Model 303A Static Mercury Drop Electrode
Instruction Manual

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Printed in USA

Advanced Measurement Technology, Inc.

a/k/a Princeton Applied Research, a subsidiary of AMETEK®, Inc.

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This Warranty shall not apply to any instrument, which our inspection shall disclose to our satisfaction, to have become defective or unworkable due to abuse, mishandling, misuse, accident, alteration, negligence, improper installation, or other causes beyond our control. This Warranty shall not apply to any instrument or component not manufactured by Princeton Applied Research. When products manufactured by others are included in Princeton Applied Research equipment, the original manufacturer's warranty is extended to Princeton Applied Research customers.

Princeton Applied Research reserves the right to make changes in design at any time without incurring any obligation to install same on units previously purchased.

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SHOULD YOUR EQUIPMENT REQUIRE SERVICE

A. Contact the Customer Service Department (865-482-4411) or your local representative to discuss the problem. In many cases it will be possible to expedite servicing by localizing the problem.

B. If it is necessary to send any equipment back for service, we need the following information.

1. Model number and serial number.
2. Your name (instrument user).
3. Your address.
4. Address to which the instrument should be returned.
5. Your telephone number and extension.
6. Symptoms (in detail, including control settings).
7. Your purchase order number for repair charges (does not apply to repairs in warranty).
8. Shipping instructions (if you wish to authorize shipment by any method other than normal surface transportation).

C. U.S. CUSTOMERS — Ship the equipment being returned to:

Advanced Measurement Technology, Inc.
801 S. Illinois Avenue
Oak Ridge, TN 37831
ATTN: Customer Service

PHONE: 865-482-4411
FAX: 865-483-2133

D. CUSTOMERS OUTSIDE OF U.S.A. — To avoid delay in customs clearance of equipment being returned, please contact the factory or the nearest factory distributor for complete shipping information.

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1. Characteristics

1.1. Safety Notice

1.1.1. Introduction

The apparatus to which this instruction manual applies has been supplied in a safe condition. This manual contains some information and warnings that have to be followed by the user to insure safe operation and to retain the apparatus in a safe condition.

The described apparatus has been designed for indoor use. It may occasionally be subjected to temperatures below 5°C without degradation of its safety.

1.1.2. Inspection

Newly received apparatus should be inspected for shipping damage. If any is noted, notify Princeton Applied Research and file a claim with the carrier.

WARNING!

THE PROTECTIVE GROUNDING COULD BE RENDERED INEFFECTIVE IN DAMAGED APPARATUS. DAMAGED APPARATUS SHOULD NOT BE OPERATED UNTIL ITS SAFETY HAS BEEN VERIFIED BY QUALIFIED SERVICE PERSONNEL. DAMAGED APPARATUS WAITING FOR SAFETY VERIFICATION SHOULD BE TAGGED TO INDICATE TO A POTENTIAL USER THAT IT MAY BE UNSAFE AND THAT IT SHOULD NOT BE OPERATED.

1.1.3. Safety Mechanism

As defined in IEC Publication 348, Safety Requirements for Electronic Measuring Apparatus, this is Class I apparatus, that is, this apparatus depends on connection to a protective conductor to earth ground for equipment and operator safety. Before any other connection is made to the apparatus, the protective earth terminal shall be connected to a protective conductor. The protective connection is made via the cable connected to rear-panel connector J1. The ground lines in this cable must pick up ground in the controlling instrument, where it is made available via the earth ground prong of the power cord plug. Thus, before any other system connections are made, it is essential that the power cord plug of the controlling instrument be inserted into a socket outlet provided with the required earth ground contact, and that the cable interconnecting the controlling instrument and J1 of the Model 303A be installed.

WARNING!

ANY INTERRUPTION OF THE PROTECTIVE CONDUCTOR INSIDE OR OUTSIDE THE APPARATUS OR DISCONNECTION OF THE PROTECTIVE EARTH TERMINAL MAY MAKE THE APPARATUS DANGEROUS. INTENTIONAL INTERRUPTION IS PROHIBITED.

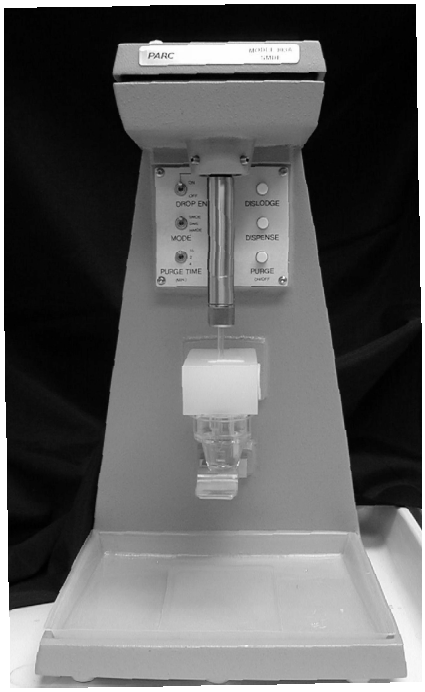


Figure 1-1, Model 303A Static Mercury Drop Electrode

1.1.4. Ventilation

There are no special ventilation requirements for the Model 303A. The power dissipation of this apparatus is quite low. As a result, operation of the Model 303A on any standard laboratory bench with open air circulation to the rest of the lab will pose no ventilation problems. If the Model 303A is operated in an enclosed space, the only requirement is that the ambient temperature not exceed 45^{o} C.

1.1.5. Defects and Abnormal Stresses

Whenever it is likely that the protection provided by the connection to earth ground has been impaired, the apparatus shall be made inoperative and secured against any unintended operation. The protection is likely to be impaired if, for example, the apparatus:

1. shows visible damage,

2. fails to perform the intended measurements,

3. has been subjected to prolonged storage under unfavorable conditions, or

4. has been subjected to severe transport stresses.

Such apparatus should not be used until its safety has been verified by qualified service personnel.

WARNING!

THE FULL OUTPUT VOLTAGE OF THE POTENTIOSTAT WITH WHICH THE MODEL 303A IS OPERATED MAY BE PRESENT AT THE COUNTER ELECTRODE. FOR THIS REASON, OPERATORS SHOULD TAKE CARE TO DISABLE THE POTENTIOSTAT WHENEVER THE ELECTRODE IS EXPOSED FOR ANY REASON.

The magnitude of the potentiostat output will vary according to the model number of the potentiostat in use, as follows.

Model 174A	±80 V at 20 mA
Model 384B	±10 V at 10 mA
Model 374	±70 V at 30 mA
Model 364	±10 V at 1 mA
Model 264A	±12 V at 5 mA

If used with a potentiostat not of Princeton Applied Research manufacture, the maximum voltage and current will differ according to the characteristics of the potentiostat in use.

1.2. Introduction to the Model 303A

The Model 303A Static Mercury Drop Electrode represents a significant advance over previously available mercury electrodes. It combines higher sensitivity, greater convenience, and lower cost in a stable, easily operated instrument. Heretofore difficult measurements become routine when the Model 303A is incorporated into the measurement system.

The Model 303A, a tri-mode electrode, is able to function as either a DME (dropping mercury electrode) or HMDE (hanging mercury drop electrode). Although dual mode electrodes are available elsewhere, they require complex, expensive mechanisms to change from one mode to the other. The Model 303A uses the same simple but elegant mechanism for both HMDE and DME operation. A solenoid-actuated valve interposed in the mercury path between the reservoir and the capillary controls each drop. When the solenoid is energized, mercury flows and a drop is dispensed. When the drop reaches the selected size, the solenoid valve, closes, stopping the mercury flow. The newly dispensed drop will hang virtually indefinitely. Measurements are always performed on static drops, even in DME operation where new drops are formed at the clock time interval. Traditionally, measurements have been made on growing drops in DME operation, with resultant errors due to charging current. By making the measurements on static drops, the dc double layer charging current due to the growing drop is eliminated and higher sensitivities are readily achieved.

Additionally, the Model 303A is easier to operate than traditional mercury electrodes. Front-panel pushbuttons give the operator control of the Dislodge, Dispense, and Purge functions. When the Model 303A is connected to a polarographic analyzer manufactured by Princeton Applied Research, there is provision for automatically regulating the dislodge and dispense functions. Moreover, the Model 264A and the Model 384B will control the purge function. Other features include a choice of glass, Teflon, or disposable plastic sample cuts and provision for simple capillary removal.

The Model 303A is specifically designed to give optimum performance with a Model 384B, with a Model 174A, with a Model 364, or with a Model 264, the full range of current Princeton Applied Research polarographs. Additionally, the unit is designed for use with future Princeton Applied Research Polarographs and can be used with apparatus not of Princeton Applied Research manufacture.

With its convenient operating characteristics, versatility, and superior performance, the Model 303A represents a significant advance, one that should prove indispensable in every laboratory where electrochemical phenomena are investigated.

1.3. Specifications

TYPE OF ELECTRODE: SMDE (Static Mercury Drop Electrode)

MODES: SMDE (Static Mercury Dropping Electrode), HMDE (Hanging Mercury Drop Electrode), and DME (Dropping Mercury Electrode with pressure feed).

DROP CONTROL MECHANISM: Solenoid-actuated valve controls flow of mercury from reservoir to capillary.

RESERVOIR CAPACITY: 5 lb of mercury.

LEVEL INDICATOR: Externally visible float gauge gives continuous indication of mercury level.

CAPILLARY: 5" (12.7 cm) long with 0.006" (0.015 cm) bore. Capillary is complete with mounting ferrule and rubber O-ring.

SAMPLE CUPS: Three types are available, a borosilicate glass cup for ruggedness and long life, a Teflon cup, and a plastic cup for economy and disposability.

N_2: Input gas at pressure not to exceed 5 psi (34.5 kPa) is required.

SIZE: 10.25" D x 9.3" W (front) x 15.7" H (26 cm D x 23.6 cm W x 40 cm H).

WEIGHT: 12 lb (casting only); 5.5 kg.

1.4. SMDE and DME Compared

To assure correct interpretation of measurement results obtained with the Model 303A, it is helpful to understand the differences between the SMDE and the DME, particularly with regard to the event sequence and resultant current waveform in a given drop cycle.

Figure 1-2 shows the drop growth and current waveform characteristics for both types of electrode. The drawings to the left apply to the SMDE, with the drop growth function above the current waveform. To the right are corresponding sketches for a conventional DME. First consider the drop-growth curves. As shown, the drop forms rapidly with an SMDE. In other words, the mercury flow rate is high, allowing a drop of the desired size to be formed in a small fraction of the typical drop time. When the desired size is attained, the mercury flow is stopped, and the drop area remains constant until the drop is dislodged. By comparison, in a conventional DME, the mercury flow rate is smaller but continuous, and the drop area continues to increase for the entire drop life. This difference in drop growth behavior causes a profound difference in the resultant current waveforms, which in turn leads to superior performance for the SMDE over the DME. Referring to the figure, note that the SMDE current rises very rapidly during the rapid dispense interval. There are three components to this current.

1. The charging current caused by the rapid drop growth.

2. The faradaic current (current due to electron exchange of chemical species at the mercury drop) produced by the rapid expansion of the drop into a solution not yet depleted by diffusion.

3. Charging current due to the increase in applied potential over the dispense interval, when the applied potential is sufficient to cause reduction or oxidation.

Because the potential changes slowly relative to the drop growth rate, this last component is small. When the mercury flow is stopped, the drop size stops changing and the charging current due to drop growth stops as well.

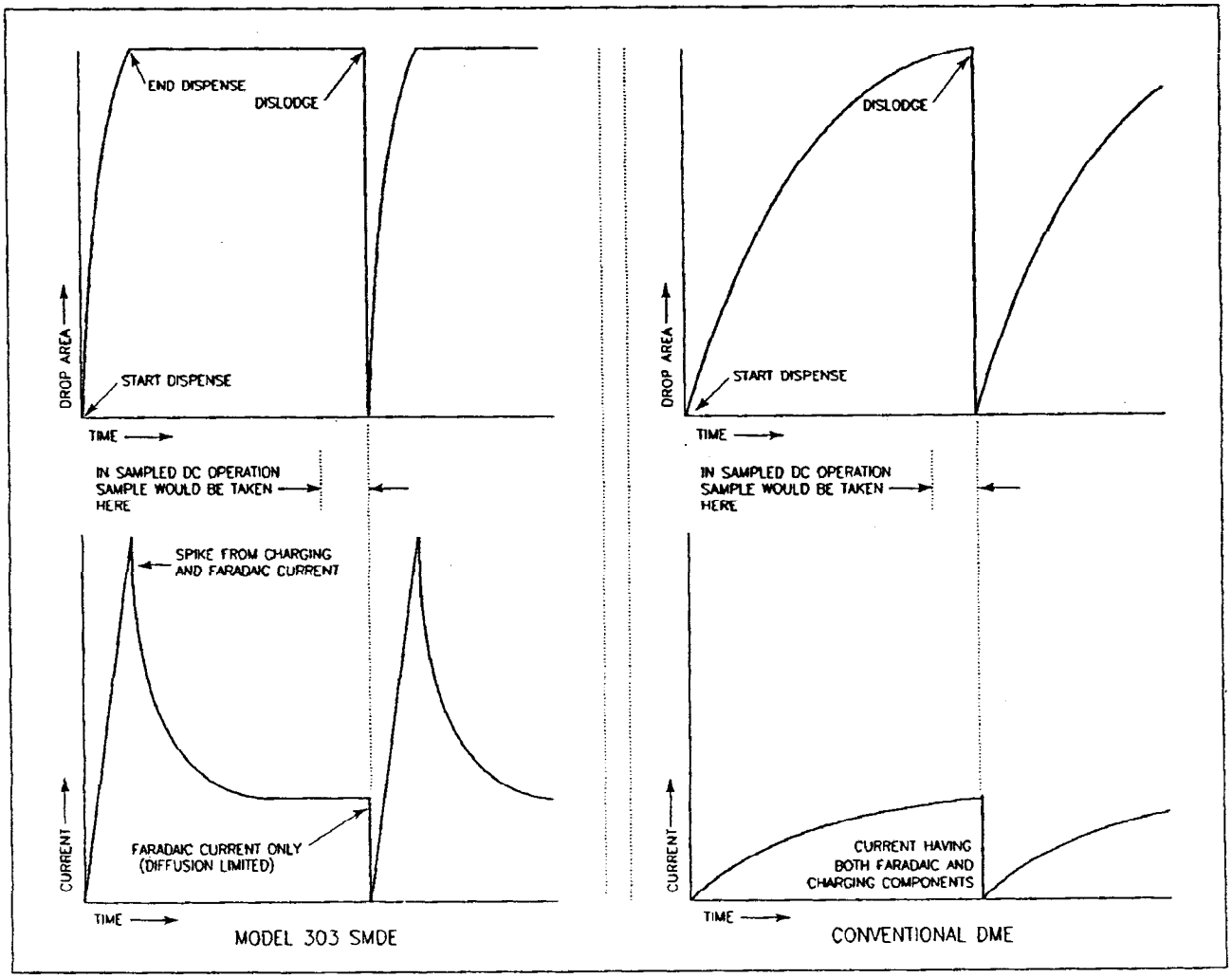


Figure 1-2, Drop Growth and Current Waveforms for Model 303A and Conventional DME

The faradaic current also decreases, asymptotically approaching the diffusion limited state. As a result, there is an overall rapid reduction in current, which approaches the diffusion-limited level. This final current does not contain the drop-growth induced charging component characteristic to a DME. With a constant potential applied, the current will be wholly faradaic. If an analog linear ramp is applied, there will be additionally the small charging component due to potential change over the drop life. Its influence can be minimized through use of a slow scan time. If the instrument has a digital applied-potential ramp, the applied potential will be constant over the life of the drop, and there will be no charging current component at all. Thus the SMDE offers the user the capability of enhancing signal-to-noise ratios over those obtainable with a DME by integrating the current for a longer period of time on each drop.

By way of comparison, note the conventional DME waveforms depicted in Figure 1-2. As shown, the drop grows continuously until it is dislodged. The spike from charging and faradaic current is not present; instead, the current increases for the life of the drop. At all times it contains a charging component due to the drop growth. By using a sampled dc current technique late in the life of the drop, when the drop area is changing relatively slowly, the component is minimized, but it is always present and always influences the measurement results. Considerations related to charging current from changes in the applied potential over the drop life are the same for both electrode systems.

Figure 1-3 is a dc polarogram generated with the Model 303A SMDE. Note that each cycle exhibits the high "spike" illustrated in Figure 1-2. The amplitude of these spikes is as much determined by the response characteristics of the measurement system as by the current magnitude. Note also that the locus formed by drawing a line connecting all of the diffusion-limited current levels will NOT parallel one drawn by connecting all of the spikes. Thus, when doing dc polarography with the Model 303A, users should bear in mind that the "true" wave is obtained by connecting the diffusion-limited levels and not by connecting the peaks. A dc polarogram produced with a DME would not have these spikes, the current during each cycle would drop to some low level at the moment of dislodgement, and then rise slowly, approaching the diffusion-limited value by the end of the drop life.

Users will not have this interpretation problem with techniques other than dc polarography. With the other techniques, the current is sampled after it has stabilized; the spike does not influence the final result. For example, a differential pulse polarogram produced with an SMDE will differ from that produced with a DME only in that it will be more sensitive, less noisy, and less subject to error.

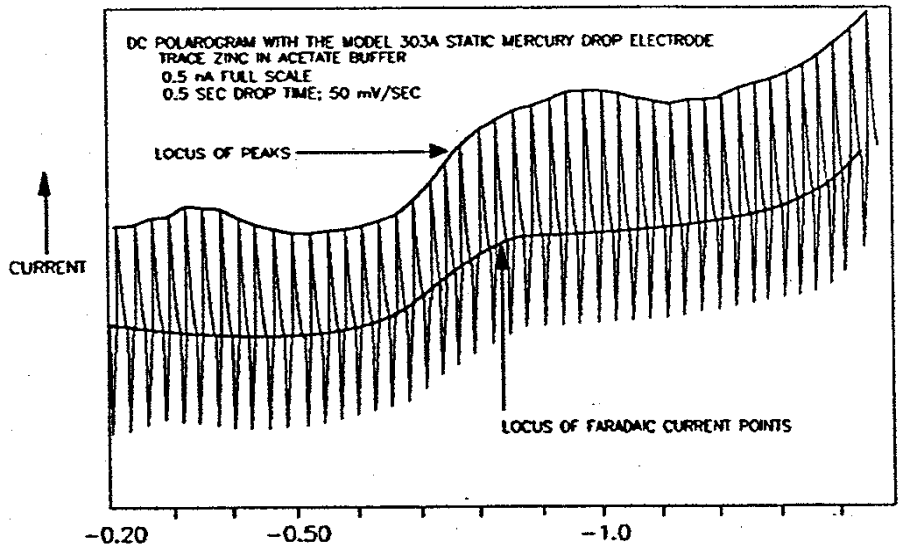


Figure 1-3, DC Polarogram Showing Peak and Faradaic Current LOCI

It will be obvious from the foregoing discussion that such techniques as high frequency or phase-sensitive ac polarography will also benefit greatly through the use of the Model 303A; drop growth induced charging-current effects will be very much reduced. It should be noted, however, that the extremely large charging current during drop formation interferes severely with phase-sensitive detection using lock-in amplifiers with either long time constants or slow recovery rates. In such experiments, it may be desirable to gate the signal to the lock-in amplifier after the period of drop generation.

Operation of the Model 303A as an HMDE is straightforward. Changeover is accomplished by simply setting the front-panel mode switch to HMDE (The Model 384B and the Model 264A automatically set the Model 303A to HMDE as long as DME is not selected on the Model 303A front panel). The large reservoir capacity of the Model 303A makes it possible to dispense many thousands of drops with high reproducibility before refilling is necessary.

2. Installation

2.1. Introduction

There are no special installation requirements for the Model 303A. Generally, it is placed anywhere on a bench within cable reach of the polarographic analyzer with which it is to be used. The heavy casting is equipped with polyurethane feet to prevent any possible scratching of the bench surface. There is no special leveling requirement. (Slopes of several degrees can be tolerated without degrading the Model 303A's performance.) The Model 303A can be positioned to either side of the associated instrumentation, whichever is more convenient. A source of oxygen-free nitrogen at a maximum pressure of 5 psi (34.5 kPa) must be connected to a port at the rear of the Model 303A. Additionally, the surface on which the Model 303A rests must be stable. Although individual drops are less likely to be dislodged than they would be with a conventional drop timer, drop-to-drop repeatability will be severely degraded by any mechanical disturbance. Any movement will cause the mercury in the reservoir to move, with resultant changes in the mercury head and thus in the size of the dispensed drops.

2.2. Cabling

2.2.1. Connecting Individual Units

The cable required depends on the unit with which the Model 303A is to be operated. For operation with a Model 264A, Model 364 or a Model 384, the part number of the interconnecting cable is C0113. The Model 384B uses cable C0193, while the Model 174A uses cable C0142.

Thus, any one of three different interconnecting cables could be used, as illustrated in Figure 2-1. However, you will probably be using the Model 303A in only one of the configurations illustrated, and so will require only one cable.

2.2.2. Connecting Multiple Units via the Model 308 Multiplex Module

A Model 384A or Model 384B can control up to four Model 303A's through the Model 308 Interface Box. The cabling required varies with the units involved.

1. *All units:* connect Cable C0193 between the controller's rear-panel CELL COMPARTMENT connector and the Model 308's 25-pin 384/384B connector.

   Model 384B: Go to Step (2).
   Model 384A (with factory upgrade to Model 384B specifications, including a Model 384B front panel)

   or

   Model 384A (with Rev. C4 B0 or higher software)

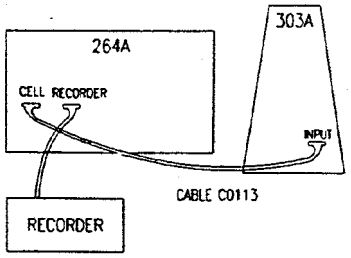
   or

   Model 384 (upgraded to a Model 384A)

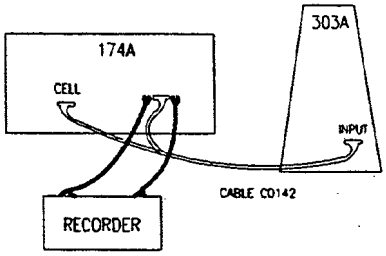
   Connect Cable C0174 between the 15-pin real-panel AUX connector and the Model 308's 15-pin AUX (384 ONLY) connector. Note: there may be a few Model 384's in the field with Rev. C4 B0 software but rear-panel AUX connector wiring that is incompatible with the Model 308's AUX (384 ONLY) connector. If a Model 384 and a Model 303A work together properly by themselves, but will not work when connected through the Model 308, it is possible that the equipment involved requires minor modification. Call or write the factory for details.

2. Use cable C0199 to connect between any of the four unlabeled 25-pin D connectors on the Model 308 and the Model 303A's rear-panel INPUT connector.

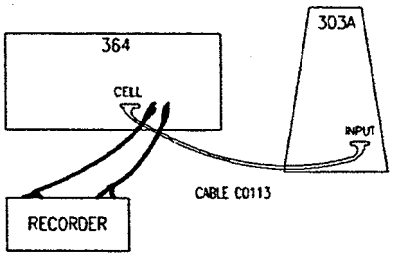
3. Repeat Step (2) for each Model 303A.



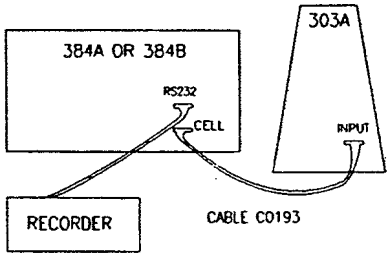
A. Model 303A in System Containing 264A



B. Model 174A in System Containing Free-Standing Model 174A



C. Model 303A in System Containing Model 364



D. Model 303A in System Containing Model 384A or 384B

2.3. Purge Gas

Aside from cable considerations, the only other installation problem of concern to the user is that of supplying oxygen-free nitrogen to the Model 303A for purging and blanketing the solution. The gas is applied to the input port at the rear of the instrument. This gas accepts standard 1/4" laboratory plastic tubing which is easily secured with a worm-drive clamp. The maximum input pressure is 5 psi (34.5 kPa). The actual input pressure or flow rate should be user adjusted as required to obtain a good purge rate as evidenced by bubbling of the purge gas through the sample. In most situations, the optimum pressure will be less than 5 psi (34.5 kPa).

For critical measurements, ordinary tank nitrogen may be too contaminated by oxygen for use as a purge/blanketing gas. It is therefore sometimes necessary that a deoxygenating system be connected ahead of the Model 303A. The Analytic Instrument Division of Princeton Applied Research makes available Application Note D-2, "Deaeration ... Why and How," which treats this topic in detail.

2.4. Electrodes

The Model 303A is shipped with the reference and counter electrode wires already in place with a plastic cup in the analysis position so that the electrode wires are protected (Figure 2-2). As part of the installation, this cup should be carefully removed to gain access to the electrodes so that assembly of the reference electrode can be performed. To remove the cup, simply rotate the spring-loaded metal support (located beneath the cup) out of the way and pull the cup straight down, exposing the electrode wires (Figure 2-3).

Facing the unit from the front, the wire to the right is the counter electrode (Pt) and that to the left is the reference electrode element (Ag/AgCl). The reference electrode glass sleeve and filling solution are shipped with the Model 303A. Once they are located, take the glass sleeve and work the "Quad" ring down to the waist constriction. Then, with the large open end of the sleeve upwards, fill it to within about one centimeter of the top with the reference-electrode filling solution supplied. Remove any air bubbles. Then carefully slip the filled sleeve up over the silver wire so that the wire is immersed in the solution. Push the sleeve up into the electrode support block until it seats securely. The "Quad" ring on the sleeve mates with the notch inside the block, preventing the sleeve from slipping downwards of its own accord. Figure 2-4 shows the sleeve in place. The sleeve can be removed by simply grasping it and pulling straight down.

This completes the installation per se. The user is well advised to return the protective sample cup to its original position and keep it there until the instrument is filled with mercury and ready to operate. In the meantime, the sample cup should be filled with distilled water. By so doing, the frit at the end of the reference electrode will be kept wet, thereby lengthening its life. Also, it may be advisable to read Subsection 2.5 (GAS SCRUBBING: WHY AND HOW) before proceeding. Many users of the Model 303A will already have polarographic analysis systems complete with a gas scrubber. However, where this is not the case, the user may have to add a gas-scrubbing system before high sensitivity analyses can be made.

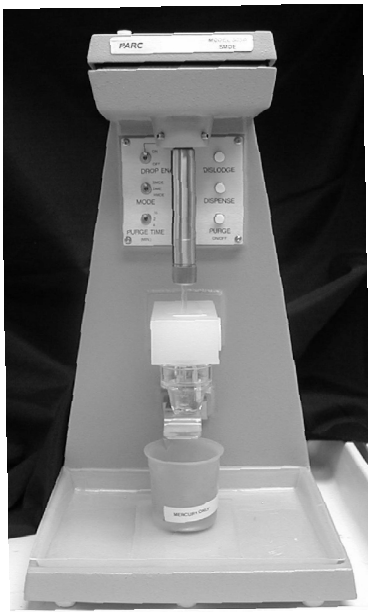


Figure 2-2, Model 303A with Cup in Position to Protect Electrode Wires

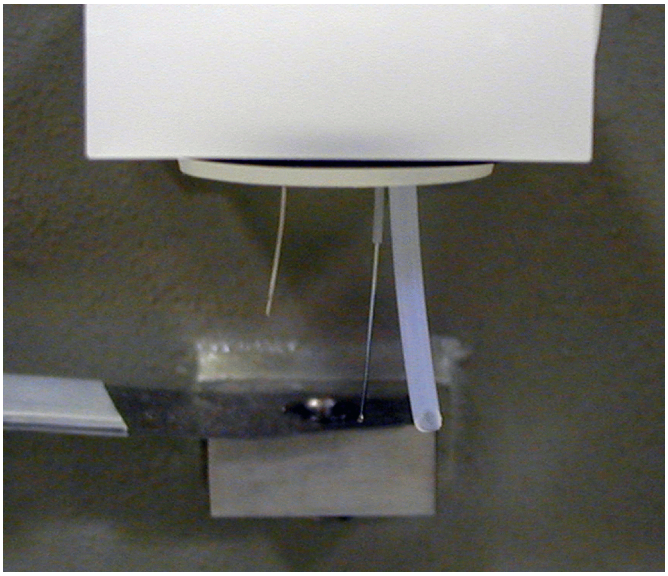


Figure 2-3, Model 303A with Protective Cup Removed Exposing Electrode Wires

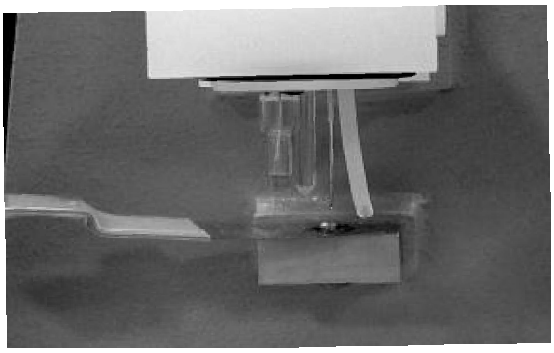


Figure 2-4, Model 303A with Filled Reference Electrode Sleeve Installed

2.5. Gas Scrubbing: Why and How

Aqueous solutions exposed to air may contain concentrations of dissolved gaseous oxygen as high as 1 mM. The presence of this oxygen can interfere with polarographic determinations because of the oxygen reduction waves that occur solutions at approximately -0.05 V and -0.9 V vs Ag/AgCl. Furthermore, the product of the oxygen reduction in unbuffered solutions may change the pH of the solution in the vicinity of the electrodes. This change in pH can interfere with the desired reaction by causing precipitation of electroactive substances at the electrode surface or by shifting reduction potentials. It is thus essential to remove the dissolved oxygen for a time immediately before the experiment is carried out. It is advisable, furthermore, to blanket the surface of the solution in the cell with inert gas during the experiment to prevent oxygen reabsorption. Nitrogen applied to the gas input at the rear of the Model 303A fills this function. This gas is used to purge the analyte or blanket it as controlled by the operator or by the polarograph with which the Model 303A is used. Purging is accomplished by sending the gas through a dip tube into the analyte. When the gas is not routed to the dip tube, it emerges from the electrode support block through an opening directly above the solution so that the solution is blanketed with the oxygen-free nitrogen.

Note that tank nitrogen may be adequate for trace analysis applications. An oxygen-scrubbing system will then be required to remove the last traces of oxygen.

A gas-scrubbing system based on a vanadous chloride scrubbing solution can be prepared as follows. The required solution is prepared most readily by boiling two grams of ammonium metavanadate with 25 ml of concentrated hydrochloric acid and diluting with water to 250 ml. The solution thus produced is usually blue or green and contains vanadium in various higher oxidation states. This solution should be transferred to a gas-washing tower, and a quantity (10-15 gm) of amalgamated zinc added to it. The amalgamated zinc can be prepared by placing about 10 g of granular or powdered zinc in a beaker, covering it with deionized water, and adding two drops of concentrated HCl. Amalgamation will occur quickly when mercury is added. The vanadous chloride solution will usually retain its original color until gas is bubbled through it for a time, at which point it will turn purple. The blue or green color returns at exhaustion. Rejuvenation is accomplished by adding some more amalgamated zinc or a few drops of concentrated HCl. A precipitate indicates that the acidity is too low. Ten percent HCl should be added to redissolve the precipitate.

With a scrubbing tower thus prepared, connect the nitrogen source to the tower input. Then connect the output of this tower to the input of a second tower, which should contain deionized water or the same electrolyte as is contained in the analysis cell. The output of this second tower is then connected to the nitrogen input port of the Model 303A. Two benefits are derived from incorporating this second tower into the gas scrubbing system. First, any vanadous chloride solution picked up by the gas will be trapped by the second tower and so not reach the cell. Second, the gas exiting the second tower will be saturated with electrolyte volatiles, thereby preventing sample concentration of electrolyte changes because of evaporation.

Alternatively, users may wish to use a commercial unit such as the Supelco Gas Purifier (#2-2315) manufactured by Supelco Corp. (Supelco Park, Bellefonte, PA 16823).

Note that the gas scrubbing system will give the longest, most efficient service if it is kept free of contact with air when not in use.

2.6. Model 303A to Model 310A Conversion

The Model 303A SMDE can be converted to a Model 310A Polarographic Detector by incorporating the items provided in the K123 Model 310 Accessory Kit. The kit includes a Liquid Chromatography Analysis Cell, together with the tubing and fittings required to operate in conjunction with a liquid chromatograph. LC detection by polarography provides excellent selectivity and sensitivity with a range of applicability that is difficult to match with any other detector. Many organic function groups exhibit polarographic activity and can be detected at nanogram levels by this technique. Also, moieties such as aliphatic carbon-chloride bonds show excellent polarographic response, but limited UV response. The polarographic detection technique also yields excellent response to dissolved metals, allowing polarographic LC detection of these substances without extensive work-up procedures. This feature is unavailable with UV or RI detectors. Contact the factory for additional information.

3. Operation

3.1. Introduction

The Model 303A allows routine analyses at sensitivities heretofore unattainable, and with a convenience and ease of operation unmatched by any other mercury electrode. Operation is simple and foolproof. There is no capillary reservoir with attendant need for frequent refilling in HMDE operation. Installation and removal of the capillary is straightforward, with little risk of accidental mercury spillage. The fixed Electrode Support Block simplifies capillary installation and greatly reduces the risk of capillary breakage. Sample cup installation is simple and secure; the spring-loaded support plate beneath the cell allows cells to be quickly changed. Front-panel switches allow mode selection and operator override of system function commands, if desired. The Model 303A takes all of its power from the Polarographic Analyzer with which it is operated. This section of the manual discusses these and other considerations germane to achieving optimum performance with the Model 303A Static Mercury Drop Electrode.

3.2. Front-Panel Switches and Pushbuttons

There are a number of toggle switches and pushbuttons mounted on the front panel of the Model 303A behind the valve body. The toggle switches are to the left and the pushbuttons to the right. A brief description of each and its function follow.

1. DROP ENABLE: In the OFF position, the Mercury Control Valve cannot be actuated and no mercury can be released from the reservoir. The instrument responds neither to the DISPENSE pushbutton nor to mercury-dispense trigger signals initiated by drop-knock commands from the polarograph. The purge function is also inhibited. The principal advantage of the OFF position is that the cell can be installed and/or removed WITHOUT SPILLING ANY MERCURY. In addition, users should have the MODE switch in the OFF position whenever installing or removing the cell or changing capillaries. The DROP ENABLE switch should also be set to OFF whenever mercury is poured into the reservoir. If it is not, the solenoid may be momentarily activated, and, if the capillary is not installed, mercury will be spilled onto the stand.

The Model 384B can control up to four Model 303A's, but it can only take data from one at a time. It commands any other 303As under its control to PURGE, and they execute this command, whether their PURGE pushbuttons are ON or OFF. If the DROP ENABLE switch is OFF, however, the PURGE function is disabled, and the operator can safely remove or replace a cell without splashing electrolyte.

When the front-panel DROP ENABLE switch is on the green DROP ENABLE lamp is turned on.

2. MODE: This three-position toggle switch allows the user to select operation as either an SMDE (static Mercury Drop Electrode), a DME (Dropping Mercury Electrode), or an HMDE (Hanging Mercury Drop Electrode). In the SMDE or DME positions, the drop knocker is triggered on a dislodge command from the controlling instrument. In typical SMDE operation, such commands are supplied at the clock interval. As each trigger pulse is applied, the drop knocker is energized (removing the existing drop from the end of the capillary). A new drop is automatically formed and any measurements are taken on the new drop while it is static and before the next drop knock is applied.

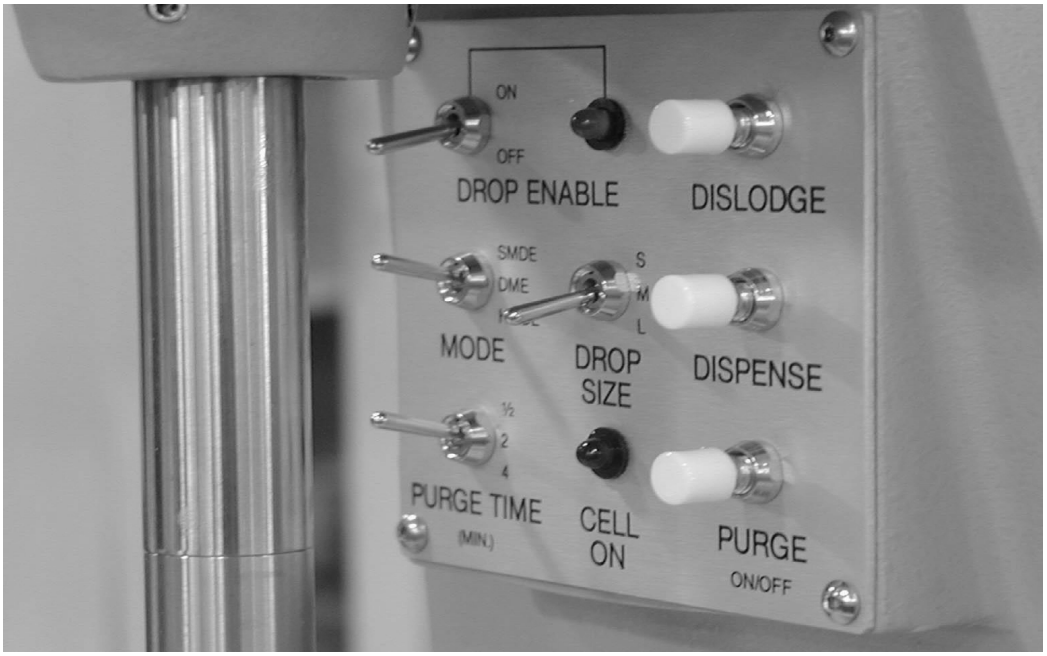


Figure 3-1, Front-Panel Pushbuttons, Lamps, and Switches

In the HMDE position, DISLODGE commands from a Model 174A or Model 384A controller are ignored. If a drop is formed prior to a run, an experiment can be performed on single drop. When the Model 303A is controlled by a Model 264A or a Model 364, it doesn't matter whether the MODE switch is in the SMDE or the HMDE position, because the controller determines how many drops should form and when they should be dislodged.

In the DME mode, the solenoid controlling mercury flow opens and mercury is pressure-fed, forming drops which grow and eventually fall off without intervention from the drop-knocker mechanism. This mode normally requires a capillary with a 0.003" bore and pressurization of the mercury reservoir. Kit 303A/99 provides the necessary apparatus.

During actual analysis, the MODE switch selects one of the three positions. The switch position must correspond to the intended function. A hanging mercury drop electrode is used for stripping voltammetry analyses and square wave polarography; a dropping mercury electrode is used for most other analytical techniques.

3. DROP SIZE: This switch gives the user the choice of three different drop sizes: S (small), M (medium), and L (large). The drop sizes are in a volume ratio of 1:2:4, corresponding to an area ratio series of 1:1.6:2.5. Sensitivity varies directly with drop area. For most applications, excellent results are assured with a small size drop. Medium and large drops give greater sensitivity at the expense of increased susceptibility to accidental dislodgment. They also exhibit greater noise.

4. PURGE TIME: Three different purge times are provided: 1/2, 2, and 4 minutes. Generally speaking, a sample should be purged as long as is necessary to reduce the oxygen peaks to where they disappear in the baseline noise. The time required will depend on the nature of the sample and the degree of oxygen contamination. Studies at Princeton Applied Research have consistently shown that, with a properly adjusted flow rate, there is no advantage to using purge times longer than the four minute maximum offered, unless the electrolyte is strongly basic, in which case a longer purge could be required.

An actual purge can be triggered by means of the front-panel PURGE ON/OFF pushbutton or by a command from the controlling instrument. When the Model 303A is operated in conjunction

with a Model 174A or Model 364, the purge must be manually initiated with the pushbutton. Pressing the PURGE pushbutton initiates the purge. Pressing it a second time terminates it, even if the selected purge period hasn't ended yet. Purges terminate automatically on expiration of the selected purge time. When the Model 303A is operated with a Model 264 or Model 384B, the purge commands come from the controlling instrument. Moreover, the purge duration is that programmed at the polarograph.

The front-panel PURGE ON/OFF pushbutton can also be used to override a PURGE command from a controlling instrument. If the button is pressed while a purge is underway, the Model 303 begins a purge whose duration is set through the front- panel PURGE TIME selection. Pressing PURGE a second time turns the purge function off.

5. DISLODGE: Each time this pushbutton is depressed, the drop knocker (located inside the electrode support block) will strike the capillary and any drop at the tip of the capillary will be dislodged. This button is most often used with a Model 174A or a Model 364 in HMDE mode to remove the old drop before forming a new drop. It is also useful in setting up and in verifying proper Model 303A operation. Note that normal dislodge action is only obtained with the capillary tip immersed in liquid.

6. DISPENSE: Each time this pushbutton is depressed, mercury is allowed to flow from the reservoir into the capillary, causing a new drop to form at its tip. Note that dispensing does NOT cause any existing drop to be dislodged. Therefore, where the goal is to produce a new electrode drop (as opposed to a larger electrode drop), the user should first press the DISLODGE pushbutton so that any drop already present will be removed.

The DISPENSE pushbutton has a second mode, activated by holding the pushbutton in continuously (minimum of one second). As long as the pushbutton is held in, continuous dispensing at the rate of three drops per second occurs. This mode is useful in that it allows the capillary to be quickly purged of any trapped air. Only a minute quantity of air can be trapped, and that air will be moved down the capillary and cleared from the system when the DISPENSE pushbutton is held in. Typically, any trapped air can be cleared by holding the DISPENSE pushbutton in for 10-15 seconds. This function is especially useful for starting mercury flowing in a new capillary.

7. PURGE ON/OFF: This pushbutton provides the user with manual control of the purge gas. Other than for setting up and verifying proper Model 303A operation, its use would normally be restricted to operation with systems consisting of the Model 303A and a Model 174A or Model 364. In the case of the Model 264 and Model 384B, the purge timing is controlled automatically. Note that dislodge/dispense commands from the polarograph are inhibited when purging.

The purge gas is turned on by pressing the pushbutton once. The purge continues for a period set with the PURGE TIME switch, unless the PURGE button is pressed a second time, in which case the purge terminates.

An external purge command terminates a purge initiated from the Model 303A's front panel.

CAUTION: The front-panel PURGE button overrides a purge initiated by a controlling instrument. If a four-minute purge command were issued by a controlling instrument, and after two minutes a four-minute purge command were initiated from the Model 303A's front panel, the experiment would begin at the conclusion of the first four-minute period, even though the Model 303A would still be purging.

Blanketing gas flows whenever a purge is NOT in progress.

8. CELL ON LAMP: This red lamp is turned on whenever the electrodes are connected to a polarograph, except when the Model 303A is purging. This lamp functions independently of the controlling instrument's CELL ON/OFF switch.

3.3. Rear Panel Features (Figure 3-2)

1. DISLODGE ADJ: This adjustment allows the operator to set the strength of the dislodgment "tap" applied to the capillary. The optimum setting is that which imparts just enough energy to the capillary to reliably dislodge the drop. This optimum can be quickly found by trial and error. Rotating the adjustment clockwise increases the force with which the capillary is struck. Rotating the adjustment counterclockwise decreases it. Again, bear in mind that normal dislodge action only occurs with the capillary tip immersed in liquid.

CAUTION!

ALWAYS BEGIN WITH THE ADJUSTMENT FULLY COUNTERCLOCKWISE. THE MAXIMUM DISLODGE TAP MAY BE ENERGETIC ENOUGH TO BREAK THE CAPILLARY.

2. TEST POINTS: Three test points are provided for monitoring the three electrode potentials. These potential are measured versus ground. The most convenient ground, if the casting is metal, is one of the four screws that secure the front-panel face plate. Otherwise, use the center terminal of the STIRRER connector. Note that the polarity at the counter electrode will be opposite that selected at the polarograph, necessary to establish the working electrode at the programmed potential with respect to the reference electrode. The reference electrode will also be at the opposite polarity, but the potential magnitude will be that programmed. The working electrode is held at virtual ground (0 V). Any potential at the working electrode test point is indicative of a system malfunction. Note that the continuity of the Hg column in the capillary can be checked by measuring the resistance between the working electrode test point and the counter electrode test point.

These test points can be used for a direct connection of an alternate cell. Leave the Model 303A cell dry and connect the electrodes to the appropriate points.

A cell containing supporting electrolyte must be in position. A normal indication on a conventional VOM will be in the range of 1 kΩ to 50 kΩ. Note that the Model 303A must be disconnected from the polarograph before making the continuity check.

3. POWER INPUT: The Model 303A takes all of its power from the instrument with which it is operated via the interconnecting cable attached to the INPUT connector.

4. STIRRER ACC CONNECTOR: An accessory connector is also provided on the rear panel of the Model 303A. It is used for remote control of the Model 305 Stirrer.

5. N_2 INLET: The blanketing/purging nitrogen is applied to this input using 1/4" plastic tubing. Pressures higher than 5 psi should not be applied. It is suggested that a worm-drive clamp be used to secure the connection.

6. CELL NO.: Use this switch to determine the address of a particular Model 303A when more than one Model 303A is being controlled by a Model 384B. If only one Model 303A is connected to a Model 384B, or if a Model 303A is connected to another instrument, the position of this switch doesn't matter.

Figure 3-2, Rear-Panel Features

3.4. Installing the Capillary

CAUTION!
SET DISLODGE ADJUSTMENT FULLY CCW BEFORE INSTALLING CAPILLARY.

3.4.1. Introduction

One of the most attractive features of the Model 303A is the ease with which capillaries can be installed or removed. To minimize any risk of shipping damage to the capillary, units are shipped without the capillary installed. The capillary is in its own packing for maximum protection.

With reference to installing the capillary, note that two procedures are provided, one that applies when there is no mercury in the reservoir, such as would be the case in the initial installation, and the other that applies when there is mercury in the reservoir, such as would be the case if a capillary had to be changed after system operation had been established.

WARNING!
MERCURY IS BOTH TOXIC AND EXPENSIVE. HANDLE IT WITH CARE AND CLEAN UP ANY SPILLS IMMEDIATELY. AVOID VAPOR BUILDUP IN CONFINED AREAS. DO NOT STORE MERCURY IN OPEN CONTAINERS.

Users should install the polyethylene tray that fits the bottom of the stand before proceeding. This tray protects the casting finish from damage by corrosive chemicals.

3.4.2. Capillary Installation, No Mercury in Reservoir

1. Hold the capillary so that it is oriented with the ferrule-end up. Be sure the capillary is completely dry and that it contains no mercury. If it does, remove the mercury with an aspirator. Note that cleaning may be required if mercury or other material has been left in the capillary bore for an extended period of time. A recommended cleaning procedure is provided further on in this discussion. There should be a rubber O-ring installed at the top of the capillary, flush with the ferrule. Capillaries may be supplied with the rubber O-ring already in place.

2. Unscrew the stainless steel capillary nut (Model 303A) from the bottom end of the mercury valve housing. Then lower the capillary through the clear plastic tubing in this nut to where the capillary ferrule is supported by the top of the clear tubing.

3. Note the slot cut into the upper surface of the electrode support block. This slot is the upper end of a channel that passes through the electrode support block from top to bottom. Gradually lower the capillary assembly through the slot (Figure 3-3), angling the capillary so that the capillary and capillary retaining nut do not strike the valve housing while the capillary is being lowered. As soon as the capillary and capillary retaining nut are low enough to so allow, orient the capillary straight up and down, and lift it to where the nut can be threaded onto the valve body.

4. Thread the retaining nut onto the valve housing as far as it will go, tightening it snugly (finger pressure only; NO TOOLS).

Figure 3-3, Installing the Capillary

3.4.3. Filling the Reservoir

Once the capillary is in place (and not before), the reservoir can be filled. The first step is to assure that the available mercury is suitable for the intended purpose. Only triply distilled or better analytical grade mercury should be used. That supplied by Bethlehem Apparatus Corporation is recommended. A quick test for mercury purity can be performed with a test tube and some distilled or deionized water. Half fill the test tube with pure water and add a few drops of mercury. Then cap the tube and shake it vigorously for a few seconds. If the mercury does not immediately separate from the suspension, the mercury is pure. It is interesting to note that most commercial triply distilled mercury tested in this manner separates immediately from the suspension, indicating that it is relatively impure. Mercury that fails this test is generally not suited for low-level stripping analysis applications, although it may be good enough for other polarographic techniques.

For very low-level work, it may be desirable to subject triply distilled mercury (containing typically 0.1 ppm non-volatile residue) to a further chemical treatment to remove base metals such as lead, cadmium, zinc, et. The following procedure is adapted from a paper by G. C. Whitnack and R. Sasseli, *Analytical Chimical Acta*, 47, 367 (1969).

A quantity of mercury (1 to 2 inches) is placed in a 1 liter flask and layered with 10% sodium hydroxide (1-2 inches). Tank oxygen (**CAUTION: NO OPEN FLAMES!**) is passed into the mercury through a disposable Pasteur pipette for a period of 12 hours. The mercury is rinsed well with deionized water and then treated in the same manner with 10% nitric acid. Following a thorough rinsing (again with deionized water), the excess water is removed and the mercury is pinholed into a polyethylene container cleaned as described in Section 3.7.

NOTE: Pinholing involves filtering mercury through a tiny hole in the bottom of a paper filer fitted to a filter funnel in the usual fashion. Any scum or water on the mercury remains on the paper filter.

Having ascertained that the mercury is of the necessary purity, proceed as follows to fill the reservoir.

1. Place a small beaker (or sample cup) beneath the capillary to catch any mercury that flows during the filling procedure. Then turn on the system power and set the Model 303A MODE switch to SMDE and DISPENSE ENABLE to ON.

2. Remove the reservoir cover (secured by a single knurled nut at the top of the unit).

3. Get a clean hypodermic syringe (10-20 ml) with needle and fill it with pure mercury.

4. Set the rear-panel DISLODGE adjustment fully counterclockwise. Then press and hold in the Model 303A DISPENSE pushbutton (system must be powered). While it is held in, incrementally inject mercury (about 0.5 ml at a time) into the small hole in the floor of the reservoir directly above the valve assembly (Figure 3-4). Allow several seconds after each injection to allow any trapped air bubbles to clear. Some operators find it convenient to tape the DISPENSE button down.

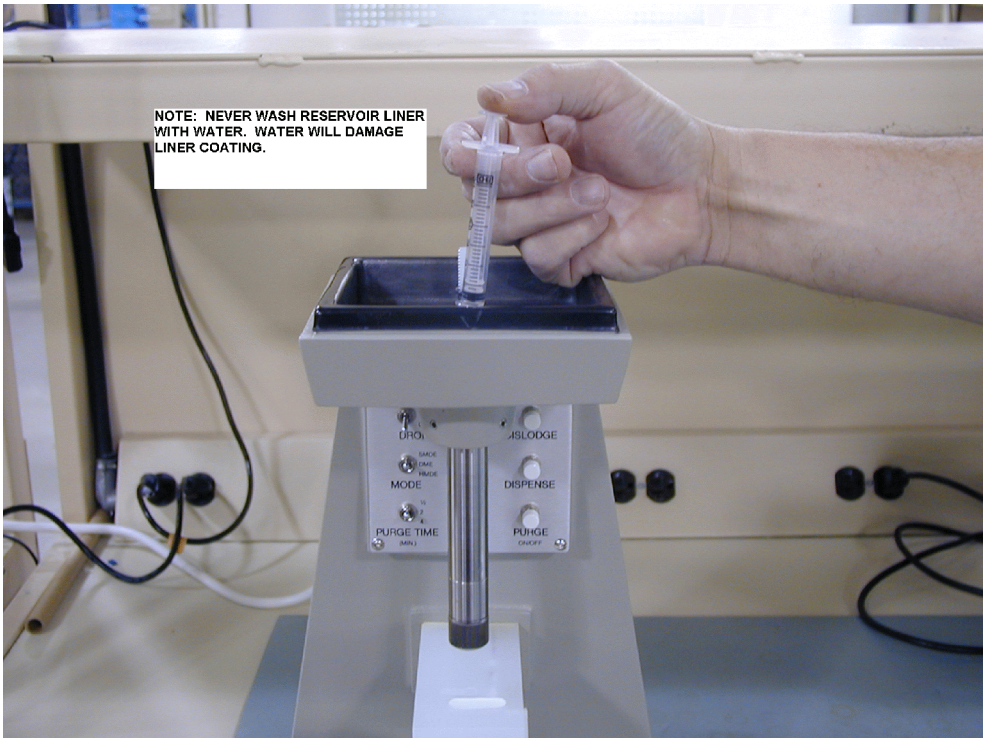


Figure 3-4, Reservoir Filling with Syringe

The interior of the mercury reservoir is lined with a polystyrene insert to insure that mercury does not contact the casting. Do not allow the syringe needle or any other sharp object to penetrate or cut this insert. The purpose of filling the solenoid by means of a syringe while dispensing is to reduce the probability of air being trapped in it, such as might occur if mercury were simply poured in.

5. After the hole is filled to overflowing, the DISPENSE pushbutton should be released, and the DROP ENABLE switch set back to the OFF position.

6. Pour the remainder of the mercury (recommended "fill" is nominally 2 kg) into the reservoir. Note that there is a black "O" ring on the shaft that the hold-down nut threads onto. The mercury level should not be allowed to go above this "O" ring "full line".

If mercury flow through the capillary occurred during the injection stage of the filling procedure, the SMDE is ready for operation. If no mercury flow occurred, there is probably a bit of air at the junction of the capillary and valve assembly. To clear the air and establish mercury flow through the capillary, proceed as follows:

1. Loosen the capillary retaining nut. Then lower the capillary. Inspect it to see if it contains mercury. If it does, remove the mercury from the capillary with an aspirator.

2. Reinstall the capillary, leaving the capillary retaining nut fairly loose (point where resistance starts as the rubber O-ring begins to compress).

3. Switch the DROP ENABLE switch ON, set the MODE switch to SMDE and hold in the DISPENSE pushbutton.

4. Continue tightening the capillary retaining nut while holding in the DISPENSE pushbutton. Mercury flow through the capillary should commence. Slowly tighten the retaining nut until it is snug (finger tight; NO TOOLS). Allow about 5 minutes for this step. Tighten the nut about 1/4 turn, wait 30 seconds, etc.

5. When the nut is tight and mercury flow through the capillary has been established, release the DISPENSE pushbutton and switch the DROP ENABLE switch OFF. Before proceeding, place the cover back on the reservoir and secure it. The cover is fitted with a built-in float to indicate the mercury level.

Note that the cover "seals" with a foam rubber gasket all around the reservoir. This is not a hermetic seal (if it were, a vacuum would be pulled in the reservoir as the mercury level dropped). Not only will the seal pass air, but it is permeable to mercury as well. Practically, this means that if the Model 303A should be knocked over, and left on its side for a period of time, there would be a gradual mercury seepage through the foam rubber seal. However, this should not prove a problem in normal operation. The Model 303A is very stable. Should it be knocked over, it is almost certain that the accident would be noticed and the unit quickly righted, thereby preventing any noticeable loss of mercury.

3.4.4. Capillary Installation, Mercury in Reservoir

1. Set the Model 303A front-panel DROP ENABLE switch to the OFF position.

2. Hold the capillary so that it is oriented with the ferrule-end up. Be sure the capillary is completely dry and that it contains no mercury. If it does, remove the mercury with an aspirator. Note that a capillary may have to be cleaned if mercury or other material has been left in the bore for a long time. There should be a rubber O-ring installed at the top of the capillary, flush with the ferrule. Capillaries may be supplied with the rubber seal already installed.

3. Unscrew the stainless steel capillary nut from the bottom end of the valve body. Then lower the capillary through the clear plastic tubing in this nut to where the capillary ferrule is supported by the inside lower surface of the nut.

4. Note the slot cut into the upper surface of the electrode support block. This slot is the upper end of a channel that passes through the electrode support block from top to bottom. Gradually lower the capillary assembly through the slot, angling the capillary so that the capillary and retaining nut do not strike the valve body while being lowered. As soon as the capillary and retaining nut are low enough to so allow, orient the capillary straight up and down, and rest the retaining nut on the electrode support block.

5. Set a small beaker in position to catch any mercury that flows through the capillary in the following steps. Then set the Model 303A MODE switch to SMDE and switch DROP ENABLE on so that mercury flow can be established.

6. Lift the retaining nut (with capillary) and thread it into the valve body until resistance begins as the rubber seal starts to compress. Then, with the system powered, hold in the DISPENSE pushbutton. With the DISPENSE pushbutton still held in, gradually tighten the retaining nut further. This technique of starting the dispense operation with the nut loose, and continuing to dispense while the nut is slowly tightened, should clear the space at the junction of the capillary and the valve assembly of any trapped air, allowing normal capillary action to be established. Tighten the nut snugly (finger tight only; NO TOOLS) as capillary flow begins. Then release the DISPENSE pushbutton.

7. Return the MODE switch to the OFF position, thereby preventing an accidental mercury spill.

3.5. Operation

3.5.1. Introduction

Once the system installation is complete, the reservoir filled with mercury, and the capillary installed, the unit is ready to operate. The user can prepare the sample (blank or standard) fill the sample cup, and run. Where the polarographic analyzer is a Model 174A or a Model 364, the operator must use the Model 303A pushbuttons to control the mercury drop in HMDE, SMDE, or DME operation. In a system including the Model 384B or Model 264A, even this minor operator duty becomes unnecessary as the appropriate control signals are generated in the polarograph. These instruments are operated according to the instructions in their respective manuals. Detailed Model 303A operating instructions follow.

3.5.2. Procedure

1. Independent of the system configuration, the user is advised to begin by washing the electrodes with deionized water from a squeeze bottle. Be sure to direct the water up into the electrode mounting holes. The drain water should be captured in a small beaker or other container. Note that the cup support spring rotates out of the way to the left to facilitate this operation.

2. Check the position of the Model 303A MODE switch. The setting should correspond to the desired operating mode. If the intended analysis technique calls for a hanging mercury drop electrode (stripping), the switch should be set to HMDE. If the intent is to do dc polarography, pulse polarography, differential pulse polarography, square-wave polarography, etc., on a static mercury drop electrode, the switch should be set to SMDE. To perform one of these analytical techniques on a Dropping Mercury Electrode, set the switch DME. (With a 0.006" bore capillary, the Model 303/99 kit will be necessary to put the mercury under pressure.)

3. A polyethylene tray, vacuum-formed to fit the bottom of the stand, is supplied with each unit. Be sure this tray is in place before proceeding. The tray protects the casting finish from damage by corrosive chemicals. Then load the sample (typically 5-10 ml) into a clean sample cup, which is then secured against the lower surface of the electrode support block by means of the cell support spring. A boss on the lower surface of the electrode support block automatically positions the sample cup so that its rim contacts against the "O" ring seal.

4. After a period of disuse, it is advisable to clear the capillary of any air trapped at its top. Such a bubble could give an "open working electrode" condition while it is in the capillary, causing the current to go to zero for the time required for the bubble to work its way through the capillary. Clearing is accommodated simply by holding in the Model 303A DISPENSE pushbutton for 10-15 seconds. Note that this operation need only be performed once. If the capillary is removed and either re-installed later or replaced with a different capillary, the capillary installation procedure should be carefully followed.

5. Program or "set up" the analysis. In other words, set the switches and controls of the associated polarograph or controller to the settings appropriate to the intended analysis. Determine whether any further steps are required at the Model 303A before starting the run. In the case of a Model 264 or Model 384B, no further operation attention at the cell is required; the purge, dislodge, and dispense operations are remotely controlled. If the Model 303A is connected to a Model 174A or a Model 364, the user will have to initiate the pre-analysis purge by pressing the Model 303A PURGE pushbutton. A purge lasting ½ minute, 2 minutes, or 4 minutes will follow. Four minutes will usually give a thorough purge for even very high-sensitivity analyses.

   If the MODE switch is set to DME, no further action will be required, other than to set the DROP SIZE switch ("SMALL" is best for most applications). If the MODE switch is set to HMDE, a new drop should be prepared. This is done in two steps. First press DISLODGE (removes existing drop). Then press DISPENSE (causes new drop to form at end of capillary).

   Take care not to hold the DISPENSE pushbutton in, as it will go into its alternate mode in which fast repetitive dispensing takes place. Should this happen, simply press DISLODGE and then DISPENSE (momentarily) to achieve the desired state, that is, where there will be a fresh drop of the proper size at the end of the capillary.

   When ready to begin, initiate the analysis according to the procedure outlined in the polarograph instruction manual. In the case of a Model 264 or a Model 384B, the analysis will go to completion automatically with no further operator attention. In the case of a Model 174A or a Model 364, some additional attention during the analysis may be required. Again, it is necessary to consult the individual instruction manuals for the required information.

   Should the measurement in question call for "spiking" the sample, as in standard addition techniques, this can be easily done. At the right side of the electrode support block is an opening to a channel that extends to the lower surface of the electrode support block directly above the sample. The channel entrance has a circular cover that pivots up out of the way to give user access. With the cover up, micropipet can be inserted to make the addition as shown in Figure 3-5.

6. If more than one sample is run, take care to rinse the electrodes with distilled or deionized water or the appropriate solvent between runs. Be sure to allow adequate time for the electrodes to drain before immersing them in the new sample. Gently blot the tip of the capillary with tissue. Also, be sure the DROP ENABLE switch is in the OFF position when sample changing. This will prevent any accidental mercury spillage. This procedure is followed as many times as there are samples to be run.

Recall that the mercury drop size is dependent on the height of the mercury column as in classical dc polarography. The mercury reservoir has been designed so that only a small change, less than 1/2%, in the mercury drop area will occur during the running of 36 samples, using the DME or SMDE mode, a 1.5 V potential range, and a small drop size. In HMDE operation, where but a single drop is used for each analysis, this source of error is inconsequential. To eliminate it in DME analyses, simply run a new standard after each series, or after each 36 samples, whichever occurs first.

When the first analysis has been completed, wash the electrodes thoroughly with deionized water (or an appropriate solvent if non-aqueous solvents are used). Set the Model 303A DROP ENABLE switch to the OFF position, thereby eliminating any possibility of a mercury spill. No further action is required to shut off the mercury flow from the reservoir when changing the capillary. When a capillary is removed, the most mercury that can escape will be a minute drop at the top of the capillary.

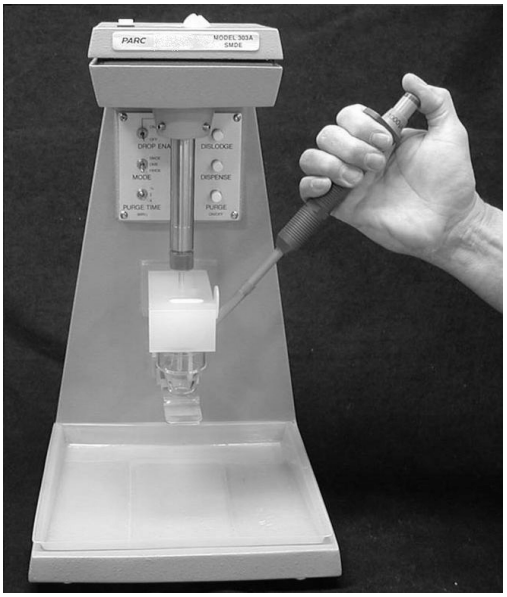


Figure 3-5, Spiking the Sample

3.5.3. Model 303A Operating Hints

Careful adherence to the following hints should help users in obtaining consistently good results when using the Model 303A.

1. CAPILLARY CLEANLINESS: A clean capillary starts easier and operates better. For this reason, prior to installing any capillary that has seen prior use, or that has been stored for an extended period, users are advised to clean the capillary. The recommended procedure is to aspirate 1 M HNO_3, water, and methanol, respectively, through the bore and then to dry the bore by blowing nitrogen through it under high pressure.

2. DROP DISLODGMENT: In addition to controlling the energy of the drop dislodgment via the rear-panel adjustment, it may occasionally be desirable to make a mechanical adjustment by varying the capillary position. When the capillary nut is loose, the capillary can be positioned over a range of about 1 mm with slight pressure. If the capillary is moved to the rear, towards the casting, the drop knock intensity will be weakened. If it is moved away from the casting, the drop knock intensity will be increased. To adjust its location, the operator must loosen the capillary nut and then apply a *slight* pressure in the appropriate direction while tightening the capillary nut. This adjust is made while the unit is dispensing.

CAUTIONS!

a. The total positioning range of the capillary at the drop knocker is only about 1 mm. Use only slight pressure to move the capillary.

b. Do not use the set screws located near the dispense solenoid to make this adjustment. The unit is aligned at the factory to center the capillary. Adjusting the set screws may damage their insulating tips and ground the working electrode.

Note that variations in the line voltage may affect the intensity of the drop knock. If significant line-voltage variations are observed or suspected, a line-voltage regulating transformer or supply should be used to provide power to the polarograph. This problem manifests itself as an occasional sudden rise (undislodged drop) or decrease (excessive knock) in the electrode current during a scan.

3. SURFACE BUMPING: When the mercury solenoid operates, it imparts energy to the mercury in the reservoir. If the reservoir cover is off, the user may notice a "bump" momentarily appear on the surface of the mercury each time the solenoid operates. The amplitude of the bump depends on the amount of mercury in the reservoir and on the amount of air trapped in the solenoid, if any. If there is trapped air, the bump will be higher than if there is none. If the reservoir is full and the solenoid is free of air, the "bumping" effect will be scarcely noticeable. If the reservoir level is low and there is considerable trapped air, the bump will be very pronounced. An understanding of what is happening may he helpful in evaluating the solenoid/capillary performance with respect to trapped air.

4. AIR IN THE CAPILLARY: Breaks in the mercury column are to be expected during and shortly after installing a capillary. Once cleared, this air should not return. If air gaps do re-appear, check the following.

    a. Capillary Ferrule Location: This dimension should be 0.110 0.01 inches from the end of the capillary to the top of the ferrule.

    b. Capillary Seal: This is the O-ring that slips over the end of the capillary and butts against the ferrule. The end of the seal should extend approximately 0.02 inches above the tip of the capillary. For proper operation, it is essential that this seal show no wear or damage. If the seal appears to be imperfect, remove it and re-install it in its reversed position. Additional seals can be purchased from Princeton Applied Research.

    c. Valve Seat: Using a light and mirror, inspect the inside surface on which the capillary seal seats. This surface can be readily cleaned by means of a cotton swab wetted with 1,1,1-trichlorthane. Allow the valve seal to dry completely before re-installing the capillary.

3.6. Cell Contamination

In parts-per-billion (ppb) level determinations, the possibility of contamination of the test solution by the sample cup should not be ignored. Three kinds of sample cups are available for use with the Model 303A. The first is a light weight, inexpensive throwaway plastic cup, which, in addition to freeing the user from dishwashing, allows very low-level analyses to be conducted with minimal risk of solution contamination through ion exchange with the cell wall.

The glass sample cups offer the advantages of permanence and transparency. However, the risk of contamination with these cells is higher than with those made of plastic. The borosilicate glass walls of the cell can act as an ion exchanger, removing metal ions at one time (via wall adsorption) and releasing them to the test solution at other times. It is therefore recommended that analyses be completed as quickly as possible. To avoid leaching metals from a cell in ppb determinations, adopt a standard practice of filling the cell with 6 M nitric acid for at least one hour (overnight, if possible) prior to the analysis, followed by rinsing the cell with deionized water only. Rinsing the cell with tap water followed by deionized water is self-defeating because the zinc and other metals in the tap water will adsorb onto the newly cleaned surface and will not be removed during the rinse with deionized water.

3.7. Standard Solutions

For good results, one should not attempt to store a standard solution more dilute than 10^{-3} M. More dilute solutions should be prepared by serial dilution on a daily basis and, if possible, the same flasks should be retained for these dilute solutions.

3.8. Purification of Supporting Electrolytes

Common electrolytes for use in stripping analysis include potassium chloride, potassium thiocyanate, acetate buffer, ammoniacal buffer, sodium nitrate, etc. Even when prepared under the most carefully controlled conditions, these solutions will contain heavy metal contaminants which originate in the reagent. It is possible to purify these supporting electrolytes by controlled potential electrolysis.

The greater the period of electrolysis, the greater the degree of purification. Residual levels of heavy metals in the purified electrolytes will be in the ppb or sub-ppb range. If desired, the cell can be allowed to operate continuously with aliquots of purified electrolyte withdrawn as required. NOTE: Strong acids should not be subjected to this type of purification procedure.

3.9. Preparation of Ultra-Pure HCL and NH_4OH by Isothermal Distillation

It is possible to prepare metal-free ultra-pure HCl and NH_4OH by means of isothermal distillation of ACS grade reagents. A 500 ml beaker half-filled with deionized water and a 500 ml beaker filled with volatile acid or base are placed in a large desiccator. The lid is placed on the desiccator and the system allowed to stand for a week to 10 days. At the end of this time the beaker of water will have come to equilibrium with the acid (or base). The strength of the purified reagent will be related to the final volume ratio of the starting and purified reagent. Since metallic impurities are not volatile and since the distillation has taken place at room temperature, obviating mechanical transfer of impurities, it is possible to prepare reagents of extremely high purity. This technique is simple and easy to set up, but requires about one week. For highest purity acid the beaker containing the water must be pretreated to remove metals from the surface. Also, it must be protected from condensate transfer from the desiccator lid. Combining isothermally-distilled HCl and NH_4OH in the proper ratio will give a highly pure ammoniacal buffer which will not require electrolytic purification.

3.10. Sample Digestion

The analysis of many matrices for low-level metals must often be preceded by an acid digestion step. During digestion, the matrix constituents are converted to volatile components such as carbon dioxide and water, leaving non-volatile metals as residue. If the matrix is being analyzed for volatile metals such as arsenic and selenium, it may be necessary to perform the digestion under reflux in a Bethge apparatus (G. Frederick Smith Co., 867 McKinley Avenue, Columbus, Ohio 43223).

Acids used for digestion should be as pure as possible to avoid introduction of metal contaminations from the digestion reagent. A family of ultra pure acids with heavy metal content typically of the order of 1 ppb or less are available and are marketed by J. T. Baker ("Ultrex" brand), BDH ("Aristar" brand) and E. Merck ("Suprapur" brand).

3.11. Intermetallics

Anodic stripping voltammetry at the HMDE can be complicated by intermetallic formation inside the mercury drop. When metals such as copper and zinc are present in solution at high concentrations, there is a tendency to form a Zn-Cu intermetallic when these metals are deposited into the a mercury electrode. Another combination that tends to be troublesome is the Zn-Ni intermetallic. When an intermetallic is formed, the stripping peaks for the constituent metals may be shifted, severely depressed, or absent altogether. The use of the differential pulse stripping technique is advantageous since deposition times can be kept short and minimum amounts of metals are incorporated into the HMDE. The HMDE used with DPASV has been found to be the most versatile electrode-technique combination, and is recommended for use over a range of 1-100 ppb. Thin Film Mercury Electrodes are recommended for operation below 10 ppb only.

3.12. Solid Working Electrodes

In applications requiring very long analysis times, or where it is necessary to achieve the absolute maximum sensitivity, it may prove advantageous to use a mercury-film working electrode, that is, a solid electrode that has been plated with a mercury film. Because a film electrode has a larger area-to-volume ratio than an HMDE, a higher concentration of the metal to be analyzed can be achieved for the same deposition time, giving an inherently higher sensitivity. However, film electrodes have the disadvantage of requiring cleaning and plating. In addition, the reproducibility as a function of such factors as stirring rate, film thickness, and exposed electrode area are more a problem for these electrodes than for the HMDE. Although one could use several different materials for the electrode substrate (gold, platinum, carbon), glassy carbon, the only one available for the Model 303A, and wax-impregnated graphite (WIG) seems to be the materials that give best results. The metal electrodes are not completely inert.

The G0197 Glassy Carbon Electrode is manufactured specifically for the Model 303A. when the G0197 is used, the MODE should be set to HMDE. Note that the plunger in the valve body will be actuated periodically; this is normal and no damage to the plunger will result. A beaker should be placed beneath the G0197 to catch the mercury when the electrode is removed.

Because the layer of deposited mercury is extremely thin, metal-film electrodes are limited to concentrations of no more than 10^{-7} due to amalgam saturation. Also, once the electrode is plated, it must be protected from oxygen to prevent oxidation of the film. This protection is provided automatically by the purging/blanketing gas system.

Prior to conditioning a film electrode, the operator must decide whether the mercury film is to be retained or removed during the conditioning operation. The conditioning potential should be set accordingly. Reliable stable operation over a period of days is frequently possible with a single film. Where this is the case, it is probably better not to do "in situ" plating, but rather to make plating a separate operation to be performed only when necessary as a result of electrode degradation. In situations where the electrodes degrade quickly, it is probably better to strip off the mercury film in the conditioning operation and to replate "in situ" during the concentration step.

WIG electrodes are quite stable and can frequently be used for several days without having to replate. However, daily replating is easily done, typically requiring 10-15 minutes. In many applications, it will prove expedient to plate the electrode during the concentration step of the analysis. Observed symptoms when an electrode requires replating include high residual current, low hydrogen over-voltage, a shift in stripping peaks to more negative potentials, and a loss of sensitivity. The potential at which the electrode is mercury plated can affect the behavior of the electrode during the subsequent analysis. Generally speaking, it is desirable that the plating potential be -0.4 V or more negative (SCE). If plating is done at a more positive potential, there is a possibility of obtaining double peaks during the subsequent analyses. One plating procedure which has proved satisfactory in a number of applications is to plate the electrode in a well stirred solution of 2.5 parts-per-million ppm (Hg^{++}) made slightly acidic with nitric acid at -0.4 V vs. SCE for five minutes. The electrode should be cleaned at a potential of 0.0 V vs. SCE for three minutes in a stirred solution before plating.

Glassy carbon is particularly well suited to use as a mercury-film substrate. Glassy carbon is a very hard vitreous carbon, with good conductivity. It can be polished to a mirror-like finish. This electrode is very rugged and can usually be cleaned simply by wiping with a tissue or filter paper. Successful "in situ" plating can generally be accomplished if the electrolyte contains mercuric ions at a concentration of nominally 2 ppm.

3.13. Operation with Non-Princeton Applied Research Equipment

The Model 303A is not constrained to use with an Princeton Applied Research Polarographic Analyzer. It can be easily incorporated into systems containing other equipment, assuming the appropriate signals for DISPENSE, DISLODGE, and PURGE are available. The necessary interconnections are made via the rear-panel INPUT connector. The table in Appendix B describes the signal/pin assignments at this connector for a typical connector.

4. Mechanical Components Theory and Service

4.1. WARNING!

THESE SERVICE INSTRUCTIONS ARE FOR USE BY QUALIFIED PERSONNEL ONLY. TO AVOID ELECTRIC SHOCK, DO NOT PERFORM ANY SERVICING, OTHER THAN DESCRIBED IN THE EARLIER SECTIONS OF THIS MANUAL, UNLESS YOU ARE QUALIFIED TO DO SO. POTENTIALLY LETHAL VOLTAGES COULD BE PRESENT INSIDE THIS APPARATUS.

Any adjustment, maintenance and repair of the opened apparatus under voltage shall be avoided as far as possible and, if unavoidable, shall be carried out only by a skilled person who is aware of the hazard involved.

When the apparatus is connected to a supply circuit, terminals may be live, and opening covers or removing parts (except those to which access can be gained without the use of tools) is likely to expose live parts. The apparatus shall be disconnected from all voltage sources before it is opened for any adjustment, replacement, maintenance, or repair. Once opened, power may be applied as necessary for the maintenance in question.

Capacitors inside the apparatus may still be charged even if the apparatus has been disconnected from all voltage sources. Service personnel are advised to wait a long period of time before assuming that all capacitors are discharged.

4.2. Mercury Feed Assembly

The Model 303A base, stand, and mercury reservoir are all part of a single massive casting that provides great stability and mechanical integrity. The mercury valve assembly projects downwards from the reservoir as illustrated in Figure 4-1. The heart of this assembly is the solenoid body (item 2) which is threaded into a bushing in the floor of the reservoir. Mercury flows through a vertical hole in the upper section of the solenoid body, and then down around the plunger in the valve stem assembly (item 4) to where it has access to the top of the capillary if the solenoid is energized. In operation, the solenoid is energized only long enough to dispense a drop, except to DME operation. The duration of the inter-dispense intervals determines whether the electrode functions as an SMDE or HMDE. The long stainless steel sleeve of the valve body (item 3) channels the mercury and supports the plunger guide (5). A compression spring (6) continuously applies a downwards force on a retaining ring (7), so that the polyurethane tip at the end of the plunger seals the capillary opening. When the solenoid is energized, the solenoid plunger is raised, working against the spring, breaking the seal between the polyurethane cap and the capillary, and allowing mercury to flow down the capillary. Note that the valve seat (10) threads into the valve sleeve, and that the capillary nut threads into the valve seat, squeezing the capillary O-ring (9) and securing the capillary. The metallic parts that contact the mercury are made of stainless steel to prevent contamination of the mercury by metal dissolved in it. The materials used in the non-metallic parts have been selected on the basis of their being insoluble in mercury and non-reactive to it.

With respect to field service, it is unlikely that anything more than changing a capillary will be required. However, if it should ever become necessary, partial disassembly is possible. Full instructions for removing a capillary are in Subsection 4.5A. Subsection 4.5D contains instructions for installing a capillary.

4.3. Electrode Support Block

In addition to the various channels it contains to provide passage for the electrodes, dip tube, and wires, the electrode support block houses the dislodge solenoid. Dislodgment is accomplished by energizing the solenoid. Whenever this is done, the solenoid plunger strikes the capillary, causing the drop to be sheared off. The force with which the plunger strikes the capillary can be adjusted from the rear panel.

4.4. Mercury Reservoir

The interior of the reservoir is lined with a polystyrene insert which is coated with a black conductive film. In order to insure that mercury does not contact the instrument casting, do not allow any sharp object to penetrate or to cut this insert. Under no circumstances should the coating be cleaned with solvent; a simple wiping action with dry lint-free tissue is recommended (Microwipes, Cat. No. 4815, available from Clean Room Products, 56 Penataquit Avenue, Bay Shore, NY 11706, Phone: (516) 968- 8282). Removal of the black coating by cleaning with solvents could result in excessively high instrumental noise levels.

Depending upon laboratory conditions, a thin film may form on the mercury surface inside the reservoir after a period in excess of a few weeks. This should not affect the operation of the SMDE. Minimal maintenance consists of the occasional removal of this film. No portion of the film should ever be allowed to enter the valve body.

There is a procedure for draining the reservoir quickly:

1. Switch DROP ENABLE off and remove the reservoir cover.

2. Remove the capillary, following the instructions in step 1 of Section 4.5A.

3. Set a beaker or other suitable container on the electrode support block so that it will catch the falling mercury. Keep in mind the quantity of mercury to be drained. It may be best to plan on having two containers, each large enough to hold half the mercury without danger of spilling. Beakers of 150 cc capacity generally work well for reservoir draining. They have adequate capacity and are small enough to allow their removal when partially filled with mercury.

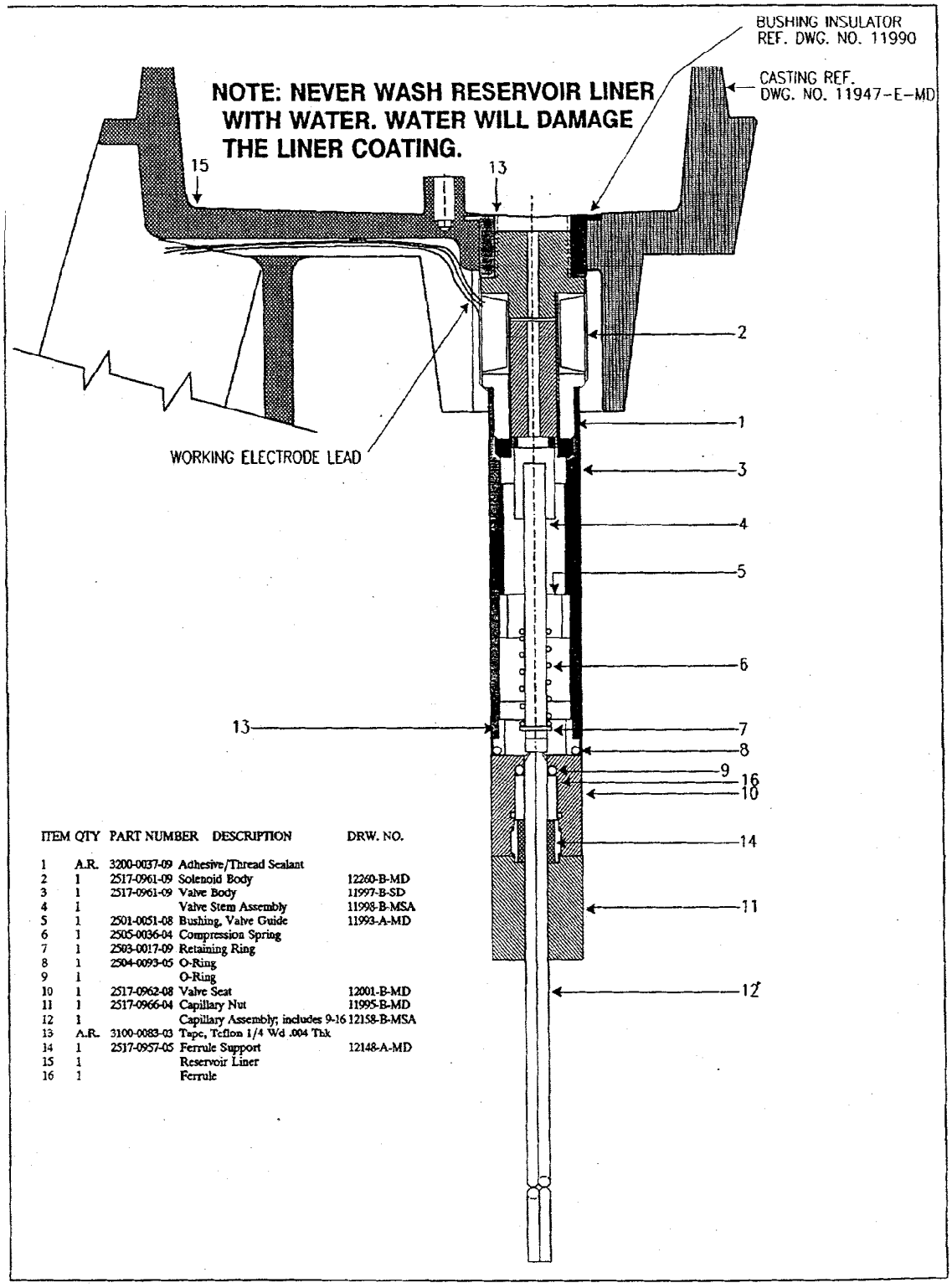
4. When ready, press and hold in the DISPENSE pushbutton. The mercury will drain from the reservoir for as long as the pushbutton is held in. If a scum or film has formed on the surface of the mercury in the reservoir, it is most prudent to prevent this portion of the mercury from passing through and contaminating the valve assembly. The recommended technique is to drain the reservoir to a low level, followed by removing the contaminated mercury by aspiration. If necessary, aspirate any drops of mercury remaining in the reservoir.

5. To drain only the valve assembly, block the valve inlet hole from above by inserting a blue or yellow Eppendorf pipet tip, thus blocking mercury in the reservoir from entering the valve.

4.5. Removing Mercury from the Valve Body

The valve body assembly consists of four discrete components: the valve body, plunger, valve seat, and capillary nut (see Figure 4-1). The valve body is secured to the reservoir via a threaded hole and is not removed during normal service. Do not adjust the four hex screws located in the underside of the reservoir; these are factory-set adjustments for proper positioning of the valve body, and they should not be removed.

Proper operation of the valve body assembly is essential to satisfactory performance of the Model 303A. The valve body is a mechanical device and requires maintenance. If questionable performance is observed, the valve body should be disassembled and cleaned as described in Section 4.5C. To assure uninterrupted operation, a spare valve body (Model 303/21) is recommended.



ITEM	QTY	PART NUMBER	DESCRIPTION	DRW. NO.
1	A.R.	3200-0037-09	Adhesive/Thread Sealant	
2	1	2517-0961-09	Solenoid Body	12260-B-MD
3	1	2517-0961-09	Valve Body	11997-B-SD
4	1		Valve Stem Assembly	11998-B-MSA
5	1	2501-0051-08	Bushing, Valve Guide	11993-A-MD
6	1	2505-0036-04	Compression Spring	
7	1	2503-0017-09	Retaining Ring	
8	1	2504-0093-05	O-Ring	
9	1		O-Ring	
10	1	2517-0962-08	Valve Seat	12001-B-MD
11	1	2517-0966-04	Capillary Nut	11995-B-MD
12	1		Capillary Assembly; includes 9-16	12158-B-MSA
13	A.R.	3100-0083-03	Tape, Teflon 1/4 Wd .004 Thk	
14	1	2517-0957-05	Ferrule Support	12148-A-MD
15	1		Reservoir Liner	
16	1		Ferrule	

Figure 4-1, Model 303A SMDE Mechanical Assembly

4.5.1. REMOVING MERCURY FROM THE VALVE BODY

1. Connect the SMDE to a Polarographic Analyzer, which supplies power for the Model 303A's mechanical and electrical components. Switch the DROP ENABLE off and set the rear-panel drop DISLODGE ADJUSTMENT to fully counterclockwise (this setting applies the minimum force to the capillary). Rinse the capillary tip with deionized water and dry thoroughly. Remove the capillary and capillary nut from the valve body by unscrewing the knurled portion of the capillary nut. As the assembly is removed, the mercury in the capillary should retract up the bore toward the valve seat, and a residual amount of mercury will flow from the coupling. Remove this residual mercury by vacuum aspiration. Set the capillary aside.

2. Place a small (150 ml) beaker below the valve body. Set the MODE switch to HMDE and the DROP SIZE selector to L. Drain the mercury from the reservoir pressing DISPENSE and holding it in until the reservoir is nearly empty.

Set the collected mercury aside, storing it in a clean container. Remove the accumulated film in the reservoir by vacuum aspiration or by careful wiping with a dry, lint-free tissue. Do not allow any of the film to enter the valve body.

3. Drain the remaining mercury from the valve body as described in Step (2).

4.5.2. Filling the Valve Body with Mercury

1. Note: to avoid accidental mercury spills, it is recommended that a capillary be installed before filling the valve body with mercury (see subsection 4.6C)

Insure that the DROP ENABLE switch is off. Obtain a clean hypodermic syringe (10 ml) with a needle and fill it with triply distilled mercury. (A recommended supplier of mercury is Bethlehem Apparatus Co., Hellertown, PA. Phone: 215-838-7034).

2. Confirm that the DROP ENABLE switch is off and slowly inject the mercury into a small hole located in the reservoir directly above the valve assembly. Continue the process until mercury is overflowing into the main reservoir.

3. Add sufficient mercury to the fill line (identified by the O-ring on the center post in the reservoir). To remove any air which may be present in the valve body, repeat Step 2 of Section 4.5A, but return the mercury to the reservoir and repeat the cycle several times. (Failure to switch the DROP ENABLE switch off will result in accidental mercury spillage from the valve.)

4.5.3. Cleaning and Disassembling the Valve Body

1. Remove mercury by following the steps outlined in Section 4.5A. Carefully remove the valve seat and plunger assembly by unscrewing the valve seat. Do not allow the valve body itself to rotate while the valve seat is being removed. Take care not to damage the O-ring on the threaded portion of the valve seat during its removal. The plunger will slip out as the valve seat is removed.

2. Set the plunger aside and inspect the valve seat. Both the inner and outer surfaces should have a mirror-like finish and be free of any dirt, pits, or obvious imperfections. Remove any surface residue with 1,1,1-trichloroethylene or methanol. Avoid exposing the O-ring to the solvent. Set the valve set aside.

3. Examine the plunger. It should have a uniform grey or black appearance with no obvious scratches or scuff marks. Remove any residue from the plunger with a lint-free tissue. The polyurethane plunger tip is securely attached to the shaft assembly. Avoid exposing the plunger tip to solvents. The plunger spring tension and length are set for optimal performance at the factory. Do not adjust or replace these parts.

4. Wipe the interior of the valve body with a lint-free swab moistened with methanol (a urethane foam swab is recommended, such as Catalog No. 632 Sof-Swab from Clean Room Products, Inc., 56 Penatqauit Avenue, Bay Shore, NY 11706, Phone 516-968-8282. It is also possible to direct a stream of methanol into the valve body from the bottom. Cap the hole in the bottom of the reservoir body to prevent methanol from contacting the reservoir coating. Dry the valve body thoroughly with a stream of nitrogen.

4.5.4. Assembling the Valve Body

1. Place the plunger back into the valve body so that only the plunger tip shows. Carefully slip the valve seat under the valve body assembly.

2. Screw the threaded portion of the valve seat counterclockwise into the valve body (finger-tight, use no tools). Some users apply two turns of Teflon tape to the threads of the valve seat to insure a leak-free seal, with the tape winding in the same direction as the threads. Teflon tape is not, however, applied to the threads during manufacturing.

4.6. The Capillary

The capillary consists of three components: an O-ring, an aluminum ferrule, and a glass capillary. The aluminum ferrule is secured to the glass capillary at the factory. The O-ring seal is the only removable component. It provides an air-tight connection between the capillary assembly and the valve seat. The capillary bore is somewhat larger than those used in conventional dropping mercury electrodes, but it still is susceptible to obstruction for foreign material. Proper operation of the SMDE depends upon scrupulous attention to periodic maintenance of the capillary. This maintenance depends upon the frequency of use, the polarographic technique, and the matrix composition of the test solution. Residual material from the test solutions may clog the capillary tip and cause premature drop loss in HMDE operation.

If the mercury drop falls off the end of the capillary after DISPENSE is pressed, suspect an imperfection in the capillary orifice, normally caused by either an obstruction, which can be removed by cleaning, or a crack in the glass at the orifice, which requires that the capillary be discarded.

4.6.1. Capillary Removal, Inspection, and Cleaning

1. Remove the capillary, following these steps: Disconnect the Model 303A from the polarographic analyzer, which supplies power to its mechanical and electrical components. Rinse the capillary tip with deionized water and dry thoroughly. Remove the capillary and capillary nut from the valve body by unscrewing the knurled portion of the capillary nut. As the assembly is removed, the mercury in the capillary should retract up the bore toward the valve seat, and a residual amount of mercury will flow from the coupling. Remove this residual mercury by vacuum aspiration.

2. Inspect the capillary. The surface nearest the ferrule should have a uniform iridescent finish that extends into the bore. There should be neither cracks nor fissures in the region of the bevel, and the capillary bore should be clear of particulate matter (use a 20X magnifier).

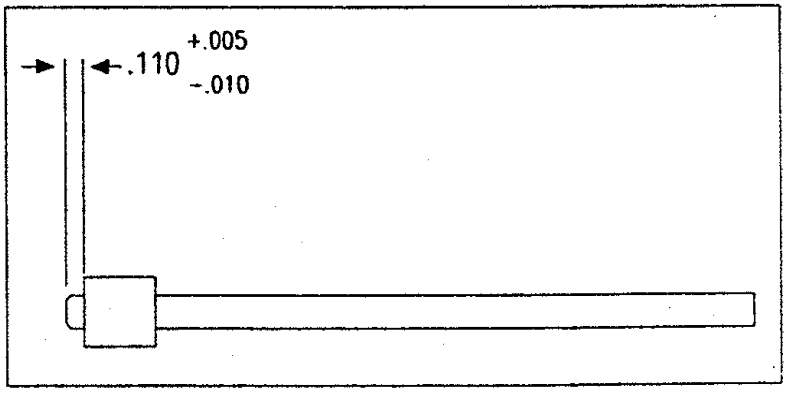


Figure 4-2, Correct Ferrule-To-Tip Distance

3. If the capillary is clogged, clean it by applying a vacuum or pressurized dry nitrogen through the bore. (Sometimes both techniques are required.) If necessary, gently tap the distal tip (ferrule end) on a hard surface covered with a paper towel to avoid scratching. Do not attempt to clear the bore with fine gauge wire, as this action will surely ruin the capillary. The ferrule-to-tip distance must be 0.110 inches (see Figure 4-2) or it is probable that the SMDE will malfunction.

4. Clean the capillary bore by aspirating several milliliters of 1 M HNO_3 followed by a deionized water rinse. Finish the cleaning cycle with a methanol rinse and air-dry the capillary at 65°C for one half-hour.

4.6.2. Siliconizing the Capillary Bore

Siliconizing the bore helps to prevent the test solution from penetrating the capillary. Once the capillary is properly cleaned, it can be siliconized by placing the tip opposite the ferrule in a fresh vial of siliconizing fluid. Do not siliconize the capillary tip nearest the ferrule. (Use Model G0092 Siliconizing Solution). Capillary action will draw the fluid partially up the bore. Remove excess siliconizing fluid from the capillary by vacuum aspiration from the end opposite the ferrule. Air-dry and cure overnight in an oven at 65°C.

4.6.3. Installing a Capillary into a Valve Body

1. Remove the capillary and capillary nut (See Section 4.5A).

2. Connect the Model 303A to a polarographic analyzer to provide power to run the dispensing solenoid.

3. Place a small (150 ml) beaker below the valve body. Switch DROP ENABLE on and select the SMDE mode with L (large) DROP SIZE. Press and hold the DISPENSE button for 10 to 15 seconds. Switch the DROP ENABLE switch off, and return the mercury to the reservoir. Repeat this step several times.

4. Insert a clean, dry capillary into the capillary nut and position them beneath the valve body. Screw the capillary nut into the valve seat - fingers only, no tools - until you can discern slight thread resistance. At this point the capillary should be fairly loose.

5. Place a small beaker beneath the capillary and switch DROP ENABLE on. Select L (large) DROP SIZE and switch the MODE SMDE. Press and HOLD dispense for 10 to 15 seconds. Mercury drops from the capillary should be unusually large and should flow rapidly. Air bubbles may appear in the bore, slowing the flow. If they don't move down the capillary, aspirate the end of the capillary with a vacuum pump, keeping the DISPENSE switch depressed so that they can be purged from the bore. When mercury flow is re-established, the capillary will rapidly dispense large drops.

6. With the DISPENSE button still engaged, gradually tighten the capillary nut in small increments until it is finger tight. The goal of this step is to tighten it just enough so that the drop knocker won't knock it loose in normal operation. There should be a slight gap between the capillary nut and the valve body. If the capillary nut fits flush against the body, suspect a slipped ferrule on the capillary.

Figure 4-3 illustrates an alternate method of initiating mercury flow. This method, one of several developed by Princeton Applied Research customers, is designed to exclude air from the capillary.

4.6.4. Checking Capillary Continuity

Maintaining electrical continuity of the mercury in the capillary is essential to the operating the Model 303A. Entrapped air, usually due to improperly filling the mercury reservoir or tightening the capillary nut, can interrupt this continuity. The following procedure is a quick check of the capillary's continuity.

1. Connect the Model 303A to a polarographic analyzer to provide it with power. Switch the analyzer to its standby mode so that it is not applying an electrochemical potential to the cell.

2. Place a polarographic cell containing a supporting electrolyte with an ionic concentration of at least 0.1 M in the Model 303A. Dispense a mercury drop.

3. Prepare an analog multimeter for resistance measurements in the range of 30 kΩ to 100 kΩ. Make sure the analyzer is in not doing a RUN. Connect the meter's leads to the rear-panel WORKING and COUNTER electrode test points.

4. Press the DISPENSE button while monitoring the meter. The measured resistance should fluctuate from 30 kΩ to 100 kΩ, but there should be no open circuit readings (infinite resistance). If there are, clear any entrapped air by following the procedure in Subsection 4.5C.

5. Hang a drop of mercury on the capillary and monitor the resistance for 10 to 15 seconds. The resistance should be constant until the drop is dislodged manually. (If the resistance changes during this check, make sure the mercury drop is still hanging at the end of the capillary. The voltage imposed by the meter can cause the drop to fall off.)

4.7. Dislodging Mechanism

The rear-panel DISLODGE ADJ control should be adjusted so that the drop knocker strikes the capillary with the *minimum* force necessary to dislodge the drop. If the knocker strikes with too much force, the capillary will vibrate excessively and next drop will also fall off.

The drop knocker itself is housed in the electrode support block. Although a rubber boot protects the knocker mechanism from the cell solution, excessive purge flow rates can deposit salts on the drop knocker, requiring commensurate increases in the dislodging force. Since it is possible increase the dislodging force until it breaks the capillary, the salts should be removed from the drop knocker by filling the cell to the very top with deionized water and purging it for several minutes.

4.8. Reference Electrode Maintenance

The reference electrode furnished for use with the Model 303A is a simple silver/silver chloride electrode that makes contact with the analyte via a porous Vycor (a trademark of Corning Glass Corporation) frit. The potential applied to the working electrode is with respect to this reference electrode. Note that potentials so defined differ from those referenced to a Standard Calomel Electrode by no more than 50 mV, and are shifted in the positive direction relative to those referenced to the SCE.

Using a Vycor frit assures long periods of reliable operation without need for refilling, and without fear that the solution in the reference electrode will poison the test solution or vice versa. For maximum frit life, avoid alternate wetting and drying of the frit. This is readily accomplished by keeping a sample cup filled with deionized or distilled water in the analysis position when the Model 303A is not in use.

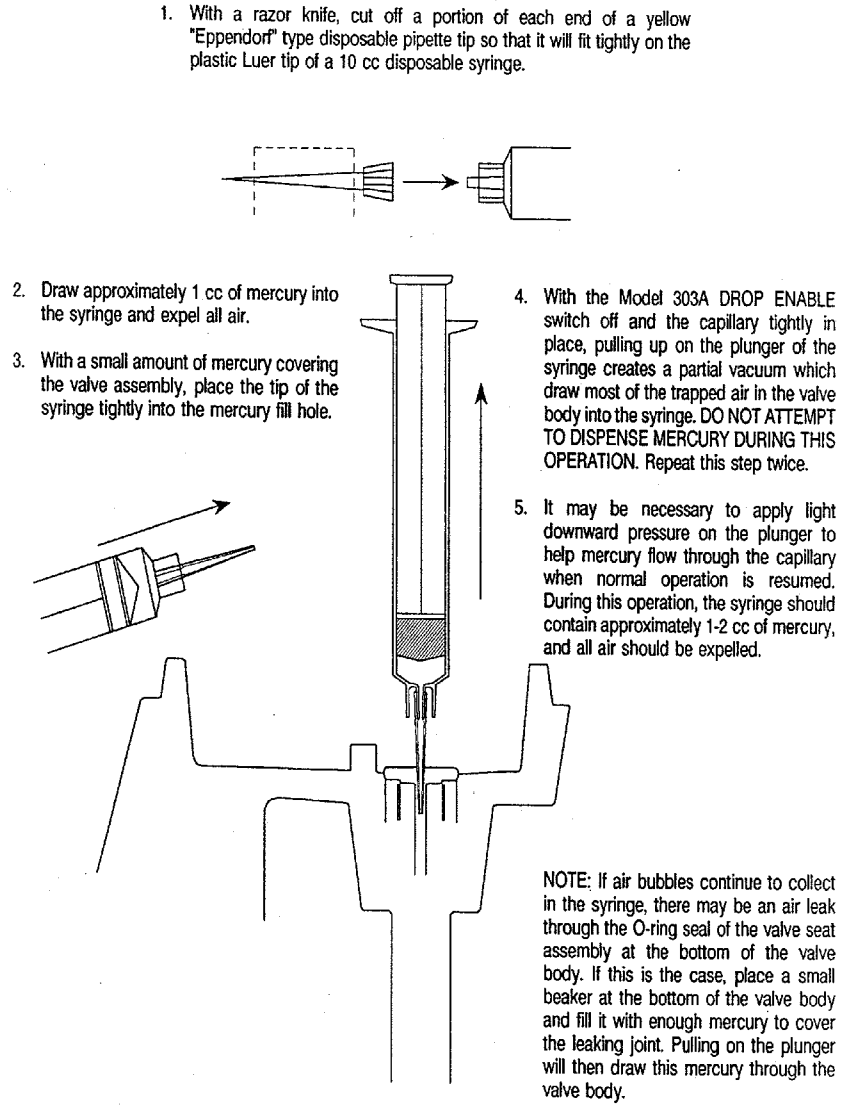


Figure 4-3, Alternate Method of Initiating Mercury Flow

A vial of electrode-filling solution (saturated with AgCl) is supplied with the electrode. During installation, the glass sleeve of the reference electrode is filled with this solution. Shake the sleeve while filling to free any bubbles. Once the sleeve is pushed up into the electrode support block, tap the sleeve to free any bubbles adhering to the electrode wire.

The only maintenance operation the user might face is replacing the unglazed Vycor frit at the end of the glass sleeve. These frits are reliable and users may expect almost indefinite operation without leakage between the inside of the reference electrode and the sample. However, it is possible that a frit will crack or dissolve in strongly alkali solutions, requiring that it be replaced. In addition, the Vycor frit may crack when exposed to extreme changes in the ionic strength or solvent character of the supporting electrolyte. A non aqueous filling solution (Model G0155) is recommended when working with non-aqueous solutions. When the frit material is thin or has a visible crack, replace as necessary. Replacement frits and the necessary Teflon shrink tubing are supplied with the Model 303A.

If the electrodes are normally stored in water, the user may notice shifting peak potentials after several days due to dilution of the of the filling solution by water entering the reference electrode. This problem may be overcome by completely replacing the filing solution.

If the Model 303A is routinely used in basic solutions, it is recommended that the Vycor frits be replaced with Model G0194 Polyethylene Disks. For experiments that require a bridge tube, such as chloride analyses, the Model K0154 Reference Bridge Tube is recommended. The Model K0154 is inserted through the sample port. (The Model K0154 is designed to be used with the K0077 Saturated Calomel Reference Electrode.)

4.8.1. Reference Electrode Removal and Inspection

1. Slip the glass Jacket Assembly (Model G0159) from the electrode support block. Add reference solution (Model SL0031) if necessary. Make sure that no air bubbles are trapped in the restricted area immediately above the frit.

2 Using a razor blade or other suitably sharp knife, cut the shrink tubing that secures the frit so that the old frit and shrink tubing can be freed and disposed of. If necessary, replace the quad-ring by carefully slipping down toward the frit.

3 Wash and dry the glass sleeve. Make sure the quad-ring groove in the cell block is clean and dry.

4.8.2. Reference Electrode Inspection and Changing the Frit

1. Insure that the silver wire is straight and will properly clear the restricted portion of the glass reference electrode jacket.

2. Replacement frits and Teflon tubing are packaged together in small plastic bags. The inside diameter of the sleeve is slightly greater than the diameter of the frit. TAKING CARE NOT TO WET THE REPLACEMENT FRITS OR MAKE FINGER CONTACT WITH THEM, grasp one end of a piece of tubing and press a frit into the other end. This step may require repeated attempts.

3. Hold the glass sleeve and orient it vertically so that the frit and the tubing can be pressed onto it. Press the tubing downwards so that the frit holds in while the tubing extends as far as it will go on the glass sleeve. Heat the Teflon tubing on all sides with a hot-air stream from a heat gun or equivalent source of dry, flameless heat. As the tubing shrinks, it will make a snug, moisture-proof seal with the glass sleeve and with the frit. Do not use a direct flame; it will char the Teflon. Allow the tubing to shrink over the disk and sleeve. Be sure to let the tubing cool to room temperature before lifting the assembly.

   Cut off the excess tubing (that is not in contact with the frit or the glass sleeve) with a razor blade so that the end of the tubing is flush with the bottom of the frit. Doing this avoids a possible air trap.

4. Fill reference electrode jacket, taking care that no bubbles are trapped. Place the filled reference electrode sleeve under the silver wire and push it into position. Ensure that the quad-ring is completely engaged in the electrode block by gently pushing the quad-ring completely into the block.

Bubbles can be freed by tapping or shaking the sleeve as it is being filled. (Most reference electrode malfunctions are caused by trapped bubbles).

The reference electrode wire (Teflon sheathed silver) is installed at the factory and should last indefinitely, unless it breaks and requires replacement. The reference electrode wire is 1.8" (4.57 cm) long and has a diameter of 0.020" (0.5 mm). The wire goes into a chamber in the electrode support block where it is soldered to a wire. To replace it, it is first necessary to gain access to the solder joint. The chamber housing the wire is filled with silicon rubber, accessible from the top of the electrode support block. By using a small spatula, it should take only a minute or two to remove enough rubber to expose the solder joint. Using a small (no larger than 25 watts) soldering iron, unsolder the old electrode wire and remove it. Then insert a new electrode wire in its place and solder it as required, using a good grade of 60/40 rosin core electronics solder. Then repot the joint with silicon rubber. NOTE: When working with the reference electrode, the user is advised to first remove the glass sleeve of the reference electrode, accomplished by simply grasping the sleeve and pulling it straight down.

4.9. Counter Electrode Maintenance

The counter electrode wire (Teflon sheathed platinum) is installed at the factory and should last indefinitely. The counter electrode wire is 2.60" (5.4 cm) long and has a diameter of 0.020" (0.5 mm). A broken electrode wire is easily replaced. The counter electrode goes into a chamber in the electrode support block where it is soldered to a wire. To replace the electrode, it is necessary to gain access to the solder joint. The chamber housing the junction is filled with silicon rubber, accessible from the top of the electrode support block. By using a small spatula, it should take only a minute or two to remove enough rubber to expose the solder joint. Using a small (no larger than 25 watts) soldering iron, unsolder the old electrode and remove it. Then insert the new electrode in its place and solder it as required, using a good grade of 60/40 rosin core electronics solder. Repot the joint with silicon rubber.

4.10. Mercury and Other Considerations Relative to Shipping

Should it ever be necessary to ship the Model 303A, it should first be drained of mercury. Then, as an added precaution against mercury being accidentally released during shipment, the unit should be placed in a sturdy plastic bag, which should be secured with a wire "twist tie" or otherwise sealed.

NOTE: One other caution with regard to shipping. Always remove the capillary and pack it separately in cotton to minimize the possibility of accidental breakage. Similarly, the glass sleeve of the reference electrode should be removed from the electrode support block and also separately packed to prevent breakage. It is probably a good idea to place a plastic sample cell in the normal operating position and tape it to the electrode support block so that the dip tube and electrode wires are fully protected.

4.11. Condensed Troubleshooting Guide

SYMPTOM(S)	PROBABLE CAUSES	WHERE DISCUSSED
Erratic, step-like current during voltammetric scan or complete loss of current.	1. Loss of electrical continuity due to trapped air within the capillary or within the valve body.	4.6C
	2. Slipped capillary ferrule	4.6A
Using the differential pulse waveform, the current suddenly increases or decreases and then slowly recovers. In other voltammetric modes, the current recovers very quickly.	1. Momentary loss of electrical continuity due to trapped air within the capillary or within the valve body.	4.6C
	2. Improper drop dislodge adjustment.	4.7
	3. Premature drop loss because of a dirty of partially clogged capillary tip.	4.6A
Inconsistent drop size, binding or scraping sound from the valve body.	1. Dirty valve body/plunger.	4.5
	2. Improper drop dislodge adjustment.	4.7
Mercury drop cannot be dispensed or mercury flows continuously from the capillary.	1. Plunger is stuck in down or up position, respectively	4.5
	2. Detached plunger tip.	4.5
	3. Dirty valve body/plunger.	4.5
Potentiostatic overload at any applied potential	Defective reference electrode	4.8
Mercury drop falls off the capillary	Defective capillary	4.6A

5. Electrical Components Theory and Service

5.1. Introduction

WARNING!

SERVICE INSTRUCTIONS ARE FOR USE BY QUALIFIED PERSONNEL ONLY. TO AVOID ELECTRIC SHOCK, DO NOT PERFORM ANY SERVICING, OTHER THAN DESCRIBED IN THE EARLIER SECTIONS OF THIS MANUAL, UNLESS YOU ARE QUALIFIED TO DO SO. POTENTIALLY LETHAL VOLTAGES COULD BE PRESENT INSIDE THIS APPARATUS.

Any adjustment, maintenance and repair of the opened apparatus under voltage shall be avoided as far as possible and, if unavoidable, shall be carried out only by a skilled person who is aware of the hazard involved.

When the apparatus is connected to a supply circuit, terminals may be live, and opening covers or removing parts (except those to which access can be gained without the use of tools) is likely to expose live parts. The apparatus shall be disconnected from all voltage sources before it is opened for any adjustment, replacement, maintenance, or repair. Once opened, power may be applied as necessary for the maintenance in question.

Capacitors inside the apparatus may still be charged even if the apparatus has been disconnected from all voltage sources. Service personnel are advised to wait a long period of time before assuming that all capacitors are discharged.

All timing and control functions are performed by a single chip microprocessor, U1. The microprocessor reads the state of the front panel switches and the Cell Number switch, S1. It also accepts inputs from the polarograph with which it is used and, if connected to a controlling polarograph manufactured by Princeton Applied Research, identifies the controlling device, adjusts its input connector's pinout accordingly, and submits to the controller's command signals. In turn, the Model 303A controls a variety of solenoids as required to achieve its functions. Timing signals are derived from a 4 MHz crystal-controlled oscillator, Y1. In addition, the circuit board contains an electrometer, U2, and a five-volt regulator, U3.

5.2. Inputs to the Microprocessor

5.2.1. Switches

All of the microprocessor's Port D and three lines from Port A are used to read the state of the front-panel switches and the Cell switch. The normal state of all the switches is high (pulled up by the resistors), unless otherwise indicated.

5.2.2. Rear Panel Connections

The Model 303A connects to the polarograph via a 25 pin D connector, J1, located on the rear panel. Referring to the schematic, note that many of the control lines have more than one designation. For example, 264 PURGE (pin 24) is different from 384 PURGE (pin 21). The individual rear-panel control signals are discussed in the following paragraphs.

1. DISLODGE AND DISPENSE SIGNALS: For the Model 384B, a Dislodge/Dispense cycle is initiated by a TTL logic 0 on either pin 22 or pin 9 of J1. There is no difference between the effect of applying a negative input to either pin. For polarographic analyzers other than the Model 384B, the control signal is still applied to pin 9 of J1. However, this signal is not TTL, but rather varies with the instrument. A transition to a logic low (negative- going edge) initiates the Dislodge/Dispense cycle. In addition, the Model 264 has a TTL Dislodge/ Dispense signal on pin 10. Transistors Q1, Q2, and Q9, together with their associated components, steer these signals and develop the required input, IRQ to the microprocessor.

The processor controls some of the gating via output line PB6, and some gating is done via pin 18 of J1, which is open when operating with a Model 384B and grounded when operating with

any other Princeton Applied Research polarograph. PB6 disables the IRQ signal, when doing critical timing operations, thereby preventing initiation of a dislodge/dispense cycle when one is already in progress.

2. PURGE AND STIR: Pin 21 is the purge input for the Model 384B. A purge will continue for as long as TTL logic low is applied to this pin. For all other polarographs, the control mechanism is the same, but occurs at pin 24 instead of at pin 21. Again, the microprocessor determines the model of polarograph connected and looks at the proper pin for purge control information. If the DROP ENABLE switch is set to the DISABLE position, these inputs are inhibited (no purge).

Pin 8 is the stir input for all polarograph models. In the case of the Model 384B, a TTL logic 1 turns the stirrer ON. For all other models, a TTL logic 0 turns the stirrer ON.

3. MULTIPLE CELL CONTROL: The lines used for Multiple Cell Control are 20 (READY), 25 (ACN), 11, and 12 (CELL ADDRESS BITS 0 and 1). These signals only matter when connected to a Model 384B. NEW 384 (pin 13), an input, is low only when the Model 303A is connected to a Model 384B. This is the line that tells the microprocessor whether it should use the information on pins 20, 25, 11, and 12. The handshake used to achieve multi-cell control is complex and beyond the scope of this circuit description.

5.3. Drive Signals

1. ANALOG ENABLE: The signal on PB4 and transistor Q7 are used to switch relay K1, which connects the three electrodes to the polarograph. In addition, the front-panel CELL ON lamp lights when K1 is energized. The processor interrupts the analog connections via K1 when purging the cell, when the DROP ENABLE switch is set to OFF, and when the Model 303A in question is not the one selected in Multiple Cell operation.

2. PURGE: The signal on PB3 and transistor Q6 are used to energize the Purge Solenoid, which controls the flow of nitrogen to the cell. When PB3 is high, purge nitrogen flows to the cell. When PB3 is low, blanketing nitrogen is applied to the surface of the analyte. When the Model 303A in question is not the one selected in multiple-cell operation, continuous purging takes place.

3. STIR: Provision is made for a Model 305 Stirrer which connects to J3. The stirrer takes its power from -15 V provided at pin 1 of J2. Logic signal PB5 controls Q8, which controls the stirrer as described in Appendix A.

4. DISLODGE: The signal on PB1 and transistor Q3 are used to energize the Dislodge Solenoid, which knocks the drop off the tip of the capillary. Capacitors C4, C5, and C6 actually store the energy that is applied to the solenoid when Q3 conducts. This provides faster, cleaner dislodge action than would otherwise be the case. The intensity of the dislodgement is controlled by R11, the rear-panel DISLODGE Adjustment.

5. DISPENSE: The signal on PB2 and transistors Q4 and Q5 are used to activate the Dispense Solenoid. In SMDE and DME operation, the signal at PB2 is applied for 50, 100, or 200 ms, as set by the DROP TIME switch (SMALL, MEDIUM, or LARGE as set by the Model 303A Drop Size switch). In DME operation Q4 is biased continuously into conduction, holding open the solenoid valve. In this condition, Q5 conducts heavily initially as C10 charges. Once C10 has become charged (time constant 120 ms), Q5 becomes a constant current source, limiting the current through the solenoid to prevent excessive heat buildup.

5.4. Electrometer

The electrometer comprises operational amplifier U2 and associated components. U3 is configured as a non-inverting, gain-of-one amplifier circuit with input protection. Its offset voltage is adjusted by R23. Note that the shield of the input line is not at ground, but rather at the U3 output level. In other words, the line is not grounded.

5.5. Test Points

There are three rear-panel test points provided for convenient monitoring of the three electrodes. The direct unbuffered reference electrode output is available at the corresponding test point. This is a high impedance point and should only be monitored with a high input impedance instrument. The potential at the reference electrode should be of opposite polarity to that programmed, but the magnitude should be the same as that programmed. The counter electrode is brought out to the correspondingly named test point. In this case, the source is a low impedance and may well be at voltages high enough to warrant caution. Wet fingers and a high counter electrode potential constitute a dangerous electrical shock hazard. As with the reference electrode, the polarity will be opposite that programmed. The magnitude of the potential will depend on the control program and on the resistance of the solution.

The working electrode test point should be at ground potential at all times. This electrode operates in the current-signal mode and a current signal cannot be monitored at a potential test point. The principal utility of the test point is as a fault indicator should a potential other than ground be measured. Such a fault would probably not be located in the Model 303A, but rather in the polarograph with which it is operated.

5.6. Troubleshooting

Despite the fact that the control mechanisms of the Model 303A are complex, troubleshooting is ordinarily quite simple. There are three integrated circuit chips that can be replaced in the field. They are U1, the microprocessor (which must be programmed at the factory), U2 the electrometer, and U3 the +5 V voltage regulator. Troubleshooting beyond the chip-replacement level is not recommended. If proper operation cannot be restored by simple chip replacement, contact the factory service department for advice.

APPENDIX A. Model 305 Stirrer

A.1. Safety Notice

As defined in IEC Publication 348, Safety Requirements for Electronic Measuring Apparatus, the Model 305 is Class III Apparatus, that is, it is apparatus in which protection against electric shock relies on the voltage in the apparatus being too low to be dangerous (the Model 305 operates from -15 V provided by the Model 303A).

A.2. Description

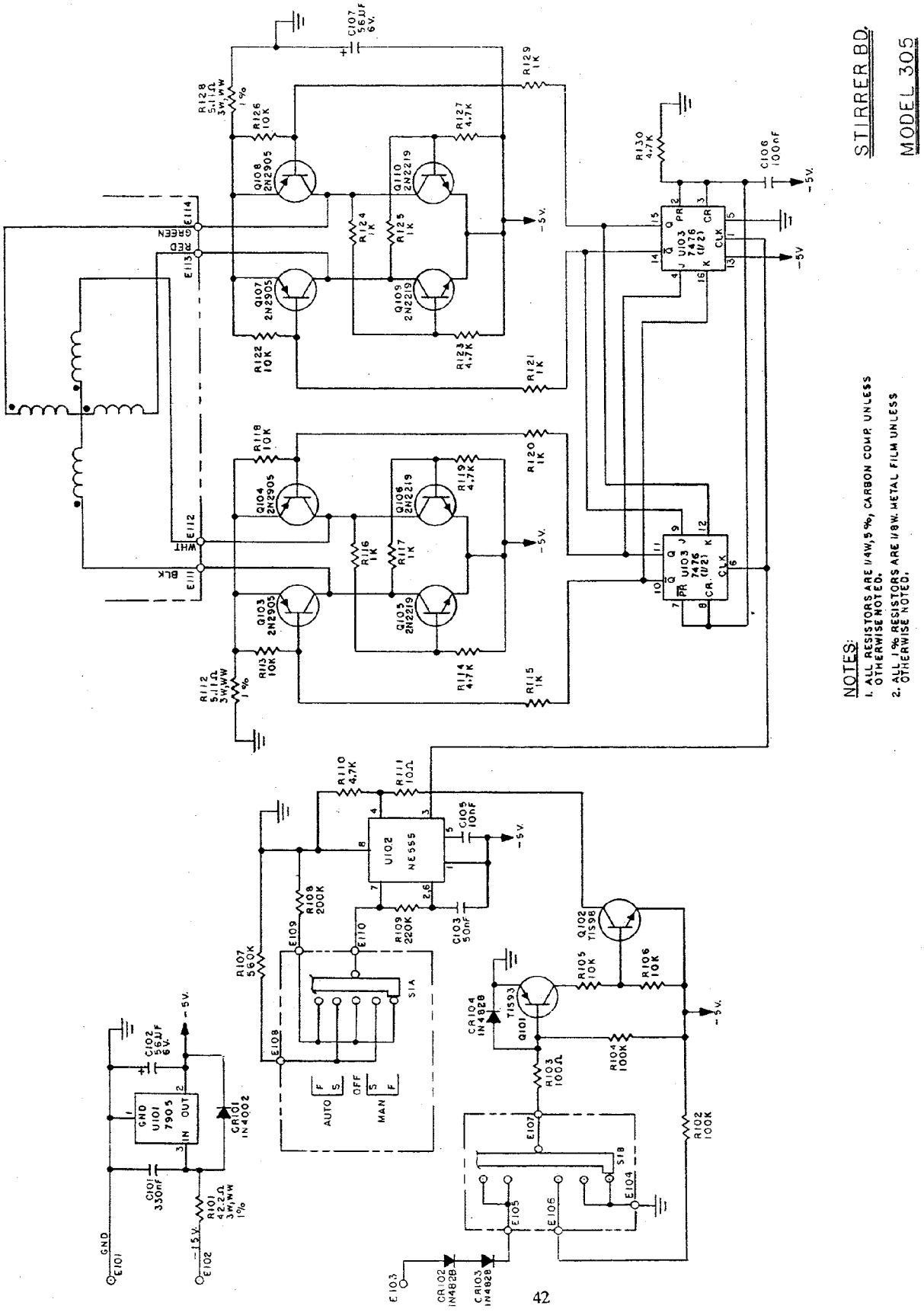
The Model 305 Stirrer is specifically designed for use with the Model 303A. The stirrer features an electronically generated rotating magnetic field (there are no moving parts) together with dual-speed operation in each of two control modes for maximum flexibility and utility. Operation is straightforward. A stirrer bar is placed in the cell, which is then secured in the usual manner. Then the stirrer is slid beneath the cell. The free end of the Model 305 cable connects to the STIRRER ACCESSORY connector on the back of the Model 303A. Stirring takes place as determined by the setting of the Model 305 Control switch and by the state of the other system components.

The Model 305 Control switch has five positions, OFF, MANUAL SLOW, MANUAL FAST, AUTO SLOW, and AUTO FAST. In the OFF position, the stirrer cannot be activated. In the MANUAL position, it is continuously activated, the only requirement being that the Model 303 be powered.

The SLOW and FAST stirrer rates are nominally 400 rpm and 700 rpm respectively, independent of the mode (MANUAL or AUTO). In the two AUTO positions, the stirrer is activated on sensing a STIR command from the polarograph. When a logic 0 is present at pin 1 of the Model 303A Stirrer Accessory connector, the Model 305 Stirrer will be inhibited. When a logic 1 is applied, the Model 305 will be activated. The timing of the control logic will depend on the user's operation of the polarograph.

The Model 305 uses solid-state circuitry for cool, reliable operation. An oscillator develops an ac signal that is then divided down to provide coil-drive signals of the proper frequency. Transistor coil-drive circuits power the individual coils to produce the rotating magnetic field. Special logic circuits monitor the level on pin 3 of the Interface Connector and switch the oscillator on or off to provide the auto-mode control.

Figure A-1, Model 303A with Model 305 Stirrer


STIRRER BD.
MODEL 305
NOTES:
1. ALL RESISTORS ARE 1/4W, 5%, CARBON COMP. UNLESS OTHERWISE NOTED.
2. ALL 1% RESISTORS ARE 1/8W. METAL FILM UNLESS OTHERWISE NOTED.
GND
E101
-15V
E102
E103
CR102 IN4828
CR103 IN4828
C102 56µF 6V.
U101 7905
C101 330nF
R101 422Ω 3W,WW 1%
CR101 IN4002
R107 560K
R108 200K
R109 220K
R110 4.7K
R111 10Ω
U102 NE555
C105 10nF
C103 50nF
E109
E110
E108
S1A
AUTO
OFF
MAN
Q101 T1593
CR104 IN4828
R105 10K
R106 10K
Q102 T1598
R104 100K
R103 100Ω
R102 100K
E107
S1B
E104
E105
E106
R112 5.11Ω 3W,WW 1%
R113 10K
R114 4.7K
R115 1K
R116 1K
R117 1K
Q103 2N2905
Q105 2N2219
R118 10K
R119 4.7K
R120 1K
Q104 2N2905
Q106 2N2219
E111
BLK
E112
WHT
R122 10K
R123 4.7K
R124 1K
R125 1K
R121 1K
Q107 2N2905
Q109 2N2219
R128 5.11Ω 3W,WW 1%
R126 10K
R127 4.7K
R129 1K
Q108 2N2905
Q110 2N2219
E113
RED
E114
GREEN
C107 56µF 6V.
R130 4.7K
C106 100nF
U103 7476 (1/2)
-5V.

APPENDIX B. Input Connector Pinout

The pinout provided here will assist users who wish to control a single Model 303A from a polarographic analyzer not manufactured by Princeton Applied Research. Any pin not mentioned in this appendix should be allowed to float. Observing the connector from the rear of the instrument, note that pins 1 through 13 are in the upper row (pin 1 to left) and pins 14 through 25 are in the lower row (pin 14 to left).

PIN	FUNCTION
1	WORKING ELECTRODE: There is direct continuity between this pin, the rear-panel WORK test point, and, if there is mercury continuity through the capillary, the mercury drop at the end of the capillary.
2	REF. ELECTRODE: This pin is returned to the output of an internal electrometer (U2). The reference electrode connects to the input of the electrometer, and to the rear-panel REF test point.
3	COUNTER ELECTRODE: This pin directly connects to the counter electrode and to the rear-panel CNTR test point.
4	SIGNAL GROUND: Connect a high-quality ground to this pin.
5	-15 V: Connect -15 V at 50 mA to this pin (350 mA if stirrer is used). Source of -15 V can be inexpensive 15 V supply.
6	+22 V: Connect +22 V at 1 A (peak requirement) to this pin. This voltage is used for solenoid power and so need not be highly regulated.
7	POWER GROUND: Connect a medium-quality ground to this pin. This is the ground for the casting and for the Stirrer Control signal return. Note that this ground is internally floated off signal ground by ten ohms.
8	STIRRER INHIBIT: A positive TTL level applied to this pin turns on an external stirrer.
9	DISL: Applying a 100 μs active-low pulse to this pin initiates a dislodge-dispense sequence.
13	NEW 384: If the Model 303A is connected to a Model 384, the logic level on this pin indicates whether it is the Model 384B (active-low) or an earlier version of the instrument (active-high). It is connected internally to +5 V through a 10 kΩ resistor. Make no connection to this pin.
14	GROUND: No ground need be connected to this pin, as it is internally connected to the Signal Ground applied to pin 4.
15	GROUND: No ground need be connected to this pin, as it is internally connected to the Signal Ground applied to pin 4.
16	GROUND: No ground need be connected to this pin, as it is internally connected to the Signal Ground applied to pin 4.
17	+15 V: Connect +15 V at 500 mA to this pin. Source of +15 V can be inexpensive 15 V lab supply.
18	174: The logic level on this pin indicates to the Model 303 which of two general types of polarograph are connected to it. A high level indicates a Model 384 or Model 300. A low level indicates all others. This pin is connected internally to +5 V through a 10 kΩ resistor. Make no connection to this pin.

21 384 PURGE: A TTL logic 0 applied to this pin will initiate a purge. The purge will continue for as long as the logic 0 is applied.

22 DISP: A logic 0 applied to this pin will initiate a dislodge/dispense sequence. There is no difference between applying a logic 0 to this input and applying it to pin 9. Note that the applied logic 0 should have a width of at least 100 μs.

23 DROP KNOCK RETURN: Connect ground to this pin. The solenoid current is returned to the 22 V supply via this line.

APPENDIX C. Pressure Kit Installation Model 303/99 or Model 303A/99

INTRODUCTION

The Model 303/99 or Model 303A/99 Option is used in polarographic applications where extremely negative potentials are needed to reduce the electrochemical species of interest. For example, formaldehyde is reduced at -1.6 V vs. SCE. (1)

The surface tension of mercury holds the drop onto the capillary. At negative potentials the surface tension decreases, and there is a tendency for solution to enter the capillary of the DME, causing the drop to fall off. (2) Barker predicted this for a large bore capillary. Therefore the Models 303/99 and 303A/99 use a small bore capillary (0.003 inches, GO200) to compensate. Pressure is needed to force the mercury down the capillary. 2-5 psi is sufficient.

Instruction on how to assemble and install the pressure option follow. A diagram is provided for clarity.

1. Remove the straight knurled plastic nut and flat washer from the cover assembly. Then remove the cover assembly.

2. Remove the "E" ring clip from the mercury level indicator and remove the plastic cover. Push out the "Rulon" bushing from the bottom side of the cover. Set these parts aside.

3. Remove the existing foam gasket and its adhesive, making sure that the gasket surface is clean and free of old gasket material. Remove the paper backing and install a silicon gasket, part number 2504-0115, in place of the foam gasket.

4. Install an "O" ring, part number 2504-0101-0, in the "O" ring groove on the underside of the tubing fitting, part number 2517-1196. Install the fitting in the level indicator hole from the top side of the cover. Then install the 3/8" nut and tighten it.

5. Reinstall the reservoir cover on the Model 303 or 303A and place the round gasket, part number 2504-0119, over the stud, followed by the plastic flat washer and nut. Tighten the nut firmly by hand.

6. **Ignore this step if top is already partially preassembled:** Assemble four 3 inch long standoffs, part number 2814-0139, to the bottom plate, part number 2517-1197, using #8-32 x ½ inch long screws. The standoffs can be mounted on either side of the plate but all four must be on the same side. Assemble four bars, part number 2517-1195, to the top plate, part number 2517-1198, using the two shoulder screws, part number 2811-0344-0, and the two springs, part number 2505-0043. The bar assemblies are to be mounted to the top plate side, opposite the countersunk holes. Then assemble the top plate assembly onto the 3 inch standoffs using four #8-32 x ½ " flat-head screws, part number 800302. Last, install four #1/4-20 x 3/4" long screws in the top plate from the countersunk side of the plate.

7. The complete clamping assembly can now be installed on the Model 303 or Model 303A from the front of the unit with the four clamping bars equally spaced about the reservoir cover. Tighten the four thumbscrews equally by making several tightening sequences.

8. Install the Nitrogen tubing, clamping it to the fitting.

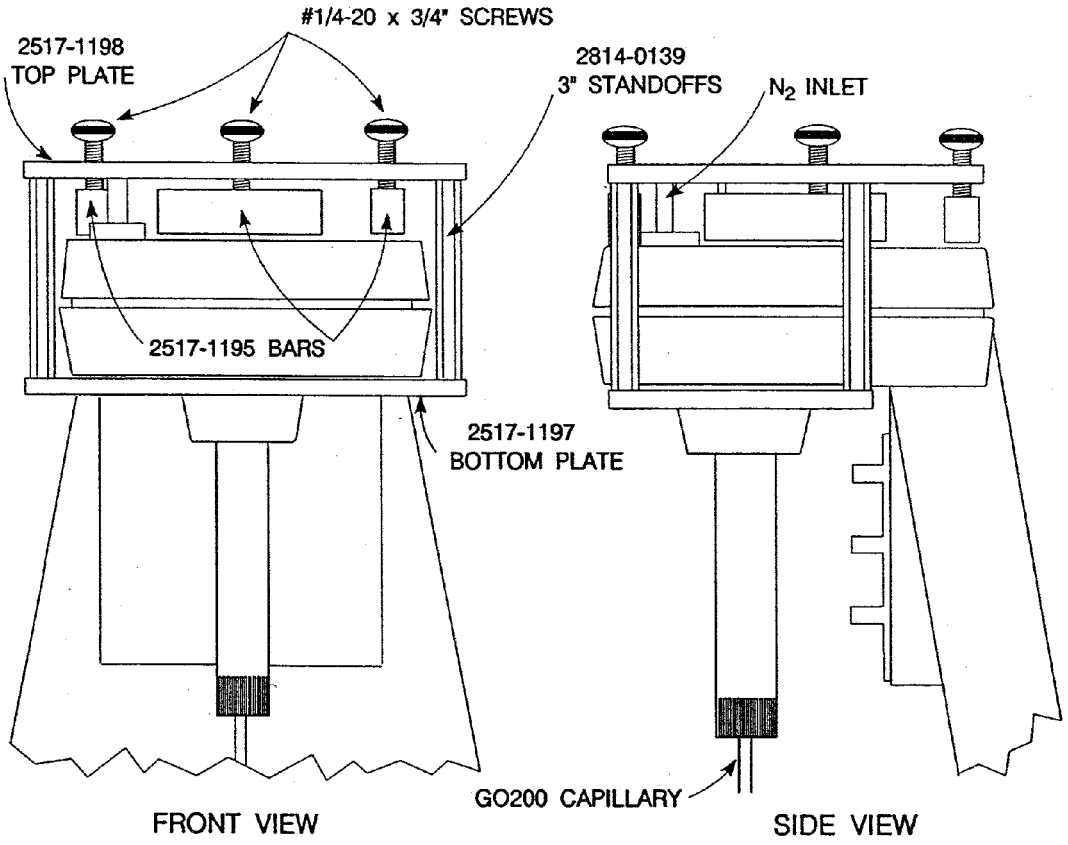
9. Install a new 0.003" bore capillary (GO200).

10. Apply Nitrogen at a pressure of 2-5 psi.

References:

1. Polarographic Determination of Formaldehyde and other Aldehydes, Princeton Applied Research Application Note F-1.
2. Barker, G.C., Square Wave Polarography and Some Related Techniques, Analytica Chimica Acta, 18, 118-31, 1958.

CLAMP ASSEMBLY - 303/99



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