

APPENDICES

CONTENTS OF APPENDICES

<u>Appendix</u>		Page
1	SPECIFICATIONS OF STANDARD DETONATORS	407
2	BRUCETON AND SAMPLE COMPARISON METHODS.....	411
3	CAVITATION OF SAMPLES	415
4	NATIONAL CONTACTS FOR TEST DETAILS.....	419
5	EXAMPLE OF A TEST METHOD FOR VENT SIZING	421
6	SCREENING PROCEDURES.....	427

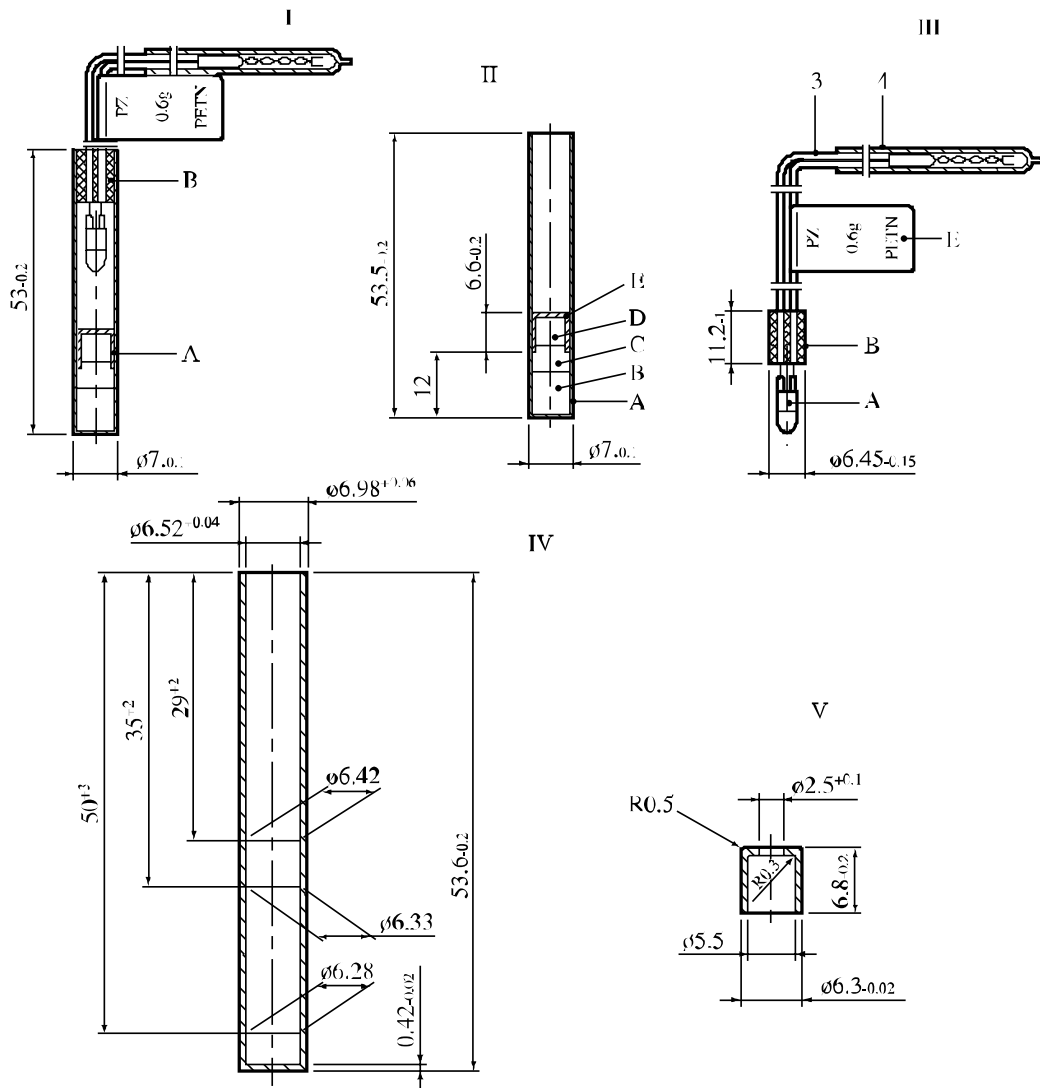
APPENDIX 1

SPECIFICATIONS OF STANDARD DETONATORS

1. Description of the standard electric blasting cap 0.6 g PETN

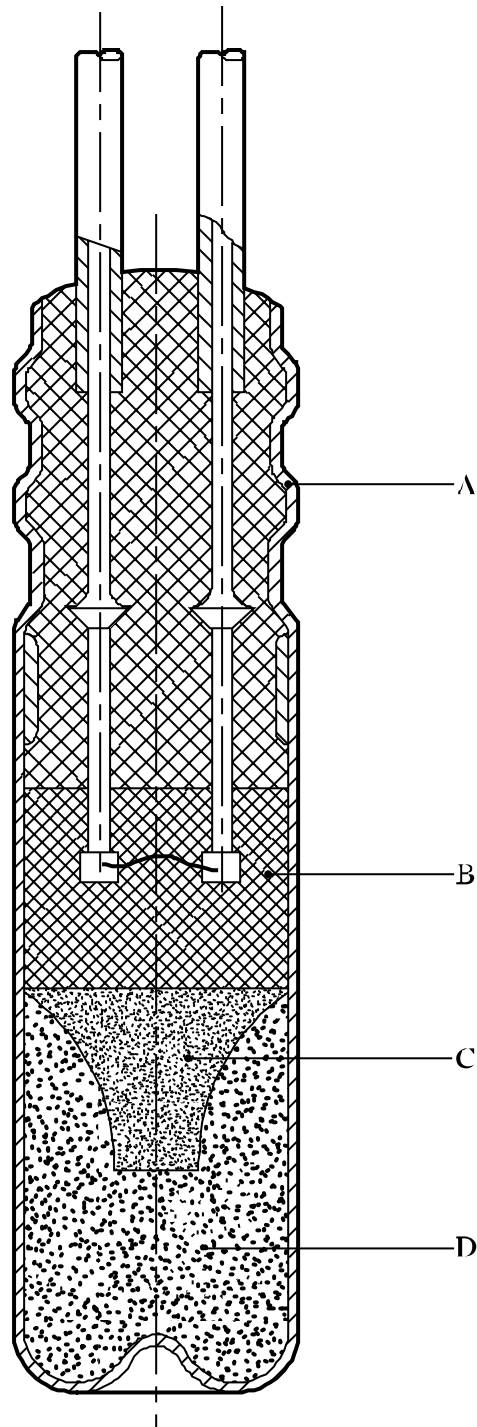
Drawing No.	Part No.	Part	Description	Remarks
I	A	Blasting cap		
	B	Fusehead	It must not undergo compression. Recommended amount of the pyrotechnic substance forming the bead: 20 mg to 50 mg	Example: Electrical fusehead Fa. DNAG, Germany, T 10 - U - with aluminium coating
II	A	Tube	Hollow-drawn tube of pure copper, (5% zinc) or of other alloys whose compositions are in the range between that of the above alloy and pure copper. The dimensions of the tube are shown in the figure. If required, the tubes for making standard detonators should be selected by checking the exact dimensions of each tube to be used.	
	B	(a) Secondary charge	Base charge: 0.40 g (± 0.01 g) PETN; compressed at 440 bar;	The PETN may contain up to 0.5% of carbonaceous matter to prevent electrostatic charges during handling and to improve the flow properties.
	C		Intermediate charge 0.20 g (± 0.01 g) PETN; compressed at 20 bar.	Total height of secondary charge 12.3 mm (± 0.6 mm)
	D	Priming charge (initiation charge)	Free choice of the substance and of its quantity. However, at least twice the minimum quantity required for initiation should be used. The total oxygen balance of the priming charge plus the secondary charge should not be more negative than -9.5% O ₂	Example: 0.30 ± 0.01 g dextrinated lead azide with a purity of 88% compressed at 440 bar
	E	Inner cup (pierced)	-	It is not required to use a pierced inner cup. Pressing the priming charge onto a highly compressed part of the secondary charge is excluded.
III	A	Fusehead	-	Example: Electrical fusehead Fa. DNAG, Germany T 10 - U - with aluminium coating
	B	Closing plug	-	No special requirements. It should however provide an absolutely tight seal (to avoid the formation of cuprous azide and to ensure the desired initiating strength). The usual commercial design is satisfactory.
	C	Wire	-	Free choice, providing the electrical risks (static electricity, stray currents) are taken into account. However, the use of an insulating sheath of plastic material inside the detonator tube is not allowed.

Drawing No.	Part No.	Part	Description	Remarks
	D	Short-circuiting tube	Plastic tube	
	E	Label		



- | | | | |
|-----|--|-----|-----------------------------------|
| I | Electric blasting cap (standard detonator) | II | Blasting cap (standard detonator) |
| III | Fusehead | IV | Tube |
| V | Inner cup | (A) | Blasting cap |
| (C) | Intermediate charge | (D) | Priming charge |
| (E) | Inner cup | | |

Figure A1.1: STANDARD DETONATOR (EUROPEAN)



-
- (A) Aluminium shell (material - 5052 aluminium alloy; length 31.8 mm; outer diameter 7.06 mm; wall thickness 0.19 mm)
 - (B) Brigewire and ignition charge
 - (C) Primer charge (0.195 g dextrinated lead azide)
 - (D) Base charge (0.447 g PETN pressed at 28 MPa)
-

Figure A1.2: NO. 8 (USA) DETONATOR

APPENDIX 2

BRUCETON AND SAMPLE COMPARISON METHODS

1. Bruceton method

Introduction: The Bruceton method is used to determine the level of stimulus at which there is a 50% probability of obtaining a positive result.

Procedure: The method involves applying different levels of stimulus and determining whether or not a positive reaction occurs. Performance of the trials is concentrated around the critical region by decreasing the stimulus by one level in the next trial if a positive result is obtained and increasing the stimulus by one level if a negative result is obtained. Usually about 5 preliminary trials are performed to find a starting level in approximately the right region and then at least 25 trials are performed to provide the data for the calculations.

Calculation of results: In determining the level at which the probability of obtaining a positive result is 50% (H_{50}), only the positives (+) or only the negatives (-) are used, depending on which has the smaller total. If the numbers are equal, either may be used. The data are recorded in a table (e.g. as in Table A2.1) and summarised as shown in Table A2.2. Column 1 of Table A2.2 contains the drop heights, in ascending order, starting with the lowest level for which a test result is recorded. In column 2, 'i' is a number corresponding to the number of equal increments above the base or zero line. Column 3 contains the number of positives ($n(+)$) or negatives ($n(-)$) for each drop height. The fourth column tabulates the result of multiplying 'i' times 'n' and the fifth column tabulates the results of multiplying the square of 'i' times 'n'. A mean is calculated from the following equation:

$$H_{50} = c + d \times \left(\frac{A}{N_s} \pm 0.5 \right)$$

where $N_s = \sum n_i$, $A = \sum (i \times n_i)$, c = lowest drop height and d = height interval.

If negative results are used, the sign inside the brackets is positive; it is negative if positive results are used. The standard deviation, s , may be estimated using:

$$s = 1.62 \times d \times \left(\frac{N_s \times B - A^2}{N_s^2} + 0.029 \right)$$

where $B = \sum (i^2 \times n_i)$.

Example of results: Using the data from Table A2.2, lowest drop height 10 cm, height interval 5 cm, sum of $i.n(-)$ 16, sum of $i^2.n(-)$ 30 and sum of $n(-)$ 12; the mean height is given as:

$$H_{50} = 10 + 0.5 \times \left(\frac{16}{12} + 0.5 \right) = 19.2 \text{ cm}$$

and the standard deviation as:

$$s = 1.62 \times d \times \left(\frac{12 \times 30 - 16^2}{12^2} + 0.029 \right) = 6.1$$

Reference: W.J. Dixon and F.V. Massey, Jr. "Introduction to Statistical Analysis, McGraw-Hill Book Co., Toronto, 1969.

Table A2.1: RECORDING DATA

Drop height (cm)	DROP RESULT																									FREQUENCY		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	+	-	
30								+																			1	
25							-		+			+				+		+									4	1
20				+		-				+		-		+		-		-		+		+					5	4
15	+		-		-						-				-						-		+		+		3	5
10		-																						-				2
																									13	12		

Table A2.2: SUMMARISING DATA

Height (cm)	CALCULATIONS USING NEGATIVES			
	i(-)	n(-)	i(-).n(-)	i ² (-).n(-)
25	3	1	3	9
20	2	4	8	16
15	1	5	5	5
10	0	2	0	0
TOTALS		N _s = 12	A = 16	B = 30

2. Sample comparison method

Introduction: This technique can be applied to any test where the Bruceton method is used. The Sample Comparison Test (SCT) is a non-parametric procedure designed to afford a high degree of confidence in any difference in sensitiveness in situations where the mean values given by the Bruceton method are close to one another.

Procedure: Samples of explosive A are tested following a normal Bruceton method, but are tested alternately with those of sample B. However, instead of following their own up-and-down programme, each sample of explosive B is subjected to the same level of stimulus as in the immediately preceding trial with sample A. Thus, at each level of stimulus as the test proceeds, one trial is performed with sample A and one with sample B. If both react or both do not react then the result is ignored for the appraisal. Only pairs of results which have afforded different responses are used for the appraisal.

Calculation of results: If there are n pairs of results which have afforded different responses and x is the number of positive reactions of the least sensitive sample from these pairs, i.e. $x < (n - x)$, then the confidence, $K\%$, that this sample is really less sensitive is calculated using Bernoullian statistics. K can be estimated by:

$$K = 100 \times \left(1 - 2^{-n} \times \left(\sum_{i=0}^x \frac{n!}{i! \times (n-i)!} \right) \right)$$

Various illustrative values of K are given in the table below for a series of values of x and n .

$x \backslash n$	15	20	25	30
2	99			
3	98	99		
4	94	99		
5	85	98	99	
6	70	94	99	
7		87	98	99
8		75	95	99
9		59	89	98
10			79	95

Where there is no real difference in two samples, the proportion of occasions where the pairs of results are the same increases and, at the same time, $(n - 2x)$ does not show a general tendency to increase as the testing proceeds.

Examples of results: HMX admixed with 0.01% of 45-63 μm airborne grit, compared with unadulterated HMX, gave $x = 3$ at $n = 13$ indicating that the former was more sensitive at the confidence level of:

$$K = 100 \times \left(1 - 2^{-13} \times \left(\sum_{i=0}^3 \frac{13!}{i! \times (13-i)!} \right) \right)$$

$$= 100 \times \left(1 - \frac{1 + 13 + 78 + 286}{8192} \right) = 95.4\%$$

Comparing a suspect sample of milled HMX with a normal sample gave $x = 6$ at $n = 11$ indicating that the former was more sensitive at the confidence level of:

$$K = 100 \times \left(1 - 2^{-11} \times \left(\sum_{i=0}^6 \frac{11!}{i! \times (11-i)!} \right) \right)$$

$$= 100 \times \left(1 - \frac{1 + 11 + 55 + 165 + 330 + 462 + 462}{2048} \right) = 27.4\%$$

showing no evidence that the suspect sample was other than normal.

NOTE: The simplest way to estimate K is to use $K = 100 \times \{0.5 + G(z)\}$ where $G(z)$ is the Gaussian area between the centre ordinate and the ordinate at abscissa z where $z = n^{0.5} - (2x+1)/n^{0.5}$. For example, where $n = 13$ and $x = 3$, $z = 1.6641$, $G(z) = 0.452$ and $K = 95.2\%$.

Reference: H J Scullion, *Journal of Applied Chemistry and Biotechnology*, 1975, 25, pp. 503 - 508.

APPENDIX 3

CAVITATION OF SAMPLES

1. German method

When a liquid is to be tested in the cavitated state, the cavitation may be achieved by passing a constant stream of gas bubbles through it. The test method is modified (see Figure A3.1) as follows:

The bottom of the tube (extended by 100 mm) is closed with a screw cap and PTFE gasket instead of the normal welded plate. A short steel tube of approximately 5 mm i.d. is welded into a central hole made in this cap. A porous glass filter is attached to the inner end of the tube by means of a flexible plastics tube so that it is positioned centrally and as close as possible to the bottom of the cap. The porous disc should have a diameter of at least 35 mm and have a pore size in the range 10 to 16 μm (porosity 4). The air, oxygen or nitrogen flow rate should be 28 ± 5 litres/hour. In order to prevent build-up of pressure the top cap should have four additional 10 mm diameter holes drilled through it.

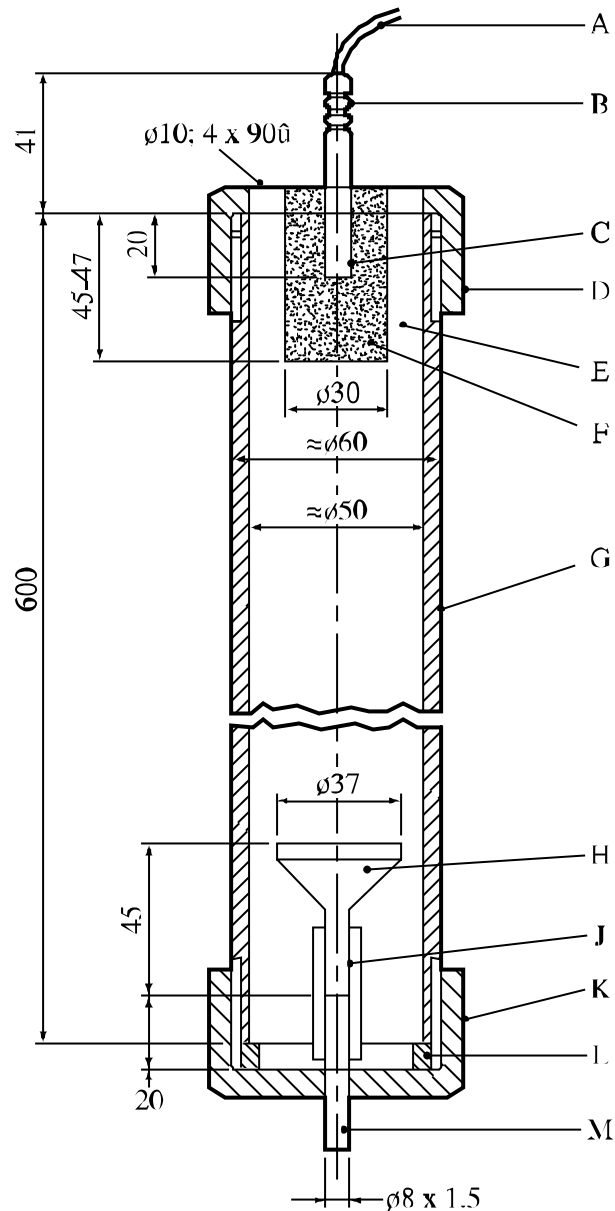
2. USA method

The apparatus for the detonation tests with cavitated liquids is the same as that for solids and uncavitating liquids except that a method of injecting bubbles into the liquid sample is provided. An example of the experimental set-up is given in Figure A3.2. The bubbles are injected by means of a 23.5 mm diameter loop of vinyl plastic tubing of the type used for medical catheterisation with an o.d. of 1.8 mm and a wall thickness of 0.4 mm located at the bottom of the sample. This loop is perforated with two rows of holes diametrically opposite to each other with the holes in each row spaced 3.2 mm apart. The holes are made by inserting a 1.3 mm diameter needle through the wall of the tubing. Because of the elastic nature of the tubing the holes contract almost completely when the needle is withdrawn, so the actual hole diameter is much smaller than 1 mm. The tubing is sealed at one end of the loop with epoxy cement and a length of the tubing from the other hand of the loop is led outside to the air supply through a hole in the steel tubing, which is sealed with epoxy cement. Air is supplied at a pressure of 30 to 100 kPa to obtain a flow rate of 1.2 litres/minute.

3. French method

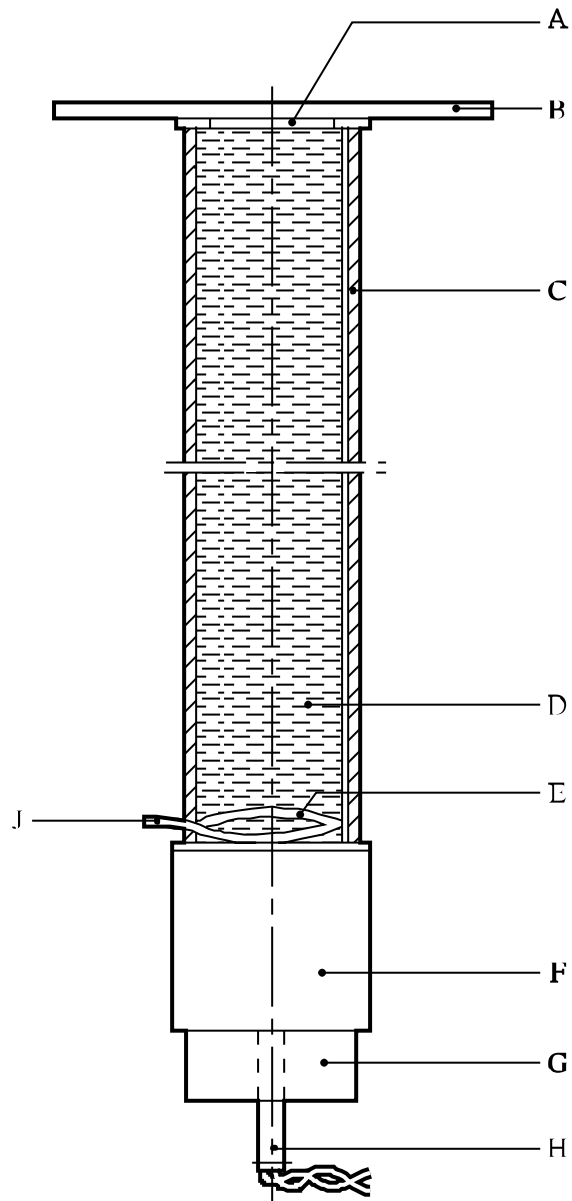
This method uses glass micro-balloons (hollow closed spheres) which are commonly used to sensitize emulsion explosives e.g. soda lime borosilicate glass bubbles, apparent density 0.15, mean diameter 50 μm , maximum diameter 200 μm and with 25% having a diameter less than 30 μm . It is applicable to liquids and pastes.

Glass micro-balloons are added, if necessary with the aid of a small quantity of dispersant which is compatible with the test substance, in the ratio of 500 mg to one litre of test substance. The mixture is agitated until formed into a homogeneous, stable dispersion and is then loaded into the firing tube.



- | | |
|--|--------------------------------------|
| (A) Lead wires | (B) Electric igniter |
| (C) Detonator | (D) Screw cap of malleable cast iron |
| (E) Substance under test | (F) Booster charge of RDX/wax (95/5) |
| (G) Steel tube to DIN 2441 specification material St. 37 to DIN 1629 specification sheet 3 | (H) Porous glass filter |
| (J) Flexible plastics tube | (K) Screw cap of steel St 35 |
| (L) PTFE gasket | |

Figure A3.1: GERMAN METHOD OF CAVITATION



-
- | | | | |
|-----|------------------|-----|----------------------|
| (A) | Spacers | (B) | Witness plate |
| (C) | Steel tube | (D) | Substance under test |
| (E) | Bubbler | (F) | Pentolite pellet |
| (G) | Detonator holder | (H) | Detonator |
| (J) | Air supply | | |
-

Figure A3.2: USA METHOD OF CAVITATION

APPENDIX 4
NATIONAL CONTACTS FOR TEST DETAILS

Country	Code	Address
CANADA	C	Canadian Explosives Research Laboratory Department of Natural Resources CANMET Complex, Bells Corners Ontario, Canada K1A 0G1
FRANCE	F	INERIS/LSE Parc Technologique ALATA B.P. 2 60550 Verneuil-en-Halatte France
GERMANY	D	Abteilung 4 Bundesanstalt für Materialforschung und -prüfung Unter den Eichen 87 D - Berlin 12205 Germany
NETHERLANDS	NL	TNO Prins Maurits Laboratory P.O. Box 45 2280 AA Rijswijk The Netherlands
JAPAN	J	Technology and Safety Division Transport Policy Bureau Ministry of Transport 2-1-3 Kasumigaseki Chiyoda-ku Tokyo 100, Japan
RUSSIAN FEDERATION	RUS	The State Committee of the Russian Federation on Defensive Branches of Industry Central Scientific and Design Bureau 20 Goncharnaya Street Moscow, 109240 Russian Federation
SPAIN	E	Laboratorio Oficial Madariaga (LOM) Alenza ly2 Madrid 28002 Spain
SWEDEN	S	Testing laboratory Bofors AB Weapons Systems Avd. VMEC S-691 80 Karlskoga Sweden

NATIONAL CONTACTS FOR TEST DETAILS (continued)

Country	Code	Address
SWITZERLAND	CH	Eidg. Gefahrgutinspektorat Postfach 212 CH-8600 Dübendorf 1 Switzerland
UNITED KINGDOM	GB	HSE, Health and Safety Laboratory Harpur Hill, Buxton Derbyshire SK17 9JN United Kingdom
UNITED STATES OF AMERICA	USA	Associate Director for Hazardous Materials Safety RSPA/DOT Washington D.C. USA 20590

APPENDIX 5

EXAMPLE OF A TEST METHOD FOR VENT SIZING

1. Introduction

This example of a method for vent sizing is used to determine the required emergency vent capacity to be fitted to a specific portable tank for a particular organic peroxide or self-reactive substance. The method is based on experimental data which indicates that, for organic peroxide or self-reactive substance formulations, the ratio of the minimum emergency vent area to the capacity of the tank is constant and can be determined using a reduced scale tank with a 10 litre capacity. In the tests, the reduced scale tank is heated at rates equivalent to that given by complete fire engulfment or, in the case of insulated portable tanks, the heat transfer through the insulation with the assumption that 1% of the insulation is missing (see paragraphs 4.2.1.13.8 and 4.2.1.13.9 of the Model Regulations). Other methods may be used provided that they adequately size the emergency relief device(s) on a portable tank to vent all the material evolved during self-accelerating decomposition or a period of not less than one hour of complete fire-engulfment.

Warning: The method does not take into account the possibility of initiation of deflagration. If this is a possibility, particularly if initiation in the vapour phase can propagate to the liquid phase, then tests should be performed which take this into account.

2. Apparatus and materials

The reduced scale tank consists of a stainless steel test vessel with a gross volume of 10 l. The top of the tank is provided with either a 1 mm opening which simulates the pressure relief valve (PRV) of the portable tank or a real PRV of a diameter which is scaled using the vent area to vessel volume ratio. A second opening simulates the emergency vent opening and is closed by a bursting disk. The diameter of this vent opening can be varied by using orifice plates with different apertures. The bursting pressure of the disk fixed to the 10 l vessel should be equal to the maximum rupture pressure of the bursting disks to be fitted to the portable tank. This pressure should be lower than the test pressure of the portable tank involved. Usually, the bursting pressure is set at a level that can cope with the pressures encountered during normal transport conditions such as hydrostatic pressure from the liquid due to turn over of the portable tank, slopping of the contents, etc. The minimum test pressure of the portable tank should be 4.0 bar gauge (see paragraph 4.2.1.13.4 of the Model Regulations). A bursting disk set pressure in the range 3.0 to 3.5 bar gauge is appropriate. For safety, the test vessel should also be provided with an extra bursting disk (bursting pressure approximately 80% of the design pressure of the 10 l test vessel) with a large opening for additional emergency venting of the test vessel in the event that the chosen orifice diameter is too small.

The outer surface of the test vessel, below the liquid level, is provided with an electrical heating coil connected to a constant power supply (proportional integral and differential control systems should not be used as the tank contents should be heated at a constant rate independent of the heat being generated by the organic peroxide). The resistance of the heating coil should be such that, with the power available, the calculated heating rate (see section 3) can be achieved. The whole vessel is insulated with rock wool.

The temperature inside the tank is measured by means of three thermocouples, two located in the liquid phase (near the top and bottom) and one in the gas phase. Two thermocouples are used in the liquid phase to check the homogeneity of the heating. The pressure is recorded by a pressure transducer(s) capable of recording slow and fast changes of pressure. The test tank is illustrated in Figure A5.1. Additional information may be obtained if the tank is mounted in a tray designed to collect any solids or liquids ejected.

The tests should be performed at a test site with suitable safety distances. Alternatively, the test can be performed in a bunker provided with sufficient ventilation and vent openings to prevent pressure build-up in it. Explosion-proof electrical equipment should be used in such a bunker to minimise the risk of ignition. ***However, the tests should be performed on the assumption that the decomposition products will ignite.***

3. Calculation of the heating rate to be used in the test

If a portable tank is non-insulated, a heat load of the shell as given in 4.2.1.13.8 of the Model Regulations is required. For an insulated tank, the Model Regulations require that the heat load to the shell be equivalent to the heat transfer through the insulation plus the heat load to the shell on the assumption that 1% of the insulation is missing.

The following information on the portable tank and organic peroxide or self-reactive substance is needed for the heating rate calculation:

F_r	=	fraction of tank directly heated (1 if non-insulated, 0.01 if insulated)	[-]
M_t	=	total mass of organic peroxide or self-reactive substance and diluent	[kg]
K	=	heat conductivity of the insulation layer	[W.m ⁻¹ .K ⁻¹]
L	=	thickness of insulation layer	[m]
U	=	K/L = heat transfer coefficient	[W.m ⁻² .K ⁻¹]
A	=	wetted area of portable tank	[m ²]
C_p	=	specific heat of the organic peroxide or self-reactive substance formulation	[J.kg ⁻¹ .K ⁻¹]
T_{PO}	=	temperature of organic peroxide or self-reactive substance formulation at relieving conditions	[K]

Heat input, q_i (W), via indirectly exposed surface (insulated part) is calculated by equations (1) and (2):

$$q_i = 70961 \times F \times (1 - F_1) \times A^{0.82} \quad (1)$$

where: F insulation factor;

$F = 1$ for non-insulated vessels, or

$$F = 2 \times \frac{U(923 - T_{PO})}{47032} \quad \text{for insulated vessels.} \quad (2)$$

In the calculation of F a multiplication factor of 2 is introduced to take into account a 50% loss in insulation efficiency in an incident.

Heat input, q_d (W), via the directly exposed surface (non-insulated part) is calculated by equation (3):

$$q_d = 70961 \times F \times F_r \times A^{0.82} \quad (3)$$

where: F = insulation factor = 1 (non-insulated)

The overall heating rate, dT/dt (K/min), due to fire engulfment is calculated by equation (4):

$$\frac{dT}{dt} = \frac{(q_i + q_d)}{M_1 C_p} 60 \quad (4)$$

Example:

For a typical 20 m³ insulated portable tank:

F_r	=	fraction of tank directly heated	=	0.01
M_t	=	total mass of organic peroxide or self-reactive substance and diluent	=	16268 kg
K	=	heat conductivity of the insulation layer	=	0.031 W. m ⁻¹ .K ⁻¹
L	=	thickness of the insulation layer	=	0.075 m
U	=	heat transfer coefficient	=	0.4 W.m ⁻² .K ⁻¹
A	=	wetted area of portable tank	=	40 m ²
C_p	=	specific heat of the organic peroxide form	=	2000 J.kg ⁻¹ .K ⁻¹
T_{PO}	=	temperature of peroxide at relieving conditions	=	100 °C

and

$$q_i = 70961 \times 2 \frac{0.4 \times 923 - 373}{47032} \times (1 - 0.01) \times 40^{0.82} = 13\,533 \text{ W}$$

$$q_d = 70961 \times 1 \times 0.01 \times 40^{0.82} = 14\,611 \text{ W}$$

$$\frac{dT}{dt} = \frac{13533 + 14611}{16268 \times 2000} \times 60 = 0.052 \text{ K. min}^{-1}$$

4. Procedure

Fill the test vessel shell with the amount of organic peroxide or self-reactive substance required to give the same degree of fill (by volume of the shell) as to be used in the portable tank (maximum degree of fill 90 %, by volume) and then install the required orifice plate¹ and bursting disk. It is common practice to fit four 250 mm diameter bursting disks to a 20 tonne portable tank. This corresponds to a test vessel orifice diameter of about 11 mm.

The vessel is heated at the desired rate by applying power to the heating coil. A higher than calculated heating rate may be applied initially until a temperature 5 °C above the self-accelerating decomposition temperature (for a 50 kg package) of the organic peroxide or self-reactive substance is reached. The calculated heating rate should be applied once this temperature is reached. The temperature and pressure in the test vessel are recorded during the entire experiment. After rupture of the bursting disk, the heating should be continued for approximately 30 minutes more to be sure that all dangerous effects are measured. ***After the test, the vessel should not be approached until the contents have cooled.***

The diameter of the orifice should be varied (if necessary) until a suitable opening is determined at which the maximum recorded pressure is not more than the test pressure of the portable tank. The step size used should be related to the options available in practice for the portable tank, i.e larger vent sizes or more vents. The test should be performed in duplicate with the minimum total vent area having sufficient capacity.

¹ *It is recommended that either small-scale vent experiments (100 - 200 ml scale) or experiments using a very strong vessel (>100 bar) be performed prior to the performance of the 10 l vent test in order to obtain information on the maximum pressure effect from the test substance and on the required orifice diameter to be used in the first 10 l scale vent test.*

5. Test criteria and method of assessing the results

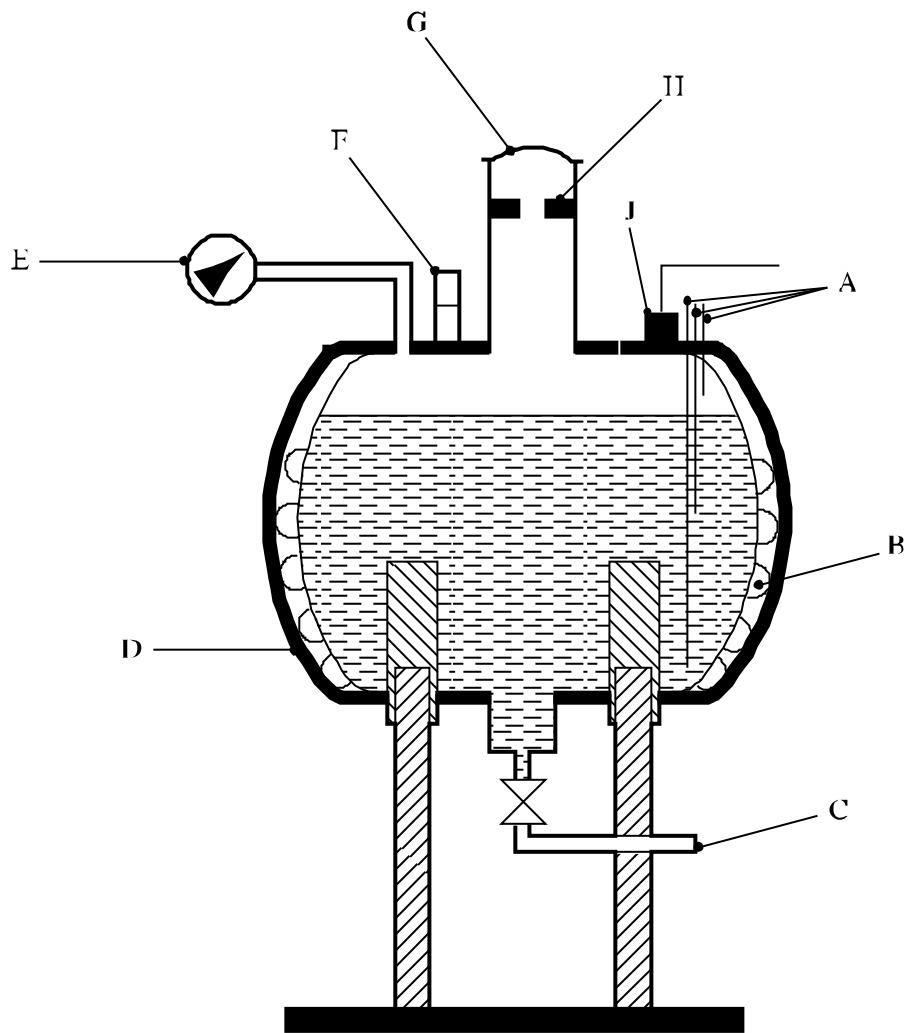
The minimum or suitable (if it is acceptable to use a vent size larger than the minimum vent size) portable tank vent area, $A_{\text{portable tank}}$ (m^2), for the portable tank can be calculated using the minimum orifice vent area, $A_{\text{test vessel}}$ (m^2), determined in the test at which the maximum pressure is not more than the test pressure of the portable tank (see paragraph 4.2.1.13.8 of the Model Regulations) and the volumes of the test vessel ($V_{\text{test vessel}}$, m^3) and portable tank ($V_{\text{portable tank}}$, m^3). The minimum total portable tank vent area is given by:

$$A_{\text{portable tank}} = V_{\text{portable tank}} \times \frac{A_{\text{test vessel}}}{V_{\text{test vessel}}}$$

Example:

For a typical organic peroxide in a 20 m^3 insulated portable tank:

$A_{\text{test vessel}}$	=	Minimum suitable orifice area found in test	=	$9.5 \times 10^{-5} \text{ m}^2$
$V_{\text{portable tank}}$	=	Volume of portable tank	=	20 m^3
$V_{\text{test vessel}}$	=	Volume of test vessel	=	0.01 m^3
$A_{\text{portable tank}}$	=	$20 \times \left(9.5 \times \frac{10^{-5}}{0.01} \right)$	=	0.19 m^2



-
- (A) Thermocouples (two in liquid on one in vapour space)
 - (B) Heating coil
 - (C) Drain line
 - (D) Insulation
 - (E) Manometer
 - (F) Pressure relief valve
 - (G) Bursting disk
 - (H) Orifice plate
 - (J) Pressure transducer
-

Figure A5.1: 10 LITRE VESSEL FOR VENTING TESTS

APPENDIX 6

SCREENING PROCEDURES

1. Purpose

1.1 Industry uses screening procedures to identify the hazard potential of raw materials, reactive mixtures and intermediates, products and by-products. The use of such procedures is essential to ensure safety during research and development and to ensure that new products and processes are as safe as possible. These procedures usually consist of a combination of a theoretical appraisal and small-scale tests and, in many cases, enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests. This reduces the quantity of material required, lessens any detrimental effect on the environment and minimizes the amount of unnecessary testing.

1.2 The purpose of this Appendix is to present example screening procedures. It should be used in conjunction with any screening procedures given in the introductions to the relevant test series. With the specified safety margin, the results from the screening procedures adequately predict when it is not necessary to perform the classification test as a negative result would be obtained. They are presented for guidance and their use is not compulsory. Other screening procedures may be used provided that adequate correlation has been obtained with the classification tests on a representative range of substances and there is a suitable safety margin.

2. Scope

2.1 A hazard evaluation for a new substance should be undertaken before it is offered for transport. Initially this evaluation can use the screening procedures given in this Appendix. If the screening procedure indicates that there is a hazard, the full classification procedure should be applied.

2.2 The screening procedures are only applicable to substances and stable, homogeneous mixtures of substances. If a mixture can separate out during transport, the screening procedure should also be performed on each reactive component of the mixture in addition to the mixture.

2.3 The remarks 1.1.2 from section 1 "General introduction" are emphasized that competence on the part of the testing authority is assumed and responsibility for classification is left with them.

3. Screening procedures for substances which may have explosive properties

3.1 The screening procedure may be used for new substances which are suspected of having explosive properties. When considering the explosive properties of self-reactive substances of Division 4.1 or organic peroxides of Division 5.2, refer to Part II of this Manual and section 5.1 of this Appendix. It should not be used for substances manufactured with the intention of producing a practical explosive or pyrotechnic effect.

3.2 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the material to be a potential explosive, the Class 1 Acceptance Procedure (see 10.3) should be applied.

NOTE: *Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than 800 J/g.*

3.3 The acceptance procedure for Class 1 explosives need not be applied:

- (a) When there are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1;

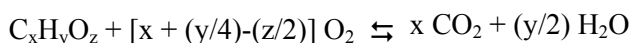
Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

or

- (b) When the substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:



using the formula:

$$\text{oxygen balance} = -1600 \times \frac{\left(2x + \frac{y}{2} - z\right)}{\text{molecular weight}}; \text{ or}$$

- (c) When the organic substance or a homogenous mixture of organic substances contain chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g.) The exothermic decomposition energy may be determined using a suitable calorimetric technique (see 20.3.3.3); or
- (d) For mixtures of inorganic oxidizing substances of Division 5.1 with organic material(s), the concentration of the inorganic oxidizing substance is:
- less than 15 %, by mass, if assigned to Packing Group I (high hazard) or II (medium hazard);
 - less than 30 %, by mass, if assigned to Packing Group III (low hazard).

3.4 When the substance is a mixture containing any known explosives, the class 1 acceptance procedure should be applied.

4. Screening procedures for mixtures which may be flammable liquids (Class 3)

4.1 The procedure only applies to possible flammable mixtures containing known flammable liquids in defined concentrations although it may contain non-volatile components e.g. polymers, additives etc. The flash point of these mixtures need not be determined experimentally if the calculated flash point of the mixture, using the method given in 4.2, is at least 5 °C greater than the relevant classification criterion and provided that:

- (a) The composition of the mixture is accurately known (if the material has a specified range of composition the composition with the lowest calculated flash point should be selected for assessment);
- (b) The flash point (closed cup as given in 2.3.3 of the Model Regulations) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions);
- (c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;
- (d) The liquid phase is homogeneous.

4.2 A suitable method is described by Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, 21, 186, (1982)). For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

5. Screening procedures for substances which may be flammable solids (Class 4)

5.1 *Substances which may be self-reactive substances (Division 4.1)*

The classification procedures (see section 20.4) for self-reactive substances need not be applied if:

- (a) There are no chemical groups present in the molecule associated with explosive or self-reactive properties; examples of such groups are given in Tables A6.1 and A6.2;

Table A6.2: EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

or

- (b) For a single organic substance or a homogeneous mixture of organic substances, the estimated SADT is greater than 75 °C or the exothermic decomposition energy is less than 300 J/g. The onset temperature and decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3).

5.2 *Substances which may be liable to spontaneous combustion (Division 4.2)*

5.2.1 The classification procedure for *pyrophoric solids and liquids* need not be applied when experience, in production or handling, shows that the substance do not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

5.2.2 The classification procedure for *self-heating substances* need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied. Examples of screening tests are:

- (a) The Grever Oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*) with an onset temperature 80 K above the reference temperature for a volume of 1 l (33.3.1.6);
- (b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. *Evaluation of the fire and explosion risks in drying powders*, Plant Operations Progress, **4** (3), 181 - 189, 1985) with an onset temperature 60 K above the reference temperature for a volume of 1.1 (33.3.1.6).

5.3 *Substances which in contact with water may react to emit flammable gases (Division 4.3)*

The classification procedure for substances which may react with water to emit flammable gases need not be applied if:

- (a) The chemical structure of the substance does not contain metals or metalloids; or
- (b) Experience in production or handling shows that the substance does not react with water, e.g. the substance is manufactured in water or washed with water; or
- (c) The substance is known to be soluble in water to form a stable mixture.

6. *Screening procedures for substances which may be oxidizing substances and those which may be organic peroxides (Class 5)*

6.1 *Substances which may be oxidizing substances (Division 5.1)*

6.1.1 For *organic compounds*, the classification procedure for oxidizing substances of Division 5.1 need not be applied if:

- (a) The compound does not contain oxygen, fluorine or chlorine; or
- (b) The compound contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

6.1.2 For *inorganic substances*, the test procedure in Section 34 need not be applied if the substance does not contain any oxygen or halogen atoms.

6.2 *Substances which may be organic peroxides (Division 5.2)*

6.2.1 Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide content of formulations (see 20.2.2).