Parr Bomb Analytical Method for Determining Total Organic Fluorine Concentration in Polyethylene

Title

Percent Fluorine in Polyethylene Film or Resin Containing Dynamar Polymer Processing Additive by Parr Oxygen Bomb Combustion Method and Fluorine Specific Ion Electrode.

Scope

This method determines Fluorine content of fluorocarbon samples via combustion by Parr Oxygen Bomb and analysis by Fluoride Specific Ion Electrode. The procedure can be used as a general method for % Fluorine in organic compounds and most inorganic material. Electrode interferences must be determined for each type of sample to be analyzed.

Principle

The sample is burned in an atmosphere of pure oxygen using a Parr Oxygen Bomb. Hydrogen fluoride is formed and is neutralized by an excess caustic/water solution. The pH of the solution is then adjusted with acetic acid to a pH of 5-6 to prevent proton or hydroxyl ion interference. After dilution, an aliquot is diluted 50/50 with TISAB II which provides a constant ionic strength background at a pH of 5.0-5.5. The fluoride concentration is then measured with a specific ion electrode.

Safety Precautions

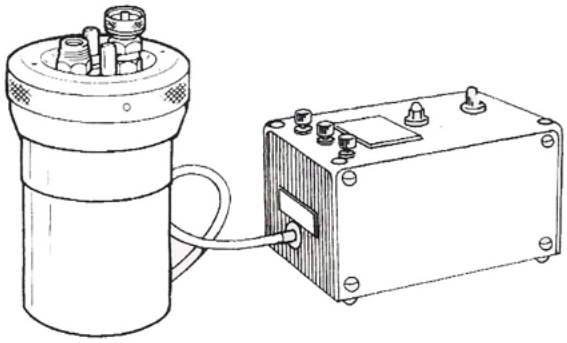
Refer to the safety precautions listed in the Parr Oxygen Bomb instruction manual. Pertinent safety precautions have been incorporated into the test procedure.

Orion TISAB II Solution and Fluoride Standard Solutions are irritating to eyes and mucous membranes. Wash all contact s with water. Avoid prolonged inhalation.

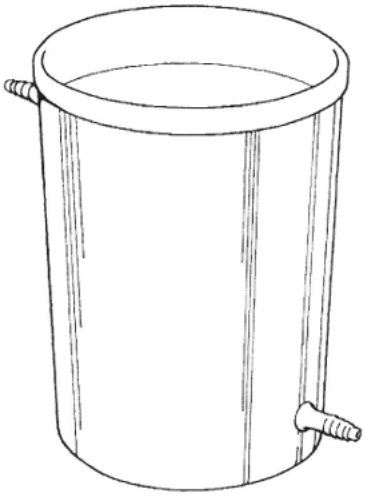
Use no oil or combustible lubricants on Parr Bomb components or fittings or any other device handling oxygen under pressure.

Although oxygen is not combustible, it does support combustion. Oxygen flow should be controlled and shut off when not in use.

FIGURE 1



Parr Oxygen Bomb Model 1108 + Ignition Unit 2901



Cooling tank

Apparatus

- Parr Oxygen Bomb (#1108 or equivalent) with ignition unit and cooling tank. (Figure 1).
- Nickel electrodes
- Fuse wire, Parr 45C10
- Oxygen source 99% pure, pressure gauge 0-55 atmospheres and connecting apparatus.
- pH meter
- Electrodes, Orion Model 94-09 Fluoride Electrode and Model 90-D1 Reference Electrode or equivalent or Model 96-D9 combination Fluoride Electrode.
- Balance, analytical, accurate to 4 decimal places.
- Flask, volumetric, 50, 100, 500 and 1000 ml
- Polystyrene test tubes, 15 ml
- Magnetic stirrer and stirring bars or equivalent
- Bottles, polyethylene
- Funnel, polyethylene
- Pipets, 1, 5, 10, 15, 25 and 50 ml

Reagents

- Acetic acid, glacial AR grade
- Distilled water stored at ambient temperature for making fluoride standards and rinsing electrodes.
- Sodium hydroxide 0.3 N - Prepare by diluting 300 ml of 1.0N certified NaOH to 1,000 ml with DI water in a volumetric flask
- TISAB II (Total Ionic Strength Adjustment Buffer), Orion Cat. # 94-09-D9.
- The buffer can be purchased commercially or prepared as follows:

Place about 600 ml of DI water in a one-liter beaker. Add 57 ml of glacial acetic acid and 58 g of NaCl. Stir to dissolve. Titrate the solution to a pH of 5 with 10 molar sodium hydroxide. Cool to room temperature and add 4 g of cyclohexylene dinitrilo tetracetic acid (CDTA). Some catalogs list this material as 1,2-diaminocyclohexane-

N,N,N', N'-tetracetic acid. Dilute to about 900 ml and stir to dissolve the CDTA. Again, titrate with 10 molar NaOH to a pH of 5.2-5.4. Transfer to a one-liter volumetric flask and dilute to volume with DI water.

- Fluoride Standard Solutions available from Orion:

		Actual F^- conc.
#04--09-06 1 ppm	50/50 distilled water/TISAB II	*0,5 ppm*
#04--09-08 10 ppm	50/50 distilled water/TISAB II	*5,0 ppm*

- Fluoride Stock Solution available from Orion:

#94--09-07 100 ppm	*100 ppm*
Prepare a 50 ppm F- standard by combining 250 ml TISAB II with 250 ml of the 100 ppm stock solution.	*50 ppm*

For alternate method of preparation of fluoride stock solutions and calibration standards, see Page 9.

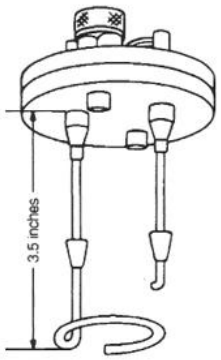
- Methyl alcohol, ethyl alcohol or acetone AR grade.

Procedure

Note: The amount of sample, sodium hydroxide or acetic acid charged, must be determined for each different type of product to be tested. The pH of solution must be greater than 7 after combustion to enhance fluoride recovery. The solution must then be adjusted to pH 5 to 6 before addition of TISAB II.

1. Sample must be run in duplicate.
2. " Polish" the fuse wire contact area of the electrode with a green Scotchbrite pad.
3. Place the bomb head on the support stand and attach a 10 centimeter length of fuse wire to the electrodes. Fasten one end to the loop electrode and the other end to the straight electrode. Make 1-1/2 to 3 wraps of fuse wire around each electrode. Make sure the fuse wire is tightly bound at each electrode to ensure a good electrical connection (Figure 2A).

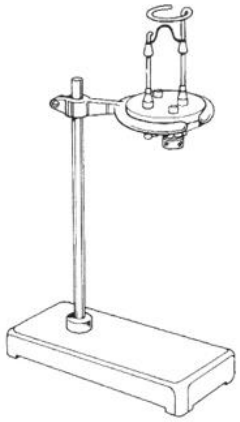
FIGURE 2



Bomb head with electrodes and loop holder which holds the combustion capsule.

The loop electrodes must not extend down more than 9 cms from the bomb head

FIGURE 2A



Bomb head held on the support stand. Wire fuse is attached to the electrodes

4. Sample preparation depends on the kind of material to be analyzed. Pellets can be weighed into the capsule. Film can be crumpled or bundled and tied with a piece of the sample. Thick films, 10 to 20 mm, can be cut in 1/4" squares. Light flaky material can be pressed into pellets.

5. Weigh the sample in the combustion capsule and record the weight to the nearest 0.1 milligram (0.0001 g). The sample weight must not exceed 0.5 g.

6. By pipet, add 15 ml of 0.3N sodium hydroxide to the bomb cylinder.

7. Place the combustion cup in the loop holder and bend the fuse wire down as close as possible to the surface of the sample. Make sure the wire does not touch the cup (Figure 3). The capsule should not touch the basic solution in the bomb cylinder. If the capsule touches the NaOH solution, combustion may be incomplete. To keep the capsule in place, rough up the outside surface of the cup and electrode contact area with a green Scotchbrite pad.

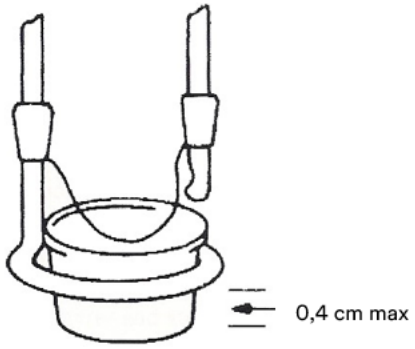
   Note: If the cup comes loose while shaking the bomb, it will dent up the interior and increase the surface area. Cleaning will be more difficult and high blank values will result.

8. By pipet, add 1 ml of AR methyl alcohol or ethyl alcohol to the combustion cup (Figure 3a).

   Note: Total combustibles (sample plus solvent or combustion aid) should never exceed 1.5 grams. Also, the sample combusted should not release more than 8000 calories when burned in pure oxygen.

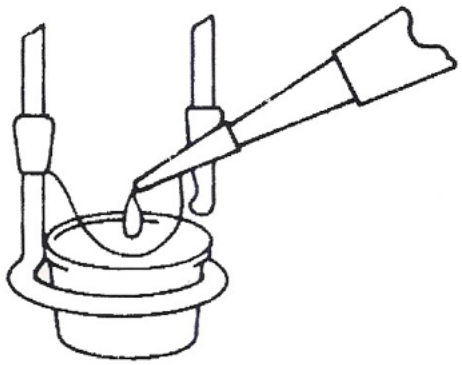
9. Assemble the bomb by placing the head into the cylinder. Tighten the bomb firmly by hand.

FIGURE 3



Bomb head is inverted on the support stand. Fuse wire connected to electrodes dips down into the combustion capsule which is held in the loop holder. The wire should not touch any metal except the electrode connections.

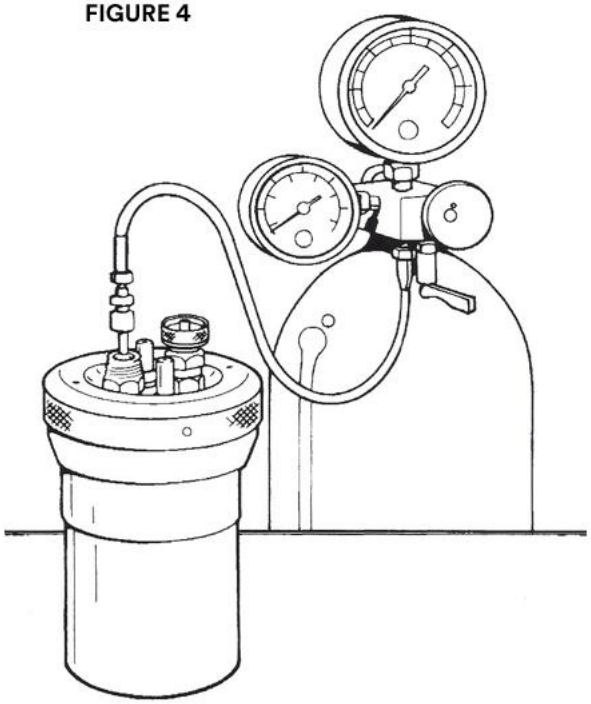
FIGURE 3A



1 ml of MeOH, EtOH or Aceton, a combustion aid, is added to the combustion capsule with a pipet.

10. Attach the oxygen hose to the inlet valve. Flush the bomb with oxygen by carefully filling it to 5 atmospheres and slowly venting. Keep the oxygen flow low to avoid splashing the combustion capsule's contents (Figure 4).

FIGURE 4



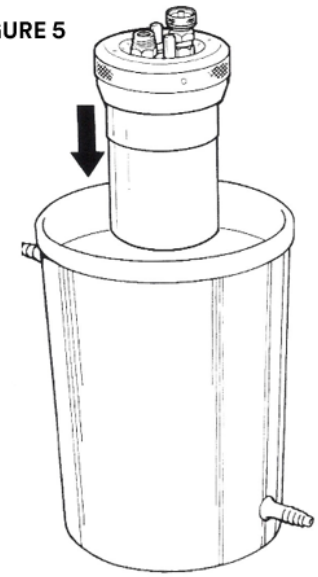
Oxygen cylinder and regulator used to pressurize the bomb with 20 atmospheres of oxygen.

11. Close the exhaust valve.
12. Fill the bomb with approximately 20atmosphere of oxygen. This must be done very slowly to avoid disturbing the combustion capsules contents. See Operating Instructions for Parr 1108 Oxygen Combustion Bomb-Oxygen Charging Pressure

    Note: The bomb pressure should never exceed 40 atmospheres.
13. Release the residual pressure in the connecting hose by pushing downward on the relief valve on the regulator.
14. Submerge the bomb in a stainless-steel container of water (Figure 5).
15. Attach the ignition wires to the bomb connectors.

    Caution: Do not have the head, hands or any parts of the body directly over the bomb during the firing period and do not go near the bomb for at least1 minute after firing (Figure 6).

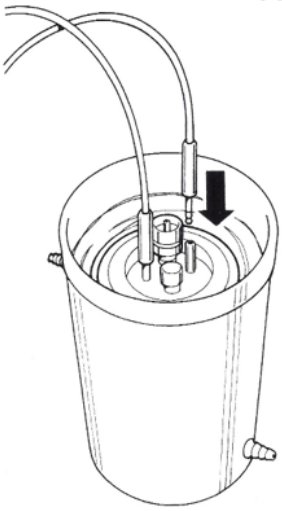
FIGURE 5



Bomb is submerged in a water bath. Check for any leaks.

Do Not Fire the bomb if any leaks are detected.

FIGURE 6



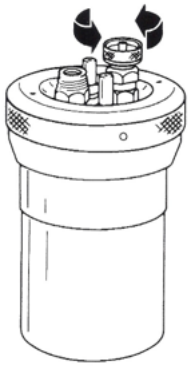
Ignition cords are attached to the electrodes after the bomb has been submerged.

During ignition stand back from the water bath. Do not hold any part of body over the bomb.

Wait 1 minute before shaking the bomb.

16. Fire the bomb by pressing the ignition button until the indicator light flashes.
17. Wait 1 minute and then shake while rotating the bomb. Bomb will be very warm due to heat of combustion.
18. Return the bomb to stainless steel container of water and allow it to cool for 10 minutes.
19. Remove the bomb from the water bath and repeat shaking as in Step 17.
20. Dry exterior of bomb and place in upright position for 1-2 minutes to drain. Open the knurled adjustable needle valve slowly and vent the gas pressure slowly over a period of not less than one minute to avoid entrainment losses (Figure 7).

FIGURE 7



After firing, shaking and cooling the bomb, it is vented by turning the knurled valve knob (outlet valve) counterclockwise. Slowly vent the bomb to avoid loss of any entrainments.

21. Unscrew the cap, lift the bomb head carefully and examine the interior for evidence of incomplete combustion. If such evidence is found the test may have to be repeated. A small amount of soot (carbon) will not affect the results.
22. Check the pH of the solution in the bomb. It should be between 5 and 6. If not, adjust the pH of the solution by adding glacial acetic acid (approximately 200 µl). Swirl the solution until the fizzing stops and recheck the pH.
23. Quantitatively transfer the contents of the bomb to a 100ml volumetric flask with a funnel by rinsing the bomb and bomb components thoroughly with distilled water. Make the volume up to 100ml with the distilled water and mix thoroughly (Figures 8 and 8A).

FIGURE 8

Bomb head and combustion capsule are thoroughly rinsed into the bomb chamber. Rinse should not exceed 80 ml.

FIGURE 8A

Bomb rinsings are transferred to a 100 ml volumetric flask and its volume is made up to 100 ml. Thoroughly mix this solution before taking a sample for reading on the fluoride electrode.

Measurement of Fluoride Anion

Remove the fluoride electrode from the storage solution (1 ppm F in 1 part TISAB II/1 part distilled water), rinse with distilled water, blot dry with a tissue and place into the lowest standard. The standards and the samples are measured in 15 ml polystyrene test tubes. After 3.5 minutes read and record the relative mV value from the meter. Remove the electrode from the standard, rinse with distilled water, blot dry and place the electrode in the next standard. After 3 minutes read and record the mV value. Repeat this procedure tor the remaining standards.

Now read the sample solutions. Combine 1 ml of the sample solution from the 100 ml flask with 1 ml of TISABII in a 15 ml polystyrene test tube and mix thoroughly. Place the electrode in the solution, read and record the mV value after 3 minutes. Repeat this procedure tor the remaining samples.

It is important that the samples and standards are the same temperature when making a measurement. (Room temperature is recommended.) To prevent any temperature fluctuations, room temperature distilled water is used tor rinsing the fluoride electrode.

After all samples and standards are measured, construct a calibration curve using graph paper or by linear regression. Calibration becomes non-linear below 0.5 ppm F^-.

Standard solutions are available from Orion or can be prepared from NaF.

Preparation of Standard Fluoride Solutions

Dry 3-5 grams of AR grade sodium fluoride (NaF) in a 110°C oven to a constant weight and cool in a desiccator. Weigh 2.2105 g of the NaF and quantitatively transfer to a 1,000 ml volumetric flask. Dissolve and dilute to volume with distilled water. Mix and transfer to a polyethylene bottle for storage. Label as 1000ppm Fluoride Stock Solution in distilled water. For a 100 ppm fluoride solution, use 0.2210 g NaF and for a 10 ppm fluoride solution, use 0.0221 g of NaF.

To prepare 100 ml of 0.5, 1, 5, 10 and 50 ppm F standards mix the following solutions as indicated below and store in tightly sealed plastic containers.

µg F-/ ml	ml of ppm NaF	ml TISAB II	Buffer ml Distilled Water
0 (blank)	0	50ml	50 ml
0.5	5 ml of 10 ppm NaF	50ml	45 ml
1	10ml of 10 ppm NaF	50ml	40 ml
5	5ml of 100ppm NaF	50ml	45 ml
10	10 ml of 100 ppm NaF	50ml	40ml
50	5 ml of 1000 ppm NaF	50ml	45 ml

An aliquot of each of the standards to be used is placed in an individual 15 ml plastic tube. Normally 0.5 ppm through 50 ppm are used to determine the calibration curve. Below 0.5 ppm the curve becomes curvalinear.

Calibration Curve

A calibration curve of μgF^- /ml vs. relative mV is plotted on 2 cycle log paper using the standard samples of NaF. The μgF^- /ml is plotted on log scale and the relative mV is plotted on linear scale. A straight line should be obtained when plotted. From this graph, the relative mV readings from the unknown samples are converted to μgF^- /ml. The values of μgF^- /ml are then used to calculate the Wt. % fluorine concentration.

Linear regression utilizes a calculator programmed to do the above. The owner 's manual tor a calculator with this capability should be consulted tor operating instructions for determining the calibration curve and reading sample concentration values from it.

When using values below 0.5 ppm F^-, a more advanced "Second Order" mathematical formula is required, or you may use a graphing technique.

Calculations

$$\text{Weight \% Fluorine} = \frac{\mu gF^-/ml \text{ (from graph or linear regression) (100 ml) (2) x 100}}{\text{Sample Weight in mg x 1000}}$$

Where: 2 = dilution factor (1 ml TISABII: 1 ml of sample solution from the bomb made up to 100 ml)

$$\text{Weight\% Fluorelastomer} = \frac{\text{Weight\% Fluorine}}{\text{\% of Fluorine Contained in the Fluorelastomer}}$$

Discussion

Cations and most anions do not interfere with the response of the fluoride electrode to fluoride. Anions commonly associated with fluoride, such as Cl^-, Br^-, I^-, SO_4^{-2}, HCO_3^-, NO_3^-, $PO4^{-3}$ and acetate, do not interfere with electrode operation. The OH^- ion is 1 electrode interference. See pH effects in the Orion Instruction Manual for Fluoride Electrode Models 94-09, 96-09. Some anions, such as CO_3^{-2}, or PO_4^{-3} make the sample more basic, increasing the OH^- interference, but are not direct electrode interferences. See Orion Instruction Manual, Fluoride Electrodes, Model 94-09-00, Model 96-09-00, Interferences, pH Effects.

A tenfold change in concentration of the standards (0.5 to 5 and then 5 to 50) should give a 54 - 60 mv (at 20°-25°C) difference in readings. This is an indication of how well the electrode is functioning and should be checked each time you use the electrode. If the value is not close for each of the two increments, i.e., within 1-1.5 mv, the "slope" is not acceptable, and the electrode may not to be accurate. Or, if the readings are drifting, you should refer to the electrode manual.

Samples should be at the same temperature as the standards when reading with the electrode. A 1°C difference in temperature will give rise to about a 2% error.

Concentrated samples or samples over 0.1 in total ionic strength should be diluted before measurement. The electrode should be stored in a 1 ppm F^- solution of TISAB II/distilled water (1:1). The electrode should always be thoroughly rinsed and blotted dry with a clean dry tissue between measurements to prevent solution carry-over.

At the lower levels of fluoride (1 ppm) the electrode response times are longer. It is recommended to expand the measuring time to allow a "stabilized" reading (≤0.1 mv/15 sec.). It is also recommended that you expand the measuring time by 1/2 minute when making your first measurement, after the electrode has been standing in the 1 ppm F^- TISAB II/water (1:1) solution.

Also, a meter reading of 0.1 mV is recommended for better precision. A 1 mV change corresponds to a 4-8% change in concentration. Better precision can also be obtained if the samples and standards are stirred during measurement.

Every time a new solution of buffer is prepared, a set of new standards must also be prepared from that buffer. It is not necessary to prepare fresh standards daily if the proper care is taken.

Proper use and care of the fluoride electrode is essential for obtaining accurate measurements. When properly calibrated, the electrode measurement will reproduce to 2%.

Problems of corrosion, pitting and poor electrical contact with the standard stainless-steel electrodes can be minimized by replacing them with nickel electrodes.

References

Orion Instruction Manual for Fluoride Electrode Models 94-09, 96-09

Orion Research – Analytical Methods Guide, Ninth Edition, December 1978.

Quality Control Test Method, Specialty Chemical Division, 3M Company, QCM #53.19% Fluorine by Parr Oxygen Bomb Combustion and Fluoride Specific Ion Electrode.

Commercial Chemicals Analytical Laboratory Methods #F-12-0480, #F-17-0382 and F-18-1 082

Total Fluorine Analysis of Carpet Fibers – Oxygen Flask Technique (3M Commercial Chemicals Division Interlaboratory Collaborative Study).

Request for Analytical Work - #21924 – 3M Commercial Chemicals Analytical Laboratory

Analytical Report #529 - 3M Commercial Chemicals Analytical Laboratory

Instructions and Methods for Parr Oxygen Bombs, Parr Instrument Company Manual No. 148.

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