Model 377A
Coulometry Cell System

Instruction Manual

4200-0160D-MNL

Advanced Measurement Technology, Inc.

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

WARRANTY

Princeton Applied Research* warrants each instrument of its own manufacture to be free of defects in material and workmanship. Obligations under this Warranty shall be limited to replacing, repairing or giving credit for the purchase price, at our option, of any instrument returned, shipment prepaid, to our Service Department for that purpose within ONE year of delivery to the original purchaser, provided prior authorization for such return has been given by an authorized representative of Princeton Applied Research.

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.

THERE ARE NO WARRANTIES THAT EXTEND BEYOND THE DESCRIPTION ON THE FACE HEREOF. THIS WARRANTY IS IN LIEU OF, AND EXCLUDES ANY AND ALL OTHER WARRANTIES OR REPRESENTATIONS, EXPRESSED, IMPLIED OR STATUTORY, INCLUDING MERCHANTABILITY AND FITNESS, AS WELL AS ANY AND ALL OTHER OBLIGATIONS OR LIABILITIES OF PRINCETON APPLIED RESEARCH, INCLUDING, BUT NOT LIMITED TO, SPECIAL OR CONSEQUENTIAL DAMAGES. NO PERSON, FIRM OR CORPORATION IS AUTHORIZED TO ASSUME FOR PRINCETON APPLIED RESEARCH ANY ADDITIONAL OBLIGATION OR LIABILITY NOT EXPRESSLY PROVIDED FOR HEREIN EXCEPT IN WRITING DULY EXECUTED BY AN OFFICER OF PRINCETON APPLIED RESEARCH.

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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Safety Instructions and Symbols

This manual contains up to three levels of safety instructions that must be observed in order to avoid personal injury and/or damage to equipment or other property. These are:

DANGER Indicates a hazard that could result in death or serious bodily harm if the safety instruction is not observed.

WARNING Indicates a hazard that could result in bodily harm if the safety instruction is not observed.

CAUTION Indicates a hazard that could result in property damage if the safety instruction is not observed.

Please read all safety instructions carefully and make sure you understand them fully before attempting to use this product.

Cleaning Instructions

WARNING Using this instrument in a manner not specified by the manufacturer may impair the protection provided by the instrument.

To clean the instrument exterior:

- Unplug the instrument from all voltage sources.
- Remove loose dust on the outside of the instrument with a lint-free cloth.
- Remove remaining dirt with a lint-free cloth dampened in a general-purpose detergent and water solution. Do not use abrasive cleaners.
- Allow the instrument to dry before reconnecting the power cord.

CAUTION To prevent moisture inside of the instrument during external cleaning, use only enough liquid to dampen the cloth or applicator.

1. INTRODUCTION

1.1. Description

Controlled potential coulometry requires a cell system that is versatile, convenient to use, and that can complete electrolyses as rapidly as possible. The Model 377A Coulometry Cell System fulfills these requirements by providing all necessary cell glassware and hardware for performing rapid, accurate, and precise controlled-potential coulometry.

The Model 377A consists of a coulometry cell mounted on a stand, complete with a stirrer motor. Separate bridge tubes are provided for the counter and reference electrodes. These bridge tubes are furnished with porous Vycor® frits to minimize diffusion between the bridge-tube solutions and the test solution, while at the same time assuring low electrical resistance. Users have the choice of a mercury pool or platinum-gauze working electrode.

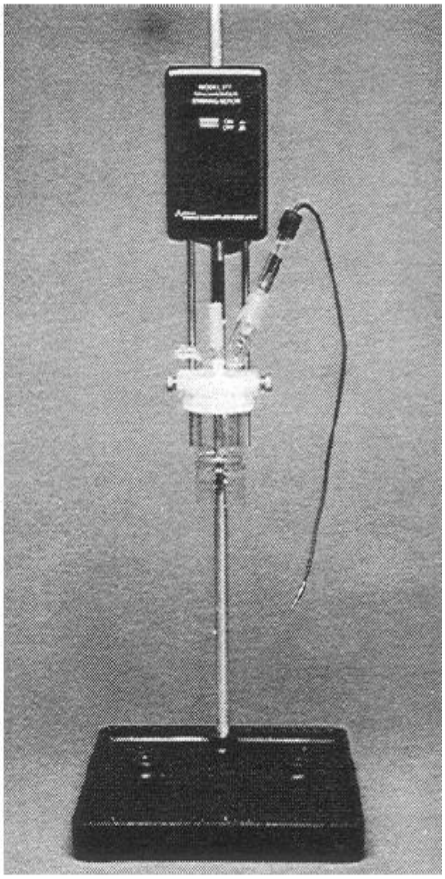

Figure 1: Model 377A Coulometry Cell

In order to use the mercury-pool working electrode, prior to operation, the cell is partially filled with mercury. The solution to be analyzed is added to the cell to a depth sufficient to immerse the lower portion of both the counter electrode bridge tube and the reference-electrode bridge tube, which are filled with the appropriate solutions. The counter and reference electrodes are inserted in their respectively bridge tubes and then connected to the coulometer. Contact with the mercury pool is made via a metal pin that passes through the bottom of the cell and into the mercury pool.

Operation with the platinum-gauze working electrode is similar except that there is no mercury in the cell and contact with the platinum electrode is made at the cell top.

During an analysis, the coulometer maintains the working electrode at a user specified potential with respect to the reference electrode. The selected control potential depends on the specific materials to be analyzed and other factors. The coulometer integrates the current to provide a reading of the total number of coulombs, and hence of the total amount of reacting material. The current is highest at the start of the analysis and drops asymptotically towards zero as the analysis proceeds. When the analysis is completed (reacting species exhausted), the current will be zero (actually some low “background” value). By continuously monitoring the current as the analysis proceeds, the endpoint can be readily determined.

1.2. System Components

The Model 377A Coulometry Cell System contains:

(1) Model K0026 Coulometry Cell Kit.
(2) Model 377/16 Synchronous Stirring Motor.

Also available is the K0027 Platinum Working Electrode Kit, which can be purchased as an accessory.

2. ASSEMBLY AND CONNECTIONS

2.1. Introduction

The Model 377A System is shipped unassembled to reduce the possibility of breaking the fragile glass components and to reduce the size of the shipping package. The recommended assembly procedure follows.

CAUTION THERE IS A VYCOR FRIT AT THE END OF EACH OF THE BRIDGE TUBES. ONCE WETTED, THESE FRITS MUST NOT BE ALLOWED TO DRY OUT. IF THEY DO DRY, THEY MAY CRACK, IN WHICH CASE REPLACEMENT WILL BE NECESSARY BEFORE THE CELL CAN BE USED.

2.2. Assembly for Mercury Pool Working Electrode

(1) Carefully unpack all items and check them against the enclosed packing lists. Also, wash and dry all glassware EXCEPT FOR THE REFERENCE AND COUNTER ELECTRODE BRIDGE TUBES.

(2) Assemble the Model K0028 Stand Kit as follows.

(a) Remove the paper backing from the adhesive of the four molded black bumper feet provided.

(b) Press the bumper feet in to position on the four corners of the underside of the base plate.

(c) Thread the jam nut onto the support rod. Then thread the support rod into the center rearmost hole in the base plate. Secure the rod firmly in place with the jam nut.

(d) Using the rubber plugs provided, plug the unused holes in the base plate.

(3) Clamp the Model 377/16 Synchronous Stirring Motor to the support rod.

(4) Remove the two screws from the underside of the Model 377/16 Motor and thread the Model MP0446 Cell Support Rods (contained in the Model K0026 Cell Kit) into the holes from which the two screws were removed.

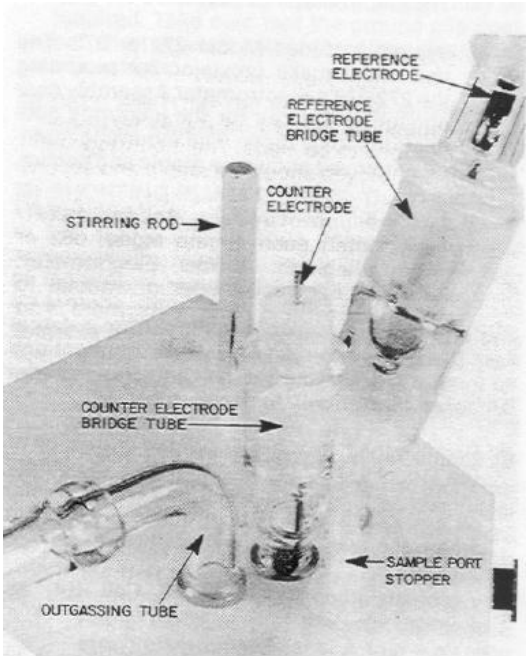

Figure 2: Top View of Assembled Cell

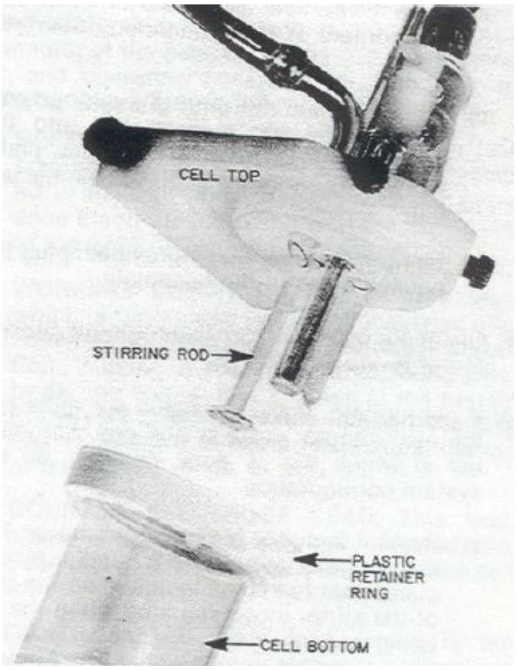

Figure 3: Completed Assembly

(5) Assemble the Model K0026 Cell Kit as follows.

(a) Install the two plastic thumb screws in the cell top. (The plastic thumb screws are used only to secure the optional platinum-gauze working electrode in position.) Then secure the Model K0029 Cell Top to the two cell support rods using the metal thumb screws.

(b) Insert the wire stem of the platinum counter electrode all the way into the adapter cap and secure it with the nylon locking screw.

(c) Slide the Model G0195 Stirring Rod into the cell top as shown in Figure 2 and secure the rod into the flexible rubber fitting of the synchronous stirring motor.

(d) Insert the outgassing tube and the Teflon® sample-port stopper into the cell top as shown in Figure 3.

(e) Rinse the Reference Electrode and Counter Electrode Bridge Tubes with distilled or deionized water. Then insert the bridge tubes into the appropriate cell top openings (Figure 3) and fill the bridge tubes with appropriate electrolyte. **NOTE:** The bridge tube frits become wetted for the first time in this step. Do not allow them to dry out.

(f) Insert the Counter Electrode and Reference Electrode into the corresponding bridge tubes.

(g) Raise or lower the cell top so that the bottom of the stirring rod is just below the end of the counter electrode bridge tube.

(h) Secure the cell bottom to the cell top with the threaded plastic retaining ring.

(i) Make the connection to the outgassing tube with 3/8" Tygon® tubing.

(k) Measure approximately 10 ml of triply distilled mercury into the cell bottom through the sample port. Then add 5 ml of the supporting electrolyte. The tips of the bridge tubes should be immersed in the supporting electrolyte, preventing the bridge tube frits from drying out.

(l) Adjust the height of the cell so that the stirrer lies in the mercury/solution interface.

2.3. Assembly for Platinum Working Electrode

The assembly is much the same as previously described except, instead of installing a G0195 Mercury Pool Stirring Rod, you would install the G0064 Paddle Type Stirrer included in the K0027 Platinum Working Electrode Kit. There is one additional step, installing the Model E0002 Platinum Working Electrode. The wire stems of this electrode are inserted into the small holes in the cell top and secured with the two plastic thumb screws. Figure 4 shows a cell top with the platinum working electrode installed.

WARNING MERCURY IS BOTH TOXIC AND EXPENSIVE. BE CAREFUL.

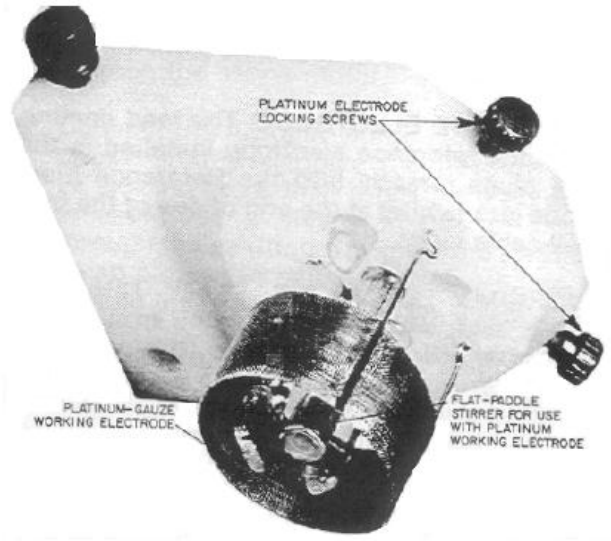

Figure 4: Cell Fitted with Platinum-Gauze Working Electrode

2.4. Cell Connections

DANGER SOME OF THE POTENTIOSTAT/GALVANOSTATS WITH WHICH THE COULOMETRY CELL IS USED HAVE OUTPUTS AS HIGH AS 100 V AT CURRENTS AS HIGH AS 1 A. THUS IT IS POSSIBLE TO RECEIVE DANGEROUS, EVEN LETHAL, ELECTRICAL SHOCKS IF THE CELL CONNECTIONS ARE TOUCHED WHEN THE OUTPUT IS LIVE. FOR SAFETY, THE CELL SWITCH OF THE INDIVIDUAL POTENTIOSTAT/GALVANOSTAT SHOULD BE SET TO THE OFF POSITION WHEN MAKING OR BREAKING CELL CONNECTIONS.

The connections are made as follows:

(1) REFERENCE ELECTRODE: The lead coming from the reference electrode installed in the cell plugs directly into the Reference Electrode jack (white) at the end of the potentiostat cell cable.

(2) WORKING ELECTRODE LEAD: This cell-cable lead, which is terminated in a green insulated clip, connects to the working-electrode contact. If using a mercury-pool working electrode, this connection is made at the cell bottom. If using a platinum working electrode, this connection is made at the cell top.

(3) COUNTER ELECTRODE LEAD: This cell-cable lead, which is terminated in a red-insulated clip, connects to the counter electrode contact at the cell top.

(4) GROUND LEAD: This lead, which is terminated in a black-insulated clip, ordinarily is not used. It is provided for those applications where a convenient source of ground may be required. Take care that the ground clip does not short against any of the other electrodes or contacts.

(5) SENSE LEAD: (if available) The sense lead (gray) is connected to the working electrode along with the working lead. As a general rule, the sense lead is required when measuring currents in excess of 200mA, but must always be connected if present on the cell cable.

3. OPERATING INSTRUCTIONS

3.1. Introduction

Properly operated, the Model 377A Coulometry Cell System can provide electrolyses in as little as five minutes. Most analyses can be carried out in the following manner. This procedure assumes that the cell has been assembled and connected as described in Section 2, and that mercury (if appropriate) and electrolyte are in the cell.

3.2. Procedure

(1) Check and, if necessary, adjust the height of the cell so that the stirrer lies in the mercury/solution interface.

(2) Turn on the stirrer motor.

(3) Connect the nitrogen purge tube to a source of oxygen free nitrogen. The pressure should be low, no more than a few p.s.i. Adjust the pressure for a steady stream of bubbles through the solution. The pressure should not be so high as to cause splashing of the supporting electrolyte against the cell top.

(4) After deaerating for five or ten minutes, pre-electrolyze the supporting electrolyte at the potential to be used for the electrolysis.

(5) When the pre-electrolysis current has decreased to an acceptable level, or after a specified time period, add the analyte to the cell.

(6) Electrolyze the analyte until the current decreases to the residual level.

(7) If desired, repetitive analyses can be performed by adding additional portions of analyte and electrolyzing.

3.3. Remarks

(1) Certain supporting electrolytes should be deaerated before contacting the mercury to prevent hydrogen peroxide from being formed, or to prevent any other undesirable redox reactions from taking place. Where this is the case, add the supporting electrolyte to the cell first, deaerate, and then add the mercury.

(2) An alternative technique for electrolyte "blank subtraction" involves a timed pre electrolysis of the supporting electrolyte with current integration. The time allowed for this step should exceed the minimum sample electrolysis time. A new aliquot of electrolyte containing the sample is then electrolyzed for the same period of time. The blank charge is then subtracted from the sample charge. This technique is preferred if accurate background compensation cannot be attained.

(3) The bridge tubes are usually filled with the supporting electrolyte used in the analysis. The Vycor frits at the bottom of the bridge tubes, once wetted, must not be allowed to dry out (they will crack). The bridge tubes can be stored in distilled water, if desired, or in a supporting electrolyte (one used routinely). Section 4 provides

additional information on handling the Vycor frits.

(4) The bottom of the stirrer should be positioned so that the mercury surface is stirred smoothly with no splashing of mercury or solution. If electrolyses consistently require more than ten minutes to complete, and are known to have no kinetic complications, the stirrer should be raised or lowered to give the most effective stirring of the mercury solution interface. This is most easily done by loosening the screws that secure the cell to the support rods and then raising or lowering the cell as required.

(5) The same cell bottom is used for electrolyses on both mercury and platinum working electrodes.

4. VYCOR HANDLING AND REPLACEMENT

The bridge tubes furnished with the Coulometry Cell System incorporate an unfired Vycor tip designed specifically to provide ultra low leakage rates with minimum IR drop through the tip. This arrangement eliminates complications arising from poisoning of test solutions by reference electrode filling solutions or by unwanted species produced at the counter electrode, and allows high sensitivity operation of potentiostats and polarographic analyzers.

The Vycor tip is deliberately sealed to the tube in a dry state. ONCE THE TIP IS WETTED, IT MUST BE MAINTAINED IN A WET STATE. What this means practically is that, when the tube is not in use, in must be stored in a solution - ideally a solution that closely approximates the solutions employed in the electrochemical experiment. If the tip is allowed to remain dry *for more than a few minutes* once it has been wetted, it will crack. A cracked tip must be replaced before the tube can be used again. Also, the tip may crack if it is exposed to drastically different environments, e.g.,

(1) A bridge tube is immersed in an aqueous environment but filled with an organic solvent (or vice versa).

(2) A bridge tube is removed from an aqueous environment and placed directly in an organic solvent (or vice versa).

If it should be necessary to use a bridge tube in different environments, i.e., organic solvents and aqueous solutions, it may be possible to prevent the tip from cracking by equilibrating the tip (inside and out) with a mixture (or mixtures) of the two environments. Alternatively, separate bridge tubes could be maintained for each environment.

The following procedure is recommended for replacing a Vycor tip.

(1) Slice off the old Teflon sleeve with a razor blade. Then discard the sleeve and the old tip.

(2) Wash and dry the bridge tube.

(3) Slide a new length of heat-shrink Teflon tubing onto the bridge tube.

(4) Stand the bridge tube on the new Vycor tip. DO NOT WET THE TIP AND AVOID FINGER CONTACT WITH IT.

(5) Heat the Teflon tubing on all sides with a hot- air stream from a heat gun. (A direct flame should not be used because it will char the Teflon.) Allow the tubing to shrink over the disk. BE SURE TO ALLOW THE TUBING TIME TO COOL TO ROOM TEMPERATURE BEFORE LIFTING THE ASSEMBLY.

Extra tips and Teflon sleeves are provided with the coulometry cell system. Replacements can additionally be purchased from Princeton Applied Research.