



Effects of various vessel materials on exothermic decomposition energy measurements

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ABSTRACT

The United Nations Recommendations on the Transport of Dangerous Goods, 1999, has specified differential scanning calorimetry (DSC) measurements as a screening method for determining the explosive properties of chemicals. In this study, we have investigated the effects of different vessel materials on the exothermic decomposition energy (Q_{DSC}) of 49 chemical substances by performing measurements with DSC. Different Q_{DSC} values were obtained for various types of sealed pressure vessels and a glass capillary tube vessel. To evaluate Q_{DSC} , all the decomposition energy values (calorific values) obtained in this study were investigated in terms of the permissible fluctuation range specified by American Society for Testing of Materials (ASTM) standards. In this manner, we have demonstrated that the material and shape of a vessel affects the measurement of exothermic decomposition energy.

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1. Introduction

The United Nations (UN) has specified certain tests (Test Series 1 and 2) to judge whether certain chemicals should be classified as explosives (UN Recommendations for the Transport of Dangerous Goods, 2009) [1]. These two test series comprise three types of tests – the UN gap test, Koenen test and time–pressure test (or internal ignition test) – and are universally used for identifying and classifying explosives. However, these tests require numerous samples and involve many examination items, and the required quantities of chemicals may not be available early in the development process. Because it is not realistic to apply these tests to all chemicals, an appendix called ‘Screening Procedures’ (Appendix 6) has been added to the UN Recommendations. The appendix contains information on the chemical groups described, indicate their explosive properties and specify the decomposition energy thresholds that are the basis for determining the need for performing the UN tests. The exothermic decomposition energy (Q_{DSC}) is an indicator of whether Test Series 1 and 2 should be performed; for example, neither tests are required if Q_{DSC} of organic materials is less than 800 J g^{-1} . Two books – Transport of Dangerous Goods and Globally Harmonized System of Classification and Labeling of Chemicals – recommend the estimation of Q_{DSC} using suitable calorimetric techniques such as differential scanning calorimetry (DSC) or adi-

abatic calorimetry (e.g. accelerating rate calorimetry (ARC)) [3]. However, measurement methods using these techniques have not been described in detail. The United Nations has recommended special care only with respect to six factors affecting the measurement, which are as follows [2]: (1) sample vessel material; (2) endotherms may immediately precede exotherms; (3) evaporation of constituents will lower the exothermicity (sealed sample vessels should normally be used); (4) the presence of air may critically affect the measured decomposition energy; (5) large differences between the specific heats of the reactants and products; and (6) rapid heating rates (for DSC, the heating rates should normally be 2–5 K/min). No clear explanations are available for the possible effects of the measurement conditions on the results, and moreover, the measurement conditions that an experimenter must use are also not clear. For example, although it is mentioned that the material of the sample vessel might influence the result, the care that must be taken by analysts is not concretely mentioned. DSC and ARC are globally recognized techniques, but the Q_{DSC} values obtained using these measurement methods are still affected by various factors. Hence, the result obtained by different experimenters evaluating Q_{DSC} for the same material may not be truly comparable.

Bodman and Chervin [4] reported that the rate of pressure increase in ARC is a better predictor of explosivity than Q_{DSC} . Further, they proposed the use of a modified version of ARC as a screening method for determining the explosive properties of chemicals; moreover, they used a glass capillary tube vessel for the DSC measurements. Judging from recent research trends

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Table 1
Samples used in this investigation.

No.	Sample name	Abbreviation	No.	Sample name	Abbreviation
1	Benzoyl peroxide (*)	BPO	22	2,2-Asobis(isobutyronitril) (*)	AIBN
2	Lauroyl peroxide	LPO	23	Azodicarbonamide	ADCA
3	tert-Butyl-perbenzoate (*)	TBPB	24	4-(Phenylazo)diphenylamine	PADPA
4	Dicumyl peroxide	DCP	25	Azoxybenzene (*)	azoxyB
5	Cumenhydroperoxide, 84%(*)	CHP	26	4,4'-Azoxydianisole	AzoxyDA
6	di-tert-Butyl peroxide	DTBP	27	1,2-Diformylhydrazine	DFH
7	tert-Butyl hydroperoxide	TBHP	28	Hydrazobenzene	HydrazoB
8	3-Chloroperbenzoic Acid	mCPBA	29	Benzhydrazide	BH
9	Trinitrophenol	TNP	30	4-(2-Pyridylazo)resorcinol	PAR
10	m-Dinitrobenzene	DNB	31	Azobenzene	azoB
11	2,4-Dinitrotoluene (*)	DNT	32	Ammonium nitrate	AN
12	2,4-Dinitroaniline	DNA	33	Isoamyl nitrite	IAN
13	Picramic acid(2-amino-4,5-dinitrophenol)	ADNP	34	Guanidine nitrate	GdN
14	2,4-Dinitrobenzoic acid (*)	24DNBA	35	Diphenylglyoxime	DPGO
15	3,5-Dinitrobenzoic Acid	35DNBA	36	Benzaldehyde oxime	BAO
16	p-Nitroaniline	pNA	37	4-Picoline-N-oxide	4PNO
17	p-Nitrophenol	pNP	38	3-Picoline-N-oxide	3PNO
18	o-Nitrophenol	oNP	39	2,3-Epoxy-1-propanol	EP
19	o-Nitroacetophenone	oNAP	40	Glycidyl methacrylate	GMA
20	N,N-Dinitrosopenta methylenetetamine	NNDNP	41	Triglycidyl isocyanate	TGIC
21	NitroGuanidine	NGd	42	N-Clsuccinimide	NCS

Seven samples marked by an asterisk were also measured by using glass capillary tube vessel.

[5–8], pressure vessels are often used for studying the relationship between the thermal reactivity and explosiveness of a chemical substance. However, chemicals have also been examined by using aluminium pans [9,10], alumina vessels [11] and glass capillary tube vessels [12]. Each researcher uses his or her preferred vessel.

We believe that it is important to clarify the influence of the measurement conditions, and hence, we are currently examining their effect on the thermal behaviour of potentially dangerous substances during DSC and ARC experiments. In particular, in this study, we have investigated the influence of various vessel materials on DSC measurements.

2. Experimental

2.1. Samples

Forty-two chemical samples were used in the first part of this investigation, as shown in Table 1. The chemical reagents were procured from Wako Pure Chemical Industries, Ltd. Hereafter, the samples are referred to by their abbreviations or the numbers listed in Table 1.

2.2. Experiment

2.2.1. DSC measurement

DSC experiments were performed using a DSC 7020 calorimeter manufactured by SII Nano Technology, Inc. (SIINT). A sample (approximately 1 mg) was sealed under air in various pressure-sealed vessels (Table 2) and heated from 25 °C to 700 °C at 5 °C/min. Note that three types of vessels could have been chosen – pressure-sealed vessel, sealed vessel and open vessel – and we chose the pressure-sealed vessel because the United Nations recommends the sealed vessel for prevention of the influence of sample evaporation [2]. The sample amount of high-energy materials is usually limited to approximately 1 mg for safety during the DSC measurements. The amount of sample was therefore unified to 1 mg throughout this report. Moreover, the United Nations recommends that the heating rates should normally be in the range of 2–5 K/min [2]; heating rates of 5 K/min were employed. Although the effects of the sample amounts and heating rates have also been investigated, we will report these results in another paper because of the enormous amount of data.

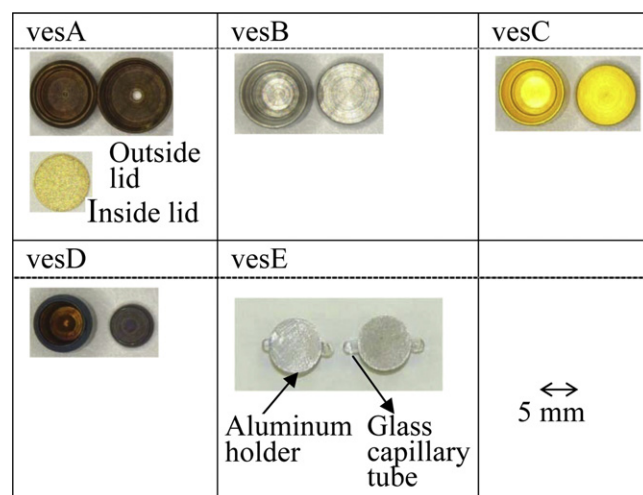


Photo 1. Appearance of the vessels.

Our investigation was focused on the effect of different sample vessels. Four types of pressure-sealed vessels and a glass capillary tube vessel were used in this experiment, and their characteristics are listed in detail in Table 2 (the manufacturer is not specified); hereafter, they are referred to by the abbreviations. Further, Photo 1 shows the five vessels. VesB and vesC were identical in all respects except that the vesC surface was gold plated. Three vessels – vesA, vesB (or vesC) and vesD – were made of slightly different stainless steel materials. In vesB, vesC and vesD, the lid was locked onto the vessel by mechanical pushing. In contrast, in vesA, the lid was screwed onto the vessel, which implied that it could be used several times since the lid can be opened after the measurements. Here, an inner lid that acts as a rupture disk was used under the outer stainless steel lid. VesE was a glass capillary tube vessel in which a sample can be sealed into a glass capillary tube that can then be inserted into an aluminium holder. All the measurements using vesE were performed at Sumitomo Chemical Co., Ltd. using a DSC 6020 calorimeter manufactured by SIINT. These measurements were conducted using only approximately seven samples (marked by an asterisk in Table 2).

The instrument was calibrated using 10 mg of four or five dedicated standard metals (In, Sn, Pb, Zn and Al) in each vessel [5,13].

Table 2
Vessel characteristics.

Notation	Volume (μl)	Weight (g)	Cp (J/gK)	Heat capacity (J/K)	Diameter (mm)	Material	Resistance to pressure
vesA	27	0.841	0.502	0.422	6	SUS316L	10 MPa
vesB	15	0.641	0.502	0.321	6	SUS303	
vesC	15	0.641	0.502	0.321	6		5 MPa
vesD	20	0.465	0.502	0.233	5	SUS304	5 MPa
vesE	5	0.019	0.670	0.013	1	Glass	^a

^a No information.

Furthermore, the device's conditions were confirmed by measuring these standard substances in the measurement mode. All the Q_{DSC} values obtained in this study were investigated in terms of the permissible range of fluctuations in Q_{DSC} specified by American Society for Testing of Materials (ASTM) standards [14,15].

2.2.2. Scanning electron microscope (SEM) observations

The sample vessels were observed and analysed using a field Scanning electron microscope (SEM) (FESEM, S5000, Hitachi Co., Ltd., Japan) with Horiba energy dispersion X-ray (EDX) microanalysis.

3. Results and discussion

Fig. 1 shows the DSC curves – temperature vs. heat flow – obtained using various sample vessels with 24DNBA as a representative sample; the Q_{DSC} values are also shown. The peak shape clearly differs depending on the sample vessel, which indicates that the thermal behaviour is affected by the vessel. Moreover, the decomposition energy value decreases in the following order: vesC > vesD > vesB > vesE > vesA.

To evaluate Q_{DSC} , all the decomposition energy values (calorific values) obtained in this study were investigated in terms of the per-

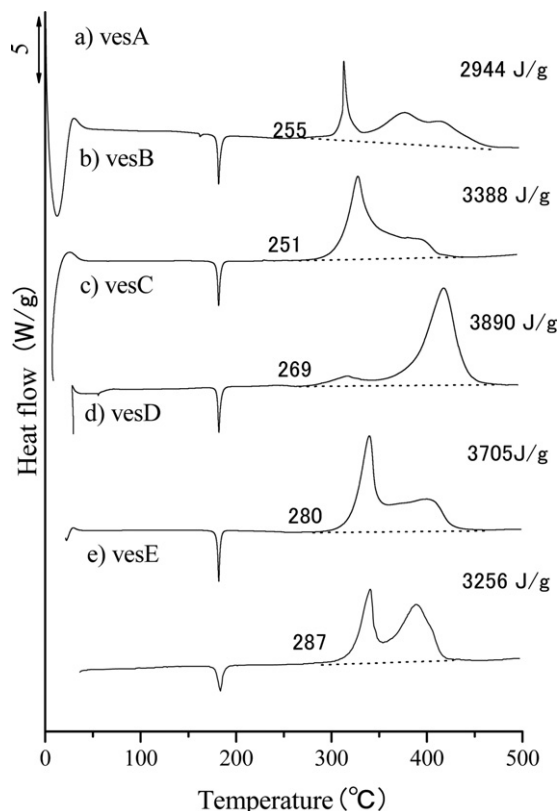


Fig. 1. DSC curves for 2,4-dinitrobenzoic acid (24DNBA).

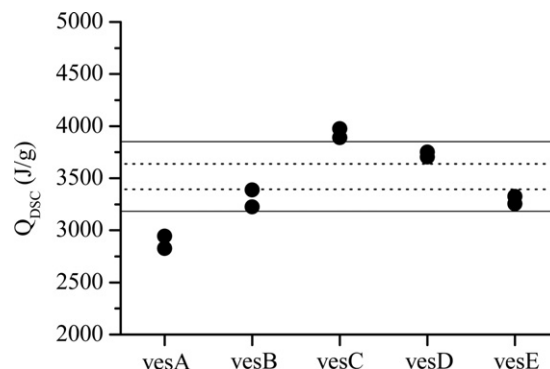


Fig. 2. Fluctuations in Q_{DSC} measured for various vessels for 24DNBA.

missible fluctuation range specified by the ASTM standards [14,15]. No universally applicable reports exist for the Q_{DSC} fluctuations. To estimate the extent of the influence of various vessel materials on the obtained Q_{DSC} , we first considered the extent of deviation of these values from the permissible range of fluctuation. The Q_{DSC} values obtained with various vessels are summarized in Fig. 2 with 24DNBA used as a representative example. According to ASTM standards [14,15], if the standard deviations of repeatability and reproducibility are within 3.5% (at one laboratory) and 4.7% (at more than two laboratories), respectively, for the same sample, the data is reliable. However, data reliability is an issue when repeatability >9.7% and reproducibility >13.2%. In Fig. 2, the dotted lines indicate the permissible range of Q_{DSC} fluctuations specified by the ASTM standard ($\pm 3.5\%$). The data becomes unreliable when the solid line ($\pm 9.7\%$ of the repeatability) is exceeded. The Q_{DSC} values obtained for vesA were remarkably lower than those for other vessels, while those obtained for vesC were comparatively higher. On the other hand, the sample vessel material did not affect the melting point; 24DNBA melts at approximately 453 K, as shown in Fig. 1. The sample vessel materials seem to affect only the decomposition phenomena.

Fig. 3 shows comparisons of the Q_{DSC} values for vesA and vesB, while those for vesD and vesB are compared in Fig. 4. Note that

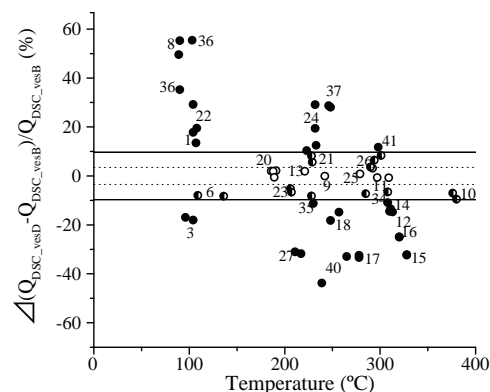


Fig. 3. Comparison of obtained Q_{DSC} for various samples in vesA and vesB.

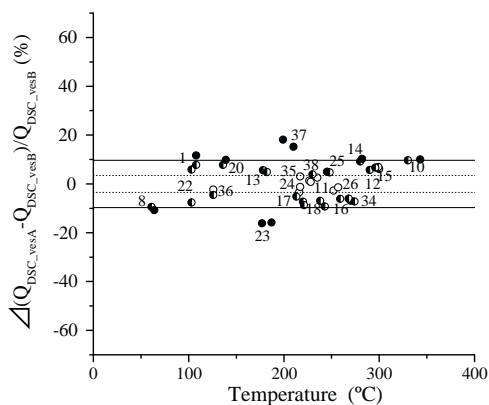


Fig. 4. Comparison of obtained Q_{DSC} for various samples in vesD and vesB.

throughout this report, all the Q_{DSC} values were compared with those obtained using vesB for the following reason. It was necessary to have a standard or control for comparison for an adequate evaluation. VesB was appropriate since it was made of uniform stainless steel in which the inner lid is not used. Although vesD is also made of uniform stainless steel, vesC is gold-plated to vesB. Figs. 3 and 4 indicate the extent to which the Q_{DSC} values obtained for vesA and vesD differ from those obtained for vesB for all samples. Moreover, the more the data points varied, the more the Q_{DSC} values for both vessels differed from those for vesB. The black circles indicate that the Q_{DSC} values obtained for both vesA and vesD were clearly different and exceeded the tolerance range of fluctuation. The unfilled circles and half-filled circles indicate that the Q_{DSC} fluctuations were within 3.5% and 9.7%, respectively. The Q_{DSC} values were different for vesA and vesB in the case of some samples, as shown in Fig. 3. In contrast, in Fig. 4, almost all the Q_{DSC} values obtained for both vessels were within the tolerance range of fluctuation. However, some black circles which the repeatability was more than $\pm 9.7\%$ were confirmed. It is not clear if the difference is significant since the data are close to the limits of reliable observations, and it may be necessary to investigate Q_{DSC} fluctuations once more.

The difference in the Q_{DSC} values for vesA and vesB may be due to the nature of the material of the inner lid rather than the stainless steel component of the vessel itself. According to an energy dispersion X-ray (EDX) microanalysis, the inner lid contained silver and copper, in addition to gold. Photo 2 shows the inner lid of vesA after the DSC measurements. A part of the inner lid had peeled and fallen off, and the substance that fell off was black on one side and gold on the other. The black colour was caused by the decom-

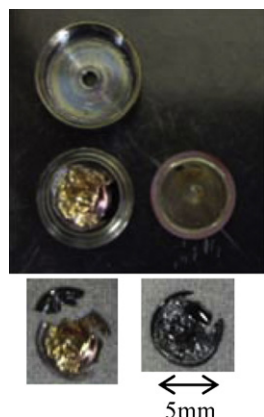
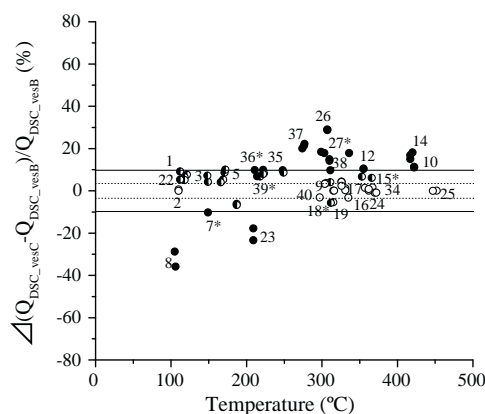


Photo 2. VesA after differential scanning calorimetry (DSC) measurements.



*Asterisks indicate cases in which the shape of the peak also changes.

Fig. 5. Comparison of obtained Q_{DSC} for various samples in vesC and vesB.

position product. Measurements were performed twice for every sample and good reproducibility was present. Identical phenomena were observed, especially when the Q_{DSC} fluctuations in both vessels were more than $\pm 9.7\%$. The inner lid certainly seems to have participated in the reaction. It is hypothesized that the effect on the gas phase reaction is large when the inner lid participates in the reaction. The material of the inner lid must also be considered. More investigations are required to determine the components that influence the DSC measurement results.

In Fig. 5, the results for gold-plated vesC are compared with those for vesB. This figure indicates the large differences between Q_{DSC} values for vesC and those for vesB regarding some samples. The asterisks indicate cases in which the peak shape also changes. Fig. 6 shows the DSC curves with 35DNBA as a representative example. In this case, although Q_{DSC} obtained for both vessels was in the permissible fluctuation range, the peak shape changed in the presence of the gold plate. The reason for this is not clear. One possibility is that the results are affected by the components. In general, gold is not known to react with any material. Photo 3 shows an SEM image of vesC. Two layers, one of gold (2 μm) and one of nickel (1.7 μm), can be clearly confirmed at the outer surface of the vessel. This vessel appears to have been plated with nickel before it was plated with gold in order to assist the gold plating. However, more complex layers were confirmed on the inner surface of the vessel than on the outer surface. In the complex layers, regions with pure carbon and pure silicon were detected in the gold layer. Moreover, complex regions including iron, chromium and aluminium were

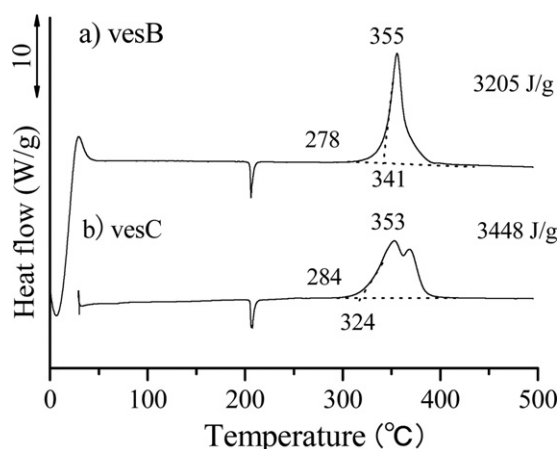


Fig. 6. DSC curves for 3,5-dinitrobenzoic acid (35DNBA).

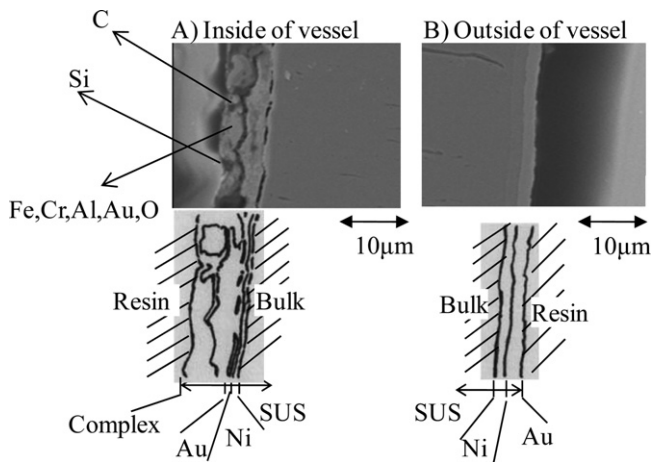


Photo 3. Scanning electron microscope (SEM) image of vesC.

also detected in addition to the regions comprising only gold. In general, the thinner the gold film, the higher the number of holes created on the surface. It is not yet clear whether the complex layers originated during the processing operation that was performed to seal the holes. The difference in the Q_{DSC} values between vesB and vesC might be a result of this complex layer. However, all the gold-plated stainless steel vessels did not have complex layers. Furthermore, SEM observations were also conducted with two types of gold-plated vessels made by another manufacturer, and differences were confirmed. The plating conditions appeared to differ with the manufacturer. Further tests are required to investigate this aspect. Note that it may be difficult to perform gold plating in small containers such as DSC vessels.

Fig. 7 shows a comparison of vesE and vesB. This comparison was performed for only 7 out of the 42 samples, but similar evaluations were conducted. In the case of TBPB (No. 3) and BPO (No. 1), the Q_{DSC} values obtained for the two vessels were clearly different and exceeded the tolerance range of fluctuation. The Q_{DSC} values of TBPB and BPO for vesE were lower than those for the metallic vessels; the reason for this is not clear. One possibility is that the tested material reacts with the metal. Fig. 8 shows the DSC curves obtained for TBPB and DNT using two types of vessels. The heat generation rate was calculated by Eq. (1) as an index as follows:

$$A = \frac{PH}{T_p - T_o} \quad (1)$$

In this equation, PH is the peak height from the baseline to the peak top while T_p and T_o are the maximum and onset tempera-

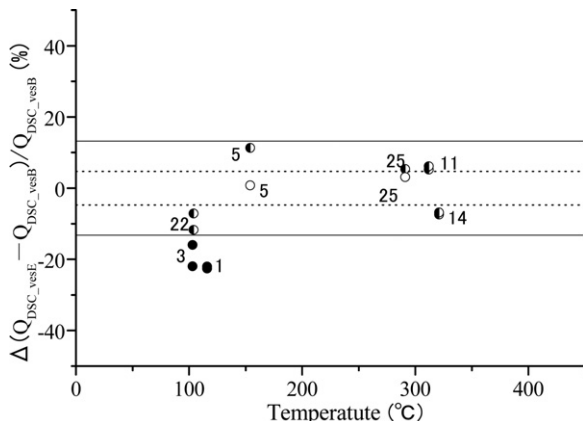


Fig. 7. Comparison of obtained Q_{DSC} for various samples in vesE and vesB.

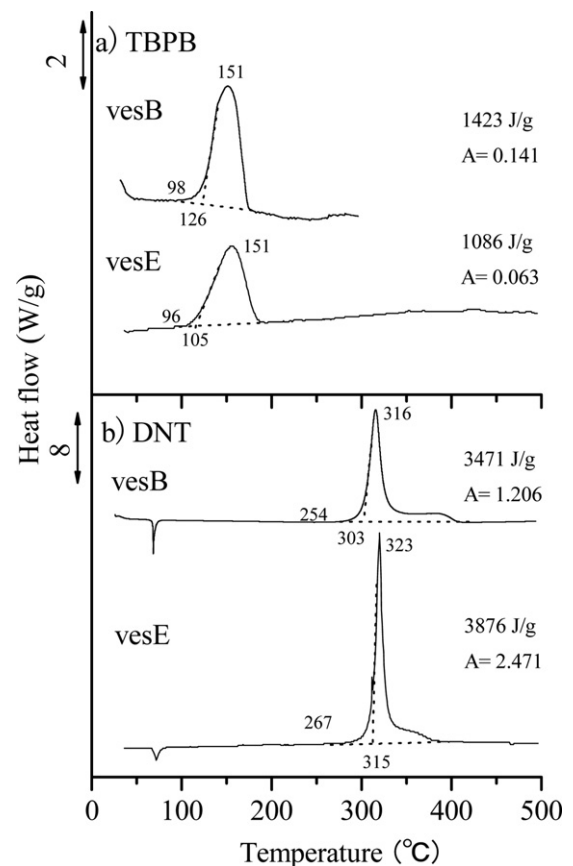


Fig. 8. DSC curves obtained when using vesB and vesE [$A = PH/(T_p - T_o)$].

tures of the peak, respectively. The obtained values of A are shown in Fig. 8. For TBPB, the peak obtained using vesE was wider than that obtained using vesB, while the heat generation rate was lower. This suggests that the glass capillary tube vessel has poor thermal responsiveness. However, in the case of DNT, the peak obtained using vesE was narrower than that obtained using vesB, while the heat generation rate was higher; this indicates that the thermal responsiveness might not necessarily always be poor when using vesE. Regarding this, it must be noted that the shape of the glass capillary tube vessel is different from that of the other vessels. The placement of the sample also differs, as shown in Fig. 9. Fig. 10 presents a comparison of the results using vesB with those of Bodman and Chervin [4] who conducted DSC experiments in a glass capillary tube vessel with 18 chemical substances. The samples were heated at $10^\circ\text{C}/\text{min}$, which, however, is different from our condition, $5^\circ\text{C}/\text{min}$. Therefore, DSC measurements using vesB were conducted for some samples at $10^\circ\text{C}/\text{min}$, and the results were compared with those of Bodman and Chervin [4]. Table 3 shows

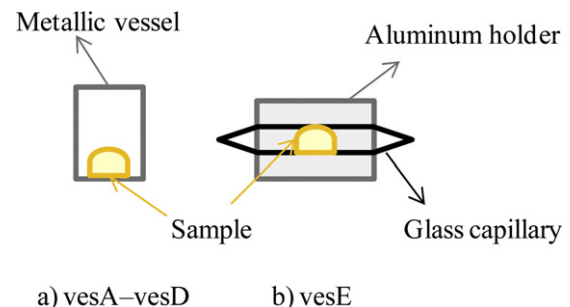


Fig. 9. Schematic comparing vesE and metallic vessels.

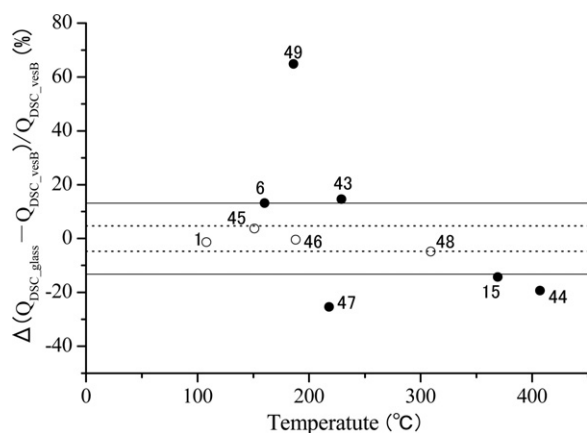


Fig. 10. Comparison of obtained Q_{DSC} for various samples in a glass capillary vessel and vesB.

the seven chemical substances that were used in the second part of this investigation. When the glass capillary tube vessel was used, the calorific value was not always lower than that obtained using the metallic vessel vesB. In addition, in the case of BPO (No.1), our results do not agree with those of Bodman and Chervin [4]. The Q_{DSC} values were clearly different and exceeded the tolerance range of fluctuation. The filling of a sample in a glass capillary tube is technically different from filling in a metal vessel and may depend on the capability of the analyst. Moreover, it may not be possible to apply the permissible range of fluctuations specified by ASTM standards to the Q_{DSC} values obtained for the glass capillary tube vessel. We must evaluate the results obtained by using the glass capillary tube vessel from various viewpoints, and although it is surmised that glass is favourable as a material to evaluate reactivity because of its inactivity, it is not yet clear whether it is preferable to use a glass capillary tube vessel. For the reference, we compared vesB with an aluminium vessel having a hole with an inner diameter of approximately 0.1 mm (PH-Al). The data obtained using PH-Al were excerpted from the literature [16], and a pressure of 30 kg/cm² was applied to the outer surface of the vessel. In the case of some samples, Q_{DSC} was smaller because of the evaporation of the sample when PH-Al was used. The influence of evaporation appeared to be considerable and exceeded expectations. Evaporation has been pointed out as the one of the six factors affecting the measurement by the United Nations as well; the evaporation of constituents decreases the exothermicity, and hence, sealed sample vessels should be used normally. In the United Nations recommendations, the definition of sealed vessels is not completely clear, and the use of open vessels has not been deprecated entirely. The hermetically sealed vessel of low pressure resistance may also be influenced by the evaporation of the sample. In addition, the aluminium in the vessel material also appeared to participate in the reaction.

Lastly, Fig. 11 shows the relationship between Q_{DSC} and the results of the UN explosive estimation test. The results using vesB, at the heating rate of 5 K/min, are plotted in this figure as the represen-

Table 3
Samples used in this investigation.

	Sample name	Abbreviation
43	2-Amino-4-chloro-5-nitrophenol	ACNP
44	3-Nitrobenzenesulfonic acid sodium salt	NBSNa
45	1-Phenyl-5-mercapto tetrazole	PMT
46	3-Thiosemicarbazide	TSC
47	2-Bromo-2-nitropropane-1,3-diol	BNP
48	2-Chloro-5-nitrobenzoic acid	CNBA
49	p-Nitrophenylhydrazine	pNPH

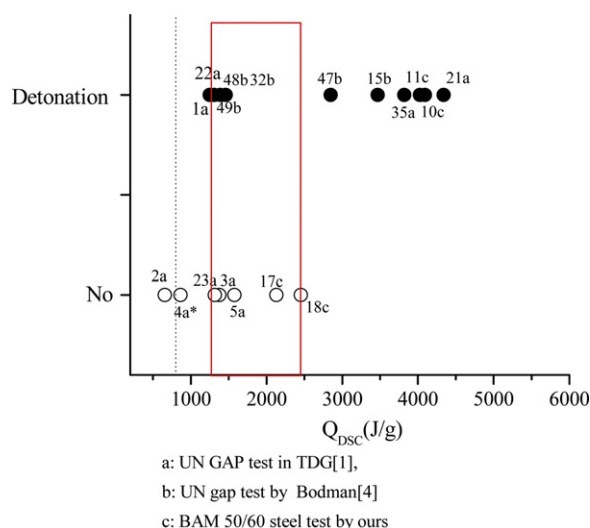


Fig. 11. Relationship between Q_{DSC} and the results of the UN explosive estimation test.

tative example. The sample with large Q_{DSC} exhibited a tendency to possess explosiveness. An estimate using Q_{DSC} can be roughly used to determine the screening of the explosion characteristic. However, the square area (indicated by the red line) implies that it is not clear whether explosiveness is present. In this area, the explosion estimation test results are negative despite the high energy. If the results observed using various vessels are also plotted in this same figure, this area becomes even vaguer. If many researchers evaluate Q_{DSC} using different vessels, it may be difficult to screen the explosion characteristics using Q_{DSC} value. However, if the type of the vessel material is specified and the data obtained using uniform stainless steel is chosen, the obtained Q_{DSC} has an approximate correlation with the criteria of the explosion estimation test, as shown in Fig. 11. This is probably because the composition of uniform stainless steel is almost identical to that of the steel pipe material used for the explosive estimation test. On the other hand, Bodman and Chervin pointed out that Q_{DSC} obtained by the glass capillary tube vessel and the explosiveness in the explosive estimation test does not have a correlation [4]. The evaluation changes remarkably depending on the used vessel. Further investigations into the DSC vessel materials are required to perform more accurate screening procedures. The measurement vessel should be made strictly and universally uniform.

In addition, it may also be necessary to reconsider the permissible fluctuation range in the threshold of Q_{DSC} on the basis of our results.

4. Conclusions

In this study, we have examined the influence of measurement conditions on Q_{DSC} for 49 chemical substances using DSC measurements. We have examined the influence on Q_{DSC} using only some of the available vessels: four types of pressure-sealed vessels and a glass capillary tube vessel. All the Q_{DSC} values obtained in this study were investigated in terms of the permissible range of fluctuations in Q_{DSC} specified by ASTM. Almost all the Q_{DSC} values obtained for two kinds of uniform stainless steel vessel were within the tolerance range of fluctuation. However, when the inner lid is used, the material of the inner lid must be considered. Our investigations have confirmed that the inner lid certainly participates in the reaction.

In the presence of gold plating on a stainless steel vessel, the obtained Q_{DSC} values were clearly different for some samples and

exceeded the tolerance range of fluctuation in Q_{DSC} . Moreover, the peak shape also changed.

When the glass capillary tube vessel was used, the calorific value was not always less than that obtained using the metallic vessel. Glass is favourable as a material to evaluate reactivity because of its inactivity. However, it is not yet clear whether it is preferable to use a glass capillary tube vessel.

Q_{DSC} obtained using various vessels showed little correlation with the explosion evaluation test results. However, if the type of vessel material is specified, for example the uniform stainless steel is chosen as the vessel material, the obtained Q_{DSC} values had an approximate correlation with the criteria of the explosion estimation tests.

The technology has recently advanced, and various manufacturers have made many vessels for DSC measurement. Researchers typically do not investigate the vessel they use before making measurements. However, the Q_{DSC} values were significantly influenced by the vessel material and vessel type. The vessel material must be chosen carefully depending on the measurement setup. The measurement methods used to determine the internationally accepted thresholds must be made stricter and universally more uniform.

References

- [1] United Nations, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, third revised ed., 1999, pp. 27–47.
- [2] United Nations, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, fourth revised ed., 2009, p. 203, 427.
- [3] United Nations, Globally Harmonized System of Classification and Labeling of Chemicals, first revised ed., 2005, p. 50.
- [4] G.T. Bodman, S. Chervin, Use of ARC in screening for explosive properties, *Journal of Hazardous Materials* 115 (2004) 101–105.
- [5] A. Berger, K.D. Wehrstedt, Azodicarboxylates: explosive properties and DSC measurements, *Journal of Loss Prevention in the Process Industries* (2010) 1–6, in press.
- [6] K.T. Lu, T.C. Chen, K.H. Hu, Investigation of the decomposition reaction and dust explosion characteristics of crystalline benzoyl peroxides, *Journal of Hazardous Materials* 161 (2009) 246–256.
- [7] M. Malow, K.D. Wehrstedt, Prediction of the self-accelerating decomposition temperature (SADT) for liquid organic peroxides from differential scanning calorimetry (DSC) measurements, *Journal of Hazardous Materials A120* (2005) 21–24.
- [8] M. Malow, K.D. Wehrstedt, S. Neuenfeld, On the explosive properties of 1H-benzotriazole and 1H-1,2,3-triazole, *Tetrahedron Letters* 48 (2007) 1233–1235.
- [9] J.H. Yi, F.Q. Zhao, S.Y. Xu, L.Y. Zhang, H.X. Gao, R.Z. Hu, Effects of pressure and TEGDN content on decomposition reaction mechanism and kinetics of DB gun propellant containing the mixed ester of TEGDN and NG, *Journal of Hazardous Materials* 165 (2009) 853–859.
- [10] U.R. Nair, G.M. Gore, R. Sivabalan, S.J. Pawar, S.N. Asthana, S. Venugopalan, Preparation and thermal studies on tetranitrodibenzo tetraazapentalene (TACOT): a thermally stable high explosive, *Journal of Hazardous Materials* 143 (2007) 500–505.
- [11] R. Gunawana, D. Zhang, Thermal stability and kinetics of decomposition of ammonium nitrate in the presence of pyrite, *Journal of Hazardous Materials* 165 (2009) 751–758.
- [12] S. Chervin, G.T. Bodman, Phenomenon of autocatalysis in decomposition of energetic chemicals, *Thermochimica Acta* 392–393 (2002) 371–383.
- [13] ISO 11357-1, *Plastics—Differential Scanning Calorimetry (DSC)—Part 1: General Principles*, first ed., 1997.
- [14] ASTM E537-07, *Standard Test Method for the Thermal Stability of Chemicals by Differential Scanning Calorimetry*.
- [15] ASTM Research Report RR: E27-1003, *Interlaboratory Test Study for E537 Assessing the Thermal Stability of Chemicals by Methods of Thermal Analysis*.
- [16] S. Tamura (Ed.), *Handbook of Chemical Process Safety*, 2000, pp. 177–412.