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### **Section 3. Polishing Guidelines**

The objective of polishing the electrode is to remove the redox reaction products that accumulate during some experiments. The rate of electrode coating (and corresponding decrease in responsiveness) depends on:

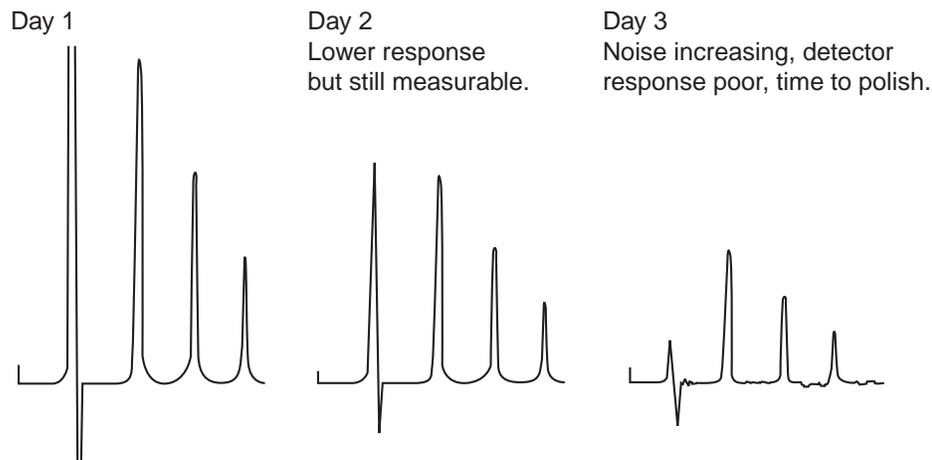
1. The analyte molecule
2. The concentration of the analyte molecule
3. The composition of the electrolyte solution (including pH)
4. The applied potential
5. The frequency of use

Electrodes used in liquid chromatography may last for several months without repolishing in some applications. LCEC has the advantage of using a flowing stream which helps to remove redox products, and deals with much lower concentrations of analytes than does voltammetry. Electrodes also can accumulate material by adsorption from the atmosphere. For example, components in cigarette smoke and aerosols of various compositions can affect electrode performance. Silver is easily oxidized under such conditions and should be carefully repolished to remove oxides prior to use.

There are many rumors and horror stories about electrode polishing. There are also some home-made polishing recipes that we specifically discourage. The use of concentrated acid is one. Use of jeweler's rouge, toothpaste, Aunt Ruth's fruitcake (vintage 1972) and other abrasive compounds should be fervently avoided. Many of these home remedies do not work and may harm the electrode. One thing is certain: The need for polishing varies dramatically with the application.

There are many potential causes for that "glitch" or noise in the baseline. Don't routinely conclude that polishing the electrode will cure all. As a rule, polishing is justified when you see a gradual decrease in the response of the electrode (Figure 3.1). You can live with decreased response if you are still able to quantitate the peaks of interest and if you periodically inject a set of standards. In many cases, a light buffing of the working electrode surface with a methanol-soaked lab tissue is all that's needed to restore the electrode. Try this first! If such a treatment improves the response only slightly, then the use of polishing abrasives is the next logical step.

Figure 3.1. Example of gradual decrease in the responsiveness of an electrode, indicating the need for polishing.



A series of one to three abrasives is used for polishing, progressing from coarser materials to very fine polishes used on soft-surfaced pads. The polishing process should remove a negligible amount of electrode material. In most cases, a single abrasive is used to lightly erode the surface and physically remove the contaminants. Precious metal electrodes or chemically modified electrodes (e.g., gold/mercury amalgam) tend to require a series of two or three abrasives to restore the original mirror-like finish.

All polishing steps require *extensive rinsing* and flushing of the electrode before moving on to the next stage. Without this washing, minute particles from the previous polishing step will be carried over and will hinder the progression towards smaller-sized particles of abrasive. Plastic squeeze bottles with thin nozzles are best for rinsing. Fill one with clean, distilled water for rinsing alumina polish. Fill another with methanol for rinsing diamond polishes. Label the bottles.

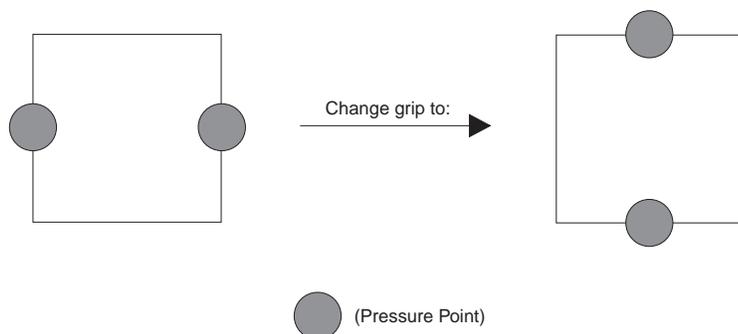
A major concern of polishing is that you do not erode the softer electrode below the surface of the surrounding plastic or glass. This can be avoided by polishing the electrode on a hard flat surface. Follow the general guidelines in Section 3.1 when handling your working electrode.

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### 3.1 General Guidelines for Polishing Electrodes

1. It is important to use the polishing materials provided by BAS and to follow the recommended procedure. The polishing kit provided with your BAS instrument gives you all materials needed for all polishing procedures. Individual polishes, pads, or the entire kit can be purchased separately.
2. Before use, shake all bottles of polishing slurry well to ensure that all the grit is evenly suspended.
3. Only one grade of polishing slurry is to be applied to the pad; that is, use a different pad for each polishing step. Do not add fresh polishing compound to pads once a particular polishing step has been initiated; add sufficient slurry at the beginning. If additional lubrication is required, add water to the pad.
4. While most individual nylon (white) polishing pads may be reused, the fine grit polishing pad (black to dark gray in color) should be used one time only. If used more than once, excess scratching may occur due to the spaces between the grit being filled in with PEEK, causing a deeper pressure scratch to occur.
5. The diamond slurries (15- $\mu\text{m}$  blue, 6- $\mu\text{m}$  orange, 3- $\mu\text{m}$  yellow, and 1- $\mu\text{m}$  gray) have an oil base, so a methanol or acetone flush of the electrode is required.
6. The pads have self-adhesive backs and are less likely to rise off the glass when wetted if applied to the glass plate the previous day. Clean the glass plate with methanol first. Then peel the pad and push down from the center out to the edge so no air pockets are trapped between pad and plate (so no high spots are produced). Label each plate for the appropriate grade of slurry to be used.
7. Moisten the pads with distilled water a few minutes prior to use. This will aid in breaking up any clumps of grit that were not rinsed off from a previous use. The excess polishing grit should always be rinsed off the pads after use to lessen the chances of clumping. Large clumps of grit will excessively scratch the gold and PEEK.
8. Rinse all surfaces of the electrode block free of any polishing compound (grit). Since the polishing schedule progresses from coarse to fine, it is very important not to mix large and small particle sizes.
9. Polish the electrode on pads attached to the heavy glass plates provided in the polishing kit. Hold the electrode surface as parallel to the surface of the glass as possible. This is especially important with voltammetry electrodes and will ensure that the surrounding plastic is not worn unevenly.

- Moving the block in a figure-eight pattern is optimal for uniform polishing. However, an alternating clockwise/counterclockwise motion is also acceptable. During all polishing steps, apply even pressure to the electrode block. This may be accomplished by alternating the position on the block to which you are applying pressure:



- Never attempt to remove the actual electrode material from the supporting plastic. This will destroy the electrode.
- Do not heat the electrode when drying. Allow it to dry at room temperature. Any heating of the electrode should be attempted with caution due to the difference in the coefficients of expansion of the electrode and the supporting plastic or glass.

### 3.2 Polishing Glassy Carbon, Silver, or Nickel

Remove a new microcloth disk from the polishing kit. (Microcloth is brown and has a soft, velvety texture.) Peel away the backing to expose the adhesive, and attach the disk to the glass plate. Use a permanent marker to label the glass with the type of polishing fluid used. It is possible to reuse the disks several times, but it is important to use the same type of polish each time. Your label will remind you which polish you used. Now follow these steps (refer to Figure 3.2):

- Rinse the electrode surface with water to flush away any encrusted material on the surface. Follow this with a methanol rinse. Wipe dry with a fresh lab tissue.
- Wet the disk surface with clean DISTILLED water. Shake the alumina suspension and add several drops of alumina polish, spacing them evenly around the pad surface.
- Place the electrode face down on the pad. Using a smooth, circular motion, and even pressure, move the electrode all over the pad. By reversing the polishing direction and rotating the electrode  $90^\circ$  at regular intervals, you will prevent uneven wear of the electrode. After 1–2 minutes, remove the electrode and rinse it well with DISTILLED water.

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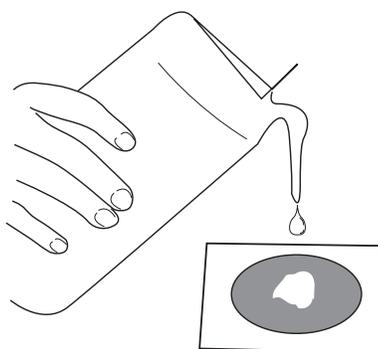
There are many rumors and horror stories about electrode polishing. There are also some home-made polishing recipes that we specifically discourage. The use of concentrated acid is one. Use of jeweler's rouge, toothpaste, Aunt Ruth's fruitcake (vintage 1972) and other abrasive compounds should be fervently avoided. Many of these home remedies do not work and may harm the electrode. One thing is certain: The need for polishing varies dramatically with the application.

There are many potential causes for that "glitch" or noise in the baseline. Don't routinely conclude that polishing the electrode will cure all. As a rule, polishing is justified when you see a gradual decrease in the response of the electrode (Figure 3.1). You can live with decreased response if you are still able to quantitate the peaks of interest and if you periodically inject a set of standards. In many cases, a light buffing of the working electrode surface with a methanol-soaked lab tissue is all that's needed to restore the electrode. Try this first! If such a treatment improves the response only slightly, then the use of polishing abrasives is the next logical step.

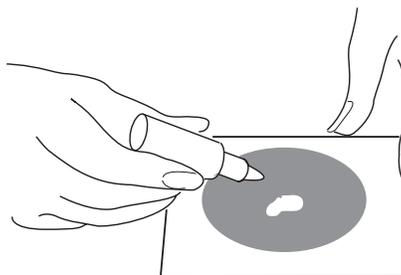
4. Electrodes may be sonicated to remove residual abrasive particles. Immerse the electrode *surface* in a *shallow* amount of DISTILLED water in a beaker that has been placed in the water of a low-power (150 watts or less) ultrasonic cleaner. Sonicate for no more than 5 minutes (longer periods may overheat and damage the electrode). Rinse again with distilled water from the squeeze bottle and shake off the remaining water.
5. Rinse the electrode briefly with methanol and wipe it dry. The electrode is now ready to use.
6. Do not touch the electrode surface with your fingers, or place the surface in contact with sharp objects or other materials which could scratch it.

Figure 3.2. Polishing steps for glassy carbon, silver, or nickel.

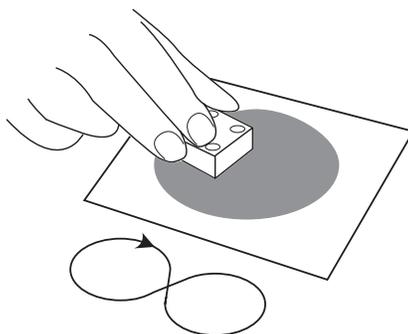
#### Wet Polishing Pad Before Adding Polish



#### Add a Small Amount of Polish to the Wet Pad



#### Use Smooth Motion and Even Pressure when Polishing



### 3.3 Electrochemical Cleaning of Platinum

Often, the gradual loss in electrode response is due to slow oxidation of the electrode surface. Sometimes, the redox chemistry depends on the presence of certain catalytic moieties on the surface which must be regenerated. This process can usually be performed electrochemically, without disassembling the cell. For many applications, the need to use an abrasive polish on a platinum electrode is rare.

Alternate the polarity of the working electrode by setting the potential to 500 mV and switching the polarity switch between (+) and (-). Perform at least 10 cycles, pausing at each potential for a few seconds. Return the potential to the desired value and test the response with a standard solution.

If the response does not improve, disassemble the cell and polish the electrode with a methanol-soaked lab tissue. Use firm pressure. Rinse the block with methanol and reassemble. Proceed to the next section only if the response is still too low compared to earlier performance.

### 3.4 Polishing Platinum and Pure Gold

Remove a new microcloth disk from the polishing kit. (Microcloth is brown and has a soft, velvety texture.) Peel away the adhesive back and attach the disk to the glass plate. Next, remove a nylon disk from the kit. (Nylon disks are white with a tight, woven texture.) Peel away the backing to expose the adhesive, and attach the disk to the OPPOSITE side of the glass plate. There are rubber feet on both sides of the glass so you can use both sides without having to place the polishing surface on your benchtop.

Label each side of the glass with the type of polishing fluid used. Use the brown microcloth with alumina polish, and the white nylon pad with the diamond slurry polish. It is possible to reuse the disks several times, but it is important to use the same type of polish each time. Your label will remind you which polish you used. Shake polishing slurries thoroughly before using. Now follow these steps:

1. Rinse the electrode surface with water followed by methanol to flush away any encrusted material on the surface. Gently wipe dry using a fresh lab tissue.
2. Wet the white nylon disk with DISTILLED water and apply a few drops of the 1- $\mu$ m diamond polish slurry (MF-2054).
3. Place the electrode face down on the pad. Using a smooth circular or figure-eight motion and even pressure, move the electrode all over the pad. Reverse direction and rotate the electrode 90° at regular intervals to prevent uneven wear of the electrode. After 1–2 minutes, remove the electrode and rinse away all remaining polishing grit with methanol, using a squeeze bottle.
4. Next, turn over the glass and wet the microcloth disk surface with DISTILLED water. Shake the alumina suspension and add several drops of alumina polish, spacing them evenly around the pad surface.
5. Place the electrode face down on the pad. Polish as in step 3 above. After 1–2 minutes, remove the electrode and rinse well with DISTILLED water.
6. Electrodes may be sonicated to remove residual abrasive particles. Immerse the electrode *surface* in a *shallow* amount of DISTILLED water in a beaker that has been placed in the water of a low-power (150 watts or less) ultrasonic cleaner. Sonicate for no more than 5 minutes (longer periods may overheat and damage the electrode). Rinse again with distilled water from the squeeze bottle and shake off remaining water.
7. Rinse the electrode briefly with methanol and wipe dry. The electrode is now ready to use.
8. Do not touch the electrode surface with your fingers, or place the surface in contact with sharp objects or other materials which could scratch it.

### 3.5 Polishing Amalgamated Gold

Gold amalgam electrodes consist of a solid gold disk that has been covered with a thin mercury film. When the mercury is gone, the gold must be repolished in several steps. In certain applications where a gold amalgam is used, the mercury is critical to the electrochemical reaction. In determination of thiols, for example, the R-SH complexes with mercury to form a product which is then oxidized. This process will tend to gradually strip away the mercury film. When the electrode performance deteriorates, you can initially try to revive the electrode by reapplying more mercury. A gold tinge is often noticeable on the surface of the working electrode when the electrode loses responsiveness.

To apply more mercury, clean the surface of the electrode with distilled water and wipe it with a methanol-soaked lab tissue. Follow this with more squirts of methanol and then air dry. Add new mercury. This procedure will often buy some extra time before a full repolishing is required. To fully repolish a gold amalgam electrode, follow the instructions in Section 3.5.1.

The final performance of thin-film mercury amalgam electrodes is very dependent on the finish of the gold substrate. A smooth, mirror-like finish produces the best results. A combined acid/abrasive procedure will achieve that goal. The acid treatment quickly removes residual mercury from the electrode surface. The grit pad and diamond polishes do the majority of the polishing, and the alumina polish burnishes the gold back to a shiny appearance in preparation for reapplication of the mercury.

***Note for Previous Users of Gold Electrodes:***

In early BAS polishing kits, used with Kel-F (white plastic) electrodes, we included a coarse grit polishing pad for use with gold electrodes. This pad had the texture of fine sandpaper and was used for a light initial polishing. In 1990, this pad was discontinued when BAS changed to PEEK plastic (light brown) electrodes. The use of the coarse grit pad caused excessive and deep scratches in both the electrode body and the gold surface, which were not easily removed by subsequent polishing steps. We have now reintroduced a grit pad (MF-1043) for initial polishing of gold PEEK electrodes. Note that this is a different pad than the coarse grit polishing pad previously sold for use with Kel-F electrodes. This dark gray (or black) pad, when thoroughly wetted with water, will produce a uniform surface on gold electrodes that can be further polished to a mirror finish.

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### 3.5.1 Polishing Gold Electrodes in PEEK

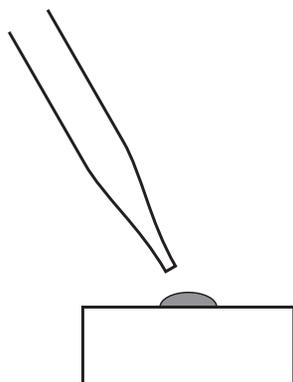
Refer to Figure 3.3 when following this procedure.

**NOTE: Always remove residual mercury film using 6 N HNO<sub>3</sub> prior to polishing!**

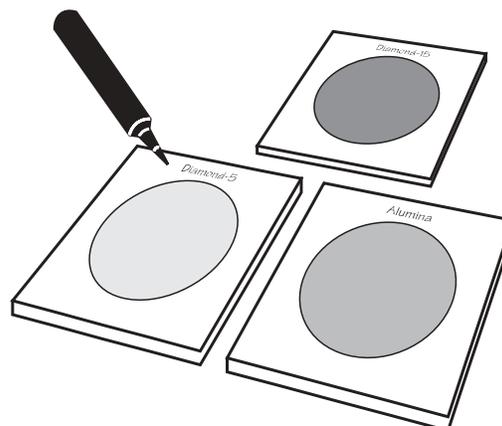
1. Rinse the electrode surface with water followed by methanol to flush away any encrusted material on the surface. Shake off the liquid and wipe the surface dry with a lab tissue.
2. Prepare for the next step using the normal precautions required when working with strong acids. Wear rubber gloves, safety glasses, and an apron, and work under a fume hood.
3. Using a pasteur pipette, apply a few small drops of 6 N NITRIC ACID (HNO<sub>3</sub>) to the electrode surface. When the color changes from grayish-black to rusty yellow, the old amalgam has been destroyed. Repeat with a second drop of 6 N nitric acid. *Do not use concentrated acid*, which will damage the plastic. After the color turns, rinse thoroughly with water and proceed.
4. Use the fine grit pad (dark gray) wetted with copious amounts of water. Polish for 5 minutes or less, until the gold appears to be of an even matte texture. The mercury has removed some of the gold, so the electrodes are recessed. The PEEK must be removed (polished away) to expose the gold electrodes to the polishing schedule. This is a critical step, so slight overpolishing is preferable to underpolishing. The gold must be exposed to the subsequent polishing and smoothing steps. Flush all surfaces of the electrode with a stream of DISTILLED water to remove grit. Clean electrode with sonication as in step 9. Use the fine grit pad only once and then discard.
5. Apply a few drops of 15- $\mu$ m diamond slurry (blue) to a water-moistened nylon pad (white). Polish until gold electrodes and PEEK are each of a uniform texture; this should take 3 to 5 minutes. This intermediate polishing step is important to impart a smooth finish to both the PEEK and the gold. As in step 4, overpolishing is preferable. The diamond slurry is oil-based, so flush the electrode surfaces with a stream of methanol, ensuring that all grit has been removed. Sonicate clean as in step 9. Wipe dry.
6. Apply a few drops of 3- $\mu$ m diamond slurry (yellow) to a water-moistened nylon pad (See 3.1, number 3). Polish the electrode for about 2 minutes. Flush and clean the electrode as in step 5. Wipe dry.
7. Apply a few drops of 1- $\mu$ m diamond slurry (gray) to a water-moistened nylon pad. Polish, flush, and clean the electrode as in step 6.

8. Apply a few drops of polishing alumina (white) to a water-moistened nylon pad. Polish for about 2 minutes. Flush all electrode surfaces with a stream of water and then methanol.
9. Stand the electrode on one side in a small beaker (100 mL). Add just enough distilled water to cover the plastic block. Clean in a bath sonicator of less than 150 watts power for 2 minutes. Flush the electrode surface thoroughly and sonicate for an additional 2 minutes. Flush the surface again with water and then methanol.
10. The electrode may be wiped dry and stored, or amalgamated for use. Prior to the addition of mercury, the gold surfaces must be rinsed with methanol and wiped dry.
11. To form the amalgam, place a drop of TRIPLE-DISTILLED MERCURY on the gold electrode. Slightly roll the drop around to make sure that it evenly touches the gold in all places. Wait 5 minutes, then use an index card to push off the excess mercury into a waste vessel. Polish the mercury surface with a lab tissue to produce an even layer.
12. Allow the electrode to rest face-up. If the surface becomes dull in 10 minutes or less, you have removed too much mercury, and your amalgam will be short-lived. If the surface remains shiny after 60 minutes, you have not removed enough mercury, and your baseline will be noisy.
13. Allow new amalgam to rest for at least 6 hours, or overnight. The electrode may be installed on a flowing LC system during this rest period, but do not apply a potential (keep the detector on the STANDBY setting). Plan on waiting overnight before using the detector for assays. If you try to use the electrode before this time, you may get a very high background and a change in electrode response over time.
14. When the electrode is not in continuous use, or you plan to store it for an extended period, remove the mercury film using 6 N nitric acid. Polish the electrode again prior to amalgamation.

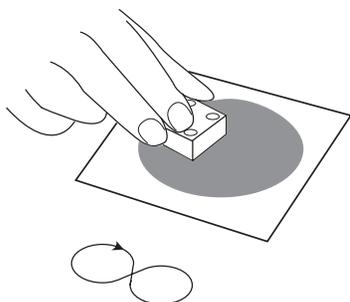
Figure 3.3. Polishing gold electrodes in PEEK (see Section 3.5.1)



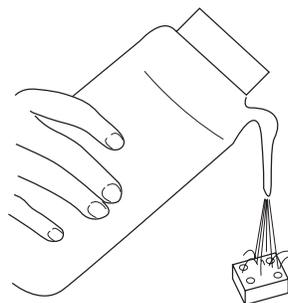
Apply nitric acid with a glass pipette.



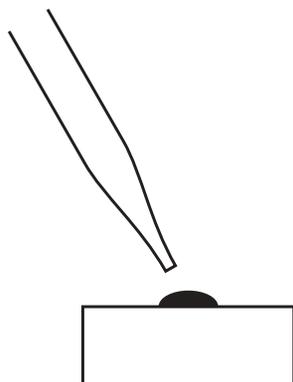
Use fresh polishing pads and label the glass with the type of polishing fluid used.



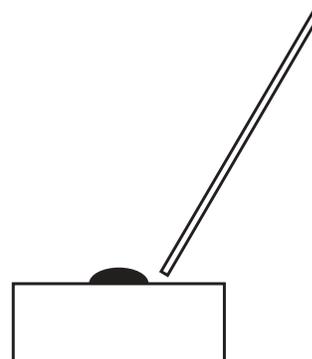
Use a figure-8 motion when rubbing the electrode on the polishing pad.



Rinse electrode frequently and extensively with distilled water.



Apply mercury drop to polished surface.



Scrape off excess mercury with a clean index card.

### 3.6 Preparing Carbon Paste Electrodes

The nice thing about carbon paste is that you don't actually polish it. Instead, you make an entirely new electrode every time. The disadvantage of paste is that it will permanently stain any piece of cloth it encounters. This provides a good excuse for wearing a shirt with a wild pattern that is complementary to abstract, black stains.

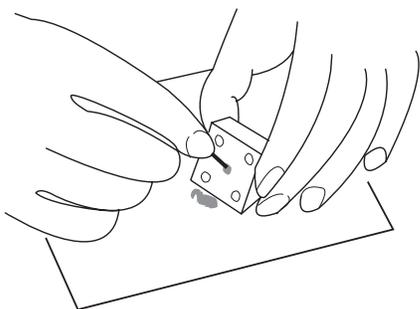
Carbon paste offers several interesting possibilities when studying compounds that are soluble in aqueous media. The electron transfer kinetics of carbon paste are markedly different than those of glassy carbon, and some users feel that the electrode offers slightly better sensitivity in some cases. It cannot be used with a high concentration of organic solvents in the mobile phase since this will erode the surface of the paste. Carbon paste compositions vary widely, including combinations of polyethylene or Kel-F powders pressed with carbon. This discussion is limited to handling of pastes currently manufactured by BAS.

Keep the vial of carbon paste closed when it is not in use. Like other forms of graphite, it can absorb contaminants from the laboratory environment. Refer to Figure 3.4 when following these instructions.

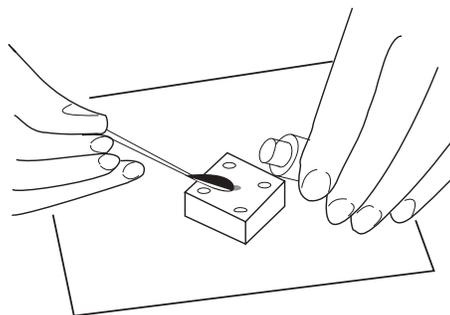
1. With a new electrode block (not previously filled with paste), begin by scooping some paste from the vial and dropping it into the open well(s) in the electrode block. In a thin-layer electrode, each well is attached to a gold connector. In a voltammetry electrode, there is an open hole at the end of the electrode rod.
2. Use the end of a glass rod to tamp down the paste evenly into the well eliminating air spaces. Keep filling and tamping it down until the well is filled with carbon paste and is mounded up slightly above the surface of the plastic block. Don't tamp too hard. You should not be squeezing the paste to the point where it begins to ooze oil.
3. Obtain a smooth, CLEAN card. Large index cards work well. Place the card on a flat, hard surface like a large piece of thick, clear glass or a seamless benchtop.
4. Turn the electrode over and draw it gently across the card, leaving a line of carbon on the paper. Then go to a clean section of the card and move the electrode in tiny, continuous circles on the surface of the card. Move to another section and repeat this until little or no paste is left on the paper surface by this action.
5. Turn the electrode over and inspect it. The surface should be even and smooth with no cracks apparent in the surface. Small dark speckles are normal parts of the paste. If any crack or obvious discontinuity is present, return the electrode to a section of the card marked with paste and continue rubbing it in this section to help fill up the cracks and smooth out the surface.

6. If you have been using an electrode and wish to resurface the paste, simply remove about a millimeter of the paste by wiping it away with a lab tissue. Then proceed by dropping a little lump of paste onto a card, pressing the electrode down onto this lump and proceeding as in steps 4 and 5.

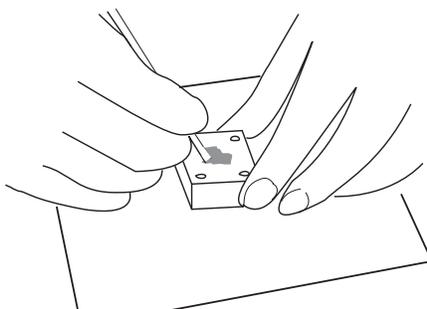
Figure 3.4. Polishing carbon paste electrodes. (See Section 3.6.)



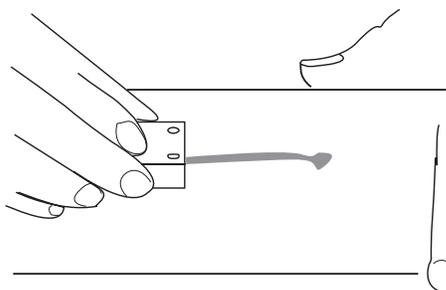
Carefully remove old paste from electrode well.



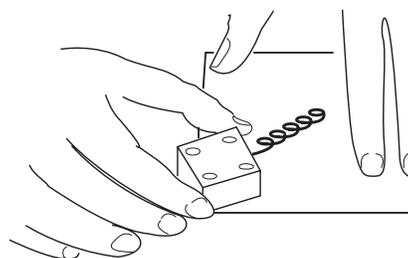
Add a small scoop of new paste to well.



Tamp into well with a small glass rod, leaving a slight mound of paste on electrode.



Rub off excess paste on a clean index card.



Keep moving to a clean area of card and use circular motion to finish polishing the paste surface.

### 3.7 Microelectrode Polishing

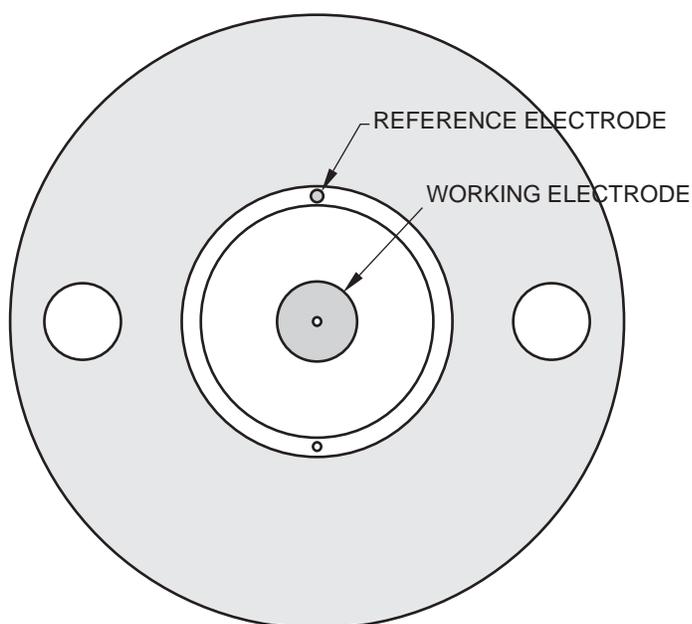
Microelectrodes are repolished using the same general parameters described previously for glassy carbon, gold, and platinum electrodes. Use smaller overall motions for microelectrodes and keep them as vertical as possible to ensure even polishing. Generally, repolishing of 10- $\mu\text{m}$  to 100- $\mu\text{m}$  diameter electrodes requires much less overall polishing time.

### 3.8 Polishing the UniJet Electrode

The surface of the UniJet electrode contains both the working electrode and the silver reference electrode (Figure 3.5). You have a choice of polishing one or both of these electrodes.

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Figure 3.5. Surface of the UniJet electrode.



The working electrode needs polishing only if response has declined and you suspect that the electrode is fouled (as discussed at the beginning of Section 3). The reference electrode needs polishing if response has declined and the bronze-colored coating has worn off. After polishing, the reference electrode must be treated to create the AgCl coating (Section 4.3).

To polish both the working electrode and reference electrode simultaneously, simply follow the instructions for whatever material the working electrode is composed of (Sections 3.1–3.6). Invert the electrode assembly onto the polishing pad so that both electrodes are polished.

To polish either the working electrode or the reference electrode independently, apply the appropriate polishing compound with a wooden cotton-tipped applicator. Use a circular motion for even polishing. Rinse with water, then methanol, and allow to air dry.