

Safety Bulletin – Methanol + Boron Tribromide

1. Overview of Incident

A researcher had used a set of syringes to transfer boron tribromide (+99%). Once the transfer was complete, the syringes (and associated needles) still contained a small amount of BBr₃. In an attempt to make the residual reagent safe, the material inside the syringes was quenched with methanol.

Approximately 200 mL of methanol was placed in a plastic beaker and was drawn into one of the syringes containing the unreacted BBr₃. At this stage, it was noted that the needle had become blocked. The researcher applied pressure to the plunger to displace the blockage and returned the "quenched mixture" to the beaker of methanol. At this point, a brief flash of light was observed, however, no immediate problem was evident.

After a few minutes, the plastic beaker containing the methanol was observed to be melting although the reason for this was not immediately clear. The methanol was transferred to a glass beaker, however, by this time the plastic beaker continued to melt and small flames could be observed. The researcher alerted their colleagues who were able to help place a fire blanket over the plastic beaker and extinguished the fire.

It appears the reaction between methanol and BBr₃ caused the methanol to ignite and melt the beaker. The flames of the methanol fire could not be observed in the well-lit laboratory. A video showing the difficulties in observing a methanol fire can be seen in the following video.

Methanol flame video: https://www.youtube.com/watch?v=1ZEEuCHdWFA

2. Lessons Learned

During the accident investigation, several lessons were identified for future improvement.

2.1 Use of Safer Alternatives

This experiment involved the use of "neat" boron tribromide (99+%). BBr₃ is also sold as 1M solutions in dichloromethane or hexanes. These commercial solutions may be less aggressive when being quenched, representing a safer alternative. It may not be practically feasible to substitute in all cases, but this should be considered.

2.2 Quenching Procedure

Drawing methanol (or other protic solvent) directly into the syringe containing unreacted material should be avoided. The use of methanol as a quenching agent is also not recommended as it is difficult to see the flames if a fire develops.

As an alternative approach, residual reagents can be diluted with an inert solvent, transferred to a flask held under nitrogen/argon, cooled in an ice bath and quenched sequentially with isopropanol and water.

Bretherick's Handbook of Reactive Chemical Hazards also suggests that small quantities of boron tribromide can be quenched by being cautiously added to large volumes of ice-water.



Whilst not immediately related to the incident, it is prudent to remind researchers that it is often cheaper and safer to dispose of unwanted pyrophoric materials through a waste contractor as opposed to quenching the reagent in-house.

2.3 Use of Plastic Container for Quenching Operations

Plastic containers should not be used to quench reagents. If a fire develops, the container may fail and result in an uncontrolled release of a burning, flammable solvent. A suitably heat-resistant container should be used for such operations.

