# Standard Operating Procedure

**Task:** Working up reactions containing nickel and carbon monoxide (quenching $Ni(CO)_4$)
**Date:** 6/30/2018

**Background**

- This SOP is recommended for any reactions containing nickel carried out under a CO atmosphere, conditions under which $Ni(CO)_4$ may be generated. The procedure utilizes methods that should destroy any $Ni(CO)_4$ that might have formed.
- $Ni(CO)_4$ is an extremely toxic liquid. The toxicity of $Ni(CO)_4$ is even greater than CO. Its LC50 for a 30-minute exposure has been estimated at 3 ppm, and the concentration that is immediately fatal to humans would be 30 ppm. Nickel carbonyl may be fatal if absorbed through the skin or more likely, inhaled due to its high volatility; *its boiling point is only 43 ˚C*.
- CO is an odorless, colorless, tasteless, poisonous gas. The permissible exposure limit (PEL) for CO set forth by OSHA is 50 ppm for eight hours. The immediately dangerous to life or health (IDLH) value set forth by the US National Institute for Occupational Safety and Health (NIOSH) is 1200 ppm. *However, if any amount of CO is detected in the laboratory, steps must be taken to stop the leakage and potential exposure to CO.* Detectors must be worn to avoid possible intoxication due to leaks. CO detectors vary in their limits of detection, but 0-500 or 0-1000 ppm are typical ranges. These detectors will have different alarm thresholds for different amounts. Values of 35 ppm will trigger a warning and typically values >50 ppm will trigger a danger alarm.

**Training Requirements:**

- Lab safety training
- Multireactor training
- Working with CO training

**Potential Hazards:**

- Exposure to extremely toxic $Ni(CO)_4$ and CO.
- Injuries from failure of pressurized gas cylinder
- Backfilling glassware cooled in liquid nitrogen will condense >50 atm CO. Injuries may result from a possible explosion upon expansion of the gas.

**Special PPE Requirements:**

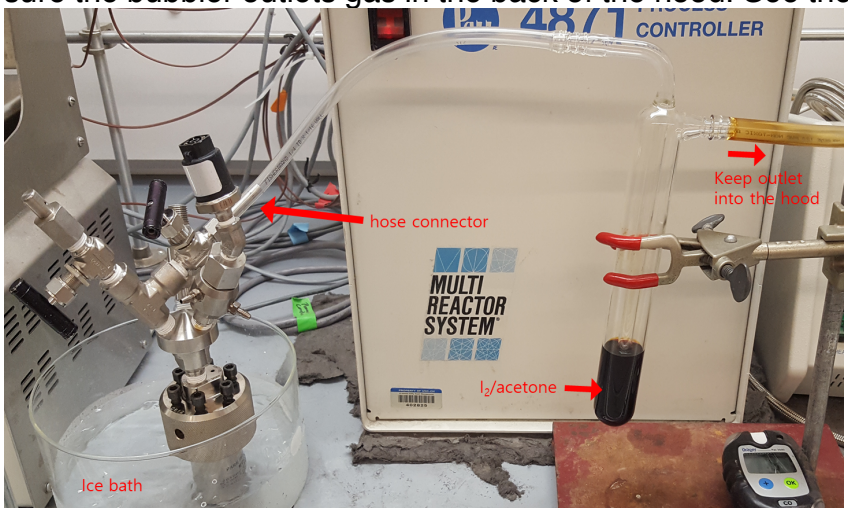
- CO detector

**Materials Needed:**

- CO detector
- Reactor vessel holder
- Schlenk line
- Bubbler
- Allen wrench

**Procedure:**

- Turn on the two CO detectors. Affix one to your lab coat, and the other in the hood.
- Set up reaction as described in Multireactor Parr MRS5000 SOP.
- Once the reaction is finished, stop heating and allow the vessel to cool close to room temperature before taking further action – See "Ending the reaction" in Multireactor Parr MRS5000 SOP for the details.
- Cool the reactor in an ice bath.
- Attach a hose connector on the vent line of the reactor. Set up a bubbler filled with $I_2$/acetone solution (100 mg of $I_2$ in 50 mL acetone) and connect it to the vent line of the reactor. Make sure the bubbler outlets gas in the back of the hood. See the image below.




- Vent the vessel through the bubbler in a hood by *slowly* opening the needle valve in the vessel head. *Fast opening may cause bumping of the reaction mixture or $I_2$ solution, more seriously damaging this setup and gas leak.* Close sash as much as possible to avoid any CO exposure.
- Close the needle valve when pressure is released. Disconnect the bubbler.
- ***Workup to analyze organic products only:***
  - Cool the reactor to –78° using dry ice/acetone bath.
  - Remove the reactor head and *immediately add excess amount of triphenylphosphine* (at least 10 equiv. to the Ni content).
  - Work up the reaction as required.
- ***Workup that separates volatile and non-volatile products (best for analysis of transition metal complexes):***
  - This procedure uses vacuum evaporation to trap the volatiles.


- Set up a vacuum trap between the vent valve of the reactor and the vacuum line. See the image.
- Evacuate the line up to the vent valve and ensure appropriate vacuum.
- Cool the trap with liquid nitrogen.
- Transfer organics into the liquid nitrogen trap by applying vacuum (slowly opening vent valve). This step may be time consuming depending on the solvent and chemicals used/produced. Plan accordingly.
- Close all the valves and detach the liquid nitrogen trap.
- Add *excess amount of triphenylphosphine* (at least 10 equiv. to the Ni content) to the trap as it thaws.
- Work up the organics in the trap as required.
- Work up the contents of the reactor vessel as required. On the bench, simply remove the reactor head and work up as required. Alternatively, the vessel can be pumped into the glovebox for workup under inert atmosphere.

**References and Related SOPs:**

- Working with CO SOP
- Tetracarbonylnickel in Encyclopedia of Reagents for Organic Synthesis https://onlinelibrary.wiley.com/doi/pdf/10.1002/047084289X.rt025m
- Nickel Carbonyl Acute Exposure Guideline Levels https://www.nap.edu/read/12018/chapter/13
- Multireactor Parr MRS5000 SOP
- Setting up trap SOP
- Vacuum Transfer SOP