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# Dynamic vacuum stability test method and investigation on vacuum thermal decomposition of HMX and CL-20

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ABSTRACT

Dynamic Vacuum Stability Test (DVST) method monitoring the reaction process continuously and directly was used to investigate the thermal decomposition of HMX and CL-20. DVST employs the built-in pressure and temperature mini-sensors combined with the data acquisition-processing unit to achieve the dynamic and real-time measurement. The eligible thermal stability of HMX and CL-20 is determined by the very little amount of evolved gas. The non-isothermal reaction model of HMX varies with experimental temperature, while that of CL-20 adheres only to one. The isothermal reaction rate constants of the two samples both increase exponentially with the rise of temperature. It may be due to the accelerating autocatalysis in the solid-state thermal decomposition. DVST as an accelerated aging method was also applied to predict the storage life of materials. DVST can replace the traditional VST method in application of thermal analysis of chemicals especially energetic materials.



## 1. Introduction

Vacuum Stability Test (VST) method is widely used to measure the stability and compatibility of many chemicals including energetic materials [1–5]. This method is operated conveniently but still has some drawbacks. For example, mercury manometer has potential danger if its pipe was broken and spilled toxic mercury [6,7]. Bourdon pressure gauge is based on the indirect pressure measurement principle [8–11]. These two methods show only the final result without the process and trend of decomposition reaction. Once the acute decomposition, combustion, or even unexpected explosion occurred during the test, these methods would fail to reflect these phenomena [12]. In recent years, interest in modifying VST has attracted considerable attention but seldom getting satisfactory result [13–16]. STABIL method employs pressure sensor to record the pressure variation successively and automatically [4], but it does not show the temperature change. NBK Lawa gasometric measuring system [17] made of stainless steel for the purpose of explosion-protection is suitable for the investigation of hazardous energetic materials. However, the reaction between metal shell material and sample has an unfavorable effect on the result.

In order to satisfy the test requirement of safety, reliability and high efficiency, a relatively new Dynamic Vacuum Stability Test (DVST) method is developed on the principle of VST pressure sensor method by our group [18,19]. DVST can supervise the dynamic changes of temperature and pressure in a reaction system continuously and directly, determining the stability, kinetics and storage security of chemical materials via programmable processing. To prove the accuracy and reliability of DVST, we focused on two widely used classical energetic materials, i.e. a well-known monocyclic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and a relatively new polycyclic strained cage nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0$^{5,9}$.0$^{3,11}$]-dodecane (CL-20). As is known to all, HMX is one of the most important energetic ingredients in various composite explosives and propellants. HMX-based energetic systems have many advantages, such as high density, potentially high specific impulse, little smoke produced, lower toxicity and lower corrosion. CL-20 as a multi-nitramine cage compound has high energetic density, good chemical stability and better performance than HMX and is considered as a most powerful elementary explosive.

So far the thermal analysis of HMX and CL-20 has been studied extensively by various methods including DSC, TG, VST, FTIR, HFC, ARC and so on [20–27]. However, the measurement of their vacuum thermolysis has not been achieved by a dynamic real-time

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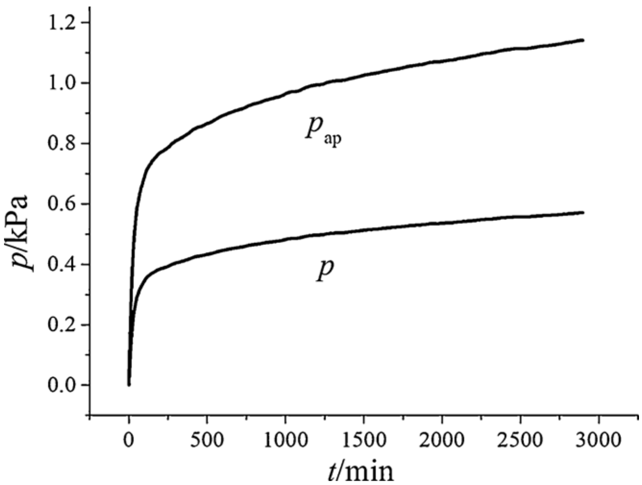


**Fig. 1.** Comparison results of $p_{ap}$ and $p$.

monitoring method. In this paper, DVST method and its studies on HMX and CL-20 are therefore introduced in detail.

## 2. Methodology of DVST

### 2.1. Principles

DVST is the abbreviation of Dynamic Vacuum Stability Test. DVST employs the built-in pressure mini-sensor and temperature mini-sensor combined with the data acquisition-processing unit to achieve real-time measurement, monitor the reaction processes continuously and directly instead of the VST method measuring data only at the experiment beginning and ending. Thus, we call the method as "dynamic" test. DVST is performed in a vacuum, heated and constant volume conditions. The glass test tube loaded with sample is pumped to vacuum and immersed in a thermostat. The decomposed gas leads to the changes of pressure and temperature in the constant-volume tube. The pressure sensor and temperature sensor probe these changes directly and dynamically. Through the data acquisition and processing, the information of the dependences of measured apparent pressure ($p_{ap}$) and test temperature ($T$) on time ($t$) are displayed on the computer. Besides temperature there are three factors affecting the apparent pressure in this study: (1) the increasing evolved gas, (2) the residual gas in the evacuated tube, (3) the drift and lag errors of pressure sensor. The first one should be measured accurately as an object of this study, while the other two should be eliminated as the systematic errors in the process of pressure standardization. The net gas-evolved pressure

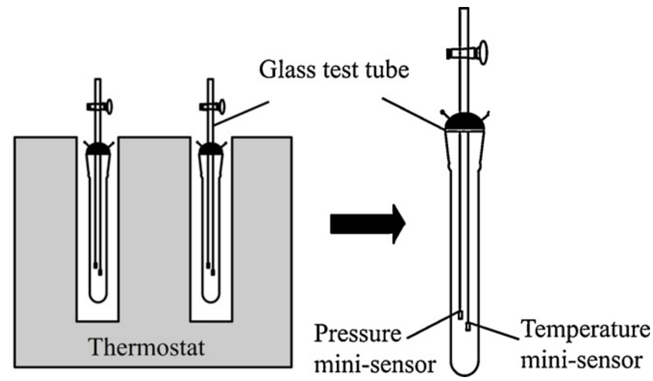


**Fig. 3.** Schematic representation of the glass test tube combined with mini-sensors.

($p$) under standard states is acquired by deducting the systematic errors and the initial pressure ($p_0$) from the apparent pressure according to the ideal gas equation of state. The comparison of $p_{ap}$ and $p$ is shown in Fig. 1.

The $p$–$t$ curve and data can be applied to the qualitative and quantitative analyses:

1) Determining the characteristic of thermal decomposition of a sample by the trend of $p$–$t$ curve.
2) Acquiring the kinetic parameters and the reaction rate constant by the data processing.
3) Evaluating the stability and compatibility of sample according to the evolved gas volume in a specific period of time.
4) Predicting the storage life of a sample by the relation of reaction rate and temperature.

### 2.2. Instruments

DVST instrument consists of the computer-control unit, the heating unit, the thermal reaction unit and the data acquisition-processing unit. The detailed components are shown in Fig. 2.

DVST test tube is fixed with the built-in pressure sensor and temperature sensor with the features of high precise, high sensitive, thermal stable as well as corrosion-resistant. The measuring range of pressure sensor is from 0 kPa to 70 kPa with the accuracy of ±0.01 kPa. The temperature sensor can measure the values varying from 25 °C to 200 °C with the accuracy of ±0.1 °C. The test tube made of explosion-proof reinforced borosilicate glass ensures the eligible air tightness. Leak test proves that the change of vacuum degree is less than ±0.05 kPa under 200 °C after 7 days. So it is safe and reliable for measurement of a small amount of hazardous energetic material. The volume of test tube approximately

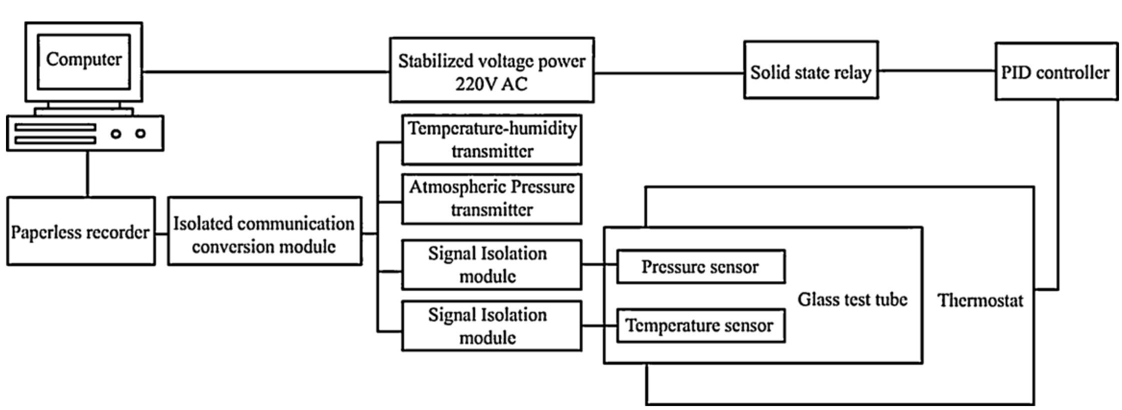


**Fig. 2.** Schematic representation of components connection of DVST.