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Determination of Specific Heat Capacity of Energetic Compounds by DSC

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Abstract: The specific heat capacity (C_p) values of four energetic compounds, 3-nitro-1,2,4-triazol-5-one (NTO), carbohydrazide(CHZ), 2,4-dinitrophenol (DNP) and picric acid (PA), were determined by differential scanning calorimeter (DSC). The least square method is applied to treat experimental data. In the range of 340 – 410 K, the C_p versus T relationship of NTO and CHZ can be expressed as a simple equation: $C_p = a + bT$. In the range of 330 – 360K, the C_p versus T relationship of DNP and PA can be expressed as a cubic equation: $C_p = a + bT + cT^2 + dT^3$. The R-Squares(COD) of measured results of NTO, CHZ, DNP and PA, are 0.9591, 0.9730, 0.9968 and 0.9972, respectively.

Key words: analytical chemistry; differential scanning calorimeter (DSC); specific heat capacity; 3-nitro-1,2,4-triazol-5-one(NTO); carbohydrazide(CHZ); 4-dinitrophenol (DNP); picric acid (PA)

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1 Introduction

Specific heat capacity (C_p) is very improtant to materials, which depends on microstructure of substance and micro movements of substance particles. Some thermochemical data of materials, such as enthalpy, free energy and entropy etc[1], are calculated basing on the specific heat capacity. Specific heat capacity of energetic material is also important to study heat of detonation, heat of combustion and critical temperature etc.

3-Nitro-1,2,4-triazol-5-one(NTO) is used as an explosive with less sensitive than hexahydro-1,3,5-trinitro-1,3,5-triazine(RDX) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Carbohydrazide(CHZ), belonging to the ramification of hydrazine, possesses intensive reduction ability and is widely used to make energetic materials as an energetic ligand. 2,4-Dinitrophenol (DNP) can be used in mixed explosives; picric acid (PA) has been widely used in many areas such as medicine, dye and explosive etc. The structure, performance, application, and process of thermal decomposition of NTO, CHZ, DNP and PA have been proposed [2-4], but the specific heat capacity values of them have been scarcely reported. This work, based on the performances of explosives, has experimentally selected the optimal experimental conditions, measurement procedures and instrument parameters. The specific heat capacity values of four energetic compounds were measured.

2 Experimental

2.1 Instrument

The Pyris 1 DSC instrument from Perkin-Elmer Inc was used, and equipped with special software for calculating specific heat capacity.

2.2 Materials

Synthetic sapphire (diameter: 3 mm; thickness: 1 mm; mass: 28.599 mg) provided by Perkin-Elmer Inc. was used to the experiments as reference materials for calibration of specific heat capacity.

Standard indium and zinc from Perkin-Elmer (99.999%; In: T_{fus} = 429.6 K, $\Delta_{fus}H$ = 28.4 J·g^{-1}; Zn: T_{fus} = 429.6 K, $\Delta_{fus}H$ = 28.4 J·g^{-1}) were used to check the calibration of the instrument and Sn (99.99%) was used to measure the specific heat capacity.

NTO, CHZ, DNP and PA are the samples purified, dried, and then restored in vacuum for 24 h prior to use.

2.3 Measured procedure

The normal method for determination of specific heat capacity by DSC in the continuous mode was well established. The heating rate was 10 K·min^{-1}, the high purity nitrogen gas was used as purifying gas , whose flowing rate

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was 20 ml · min^{-1}. The mass of the sample was less than 5 mg for the NTO, CHZ, DNP and PA. The procedure used in this work to measure the specific heat capacity as a function of the temperature is illustrated in Fig. 1. Each C_p vs. T determination requires three consecutive runs. In the baseline experiment (curve C) the reference and sample-measuring tubes contain empty crucibles. In the second one (curve A) the crucible previously contained in the sample-measuring tube, filled with sapphire and the measured procedure was at same conditions with the baseline one. At last experiment (curve B), the crucible used in the second experiment was filled with sample and was pressed to be a circular tablet, and the measured procedure was same as above. When experiments completed, the computer software automatically processed the data.

The heat flow rate into the sample is related to the specific heat capacity of sample, and the relation is given by[5]

$$\frac{dH}{dt} = mC_p \frac{dT}{dt} \qquad (1)$$

Where $\frac{dH}{dt}$ is the heat flow rate, m is the sample mass, C_p is the specific heat capacity, $\frac{dH}{dt}$ is the heating rate. From which we can see the heat flow rate is in direct proportion to the specific heat capacity of sample. From equation (1) we can get:

$$\frac{C_p}{C_p'} = \frac{m'\Delta Y}{m\Delta Y'} \qquad (2)$$

Where $\Delta Y'$ and ΔY are the ordinate deflections due to the standard and the sample, C_p' and C_p are the specific heat capacity of the standard and sample, m' and m are the mass and specific heat capacity of standard and ample, respectively.

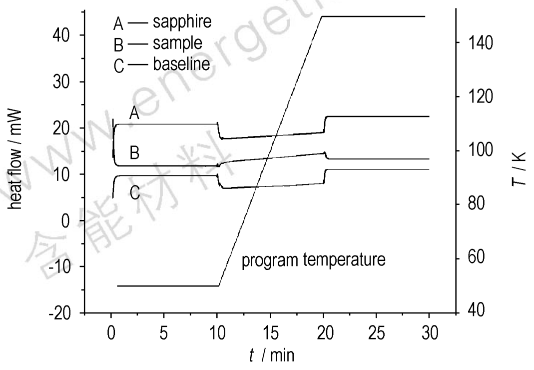

Fig. 1 DSC heat flow curves of sample, sapphire and baseline to be determined

3 Results and discussion

3.1 Examination of the precision

First of all, the Pyris 1 DSC baseline was calibrated, and then the temperature and heat flow were calibrated by measuring the melting point and the enthalpy of In and Zn. The results are show in Table 1. It can be clearly seen from Table 1 that all the relative deviations are within 1%. The precision of the instrument is high.

In order to examine the precision of method for the measurement of specific heat capacity, five parallel experiments were carried out for standard Sn (99.99%) at 340 – 410 K. The heating rate was 10 K · min^{-1}, hold for 10 min at the initial temperature and the end temperature, the specific heat capacity at 400 K calculated by the software of the DSC instrument is listed in Table 2.

Table 1 The melting point and melting enthalpy of In and Zn

materials	ref. values		exp. values		relative deviation	
	T /K	$\Delta_{fus}H$ /J · g^{-1}	T_{fus} /K	$\Delta_{fus}H$ /J · g^{-1}	T /K	$\Delta_{fus}H$ /J · g^{-1}
In	429.75	28.45	429.70	28.38	0.03%	0.23%
Zn	692.62	108.37	692.82	107.27	0.05%	1%

Table 2 Measured results of C_p for Sn at 400 K

parameters	m / mg					average value	ref. value	relative deviation
	9.79	9.39	6.25	11.97	10.89			
C_p /J · g^{-1} · K^{-1}	0.245	0.229	0.246	0.239	0.237	0.239	0.243	1.65%

From Table 2, it can be found that the repeatability of five measurements is good, and the relative deviation is little. This shows that this metrical method is quite satisfactory in the measurement precision and the specific heat capacity of the energetic compounds can be measured by this method.

3.2 Measured results

The C_p values of four energetic compounds were measured by DSC. Three parallel experiments were carried out, and the average results were obtained from the measured values.

Measured values of specific heat capacity of the NTO at different temperature are listed in Table 3, and for the sake of comparison, literature values[6] are also given. The measured values are a little different from literature ones. It may be caused by the difference of the state of measured sample and measuring conditions.

The average values of three measurements for the specific heat capacity of NTO and CHZ at the temperature range of 340 − 410 K are listed in Fig. 2. The average values of three measurements for the specific heat capacity of DNP and PA in the temperature range of 330 − 360 K are listed in Fig. 3. The C_p vs. T relationships of 4 samples are shown in Table 4.

Table 3　Specific heat capacity values of NTO　$J \cdot g^{-1} \cdot K^{-1}$

T/K	first	second	third	literature values[6]
360	1.190	1.181	1.205	1.112
370	1.228	1.215	1.210	1.150
380	1.261	1.231	1.244	1.189
390	1.286	1.250	1.273	1.227
400	1.297	1.269	1.270	1.266

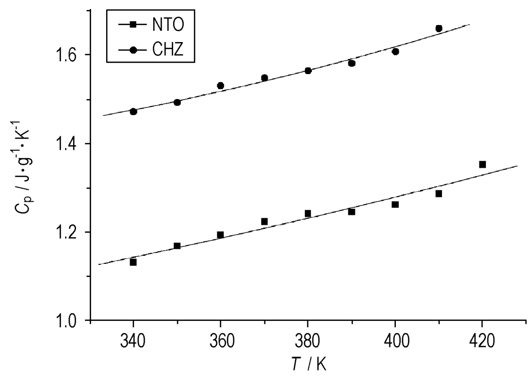

Fig. 2　The relationships of C_p vs. T for NTO and CHZ

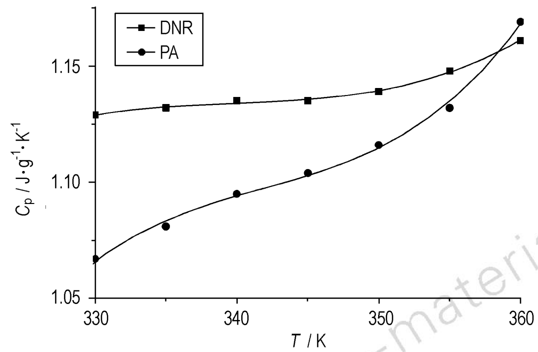

Fig. 3　The relationships of C_p vs. T for DNP and PA

It can be clearly found from Table 4 that the relationships can objectively reflect the measured values in Fig. 2 and 3. The C_p vs. T relationships of NTO and CHZ can be expressed as simple equation, and the R-Squares (COD) of results are 0.9591 for NTO and more than 0.97 for CHZ. The C_p vs. T relationships of DNP and PA can be expressed as cubic equation, and the R-Squares (COD) of results are above 0.99. The standard deviation (SD) of all of them is very small and fitted results are very compatible with the relationships.

Table 4　The temperature dependence of C_p for NTO, CHZ, DNP and PA

sample	T/℃	relationships	R-Square	SD
NTO	340 ~ 410	$0.4520 + 0.0021\ T$	0.9591	0.01118
CHZ	340 ~ 410	$0.6425 + 0.0024\ T$	0.9730	0.01075
DNP	330 ~ 360	$-103.5439 + 0.9238T - 0.0027T^2 + 2.6667 \times 10^{-6} T^3$	0.9968	8.908E − 4
PA	330 ~ 360	$-265.8844 + 2.3394T - 0.0068T^2 + 6.6667 \times 10^{-6} T^3$	0.9972	0.00256

4　Conclusions

The specific heat capacity values of NTO, CHZ, DNP and PA were measured by DSC. Their C_p vs. T relationships were obtained. In the temperature range of 340 − 410 K, the $C_p = 0.4520 + 0.0021\ T$ for NTO, $C_p = 0.6425 + 0.0024\ T$ for CHZ, and in the temperature range of 330 − 360 K, $C_p = -103.5439 + 0.9238T - 0.0027T^2 + 2.6667 \times 10^{-6} T^3$ for DNP $C_p = -265.8844 + 2.3394T - 0.0068T^2 + 6.6667 \times 10^{-6} T^3$ for PA. The relationships show the variation regularity of the C_p with T, and the R-Squares (COD) of results are 0.9591 for NTO and more than 0.97 for CHZ, DNP and PA, providing important information for calculating characteristic parameters.

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4 结　论

（1）当燃烧热固定时，随着药剂配方氧差绝对值的减小，红外照明剂的火焰辐射温度升高，增幅趋向于平缓，火焰的总体辐射能力增强。

（2）随着氧差趋于零，红外照明剂的近红外和可见光辐射强度均有提高，且近红外辐射强度增幅较大。表明零氧差配方能明显提高红外照明效果。

因此，配方设计中，考虑燃烧热的同时应尽量选择负氧差绝对值较小的配比，理论上零氧最好。由于实际燃烧过程中，必然有部分空气中的氧参与反应，可调节氧差值，使其略小于零，故负氧差绝对值较小的配方既可部分利用了空气中的氧，又提高了红外照明效果。而正氧平衡时氧量过剩，会造成浪费，一般不提倡。

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Influence of Oxygen Balance on Flame Radiation of Infrared Illuminating Composition

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Abstract: The different illuminating composition with different oxygen balance which have the same quantity of reaction heat were designed and tested by a moment transform lamp-house radiometer. The results show that when oxygen is deficient，the burning temperature of illuminating composition increases along with the oxygen balance tending to zero，and radiant intensities of the near-infrared (0.7－1.0 μm) and visible light (0.4－0.7 μm) are improved at one time，and the extent of near-infrared radiant intensity is much larger that of visible light. It's inferred that the radiancy is preferable when oxygen balance close to zero.

Key words: physical chemistry; infrared illuminating composition; oxygen balance; combustion heat; radiant temperature; radiant intensity

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用差示扫描量热法测定含能化合物的比热容

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摘要：用差示扫描量热仪（DSC）测定了含能化合物 3-硝基-1，2，4-三唑-5-酮（NTO）和碳酰肼（CHZ）在 340～410 K 温度区间内、苦味酸（PA）和二硝基苯酚（DNP）在 330～360 K 温度区间内的比热容，对所测温度区间内物质的比热容随温度变化的曲线进行了拟合，NTO 和 CHZ 的比热容在所测温度区间内比热随温度变化符合一次函数：$C_p = a + bT$，而 DNP 和 PA 符合三次函数：$C_p = a + bT + cT^2 + dT^3$。NTO、CHZ、DNP、PA 拟合曲线的相关度分别是 0.9591、0.9730、0.9968 和 0.9972。

关键词：分析化学；差示扫描量热法（DSC）；比热容；3-硝基-1，2，4-三唑-5-酮（NTO）；碳酰肼（CHZ）；二硝基苯酚（DNP）；苦味酸（PA）

中图分类号：TJ55；O642　　**文献标识码**：A