

Preparation of samples for analysis in SEMLAB

Basic Imaging:

Images are generated from the emission of secondary electrons (SE), or of back-scattered electrons (BSE) from the sample. For imaging in a scanning microscope, the sample should be moisture and contaminant free, and should have a conductive surface. The conductivity is important for two reasons: 1) With a non-conductor, electric charge builds on the sample surface. This can result in a very bright surface effect which can obscure surface characteristics, and can also deflect (via electro-static repulsion) the electron beam from its intended target location. Both interferences result in a much poorer resolution. 2) Under the electron beam's influence, secondary electrons, which are liberated within the first 50 nanometers of the sample, make their way via elastic and inelastic collisions to the sample surface. If their energy exceeds the surface work function, they can escape the surface and are "counted" by the SE detector to assign a grey-scale to the pixel being scanned. The lower the conductivity, the greater the amount of energy the SE must have to escape (resulting in fewer SEs reaching the detector). To overcome this problem, it is possible to vapor-deposit a nano-thin layer of a conductive metal on the sample surface which results in a reduction of the work function (allowing more SEs to escape the surface), and also eliminates the surface charging which degrades imaging and causes deflection of the electron beam. The reason that the sample should be moisture free is because the analysis is conducted in a sealed chamber under high vacuum; the moisture "boils" off and creates a diffuse gas layer above the sample, which causes beam dispersion and very poor imaging. The physical morphology of the sample can also suffer as the moisture leaves the structure.

If the sample(s) to be imaged are non-conductive, or poorly conductive, SEMLAB has a sputter-coater which can deposit a user-defined thickness of a platinum-palladium alloy on the sample surface to avoid these effects. Facility users should consider the conductivity characteristics of their samples to evaluate the need for coating when planning an analytical session.

Surface charging has less of an effect on images compiled from back-scattered electrons, but the resulting BSE images typically have less resolution than the SE images. Where secondary electrons produce the highest quality images, the BSE images are useful in visually highlighting the differences in density within domains in the sample matrix.

Some semi-moist samples can be imaged using differential vacuum, where the electron source (the Schottky Emitter) is maintained and protected in a very hard vacuum by an objective aperture while the chamber pressure is allowed to increase to a maximum of 150 Pascals. This partial pressure in the chamber allows a reduction in surface charging as the charge can be carried away by the rarified-but-conductive atmosphere within the instrument. As a consequence of the partial vacuum, beam dispersion again becomes a factor and results in a much poorer resolution image and a reduced magnification range. Note that a special SE detector... the

LVSTD detector, must be used when operating at reduced vacuum since the rarified atmosphere in the chamber will allow arcing from the attractor plate to the SE detector window. The LVSTD has a built-in turbo-molecular pump to reduce pressure at the detector face to prevent burnout.

Although a larger sample (up to 100 mm) can be accommodated within the chamber, samples are typically reduced to ~ 10 mm and are carbon-mounted onto aluminum stubs which then can be analysed in groups of six without venting the instrument. It is helpful if the samples are approximately the same height to avoid collision with the objective while working a short working distances. In cases where the sample is cast in mounting/polishing resin, the maximum thickness of the resin should be about 8 – 10 mm, and the mould diameter should be either 1” or 1 ¼” across. The mold, resin, and polishing equipment is located in EME 1215. The aluminum mounting stubs, the carbon sticky tabs and the metal sputter-coater are all available in the SEMLAB facility, where the final preparation for analysis is conducted.

EDX Elemental analysis:

For elemental analysis, the instrument uses an Oxford X-Max silicon-drift X-ray detector. When the electron beam strips an inner shell electron from a constituent element in the sample (inner-shell ionization), a transition of an outer-shell electron to fill the inner-shell void occurs. The energy difference between the two orbitals is emitted as an X-ray photon which is unique to the electronic structure of the element being probed. Prior to analysis, the detector is calibrated against pure copper, establishing the instrument response and the reference position of the emission peaks in the energy spectrum. Therefore, knowing the energy of the emitted X-ray, we can ascertain the identity of the emitting element. All X-ray emissions between 0 and 20,000 electron volts are recorded and displayed as an energy spectrum, where each emission peak is assigned to its respective element, and the total counts normalized to 100%. Thus, elemental concentrations are reported as a percentage of the total X-rays received, with a quantitation limit of 0.1% of the total counts.

EDX analyses suffer from the same interferences as when imaging; analysis works best when the sample is conductive, or coated with a thin conductive metallic layer. For coated samples, the analytic program employs a complex algorithm which accounts for the absorbance and re-fluorescence (XAF) of emitted X-rays by other elements in the sample. By defining the thickness and density of the coating material, the X-rays produced by the coating alloy, and its interference with X-rays from resident elements can be de-convoluted and eliminated from the quantitation output. Please note that the XAF algorithm is predicated on having a perfectly smooth and perfectly flat sample surface... the further the sample deviates from smooth/flat (rough surfaces, powders, etc.), the resulting quants become less reproducible and reliable.

In the case of resin-mounted ceramic or metal samples, the 1 or 1 ¼” resin block should be no greater than 10 mm thick. After mounting the sample in a SEM holder, a strap of copper tape is positioned across the edge of the imbedded sample and grounded firmly to the aluminum holder. A thin coat of platinum-palladium alloy is sputtercoated over the entire sample to eliminate charging. These preparations are conducted in the SEMLAB facility. Methodologies for the automated equipment in EME 1215 for cutting, mounting and polishing samples for EDX, are compiled at the end of this descriptive.

EBSD Crystallographic analysis:

For crystallographic analyses, the instrument uses a Nordlys “Fast” Electron Back Scattered Diffraction detector. In this mode, a finely polished crystalline sample (usually resin mounted) is mounted at 70 degrees from the horizontal on an extended mount. Using geometric transformations to correct for the 70° orientation, a high energy, high current beam is focussed on the sample. If the angles of the crystal lattice satisfy Bragg’s Law, the electrons will be channelled along the crystal lattice and form a diffraction pattern (Kikutchi pattern) on a phosphorescent screen in front of a high speed camera. The pattern represents the physical properties of the crystal; the thickness of the Kikutchi bands corresponds to the thickness of the inter-lattice spacing, and the angles of the band interceptions corresponds to the angles of lattice intersection. If fully optimized with a well prepared sample, the instrument can obtain full elemental data, and by transformation of the Kikutchi patterns, can identify the crystal phase, grain size and crystal orientation at a rate of up to 400 scans per second.

In the case of EBSD, sample preparation is the key to fast and reliable analyses. Past experience has shown that diamond-polished samples are typically too rough to generate or reliably index Kikutchi patterns. Limited success has been reported for samples carefully polished with colloidal silica; however the best results are derived from samples which have been electro-polished.

The electropolish technique used for EBSD preparation depends on the material to be analysed. Struers produced a list of 12 different electrolytes, each specific to a particular metal or alloy group. A complete list of these electrolytes and their constituents are included at the end of this descriptive.

NOTE: Do not attempt to use any of the sample preparation equipment without authorization and training. Under NO CIRCUMSTANCES should users try to mix electropolishing electrolytes without authorization and supervision. Some reagents are EXTREMELY HAZARDOUS !!

Struers CitoPress – Hot Mounting Press

The Struers CitoPress is a hot mounting device. It allows for fast and clean mounting of samples.

Mounting Resin

Two different resins are available at the SPSL laboratory: MultiFast and ConduFast.

Multifast is a thermosetting Bakelite resin. This standard resin is to be used in most of the cases.

ConduFast is an acrylic based conductive resin with iron filler. This resin allows electrolytic polishing of samples

Handy Doser

The Handy Doser is a tool for fast and clean filling of the cylinder with resin. One unit, i.e. one revolution of the wheel, delivers approximately 5 ml. Please check how much resin you need, referring to the table in the lab. Finished specimen should be approximately 8 – 10 mm deep in pressed resin,

Prior to use

Open the water valve: turn the handle on the pipe against the wall behind the polisher.

User interface

The screen displays all the information and settings of the machine. In the main menu you can select “Process”, “Configuration” or “Service”. To perform polishing choose process using the pink ← key. All parameters of the machine are displayed in this menu. Browse and change any parameter you want.

Please note that when starting the machine, it may already be in the “Process” menu.

Procedure of use

Turn the main on-off switch. This switch is located behind the machine, on the right hand side. Bring the piston up with the double arrow yellow key. Apply AntiStick powder on the top of the piston. Place the sample with the face to be studied downwards. Lower the piston using the double arrow key. Fill the cylinder with the adequate quantity of resin. Refer to the parameters sheet to know how much you need. Close the cylinder. There is no need of strength to screw on the cap. If you feel resistance, realign the cap and try to screw it again. Set the heating and cooling parameters. The parameters suitable for your mount are dependent on the resin used and the diameter of the cylinder. Refer to parameter sheet. Before starting, make sure the water is open. Launch the procedure (green key to start). At the end of the mounting, open the chamber. Bring the piston up to liberate the cover and your mounted sample.

Do not forget to turn off water after use. The machine must also be switched off.

Please clean your work plan and the machine. Put everything in its place before leaving the lab.

Struers Tegramin 30 – Automatic Polisher

Struers Tegramin-30 is an automated polisher. It allows polishing up to 6 samples at the same time. The programmable polishing method database ensures a high level of reproducibility during preparation. Built in fluids dispenser saves time and limits the sources of contamination.

The disks

Various disks are available for polishing. Each disk is dedicated to a specific use. Follow the information provided on the polisher's screen. Take care not to interchange two discs otherwise they will become contaminated and must be discarded. Note that the SiC Foils are simply applied onto the MD-Gekko disks.

Fluids

All fluids are automatically dispensed by the polisher. The flows can be adjusted. Low fluid level alerts are part of the system.

Prior to use

Open the water valve, and gas cylinder before you start using the polisher.

Water: Turn the handle on the pipe against the wall behind the polisher

Gas cylinder: The gas bottle is located in front of the window next to the clean room. Open both taps and verify that the pressure regulator is in the range between 600 kPa (87 psi) and 1000 kPa (145 psi).

Do not forget to close them once polishing is over.

Control Panel

All actions are monitored through the control panel and the screen.

- The orange coloured keys control the rotating plate and fluids dispenser. The left-hand button manually starts and stops the rotation of the plate. The second button turns the water on. The water flow can be adjusted with the wheel on the left side of the machine. The third button dispenses diamond paste. The last button dispenses the oxide polishing suspension.
- The sample holder can be moved using the yellow buttons. The top two move the sample holder left and right. The positioning of the sample holder has some importance – the samples must always be placed a few millimetres over the end of the disc to avoid the formation of a ridge on the polishing cloth. The bottom left button lowers or raises the sample holder. The bottom right button turns half the sample holder to facilitate samples pick up.
- The green and the red buttons are used respectively to start and stop the automatic polishing steps. The wheel and esc key are used to browse the on-screen menu and create an automated polishing program.

Struers Tegramin 30 – Polishing Procedure

The main menu allows you to choose between different submenus.

- Note that we always use “single sample methods” even though the sample holder can carry up to 6 samples. For polishing, select your polishing method among the Struers or SPSL’s methods. A personalized methodology can also be created and saved.
- Place your samples in the sample holder and follow the instructions on the screen. Move on any parameter and click it to set. Please check fluid flow during polishing and adjust it. The grinding disk should be moist. Adding too much diamond paste is just a waste. If one step was not satisfactory, you can run it again by moving on it with the wheel and click it.
- Between two polishing steps, wash your samples and the sample holder carefully in the sink. Use water and soap; rub them with cotton balls. Wipe the side of the rotating plate with paper towels to avoid contamination. Do not remove diamond pastes from the disks as it is expensive and is not worn after use.
- After using the oxide polishing suspension wash carefully the cloth. Use the comb to extract as much oxide particles as you can. If this operation is not carried out, the cloth will be ruined when dry.

After use, switch off the machine and wash it. Clean your work plan. Put everything back in place before leaving the lab. Do not forget to close water and gas!

A few reminders:

- 1. Make sure to clean and wipe down the MD Disc after use**
- 2. Always leave last SiC paper on MD Gekko to protect the surface**
- 3. Make sure to always polish off the edge**
- 4. Make sure to wash the 6-sample mover plate between polishing stages and after final polish**
- 5. Clean the Tegramin Tank with one or two litres of water from the sink**

Struers Discotom 6 – Cut-off machine

The Struers Discotom-6 cut-off machine is an easy-to-use cutting machine. It can perform automated cuts with its automatic feeding table. Manual mode is also available.

Cut-off wheels

Two wheels are presently available at the SPSL laboratory. The 40A25 is meant to be used with ferrous materials, while the 10S25 is to be used with non-ferrous materials such as aluminum.

Cooling

Always make sure cooling is working properly during cutting. If no cooling fluid is thrown against the blade, do not cut.

Samples Holders

Various sample holders are available. Make sure to use the one that fits your sample. Take care not to cut the sample holder!

Procedure of use

Turn on the main on-off switch on the saw. The switch is on the right side. Fix your sample on the table. Close the protection guard. The saw cannot be started as long as the protection guard is open. If the machine does not start, make sure the protection guard is well closed.

The green button gets the disc rotation started as well as activates the cooling. In manual mode, just pull the handle to cut your part. In automatic mode, the start button also activates the table advance. In this mode, set the disc height before starting the cut and lock it with the black handle on the right of the machine. Take care to not overtighten the black handle. An “Auto” light notifies whether auto mode is on. Use “Auto” blue button to switch from manual mode to automatic mode and vice-versa. To stop the cutting blade, use the red button.

The speed of the automatic table motion is set by the table feed speed wheel, and can be varied from 0.1 mm/s to 2.5 mm/s. A LED-bar indicates the load placed on the cutting motor; the optimal speed is reached when about 3 led are lit. The table can be moved at anytime with the yellow double arrows buttons. Hitting the wheel with your sample or the table may damage both. Be careful when moving the table.

Please wash machine after each use with flush hose located on the left of the machine. Rotate the black knob prior to washing. After washing, leave the protection guard open to allow for drying. Do not forget to turn the main switch off after use!

Struers Metason 120T – Ultrasonic cleaner

The Struers Metason 120T is an ultrasonic cleaner. It provides a high level of sample cleaning, removing most of the surface contaminants. Sample cleaning using the ultrasonic cleaner is required in the case of difficult cleaning scenarios and to avoid contamination during polishing.

Procedure of use

Place the samples in a container and cover with a liquid. Although DI water can be used, ethanol is a more common cleaning agent and achieves very good results (tap water should NOT be used on your sample). Place the container into the ultrasonic water bath. The water should wet at least 3-5 cm of the container's height as all areas of the sample that are not in contact with water will not be properly cleaned.

The usual cleaning time is 4 to 5 minutes. Once the ultrasonic cleaning is accomplished, it is important to dry the samples with hairdryer or compressed air gun to avoid residual marks on the surface.

List of Electrolytes and suggested uses

A-2	A-3	A-5	A-6
Aluminum Antimony* Beryllium Iron steel stainless steel Nickel Silver Tin Titanium	stainless steel (large areas) Manganese* Molybdenum Titanium Vanadium Zirconium	Lead Uranium Tin	Cobalt Aluminum steel Tin*

A-8	AC-2	B-1	C-1
Chromium Hafnium austenitic steel Nickel Thorium* Titanium*	cast Iron Magnesium low C steel stainless steel Beryllium Nickel	Antimony* Cobalt* Germanium Gadolinium Holmium Magnesium	Cadmium Magnesium Zinc Lead

D-2	E-2	E-5	F-1
Copper brass Gold*	Cerium* bronze brass Gold* Indium* Neptunium*	bronze brass [examination of inclusions] [materials with strongly varying structural elements]	Tungsten hard metal (sintered carbides)

*suggestion for applicable electrolytes – other possibilities exist

RECIPES FOR ELECTROLYTES

Recommended Electrolyte Formulas for use in
Struers Electrolytic Equipment

**NOTE: HAZARDOUS CHEMICALS!!! OBTAIN INSTRUCTION AND
PERMISSION BEFORE PRODUCING THESE ELECTROLYTES**

A-2

90 ml Distilled Water
730 ml Ethanol (Ethyl Alcohol)
100 ml Ethylene glycol monobutyl
ether
78 ml Perchloric Acid

The perchloric acid should be added to the mixture of ethanol, ethylene glycol monobutyl ether, and water immediately before use.

A-3

600 ml Methanol (Methyl Alcohol)
360 ml Ethylene glycol monobutyl
ether
60 ml Perchloric Acid

Like A-2, the perchloric acid should be added immediately before use.

A-5

600 ml Ethanol
180 ml Acetic Acid
32 gm Sodium Hydroxide
27 gm Sodium Acetate Anhydrous
18 ml Distilled Water
90 ml Perchloric Acid

The sodium hydroxide should be dissolved in the mixture of water, acetic acid, and 100ml ethanol. After dissolution, dilute with remaining ethanol. The sodium acetate is added to this solution, which dissolves when the perchloric acid is added just before use.

A-6

120 ml Distilled Water
700 ml Ethanol
100 ml Ethylene glycol monobutyl ether
50 gm Tartaric Acid
78 ml Perchloric Acid

The tartaric acid is dissolved in the mixture of distilled water and ethanol. Add to this solution the ethylene glycol monobutyl ether. Add the perchloric acid immediately before use.

A-7

200 ml Glycerol
700 ml Methanol
100 ml Perchloric Acid

Follow the same mixing conditions for A-2

A-8

950 ml Acetic Acid
50 ml Perchloric Acid

Follow the same mixing conditions as for A-2

AC-2

60 gm sodium thiocyanate dihydrate

(or 41.5 g sodium thiocyanate anhydrous and 18.5 ml distilled water)

75 gm Citric Acid
800 ml Ethanol
100 ml Propanol
10 gm Hydroxychinolin (Known as #8 Hydroxyquinoline)
15 ml Perchloric Acid

Propanol and ethanol are mixed, and the hydroxychinolin is dissolved. After dissolution, the sodium thiocyanate is added. After dissolution, add the citric acid. When the citric acid is added, the liquid turns muddy, but clears again when everything is dissolved and the perchloric acid is added.

If mixing and dissolution are not completed, the citric acid and the sodium thiocyanate in the liquid without perchloric acid will develop a sediment which cannot be dissolved, even after the perchloric acid is added. In this case, the following method must be used:

The hydroxychinolin is dissolved in the alcohol mixture, and then the citric acid. Just before use, the sodium thiocyanate is dissolved in the mixture, after which the perchloric acid is added.

B-1

1000 ml Methanol
10 ml Hydrochloric Acid

To be mixed.

The copper (II) nitrate should be dissolved in the methanol by heating slowly. After cooling, the nitric acid is added cautiously, but not until just before use.

C-1

160 gm sodium thiocyanate (or 110 g sodium thiocyanate anhydrous and 50 ml distilled water)
800 ml Ethanol
80 ml Ethylene glycol monobutyl ether
20 ml Distilled Water

The sodium thiocyanate should be dissolved in the mixture of distilled water and ethanol. Then add the ethylene glycol monobutyl ether.

D-2 - Corrosive

500 ml Distilled Water
250 ml Phosphoric Acid
250 ml Ethanol
50 ml Propanol
5.0 gm Urea

To be mixed.

E-2

300 g Copper (II) Nitrate
900 ml Methanol
30 ml Nitric Acid

E-5

400 gm Cobalt (ii) Nitrate
40 gm Iron (III) Nitrate
4.0 gm Urea
140 gm Tartaric Acid
900 ml Methanol, pure
140 ml Propanol
120 ml Acetic Acid
200 ml Ethylene glycol monobutyl ether

Methanol and Propanol are mixed, and then the tartaric acid is dissolved in the mixture. Then the cobalt nitrate, iron nitrate, and the urea are dissolved. Then the acetic acid and ethylene glycol monobutyl ether is added.

F-1

20 gm Sodium Hydroxide
1000 ml Distilled Water

The sodium hydroxide should be dissolved in water.

Chemicals required for electrolyte manufacture: (NOTE: Be sure to request Material Safety Data Sheets when ordering the chemicals).

CAUTION: For all solutions containing perchloric acid, a bi-distillation of the solvents must be avoided otherwise there is a risk of violent explosion.

GET INSTRUCTIONS... READ THE MSDS !!!!!

Acetic Acid:	99% CH ₃ COOH Sp. gr. 1.055
Ethylene glycol monobutyl ether:	Ethylene Glycol Monobutyl Ether, CH ₃ (CH ₂) ₂ CH ₂ O CH ₂ CH ₂ OH
Citric Acid:	(COOH) CH ₂) ₂ COH COOH, H ₂ O
Cobalt (II) Nitrate:	CO (NO ₃) ₂ , 6 H ₂ O
Ethanol:	Ethanol 96% vol. CH ₃ CH ₂ OH, sp. gr. 15 ⁰ /15 ⁰ 0.81
Glycerol:	about 85% HOCH ₂ -CHOH-CH ₂ OH, sp. gr. 1.23
Hydrochloric Acid:	about 36% HCl, sp. gr. 1.19
Hydroxyquinolin Ortho:	C ₉ H ₇ NO-Also known as No. 8, Hydroxyquinoline
Iron (III) Nitrate:	Fe (NO ₃) ₃ 9H ₂ O
Methanol:	100% CH ₃ OH
Nitric Acid:	ABT. HNO ₃ , sp. gr. 1.40
Perchloric Acid:	60% HCl ₄ , sp. gr. 1.54
Phosphoric Acid:	Ortho Phosphoric Acid 84%, H ₃ PO ₄ , sp. gr. 1.70
Propanol:	Propanol 100% CH ₃ CH ₂ CH ₂ OH
Sodium Acetate Anhydrous:	Propanol 100% CH ₃ CH ₂ CH ₂ OH
Sodium Hydroxide:	NaOH (pellets)
Sodium Thiocyanate:	Sodium Sulphocyanide NaSCN, 2 H ₂ O or Anhydrous
Tartaric Acid:	(CHOH-COOH) ₂
Urea (Carbamide):	CO (NH ₂) ₂
Distilled Water:	H ₂ O