transfer the samples by either directly filling the etched sample chamber of the nanocalorimeter using cotton swabs or by vacuuming.

The nanocalorimeter is not designed for vapor samples because the size of its sample chamber is too small to store enough amounts of vapor for thermal analysis, especially for explosives detection. The vapor pressures of most common explosives are between around 1 ppm and 1 ppt (Steinfeld & Wormhoudt, 1998). The low-pressure explosives such as C-4, semtex, and detasheet do not produce enough vapor to be detected from their vapor. In this case, swiping-based detection and bulk detection such as X-ray become preferred detection methods.

6.2   Sample Loading

The liquid explosives of the U.K. foiled plane-bombing plot in August 2006 highlighted the need of new types of hand-held explosives detection device, such as the nanocalorimeter system. This nanocalorimetry device is able to analyze condensed

energetic substances in both liquid and solid phases. The sample enclosure design and loading process of the nanocalorimeter system 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 will be 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 keep the sample confined during the run. A sealed sample of ammonium iron (III) sulfate dodecahydrate in the nanocalorimter cell is as shown in Figure 9.
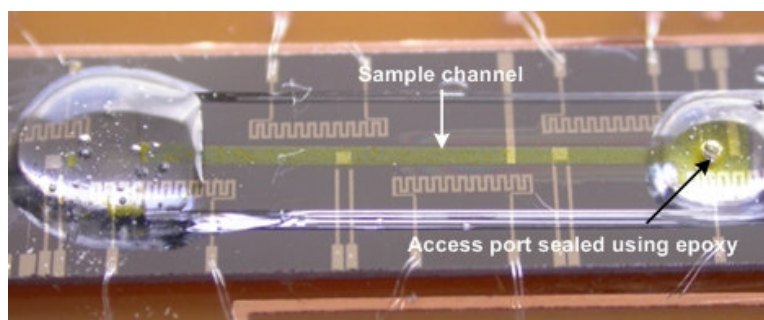
**Figure 9.** Sample of ammonium iron (III) sulfate dodecahydrate.

CHAPTER VII

DATA ACQUISITION AND ANALYSIS

7.1   Control Algorithm

The control algorithm and associated data acquisition system for a DSC type instrument adapts the power-compensation DSC principle. A simplified control circuit for a DSC based on proportional controllers is shown in Figure 10. When a reaction or any thermal event occurs in the sample there is a temperature difference between the two chambers. This temperature difference is fed to a proportional controller which tries to compensate the reaction heat-flow rate by increasing or decreasing an additional heating power 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 proportionality constant.   A heat flow-rate, $\varphi = K_2 \, \Delta T$, is then assigned to the measured temperature difference, where K_2 is determined from calibration (Höhne et al., 2003). A proportional-integral-derivative (PID) control algorithm is written based on the discussed power-compensation principle using the LabVIEW Express^{TM} 7 code.

The control algorithm is 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 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 FieldPoint modules using LabVIEW Express[TM] 7 software.
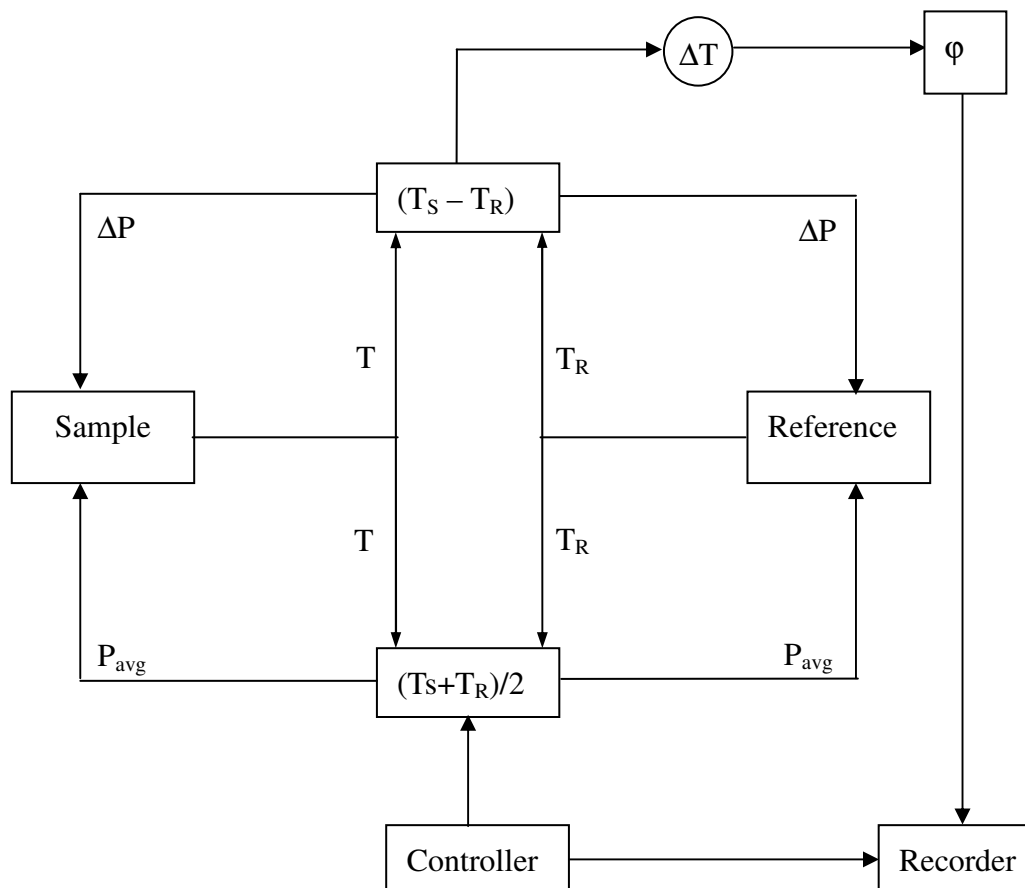
Figure 10. Control circuit for power compensating DSC.

T_S – Sample temp ; T_R – Reference temp; ΔP – Electric heating power to compensate between T_S and T_R; Pavg. – Average heating power to maintain heating rate based on average T_S , T_R ; φ - Calibrated ΔT signal

7.2   RTD Calibration

Calibration of the temperature sensors were performed by placing each device in an oven and monitoring the RTD resistance at a series of temperatures in the vicinity of

operation. A fit to these data provides a calibration curve for the temperature response, which is expected to be linear within the range of interest for these applications. On-chip temperature control will be achieved by resistive heating in response to a potential applied to the heater elements using feedback control from the RTD sensors. The LabVIEW system is used to monitor and control the thermal output, as well as measure the changes in power applied to the heaters in order to identify associated thermal transitions.

7.3   Flexible Modular Design

The modular design of the LabVIEW-based virtual instrumentation hardware and software allows 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 Windows-based laptop computer or Personal Digital Assistant (PDA) to perform instrument control and data acquisition operations outside the laboratory environment.

CHAPTER VIII

EXPERIMENTAL RESULTS

8.1   RTD Calibration for Acetone

To test the concept of the nanocalorimeter design, the thermal transition associated with the boiling point of acetone ($T_{b.p.}$ = 56.2 °C) was studied. A 350 nL volume of acetone was loaded into the sample channel of the prototype device, after which access holes were sealed with epoxy to fully encapsulate the sample. The RTD sensors were calibrated to obtain a linear relationship of temperature vs. resistance, as shown in Figure 11.
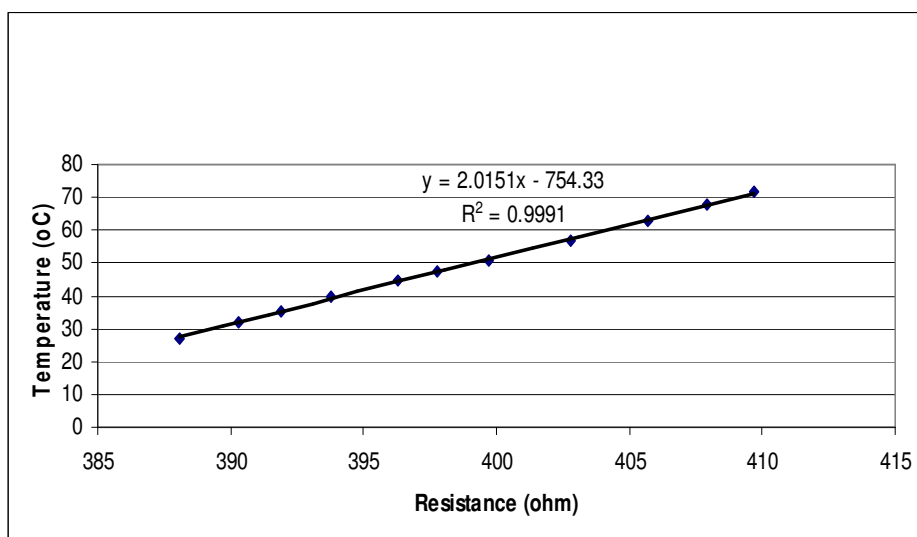
Figure 11. RTD calibration for acetone.

8.2   Boiling Point of Acetone

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 Figure 12.
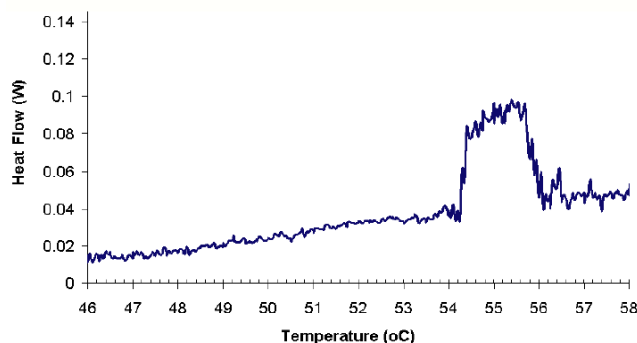
Figure 12.   Thermal analysis data from the nanocalorimeter prototype.
Plot of heat flow as a function of temperature during a 1°C/min heating scan of a 350 nL acetone sample using the prototype nanocalorimeter device.   The observed curve centered near 55.2 °C is roughly consistent with literature values for the boiling point (56.2 °C).

8.3   Redesign and Improvements

The preliminary results obtained in the prototype device illustrated proof of concept for calorimetry, and the nanocalorimetry cell was then redesigned and fabricated. Key improvements incorporated in this nanocalorimeter cell design, shown in Figure 13 a, include:

▪   <u>A reduction in thermal mass</u>.   With simplicity and ease of fabrication in mind, a reduction in the device surface area footprint is about 11% of the prototype size.

Figure 13. 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 4-lead RTD arrangement.
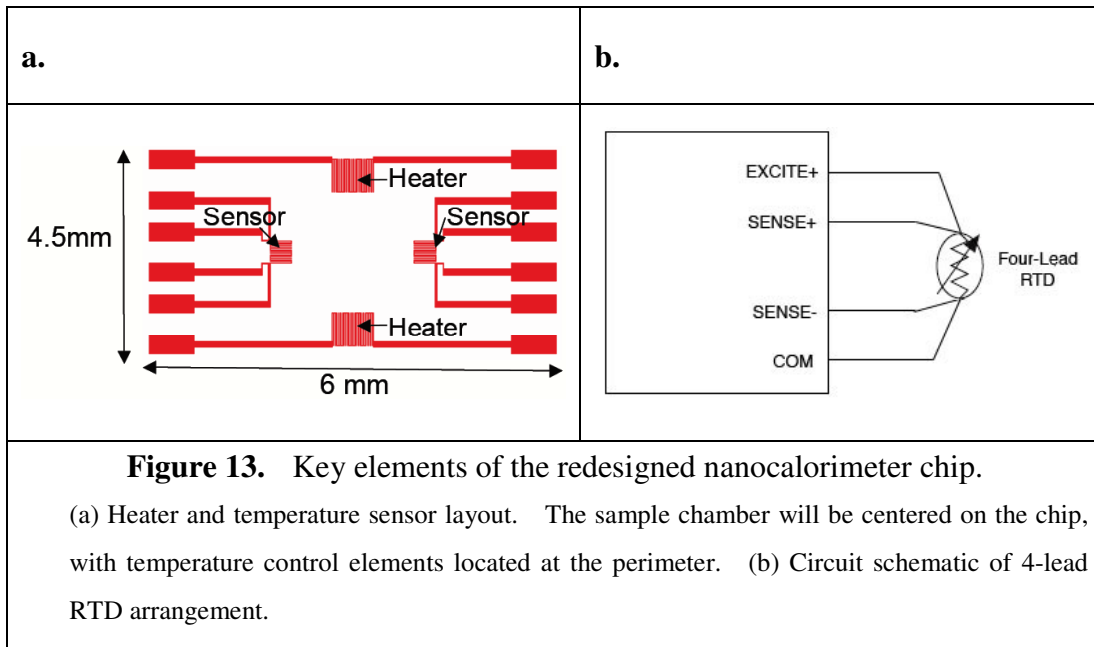
- A simplified single-mask layout.   By moving the temperature sensors to the outer perimeter of the sample chamber, the sample is not in direct contact with the sensing elements. Consequently, passivation layer deposition and the corresponding second lithography step to etch the contacts are not necessary. This reduces time and costs associated with fabrication.   The photomask of the new chip layout was drawn using L-edit Pro, a CAD software, after a series of designs and metals were compared (Figure 13). Redesign of the thermal control elements to use aluminum instead of platinum metal can further reduce fabrication costs.

- An improved temperature sensing circuit.   A four-wire RTD element (Figure13 b) is employed in the redesigned device in order to provide a more accurate

measurement of temperature localized at the sample chamber. This is achieved by adding two additional wires and operating the circuit with the lead resistance canceled so that only resistance changes at the sensing element are detected.

- ▪ <u>Improved thermal isolation</u>. Because of the small device size, sample and reference cells can be physically separated and placed in an enclosed environment to eliminate thermal crosstalk and heat isolation issues.

8.4 Experimental Results

The boiling point of pentane was measured using the new nanocalorimeter cell, as shown in Figure 14. For the redesigned device, the measured input energy is about 0.680 J, or about 4.8 times the required input energy for the liquid-vapor transition of pentane (~0.140 J). In the original design, the measured input heat during the vapor-liquid transition of acetone was about 4.50 J, or about 32.4 times the required input energy for this phase change (~0.139 J). Thus, the reduced input energy reflects the reduced thermal mass in the redesigned device. In addition, the measured phase transition temperature, 38.7 °C, is shifted from literature values for the boiling point (36.2 °C) because of several possible factors such as thermal lag from the sample to the RTD sensors and heaters, 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. When the depth of a thin film is less than 100 nm, interfacial forces can have a controlling effect on phase change processes. The dynamics of a fluid nanodomain is controlled by the sum of excess intermolecular interactions, which manifest as the disjoining pressure. Examples of

intermolecular/surface forces are apolar van der Waals, polar acid-base, electrostatic, structural, vapor thrust, and curvature-effect.
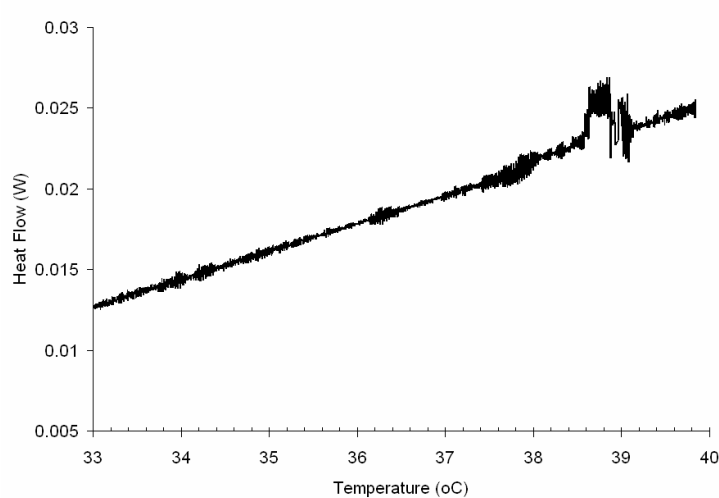
Figure 14. Thermal analysis data from the redesigned chip.

Plot of heat flow as a function of temperature during a 1°C/min heating scan of a 600 nL pentane sample using the redesigned device. The observed curve centered near 38.7 °C is shifted from literature values for the boiling point (36.2 °C).

CHAPTER IX

OPERATION

9.1. Energetic Substances

Operation of the calorimetric system can be verified through the use of well-characterized calibration standards, as shown in Table 8 (Höhne et al., 2003). The onset temperatures, reaction enthalpies, and other reaction parameters can be measured in the nanocalorimeter with sample sizes of ~ 1 μg 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.

Table 8. Typical calorimetric calibration standards (Höhne et al., 2003)

Material (transition)	T_{trans} (℃)	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
Aluminum (s → l)	660.3	398

An extensive library of experimental data for over 1,000 chemicals, mostly measured using ARC and APTAC, are provided by industrial partners (Table 9). The decomposition parameters for the selected compounds can also be compared with DSC

measurements on the same compounds reported by Grewer (Grewer, 1994), Ando (Ando et al., 1991), and Eastman Kodak Co.(Chervin & Bodman, 2001).

Table 9. Library of energetic compounds to be used for instrument testing

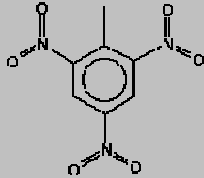| Sr. no.	Chemical	Mass gm.	Onset temperature ^{o}C	Max. temperature ^{o}C	Heat of reaction cal/g
1	Di-ter-butyl peroxide in toluene	0.71	115	184	49
2	Hydrogen peroxide	8	130	240	700
3	Ammonium nitrate	0.5	201	291	-
4	Styrene	2.2	100	201	172
5	Nitro-styrene	0.95	170	264	297
6	Acrylonitrile	0.79	-	-	389
7	1,3 Butadiene	12	158 ± 10	445 ± 19	260
8	50 wt.% hydroxylamine	2	133	216	420
9	Hydroxylamine nitrate	4.2	171	196	350
10	Hydroxylamine sulfate	4.5	151	185	-

9.2   Explosives
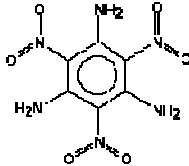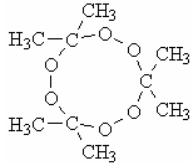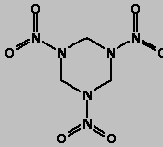
A calorimetric experiment captures thermal transitions (phase change, reactions) that occur within the system. For solid explosives the thermal events expected within a calorimetric run are: phase transition from one solid state to the other (e.g., α-phase → γ-phase), melting or sublimation, and thermal decomposition. These transitions can be exothermic or endothermic as indicated by a positive or negative deflection in the measured power. A library of representative explosives, shown in Table 10, can then be

tested to benchmark the performance of the nanocalorimeter relative to other conventional hardware. A comprehensive analysis database package containing such chemical libraries is discussed in Section 10.3.

9.3   Pressure inside the Sample Cell

Highly energetic substances and explosives 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 to 1000 times of the original sample volume depending on the reaction conditions. With the increasing vapor volume, the pressure inside the sample cell will also increase significantly. For the hybrid glass/silicon design, the tensile strength of glass will be the limiting parameter.   The working pressure of Pyrex® borosilicate glass can be 800 psi using characteristic dimensions. 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. The single-use disposable format of the sample cell can eliminate mechanical degradation arising from repeated temperature and pressure cycling. In addition, with nanogram amounts of samples, consequences of rapid runaway reactions will be minimized.

Table 10. Common explosives

Explosive	Chemical Formula
Ethylene glycol dinitrate (EGDN)	$(CH_2ONO_2)_2$
Nitroglycerine (NG)	CH_2ONO_2 $HCONO_2$ CH_2ONO_2
Trinitrotoluene (TNT)	
Ammonium Nitrate (AN)	NH_4NO_3
Urea Nitrate (UN)	$NH_2(CO)NH_3^+NO_3^-$
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	
Pentaerylthritol tetranitrate (PETN)	CH_2ONO_2 $O_2NOCH_2CCH_2ONO_2$ CH_2ONO_2
Triacetone Triperoxide (TATP)	
Cyclonite, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	

CHAPTER X

CONCLUSIONS AND FUTURE WORK

10.1   Conclusions

Calorimetric techniques are widely used for material characterization by monitoring the thermal energy required to heat or cool a sample material at a constant rate. The hand-held nanocalorimeter will serve as a new generation of identification and detection tools for explosive and energetic compounds directly in the settings where they are needed with high efficiency, reduced cost, 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, developing a trace analysis software to link it to a database of explosive information, and adapting different fabrication procedure for high temperature operation and large scale production.

10.2   Substrate Design

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 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. In addition, to further eliminate heat loss from samples to thermal encapsulation modules, smaller thermal mass of the silicon substrates can be achieved by switching from 500 µm to 100 µm thick silicon wafers.

10.3   Comprehensive Analysis Database Package

Based on the values calculated from a calorimetric run, the likely candidates exhibiting similar thermal behavior can be identified based on a database of chemicals. Energy of decomposition and onset temperature for over 1,000 common chemicals are available. For the existing compounds, additional properties such as melting / boiling points, appearance, and odor will be gathered. A chemical incompatibility database, similar to the NOAA Worksheet, is also included in the analysis database package because many common chemicals can become highly unstable and energetic if mixed with other

chemicals. For example, the Bhopal incident in 1984, the worst industrial disaster in history, was caused by the introduction of water into a MIC holding tank. MIC is an intermediate in carbaryl manufacture. For air travel, liquid and gel explosives can be made easily by mixing several non-energetic substances.

In addition, a Material and Safety Data Sheet (MSDS) will be electronically linked for every chemical in the databank. The aim of collecting this additional data is to aid in the onsite identification and provide additional useful hazard information for choosing mitigation measures. Following an onsite calorimetric run and peak-shape analysis, the user will have the option to screen through the database to determine the most likely candidates.

Peak-shape Analysis

A positive deflection or peak in the power corresponds to an exothermic process and a negative deflection or dip corresponds to an endothermic one. As an example, a typical DSC curve for 2,4,6-trinitrotoluene (TNT) is shown in Figure 15 (Folly, 2004). The next few paragraphs discuss the peak-shape analysis following a calorimetric run to quantify thermal transitions for explosive potential characterization.

A software program will be developed to extract the following characteristics from the thermal analysis curve:

- Melting point (m.p.) / boiling point (b.p.)

- Enthalpy of reaction ($-\Delta H$)

- Aspect ratio (peak height / peak width)

The energy associated with a thermal transition (reaction or melting) is calculated as the

area under the curve from the power (Watts) vs. time (seconds) plot. From the thermal analysis curve, the software would allow a user to choose the onset temperature (T_o) and maximum temperature (T_{max}) for a given profile. Numerical integration will then be performed between the two temperatures end-points (T_o, T_{max}) using Simpson's 3/8 rule.
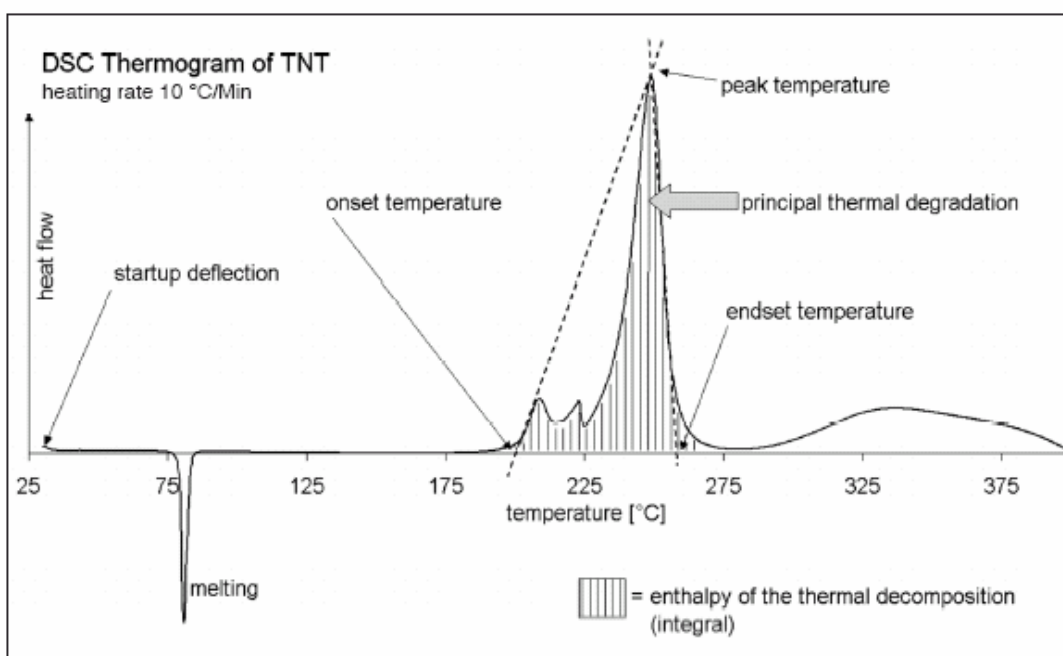
Figure 15. DSC curve for TNT (Folly, 2004).

The calculated area is thus the difference between the measured heat flow and the baseline. The baseline represents the theoretical profile, which would have been measured if the reaction/decomposition would have taken place without any heat release. Within a peak or a dip the unknown baseline must be interpolated, which is an error prone task. The software will offer a choice of interpolation methods (linear, quadratic, spline) to the user.

Although there is a choice of baseline for accurate measurements, it is not expected to significantly affect heats of reaction for explosives because of the high magnitudes of the observed power output.

For certain systems, a thermal analysis curve may show multiple peaks or dips. The exothermic peaks, which are of primary interest to this project, typically correspond to different reaction mechanisms within the system. The integration software would provide user with the flexibility of choosing end-points for the different peaks observed during a run.

The explosive potential of a system will be based on the following parameters:

- Aspect ratio (W/ g ^{o}C): The aspect ratio (S) is defined as the ratio of peak height (W) to peak width (^{o}C), and is a reflection of the rate of energy release within a system. The peak width is measured at half the peak height. Generally, systems with higher peak heights and narrower peak widths represent a higher explosion potential.

- Onset temperature (^{o}C): The temperature at which a system first exhibits exothermic reaction is called the onset temperature (T_o) and thus denotes a rate of reaction significant enough to be measured by the calorimeter. The detected onset temperature is thus a measure of reaction kinetics of the substance. Typically, if a system reacts at a significant rate at lower temperatures, it is unstable and can pose an explosion hazard if there is sufficient energy that can be released.

10.4 Higher Temperature Operation and Large Scale Production

The sample enclosure and thermal control components can be bonded using a

standard anodic and/or thermal fusion process. Fusion bonding can be achieved by etching alcoves at appropriate locations so that the metal will not be in direct contact with the encapsulation substrate (Krishnan et al., 2002). These bonding steps can be performed prior to dicing so that an entire wafer of devices can be assembled in parallel. If bonding is to be performed on the scale of an entire wafer, access holes can be machined using an automated laser drilling process.

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APPENDIX

STATEMENT OF ACADEMIC ENGINEERING RESEARCH

This research project funded by the Safety Center is aimed to reduce the losses of lives and properties. The Center, as an engineering research institute, does not take a stand of any political or religious group. The following are the 2005 Nobel Lecture by Mohamed ElBaradei (ElBaradei, 2005):

- There is no religion that was founded on intolerance – and no religion that does not value the sanctity of human life.

- Islam declares that killing one person unjustly is the same as killing all of humanity.

- Hinduism recognizes the entire universe as one family.

- Buddhism calls on us to cherish the oneness of all creation.

- Christianity says we should treat our neighbours as we would be treated.

- Judaism asks that we value the beauty and joy of human existence.

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2. Liu, Y.-S., Ugaz, V.M, Rogers, W.J., & Mannan, M.S. (2006). Screening Reactive Chemical Hazards. *Chemical Engineering Progress*, *102* (5), 41 – 47.

3. Liu, Y.-S., Ugaz, V.M, Rogers, W.J., Mannan, M.S, Saraf, S.R. (2005). Development of an Advanced Nanocalorimetry System for Material Characterization. *Journal of Loss Prevention in the Process Industries*, *18* (3), 139-144.

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