

Purge Gas Effectiveness for Removal of O₂ from Thermo-gravimetric Analyzers

A number of materials and procedures are useful to determine the effectiveness of an inert purge gas to replace oxygen from a thermogravimetric analyzer (TGA). A big question is how "oxygen free" must TGA be? This depends on the type of experiment being conducted. Most commercial TGAs are constructed to be "oxygen" free in the sense of oxidation of hydrocarbons or polymers. Absolutely oxygen free is something else. The presence of oxygen can be tested with inexpensive materials and a well planned experiment.

Carbon Black (Activated Charcoal)

Carbon black oxidizes to carbon dioxide at high temperature. Carbon black isothermally heated at temperatures above 700°C will oxidize and lose weight in the presence of O₂. Little or no weight loss indicates an effective purge with an inert gas and that a system is not leaking oxygen. Results will vary depend on the instrument and the type of carbon black used. A good goal would be a loss of 0.1 micrograms per minute or less for a well-plumbed TGA. An advantage for carbon black is that it is inexpensive. An older sample is preferable since extremely reactive sites would be passivated. Any type of crucible can be used with carbon black. Mass losses of micrograms per minute suggest a leaking system. It is interesting to watch long isothermal experiment to determine just how long purging may be necessary to eliminate trace oxygen from the instrument. You can also use an isothermal experiment to determine if a high initial purge rate can reduce the overall purge time to essentially eliminate oxygen from the system. Purging a system up to 15 minutes at a high flow rate before beginning the experiment can reduce oxygen levels more quickly.

Oxidizable Metals

A more stringent test might use oxidizable metals, such as, Ti, Zr or W in fine powder form. Fine metal powders, however, may be inhalation and explosion hazards especially anywhere near an open flame.

Another option for checking oxygen presence uses copper oxalate. Copper oxalate loses oxalate at about 325°C leaving finely divided fresh (salmon pink) particles of copper on the sample pan. These particles are sensitive to oxidation. The high surface to volume ratio of the fine particles and the fresh copper surfaces enhance sensitivity to oxygen. While copper oxalate is somewhat difficult to find commercially, it does not have sample preparation and repeatability challenges of carbon. Pure powdered copper can be used to monitor weight gain or copper (II) oxalate hemi-hydrate can obtain from Alfa/Aesar in the USA.

High Initial Flow Rates

High initial flow rates are especially useful to minimize oxygen. Rates up to 300 mL per minute for up to 30 minutes may be necessary between runs for critical work. Thermo balances with a lot of corners where air pockets can remain may require even higher rates and longer times especially when first changing over from air or oxygen to an inert gas. Each time the furnace is opened, this compartment must be re-purged. Opening the furnace only as long as necessary reduces purge times.

If a system seems to continue leaking oxygen, verify that O-rings and connectors are properly seated. Use high purity gas. Use metal tubing transfer lines if possible, such as stainless steel or metal flex tubing. Use Mass flow controllers with swagelok connectors instead of rotameters. Install a heated gas purifier at the inlet if possible. If the maximum temperature is low enough and there is some space in the TGA furnace, some copper windings or a metal sponge in a corner can scavenge O₂ during the analysis.

Calcium Oxalate Flow Rates

Another indicator is a calcium oxalate "validation" run. The product should be gray after heating to ~1000°C. On cooling, if the material turns white you have a leak.

Leaks

To obtain the highest levels of oxygen purity, polymer tubing used in the purge gas feed system should be replaced with clean stainless-steel tubing. Virtually all polymer tubing is permeable (at some level) to oxygen and so low levels of oxygen permeate into the system. Copper tubing should be avoided because it usually is oxidized resulting in the possibility that oxygen will come off the surface into the purge gas.

Other Oxygen Sources

Do not use ceramics such as alumina anywhere in the TGA oven. Alumina off gases O₂ as the furnace warms up and reabsorbs O₂ when the oven cools and is open to the atmosphere.