Combustion with oxygen in a sealed Parr bomb has been accepted for many years as a standard procedure for converting solid and liquid combustible samples into soluble forms ready for chemical analysis. It is a reliable whose effectiveness stems from its ability to treat samples quickly and conveniently within a closed system, thus ensuring complete retention and potential recovery of all combustion products. The bomb combustion method is an essential step in standard ANSI/ASTM methods for determining sulfur and chlorine in coal, and it has been applied successfully to the determination of arsenic, phosphorus and other elements as well.

The methods given here for sulfur and chlorine correspond to the basic ASTM reference methods for these elements, each of which calls for a gravimetric finish. Although these are reliable procedures, other less time consuming volumetric, nephelometric or ion chromatographic methods can be used for estimating these elements after recovering the bomb washings. Such alternatives are suggested in the references which follow.

**Sulfur in Combustible Solids.** Burn a 1.0 gram sample and collect the washings as described in the basic procedure for using the 1108 oxygen bomb. Let the bomb stand for at least 5 minutes after firing; then remove it from the water and release the residual gases slowly and at an even rate so that the pressure is reduced to atmospheric in not less than one minute. Open the bomb and wash all parts of its interior, including the combustion capsule, valve passages and electrodes, with a fine jet of distilled water containing 1 ml of a saturated solution of methyl orange indicator per liter. Wash until no acid reaction is observed, collecting the washings in a beaker. If necessary, use a rubber policeman to transfer any precipitate from the bomb or capsule to the beaker. After neutralizing the solution, add 1 ml of ammonium hydroxide, heat the solution to boiling, and filter through a rapid qualitative paper. Wash the residue and filter paper with hot distilled water and add sufficient water to bring the total volume of solution to approximately 250 ml. Neutralize with concentrated hydrochloric acid and add 2 ml in excess. Add 10 ml of saturated bromine water and evaporate to approximately 200 ml on a hot plate or other source of heat. Adjust to a slow boil and stir constantly while adding 10 ml of a 10% barium chloride solution from a pipette. Continue stirring for two minutes, cover with a fluted watch glass and keep just below boiling on a steam bath or hot plate until the volume is reduced to 75 ml, then allow the precipitate to settle for another hour while cooling. Filter through an ashless filter paper and wash with warm water until free from chlorides.

Transfer the paper and precipitate to a weighed crucible, dry at low heat, char the paper without flaming, then raise the temperature to a good red heat (approximately 925 °C) and heat to a constant weight. If the crucible is placed in a cold electric muffle furnace and the current turned on, drying, charring and ignition will usually occur at the desired rate. After ignition is complete, allow the crucible to cool to room temperature and weigh. Determine the exact weight of the barium sulfate precipitate and calculate the percentage of sulfur in the sample as follows:

\[
\text{Sulfur, } \% = \frac{\text{Wt. } \text{BaSO}_4 \times 13.734}{\text{Wt. Sample}}
\]

**Sulfur in Combustible Liquids.** For oils or other liquids containing 5% sulfur or less, use a sample weighing from 0.6 to 0.8 gram. If the sample contains over 5% sulfur, use a sample weighing from 0.3 to 0.4 gram and add an equal amount of sulfur-free U.S.P. white oil. If the sample is not readily miscible with white oil, some other low sulfur combustible diluent may be used. However, the combined weight of sample and white oil or other combustion aid must not exceed 1.0 gram. If the sample is volatile it must be weighed in a sealed holder. The procedure for filling the bomb, firing, recovering the washings and determining sulfates is the same for liquid samples as described in the preceding method for solids.

Other less time consuming procedures have been suggested as an alternative to the gravimetric methods described here for estimating sulfur in the bomb washings. Among the titrimetric methods: Hicks\textsuperscript{21}, et al titrates with lead perchlorate and determines the equivalence point using a lead ion specific electrode. Callan\textsuperscript{11} suggests converting to benzidine sulfate and titrating with standard hydroxide solution. Siegfriedt\textsuperscript{41} titrates with barium chloride solution using tetra-hydroxyquinone as an indicator. Randall\textsuperscript{37} adds barium chloride in excess and back titrates with disodium hydrogen phosphate with the addition of alcohol. Herrig\textsuperscript{20} back titrates with Tritiplex III using phthalein purple as an indicator. A conductometric method has been suggested by Barthel\textsuperscript{6}. Nephelo-
Analytical Methods for Oxygen Bombs

metric methods for trace amounts of sulfate have been suggested by Toennies\textsuperscript{43} and Bailey\textsuperscript{5}.

Chlorine in Combustible Solids and Liquids. Platinum combustion capsules and platinum ignition wire are recommended for these tests because of the extremely corrosive nature of chlorine and its compounds. After repeated use with such samples, the inner surfaces of the bomb will become etched to the point where appreciable amounts of metal salts will be introduced during each combustion. The ability of the bomb to withstand such corrosion can be improved by keeping the inner surfaces highly polished. Any bomb which is being used for chloride determinations should be repolished at regular intervals to prevent the development of deep pits. The alternative to this procedure is to use an 1108CL bomb which offers much better resistance to chlorine than the standard 1108 bomb. Or for ultimate protection, use an 1105C or 1106C bomb with a platinum liner.

Samples containing more than 2% chlorine by weight should be diluted with U.S.P. white oil or some other non-volatile, chlorine-free diluent. The suggested amounts of sample and diluent are shown in the following table, but the user is cautioned that the combined weight of the charge must not exceed 1.0 gram.

<table>
<thead>
<tr>
<th>% of Chlorine in Sample</th>
<th>Grams of Sample</th>
<th>Grams Of White Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 2</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>2 to 5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>5 to 10</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>10 to 20</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>20 to 50</td>
<td>0.05</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Place about 5 ml of a 5% sodium carbonate solution (135g Na\textsubscript{2}CO\textsubscript{3},10H\textsubscript{2}O per liter) in the bomb, assemble and fill with oxygen to a pressure of 35 atmospheres. Immerse the bomb in a bath through which cold water is circulating. Attach the ignition wire to the bomb terminal, then stand at least six feet from the bath when firing the charge. Keep the bomb in the bath at least five minutes before removal. Release the residual gas slowly and at an even rate so that the pressure is reduced to atmospheric in not less than one minute. Open the bomb and examine for traces of unburned sample or sooty deposits. If found, discard the determination and clean the bomb thoroughly before using it again.

If the combustion was satisfactory, wash the sample cup and all interior surfaces of the bomb with a fine stream of distilled water, collecting the washings in a 600 ml beaker. Scrub the interior of the cylinder and the underside of the head with a rubber policeman. Continue washing until no acid reaction is observed on any bomb parts or passages, which will normally require at least 300 ml of wash water.

Acidify the solution by adding 1:1 nitric acid dropwise until the methyl red endpoint is observed; then add 2 ml excess acid. Filter through a qualitative paper and collect the filtrate in a 600 ml beaker. Heat to about 60 °C; protect from strong light and slowly add 5 ml of silver nitrate solution (50 g per liter) while stirring. Heat almost to boiling and hold at this temperature until the supernatant liquid becomes clear. Add a few drops of silver nitrate solution to test for complete precipitation. If cloudiness appears, repeat the above operation.

Allow the beaker to stand in a dark place for at least one hour. Filter the precipitate by suction onto a weighed fritted glass filter. Wash with distilled water containing 2 ml of 1:1 nitric acid per liter. Dry the precipitate and crucible at 110 °C for one hour. Cool in a desiccator and weigh.

Make a blank determination with 0.7 to 0.8 gram of white oil, omitting the sample; then calculate the chlorine content of the sample by substituting in the following equation:

\[
\text{Chlorine, % by wt.} = \frac{(P-B)}{24.74} \times \frac{m}{m}
\]

where,

- \(P\) = grams AgCl obtained from sample
- \(B\) = grams AgCl obtained from blank
- \(m\) = mass of sample in grams

**ASTM Methods for Sulfur and Chlorine.** Oxygen bomb procedures for determining sulfur and chlorine in a broad range of combustible materials are given in the following standard methods published by the American Society for Testing and Materials, copies can be obtained from ASTM at [www.astm.org](http://www.astm.org).


**ASTM Method D808**, “Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method)”.
Analytical Methods for Oxygen Bombs


Halogen Determinations. Other halogens in addition to chlorine can be determined by the oxygen bomb method. Agruss used the oxygen bomb to determine chlorine, bromine and iodine mineral oils. Longo applied this method to many different organic compounds, with particular emphasis on the determination of iodine. Intonti used an oxygen bomb for analyzing insecticides and antifermantatives. Bradford describes a bomb method for determining fluorine in coal. Bailey and Selig describe the use of platinum lined bomb for determining fluorine. The Monsanto Co. uses the oxygen bomb combustion method for determining small amounts of pentachlorophenol and similar chlorophenols in wall board, wood, paperboard, fish net, rubber etc. Recently, Nadkarni has used halogen selective electrodes to determine fluorine, chlorine, bromine and iodine in coal samples and polymers after combustion in an oxygen bomb.

Arsenic Determinations. It has been shown by Carey that combustion in an oxygen bomb is a reliable way of preparing samples for the determination of arsenic by the Gutzeit method, or by the Marsh-Berzelius method. In this application the oxygen bomb replaces the acid digestion generally used in the standard methods for arsenic.

Mercury Determinations. Borchardt used an oxygen bomb to determine mercury in paper. Fujita determined mercury in rice, rice hulls and hair, while Ukita used the bomb method for mercury determinations using atomic absorption spectrometry for the final measurement.

Phosphorus Determinations. Oxygen bomb methods for determining phosphorus have been given by Piercy, Conrad, Wreath, and Buss. One problem associated with this determination is the formation of a phosphoric acid mist in the bomb which does not settle out after combustion. To dissipate the mist, apply 20 v.d.c. to the electrodes. To minimize the formation of phosphoric acid mist, add one gram of sodium carbonate to the sample, mix some sodium naphthenate or zinc oxide with the sample.

Boron Determinations. An oxygen bomb technique suggested by Hill has been found excellent for the destruction of animal and vegetable tissue preparatory to chemical analysis. A similar technique for the analysis of blood samples has also been recommended. This procedure has been used successfully for determining small amounts of boron in animal and vegetable matter, and it seems reasonable to assume that it would work equally well for determining other elements. Burke, Conrad, and Kuck also describe methods for determining boron after combustion in an oxygen bomb.

Other Elements. Selenium, Zinc, Lead, Titanium, Iron, Sodium, Potassium, Calcium, Magnesium, Copper, Carbon, Hydrogen, Oxygen, Tritium, Beryllium, Chromium, Manganese, Nickel, Vanadium and Carbon-14, all can be determined by oxygen bomb methods.

Selenium has been determined in solid wastes by Johnson and in plant and animal tissue by Dye. Zinc in rubber and copper in mushrooms has been reported by Przybylski. Edwards has sodium, potassium, calcium and magnesium in fuels. Fujiwara describes methods for determining iron, aluminum and titanium in polyethylene, and Anduze on titanium in polyethylene. Lead in piston deposits has been determined by Conrad. Lead in coal has been determined by Lindahl.

Carbon determinations by the oxygen bomb method have been reported by Adam, Lambris, Thomas, Mehta and Nishioka. Hydrogen has been determined by Mehta and Nishioka and Zhokovskay. The use of two bombs for determining oxygen is described by Witaker.

Nadkarni has determined nitrogen in coal samples using a chemiluminescent method following combustion in an oxygen bomb. This method is much faster than the traditional Kjeldahl method, requiring only a minute to determine nitrogen concentration.
A method for determining H3 and C14 in biological materials is described by Sheppard40.

Fujiwara19 gives an excellent review of methods for determining trace elements in organic compounds by the oxygen bomb method.

Lindahl29 describes a particularly useful method for the determination of beryllium, chromium, manganese, nickel, vanadium, copper, lead and zinc in coal.

A procedures manual issued by the U.S. Environmental Protection Agency recommends combustion in a Parr Oxygen Bomb for preparing all combustible materials for inorganic analysis. Specific procedures are given for mercury, antimony and arsenic.

**Procedures For Determining Trace Elements Using A Quartz Liner In the 1108 Oxygen Bomb**

Trace amounts of heavy metals in coal and other combustible samples can be determined by the bomb method but usually these procedures have required the use of an expensive platinum liner in the bomb to avoid problems introduced by the leaching of trace amounts of heavy metals from the bomb walls and electrodes during combustion. This problem has now been resolved with the introduction of a cup and cover which can be used in any 1108 Parr oxygen bomb to hold the combustion products. Although a quartz liner does not offer the complete protection obtainable with a platinum liner, it is nevertheless an effective means for preventing heavy metal contamination in certain combustion procedures.

**The 513A Quartz Liner**

The quartz liner now offered for use in the 1108 oxygen bomb consists of a quartz cup, 61 mm dia. x 86 mm deep, with a flat quartz cover which rests on top of the cup. Holes are provided in the cover for inserting platinum electrodes which extend into the cup to support a short length of platinum fuse wire and a fused silica sample holder. All of the parts needed to add this liner to an 1108 oxygen bomb are provided in the 1912 Conversion Set listed below.

**Kraft (TRW) Procedures**

Some of the earlier combustion procedures using a quartz-lined oxygen bomb were developed by M.L. Kraft of TRW, Inc., Defense and Space Systems Group, who used this method to prepare spark source mass spectrometry samples of coal, oil and other organic matter. In the Kraft methods the sample is burned in a fused silica capsule using 10 ml of 1:1 nitric acid in the bottom of the quartz liner to absorb the combustion products. Kraft found that background quantities of Cr, Fe, Ni and Mn were completely eliminated by this arrangement.

**Lindahl Procedures For Trace Elements In Coal**

Extensive studies by Peter C. Lindahl29 of the Exxon Production Research Company have shown that a quartz-lined Parr 1108 oxygen bomb provides a rapid and accurate method for treating coal samples to determine trace amounts of Be, Cd, Cr, Cu, Pb, Mn, Ni, V and Zn by atomic absorption spectrometry. The basic Lindahl combustion is described below. Further details covering final assays for each element are provided in the complete Lindahl Paper, a reprint of which can be obtained from Parr Instrument Company on request.

Weigh a pelletized coal sample (1.0-1.2g) in a silica capsule. Transfer 10 ml of 1:10 HNO3 to either the combustion bomb or to the quartz liner. Assemble the bomb and charge it with oxygen to 15 atm. Place the bomb in a cooling water bath and ignite the sample. Allow the bomb to remain in the bath for 5 minutes, then remove the bomb and release the pressure slowly. Open the bomb carefully and rinse all parts thoroughly into a Teflon beaker; then evaporate the washings to dryness on a hot plate or in a microwave oven.

Treat the residue in the Teflon beaker with 5 ml of aqua regia and 5 ml of HF and heat to dryness. Treat the residue with the appropriate volume of HNO3 along with water to make the final solution 1% in HNO3 after dilution to volume. For ash contents up to 5%, dilute to 25 ml. For ash up to 10% dilute to 100 ml.

In Lindahl’s work, final assays were performed by atomic absorption spectrophotometric methods. Flame absorption analyses were run on a Perkin-Elmer Model 5000 AA Spectrophotometer. Flameless analyses were performed using a Perkin-Elmer Model 703 AA Spectrophotometer equipped with a Model 400 HGA. Hollow cathode lamps were used in all analyses except for cadmium and lead analysis in which electrodeless discharge lamps were used.

**Quartz Liner Conversion Set**

All of the parts needed to install a quartz liner in an 1108 oxygen bomb are provided in a conversion set (No. 1912) obtainable from Parr. The set consists of:

1. 513A Quartz liner
2. 4AFB Platinum electrode, straight
3. 5AFB Platinum electrode, loop
4. 68AC Lock nuts, T303SS
5. 45C3 Platinum fuse wire, 300 cm
6. 43A3 Combustion capsules, fused silica

Any of the above items can also be purchased separately.
Procedure For Installing The Liner

1. Unscrew the two alloy electrodes from the bomb head. Insert 4AFB platinum electrode through the hole nearest the center of the quartz cover; attach a 68AC lock nut to the straight electrode and screw the electrode into the insulated terminal in the bomb head.

2. Insert the 5AFB loop electrode into the opening nearest the edge of the quartz cover; attach a 68AC lock nut to the electrode and screw it into the bomb head.

3. Position the straight electrode with the hook pointed outward and tighten the lock nut gently; then turn the loop electrode to its center position and tighten the lock nut. Bring the loop electrode to its final position by gentle pressure in the loop itself, but remember that platinum is soft and the threads on the electrodes can be damaged by tightening lock nuts more than necessary. Also, it may be necessary to bend the loop electrode slightly to allow the cover to slide freely on the electrodes and still remain concentric with the bomb cylinder.

4. Use either fused silica or platinum combustion capsules with this assembly, and always use platinum fuse wire, either 36 ga. or 26 ga. wire in the same manner as the regular 45C10 alloy wire. If the heavier 26 ga. wire is used, wrap two or three turns around each electrode and shape the wire into a running loop around the periphery of the capsule. This will allow the capsule to be inserted and removed without disturbing the fuse. It will also keep the wire out of the direct flame and reduce the possibility of a melt.

Always add an auxiliary fuse to the heavy 26 ga. wire, using either cotton or nylon thread or a thin strip of filter paper for this purpose.

5. When firing the 26 ga. fuse do not hold the firing button down more than one or two seconds. A longer ignition period will melt the wire. If the wire melts, use the 7 cm terminals on the ignition unit to obtain a lower firing voltage; or add a heavy, one-ohm resistor to the 10-cm firing circuit to lower the voltage.

6. To assemble the bomb, slide the quartz cup into the cylinder and lower the head and quartz cover into the bomb gently so as not to break the cover.

7. For zinc and cadmium determinations, the 230A synthetic rubber sealing ring on the bomb head should be replaced with a similar ring made of Viton, Part No. 230AJV.

8. Handle the quartz cup and cover carefully as these parts are easily broken. And, although quartz is noted for its good resistance to thermal shock, these parts can be broken by a non-uniform burn or other unusual conditions in the bomb. Breakage can be minimized by always leaving as much moisture in the sample as possible (up to 40% in some cases) to avoid the sometimes explosive reaction which may result from burning a bone dry sample.


