

Health and Safety Executive OC 431/13

Field Operations Division

To

FCG Specialist Inspectors (Fire and Explosion)

Factory Inspectors in Chemical Groups

CHEMICAL REACTOR SAFETY

TEST METHODS FOR EXOTHERMICITY

Introduction

1. This OC is based on TD Minute 5C/T/7/90. It describes the main tests which are available for assessing the exothermic behaviour of materials used or formed in chemical reactors and gives guidance on the selection of suitable test regimes. The advice is primarily aimed at FCG fire and explosion specialists but may also be of interest to chemical group inspectors.

2. It is clearly not safe to test unknown reactions or compounds by heating them in a full-size reactor vessel, as a vigorous exotherm may well overcome any protection systems provided. Various small-scale tests have therefore been devised, aimed at providing data on the degree of exothermicity and on the likelihood and severity of a runaway reaction. They vary from basic heating tests to sophisticated simulations of full-size plant. There is unfortunately no single test which can provide all the data required for a particular process; selection from a range of tests is necessary, depending on the type of substances involved and on the process. Also, the assessment needs to cover not just the intended reaction but also unwanted or unexpected side-reactions and the possible decomposition of individual compounds in the reaction mixture.

Test types

3. The main types of test are:

- 1) basic screening tests;
- 2) isothermal calorimetry, aimed at quantifying reaction kinetics, heats of reaction, etc for particular reaction systems;
- 3) adiabatic calorimetry, used mainly for examining the runaway potential of reactions and individual compounds; and
- 4) combination instruments intended not only to give thermal data but also to calculate appropriate reactor vent sizes.

4. These tests tend not to give absolute results, in that the experimental conditions may affect the data obtained. Factors such as sample size, container material, heating rate, thermal inertia and endothermic effects (eg evaporation, gas evolution and phase changes) can all affect the result. The work, therefore, needs to be carried out by persons who are adequately trained and experienced in this type of investigation, to ensure that in each case suitable techniques are employed and adequate account is taken of experimental variables.

Basic screening tests

5. If the properties of the compound are completely unknown it may be necessary to start with the assumption that the material could be unstable or even explosive. Various tests are available for such properties, starting with calculation of an oxygen balance. This is useful where oxidising groups such as nitrate and chlorate are present. For a molecule $C_xH_yO_z$ (ignoring other atoms) the oxygen balance is:

$$-1600 (2x + y/2 - z)$$

Molecular Weight

Any result more positive than -200 should be treated as potentially explosive and more screening tests should be carried out. Examples are the Trauzl lead block test and the Koenen tube test for deflagration. Further information on these tests and on potentially explosive substances can be obtained from TD 5.

6. The most common screening tests for exothermicity are differential scanning calorimetry (DSC) and differential temperature analysis (DTA), with the former being more widely used. DSC equipment consists of 2 identical pans, one containing a small sample (up to 20 mg) of the compound of interest and the other an inert material, to act as a reference. Both are heated at the same rate (0.1-10°C/min), and the difference in the power inputs required to maintain them at the same temperature is recorded. The temperature trace of the compound will indicate, by means of peaks, troughs or discontinuities, any exothermic or endothermic activity. The total amount of energy released and the rate of release can be estimated from the area under the curve and the slope of the trace respectively.

7. The DTA method is similar but with the important difference that it allows the temperature of the sample to vary under the influence of the heating programme. A measurement is taken of the temperature difference between the sample and the reference rather than the power difference. The output can therefore give a clear graphical indication of how the sample temperature varies from the programmed oven temperature. It is not easy however to obtain accurate values for heats of reaction or transition, mainly because of calibration difficulties.

8. With regard to chemical reactors, the main disadvantages of these techniques are that the test conditions tend towards being isothermal (whereas reactor runaways occur in conditions more akin to adiabatic), that the sensitivity of the standard test is relatively low (1-5 W/kg), and that the measured onset temperature at which a reaction begins is a function of the sample heating rate. In addition, the small sample size may lead to it being unrepresentative of plant materials. In particular, the onset temperature may be significantly lower in a full-size reactor system, and also, unless sealed pans are used, evaporation losses can lead to errors.

Isothermal calorimetry

9. Isothermal calorimeters are mainly used for measurement of the heat flow in semi-batch reactors, where one or more reactant is charged into the reactor and the final reactant added at a controlled rate throughout the reaction. With careful design they can simulate a range of process variables, including feed rate, stirring, distillation and reflux. A typical mode of operation is to remove the heat of reaction from a glass mini-reactor (holding up to 2 kg of material) as fast as it is produced, using a hot oil circulation system, so that the temperature of the reactants remains the same. The temperature difference between the reactor and the oil jacket is proportional to the heat produced by the reaction. The Mettler calorimeter is typical of this type. Chemical Manufacturing (CM) NIG (Area 17) hold a video made by Mettler which describes the use of this instrument. The video may be borrowed from the NIG on request. Appendix 1 shows the reactor of a typical heat-flow calorimeter.

10. A problem with this type of calorimeter is the difficulty in removing the heat fast enough to maintain isothermal conditions. One solution is to maintain a constant temperature difference between the calorimeter contents and the jacket and to reduce the input to the electrical heater to balance the chemical heat produced. The amount of reduction in electrical power is a measure of the heat of reaction. Heat losses are minimised by enclosing the calorimeter in an oven and for additional accuracy account can be taken of power supplied via the stirrer and lost by evaporation.

Adiabatic calorimetry

11. Adiabatic calorimeters are mainly used for investigating runaway conditions, when the heat generated by the reaction is more than the heat loss from the reactor. By minimising heat loss to the test container and to the surroundings these instruments can detect thermal activity at relatively low onset temperatures. The sample temperature is used as the set point for the heater control, so that as an exotherm begins and the sample starts to heat up the oven temperature is increased as quickly as possible to match it, thereby minimising heat loss from the sample. Use of a lightweight container or a relatively large sample helps to minimise losses arising from the thermal capacity of the container.

12. The best-known commercial instrument is the Accelerating Rate Calorimeter (ARC), marketed by Columbia Scientific Industries (see Appendix 2). This uses a titanium or hastelloy container of 10 g capacity with temperature and pressure transducers. The container is suspended within a copper vessel containing heaters and the whole system is enclosed in a steel safety casing. The instrument is normally operated in a step-wise temperature regime - the "heat/wait/search" technique. At each temperature step the ARC waits to see if any self-heating is detected ($0.02^{\circ}\text{C}/\text{min}$ or more). If so, the instrument progressively increases the temperature of the container to follow the rise, recording the elapsed time, temperature and pressure at intervals of 1°C . Output graphs of temperature against time enable minimum reaction onset temperatures to be determined (see Appendix 3).

13. The ARC can also measure induction times, ie the time for a sample to reach a maximum rate of decomposition at a given fixed temperature, which because of the instrument's sensitivity, can be quite low. This is useful for setting safe storage conditions for reactive materials. Other applications include study of autocatalytic effects and measurement of heats of reaction, rates of heat release and reaction kinetics. Disadvantages include difficulty in filling the container, particularly if viscous or solid materials are involved, the relatively large correction required for container heat capacity and the several hours needed for each run.

14. Another type of adiabatic instrument is the Dewar calorimeter (see Appendix 4). This uses a simple Dewar flask in an oven and has the advantage of low heat loss, both to the flask itself and to the surroundings. Other benefits include relative cheapness and ease of use, making it particularly suitable for rapid initial assessment of reaction hazards. Use of a stirrer allows addition of reactants during an experiment. More accurate data can be obtained by using a thermostatic bath and an internal heater to make up heat losses (the power-compensated Dewar). Pressurised versions are also available, using a stainless steel flask capable of operating at up to about 20 bar, enabling reflux reactions to be studied. An external oven is used, following the reaction temperature in the same way as the ARC. The type of data that can be obtained includes rate and quantity of heat generated, the rate of gas evolution and final decomposition pressure. A major drawback (also shared by the ARC) is the cost of the systems used to control the reaction and obtain the data, and of the pressure protection required for the safety of the operator.

Combination instruments

15. The instruments described above produce data which can be used, amongst other purposes, for sizing the emergency vent required to safely relieve a runaway exotherm in a reactor. Improvements in the accuracy and scope of equations to calculate vent sizes means that it is feasible to connect a calorimeter to a computer to produce the vent size directly from the test data. One commercial application is the Fike Vent Sizing Package (VSP). This uses a 120 ml heated test cell with a pressure control system which balances the internal and external cell pressure, allowing the cell to be of relatively weak material and of low thermal capacity, thereby minimising heat losses. The cell can operate in closed or open mode, the latter using a vent pipe into the outer containment vessel. As well as heats of reaction, maximum temperature and pressure, etc, data can be obtained on vapour/pressure relationships and on the flow behaviour of discharging runaway reaction masses. The computer then calculates the required vent size. Limitations include the need to avoid carry-over of liquid when venting, as this could allow reaction to continue in the containment vessel.

16. A more recent development is the Phi-tec adiabatic calorimeter from Hazard Evaluation Laboratory Ltd (HEL). It is broadly similar to the VSP but has a variable-volume test cell and the cell contents can be vented

outside the equipment rather than into a containment vessel. It has better thermal sensitivity and is more nearly adiabatic in operation.

Consultancy services

17. One of the problems of the instruments described is their cost, which can be in the range of £30-80,000 for the more sophisticated items. This severely limits the use of the techniques, particularly for smaller companies. Several organisations however operate consultancy services, whereby reactions can be investigated for a fee. These range from simple tests using one piece of apparatus to comprehensive investigations using a variety of techniques. The Polytechnic of the South Bank has probably the widest range of equipment, (partly as a result of funding via HSE research projects). Others include HEL and Columbia Scientific Industries - see Appendix 5 for addresses.

New calorimeters

18. Cheaper calorimeters are now starting to appear on the market, the manufacturers having realised that the market for more expensive equipment is approaching saturation. One such calorimeter is the Reactive System Screening Tool (RSST) made by Fauske, the originators of the VSP system. It consists of an insulated 10 ml glass test cell in a pressure container. The same heater is used to initiate the reaction and balance heat losses. The RSST can operate in an adiabatic mode, increasing the temperature as the reaction gives off heat, or isothermally, maintaining the sample at a specified temperature. Magnetic stirring is used, and materials can be added during a test run. Gas evolution rates are obtained from pressure rise data. Current prices start from around \$10,000.

19. Another recently-introduced device is the Quantitative Reaction Calorimeter from Columbia Scientific Industries. This is a 250 ml metal vessel within a cylindrical adiabatic shield intended to create a zone around the vessel at the same temperature as the vessel contents. Reactants are added via spiral tubing within the zone, allowing time for them to reach the reaction temperature. The vessel sits directly on a heat exchange system, consisting of a thin foil heater on top of a cold zone maintained at (typically) 30°C below the vessel temperature, using thermal oil circulating through the base of the unit. As no heat escapes via the top or sides of the vessel, all heat supplied to the vessel from the foil heater is dissipated via the oil. When reagent is added and the reaction starts to generate heat, the system seeks to correct this by reducing electrical power to the foil. This power reduction is proportional to the heat generated by the reaction.

Advice to inspectors

20. The above description of test equipment is intended to act as a guide to specialist inspectors on the test methods currently available. The choice of test regime will depend on how much is already known about the material and the degree of detail and accuracy required. A simple process with low rates of heat or gas evolution and a stable reaction/product mixture can be assessed using relatively simple methods, whereas a complex process with potentially hazardous reactions requires detailed investigation using more sophisticated techniques. Appendix 6 shows a typical procedure.

21. For a material with unknown properties it is better to start from the assumption that it is unstable and carry out screening tests for explosivity, including calculation of the Oxygen Index if the formula is known. The next step, particularly if basic information is required quickly, would probably be to carry out some small scale tests. This type of test, although not particularly representative of reactor conditions, would give an indication of the onset temperature of exothermic behaviour under conditions of steady heating. For more precision on this aspect and for information on heats of reaction, rates of heat release, and behaviour on runaway, an adiabatic calorimeter such as the ARC or a Dewar vessel can be used. Where study of an intended reaction is required, as opposed to an unwanted potential runaway, an isothermal heat-flow calorimeter such as the Mettler would be appropriate.

22. Should a need arise for HSE to obtain reactivity data, for example after an incident, RLSD EFL at Buxton should be contacted in the first instance. Representative samples of the materials may be needed for

analysis, and these should be taken and handled using the standard procedures. Further advice for occupiers on the suitability of different test methods can be obtained from TD 5, who should also be kept informed of approaches to RLSD.

Further guidance

23. An I Chem E handbook is being prepared, giving advice on exothermic reactions in general, including calorimetry aspects. RLSD, TD 5 and TD 6 are represented on the drafting committee.

24. CM NIG is producing a training video on the prevention of runaway chemical reactions and which describes some of the laboratory test methods for determining the potential for runaway. The video is expected to be completed and distributed to all areas in Spring 1991.

25. *Guidelines for Chemical Reaction Hazard Evaluation* produced by the Association of the British Pharmaceutical Industry (file 431) contains advice on the measures necessary to help prevent and control the hazards of exothermic chemical reaction.

11 February 1991

(1822/FOD/1990)

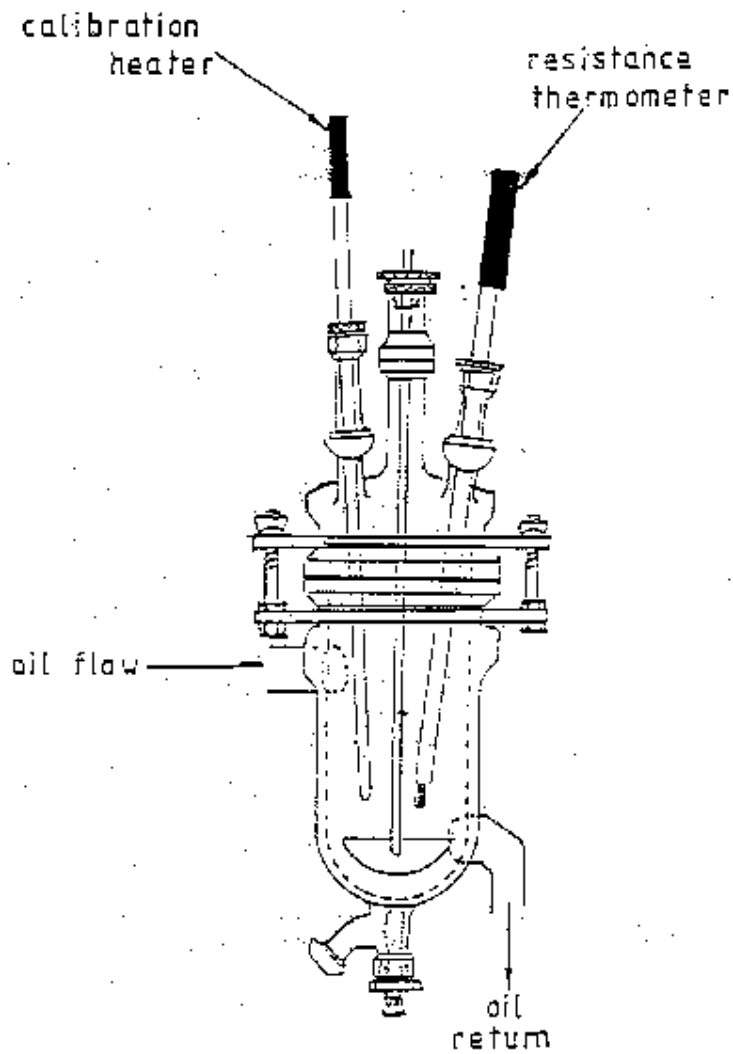
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ASI headings

Calorimeters: chemicals - manufacture: exothermicity: instruments: reactors.

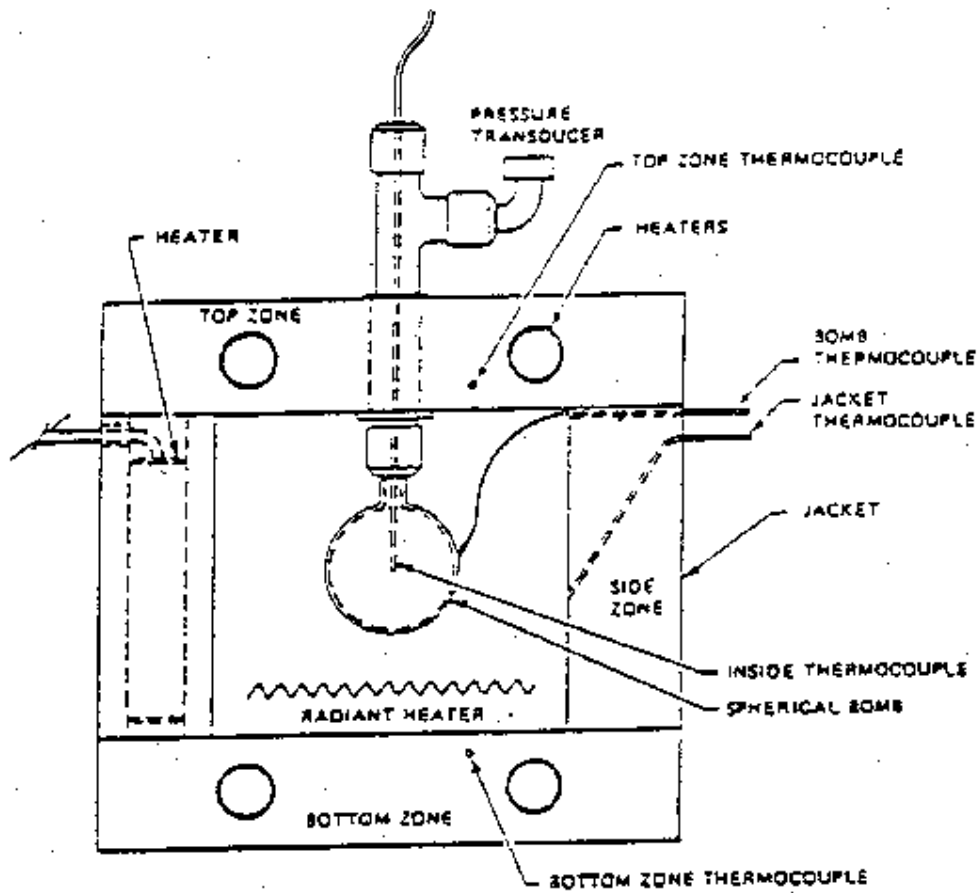
APPENDIX 1
(para 9)

Reactor of heat-flow calorimeter



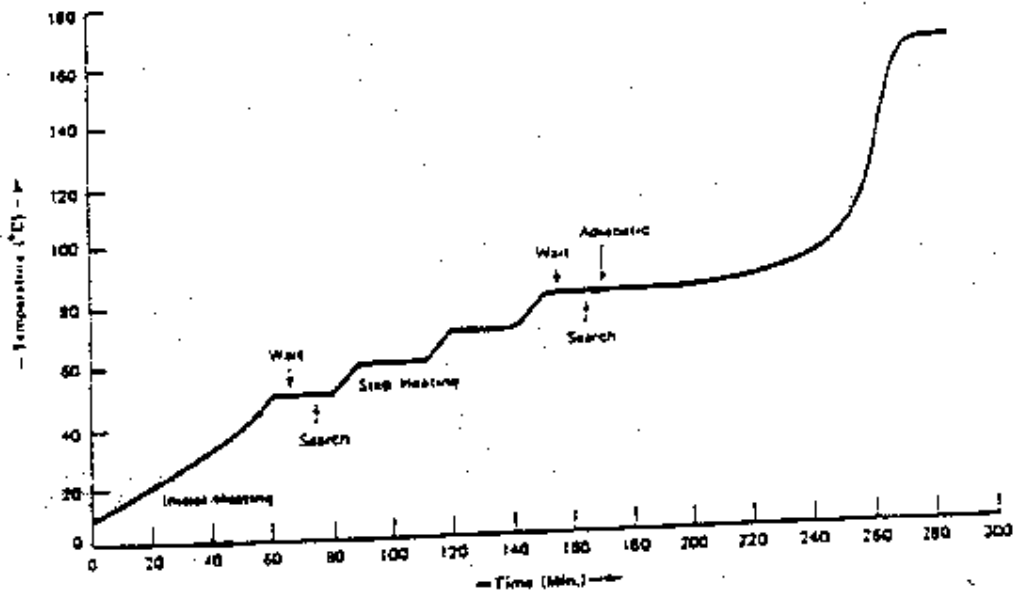
APPENDIX 2
(para 12)

An accelerating rate calorimeter



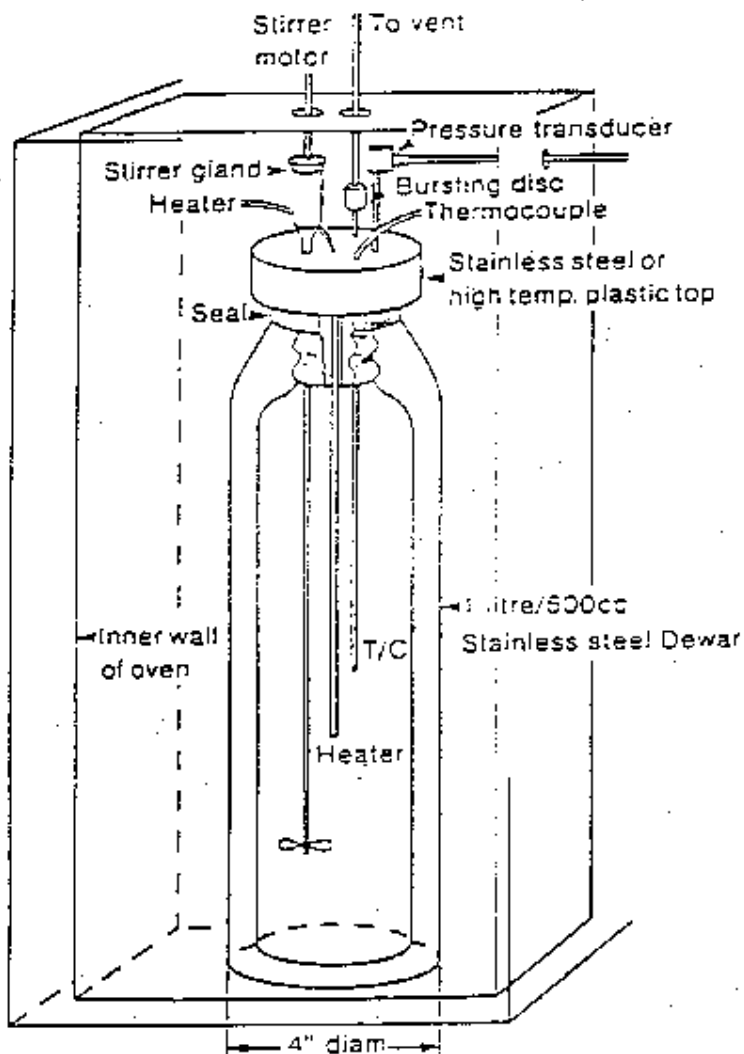
APPENDIX 3
(para 12)

The heat—wait—search operation mode of an accelerating rate calorimeter



APPENDIX 4
(para 14)

ADIABATIC DEWAR



APPENDIX 5

(para 17)

ADDRESS OF ORGANISATIONS ABLE TO CARRY OUT TESTING

Chemical Reaction Hazards Centre

Department of Chemical Engineering

South Bank Polytechnic

Borough Road

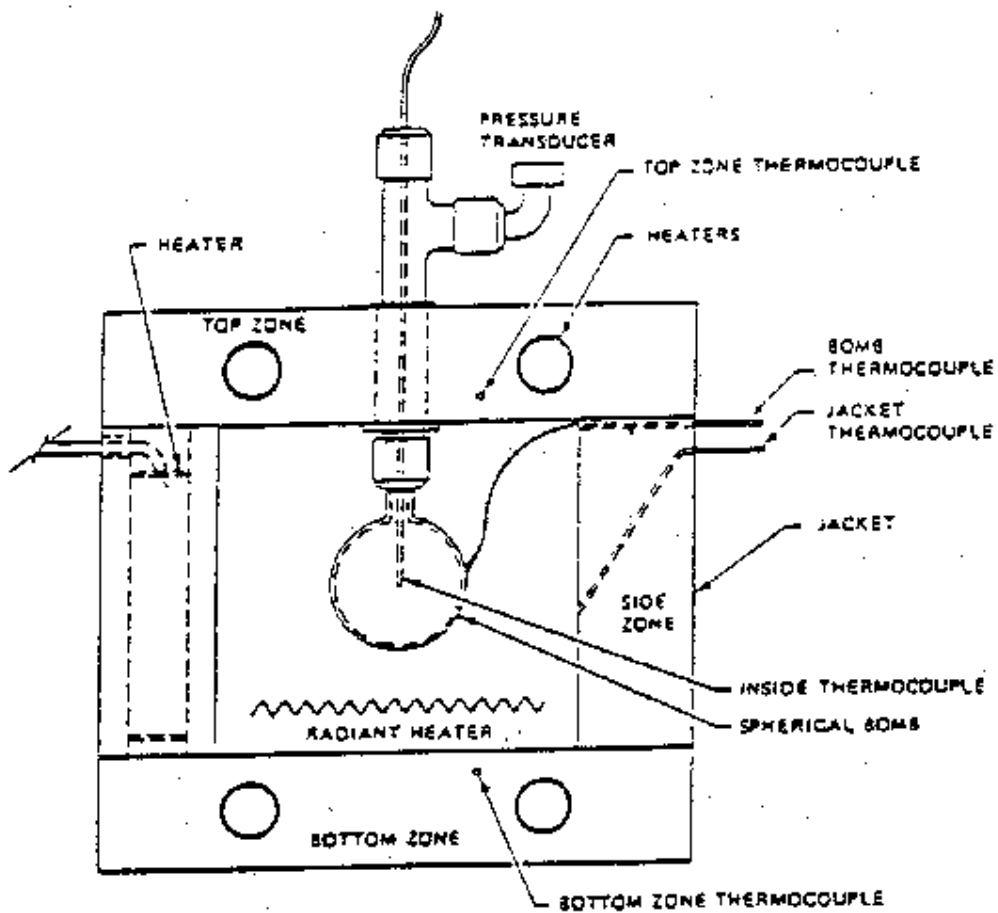
London

SE1 0AA

Hazard Evaluation Laboratory Ltd

APPENDIX 2
(para 12)

An accelerating rate calorimeter



Fire

Research Station Site

Melrose Avenue

Borehamwood

Herts

WD8 28L

Columbia Scientific Industries

101 Garamonde Drive

Milton Keynes

MK8 8DD

APPENDIX 6
(para 17)

