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Office of Sponsored Programs
110 Technology Center Building
University Park, PA 16802 -7000

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RPPR Final Report
as of 18-Oct-2018

Agency Code:

Proposal Number: 70117EGRIP **Agreement Number: W911NF-17-1-0151**
INVESTIGATOR(S):

Name: Stefan T Thynell Thynell@ps
Email: Thynell@psu.edu
Phone Number: 8148630977
Principal: Y

Organization: **Pennsylvania State University**
Address: Office of Sponsored Programs, University Park, PA 168027000
Country: USA
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Begin Performance Period: 15-Jul-2017 **End Performance Period:** 14-Jul-2018
Report Term: 0-Other
Submitted By: Stefan Thynell Email: Thynell@psu.edu
Phone: (814) 863-0977
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STEM Degrees: 0 **STEM Participants:** 0

Major Goals: Purchase and install a thermogravimetric analyzer (TGA), to be interfaced with an existing FTIR spectrometer

Accomplishments: The TGA system was purchased and successfully installed.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Stefan T. Thynell
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 18-Oct-2018

Abstract

The funds for this equipment proposal were used to upgrade a species diagnostic system used in thermolysis of energetic materials. Specifically, the funds were used to purchase a combined thermogravimetric analyzer (TGA), differential scanning calorimeter (DSC) and differential thermal analyzer (DTA). The evolved gases from the TGA are sent via a heated tube to an interface attached to an FTIR spectrometer. As such, the species evolved from the thermolysis can be associated with the mass-loss profile. The system is used in two existing projects. In the first ARO-sponsored project, it will be used to identify species from mixtures of RDX with a high-nitrogen compound as well as HMX and mixtures of HMX with a high-nitrogen compound. In the second project funded by AFOSR, the diagnostic system is used to identify species evolution of energetic materials containing catalytic nanoparticles. These species measurements provide guidance to a quantum mechanics investigation, in which the transition states and reaction pathways are sought. The overall objective for these combined experimental studies and quantum mechanics investigations is to identify the relevant reaction channels at low and high heating rates and to develop reaction mechanisms, which can be used in computational fluid dynamic studies of ignition and combustion of solid and liquid propellants used in propulsive devices.

Cost and Technical Specifications of the Purchased TGA/DSC/DTA System

Table 1 lists the components and their costs of the purchased TGA interface, which is attached to an existing FTIR spectrometer. Table 2 lists the technical details of the purchased TGA/DSC/DTA system, Table 3 shows the relevant technical specifications of the TGA system, and Fig. 1 shows an image of the various components in the overall setup.

Table 1. Components and Costs for a TGA Interface which is attached to the existing Bruker model Vertex 80 FTIR spectrometer. (Mr. Dana Kelley, Bruker Optics Inc., 19 Fortune Drive, Billerica, MA 01821, (978) 439-9899, dana.kelley@bruker.com)

Item	Material/Description	Quant.	Unit price	Amount
1	**A171/Z-L (Mirror)** Adaption set for connection of external accessories to the left side of the spectrometer. The set contains computer controlled beam-steering mirror, window and window flange.	1	$2,754.00	$2,754.00
2	**W162/B (Window flange)** Window flange for mounting of windows in input/output ports for TENSOR and VERTEX 70/80 (without windows) Required: F162-x window	1	$71.01	$71.01
3	**F162-5 (Window)** KBr window, 45x3mm, wedge 6mrad for window flange W162/B or W162/3 Note: not to be used for A131-2 and A132-2.	1	$176.08	$176.08
4	**A588-S1 (TGA Coupling)** TGA-IR-service set 1 consisting of:	1	$1,081.35	$1,081.35

	- 2x sets of O-rings (PN: 17271, 83881, 82397) - 2x KBr window (PN: 5665) - 2x ZnSe window (PN: 17336) - 2x spacer (PN: I10486)			
5	**A588-S2** TGA-IR-service set 2 consisting of: - 2x set O-rings (PN: 17271, 83881, 82397) - 2x spacer (PN: I10486)	1	$129.33	$129.33
6	**A588-S3** TGA-IR-service set 3 consisting of: - 5m Teflon tube (od: 3mm, id: 2mm) - 5 pieces support sleeve - 5 pieces lock nut.	1	$129.33	$129.33
7	**A588-S4** TGA-IR-service set 4 consisting of: - 5 pieces of O-rings (PN: 83881)	1	$125.55	$125.55
8	**A588LB-N** External TGA-IR coupling unit, coupling to the left side of the spectrometer prepared for connecting the transfer line from NETZSCH thermo- balances (w/o TGA-unit). Currently installed NETZSCH thermo balances will need to be modified for connection with a Bruker FTIR spectrometer. The coupling unit includes OPUS/Search Software(O/SR) and a liquid nitrogen cooled MCT-detector D316/Bx; Additionally required: OPUS/CHROM, OPUS/3D, adaption A171/x-L	1	$26,460.00	$26,460.00
9	**O/CH-N** OPUS/CHROM, Chromatographic coupling package. Recommended: in order to support 3D data calculations we recommend to use OPUS/3D. In order to use OPUS/CHROM the upgrade for the current version of OPUS/IR is required.	1	$2,308.50	$2,308.50
10	**B-PNNL-1** Quantitative vapor-phase infrared spectral library from PNNL 470+ spectra, Resolution 4cm-1, 1ppmm. The spectra have been recorded by PNNL. Handling fee.	1	$363.15	$363.15
11	**I9429** BRUKER EPA/NIST Gas-phase Library; about 5,000 spectra, structure information for most spectra included	1	$1,755.00	$1,755.00
12	**S941-U05** (Installation of TGA interface on spectrometer). On-site Professional Service (1/2 Day Rate) (Does not include parts and travel charges - see travel)	1	$1,800.00	$1,800.00
13	**S941-U1** On-site Professional Service (Daily Rate) (Does not include parts and travel charges - see travel)	1	$2500.00	$2500.00

14	**S962** (two trips required) Travel Charge	1	$1,225.00	$2,450.00
15	**S955-U** On-site application training daily Rate. Does not include travel charges. See travel S962	1	$2,850.00	$2,850.00
16	**S119/B** Desiccant cartridges, package of 2 pieces	1	$268.65	$268.65
17	**A105-X** Holder for samples or optical filter with a diameter of 25mm	2	$126.09	$252.18
	Total Price			$ 45,474.13
	Academic discount (10%)			-$ -4,547.42
	Total cost for Bruker Components for interfacing the TGA to the FTIR spectrometer			**$40,926.71**

Table 2. Components and Costs for the Netzsch STA 449 F5 Jupiter Simultaneous Thermal Analyzer (TG-DSC/DTA Apparatus) covering room temperature to 1600ºC, which is interfaced to the existing Bruker model Vertex 80 FTIR spectrometer. Total cost for both Bruker and Netzsch components is at bottom (NETZSCH Instruments North America, LLC,129 Middlesex Turnpike, Burlington, MA 01803, contact person: Dave Shepard, phone: +1 781 418 1810, e-mail: dave.shepard@netzsch.com; new sales person is Daniel van Ness Daniel.vanNess@netzsch.com)

Item	Material/Description	Quant.	Unit price	Amount
1	**STA400F5A11.000-00** DSC-TGA instrument combination for simultaneous determination of caloric effects and mass changes for measurements from RT up to 1600°C. The STA 449 F5 Jupiter is equipped with a top-loading, highly sensitive micro balance which provides high measurement accuracy and low drift even with large sample weights. A pivoting, motorized furnace hoist enables the easy and safe exchange of sample crucibles and sample holders which utilize Quick-Connect connectors. The system comes standard with three mass flow controllers (MFC) for precise control of protective and purge gases, enabling measurements in dynamic and static gas atmospheres. The system is vacuum-tight. An easy upgrade allows for evolved gas analysis using QMS, GC-MS, and/or FTIR. The sophisticated measurement and evaluation software Proteus® for MS Windows is included. The TGA-BeFlat® feature for automatic base line correction eliminates time-consuming correction measurements, if requested.	1	$60,720.00	$60,720.00
2	**6.226.1-90.6.00** Refrigerated bath circulator, cooling capacity 260 W (at 20°C), heating capacity 2000 W, multifunction display, connection parts, power supply 115 V / 60 Hz	1	$3,320.00	$3,320.00
3	**SW-BIR-69X.1B** Software extension for the coupling with Bruker-FTIR with OPUS software. Start/Stop support of Bruker-FTIR measurement by Proteus, data exchange between OPUS and Proteus with storage in the data files of both software packages. OPUS data from coupling with Bruker-FTIR can be loaded/imported, presented and evaluated comparatively with TGA/DSC/dL measurement curves of the Proteus software.	1	$130.00	$130.00
4	**6.223.5-91.3.00** Calibration sample kit with 8 substances 400 mg each (Indium, Tin, Bismuth, Zinc, Aluminium, Silver, Gold, Nickel) for DSC/DTA calibration of enthalpy and	1	$1,060.00	$1,060.00

	temperature. Temperature range ambient ... 1500°C, in wooden case with foam lining and certificate of compliance, for use in Al2O3 crucibles			
5	**HTP40000B18.010-00** Adaptor for gas transfer system (FTIR and/or QMS 403 C Aëolos/GC-MS), for furnaces HTP40000A81...-A85, heatable up to 300°C - depending of the connected transfer line. For use with temperature controller TRG00400xxx	1	$7,560.00	$7,560.00
6	**HTP40000B18.620-00** Transfer line for adapter HTP40000A18.xxx, heatable to 230°C max., length 2 m, with exchangeable gas tubing from Teflon, control thermocouple type K, suited for Bruker FTIR instruments. For use with temperature controller TRG00400A1x.	1	$3,120.00	$3,120.00
7	**TRG00400B12.000-00** Multi-channel temperature controller for temperature control (RT...300°C) of up to two NETZSCH-heater (coupling adaptor, transfer lines etc.). Set point adjustment, actual value display and heater information are supplied trough an easy operable touch display.	1	$4,450.00	$4,450.00
8	**GB399972** Sample crucible from Al_2O_3, outer bottom Ø 6.8 mm, 85 µl	5	$33.50	$167.50
9	**GB399973** Lid from Al_2O_3 (for pan GB399972)	5	$18.00	$90.00
10	**AI-STA449FS** Installation and commissioning of the STA 449 F1/F3/F5 with a standard furnace including a basic instruction by a NETZSCH service engineer.	1	$2,780.00	$2,780.00
11	**SHIPPING COSTS** Shipping Costs; FOB Destination	1	$0.00	$0.00
	Total Price			$83,397.50
	Academic discount			-$17,735.85
	Total cost for Netzsch TGA system interfaced to Bruker FTIR spectrometer			**$65,661.65**
	TOTAL COST $40,926.71+ $65,661.65			**$106,588.36**

Table 3. Technical details of the STA 449 F5 Jupiter TGA/DSC/DTA apparatus by Netzsch.

Item	Property
Temperature range	RT to 1600C
Heating range	0.001 to 50 K/min
Mass range	Micro balance with digital resolution of 0.1 µg over a measurement range of 35g
Atmosphere	Static, dynamic, inert, oxidizing
Vacuum tightness	10E-02 mbar
Furnace	SiC furnace with electromechanical hoist
Temperature Measurement	TGA-DSC sample holder with thermocouple type S
Mass flow	3 integrated mass flow controllers (MFC): 0 … 250 ml/min, increment 1 ml/min
Vacuum system	Rotary vane pump (4 m^3/h) with AutoVac function
Power	115/230 V, 50/60 Hz

Figure 1. Components of the TGA/DSC/DTA interfaced to the Bruker Vertex 80 FTIR spectrometer are shown. The left component is the TGA, and the Vertex 80 is to the right. In the middle, attached to the Vertex 80, is the TGA interface. On the floor and not clearly shown are the chiller and the vacuum pump.

Use of TGA System

Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX, ARO Grant # W911NF-15-1-0202 (PI: S. Thynell, Program Manager: Dr. R. Anthenien)

Our research effort so far has focused on the chemical kinetics of RDX. This compound has a low melting temperature of 204ºC but a decomposition temperature that is higher by about 50ºC. Thus RDX largely vaporizes in slow-heating-rate TGA studies. It does decompose in our fast thermolysis studies, however, where the heating rate is 2,000K/s. RDX mixtures with a high-nitrogen compound has shown to have a lower decomposition temperature, and such studies will be undertaken once our modeling effort on RDX is near completion. In our future studies, HMX and its mixtures with a high-nitrogen compound are expected to be much different. The melting temperature of HMX is 276ºC, and it is known to decompose in the solid phase beginning with a phase transition. Thus, the TGA and its interface with the spectrometer is expected to provide very useful information about mass loss and the corresponding species profiles. We are now obtaining small amounts of pure HMX, since an ATF license is available.

Existing Research Capability is Enhanced

The TGA system will enhance our capabilities to study decomposition of energetic materials. In general, it will provide information about mass loss and species evolution at slow heating rates. Such capability is not available here on campus. The system, which is interfaced to an existing FTIR spectrometer, allows decomposition studies of both solid and liquid samples. The TGA system can also also used to examine the residue remaining on the aluminum foil after our fast thermolysis studies, conducted in a completely different apparatus. Finally, an often overlooked aspect is that the mass loss during slow decomposition can be directly correlated to specific species, which is needed in our analysis and chemical reaction mechanism reduction for the condensed phase, as well as growth modeling of bubbles in the foam layer.

Current Projects

November 1, 2012 - October 31, 2018 (incl. 1 year no-cost extension), "MURI-Smart Functional Nanoenergetic Materials," AFOSR Grant # FA9550-13-1-0004 (PI: R. Yetter, Co-PI: S. Thynell, Program Manager: Dr. M. Birkan), approx. $750k/5 years.

May 1, 2015- April 30, 2020, "Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX," ARO Grant # W911NF-15-1-0202 (PI: S. Thynell, Program Manager: Dr. R. Anthenien), approx. $980k/5 years.