



introduce one harmonized pressure vessel test into the UN Manual of Tests and Criteria. So far the development of a harmonized PVT has been included in the UN working program three periods as follows: (1) from 1997 to 1998 a harmonized UNPVT was developed; (2) from 1999 to 2000, test procedures, conditions and criteria for the MCPVT were defined, and MCPVT round robin would be conducted, where MCPVT was included as a screening test and possible replacement of test series E by MCPVT was studied; (3) from 2001 to 2004, MCPVT round robin test will be continued for a screening test. Based on many fundamental works [2,3], round robin tests were firstly initiated in Japan with three organic peroxides in order to obtain that (1) Reproducibility of MCPVT under the same conditions; (2) Valuable benchmark for further design improvement and validation; (3) Extensive utilization of this apparatus in runaway hazard evaluation for unstable substances [5].

## 2. Round-robin experiments

Closed vessel measurements were made using a Japanese modified type MCPVT vessel which is illustrated diagrammatically in Fig. 1. MCPVT

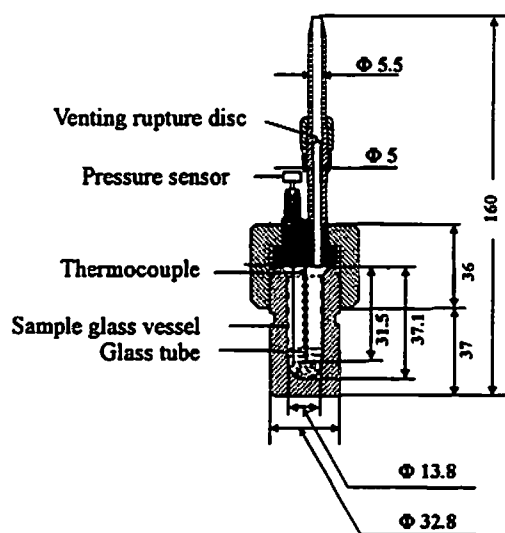


Fig. 1 MCPVT vessel

is a kind of the larger scale DTA system which allows the measurement of pressure as well as temperature. There are three holes through the lid of the vessel, one for a strain type sensor with a vibration frequency of 1 MHz through a capillary

tube of 30 mm length to measure pressure, second one for a K-type thermocouple to measure temperature and third one for a rupture disc (Ni-Mo alloy, activation pressure is 35 MPa at 450°C) for venting. To avoid catalyzing effect on the decomposition of the sample, a glass tube was used as a sample container inside the steel vessel and the thermocouple was protected in a glass sheath. The autoclave had a free volume of  $6.0 \times 10^{-6} \text{ m}^3$ . The assembled vessel with sample and sensors for temperature and pressure measurement was put in an electrical heating furnace whose heating condition could be controlled by a digital program. Digital data with the sampling rate of 0.2 kHz were obtained and the maximum rate of pressure rise,  $(dP/dt)_{\text{max}}$ , was calculated from two points smooth of the first derivative of the pressure-time curve.

Three organic peroxides provided by Kayaku Akzo Co. Ltd. shown in Table 1, were chosen as samples. Following X. Liu and K. Hasegawa [5,6], test conditions were selected as below:

Vessel volume:	$6.0 \times 10^{-6} \text{ m}^3$
Heating rate:	9-10 °C/min
Sample mass:	1 ( $\pm 0.1$ ) g
Measuring items:	pressure and temperature
Data sampling rate:	0.2 KHz

Three research groups participated in the round-robin tests, that is, the National Research Institute of Fire and Disaster (NRIFD), Tokyo, Nippon Kaiji Kentai Kyokai (NKKK), Yokohama, and Kayatech Co. Ltd., Yamaguchi prefecture.

## 3 Results and discussion

To make sure of no leakage, the MCPVT must be closed with a very strong torque and all threads must be lubricated very well. In Fig. 2, it indicates that results of measurements of vapor pressure of water during being heated are very close values with those in the reference [7]. The vessel has to be heated until at least 250 °C. It means MCPVT gives good data when it is closed quite well and no leakage is made in the system during the whole heating process.

Figure 3 shows the pressure and temperature histories for three runs carried out for BPB by NRIFD and corresponding rates of pressure rise in order to get the maximum values. These data

Table 1 Samples used in the test

Code	Sample name	State	Purity
BPB	t-Butyl peroxy benzoate	liquid	99.9%
DBTO	2,5-Di-methyl 2,5-di-(t-butyl peroxy) hexane	liquid	85.5%
BPO	Benzoyl peroxide	solid	74.3%

Samples used here were provided by Kayaku Akzo Co. Ltd.

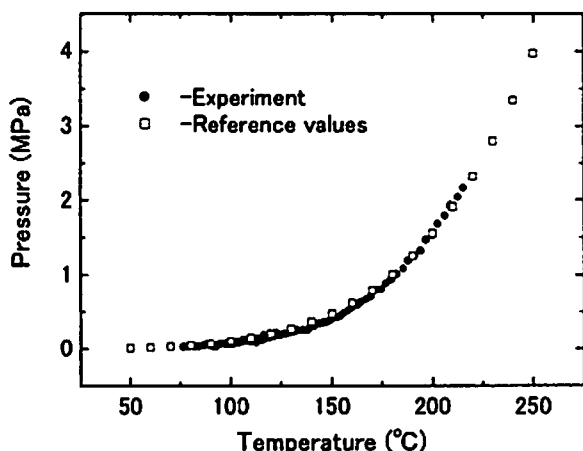


Fig. 2 Vapor pressure of water versus temperature [7]

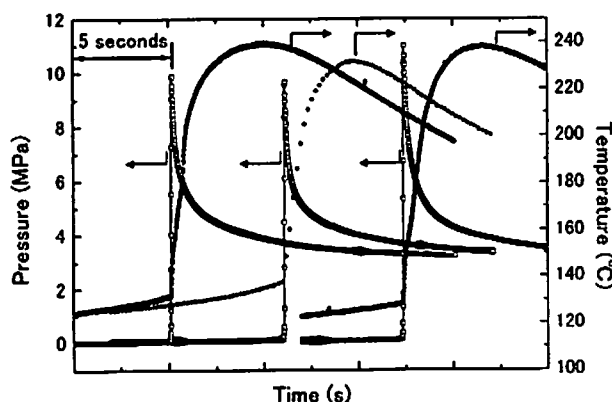


Fig. 3(a) Pressure and temperature behaviors of BPB for three runs in MCPVT  
□: Pressure ●: Temperature

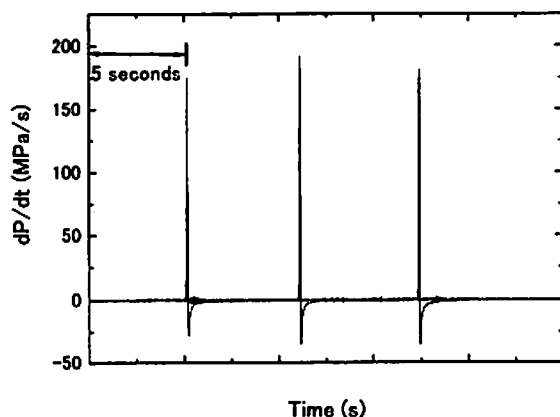


Fig. 3(b) Rates of pressure rise of BPB for three runs

imply that repeatability of test results obtained by the same operator is acceptable. The sample at first is heated by the rate of 10 °C/min under a ramp mode. At the onset temperature of decomposition of the sample, pressure and temperature go up steeply as gas and heat release. Here onset temperature ( $T_0$ ) is defined as the temperature at which  $dP/dt$  is the maximum and  $T_p$  is the highest temperature at which the reaction can proceed. The major products of BPB are toluene, benzene, propanone, methane and carbon dioxide [8]. The experimental research [9] has revealed that a very short-term wave of gases of both “dry” and “wet” products with intense heat release arises from the vessel into atmosphere, and vents directly through the duct to pressure transducer sensor, which build up a quite high overpressure sharply at the position of pressure transducer. So there appears a sharp peak on the pressure curve at which pressure rise attains the maximum value. Then the pressure decreases to a constant lower level. There are two reasons. The first is that the former high-speed gas flow leads to a pressure imbalance between the vessel and the duct, that is, the pressure in vessel is lower than that in duct. The imbalance in turn causes an inverse gas flow from the duct into the vessel soon after the pressure attains the highest. The second reason is that due to the biggest temperature difference between inside and surrounding when the sample decomposes violently, heat generated from the reaction is lost to the ambient quickly and as a result temperature of the sample tends to go down again to the ambient. Especially the “wet” fractions in the products, such as toluene and benzene, condense again, which lead the pressure to decrease until a new balance is established. The similar phenomena are also observed in the measurement of DBTO and BPO whose products are benzene and carbon

Table 2 Repeatability in MCPVT

Sample	$P_{max}$ (MPa)	$(dP/dt)_{max}$ (MPa/s)	$T_o$ (°C)	$T_p$ (°C)	Konen PVT	Dutch PVT	USA
BPB	10.3±0.6*	183.5±5.6*	133.8	232.3	Violent	Violent	Medium
	10.3 **	221.8 **					
DBTO	12.7±0.3*	201.4±18.5*	172.8	299.2	Medium		Violent***
BPO	8.1±0.7*	398.2±21.7*	101.6	193.2	Violent	Medium	Violent****
	8.6 **	333.2 **					

\* The ranges mean the value of standard deviation.

\*\* Data were obtained by different operators. (Samples were from Nippon Oil & Fats Co. Ltd.) [5]

\*\*\* Disc ruptured at orifice diameter of 9.0 mm in USA-PVT

\*\*\*\* Disc ruptured at orifice diameter of 18.0 mm in USA-PVT

Table 3 Reproducibility of round robin test

Sample	NRIFD		NKKK		Kayatech	
	$P_{max}$ (MPa)	$(dP/dt)_{max}$ (MPa/s)	$P_{max}$ (MPa)	$(dP/dt)_{max}$ (MPa/s)	$P_{max}$ (MPa)	$(dP/dt)_{max}$ (MPa/s)
BPB	10.3	183.5③	10.4 (+1%)	107.3③ (-41%)	8.7 (-15%)	174.0③ (-5%)
DBTO	12.7	201.4②	8.8 (-30%)	118.6② (-41%)	12.4 (-2%)	187.5② (-6%)
BPO	8.1	398.2①	5.2 (-35.8%)	141.3① (-64%)	8.3 (+2%)	357.1① (-10%)

Data were obtained by each operator at least three runs.

The percentages in parentheses mean the mean deviation from data of NRIFD

①~③ are rankings for violence of decomposition.

dioxide [8].

Table 2 compares the data obtained from NRIFD using samples from Kayaku Akzo Co. Ltd. by authors and Nippon Oil & Fats Co. Ltd. by other operators. It shows very close results provided that the vessel is the same, regardless of the suppliers of samples. In Table 2, the data from MCPVT are also compared with test results in the UN Recommendation using the Konen Test, the Dutch test and the USA test [1]. It is noted that these three methods only provide rough classification, and even to do so, results of ranking three samples by three test methods shown in the UN recommendations are quite inconsistent. For example, BPB decomposition is concluded to be violent in the Konen and the Dutch tests, while it is medium in the USA test. DBTO is concluded to be medium in the Konen test but violent in the USA test. BPO is violent in the Konen and in the USA tests but medium in the Dutch test. It can be seen that there is no evident correlation between either two of them at all. However, in MCPVT,

when  $(dP/dt)_{max}$  is adopted as a parameter, the decomposition ranking is concluded as BPO>DBTO>BPB. Their  $(dP/dt)_{max}$  decreases in the same order as those from orifice diameter increase for disc rupture in the USA PVT test. For instance, BPO, DBTO and BPB decompositions cause disc rupture at orifice diameters of 18.0 mm, 9.0 mm and 8.0 mm, respectively.

To look through the reproducibility, results obtained by different operators in different laboratories. Table 3 lists the data from the other two participants, NKKK and Kayatech Co. Ltd., and  $(dP/dt)_{max}$  values obtained by Kayatech Co. Ltd. are in accordance well with those of NRIFD, though NKKK data is still not so good. It should be noticed that on one hand, when MCPVT is used for classifying the extent of hazards in laws or in regulations, the size of vessel, the mass of sample and heating rate should be identical and defined clearly. On the other hand, measurement of  $P_{max}$  may still have some problem because measurement of pressure is very difficult to control from

laboratory to laboratory, affected by various factors, such as the size of vessel, the mass of sample, the resolution of amplifier, heat rate and even the type of recorder. Compared to  $P_{\max}$ ,  $(dP/dt)_{\max}$  is more important parameter to determine the ranking for substances' decomposition. In table 3,  $P_{\max}$  of BPO is the lowest among the three samples, while it is known that its decomposition should be much more vigorous than BPB and DBTO, because of their characteristics of chemical structure. With the data of  $(dP/dt)_{\max}$  from the three laboratories, it is more preferable to give good agreement in the ranking of BPB, DBTO and BPO. Therefore, if  $(dP/dt)_{\max}$  can be adopted as a criterion, MCPVT has a great potential to be a new quantitative and reliable test method, substituting for the present UN standard tests.

Furthermore, for extensive utilization, other facts involves in a device design are: (1) a glass-sheathed thermocouple, which inserts into the sample, can directly measure the temperature of sample. It is found that there is divergence for temperatures among sample and furnace and temperature distribution in a vessel. Seeing all curves in recent experiments and calculating the heating rates, the existing condition can guarantee that sample is heated by the rate of 9-10 °C/min. (2) Aluminum spacer and silicon oil should fill the capillary tube to prevent corrosion. But so far we did not use aluminum spacer and silicon oil for substitution often since corrosion does not influence on the test result so much.

#### 4. Conclusions

The round robin test data of MCPVT demonstrated good repeatability for three samples and good reproducibility among different laboratories provided when the same type vessels were used in these tests. It is suggested that if  $(dP/dt)_{\max}$  can be adopted as a criterion, MCPVT is used for classifying the extent of hazards in laws or in regulations, but only when the size of vessel, the mass of sample, heating rate and other details should be identical and defined clearly. The data

in this paper support the extensive utilization of MCPVT for classification of materials with unstable decomposition. Furthermore, these data are able to serve as benchmark data for worldwide round robin tests.

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