

Safety Incident Report (5/20/16)

Glovebox Regeneration Odor in FRNY 3140 and Subsequent Building Evacuation

Background

Gloveboxes are used to provide an inert atmosphere for air and moisture sensitive chemicals. A major part of our research is amine-thiol mixtures, both of which are odorous, especially the thiols. The human nose can easily smell thiols in the part per billion range. The gloveboxes have a molecular sieve solvent trap to remove solvent vapors from the glovebox atmosphere, as well as a molecular sieve/copper catalyst oxygen/moisture trap to remove oxygen and moisture from the glovebox atmosphere. Both traps need to be regenerated after a given amount of time (every 2 weeks for the solvent trap, and every 2-3 months for the oxygen/moisture trap). Regeneration of the solvent trap is performed by heating up the trap and purging with inert gas (nitrogen) in cycles over ~16 hours. Regeneration of the oxygen/moisture trap is performed by heating the trap, flowing a 5% hydrogen, 95% nitrogen mixture over the catalyst, and then purging with inert gas. This performed in a number of cycles over ~16 hours.

Description of Incident

On May 19, 2016, the solvent trap had been regenerated, which proceeded as normal. On May 20, the regeneration of the oxygen/moisture trap was started. This had been running for about 3 hours when a member of the custodial staff entered the lab and encountered an extremely strong smell. They contacted the Fire Department; on arrival they detected low levels of H₂S, CO, and VOCs and pulled the fire alarm. The emergency personnel returned to the lab later, but detected nothing in the general lab atmosphere. The H₂S readings were likely false readings caused by other sulfur containing compounds such as thiols. For the last 3 years of glovebox use, a strong odor was observed during regeneration, however, during this incident, the odor was likely much worse. The major cause was later identified to be a broken flow meter, which leaked the exhaust of the oxygen/moisture trap into the room. A bypass is installed to prevent the flow meter from being in contact with the solvent vapors in the glovebox atmosphere; however, this was not used during this particular regeneration cycle.

Causes and Issues

Major

The major cause of this incident was the failure of the flow meter. The flow meter gets contaminated because it is located after the catalyst. This is for two reasons: (i) it makes sure that gas is flowing through the catalyst bed, and (ii) it acts as an indicator of the condition of the catalyst (by Mbraun technician). Normally, the flow meter can stand for several regeneration runs and it will stop working if it is not compatible with exhaust gas. Therefore, a bypass for the flowmeter was installed on the setup. On this particular regeneration, the user installed a new flow meter, but wanted to see the condition of the catalyst (check color in the flow meter) after regeneration, thus did not switch to the bypass valve. Due to the heavy amines, thiol usage of the glovebox, and glovebox troubleshooting and maintenance work caused an abnormally long (one and a half month) interval between the last solvent trap regeneration, the catalyst absorbed a higher amount of aggressive solvents that was thought to be able to be removed by the solvent filter trap before the catalyst. During regeneration, the sulfur, oxygen, and chlorine compounds are heated and may react with H₂ gas to generate acid gas (such as H₂S, H₂SO₃, H₂SO₄, HCl etc.) As the exhaust gas passed through the flowmeter, it reacted with the flow meter and dissolved it, leading to a gas leak in the room.

Minor

There could have been some other sources of gas leaks which might have played a role...

Permeability of tubes and Condenser Trap - Some portion of the tubing used to carry the regeneration exhaust gas is composed of Teflon coated PVC, which has some gas permeability.

Delay in regeneration process - Ideally, solvent trap regeneration is completed every two weeks. On this occurrence, it was delayed by four weeks as the delivery of one of the connections needed for the catalyst regeneration process was delayed. The solvent trap became saturated, so some of the solvents were instead absorbed by the catalyst.

Improper procedure when using solvents - The solvent trap cannot trap certain solvents (like amines, thiols, phosphorous, halides), and it can only trap certain aromatic organic solvents and aliphatic organic solvents. Therefore, amine and thiol solvents migrate to the oxygen moisture trap, poisoning the copper catalyst. Ideally, no solvent should be absorbed by the catalyst in the oxygen/moisture trap.

Insufficient communication of Glovebox regeneration - The group was notified via email several days in advance of the pending regeneration. However, there was no sign on the door to notify the custodial staff about this. Additionally, the doors were not locked due to user error.

Changes Made to Prevent Future Incidents

A number of changes were made to address the causes:

- The damaged flow meter was replaced as soon as it was discovered
- The oxygen and moisture catalyst was replaced on all gloveboxes in all of our labs.
- The SOP was modified such that the usage of solvents is more in line with the capabilities of the glovebox's solvent trap. Some of the SOP modifications are:
 - The bypass flow meter procedure is added in the catalyst regeneration section.
 - A door sign is required during both catalyst and solvent filter regeneration.
 - Turn off the catalyst-glovebox circulation or use quick purging if necessary during some lab procedures, to avoid overloading of catalyst with solvent vapors.
 - Chemicals that are not oxygen/moisture sensitive won't be stored in the glovebox.
 - Volatile thiol, amine, phosphorus, and halide solvents must be placed in a sealed secondary containment vessel to avoid damaging the catalyst.
 - Keeping an accurate inventory (log sheet) of solvent storage and usage was implemented for each glove box.
 - Regenerations will be performed during the day so that lab members are present to monitor the status of the regeneration and address any issues that may arise
- All the polymer tubing on the exhaust lines were replaced with stainless steel tubing to mitigate the permeation of the exhaust gas into the room.
- A new condenser trap made from glass was ordered and will be cooled using ice water, dry ice, or liquid nitrogen in order to prevent condensation in the elephant trunks.
- Heating tape will be placed on exhaust lines before the condenser trap to prevent any liquid from condensing there.
- The final exhaust line from the condenser trap to the elephant trunk was redesigned to minimize the amount of tubing before exhaustion.
- The modifications including new catalyst, exhaust lines, condenser trap, and heating tape were also made to another glovebox in the lab that also uses volatile solvents.

These changes should significantly reduce, and hopefully eliminate, any smell that previously occurred during regeneration.

Lessons Learned

- Thoroughly read the equipment manual provided by the manufacturer. While these manuals can be lengthy and dull, they often contain valuable information that might otherwise be overlooked. In our case, the manual suggested that quick purging be used when large amounts of solvent vapor may be present. We had not been doing this, causing an unnecessary load on our solvent trap, and also exposing the oxygen/moisture trap catalyst to be poisoned by sulfur containing solvents.
- Make sure to keep the SOP up to date. In our case, the flow meter bypass was neglected, causing the failure of the flowmeter and the subsequent release of exhaust gas into the lab. This bypass procedure was not included in the SOP.
- Just because something has been common practice does not mean it is the correct practice. We had always had very strong odor during both solvent trap and moisture/oxygen trap regeneration; however, eliminating the source of this smell should have been addressed much earlier.
- General lab SOPs, such as the lock up policy, need to be reviewed periodically with lab members. Additionally, all lab members need to have the cell phone number of the PI.

Brief Timeline of Incident

Friday 05/20/2016

4:00 pm - Glovebox super users begin the regeneration process for the GB1/GB2 catalyst.

7:40 pm - Custodian enters lab, smells odor, leaves immediately and calls fire department.

8:00 pm - Fire department arrives, enters lab, takes readings. Fire alarm is pulled by emergency personnel and building is evacuated.

8:15-9:30 pm – The primary contact for FRNY 3140 listed on the door post is called by the emergency responders and arrives to campus shortly. Other safety officers arrive later.

10:00 pm – Glovebox super user asks the fire officer to turn off the H₂/N₂ regen gas supply by turning off the H₂/N₂ regen gas cylinder valve. Emergency responders put on hazmat suits and enter laboratory. Officer turns off the N₂ tank feeding the glovebox instead of H₂/N₂ cylinder, which caused the regeneration process to pause. Laboratory readings are at zero.

10:30 pm - Emergency responders enter laboratory again to confirm zero readings.

11:15 pm - Emergency responders check level of CO, H₂S and VOCs in building hallways and reopen the building, except FRNY 3140.

Monday 05/23/2016 - REM officers inspect FRNY3140 along with Dr. Gabriela Nagy, glovebox superusers and group safety officers and confirm zero readings. The lab was reopened for all lab users. Safety officers keep lab closed for 2 more days due to unpleasant odor. During these two days there is ongoing inspection and discussion regarding how to solve problems in glovebox.

Wednesday 05/25/2016 – Safety officers clear the lab for general lab use (no unpleasant odors)

Friday 05/27/2016 - Solar group members along with Prof. Agrawal investigated the causes of this incident, and identified the broken flowmeter, which was replaced with a new one immediately.

Monday, 6/13/2016 – The catalysts for all the gloveboxes were changed to new ones and the exhaust lines were replaced with stainless steel tubing. Most of the volatile amine and thiol solvents were moved from the gloveboxes.

Tuesday 06/14/2016 - The SOP was updated.

Monday 06/20/2016 - All lab members were trained on the new SOP and gloveboxes were back to normal operation.