QUICK HAZARD SCREENING BY CLOSED CELL ARSST USING STANDARD ARC™ BOMBS

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Abstract: Reaction hazard assessment at the early stages of compound development requires tools that are fast and accurate, and laboratory screening tests must quickly identify potentially hazardous materials or conditions while using a minimum amount of sample. Since 1989 the Advanced Reactive System Screening Tool (ARSST™) concept has provided process safety professionals with an easy-to-use low φ-factor safety calorimeter to generate data for reactive system vent sizing by DIERS direct scale-up methods. In recent years the ARSST has seen increasing use by process development chemists for applications such as thermal stability, material compatibility, and simple reaction chemistry. An advantage is the sample size (up to 10 ml) which allows for a representative well-mixed sample while minimizing risk and expense. This article focuses on high φ-factor screening using standard ARC™ test cells to illustrate the convenience of closed-cell ARSST testing, particularly with regard to observed reaction onset temperature. Low gas generation rates such as might be expected at normal process conditions, or at onset of an undesired reaction, are readily observed using the described closed cell ARSST methods, often at temperatures lower than the observed onset of thermal activity. Specific examples are presented to compare closed cell ARSST results with published data from other screening instruments, demonstrating the utility of the method as a simple general-purpose screening technique suitable for laboratory-scale process development.

Keywords: Safety Calorimeter, Hazard Screening, Process Safety, Thermal Stability, Onset Temperature

INTRODUCTION

Since 1989 the Advanced Reactive System Screening Tool (ARSST) concept has provided process safety professionals with an easy-to-use low φ-factor adiabatic safety calorimeter [1, 2, and 3]. Engineers responsible for reactive system vent sizing by DIERS direct scale-up methods find the standard ARSST combination of low thermal inertia (φ), open test cell design, and large containment volume particularly useful for gassy systems (i.e. decompositions) because the (sometimes high) gas generation rate at venting is effectively and safely measured.

More recently the ARSST has been adopted by process development chemists for applications such as material compatibility, thermal stability, and reaction chemistry. The ARSST scale (~10 ml) allows for representative well-mixed samples while minimizing risk and expense. Low gas generation rates, such as at normal process conditions or at onset of an undesired reaction, are readily observed using closed cell ARSST methods [4]. This article presents examples using closed cell ARSST methodology as a simple general-purpose screening technique suitable for laboratory-scale process development.

CLOSED CELL ARSST TESTING

BEFORE VENT SIZING

Laboratory screening tests must quickly identify potentially hazardous materials while using a minimum amount of sample material. Low φ-factor data are not critical to this effort, and various high-φ reactive system screening tools are described in the literature [5]. Unlike most ramped screening tools, the ARSST effectively applies constant power to the sample and compensates for heat losses. This quasi-adiabatic method provides a reasonably steady ramp rate (typically 2°C/min), and endotherms (such as melting of a solid) are easily handled without increasing the driving potential for heat transfer to the sample. Thus there is no heater “wind up” effect which might be misinterpreted as a false exotherm.

The purpose of this article is to illustrate the convenience of closed-cell ARSST testing and focus on high φ-factor screening using standard ARC test cells (bombs). Of particular interest is the observed onset temperature, a parameter which is generally understood to be instrument dependent, with ARC results often taken as the reference standard. The present approach, consistent with [5], can be useful in early "value judgment" screening but should be part of a comprehensive hazards assessment using various tools and methods. Screening results are not a substitute for thermal explosion theory analysis [3, 6].

EXPERIMENT DESIGN

Closed cell ARSST testing has been in use for several years [4]. In this configuration a pressure tube attaches directly to the test cell. For low φ-factor testing there are several styles of all-glass test cells available, with volumes from 5 to 20 ml, and combination test cells with glass bodies and metal necks. Low-φ glass cells can often withstand substantial internal pressure (more than 200 psi), but even if the test cell ruptures the contents are safely contained without damaging any expensive parts (i.e., similar to a conventional open cell ARSST test).

For reactivity screening, low φ-factor and scalable rates are sometimes less important than quick identification of hazards with a reasonable estimate of reaction onset. For secure metal-to-metal connection a standard ARC bomb can be used as the test cell, and is simply attached on the underside of the vessel lid (Fig. 1). The heater connections are also made through the lid. A short heater belt (same as for 5 ml glass cells) works well, and the assembly is wrapped in foil (not shown). A "nest" of insulation is placed inside the containment vessel to receive the test cell. The pressure transducer is mounted external to the containment vessel, while the sample thermocouple passes down inside the pressure tube. Good agitation is achieved using a small magnetic stir bar.

Fig. **1 Vessel assembly for closed cell ARSST**

RECOMMENDATION

In the closed-cell configuration pressure is measured directly in the test cell. Since the available void space (free board volume) is much less than for an open cell vent sizing test, it is recommended that the test cell fill fraction be substantially less than in vent sizing tests, particularly for gas generating systems. For screening applications it is suggested to start with no more than a 1 or 2 gram sample. Pressure transducers of the type used in the ARSST are available in a variety of ranges, from 45 to 20,000 psig full scale. For most screening applications a standard 1000 psig (70 bar) transducer works well, but for better pressure resolution (say for isothermal testing) a lower range model may be preferred. Where possible, it is good practice to estimate a priori the peak pressure that might be generated.

The easiest way to load the sample is to preload the test cell before it is installed. Another method is to remove the pressure/temperature tree from atop the vessel and use a long syringe needle or tubing segment to add liquid sample directly to the installed test cell. A flexible plastic tip can be pushed all the way to the bottom of the test cell. This also allows liquid to be removed and replaced after a test without removing the test cell from the containment vessel.

Post-test cooling is very fast since the heater itself is lightweight. Cooling can be enhanced by removing the test cell and lid assembly to allow the cell to cool naturally. Or one could remove the test cell heater belt and submerge the still mounted test cell into a container of cool water. In this way the time between tests is reduced to just a few minutes.

EXAMPLES

Table 1 compares closed cell ARSST results for several thermally unstable compounds against published onset temperatures derived from several different instruments [5]. It is acknowledged that sensitivity and thus onset determination can vary from instrument to instrument, so the ARC results reproduced here may not reflect results from newer equipment. ARSST onset determination has been done graphically using composite plots of self-heat rate, pressure rate, and measured pressure vs. temperature. Plots of temperature or pressure versus time generally are less useful (giving higher apparent onsets), except in the case of long term isothermal hold tests where developed pressure indicates reactivity. Results tabulated here are simply intended for comparison and illustration.

Test data are shown in Figs. 2 to 7. For convenience the rates of pressure and temperature rise (dP/dt and dT/dt) are plotted, together with the absolute pressure P, versus reciprocal absolute temperature. In most cases the ARSST data were generated using a constant power polynomial ramp (at about 2ºC/min), and sample sizes ranged from 0.5 to 2 g. All tests used titanium ARC bombs (Fauske part FT4, approximate tare mass 6.4 g). The pressure transducer had a nominal range of 1000 psi (70 bar), but periodic calibration checks demonstrated good linearity to at least 1600 psi. Additional details are given below:

1) **2-amino-4-chloro-5-nitrophenol -** 0.5 g sample. Post-test, the lid assembly was removed to allow the test cell to quickly cool down in ambient air (cooled from 600°C to ambient within 20 minutes).

2) **4-amino-1,2,4-triazole** - 0.64 g sample. To expedite the test the heater power was initially "dialed up" to give about 5°C/min until the sample reached 100°C, after which a lower 2°C/min rate was used.

3) **3-methyl-4-nitrophenol -** 1.7 g sample melted at about 128°C. Continued heating led to an energetic decomposition. This caused the test cell to rupture (peel open) but was safely contained in the surrounding 450 ml containment vessel with negligible damage (the thermocouple and pressure tube connection had to be replaced).

4) **di-benzoyl peroxide -** 2 g sample was tested first (4a) with a constant power ramp (standard mode) and then (4b) with stepwise heating by PID control (PID parameter values were PB%=10, RT=1, DT=0.1). Isothermal steps lasted one hour each, but they could be much longer to get better resolution of small pressure changes and infer an average pressure rate from the net pressure change at that temperature.

5) **di-tert-butyl peroxide -** 1.6 g sample was tested first (5a) with a constant power ramp and then (5b) with a single PID ramp (so called "DSC mode" to scan at a constant temperature rise rate) using the same PID settings as noted above. In DSC mode the heater power can be examined to infer the onset of thermal activity. This method has been used previously to study isothermal stability of lithium battery materials by closed cell ARSST [7].

CONCLUSION

Closed cell ARSST testing using ARC bombs represents an effective choice for reactive hazards screening at the process development stage. This robust, safe, and efficient method provides excellent sensitivity to small gas generation rates and rapid test turnaround. Multiple testing modes provide flexibility to study thermal stability in different ways (e.g., constant power ramp, long duration isothermal hold, step-wise heating, etc.) And of course the ARSST retains the ability to run low φ-factor tests for straightforward development of kinetic models and quantitative scale-up applications like vent sizing.

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Table 1 Summary comparison of materials tested and observed decomposition onsets [5]

	Chemical Identity	**mp**	**DSC**	**C80**	**ARC**	**TSu dP/dt**	**TSu dT/dt**	**ARSST dP/dt**	**ARSST dT/dt**	**ARSST Watts**
		(°C)	**(°C)**	**(°C)**	**(°C)**	**(°C)[1]**	**(°C)[2]**	**(°C)[1]**	**(°C)[2]**	**(°C)[3]**
1	2-amino-4-chloro-5-nitrophenol	225	205	187	166	180	200	180	180	---
2	4-amino-1,2,4-triazole	85	260	200	190	192	240	200	220	---
3	3-methyl-4-nitrophenol	128	247	188	181	193	240	155	180	---
4a	dibenzoyl peroxide	105	99	93	86	95	95	93	95	---
4b	dibenzoyl peroxide (isothermal hold steps)	105	---	---	---	---	---	90	---	---
5a	di-tert-butyl peroxide	bp 109	164	120	116	130	150	115	115	---
5b	di-tert-butyl peroxide (PID scan at 2°C/min)	bp 109	---	---	---	---	---	115	---	120

1=°C onset detected from pressure rate plots
2=°C onset detected from heat rate plots
3=°C onset detected from heater power

DSC - Differential Scanning Calorimeter (Mettler Toledo)
C80™ - Microcalorimeter (Setaram, France)
ARC™ - Accelerating Rate Calorimeter (Columbia Scientific)
TSu™ - Thermal Screening Unit (HEL, UK)
ARSST - Advanced Reactive System Screening Tool (Fauske, USA)

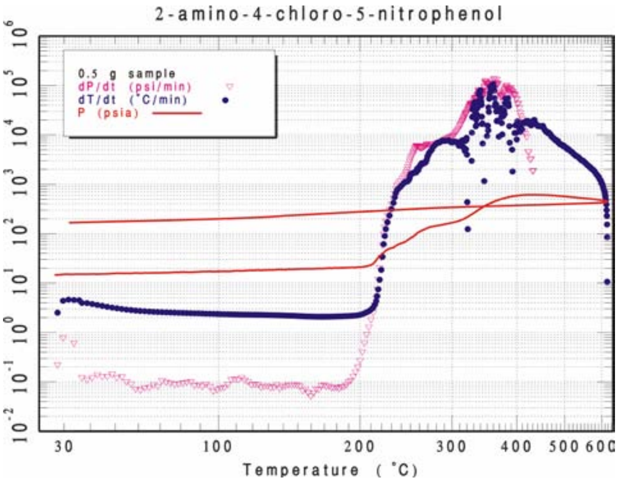

Fig. **2 Pressure and temperature rates and pressure data for example 1**

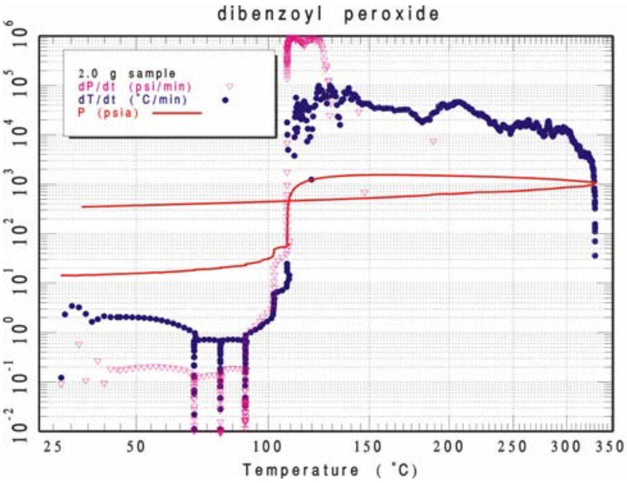

Fig. **5 Pressure and temperature rates and pressure data for example 4b (stepwise heating by PID control)**

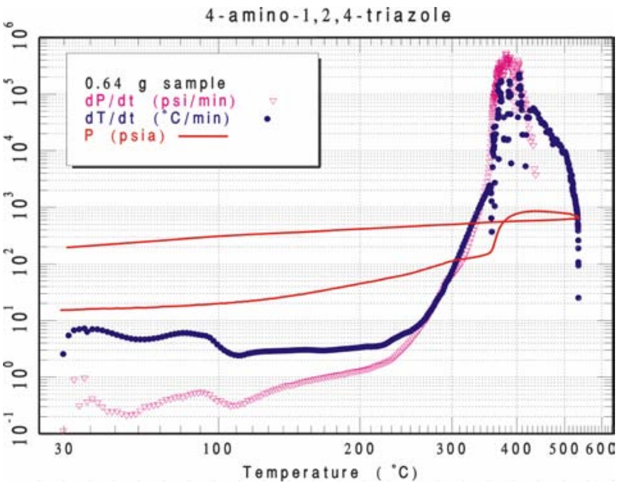

Fig. **3 Pressure and temperature rates and pressure data for example 2 (shows initial faster heatup rate)**

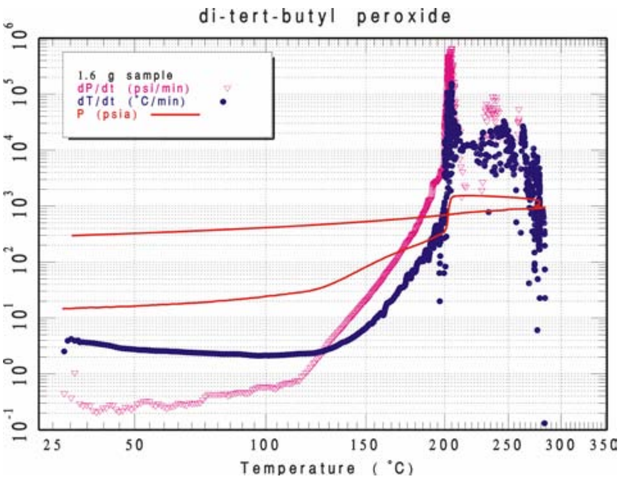

Fig. **6 Pressure and temperature rates and pressure data for example 5a**

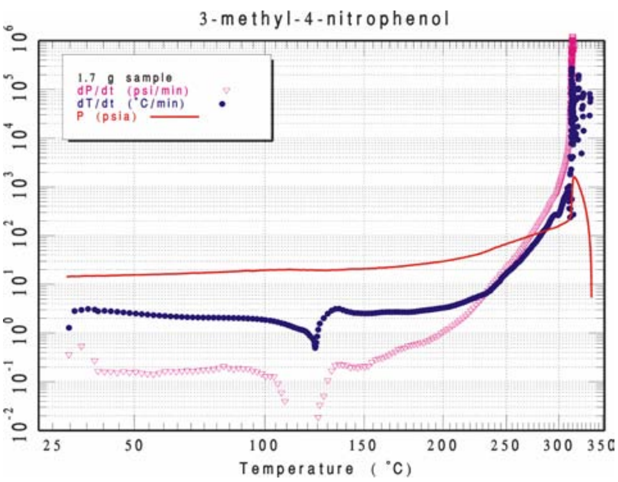

Fig. **4 Pressure and temperature rates and pressure data for example 3 (shows melt and rupture)**

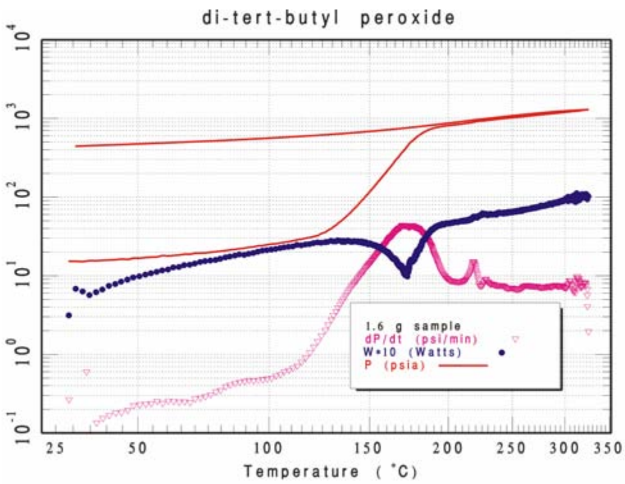

Fig. **7 Pressure rate, heater power and pressure data for example 5b (PID ramp at 2°C/min)**