

## A Bomb Method for Rapid Combustion of Samples

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### INTRODUCTION

This paper describes a highly efficient method for combustion of organic samples up to 20 g or so in weight. The method and apparatus described have been developed primarily for combustion of radiocarbon dating samples but may also have applications to other cases in which relatively large samples must be dealt with.

Before discussing the equipment and its operation and performance it is necessary to consider briefly some practical limitations imposed on samples for radiocarbon dating, the difficulties met in combusting these materials satisfactorily by conventional methods which led to the development of the improved method of combustion and an outline of this development.

For the purpose of obtaining radiocarbon dates, natural Carbon-14 can be measured in a number of ways among which internal gas and scintillation counting are generally preferred. Some more exotic techniques for precise measurement of natural Carbon-14 have also been tried or proposed such as, among others, the use of nuclear track plates,<sup>1</sup> thermoluminescence dosimetry<sup>2</sup> and a bubble chamber method.<sup>3</sup> But the starting point common to the preparative chemistry of all existing methods of measurement is, with one exception, the combustion to carbon dioxide of the sample material for which a date is being sought. The exception is the preparation of acetylene from lithium carbide formed by direct high temperature reaction of wood charcoal with lithium metal.<sup>4</sup> This procedure is not widely used and need not be considered further here.

Because of the low specific activity of natural Carbon-14 — about 14 disintegrations per minute per gramme of carbon — it is not usually practicable to measure less than about 1 g of carbon if the sample concerned has an age of more than a few hundred years. Ideally, in order to arrive at a date with an acceptably small associated error term within a reasonable counting period by gas proportional or scintillation measurement about 5 g of carbon are needed for samples in the age range usually encountered, that is, up to about 50,000 years old. For most common sample materials this means that a minimum of about 10 g of pre-treated sample must be burnt initially. In most cases, though by no means always, it is generally possible to obtain enough archaeological or geological sample

material to provide at least this amount for combustion, allowing for some unavoidable wastage during the preliminary treatment for removal of possible age contaminants.

Conventionally the samples are combusted in a scaled-up version of the kind of silica tube furnace used in classical quantitative microchemical analysis for carbon and hydrogen, usually incorporating a wire form copper oxide packing and followed by a variety of alternative wet purification trains depending on the individual laboratory's preferences. However, the combustion of 10 g or more of sample material in such large-scale tube furnaces is a tedious, unproductive process often taking more than 2 h for each sample and, more importantly, requires constant supervision. This type of apparatus is rather troublesome to operate properly and over the long period needed for each combustion there is a strong tendency for bubblers and traps to become blocked and for leaks to develop with the attendant risk of loss or contamination of samples.

For these reasons the idea is attractive of a more or less instantaneous bomb method of combustion, as utilised for example in the estimation of calorific values of fuels but on a larger scale, and with these considerations in mind H. Barker began experimenting with a combustion bomb for radiocarbon samples at the British Museum Research Laboratory more than a decade ago. There were, however, practical difficulties in extracting the mixture of carbon dioxide and excess oxygen at about 10–15 atm pressure from the bomb after a combustion such that there was no appreciable saving in time over the tube furnace method and the idea was not taken any further at the time.

Eventually this difficulty was overcome by means of a semi-automatic system for extraction and separation of the gas mixture from the bomb so that its routine use for sample combustions then became practicable.<sup>5</sup> Meanwhile, V.R. Switsur of the University of Cambridge Radiocarbon Dating Laboratory developed a more sophisticated bomb having a spin ring closure instead of a lid bolted to a flange welded to the body of the vessel as in the case of the original British Museum bomb.<sup>6</sup> The first British Museum bomb was a thick-walled stainless steel vessel converted at AERE, Harwell from its original use as a lithium furnace for large-scale preparation of acetylene<sup>7</sup> and, although properly engineered and tested at the time, was basically of a design which would not now be regarded as fully satisfactory for the purpose to which it had been adapted. This bomb finally failed in use after several hundred successful combustions<sup>8</sup> and was replaced by the purpose-built version incorporating Switsur's spin ring closure principle and this is the equipment which will now be described. Just before leaving the background to the development of these combustion bombs it should be added that Dr. Switsur has now taken this a stage further with a horizontally oriented bomb of advanced design having a hinged door and many other new features, which he has recently described in detail.<sup>9</sup> This equipment<sup>a</sup> could also be used for more fundamental work such as the study of the kinetics of combustion processes.

#### DESCRIPTION OF THE EQUIPMENT

The combustion bomb, which is commercially available,<sup>b</sup> is shown diagrammatically in Fig. 1 and consists of a stainless steel cylinder some 4.5 in (115 mm) in internal diameter, 15 in (480 mm) in length and of nominal 4 litre volume,

<sup>a</sup> High Pressure Combustion Unit manufactured by Phonon Particle Beams Ltd., 356 Wimpole Road, Lords Bridge, Barton, Cambridge CB3 7AE, England.

<sup>b</sup> Manufactured by Interskill Ltd., 121 Cambridge Road, Milton, Cambridge CB4 4AT, England.

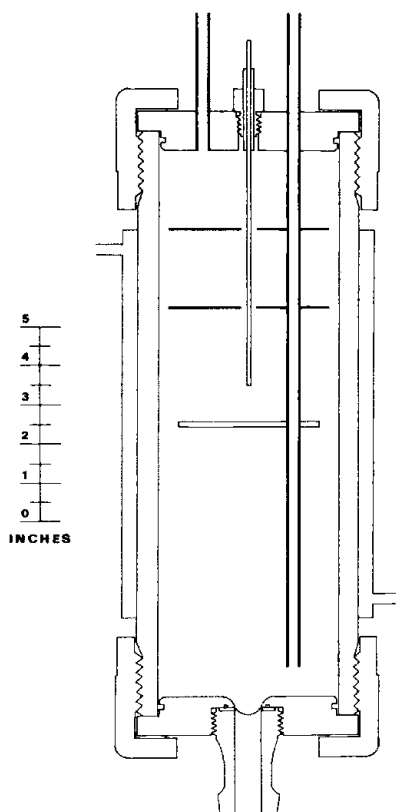


Fig. 1. Diagram of construction of combustion bomb (firing wire and sample crucible not shown).

having 0.5 in (12 mm) walls heavily threaded externally at both ends to take the large aluminium bronze spin rings which secure 1 in (25 mm) thick stainless steel end plates. A cooling water jacket is fitted to the outside of the vessel which is held vertically in a tripod stand bolted in turn to a bench. Gas inlet and outlet tubes with shut-off valves attached and an insulated lead-in for the electrically heated firing wire pass through the top plate. This plate also has an attachment point for a cable and counterweight arrangement so that the whole assembly, including the heavy spin ring, can be easily raised and lowered when placing the sample in position and for servicing and cleaning. In the centre of the bottom plate there is a high pressure relief valve in the form of a stainless steel bursting disc 0.625 in (15 mm) in diameter and two thousandths of an inch (0.025 mm) thick, rated at 1500 lb/in<sup>2</sup>. Both the end plates have stepped profiles and are thus retained by the spin rings against the ends of the vessel walls but also form, with an 'O' ring in their inner edges, a piston fit inside the cylinder. The gas inlet tube reaches almost to the bottom of the closed vessel to facilitate purging with oxygen before filling. A ring which supports the sample crucible and above this two heat shield plates are all attached to the inlet tube by bayonet fittings and the tube also provides a convenient earth connection point for the firing wire. All the internal metal components are of stainless steel.

The vessel, without the bursting disc fitted, that is with a blank baseplate, has

been subjected to a British Standard Specification static pressure test of 2250 lb/in<sup>2</sup> at the Ministry of Technology, Explosives Research and Development Establishment and carries a test certificate to this effect.

The firing wire is powered by a transformer circuit with an output of about 4 A at 12 V located close to the bomb but operated remotely via switches and relays. The firing wire is a loose coil, about 0.125 in (3 mm) in diameter, of iron or nichrome resistance wire about 0.2 mm thick connected by heavier tinned copper wires between the insulated lead-in and earth. Oxygen from a standard size J cylinder (200 ft<sup>3</sup>) is supplied to the bomb through a heavy duty regulator having a maximum outlet pressure of 600 lb/in<sup>2</sup>, fitted with a flame arrestor and connected by flexible high pressure oxygen hose to a needle valve and a pressure gauge which allows the filling pressure to be monitored. After combustion the gas mixture is extracted and separated by pumping through a series of refrigerated glass traps (e<sub>1</sub>, e<sub>2</sub>, e<sub>3</sub>). The pressure in this system being controlled by a modified oxygen cylinder regulator and an electromagnetic valve operated from contacts on a mercury manometer. Figure 2 is a diagram of the filling and extraction system.

Obviously it would not be difficult to devise a more elegant arrangement for

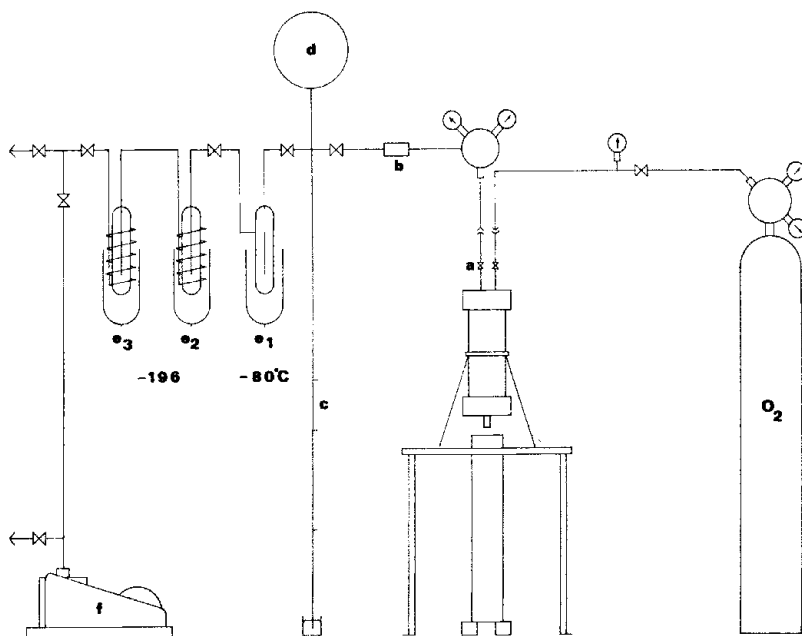


Fig. 2. Schematic layout of combustion bomb filling and extraction system. The procedure for filling the bomb is explained in the text. After a combustion CO<sub>2</sub> is separated from excess O<sub>2</sub> by evacuating the gas mixture through refrigerated traps (e<sub>1</sub>, e<sub>2</sub>, e<sub>3</sub>). By careful control of pumping conditions all CO<sub>2</sub> is retained in traps e<sub>2</sub> and e<sub>3</sub> and O<sub>2</sub> is vented to atmosphere. To initiate this process outlet valve a, an intermediate regulator, and electromagnetic valve b are opened and stopcocks adjusted in the line to pump f (see text for details). Pumping then continues until the bomb is emptied (about 40 min), the gas flow being automatically controlled by valve b which operates, in response to pressure changes, from contacts on manometer c (via relays, not shown). A buffer volume d ensures that pressure changes in the line are not too rapid.

recovery of the carbon dioxide from the bomb, but the system in use is simple and effective and has been trouble-free over a long period.

#### OPERATION OF THE EQUIPMENT

Samples for radiocarbon dating are, with a few special exceptions, all once-living materials such as wood, charcoal, bone, cloth, plant remains and various other typical substances. These have first to be treated by fairly straightforward chemical methods to remove possible age contaminants. In the case of bone and antler, for reliable results the protein fraction (collagen) must be freed of its inorganic matrix which, since it contains carbonates, is liable to have undergone exchange with (usually) more recent carbon. After treatment the sample materials are generally in the form of coarsely particulate solids. To avoid very rapid combustion, particularly of finely divided materials such as charcoal, it is advisable to moisten and compress the samples into the form of large pellets. We achieve this by means of a press designed for embedding specimens for metallographic examination which happens to be conveniently available in a neighbouring laboratory but presses specifically designed for pelleting combustion samples are obtainable commercially. In our case the pellets are about 1 in (25 mm) in diameter and up to 0.5 in (12 mm) thick and there are one or two such pellets for an optimum sample of about 12 g of typical pretreated material.

The sample pellets are placed in an 80 mm silica crucible supported centrally in the bomb, making sure that there is good thermal contact with the firing wire coil. A small amount of distilled water (nominally 50 ml) is placed in the bomb which is then closed, purged briefly with oxygen and, with the outlet valve shut off, filled to 100–125 lb/in<sup>2</sup> (representing about a five-fold excess of O<sub>2</sub>) over a period of about 2 min. With pelleted samples there is a negligible risk of a dust explosion caused by sample material ejected into the bomb atmosphere during filling. The oxygen is not purified before admission to the bomb but is known not to contain a significant quantity of carbon dioxide (stated to be less than 5 v.p.m.). However, to allow for decay of Radon-222 (3.8 day half-life), almost certainly present in small amounts in the oxygen and which might possibly get through physically to the final counting sample, fresh cylinders of oxygen are aged by storage for 4 weeks or so before use.

When filling is complete the inlet valve is closed, the filling line disconnected and after clearing personnel from the area the bomb, with cooling water flowing, is fired remotely from an adjacent room. A pilot light visible from the firing point indicates firing wire continuity. Failure of this to illuminate after operating the firing switch is taken as a simple indication of a successful combustion (in which the wire is always destroyed) and this has proved reliable in practice. As a safety measure the firing switch cannot be operated successfully without first turning a separate key switch. The operator keeps this key in his possession while he is charging the bomb.

After combustion, which probably takes place in about 30 s or less, the mixture of carbon dioxide and excess oxygen is separated by pumping through the cold trap system already mentioned using a large rotary vacuum pump. The extraction line has three fairly large pyrex glass traps and a 5 litre ballast volume to prevent oscillation of the electromagnetic valve which would be caused by rapid pressure changes. The first trap is a simple one, cooled with dry-ice/acetone slush, in which the pressure is kept at about 30 cm Hg to remove water vapour, and the other two are specially designed spiral traps cooled with liquid nitrogen for collection of the carbon dioxide most of which is held back in the first of these (Fig. 2). By careful adjustment of the stopcocks in the extraction line the pressure of the gas mixture pumped through the liquid nitrogen traps can be

maintained at about 7.5 mm Hg. This ensures that the excess oxygen does not condense as a liquid in the cold traps but is vented to atmosphere while at the same time allowing virtually complete stripping and retention of carbon dioxide. When these initial settings have been made the system can be left to operate unattended until all the gas has been pumped out of the bomb which takes up to about 40 min. The carbon dioxide is converted via acetylene to benzene for radiocarbon age measurement by liquid scintillation counting.<sup>10</sup>

The safety aspects of the use of the bomb have been considered in some detail. Apart from the need common to all high pressure systems to maintain adequate standards of care and cleanliness in operation, the combustion bomb is regarded as inherently very safe. So far as it can be ascertained the pressure rise on combustion is small. The bursting disc provides a safety factor which is probably at least an order of magnitude greater than the pressure increases which occur in normal operation. The bomb is mounted over an asbestos tube about 5 in (125 mm) in diameter into which the orifice of the bursting disc assembly is directed. If the disc did burst the escaping hot gas mixture and any minor debris would be ducted harmlessly away, probably the most serious consequence being the loss of a sample.

The bursting disc is exposed to quite strongly acidic conditions each time a sample is combusted. Since it is a component too expensive to replace routinely, the disc is microscopically examined at regular intervals for signs of stress corrosion. This could weaken the disc and if neglected might cause its failure at normal operating pressures resulting in the otherwise avoidable loss of a sample. So far no such corrosion has been observed and indeed one disc deliberately burst after 35 combustions still failed very close to the rated pressure of 1500 lb/in<sup>2</sup>. Damage caused by normal handling of the relatively fragile disc is most likely to make its replacement necessary long before it has been significantly weakened by corrosion.

#### PERFORMANCE OF THE EQUIPMENT

The performance of the combustion bomb is very satisfactory. The equipment described here has been in routine use in our laboratory for some 18 months and about 150 combustions have been carried out with it in this time. Compared with the alternative tube furnace method the bomb method is easy to operate and requires only about 20 min of full-time attention by an operator for each combustion against 2 h or more of constant supervision for an equivalent tube furnace combustion. There is no doubt that the kinds of sample material commonly met in radiocarbon dating are completely burnt in the bomb. Generally little or no ash remains after the combustion<sup>a</sup> and almost all (probably better than 99%) of the carbon dioxide can certainly be recovered. The purity of the gas is high as traces of oxides of nitrogen and sulphur formed during the combustion are mostly dissolved in the small amount of distilled water deliberately placed in the bomb for this purpose

<sup>a</sup> It is of some interest to note that in certain cases, usually when charcoal is burnt, numerous glassy microspheres, generally greenish or brownish in colour and of sub-millimetre dimensions, are afterwards found in the sample crucible. Superficially, these closely resemble some forms of lunar spheres in appearance and it is known that similar spherules can be produced in a number of other ways, for example in the manufacture of mineral wool<sup>11</sup> and occasionally by steam locomotives.<sup>12</sup> In this particular case the spherules must be derived from fusion of small amounts of silica and metallic oxides sometimes present in the sample materials.

before firing. These impurities are usually much more difficult to remove satisfactorily from carbon dioxide obtained by tube furnace combustions. After final drying carbon dioxide from the bomb combustion can be reacted directly, without the need for further purification, to form acetylene via lithium carbide (and subsequently to benzene for liquid scintillation counting). Carbon dioxide obtained by bomb combustion would of course still require further purification if the intention was to measure the Carbon-14 activity directly by internal gas counting.

In our laboratory the optimum sample size for our purposes is 12 g and this amount yields about 9 litres of carbon dioxide from most common sample materials. Samples of comparable carbon content (30–50%) up to at least 20 g in weight could easily be combusted and the filling pressure of oxygen could be increased up to 250 lb/in<sup>2</sup> if necessary. With some difficulty larger samples containing as little as 5% or less of carbon could most probably be successfully combusted. Any samples much smaller than about 1 g in weight would probably still be more conveniently combusted in a tube furnace.

Finally, the equipment can be easily disassembled for cleaning after each combustion so there is ordinarily no risk of memory effects, at least when dealing with radiocarbon dating samples. Provided that total activities higher than a few tens of disintegrations per minute are not introduced to the bomb there is no reason to suppose that there will be memory problems in other applications.

## CONCLUSIONS

The bomb combustion method described has, at least in its application to radiocarbon dating samples, distinct advantages over the numerous variants of the more conventionally used large-scale tube furnace combustion method in terms of time saved and improved yield and purity of the resultant carbon dioxide. These advantages soon repay the fairly high initial cost of the equipment (about £1000). It seems possible, therefore, that this type of equipment may also have applications in other fields, particularly where the problem may be one of dealing with large samples of intrinsically low radioactivity. The productivity of the equipment does not of course compare with that of commercial automatic combustion units intended for smaller and normally higher activity samples and a maximum of about five or six combustions per normal working day seems a probable figure. However, this will often be more than adequate in low level applications in which there may follow several more stages of sample preparation chemistry and where finally, to obtain the required precision, it may take a week or so to evaluate a small group of samples by scintillation counting.

## ACKNOWLEDGEMENTS

For the benefits of their most helpful advice and discussions I am greatly indebted to my colleagues at the British Museum Research Laboratory, Mr. H. Barker, who initiated this work, Mr. N.D. Meeks who constructed much of the apparatus and has carried out most of the combustions and to whose expertise the success of the work is largely due, and Mrs. J. Lang who has provided metallographic information and facilities; to Dr. V.R. Switsur of the Sub-Department of Quaternary Research, University of Cambridge and to Mr. J.M. Cleland of Interskill Limited, Milton, Cambridge.

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## DISCUSSION

C.R. Jones: What was the cost of manufacture of the bomb?

R. Burleigh: £800-£1,000.

B. Scales: Do you have any problems in maintaining a steady low pressure which is sufficient to prevent condensation, but gives good recovery of carbon dioxide in the liquid nitrogen-cooled traps?

R. Burleigh: No. Liquid oxygen is a hazard which we certainly take note of, but at the low pressures maintained by our large rotary pump, the recovery of carbon dioxide in our carefully designed traps is better than 99%.