

Working with chemicals

February 2023

General

- Arbo & Milieu Dienst (AMD)
 - contact for safety and Dutch labor laws (ARBO) at the University
 - AMD email address: amd@science.leidenuniv.nl
 - AMD website for information and contact persons can be tricky to find:
 - For staff members:
 - Go to universiteitleiden.nl
 - Click Staff members
 - Select unit: Science, Leiden Institute of Physics
 - Search for 'Working in a lab'
 - For students:
 - Go to universiteitleiden.nl
 - Click Students
 - Choose your study programme
 - Search for 'Safety'
- BSc, MSc students and interns form a special group of employees for Dutch labor law. They always work under the supervision of a PI, PhD or Postdoc
- High risk work is never allowed outside working hours 8.00-17.00
 - High risk works should not be done by BSc students
 - Working with HF is only allowed after following a specific HF safety instruction
 - Working with HF is only allowed with a buddy who has also followed the HF safety instruction

General

- Emergency telephone number is 4444 from a lab telephone and 071-5274444 from a mobile phone
- Never transport dangerous goods such as chemicals in the normal elevator; use the stairs or the dedicated freight elevator
- Always wear closed shoes and long trousers in the lab
- Report incidents via the incident report form, to the responsible technician and your supervisor
- All beakers, flasks, bottles, etc. containing chemicals must be labelled when left unattended.
The label should contain: substance name, user name, starting time and end time.
- We give a standard cleanroom safety training for cleanroom users, after this training you are allowed to work in the cleanroom and use the standard organic solvents: Acetone, Ethanol and Iso-Propanol (IPA)
- If you're planning to work with chemicals, consult with your daily supervisor if there is a work protocol and get familiar with the work protocol. Consult with the responsible lab technician how you are going to perform the experiments in the lab.

Work protocol

1. Purpose and application
2. Hazards
 - a. Look up hazards in a Material Safety Data Sheet
 - b. Make a Task Risk Analysis
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment
6. Workplace, storage of chemicals and waste
 - a. Workplace
 - b. Storage of chemicals
 - c. Waste
7. Cleaning up
8. Work procedure
9. First Aid and Emergency Procedures
 - a. What to do in case of:
 - i. Eye contact
 - ii. Skin contact
 - iii. Inhalation
 - iv. Ingestion
 - v. In case of a spill
 - vi. In case of fire

Purpose and application

1. ***Purpose and application***

2. Hazards

3. Incompatible chemicals and materials

4. Equipment, chemicals and supplies

5. Personal Protective Equipment (PPE)

6. Workplace, storage of chemicals and waste

7. Cleaning up

8. Work procedure

9. First aid and emergency procedures

What is the goal and application of the process you are performing?

Can you use an alternative safer process?

E.g. removing organic residue can be done with Piranha, but often also with oxygen plasma cleaning which is less dangerous

Can you make the process safer?

E.g. we had been working with a 48% HF solution for many years to prepare our substrates. We found a 14% HF solution to work too and the results were indistinguishable. Using a lower concentration HF solution greatly reduced the risks

1. Purpose and application, Chromium etching:

Etching 50nm sputtered chromium from a fused silica sample with wet etching.

Use pre-mixed chromium etchant, no safer alternatives known. Dry etching not suitable for 50nm thickness since it will etch through the PMMA mask.

Hazards

1. Purpose and application
2. **Hazards**
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Write down all hazards associated with the process

- Read the Material Safety Data Sheet (MSDS) of the chemicals you wish to use. A CAS number is a unique identification number of a chemical, with this number you can find the MSDS
- Often the supplier of the chemical will provide an MSDS on their website
- Write down Hazard and Precaution sentences from MSDS
- Ask experts or experienced users for help
- Look up legal information on maximum allowed values. Rules are different per country, make sure to check the Dutch law
<https://www.ser.nl/nl/thema/arbeidsomstandigheden/Grenswaarden-gevaarlijke-stoffen/Grenswaarden>

2. Hazards, Chromium etching:

1. Purpose and application

2. Hazards

3. Incompatible chemicals and materials

4. Equipment, chemicals and supplies

5. Personal Protective Equipment (PPE)

6. Workplace, storage of chemicals and waste

7. Cleaning up

8. Work procedure

9. First aid and emergency procedures

- SDS retrieved from supplier Sigma Aldrich
- Hazardous components in Chromium etchant are:
 - Diammonium hexanitratocerate, CAS 16774-21-3
 - Nitric acid, CAS 7697-37-2
 - We could look up both hazardous components separately, but Sigma Aldrich provides a SDS specifically for this mixture
- write down H and P sentences from section 2 in the SDS
- Hazard statement(s)
 - H272 May intensify fire; oxidizer
 - H290 May be corrosive to metals
 - H314 Causes severe skin burns and eye damage
 - H317 May cause an allergic skin reaction
 - H411 Toxic to aquatic life with long lasting effects
- Precautionary statement(s)
 - P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking
 - P220 Keep/Store away from clothing/ combustible materials
 - P260 Do not breathe dust/ fume/ gas/ mist/ vapours/ spray
 - P280 Wear protective gloves/ protective clothing/ eye protection/ face protection
 - P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
 - P370 + P378 In case of fire: Use dry powder or dry sand to extinguish

Hazards

Task Risk Analysis

Risk (R) = E x B x W		
> 400	Very high risk	stop work!
200 – 400	High risk	directly take measures
70 – 200	Important risk	directly take measures
20 – 70	Possible risk	directly take measures
< 20	No risk	no more measures needed

Effect			Exposure frequency (B)		Probability (W)		
40	Disaster	several deaths	10	Continuous	10	Expected	>50%
15	Very serious	One dead	6	Regularly	6	very well possible	10-50%
7	Serious	Invalidity	3	Once in a while	3	unusual	1%
3	Important	injury with sick leave	2	Sometimes	1	Unlikely but possible	0.1 %
1	Limited	injury without sick leave	1	Seldom	0.5	Thinkable but unlikely	0.01%
			0.5	Very seldom	0.2	Practically impossible	0.001%
					0.1	Nearly unthinkable	0.0001%

1. Purpose and application

2. **Hazards**

3. Incompatible chemicals and materials

4. Equipment, chemicals and supplies

5. Personal Protective Equipment (PPE)

6. Workplace, storage of chemicals and waste

7. Cleaning up

8. Work procedure

9. First aid and emergency procedures

1. Purpose and application

2. **Hazards**

3. Incompatible chemicals and materials

4. Equipment, chemicals and supplies

5. Personal Protective Equipment (PPE)

6. Workplace, storage of chemicals and waste

7. Cleaning up

8. Work procedure

9. First aid and emergency procedures

2. Hazards – Task Risk Analysis, Chromium etching

Action	Hazard	Risk classification				Measures: -source -collective	Measures: -procedures -Instructions -PBM's	Risk classification			
		E	B	W	Score			E	B	W	Score
Pouring etchant in beakers	Spilling etchant on hands and limbs	3	6	3	54	Work in a fume hood	use suitable chemical gloves and lab coat	1	6	3	18
Dipping sample in etchant	Spilling etchant on hands and limbs	3	6	3	54	Work in a fume hood	use suitable chemical gloves and lab coat	1	6	3	18
Cleaning up waste and workspace	Spilling etchant on hands and limbs	3	6	3	54	Work in a fume hood	use suitable chemical gloves and lab coat	1	6	3	18
	Inhaling vapour	3	10	10	300	Work in a fume hood		3	10	0.5	15

Incompatible chemicals and materials

1. Purpose and application
2. Hazards
3. ***Incompatible chemicals and materials***
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Some examples:

- HF should never be used in glass beakers
- Never use plastic tweezers when working with a piranha solution
- Organic solvents can react violently with CrO₃ precursor material

3. Incompatible chemicals and materials, Chromium etching:

From MSDS section 10:

Alkali metals, **Organic materials**, Acetic anhydride, Acetonitrile, **Alcohols**, crylonitrile, Strong reducing agents, Powdered metals

Equipment, chemicals and supplies

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. **Equipment, chemicals and supplies**
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Make a list of needed equipment, chemicals and supplies

- Determine which tweezers are suitable for your process
- Use a small amount of chemicals. Do not use the large containers for daily work, prepare a small work supply. If possible order small pre-mixed containers

4. Equipment, chemicals and supplies, Chromium etching:

- pre-mixed chromium etchant
- 5 glass beakers
 - 1 for etchant
 - 1 for demi-water with clean sample
 - 3 for rinsing and diluting
- spray bottle with demi-water
- timer
- clean* carbon fibre tweezers

Personal Protective Equipment (PPE)

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. **Personal Protective Equipment (PPE)**
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Make a list of needed PPE

- Glasses
 - Use suitable safety glasses, they are available in every chemical lab
 - People with prescription glasses need to wear overlay safety glasses.
- Gloves
 - Check chemical resistance and break down time
 - More info on gloves from the AMD
- Lab coat
- Other
 - Sleeve protection
 - Dust mask
 - Apron
 - ...

5. PPE, Chromium etching:

- ❑ lab coat
- ❑ shieldskin chem neo nitrile 300 gloves
 - ❑ 122 min for 70% nitric acid
 - ❑ tested gloves in MSDS are 0.11mm nitrile. These gloves 0.25mm nitrile

we will be working in a fume hood, hence we only need these PPE

Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Workplace

- You should know where to find:
 - shower
 - eyewash
 - fire extinguisher
 - lab telephone
 - emergency exit
- Where are other people on the floor? Do you know these people? Do they know you? Are they experienced?
- Do not call 112 for help, always use the internal emergency number, 4444 from a lab phone, 071- 527 4444 from a mobile phone.

Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Workplace - Fume hood

- What should always be done in the fume hood:
 - Toxic chemicals
 - Carcinogenic chemicals
 - Mutagenic chemicals
 - Teratogenic chemicals (substances that may cause birth defects)
 - Reproductive toxic chemicals
 - Explosion risk chemicals
 - Strong acids and bases
 - Stench/strong odor processes (e.g. thiols)
 - Volatile chemicals with low exposure limit -> calculate VHI
 - $VHI = SVP / WEL$, ratio between saturated vapor pressure and workplace exposure limit
 - If vapor pressure is high (easily evaporates) and exposure limit is low (dangerous substance) VHI is high
 - <https://www.icheme.org/media/9860/xix-poster-02.pdf>
- Fume hood does not only offer vapor protection, but also splash protection
- Using a fume hood can be a good idea if you want to leave your process unattended overnight

Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Workplace - Using the fume hood

- Set fume hood window to correct/indicated height
- Ensure that the fume hood exhaust is on and the flow indicator is green (only applicable to newer fume hoods)
- Fume hood is not a storage place for chemicals
- Leave a clear note when leaving stuff behind

6. Workplace, storage of chemicals and waste, Chromium etching:

Workplace: fume hood.

P260 Do not breathe dust/ fume/ gas/ mist/ vapours/ spray

P280 Wear protective gloves/ protective clothing/ eye protection/ face protection

Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Storage of chemicals

- Follow the categories that are used in the chemical cupboard, don't mix categories.
 - Bases
 - Acids
 - Flammable materials
 - Solvents
 - Oxidizing agents
 - Corrosive substances
 - Salts
- Place chemicals in a leak tray
- Chemicals can be stored below the right fume hood in lab HL725 because there is air ventilation. The left fume hood doesn't have a cabinet with ventilation so you cannot store chemicals there!
- CMR substances (carcinogen, mutagen and reproductive toxins) should always be stored in a locked chemical cabinet

6. Workplace, storage of chemicals and waste, Chromium etching:

Storage of chemicals: Store with oxidizing agents in a ventilated cabinet.
H272 May intensify fire; oxidizer. Storage class (TRGS 510): Oxidizing hazardous materials.

Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Waste disposal

Full waste containers and full waste bags are collected in the hallway near the cryogenic department

- General lab waste,
 - tissues, gloves, etc go into the bins with yellow trash bags
- Solid waste
 - solid waste that cannot go into the yellow trash bags (still dangerous)
 - mark the waste buckets with contents and your name
 - solid waste has to be brought to the expedition in the Gorlaeus building
 - solid waste contaminated with nanomaterials needs to be put in a sealed bag into the white buckets to avoid release when opening the container
- Sharp waste
 - into the small yellow containers with red lid
- Glass waste
 - in the proper glass disposal container



Workplace, storage of chemicals and waste

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Waste disposal - Liquid waste

The university works with 5 categories for liquid waste. Liquid waste is collected in 20L jerry cans and are marked with a color on top of the container

- Black – watery solutions $\text{pH} > 5$
- Blanco/no marking – inorganic solution with $\text{pH} < 5$
 - 2 exceptions (HNO_3 and H_2CrO_4), use a suitable container and collect separately
- Red – organic solvents without halogens
- Blue – organic solvents with halogens
- Green – oil and grease waste



markering **ZWART**

waterige oplossing $\text{pH} > 5$
>50% waterig vloeibaar afval dat verontreinigd is met gevaarlijke stoffen



markering **BLANCO**

waterige oplossing $\text{pH} < 5$
mengsels van anorganische zuren met uitzondering van salpeterzuur en chroomzuur



markering **ROOD**

organische oplosmiddelen
mengsel van >50% halogeenaarne organische oplosmiddelen



markering **BLAUW**

organisch halogeenvrij
mengsels van halogeene (Cl, Br, F, I) bevattende organische oplosmiddelen



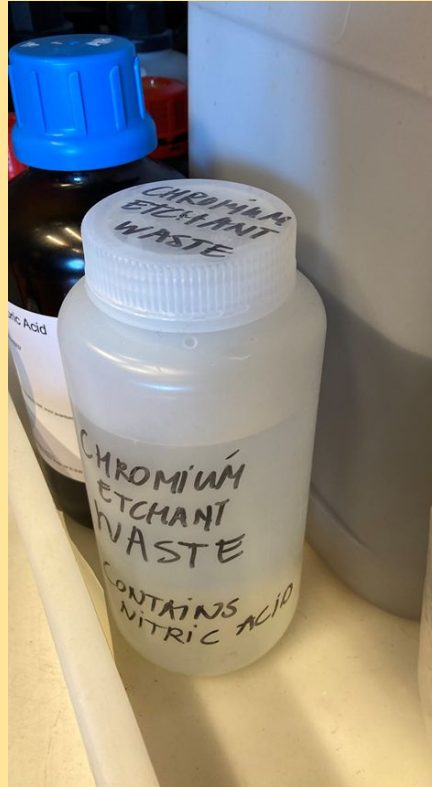
markering **GROEN**

Olie en vet uit werkplaatsen
Alle afval van smeeroliën en vetten van werkplaats en lab-apparatuur

6. Workplace, storage of chemicals and waste, Chromium etching:

Waste has to be collected separately since it contains nitric acid, HNO₃.

Use chemical resistant HDPE bottles for the waste. Mark contents of bottle clearly. Bring waste to expedition.



1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. **Workplace, storage of chemicals and waste**
7. Cleaning up
8. Work procedure
9. First aid and emergency procedures

Cleaning up

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. **Cleaning up**
8. Work procedure
9. First aid and emergency procedures

Always clean your workspace directly after use!

- Rinse dirty beakers a few times with water, this water also has to be disposed as chemical waste
- Wash you beakers and other tools immediately when you're done
- Clean up you work space

7. Cleaning up, Chromium etching:

No special clean up needed, make sure fume hood is empty.

E.g. for bio-samples you might need to disinfect your workbench afterwards.

Work procedure

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. **Work procedure**
9. First aid and emergency procedures

Write down step by step what you are going to do. Use the TRA you made

- For a high risk process it is worthwhile do to a test run without the dangerous substances
- Having a buddy around can be really useful to have an extra pair of hands
- If you need to leave chemicals for a longer period, make sure this is not a threat to other people and always **label** precisely which chemicals you are using.
The label should contain: substance name, user name, start time and end time

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. **Work procedure**
9. First aid and emergency procedures

8. Work procedure, Chromium etching:

1. get demi-water from 10th floor
2. clean fume hood from all organic residue
3. make sure no alcohols are in the fume hood
4. make sure waste bottle is within reach
5. prepare beaker with etchant, put etchant back in chemical cabinet
6. prepare 4 beakers with demi-water
7. dip sample in etchant for xx minutes (determine etch time based on chromium thickness)
8. remove sample from etchant and dip in first beaker, then dip in second beaker, lastly the third beaker and swirl sample around
9. put sample in clean demi-water beaker
10. clean tweezer
11. remove sample and dry with n2
12. collect all liquids from beakers in waste
13. rinse beakers and collect dirty water in waste, put waste container back in waste leak tray
14. clean fume hood
15. clean beakers with detergent

First aid and emergency procedures

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. ***First aid and emergency procedures***

What to do in case of emergency?!

- Call the emergency number 4444 with a lab phone, or 071-527 4444 with a mobile phone and look for help
- If there is a victim, look for help, then help the victim
- Write down for your process what to do in case of
 - Eye contact
 - Skin contact
 - Inhalation
 - Ingestion
 - In case of a spill
 - In case of fire

First aid and emergency procedures

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. ***First aid and emergency procedures***

Eye contact

Check specifically for your chemicals!

In general:

- Call for help asap
- Use the eyewash for at least 15 min, we have small bottles in each lab for a quick rinse
- If the BHV is there with a mobile eyewash, use that one
- If you run out of eyewash, use demi-water (or if not available, use tap water)

Skin contact

Check specifically for your chemicals!

Rinsing with water is often the correct way as a first measure.

Inhalation

Check specifically for your chemicals!

Bringing the victim to fresh air is often the correct way as a first measure.

First aid and emergency procedures

1. Purpose and application
2. Hazards
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment (PPE)
6. Workplace, storage of chemicals and waste
7. Cleaning up
8. Work procedure
9. **First aid and emergency procedures**

Ingestion

Check specifically for your chemicals!

In case of spill

Check specifically for your chemicals!

- Each chemical can require specific materials for clean-up! E.g. cleaning up Piranha spills with regular tissues can result in a fire.
- In case you get chemicals on your gloves
 - Remove the contaminated glove wrist-first and carefully pull it inside-out
 - Hold it in the non-contaminated hand and pull the other glove over it
 - Dispose as solid chemical waste
- In case you get a lot of chemicals on you, use the showers in the hallways

In case of fire

Check specifically for your chemicals!

- Activate the fire alarm
- Be aware of the risk to stay close to a fire, this quickly gets dangerous!

9. First aid and emergency procedures, Chromium etching:

1. Purpose and application

2. Hazards

3. Incompatible chemicals and materials

4. Equipment, chemicals and supplies

5. Personal Protective Equipment (PPE)

6. Workplace, storage of chemicals and waste

7. Cleaning up

8. Work procedure

9. **First aid and emergency procedures**

- General info from MSDS
 - Consult a physician. Show the safety data sheet to the doctor in attendance.
- Eye contact
 - Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.
- Skin contact
 - Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Consult a physician.
- Inhalation
 - If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.
- Ingestion
 - Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.
- In case of a spill
 - Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations. (Wet-brushing is just cleaning up with wet paper towels, contaminated towels have to go in the solid waste afterwards).
- In case of fire
 - Suitable extinguishing media: Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Recap

1. Purpose and application
2. Hazards
 - a. Look up hazards in a Material Safety Data Sheet
 - b. Make a Task Risk Analysis
3. Incompatible chemicals and materials
4. Equipment, chemicals and supplies
5. Personal Protective Equipment
6. Workplace, storage of chemicals and waste
 - a. Workplace
 - b. Storage of chemicals
 - c. Waste
7. Cleaning up
8. Work procedure
9. First Aid and Emergency Procedures
 - a. What to do in case of:
 - i. Eye contact
 - ii. Skin contact
 - iii. Inhalation
 - iv. Ingestion
 - v. In case of a spill
 - vi. In case of fire