DIONEX

ED40 ELECTROCHEMICAL DETECTOR OPERATOR'S MANUAL

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1 • Introduction

1 • Introduction

1.1 Overview

The ED40 Electrochemical Detector measures current resulting from the application of potential (voltage) across electrodes in flow-through cells. Depending on the method by which the potential is applied and the current measured, several different properties of the flowing solution can be determined. These measurements help answer the major questions analytical chemists ask: What's in it and how much?

Of course, there are other detectors used in high performance liquid chromatography (HPLC). The UV-visible absorbance detector dominates all other forms of detection. Sensitivity is excellent for many analytes, especially aromatic species, and transparent mobile phases are readily available. However, there are numerous analytes that have very poor absorbance and are not detected with sufficient sensitivity by UV absorbance. Most of these nonchromophoric molecules are aliphatic organic molecules and inorganic ions. Low wavelength UV detection can be used, but at a loss in selectivity. Refractive index detection can also be used. However, maintaining a stable baseline can be difficult, and RI detection is less sensitive and substantially less selective than UV detection.

Fortunately, a wide variety of nonchromophoric molecules can be detected with good or excellent sensitivity by one of several forms of electrochemical detection. These molecules include carboxylic, sulfonic and phosphonic acids; alcohols, glycols, aldehydes and carbohydrates; primary, secondary, tertiary and quaternary amines; sulfates, sulfoxides, thiols, sulfides and mercaptans; and inorganic anions and cations. In addition, electrochemical detection provides substantial improvements in sensitivity and selectivity compared to UV absorbance detection for amine and hydroxy-substituted aromatics such as catecholamines.

Several forms of electrochemical detection have become popular for certain HPLC applications. Conductivity is the workhorse detection method in ion chromatography, just as UV detection is for HPLC. DC amperometry is the preferred method for neurochemical analyses. Pulsed amperometry is now established as the superior detection method for carbohydrates. For most of the numerous analytes listed in the previous paragraph, detection by UV-visible absorbance is poor, while one of the three main techniques of electrochemical detection provided by the ED40 provides superior sensitivity and selectivity.

Electrochemical detection is not a substitute for UV-visible absorbance detection, but is an important complement. A liquid chromatograph equipped with both a Dionex AD20 Absorbance Detector and an ED40 Electrochemical Detector is a truly versatile and powerful analytical instrument.

1.2 Modes of Detection

The ED40 provides the three major forms of electrochemical detection: *Conductivity, DC Amperometry*, and *Integrated Amperometry*. *Pulsed amperometry* is a form of integrated amperometry.

- *Conductivity detection* is based on the measurement of the magnitude of electrical current carried by dissolved ions in an electric field.
- *DC amperometric detection* is based on the measurement of current resulting from oxidation or reduction (electrolysis) of analyte molecules at the surface of an electrode.
- *Integrated and pulsed amperometric detection* are similar to DC amperometric detection in that molecules are oxidized or reduced at the surface of an electrode. However, current is measured by integration during a portion of a repeating potential vs. time waveform.
- In addition the *Voltammetry* mode is used to determine potentials used in DC and Integrated Amperometry.

1.3 About This Manual

This Operator's Manual is modular in design and intended to be an ongoing reference for operating and maintaining the ED40 Electrochemical Detector. The manual describes physical and functional aspects of the ED40. It provides step-by-step installation and operation instructions.

Chapter 1, **Introduction**, provides an overview of the ED40.

Chapter 2, **Description**, is a description of the physical aspects of the ED40, followed by a functional description of the operating features.

Chapter 3, **Operation and Maintenance**, discusses the operating features and methods. Routine preventive maintenance requirements are included in this chapter.

Chapter 4, **Troubleshooting**, lists possible causes of problems and provides step-by-step instructions to isolate and eliminate their sources.

Chapter 5, **Service**, presents step-by-step instructions for service and parts replacement procedures.

Chapter 6, **Electrochemical Detection**, describes electrochemical detection and what it is used for.

Appendix A, **Specifications**, contains the ED40 specifications and facility requirements.

Appendix B, **Installation**, describes the installation and interface necessary to place the ED40 into operation. It includes the setup procedures that will enable you to operate it in a stand-alone environment or to connect it to other Dionex products.

Appendix C, **User Interface**, describes the front panel display and keyboard controls. Menus and screens are illustrated. The second part of this Appendix describes the ED40 Diagnostics program included in the detector's Moduleware™ to diagnose operating conditions and to identify problems.

Appendix D, **Signal Processor Functions**, lists the functions of the Signal Processor (SP) card.

Appendix E, **Connector Pinouts**, describes the pinouts for all of the ED40 connectors.

Appendix F, **Further Reading**, provides a comprehensive bibliography for electrochemical detection.

1.4 Conventions

Screen is used alternately to signify:

- The liquid crystal display itself.
- The information that appears in the display.

Menu signifies a display that offers a list of screens or additional menus that you can choose for specific functions.

The following typographical conventions are used in this manual:

- Front panel keys, when reference is made to the key itself rather than its function, are in capitalized, bold print, such as:

  Press **Enter** to start the method running.

- The reference is in normal typeface and case when it is to the key's function, as the word *enter* in this example.

  You can enter changes only in reverse video fields.

- Names of screens, menus, and entries in the displays are in uppercase bold type with the case matching the actual display when referring to the screen, such as:

  Call up the **MENU of SCREENS**.

  Move the cursor to the **EDIT** field.

- The reference is in normal typeface and case when it is to the screen or display function, as the word *edit* in this example:

  Move the cursor to the field you want to edit.

1.5 Product Safety Information

This instrument has been designed to comply with the requirements for safety set forth in IEC 1010 *Safety Requirements for Electrical Equipment for Measurement, Control, and Laboratory User.*

Sections of this manual are flagged with the following symbol to denote the nature of any hazard or precaution necessary. These safety directives apply to all operators and service personnel.

CAUTION — Indicates a potential hazard to the operator or damage to the instrument or other property. Example: Overtightening a connector may break it off.

2 • Description

2.1 Physical Description

The ED40 Electrochemical Detector is housed in a Dionex DX 500 enclosure. The detector is designed to be stacked on top of other DX 500 units to a recommended maximum height of four units. Figure 2-1 illustrates the ED40 enclosure.

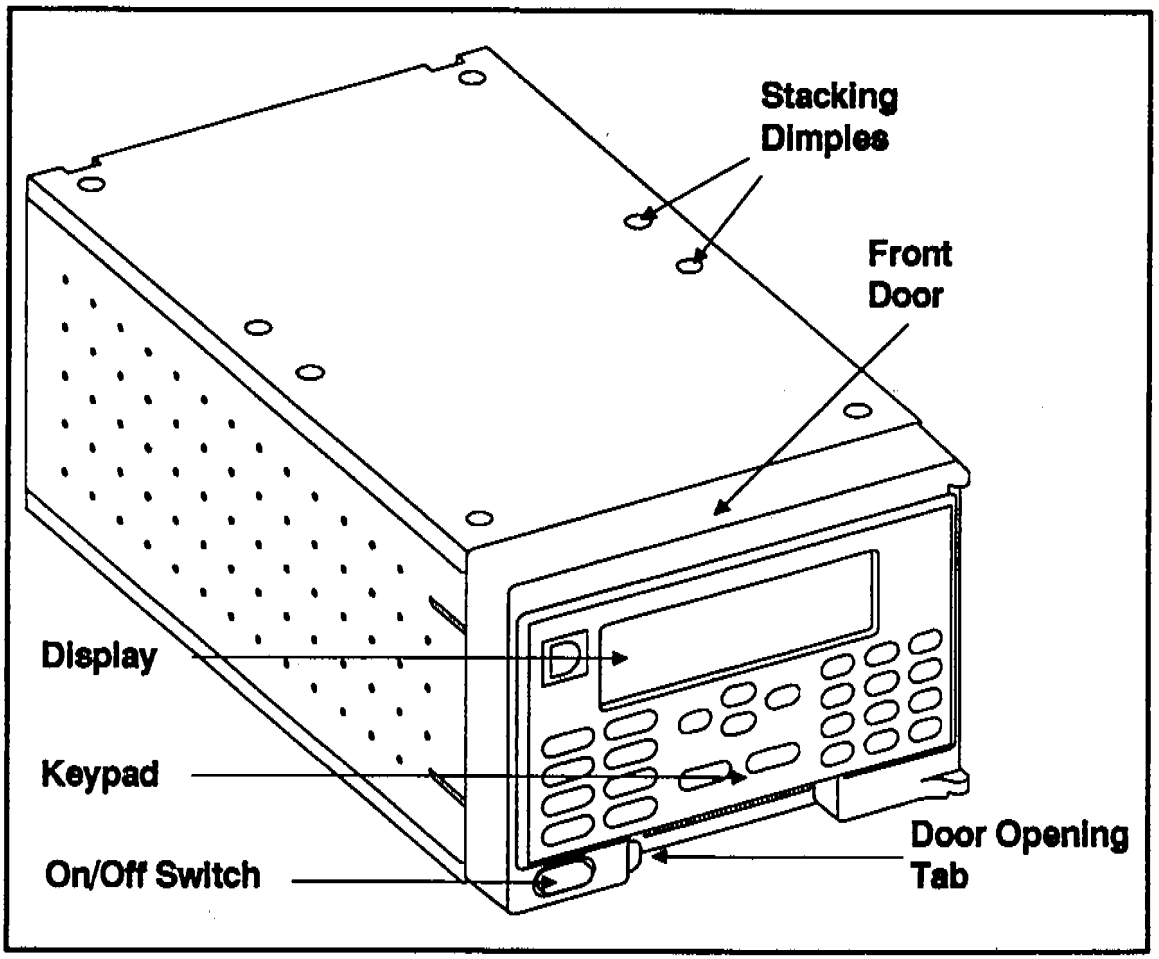


Figure 2-1. ED40 Enclosure

2.1.1 Power Switch

The power switch is labeled with a vertical stroke in a circle, which indicates an alternating action power switch. The position of the switch actuator on the front panel does not necessarily indicate the state of the power switch. When powered, the status LED, located inside the front door, indicates powered operation. The actual switch is inside the front door panel. The power is on when the switch is pushed in.

2.1.2 Tilt Front Panel

The keypad and display can be tilted to four different positions to maximize visibility and ease of use.

- To increase the viewing angle, support the door at the left side to prevent it from opening and lift firmly on the tab located in the middle of the recess below the keypad. After the fourth position up is reached, the panel will swing free of the stops.
- To decrease the viewing angle, press firmly on the tab until the panel is set to the desired position.

2.1.3 Using the Front Panel

The display, cursor, and operating parameters are controlled by entering data into the screens with the keypad. Use the four directional keys to move the cursor into position, enter the desired parameter with the numerical keys, and press **Enter** to execute the change. Press the **Menu** key to display the **MENU of SCREENS**.

NOTE

You must press Enter to execute a numerical value. If you move the cursor to another field without pressing Enter, the value will not have any effect.

Parameter changes can only be entered in the fields shown in reverse video on the screen, and with the cursor positioned in the field to be changed. Entries into changeable fields are by two methods:

- Enter the numerical value (only for numeric entries).
- Select a predetermined value with the **Select** keys.

The **METHOD** and **WAVEFORM** screens are in tabular form. On these screens, it is not necessary to fill each cell with a parameter. In each column, the top entry will continue in effect through succeeding rows where the cell is blank until a parameter is entered. This entry will then continue in effect until another parameter is entered, etc.

The **MAIN** screen displays certain information in enlarged characters to make viewing from a distance easier.

You will hear a beep when you press a keypad button. If an error occurs, the beep will be lower in frequency. Keypad beeps can be disabled in the **MODULE SET-UP** screen (see Section C.1.18).

2.1.4 Keypad

This section describes the front panel keypad. Use the keypad to enter new values for parameters, to select any of the available display screens, and to initiate or cancel operations.

When you press a key, a beep signals that the keystroke has engaged. If an error occurs, the beep is a lower frequency. You can disable the keyboard beeps, if desired, from the **MODULE SET-UP** screen.

The keypad contains function keys, cursor movement keys (arrows), and a numeric keypad. Figure 2-2 shows the ED40 keypad layout.

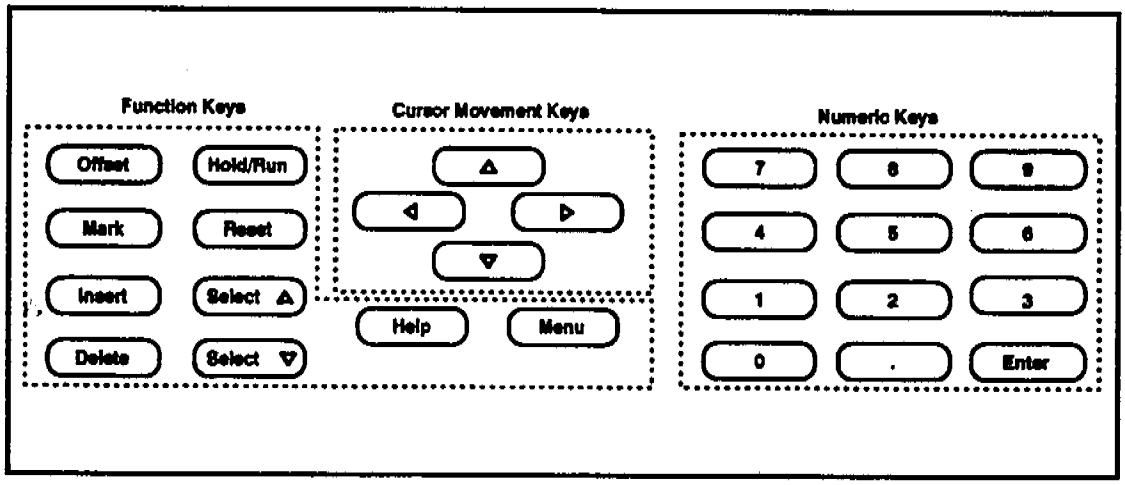


Figure 2-2. ED40 Keypad Layout

Menu

The **Menu** key displays the **MENU of SCREENS** from any of the basic user interface screens. From any of the diagnostic screens, this key returns you to the **DIAGNOSTICS MENU**. Press the key a second time to return to the **MENU of SCREENS**.

Cursor

Four cursor directional keys (arrows up, down, left, and right) move the cursor to the adjacent changeable field, if there is a changeable field in that direction. If not, the cursor moves diagonally or stays where it is. When the cursor is moved with these keys to a new field, the field's value is restored to what it was when **Enter** was last pushed (at this location). Line wraparound to the right advances down to the beginning field in the next line. Line wraparound to the left advances up to the last field in the line above.

Offset

The **Offset** key, sometimes referred to as auto-zero or auto-offset, returns the analog (recorder) output to a predetermined baseline and zeros the display. The resultant value of the offset required is displayed on the **DETAIL** screen. This function can be programmed within a method.

Hold/Run

The **Hold/Run** key turns the method clock off (Hold) and on (Run).

When in Hold mode, this key starts the method clock. A new method begins with the initial step and immediately executes the 0.00 step and then the succeeding steps, when **Run** is pressed. An interrupted method begins running at the point where it was interrupted.

When a method is running, this key stops the method clock, thereby holding the method and freezing the current conditions.

Mark

The **Mark** key sends a 10% positive event mark to the analog (recorder) output. A mark is typically used to indicate a sample injection. This function can be programmed within a method using the **METHOD** screen.

Reset

The **Reset** key changes the method clock time to **INIT**ial conditions. If the method is running, it continues running beginning with the time zero step.

Insert

The **Insert** key inserts a timed step into a method or waveform. You need to fill in a time value as the time field will be blank. If you do not fill in the time value before moving the cursor to a different field, the inserted step will be incomplete and will disappear. Timed steps are automatically ordered chronologically when entered.

Delete

In the **METHOD** and **WAVEFORM** screens, the **Delete** key blanks step parameter values (meaning no change from the previous step).

In the other screens, this key blanks number values in all spaces. If the cursor is moved from the field before a new value is entered, the old value is restored. For fields with a valid selection of **OFF**, this key causes **OFF** to be set.

The first time **Delete** is pressed at a method or waveform time field, the time is blanked and a confirmation displays at the bottom of the display. Press **Delete** a second time to delete the step.

Select ^/Select v

These keys toggle the parameter at the cursor position. When there are more than two possible values, the **Select ^** key increments to the next higher selection and the **Select v** key decrements to the next lower value. Press **Enter** to place the new value into effect.

Help

Press **Help** to display a help screen specific to the current display field.

Enter

Changes are saved when you press **Enter**. The cursor will be one or more spaces from the left if you have entered any data in the field. When you press **Enter**, the cursor moves back to the left margin within the same field. The cursor does not move to the next data field.

In the **METHOD** or **WAVEFORM** screens, after changing one or more parameters, you must move the cursor to the **SAVE TO** field, type in the number to save the method to, and press **Enter**.

Numeric Keys

Press the numeric keys to enter numeric values into fields where the cursor is positioned. The numeric keys are 0 through 9 and a decimal.

Power-Up Screen

When the detector has successfully powered-up (passed all diagnostic tests), it briefly displays the **POWER-UP** screen as shown in Figure 2-3.

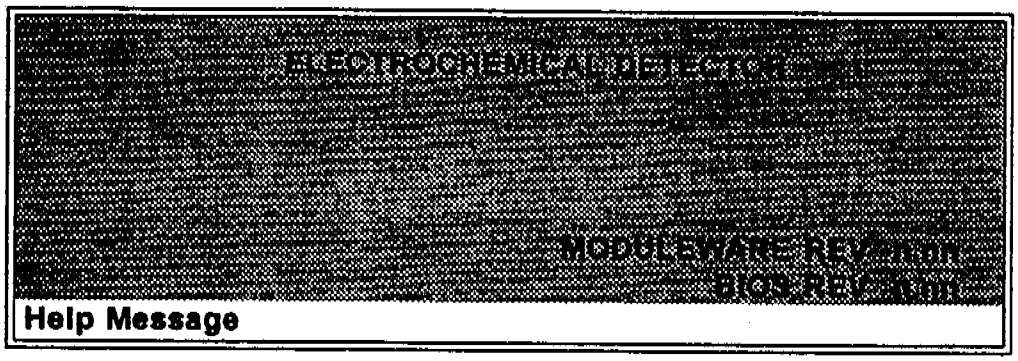


Figure 2-3. Power-Up Screen

The revision codes shown here are for illustration only. These codes are displayed to identify the Moduleware™ in the event service is needed. When equipped with a DX LAN™ connected to a Dionex PeakNet™ Workstation, new Moduleware updates may be downloaded over the DX LAN.

Main Screen

After 6 seconds, the display proceeds to the **MAIN** screen as shown in Figure 2-4. The ED40 **MAIN** screen is unique to each of the four detection modes. This example shows the Conductivity **MAIN** screen.

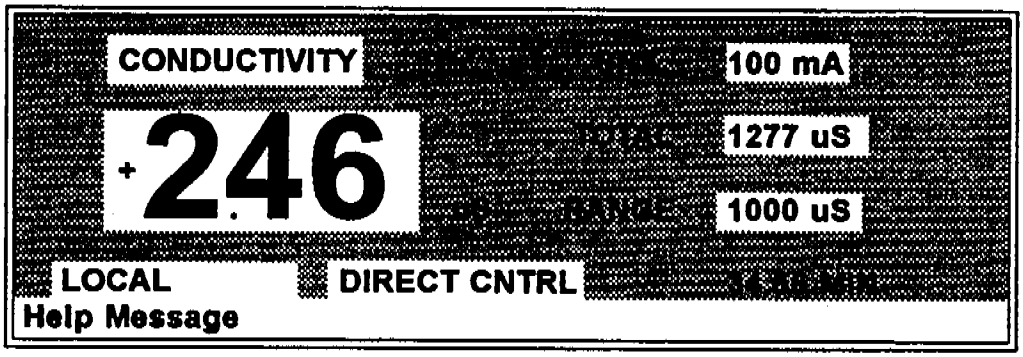


Figure 2-4. Main Screen — Conductivity

Press the **Menu** key to go to the **MENU of SCREENS**. Refer to Appendix C, *User Interface*, for a description of screens that you can select from the **MENU of SCREENS**. Also refer to Appendix C for a description of the screens that you can select from the **DIAGNOSTIC MENU**.

2.1.5 Electronic Service Chassis

All the electronics and connections are accessible from the front of the detector, just behind the front door. Figure 2-5 shows the position of the electronics components with the front door open.

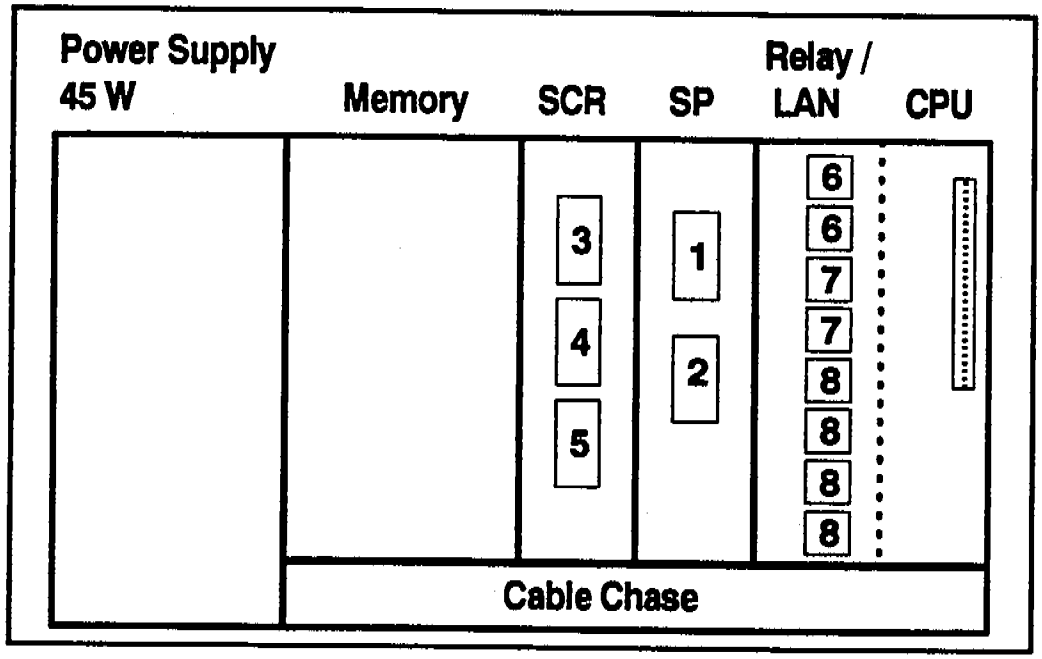


Figure 2-5. ED40 Inner Front Panel

Connectors

Electrical connections to the detector are made to three cards on the inner front panel. The numbers refer to the connectors identified in Figure 2-5.

- 1 — **Amperometry Cell** — Provides all connections to the amperometry cell.
- 2 — **Conductivity Cell** — Provides all connections to the conductivity cell, including temperature compensation.

- 3 — **Analog Output** — Provides for easy attachment of hook-up wire leads using a small screwdriver. This connector is typically used with a recorder/integrator or diagnostics instruments. See Table E-1 for the connector pinout descriptions.
- 4 — **SRS** — Provides for all connections, including power, to the Self-Regenerating Suppressor (SRS™).
- 5 — **DS3** — Provides for all connections, including power, to the DS3 Detection Stabilizer.
- 6 — **Relay** — Provides 2 relay output connector plugs for easy attachment of hook-up wire leads, using a small screwdriver.
- 7 — **TTL Output** — Provides 2 TTL output connector plugs that can be used to connect to another TTL-compatible instrument.
- 8 — **TTL Input** — Provides 4 TTL input connector plugs that can be used to control the detector from another TTL-compatible instrument. Note that these connectors are identified as TTL-1 through TTL-4 on the **TIME FUNCTION IN** screen.
- **60-pin ribbon connector** — Provides the connector plug for the 60-pin ribbon connector to the front panel (display and keypad).

The main components for the control of the detector are packaged as modules which are interconnected internally from the backplane. There are no user-serviceable components within these modules. You may, however, replace the modules, cables, and fuses.

Power Supply

The Power Supply card provides 45 Watts of power for the detector electronics.

Memory Card

The memory card contains memory chips that are used by the CPU card.

Supply Control/Relay Card

The Supply Control/Relay (SCR) card interfaces to the CPU and contains the following three functions:

- *16-bit Recorder Output Digital-to-Analog Converter*—This function includes an electronic switch to allow selection of full-scale outputs of 0.01, 0.1, and 1.0 V.
- *SRS Power Supply*—This function supplies a user-settable regulated current of 50, 100, 300, or 500 mA to a Self-Regenerating Suppressor. An overvoltage detector shuts the power off if the voltage exceeds 8.5 V. An over-temperature detector shuts the power off if the SRS temperature exceeds 40 °C. In either case, this card sends an error message to the CPU which is displayed as **SRS Alarm**.
- *DS3 Power Supply*—This function supplies heating power to the DS3 Detection Stabilizer. While warming, or cooling to a lower set point, a **BELOW TEMP** or **ABOVE TEMP** message is displayed. When a set point in the range of 25 to 45 °C is reached, proportional heat control is used to keep the temperature constant.

Signal Processor Card

The Signal Processor (SP) card contains all analog circuitry necessary for the four detection modes, and the digital circuitry to interface to the CPU. The card contains circuit sections which are shared by the four detection modes; see Table D-1.

CPU/Relay Card

The CPU logic and Relay I/O cards occupy two slots in the card cage but engage only the first (rightmost) socket. The Relay I/O card is a half card which leaves room behind it for the optional LAN half card that engages the second socket. The CPU provides control and monitoring of the other modules. A 60-pin ribbon cable assembly links the logic to the display and keypad. Control Moduleware for the detector resides on this card. When equipped with the optional DX LAN card and software, Moduleware updates may be downloaded from a Dionex PeakNet Workstation.

The Relay I/O card mounts piggyback to the CPU and leaves room behind it. This card provides two isolated low voltage relay outputs, two TTL outputs, and four TTL inputs.

At the bottom of the I/O connections is a multi-color LED that indicates the state of the power supply.

- Green indicates normal operation.
- Red or yellow indicates a fault. The ED40 will enter its diagnostic state and no other control is permitted.

2.1.6 Rear Panel

The rear panel of the ED40 contains connectors for line power, the fuse, and a connection for an optional DX LAN. In addition, cables can be routed from the front panel out the rear of the detector through the cable chase.

Power Entry

The power entry, fusing, and EMI filter are mounted on the rear of the 45 W power supply module. The power entry is socketed for a standard IEC 320 C13 modular line cord. The detector requires a grounded, single-phase power source. The unit may be operated from 85 to 270 Vac, 47 to 63 Hz power. The input power is 50 W maximum. No user adjustments are required for line voltage selection.

SHOCK HAZARD — Unless a grounded receptacle is used, a shock hazard may result. Do not operate or connect the ED40 to AC power mains without earthed ground connections.

Fuses

The detector uses two 3.15 slow-blow IEC 127 type 1 fuses. For continued protection against risk of fire or shock, replace with the same type and rating fuse.

The line fuse is mounted in a pocket drawer in the power entry module. To access the fuse, disconnect the line cord from the detector and pinch the release clips on the fuse drawer in the power entry module with your fingernails. The drawer is spring loaded and will open only after both clips are released. Remove the fuse drawer and replace the fuses. Before reinstalling the fuse drawer, note the orientation of the slot and the key in the drawer and power entry module.

Remote Network Connection (LAN Option)

When using a computer to control the ED40, the DX LAN I/O board must be installed. When present, a standard BNC connector is visible at the upper left on the rear panel of the ED40. If not present, a cap-plug covers this port.

External Connection Access

Connections to the front of the electronics modules can be routed to the back through the cable chase opening in the bottom of the electronics bay. Cables may also be passed through slots at the front of the detector, visible when the front panel is open.

2.1.7 Conductivity Cell

The flow-through conductivity cell has an active volume of approximately 1.0 µL. The PEEK cell body contains two 316 stainless steel electrodes which are permanently sealed into the cell. The detector cell constant has a nominal value of 200 cm^{-1} and is calibrated electronically. A sensor located slightly downstream from the electrodes senses the temperature of the liquid as it exits the cell. The measured value is used for temperature compensation.

Temperature Control and Compensation

Temperature directly affects the conductivity of a solution. As solution conductivity increases, the effect of temperature changes becomes more pronounced. Often, the building temperature control system causes a regular oscillation in the baseline. This change can, in turn, affect the reproducibility of a determination. In ion chromatography, suppressing the eluent conductivity reduces the effect of minor temperature variations. At high sensitivities, however, conductivity changes resulting from even small temperature variations represent a significant percentage of the total conductivity.

The optional DS3 Detection Stabilizer reduces these effects to below the detection limit. Temperature compensation in the detector further reduces the effects of temperature by normalizing all measured conductivities to 25 °C.

2.1.8 Amperometry Cell

The ED40 amperometry cell is a miniature flow-through electrochemical cell that contains three electrodes:

- Working—Choice of:
  Gold (P/N 044112)
  Silver (P/N 044114)
  Platinum (P/N 044113)
  Glassy Carbon (P/N 044115).
- Counter—Titanium (part of the cell body).
- Dual Reference—Silver/Silver Chloride and pH (P/N 044198).

Oxidation or reduction of analyte molecules is accomplished by applying a potential between the working and reference electrodes. The reference electrode is chosen so that the potential difference between it and the solution is fixed by an electrochemical redox couple. (The ED40 amperometry cell reference electrode is a combination pH-silver/silver chloride electrode. Either of these half cells can be used as the cell reference electrode.) Any changes in the potential applied between the working and reference electrode will be developed between the working electrode (where analyte reduction or oxidation takes place) and the solution. To maintain a constant potential difference between the reference electrode and the solution, the cell current must be prevented from flowing through the reference electrode. A section of the ED40 electronic circuit (the *potentiostat*) causes the cell current to flow instead through the counterelectrode. The potentiostat automatically compensates for the solution resistance between the reference electrode and the counterelectrode.

The ED40 amperometry cell is a thin-layer design. The mobile phase flows in a thin channel parallel to the surface of a flat disk electrode. The resulting smooth flow produces low noise. The low volume (0.3 µL) of the channel also allows high efficiency and narrow bore columns to be used. The cell is designed so that the electrical resistance between the working electrode and the counterelectrode is as low as possible. This results in a wide linear dynamic range. Low resistance is accomplished by locating the counterelectrode (the titanium cell body) directly across the thin-layer channel from the working electrode.

The counterelectrode is connected to ground along with a length of titanium inlet tubing. This shunts minute electric currents that might conduct from the pump through the flow stream into the working electrode. The working electrode current is processed using low noise analog amplifiers and filters and additional digital filtering of the analog output is selectable.

The ED40 amperometry cell is installed directly after the column. A suppressor is typically not used. A second detector, such as the AD20 Absorbance Detector, may be installed in-line with the amperometry cell, as long as the pressure at the amperometry cell inlet is less than 700 kPa (100 psi). Because of the volume within the reference electrode section of the cell (67 µL total cell volume), some band broadening may be noticed at the second detector. However, this is reduced by the precision flat bottomed reference electrode.

NOTE

In certain applications, light may activate a compound to become electrochemically active. In such cases, plumb the AD20 Absorbance Detector ahead of the amperometry cell. Also, the AD20 does not add as much dispersion as the amperometry cell.

2.1.9 Combination pH-Ag/AgCl Reference Electrode

The ED40 reference electrode is a standard combination pH electrode containing a glass membrane pH half cell and a silver/silver chloride (Ag/AgCl) half cell. The combination electrode is used to monitor mobile phase pH, which is displayed on the **DETAIL** screen and is also available as an analog output. To obtain an accurate pH readout, the electrode should be calibrated before use (see Section C.2.11). The Ag/AgCl half cell is normally used as the amperometry cell reference electrode. The pH half cell can instead be used as the cell reference electrode to minimize changes in the baseline during a pH gradient. The potentials at which many redox reactions take place on metallic electrodes are pH dependent, with the potential shifting -0.059 V per pH unit. This is especially true for metal oxide formation and reduction reactions. Since the reference potential of the pH half cell also shifts by -0.059 V per pH unit, pH dependent potential shifts at the working electrode are canceled.

At a mobile phase pH of 7, the reference potential of the pH half cell is the same as that of the Ag/AgCl half cell. As the mobile phase pH is increased, the pH half cell potential decreases approximately 0.059 V per pH unit. For example, at a mobile phase pH of 12, the reference potential of the pH half cell would be -0.295 V relative to the Ag/AgCl half cell. Therefore, at pH 12, the potentials applied to the working electrode must be raised approximately 0.3 V when switching from the Ag/AgCl reference to the pH reference. In acidic mobile phases, the reference potential of the pH half cell is positive with respect to the Ag/AgCl half cell, and all applied potentials must be decreased by 0.059 V per pH unit when switching from the Ag/AgCl half-cell reference to the pH reference.

2.2 Functional Description

This section describes the ED40 functional operation. It includes descriptions of the operating modes and controls.

2.2.1 Modes of Operation

The detector has two modes of operation: ***Local*** and ***Remote***. When the detector is powered up, it is in Local mode. The mode of operation can be changed from the **MAIN** and **DETAIL** screens. To change to Remote mode, move the cursor to the **LOCAL** field and use the **Select** keys to toggle the mode. Press **Enter** when the mode is properly selected.

Local Mode

Local mode allows two types of entry:

- Directly from the front panel keypad.
- Relay and TTL inputs.

Relay and TTL control is defined using the **TIME FUNCTION IN** screen. Simple TTL logic levels or relay contact closures are used to control any selected four of the following detector functions:

- OFFSET
- HOLD/RUN
- SRS OFF/ON
- METHOD NUMBER INCR
- METHOD NUMBER DECR
- MARK Recorder
- Increase RANGEX10

These functions allow you to use a remote controller or the timed event function of an integrator to control the ED40. You must use the ED40 front panel switches to control all other detector functions.

No special setup or switch is required for Relay and TTL control. This control method is always available in Local mode. In addition, front panel control is still active.

Remote Mode

In Remote mode, the detector is computer controlled via the DX LAN. Remote control can be either Remote or Locked Remote. The Remote mode can be selected either from the **MAIN** screen or **DETAIL** screen with the keypad, or through the Peaknet Workstation. When making the selection from the keypad, move the cursor to the **LOCAL** or **REMOTE** display on the screen, press either **Select** key to toggle the operation of your choice, and then press **Enter**. If you are selecting **REMOTE**, you will be prompted to confirm that you want to select remote operation.

While operating in the Remote mode, all keys on the keypad function except **Hold/Run** and **Enter**. The **Enter** key will work for selecting display functions that do not interfere with LAN remote control of a method while it is running. When in the Remote mode (with the cursor on the **REMOTE** display), you can push either **Select** key to toggle the display to **LOCAL** and press **Enter** to select the Local mode. When the computer changes the ED40 from Local to Remote mode, the ED40 will immediately display its **MAIN** screen with the cursor positioned on **REMOTE** or **LOCKED RMT**.

The **LOCKED RMT** mode can be selected only from the computer. It locks out all parameter changes from the ED40 front panel. You can clear **LOCKED RMT** only from the computer or by powering the ED40 down. The ED40 always powers-up in Local mode.

If the ED40 is running a method when you change to the Remote mode, the computer will not interrupt the method, unless you select an *abort* command or download a method.

After the PeakNet software downloads a method to the ED40, the computer activates the method number with a LAN command. The **INITial** conditions step is activated. If a method is running when the computer activates a method number, the old method will be interrupted and the detector method clock will reset to **INITial** conditions.

A subsequent **RUN** command causes the ED40 method clock to run, activating the timed event starting with the time-zero step of the method.

2.2.2 Control

There are two types of control in either Local or Remote mode: ***Direct*** control and ***Method*** control.

Direct Control

In Direct control, commands are executed immediately when entered. Since there is no time-based program, the method clock is not used. The **Hold/Run** and **Reset** keys are not operable.

To select Direct control, first select either the **MAIN** or **DETAIL** screen. If **DIRECT CNTRL** is displayed, the mode is already selected and no further action is necessary. If **METHOD** is displayed, move the cursor to **METHOD** and press either **Select** key to toggle between **DIRECT CNTRL** and **METHOD** in the display. Press **Enter** to activate your selection.

If a method is running when you select Direct control, the method will be aborted and the method clock will be reset.

Method Control

In Method control, commands are executed as programmed in a method containing time-based program steps. The following parameters are programmed and cannot be changed from the front panel:

- Detection mode (Conductivity, DC Amperometry, Integrated Amperometry)
- Analog range
- Offset
- Mark
- Relays and TTLs
- SRS current (Conductivity)
- DS3 temperature (Conductivity)
- Temperature Compensation factor (Conductivity)
- Potential (DC Amperometry)
- Waveform number (Integrated Amperometry)

All of the above parameters may be changed by:

- Editing the currently running method and saving the changes. The changes are implemented when the method is saved.
- Switching to a different method.
- Aborting the method, going to Direct control, and entering the new parameters directly.

Methods are programmed and controlled from the **METHOD** screen. Besides storing and running methods, the ED40 allows you to run the detector under Method control while you are entering or editing any method, even one that is currently running. See Section 3.6 for instructions on programming methods.

When saving changes to the currently running method or switching to a different method, the method clock continues running unaffected. Only those parameter changes which affect the method after the current time will be implemented in the current run. Of course, you may intentionally press **Reset** to implement the initial conditions.

The front panel may be used to enter non-method programmed parameters, as well as to change screens to monitor detector operation.

To select Method control while in Direct control, call up either the **MAIN** screen or **DETAIL** screen. Move the cursor with the cursor directional keys to **DIRECT CNTRL** and press either **Select** key. Press **Enter**. **METHOD** will replace **DIRECT CNTRL** in the display.

There are 100 methods (00 through 99) available. The actual number that can be stored is memory-dependent. Typically, the maximum number will be less than 100. Each method can contain up to 50 separate time-based steps, starting at time **INIT** conditions. A method is entered by first selecting a method number from 0 through 99. Once the method number is selected, the time-based steps are entered one-by-one by first entering a time, followed by the operating parameters you want to be in effect at that time. Methods are retained in memory even when the detector is powered-down.

3 • Operation and Maintenance

3 • Operation and Maintenance

3.1 General Notes for Operation

The ED40 Electrochemical Detector may be controlled from the front panel or by the DX LAN. If the recorder outputs, TTL, or Relay I/O are used, the control set-up parameters should be configured before beginning operation. Preparation of the chromatographic system (eluents, columns, and apparatus) will vary depending on the analysis.

3.2 Start-Up

After installing the detector, or whenever the detector power has been off, use the following check list to place the detector back in operation:

For all Modes:

- ☐ Verify that all cables are correctly connected.
- ☐ Verify that the detector is plugged into the main power.
- ☐ Press the power switch located on the front panel to turn on power to the detector. See Section 3.3 for detailed information.
- ☐ The detector undergoes a self test. Verify that the detector passed all the tests (see Section 3.3 for detailed information).

For Conductivity Mode:

- ☐ If you are using a DS3 Detection Stabilizer, turn its power as soon as the proper temperature has been set. When used in an LC30 Chromatography Oven, this temperature should be at least 5 °C above the oven temperature. Otherwise, set the temperature at least 5 °C above the highest expected ambient temperature surrounding the DS3. The DS3 warms at about 1 °C / minute. After reaching the set temperature, the baseline conductivity should stabilize.

☐ Turn the suppressor on as soon as the proper current is determined and eluent is flowing through the suppressor at the proper rate. It may take longer for the suppressor to stabilize than the DS3. The drift usually goes down as suppressor efficiency improves.

☐ While waiting for acceptable drift, you may want to select a lower sensitivity. Set the offset to 50%.

☐ When starting a run, select the desired sensitivity and offset. Press **Offset** before injecting and during a run if necessary.

☐ The supressor is programmed and monitored from the **DETAIL** screen. Operational requirements for the suppressor are presented in the manual shipped with the suppressor:

- Document No. 034650 for the anion suppressor.
- Document No. 034651 for the cation suppressor.

For Integrated Amperometry Mode:

☐ Create a potential vs. time waveform or edit an existing waveform. In Local mode, use the **WAVEFORM** screen. Verify that the correct waveform is selected on either the **MAIN** and **DETAIL** screen, or in the **METHOD** screen if you are using a method.

☐ If necessary, calibrate the reference electrode (Section 3.12.2).

☐ Polish the working electrode (Section 3.12.3).

☐ Verify that the cell is connected and that all tubing has been properly connected.

☐ Turn on the pump.

☐ Turn on the cell and allow the baseline to stabilize. The detector output will normally drift downward for about one hour as the baseline stabilizes.

For DC Amperometry Mode:

- ☐ Enter the applied potential on the **MAIN** or **DETAIL** screen, or in the method.
- ☐ If necessary, calibrate the reference electrode (Section 3.12.2).
- ☐ Polish the working electrode (Section 3.12.3).
- ☐ Verify that the cell is connected and that all tubing has been properly connected.
- ☐ Turn on the pump.
- ☐ Turn on the cell and allow the baseline to stabilize. When a glassy carbon working electrode is used, the detector output will normally drift downward for up to one day. Baseline noise will diminish considerably during this period. Set up the detector the day before it will be used and allow the baseline to equilibrate overnight. Slow the flow rate to one fourth of the value to be used for analyses to conserve mobile phase. The detector will stabilize quickly the next morning when the flow rate is increased to the proper value.

3.3 Powering Up

Set up the ED40 as described in Appendix B.

The power switch is labeled with a vertical stroke in a circle, denoting an alternating action power switch. When turned on, the detector conducts an internal diagnostic check. If the detector is in Conductivity mode, the conductivity cell is turned on and the amperometry cell is off. If the detector is in one of the other modes, both cells are off.

The position of the switch actuator does not indicate the state of the power switch. When powered, the status LED indicates powered operation. The true power switch is located inside the door panel. The switch is engaged when it is pushed in.

3.4 Navigating the Menus

The control display is organized as a series of screens that is navigated using the **Menu** key. Figure 3-1 shows the ED40 Menu Map. In each operating mode, some screens are not applicable and do not appear. For example, in Conductivity mode, the **WAVEFORM** screen does not appear. Each screen is illustrated and described in detail in Appendix C.

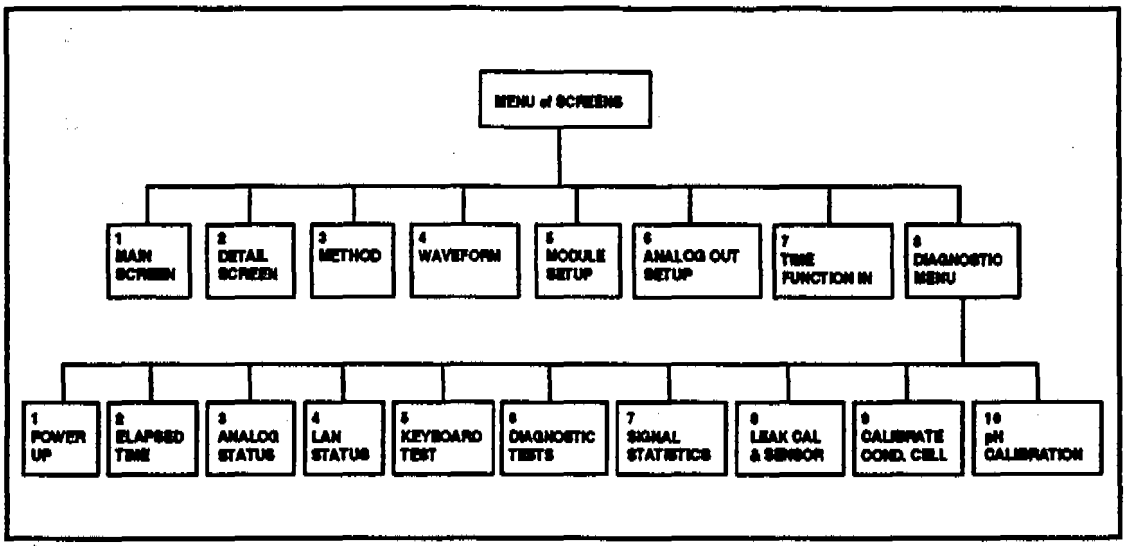


Figure 3-1. ED40 Menu Map

Notice that there are two hierarchical levels of screens.

- Pressing the **Menu** key from any of the first-tier screens moves you directly to the **MENU of SCREENS.**
- Pressing the **Menu** key from any of the second-tier (diagnostics) screens moves you to the **DIAGNOSTICS MENU.** To move from the **DIAGNOSTICS MENU** to the **MENU OF SCREENS,** press the **Menu** key a second time.

The bottom line of every screen is the *help line*, which describes each function displayed as the edit cursor is moved. Additional information for each displayed function can be accessed by pressing the **Help** key.

Because each of the four operating modes requires different parameters, the **MAIN**, **DETAIL**, **WAVEFORM**, and **METHOD** screens are unique to their respective modes.

3.5 Direct Control

When using Direct control, all detector settings are in effect until you change them. Changes to parameters are then executed immediately when entered. Because there are no time-based steps, the clock is not used and the **Hold/Run** and **Reset** keys are not operable. To change a parameter, move the cursor to the parameter location on the screen, key in the parameter, and press **Enter**.

To select Direct control, first select either the **MAIN** or **DETAIL** screen. If **DIRECT CNTRL** is displayed, the mode is already selected and no further action is necessary. If **METHOD** is displayed, move the cursor to **METHOD** and press either **Select** key to toggle between **DIRECT CNTRL** and **METHOD** in the display. Press **Enter** to activate your selection.

3.6 Methods

A method is a programmed series of timed events. You create and modify methods using the **METHOD** screen. Methods can be saved in memory to be reused at a later time. You can create up to 100 methods (numbered 0 to 99). Methods are retained in memory, even when the power is turned off.

The parameters that may be controlled by a method depend upon the operating mode of the detector. See the following sections for detailed information about the method parameters:

- Conductivity — Section C.1.4
- Integrated Amperometry — Section C.1.8
- DC Amperometry — Section C.1.13

There are two ways to run a method:

- Call up the **MAIN** or **DETAIL** screen. Toggle from **DIRECT CNTRL** to **METHOD** if necessary, enter the desired method number, and press **Enter**.
- Use the **METHOD** screen. Move the cursor to the **RUN** field, enter the desired method number, then press **Enter**.

If the clock on the **MAIN** or **DETAIL** screen is **INIT** when you press **Enter**, the ED40 uses the method **INIT**ial condition parameters to control the module. If the method clock is greater than zero when you press **Enter**, the ED40 uses the method parameters in effect at that time.

Pressing **Run** on the keypad starts the method clock. From the **INIT**ial conditions, the time zero step is executed as soon as **Run** is pressed. The remaining steps are executed according to their programmed times.

When there are more steps in a method than can be displayed on one screen, they can be viewed by stepping the cursor to the top or bottom screen entry and then stepping one more line. A small **v** next to the time entry at the bottom of the screen indicates that you need to move the cursor down to view the additional steps. Similarly, a caret **^** adjacent to the top time entry indicates that you must move the cursor up to view the additional steps.

3.6.1 Entering a New Method

You can create a new method at any time: Call up the **METHOD** screen and enter a new method number in the **EDIT** field. Then enter the same number in the **SAVE TO** field.

Time-programmable events are entered into the method field-by-field. In Conductivity mode, SRS current, DS3 temperature, and temperature compensation remain constant throughout the method and are displayed on the **METHOD** screen.

The first step of a method is an initial conditions step with **INIT** in the time parameter column. The second step is always a time-zero step with 0.00 in the time parameter column. The parameters in these beginning steps can be changed, but the steps cannot be deleted. Figure 3-2 shows the **METHOD** screen for Conductivity.

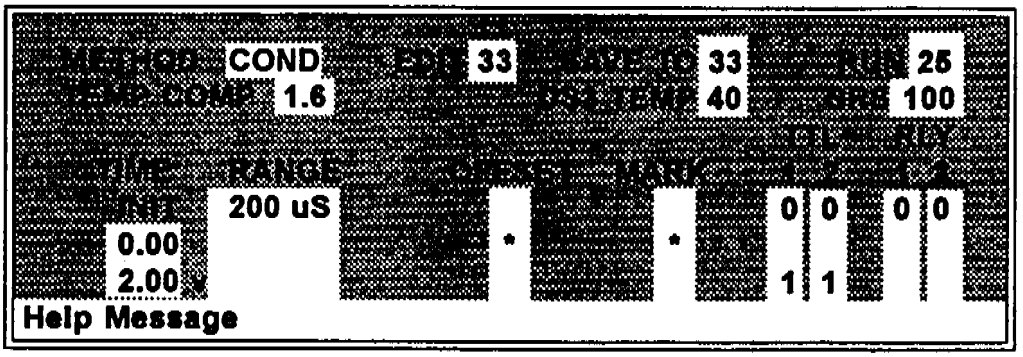


Figure 3-2. Method Screen — Conductivity

A new method step is initiated by entering the total elapsed time. The first step will always be 0.00. Move the cursor to the **TIME** field and enter the time followed by the remainder of the parameters.

When a method is entered, the method steps are stored in memory and become effective when the method is saved.

3.6.2 Editing a Method

After entering a method, you can later modify it by changing, adding, or deleting steps and parameters. If the method being edited is currently running, the changes are stored in memory when you **SAVE TO** the method number. Changes take effect as soon as you save them.

Be sure to save changes before you leave the **METHOD** screen. If you leave without saving, your changes will be lost.

After the changes are saved, there is no way to recall the original method. Therefore, if you plan to make experimental changes to a method, but want to retain the original method in its unmodified form, save either your new method or a copy of the original method under a different method number.

Adding a Method Step

To add a method step to an existing method, enter the time and the desired parameters in the **METHOD** screen. The step will be inserted automatically into the method at the correct chronological point. Or, place the cursor on the line which will precede your new step and press **Insert**. A new blank line will appear below where you placed the cursor.

Deleting a Step

To delete a time-based method step, move the cursor on the **METHOD** screen to the time of the step to be deleted, then press **Delete** twice.

3.6.3 Deleting a Method

To delete an entire method, move the cursor on the **METHOD** screen to the **EDIT** entry, then press **Delete** twice.

3.6.4 Running a Method

To run a method, enter the method number in the **RUN** field of the **MAIN**, **DETAIL**, or **METHOD** screen and press **Enter**. If the clock is not already running, the initial conditions will be applied.

3.6.5 Changing the Method Number

To change from the method currently running to a different method, enter the new method number in the **RUN** field on the **MAIN**, **DETAIL**, or **METHOD** screen and press **Enter**.

Interrupting the execution of a method by pressing **Hold** stops the clock and freezes the parameters at the point of interruption. When **Run** is selected again, the method continues from the previously frozen time.

3.6.6 Controlling Another Instrument

The ED40 can control another instrument through the TTL and Relay ports, which are programmable within methods and can also be controlled immediately through Direct control. Similarly, another instrument, such as the GP40 Gradient Pump, can control the ED40 Electrochemical Detector by a method in the pump through the TTL input ports in the ED40.

Typically, the chromatography system is set up so that one module (such as the pump) contains the method control and drives other modules (such as the ED40 Electrochemical Detector and the AD20 Absorbance Detector).

3.7 DX LAN Remote Operation

A computer equipped with PeakNet software connected to the ED40 via DX LAN allows you to monitor the detector status remotely and to control all of the detector functions from the computer. When the DX LAN cable is connected to the BNC connector on the ED40 rear panel, and the detector is in Remote mode, the computer has complete control of the detector.

3.8 Optimizing Temperature Compensation

The optional DS3 Detection Stabilizer maintains a constant temperature to improve conductivity detection.

3.8.1 With a DS3 Detection Stabilizer

If you are using a DS3 Detection Stabilizer, the temperature variations of the liquid reaching the cell should be negligible. Set and leave the temperature compensation setting at 1.7% per °C.

If temperature-induced baseline cycling is evident, it is probably due to another chromatography component. If the variation increases as the eluent reservoir empties, try the following:

- Put the reservoir in a more temperature-stable environment.
- Wrap the reservoir in insulation.

3.8.2 Without a DS3 Detection Stabilizer

If a DS3 is not used, the baseline will drift up and down as the laboratory temperature fluctuates. This is especially noticeable in laboratories with thermostatically controlled temperature as the thermostat cycles on and off. The effect of changing temperature can be minimized by properly setting the temperature compensation factor. The temperature compensation setting is generally between 1.5% to 2% per °C for most systems, suppressed or not. Start with a setting of 1.7%.

If a sinusoidal baseline variation of the same period as the laboratory cooling or heating occurs, change the detector temperature compensation setting higher or lower. Continue adjusting until you find the optimum setting.

If your laboratory does not have a temperature control system, and has a slowly increasing or decreasing temperature pattern, look for a corresponding baseline drift. If this drift occurs, try a slightly higher or lower temperature compensation setting. Continue adjusting until you find the optimum setting.

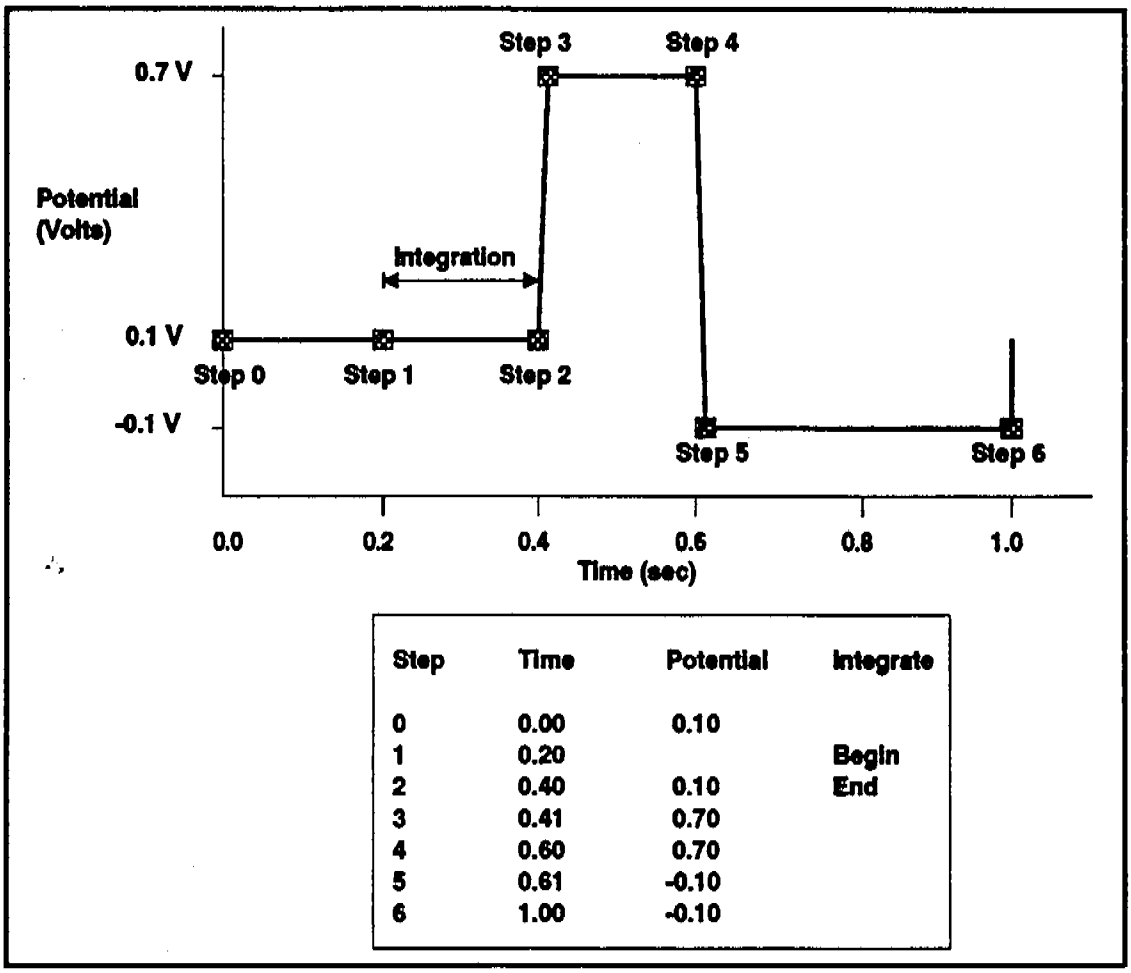
3.9 Operating Temperature

The DS3 temperature operating range is 25 to 40 °C (50 to 104 °F). Do not operate the DS3 in ambient temperatures outside of its normal operating range. If the ambient temperature is less than 25 °C, the DS3 may not be able to reliably maintain the set temperature. If the ambient temperature is greater than 40 °C, damage to the DS3 may result.

CAUTION — When using the DS3 in a LC30 Chromatography Oven, do not set the oven temperature above 40 °C (104 °F). Higher temperatures may damage the DS3 permanently.

3.10 Waveforms

Waveforms must be defined for the Integrated Amperometry and Voltammetry modes. Entering a waveform is similar to entering a method. A waveform is a series of steps, defined as points on a plot of potential vs. time. Figure 3-3 shows an example waveform and the waveform program that created it.



Step	Time	Potential	Integrate
0	0.00	0.10	
1	0.20		Begin
2	0.40	0.10	End
3	0.41	0.70	
4	0.60	0.70	
5	0.61	-0.10	
6	1.00	-0.10	

Figure 3-3. Sample Waveform

Notice that for Step 2, the potential does not need to be entered because it does not change from Step 1. Also notice that after Step 6, the waveform automatically reverts to the Step 0 potential.

3.11 Voltammetry

The Voltammetry mode is used to develop waveforms for Integrated Amperometry and to determine appropriate potentials for DC Amperometry. It is similar to Integrated Amperometry in that a repeating potential vs. time waveform is applied to the cell. It differs in that the ED40 detector output is the cell current, which is continuously monitored and reported as in DC Amperometry. The information gained by studying instantaneous cell current can be useful for developing waveforms used in Integrated Amperometry. The ED40 can also be used to perform cyclic voltammetry by programming a triangle wave as the waveform.

3.11.1 Cells for Voltammetry

With the pump on and the mobile phase and analyte flowing through the amperometry cell, results are similar to those obtained by rotated disk voltammetry in a standard beaker cell. With the flow off, rapid depletion of analyte next to the working electrode is typical of thin-layer voltammetry. Cells other than the ED40 cell can be used by making the appropriate working, reference, and counterelectrode connections to the amperometry cell cable. Pin identification is listed in Table E-8. *However, you must short pins 1 and 7 to avoid a cell disconnected error message.*

3.11.2 Recorder Connections

Cell current is monitored in the Voltammetry mode by connecting the ED40 analog output to a recording device. Use the recorder negative and positive connections on the SCR card (pins 1 and 2). Data output from cyclic voltammetry is traditionally plotted as current vs. potential rather than time. This is accomplished by connecting the Amperometry Cell Drive output on the SCR card (pin 7) to the X axis of an X-Y recorder, oscilloscope, or a computer equipped with A/D conversion and X-Y plotting software.

3.11.3 Programming the Voltammetry Waveform

Waveforms are programmed using Screen 4. There is only one Voltammetry waveform; it must be edited to create a different waveform.

Waveforms are defined by points on an X-Y graph of potential vs. time, as in Integrated Amperometry. See Figure 3-4 for an example of a triangle wave used in cyclic voltammetry.

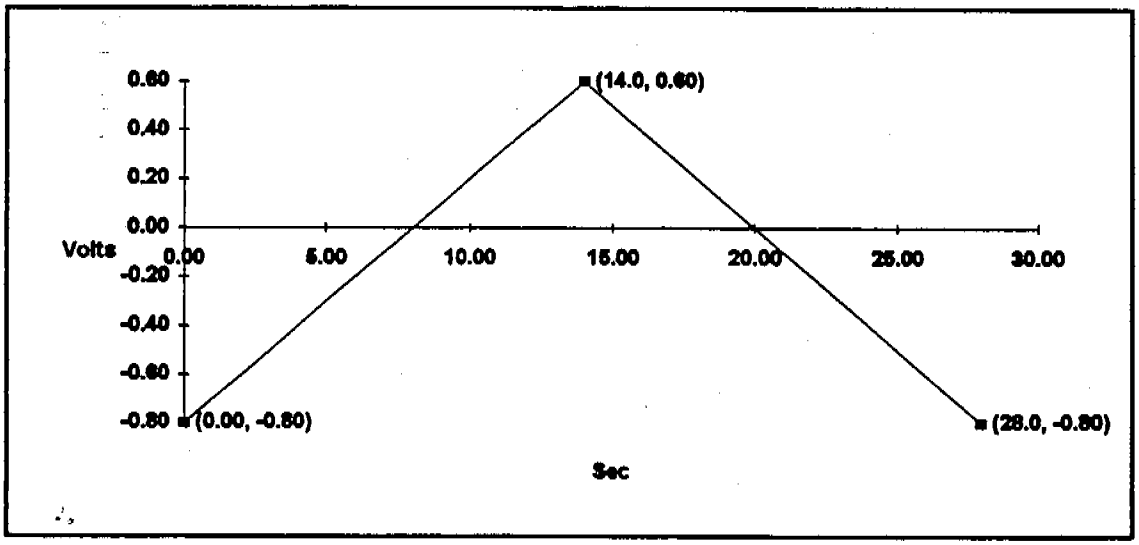


Figure 3-4. Cyclic Voltammetry Example

In this example, the potential is cycled between -0.80 and +0.60 V at a sweep rate of 0.1 V/s. Cyclic voltammetry programs contain three steps, with the potential at the first and third steps being equal. The first waveform step at 0.00 s is the initial potential of -0.80 V. To calculate the time for the second step, divide the total voltage scanned by the desired sweep rate.

$$\frac{Total\ Voltage\ Scanned}{Sweep\ Rate} = \frac{1.4\ V}{0.1\ V/s} = 14\ s$$

The time for the second step is 14 s. The third step is an equal interval later, or 28 s.

Waveform steps are created by first entering the time, followed by the potential. The first step of the waveform is at time zero. Since this cannot be changed, the first value to enter is the first potential. The remaining times and potentials are entered in sequence until the waveform has been completed. Be sure to save the waveform before exiting the screen.

In the Voltammetry mode, the ED40 measures and reports the current every 10 ms. Since the change in potential during each measurement period must be equal, the available potentials are limited to ensure that the potential change is an integer number of mV per 10 ms. (The slowest scan rate is therefore 1 mV per 10 ms, or 0.1 V/s.) If you enter a potential that results in a noninteger change, the ED40 will substitute the closest acceptable potential. You can also use the **Select** keys to find available potentials.

3.11.4 Running the Waveform

When the cell is turned on, the ED40 applies the initial potential programmed at time zero. Press **Run** to begin the waveform. Press **Hold** to freeze the scan at the current potential; press **Run** to continue from that point. **Reset** returns to the initial potential but does not stop the scan. To return to the initial potential and hold at that potential, press **Hold** and **Reset**, in that order.

3.12 Routine Maintenance

The ED40 Electrochemical Detector electronics require no routine maintenance. Periodically check the liquid line connections to both cells (located inside the Chromatography Module) for leaks and clean up any spills. Depending on the application, the amperometry cell working electrode may need periodic polishing. The amperometry cell reference electrode may also require occasional cleaning.

3.12.1 Calibrating the Conductivity Cell

Use the **DIAGNOSTIC MENU** screen 9. Note that a conductivity cell constant is displayed along with a conductivity reading. The cell constant is a number stored in permanent memory. It is used to calculate the measured conductivity. You may enter a new value using the keyboard regardless of whatever is in the cell. Or, you can cause a new value to be entered automatically by performing the following procedure.

Every cell is calibrated at the factory and the cell constant is recorded on a tag attached to the cell cable near the cell body. This value will normally remain the same over time, unless the cell is damaged. If this value is not entered in your detector, do so and then you can use the detector with reasonable confidence in the accuracy of the readings.

If you wish to check the calibration yourself, perform the following procedure to calibrate the cell at 147 µS.

1. Disconnect the pump output line from the LC10 Chromatography Organizer, LC20 Chromatography Enclosure, or LC30 Chromatography Oven.
2. Connect the pump output directly to the DS3 or shielded cell inlet.

3. Pump 0.001 M KCl calibration solution through the cell at 8.0 mL/min. Conductivity is slightly flow-rate sensitive. Calibrate the detector at the flow rate used in the majority of your work.
4. Set **TEMP COMP** to 1.7%.
5. Set the DS3 temperature (if used) to the intended operating point. Wait until the DS3 READY message appears.
6. Wait until the conductivity reading is stable (within 0.1 µS).
7. Note the conductivity reading which will probably be off by a small number of µS. Perform the calibration. The conductivity reading should now be exactly 147.00 µS and a new value for the cell constant will appear and be entered in memory. If the new and old values differ by more than 5 to 10, it is possible that a problem is developing in the cell or module electronics. Refer to the troubleshooting chapter for more information.
8. Pump deionized water through the DS3 or cell lines until the conductivity reading drops to near zero to flush the calibration solution from the system. Then stop the pump.
9. Disconnect the pump from the DS3 or cell.
10. Reconnect the pump to the LC10, LC20, or LC30.
11. Reconnect the liquid line from the suppressor outlet to the cell inlet.
12. Reset the **TEMP COMP** to the optimum value for the eluent.
13. Set the pump to a flow rate that is safe for the system in use.

The ED40 is now calibrated and ready for making conductivity measurements.

3.12.2 Calibrating the pH Reference Electrode

All pH electrodes must be calibrated when installed to produce accurate pH readings. Although it is possible to calibrate the electrodes by pumping pH buffers through the cell, Dionex recommends that you follow the procedure below. Calibration is performed with the cell turned off and the pH electrode removed from the reference electrode chamber within the cell body.

Calibrating the pH reference electrode when installed in the cell with the cell powered on may cause oxidation or reduction of some components of the pH calibration buffers. This may poison the working electrode surface. If this occurs, you must restore the working electrode surface by polishing it.

Reference electrodes that have been used recently in strong acidic or basic solutions should be soaked overnight in saturated KCl prior to calibration.

1. Begin with two buffer solutions. The first must be at pH 7. The second must be at least 1 pH unit away from pH 7, but no greater than pH 12. Buffer solutions of pH 4 or pH 10 are commonly used. Note, however, that the chosen buffer solution should ideally be as close as possible to the mobile phase pH.
2. Verify that the amperometry cell cable is connected to the cell and to the detector.
3. Make sure that the cell is off.
4. Remove the electrode from the soaker bottle by first partially unscrewing the lid, then pulling the electrode out of the O-ring groove within the lid. Rinse the electrode in deionized water. Be sure to rinse off any precipitated salt.

NOTE

Do not discard the soaker bottle and lid, as these are required for safe storage of the electrode when the cell is not in use.

5. Connect the pH electrode lead wire to junction J2 on the cell pre-amp board and place the electrode into the pH 7 buffer solution.
6. Press the **Menu** key on the ED40 front panel. Select the **DIAGNOSTIC MENU** and then select **pH CALIBRATION**.
7. With the pH electrode in the pH 7 buffer solution, select **CAL** and press **Enter** on the ED40 detector keypad and wait for the pH 7 *Calibration Complete* message to appear.
8. Remove the pH electrode from the pH 7 buffer solution and rinse it well with deionized water.
9. Place the pH electrode into the second buffer solution. Enter the pH value for the second buffer solution and press **Enter**. Wait for the *Calibration Complete* message to appear.
10. The pH electrode is now calibrated. Rinse the electrode with deionized water and install it into the cell body.

The ED40 is equipped with an automated sodium correction option. This option corrects for sodium and alkaline errors above pH 12 and is particularly useful for sodium hydroxide mobile phases. This option should not be used with potassium hydroxide or other cation hydroxide mobile phases. The best accuracy is obtained in the pH 12 to 13 range. Accuracy is less in pH ranges greater than 13.

3.12.3 Maintenance of the Amperometry Cell

Be careful to keep the polished surface of the cell body along with the gold, spring-loaded working electrode contact clean and dry. Be sure not to allow any type of *salt bridge* to form an electrical short between the spring-loaded working electrode contact and the cell body.

Shutdown

Whenever the cell is not being used, remove the pH reference electrode to prevent the diffusive interface of the pH reference electrode from drying out and becomming clogged. The following steps should be taken to ensure safe storage of the electrode.

1. Prepare a saturated solution of KCl in deionized water.
2. Remove the cap of the soaker bottle in which the electrode was shipped.
3. Fill the soaker bottle at least 3/4 full with the prepared KCl solution.
4. Remove the pH reference electrode from the cell.
5. Slip the electrode through the hole in the soaker bottle lid until the electrode cap bottoms out on the top of the lid.
6. Screw the soaker bottle lid with the electrode attached to the KCl filled soaker bottle.
7. Store the assembly in the original shipping box.

Regenerating

After using the reference electrode for a long time (months) at high pH, the reference frit may become clogged. This may cause sudden changes in the baseline or produce random spikes. If you have a reference electrode that may have partially dried out, it may be possible to regenerate (unclog) it by soaking it in a saturated KCl solution for 1 to 3 days. If this fails, then you must replace the defective electrode (P/N 046338).

Replacing the O-Ring

If you observe leaks emanating from the pH reference electrode or compression nut area when the cell operating pressure is below 700 kPa (100 psi), you may need to replace the pH reference electrode O-ring. Removing the O-ring destroys it. Always replace the old O-ring with a new one.

1. Remove the pH reference electrode from the reference electrode cavity.
2. With a sharp instrument (such as a pin), stick the O-ring and pull it out. Be sure not to misplace the stop ring (P/N 045967) located in the reference electrode cavity below the O-ring. This stop ring is necessary to prevent the pH reference electrode from bottoming out and damaging the electrode. Be sure not to scratch the cell body.
3. Prior to replacing the new O-ring, verify that the stop ring is in place at the bottom of the cavity.
4. Using a blunt instrument, push the new O-ring into the groove within the cavity. Be sure that the replacement O-ring is seated properly before reinstalling the pH reference electrode.

3.12.4 Polishing the Working Electrode

The working electrode must be polished before it is installed in the amperometry cell. To maintain sensitivity after the initial installation, polish the working electrode surface whenever you observe high background current, a decrease in sensitivity, or other degradation in the detector output. Figure 3-5 shows the amperometry cell assembly.

1. Unscrew the wing nuts holding the working electrode to the cell body, and carefully separate the parts. Handle the cell gasket and the inside surfaces of the cell carefully, to prevent scratches which may cause leaks.

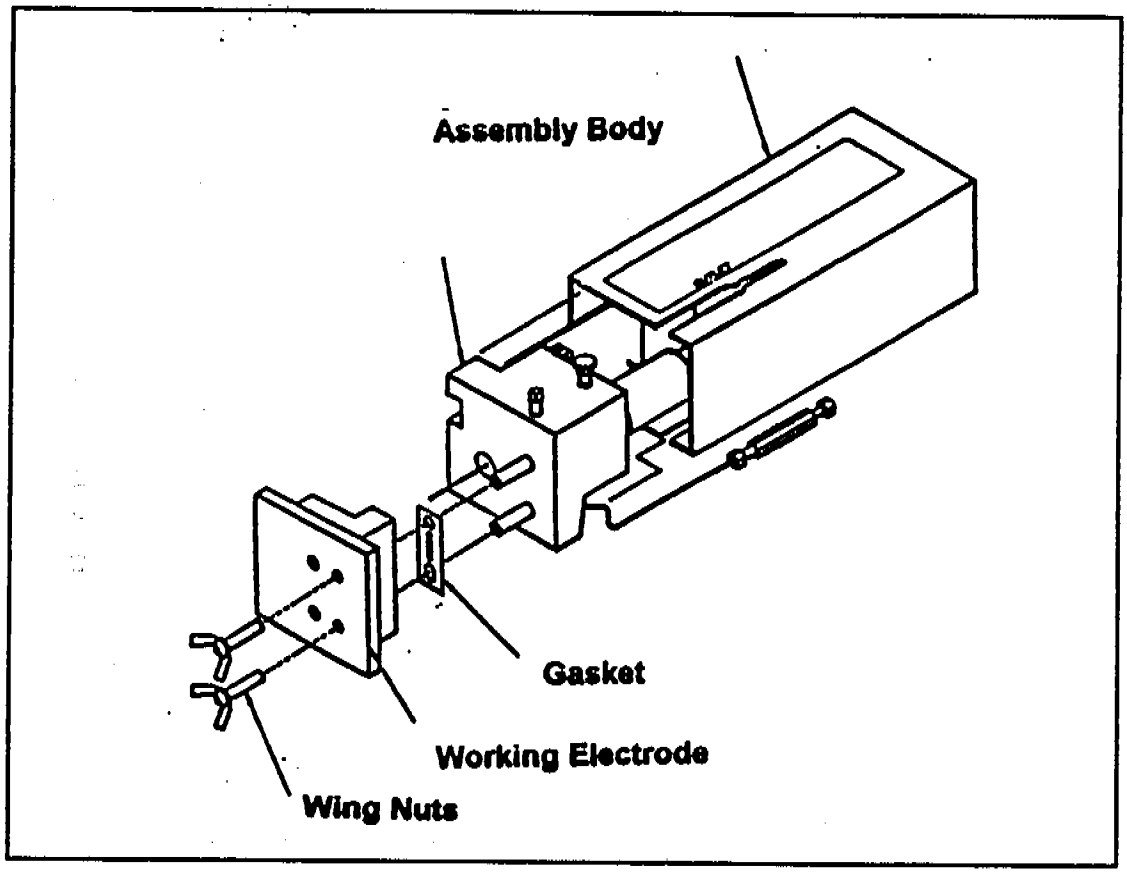


Figure 3-5. Amperometry Cell Assembly

2. Locate the polishing kit (P/N 036313) in the Ship Kit. The kit contains two polishing pads, a bottle of fine polishing compound, and a bottle of coarse polishing compound. Using indelible ink, mark the plastic side of each pad to designate whether it is to be used with the coarse or fine polishing compound. Also mark the fine pad to designate for which working electrode type it is to be used.

NOTE

Polishing more than one type of working electrode with the same fine polishing pad may contaminate the electrode surface with microparticles from the other working electrodes. A separate polishing pad is shipped with each type of working electrode. Using indelible ink, mark each pad to indicate the working electrode with which it is used.

3. Moisten the plastic side of the fine polishing pad slightly with water and place it on a smooth, flat surface.
4. Sprinkle about one-half gram of fine polishing compound (P/N 036316) in the center of the suede side of the polishing pad. Add enough deionized water to make a thick paste.
5. Using the working electrode block, spread the paste evenly over the pad. Then, using firm pressure, polish the surface of the electrode block for approximately one minute. Add more water sparingly if the pad dries out while polishing.
6. Use deionized water to rinse off all polishing compound from the electrode block. An ultrasonic cleaner is effective for thoroughly cleaning the electrode block. Carefully wipe the surface of the block with a soft damp cloth or damp paper towel. Inspect the surface of the working electrode to make sure that it is clean.

NOTE

The polishing pads are reusable. Do not rinse the polishing compound from the pads after polishing is complete. After the initial use, add only enough polishing compound to maintain the coating on the pad.

NOTE

During the normal operating life of the working electrode, the surface will gradually become pitted. If you notice any degradation in performance, such as a noisy baseline or tailing peaks, polish the working electrode using the coarse polishing compound. Then, rinse the electrode thoroughly, wipe the coarse polishing compound from the surface of the electrode, and polish with fine polishing compound. You may use the pad designated for use with coarse polishing compound on all electrodes.

7. Reassemble the working electrode.

3.12.5 Replacing the Plumbing

Although PEEK is a plastic, the creep rate is slow. However, over time, it is possible for the PEEK tubing and fitting components to loosen and leak or pinch off and plug. Inspect the tubing for leaks and watch for increasing pressure. Tubing and fittings are user serviceable.

4 • Troubleshooting

4 • Troubleshooting

This chapter provides you with a guide to troubleshooting common problems in the ED40 Electrochemical Detector. To use this Guide, turn to the section that best describes the operating problem. There, you will find the possible causes of the problem listed in order of probability. If you cannot eliminate a problem on your own, notify the nearest Dionex Regional Office.

If you cannot locate the problem from the Troubleshooting Guide, refer to Appendix C for instructions on how to run the ED40 Diagnostics Program.

4.1 Troubleshooting Guide

4.1.1 No Detector Response

- **The cell is turned off.**

  Turn the cell on using the **MAIN** or **DETAIL** screen.

- **The analog output range is set too high. The display indicates a response, but no recorder response is observed.**

  Select a more sensitive analog output range.

- **Wrong full-scale output selected.**

  Select 0.01, 0.10, or 1 V Full-Scale.

- **Pump is not pumping.**

  Check the pressure reading on the pump to ensure that the pump is on.

- **Detector offset out of range.**

  Press **Offset**.

4.1.2 Low Detector Output

- **The analog range to the recorder is set too high. The display indicates a response, but little or no recorder response is observed.**

  Select a more sensitive analog range.

- **An insufficient sample is injected.**

  Increase the injection size or concentration.

- **Conductivity cell is out of calibration.**

  Recalibrate the Conductivity cell (see Section 3.12.1).

- **Working electrode is fouled.**

  Polish the working electrode (see Section 3.12.4).

4.1.3 High Detector Output

- **Auto offset has not been activated recently.**

  Press **Offset** before making an injection.

- **In Conductivity mode, the regenerant is not suppressing the background.**

  Use a higher regenerant flow rate.

- **In Integrated Amperometry mode, there are too many integration periods. Integration periods were not properly deleted during editing.**

  Delete unnecessary integration periods.

4.1.4 Noisy or Drifting Baseline

- **Air trapped in the cell; excessive regular pulses in the baseline.**

  Remove trapped air. Increase the length of the waste line to increase the backpressure on the cell.

- **There is a flow system leak ahead of the cell; the baseline is erratic.**

  Check all fittings and liquid lines for leaks. Tighten any leaking fittings fingertight, then tighten an additional 1/8 turn. Tighten further only if the leak continues. **DO NOT OVERTIGHTEN**. If tightening does not stop the leak, remake the fitting.

- **In Conductivity mode, operating conditions for the suppressor are inappropriate.**

  Operate the suppressor as directed in the suppressor manual.

- **Pump is not properly primed.**

  Prime the pump.

- **In Integrated Amperometry, there arae regular baseline oscillations caused by trace contamination of water used to prepare the eluent.**

  Use high purity DI water which does not contain trace sugar contaminants.

- **In DC Amperometry and Integrated Amperometry modes, there are frequent, random spikes in the baseline caused by a plugged reference electrode.**

  Regenerate the reference electrode or replace the reference electrode (see Section 3.12.2).

- **In DC Amperometry and Integrated Amperometry modes, there is regular baseline oscillation on high-sensitivity ranges caused by not using the short stainless-steel tubing on the cell inlet.**

Reconnect the stainless steel tubing to the cell inlet.

- **In DC Amperometry and Integrated Amperometry modes, the working electrode is dirty.**

  Polish the working electrode (see Section 3.12.4).

- **There are rapid temperature changes in the laboratory. A heater or air conditioner is blowing directly on the cell.**

  Direct heating and air conditioning vents away from the cell.

  Install the cell in an LC30 Chromatography Oven.

- **Insufficient system equilibration following any changes to the operating parameters; especially apparent when operating at high sensitivities.**

  Allow longer system equilibration before beginning operation.

- **In Conductivity mode, the temperature compensation setting is not optimized.**

  Optimize the selected setting (see Section 3.8.2).

  Install the cell in a DS3 Detection Stabilizer.

4.1.5 pH Readout from Amperometry Cell Always 7.0

- **Short circuit in pH reference electrode.**

  Check connections to the cell preamp PC board.

  Look for salt on the cell preamp PC board.

  Replace the pH reference electrode.

4.1.6 No pH Readout from Amperometry Cell

- **One or two pH electrode wires disconnected or broken.**

  Fix connections or replace electrode.

- **pH electrode not calibrated.**

  Calibrate the pH reference electrode (see Section 3.12.2).

4.1.7 pH Readout from Amperometry Cell Cannot be Set to 7.0

- **Calibration buffer not accurate.**

  Use a separate pH meter to check the pH of the buffer.

- **pH reference electrode contaminated.**

  Soak the electrode in a 1 M KCl, 1 M HCl solution.

  Replace the electrode.

4.1.8 pH Reference Electrode Discolored

This is not a problem. The electrode will normally become discolored from prolonged use at high pH. It will still function well.

4.1.9 Faulty DX LAN Communications

- **Each unit is connected with a tee, and the tee daisy chains the connection to the next unit. Both end units in the chain must have a terminator at the tee output.**

  Other connections add reflections, use the daisey chain.

  Is the terminator plug only on the last unit? Missing or multiple terminators add reflections.

4.2 Diagnostics

Diagnostic screens are accessed by selecting the **DIAGNOSTICS MENU** from the **MENU of SCREENS** (see Figure 4-1). While in the diagnostic system, pressing the **Menu** key will bring up the **DIAGNOSTIC MENU**. From the **DIAGNOSTIC MENU**, pressing the **Menu** key twice returns you to the **MENU of SCREENS**.

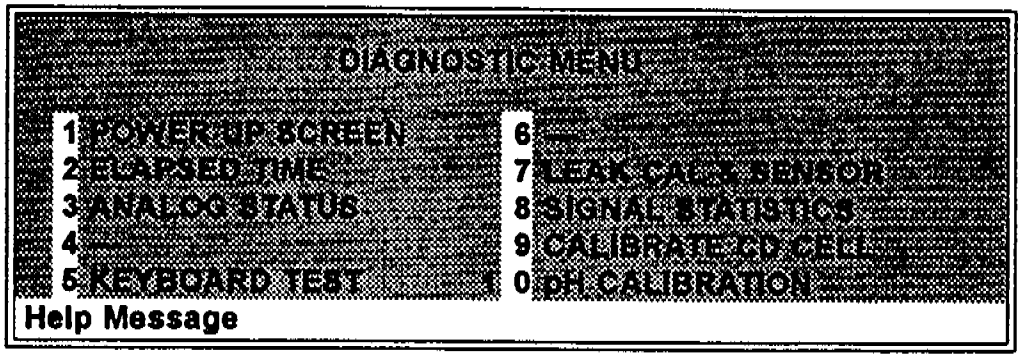


Figure 4-1. Diagnostics Menu

The Diagnostic screens and procedures for using the ED40 Diagnostic Program are contained in Appendix C.

5 • Service

This chapter describes service and repair procedures for the ED40 detector and cells. Since there are no moving parts, relays, or frequently used switches and only one potentiometer, the detector is not prone to wear out. The fluorescent backlight on the liquid crystal display screen should last the life of the detector.

Each procedure in this chapter specifies the problem it is intended to eliminate. Before replacing any part, refer to Chapter 4, *Troubleshooting*, to isolate the cause of the problem. When ordering replacement parts, please include the model and serial number of the detector, along with the part numbers. Where applicable, also include the revision number of the parts.

The detector features a series of diagnostic tests designed to determine the source of many electronic problems. Before beginning these tests, consult Chapter 4, to isolate any non-electronic problems. Electronic components are not customer-serviceable but cables and electronic modules can be replaced. Any repairs involving electronic components must be performed by Dionex.

5.1 Tube Fitting

The ED40 is plumbed with Dionex ferrule fittings (P/N 043276), 10-32 fitting bolts (P/N 043275), and 1.6-mm (1/16-in) PEEK tubing. For more information, refer to the Document *Installation of Dionex Ferrule Fittings*, included in the ED40 Ship Kit.

5.2 Trapped Air in the Cell

Air trapped in the cell may respond to pump pulsations and cause a regular pulsation of the baseline. Bubbles may also cause random noise and low readings. The trapped air may be a result of air in the columns, introduced during installation, or from eluent outgassing. A small amount of backpressure on the cell will prevent it from trapping air.

NOTE

Make sure the proper backpressure tubing is installed. Use a length of 0.25 mm (0.010 in) ID tubing (P/N 042690), with fittings on both ends, between the cell outlet and the waste. A cell backpressure tubing of 0.20 mPa (30 psi) is recommended. Use 1 m at 1 mL/min, 2 m at 0.5 mL/min, etc. Use large diameter tubing, at least 1 mm (0.04 in), the rest of the way to the waste container. Avoid large flow rate increases that would result in more than 1.4 mPa (200 psi). Use a union (P/N 042627) to connect the backpressure tubing to the waste line.

5.3 Detector Diagnostics

The detector microprocessor Moduleware features diagnostic tests which check the operation of the detector electronic components, simplifying isolation of any malfunction. Turning the power on activates a basic diagnostic testing function. Further tests can be selected using the display screen and keypad.

Most of the circuitry on the Signal Processing (SP) board is exercised and checked for proper operation during the comprehensive diagnostic test. Error messages identifying the circuit section and type of malfunction then appear on the display.

Individual diagnostic tests can be run from the **DIAGNOSTICS TESTS** screen. See Section C.2.7.

6 • Electrochemical Detection

6 • Electrochemical Detection

This chapter describes the fundamentals of electrochemical detection methods. The better you understand electrochemical detection, the more successful you will be at exploiting the ED40's capabilities. Then you can use the powerful detection capability of the ED40 to solve problems in analytical chemistry.

6.1 Electrochemical Detection Modes

The ED40 Electrochemical Detector is used for three different detection modes. During conductivity detection, current conducted by ions in solution in an electric field is measured. In DC Amperometry, a constant voltage is applied to the working electrode in the amperometry cell and the resulting current is the detector output. Integrated Amperometry is similar to DC Amperometry in that the same cell and associated circuitry are used. After the initial stages of signal processing, however, the cell current is integrated and the resulting charge is the detector output reported for each integration period. A user-programmed waveform, or repetitive series of potentials, is applied to the cell, and the same waveform program sets the start and finish of the integration period. The program is entered using the keypad on the **WAVEFORM** screen.

An important distinction between conductivity detection and the forms of amperometric detection is that no electron transfer reactions occur during conductivity detection. During DC and integrated amperometric detection, electrons are actually transferred between the electrode and the analyte molecules. This concept is illustrated in Figure 6-1.

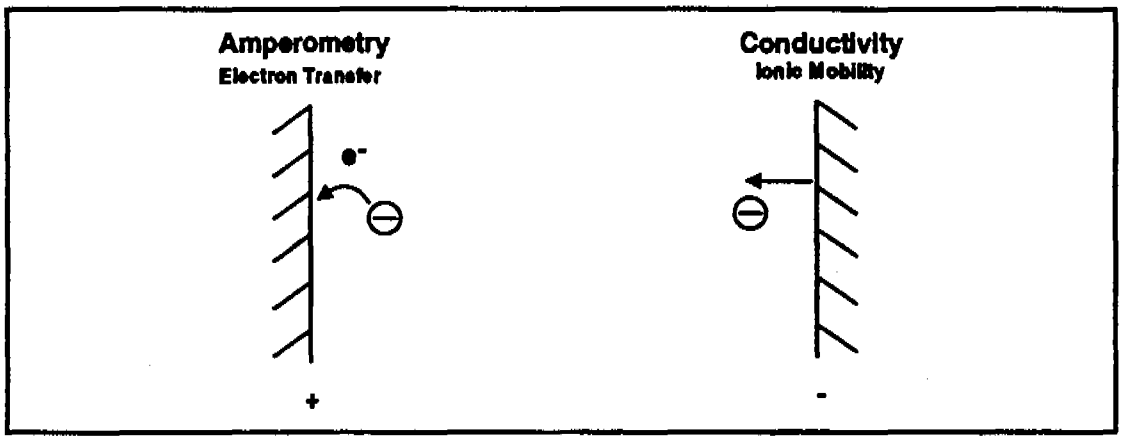


Figure 6-1. Electrochemical Properties Measured

Although in theory the same detector cell could be used for all three detection modes, a cell optimized for conductivity is not appropriate for amperometry, and vice versa. For this reason, the ED40 uses two detector cells, one for conductivity and another for DC and integrated amperometry.

6.2 Equivalent Circuits

The detector accomplishes all three detection modes by measuring current resulting from the application of potential (voltage) across electrodes in a flow-through cell. The three forms of electrochemical detection differ in the manner used to apply the potential and measure the current.

To understand how the ED40 can perform three different detection modes simply by applying voltage and measuring current, it is useful to model electrochemical cells in the equivalent circuit shown in Figure 6-2.

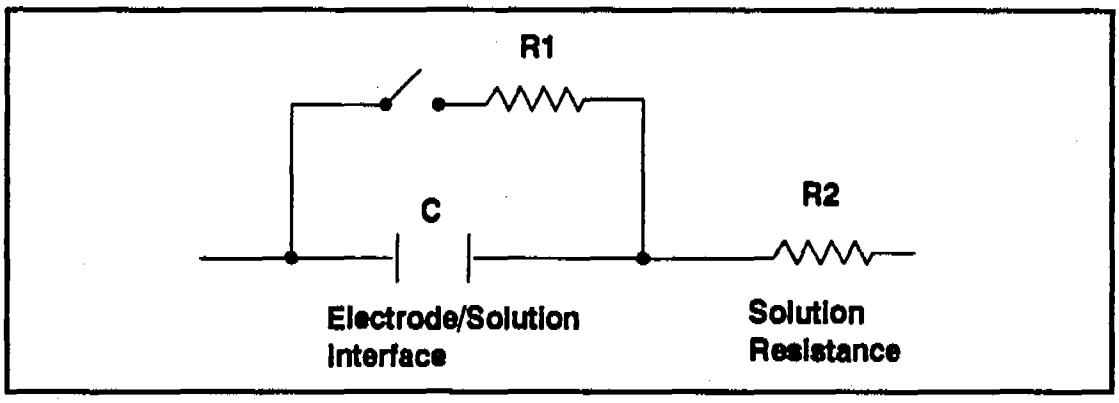


Figure 6-2. Equivalent Circuit

This circuit is designed to mimic the electrochemical behavior of conductivity and amperometry cells. R_2 represents the resistance to the migration of ions caused by the electrical field applied between the electrodes, measured during conductivity detection. The interface between the solution and the electrode acts as a capacitor, C, in the circuit. (Only one interface is shown in the figure.) When the applied potential is high enough, electrons transfer to or from molecules in solution. This is represented by closing the switch. The resulting current measured during amperometry is controlled mostly by the rate of diffusion of analyte to the electrode surface. A resistance (R_1) may be defined which is inversely proportional to the rate of analyte diffusion to the electrode surface.

6.2.1 Conductivity

The quantity we wish to measure during conductivity detection is the inverse of the solution resistance R_2. It can only be measured when all of the applied potential develops across R_2. This is accomplished by applying a high frequency alternating potential across the electrodes. When an alternating potential of several kHz is applied across a capacitor, its resistance to current flow drops to near zero. With zero resistance (more accurately, reactance) at the interface between the electrode and the solution, all the applied potential develops across the solution resistance R_2.

Since we know the applied potential and the current is measured, R_2 is calculated from Ohm's law:

$$R = \frac{E}{i}$$

The inverse of the solution resistance R_2 is the *conductance*, G. The measured conductance is then corrected by the conductivity cell constant K to produce the conductance which would be measured in a cell containing electrodes of 1 cm^2 surface area held 1 cm apart. This quantity is the *conductivity*, κ and the units are siemens per cm, S/cm. Stated as equations:

$$G = \frac{1}{R} = \frac{i}{E}$$

$$\kappa = K \bullet G$$

6.2.2 DC, Integrated, and Pulsed Amperometry

The addition of a supporting electrolyte in high concentration greatly lowers the solution resistance, R_2. (An *electrolyte* is simply a solution containing dissolved ions.) Generally, acids, bases or salts in concentrations of 1 to 100 mM are used. The addition of a supporting electrolyte plus the application of a DC or very low frequency alternating potential waveform causes nearly all the applied potential to develop across the interface between the electrode and the solution. The potential difference between the electrode and the solution can easily be made high enough to cause electron transfer reactions to occur (closing the switch), oxidizing or reducing species in solution. During an oxidation reaction, electrons are transferred from the analyte to the electrode. During a reduction reaction, the reverse occurs; electrons leave the electrode and enter the analyte.

During amperometry, the current is reported directly to the recording device. With the other modes (Conductivity, Integrated and Pulsed Amperometry) the detector converts the measured current into other, proportional, units. The detection modes and the three properties of the solution measured are listed in Table 6-1.

Mode	Quantity Measured	Units
Conductivity	Solution conductivity	Siemens (S)
DC Amperometry	Current caused by reduction or oxidation of solution species	Amperes (A)
Integrated and Pulsed Amperometry	Integrated current (charge) from reduction or oxidation of solution species during a portion of a repeating potential vs. time waveform	Coulombs (C)

Table 6-1. Electrochemical Properties Measured

In summary, the detection method is determined by the applied potential waveform, regardless of whether a supporting electrolyte is added, and the manner in which the current is measured.

6.3 Conductivity Detection

To understand conductivity detection, it is useful to review how individual ions contribute to the total conductivity of solutions.

6.3.1 Conductivity of Solutions

The conductivity of a dilute solution is the sum of the individual contributions to the conductivity of all the ions in the solution multiplied by their concentrations (i.e., conductivity is directly proportional to concentration). This is called Kohlraush's law of independent migration. It states that each ion carries its portion of the total conductivity without being affected by any of the other ions in solution.

Stated as an equation:

$$\kappa = \frac{\sum_i \lambda_i^o c_i}{1000}$$

where:

- κ is the measured conductivity in S/cm.
- c_i is the concentration of the ions in equivalents/L. (Equivalents/L equals moles/L times the charge on the ion.)

The *ionic limiting equivalent conductivity*, λ_i^o is specific for each ion. It is the conductivity of the ion divided by the concentration and extrapolated to infinite dilution. Table 6-2 lists limiting equivalent conductivities for a number of organic and inorganic ions. The unit for λ_i^o is $S \cdot cm^2$/equivalent.

Anions	λ_i^o	Cations	λ_i^o
OH^-	198	H^+	350
F^-	54	Li^+	39
Cl^-	76	Na^+	50
Br^-	78	K^+	74
I^-	77	NH_4^+	73
NO_3^-	71	Mg^{2+}	53
HCO_3^-	45	Ca^{2+}	60
SO_4^{2-}	80	Sr^{2+}	59
$Acetate^-$	41	$CH_3NH_3^+$	58
$Benzoate^-$	32	$N(CH_3CH_2)_4^+$	33

Table 6-2. Limiting Conductivities at 25 C

Values of λ_i^o from this table can be used to calculate conductivities of solutions containing ions. For example, the limiting equivalent conductivity at 25 °C for NaCl is the sum of the ionic limiting equivalent conductivity for Na^+, 50.1, plus that of Cl^-, 76.4, or 126.5. A 0.1 mM solution of NaCl at 25 °C has a conductivity of 0.1 X 126.5, or 12.65 µS/cm. The conductivity of a solution containing 0.1 mM NaCl plus 0.1 mM Na_2SO_4 would be:

Ions		Charge		Conc.		λ_i^o		µS/cm	
3	X	1	X	0.1	X	50.1	=	15.0	(Na^+)
1	X	1	X	0.1	X	7.6	=	07.6	(Cl^-)
1	X	2	X	0.1	X	80.0	=	16.0	(SO_4^{2-})
					Total			38.6	

So far, only dilute solutions have been discussed. As concentration increases, the direct proportionality between conductivity and concentration is lost. However, at the analyte concentrations normally encountered in ion chromatography (below 1 mM), conductivity is generally proportional to concentration. For example, the equivalent conductivity at 25 °C of KCl at infinite dilution is 149.9; and at 1 mM, 146.9, a decrease of only 2%. However, the conductivity of an eluting analyte cannot be assumed to be directly proportional to concentration, because ionic components of the mobile phase may be contained in the eluting volume.

If the electrolyte is a weak electrolyte such as an acid or base with only partial dissociation, then c_i must be replaced by the concentration of the dissociated ions only, since only they contribute to conductivity. For acids and bases, the pK values and the solution pH can be used to calculate the extent of dissociation.

6.3.2 Effect of Hydration Sphere and Solvent on Conductivity

The limiting equivalent conductivity of an ion, λ_i^o, is a measure of the mobility of the ion. Ionic mobility is greatly affected by the properties of the ion in the solvent. Ions with large hydration spheres are less mobile, and therefore less conductive, than ions with small hydration spheres. This explains why λ_i^o for extensively hydrated fluoride (55.4) is lower than λ_i^o for chloride (76.4), which is less hydrated. The viscosity of the solvent also affects ionic mobility, with ions being more mobile in solvents of lower viscosity.

It is not necessary to know values such as hydration sphere and viscosity, since quantitative analysis is performed by comparing the conductivity of the analyte in the sample to the conductivity of the same analyte in a standard (or standards). Even if a solvent gradient is used, the composition of the solvent during the elution of the analyte will be the same in both the sample and the standard.

6.3.3 Effect of Temperature on Conductivity

Ionic mobility, and therefore conductivity, is greatly affected by temperature. The conductivity of an aqueous solution is found experimentally to rise about 2% per °C. (This dependence is described in a complex equation developed by Onsager.) Therefore, it is necessary to hold the mobile phase temperature as constant as possible to maintain a stable baseline. This is accomplished by the DS3 Detection Stabilizer, which maintains the cell at a set temperature. In addition, the ED40 corrects the measured conductivity to that which would be measured at 25 °C by measuring the cell temperature with a thermistor and multiplying the conductivity by a temperature dependent constant. This constant, the *temperature compensation factor*, is expressed in units of %/°C. When the DS3 is not used, setting an accurate temperature compensation factor minimizes baseline drift caused by laboratory temperature changes.

6.3.4 Species Detected by Conductivity

Conductivity detection is typically the mode of choice for species which are ionic when they enter the detector cell, especially those with weak UV absorbance. This includes both organic and inorganic ions. Conductivity detection is best suited to anions and cations of strong acids and bases, such as chloride, sulfate, trifluoroacetate, sodium, and potassium. Ions of weaker acids and bases are detected, provided that the mobile phase pH is chosen to maximize analyte dissociation. (When a suppressor is used, the mobile phase pH which determines whether an ion will be detected is the pH after suppression.)

Anions

Sensitivity is best for anions with pKa values below 6. As analyte ionization (dissociation) decreases, so does sensitivity. Anions with pKa values above 7 can be detected under certain conditions, but signal-to-noise ratios are generally poorer. Fortunately, all organic acids with either carboxylate, sulfonate, or phosphonate functional groups have pKa's below 4.75, so conductivity is the preferred detection method for these species. Common inorganic strong acid anions include chloride, nitrate, phosphate, and sulfate.

Cations

Inorganic cations detected include the alkali metals and alkaline earths. Most transition metal cations are not detected since they either hydrolyze water to form anions or precipitate in the suppressor. These metals are usually detected by visible wavelength absorbance following postcolumn reaction with a chelating indicator. Nearly all organic cations are amines. Aliphatic amines have pKa's around 10 and are easily detected. Aromatic and heterocyclic amines have pKa's between 2 and 7, too low to be detected by suppressed conductivity following

cation exchange separation. Although nonsuppressed detection can be used for these species, sensitivity is generally poor. These amines can be detected by UV absorbance or by DC or Integrated Amperometry.

Zwitterions

Amphoteric or zwitterionic molecules are difficult or impossible to detect by conductivity. These molecules contain both cationic and anionic functional groups. Amino acids are good examples. They contain both ammonium cationic functional groups and carboxylic acid anionic functional groups. With suppressed conductivity detection, they are generally removed by the suppressor and do not reach the detector. Using nonsuppressed conductivity detection, they can be detected provided the mobile phase pH is at a value which results in a net charge on the molecule. Since most zwitterions contain primary, secondary, or tertiary amine functional groups, Pulsed or Integrated Amperometry is often the best detection method. UV absorbance can be used for aromatic zwitterions.

6.3.5 Chemical Suppression

Species detected by conductivity are by their nature ionic, so ion exchange and ion pair chromatography are by far the most commonly used separation methods. These methods both require mobile phases containing strong electrolytes. This causes a problem: how to detect the ionic analytes without the detector being overwhelmed by the ions in the mobile phase. The best method of solving this problem is by neutralizing the mobile phase in a suppressor.

The suppression mechanism occurring inside an Anion Self-Regenerating Suppressor (ASRS) using sodium hydroxide as the mobile phase for anion-exchange separation is illustrated in Figure 6-3.

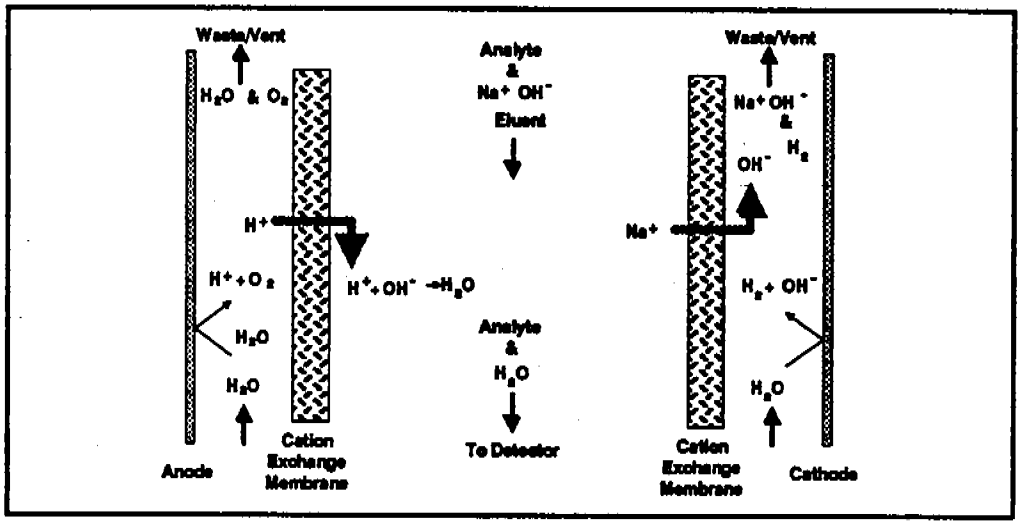


Figure 6-3. Chemical Suppression (Anion Exchange)

Analyte anions elute from the column with sodium counterions. Two electrodes, one on the side of each membrane opposite to the mobile phase, hydrolyze water to hydrogen and hydroxide ions. Hydrogen ions diffuse across the membrane next to the anode, neutralizing the mobile phase hydroxide to water, while sodium ions from the mobile phase diffuse across the other membrane, providing counterions to the hydroxide being generated at the cathode. In effect, sodium hydroxide from the mobile phase is transferred across the membrane, and does not reach the detector. The resulting mobile phase background conductivity is near zero, considerably lower than before suppression. Also, the counterion to the anion analytes is now a hydrogen ion, which has a conductivity seven times higher than the original sodium counterion. Since both the anion analyte and the cation counterion produce the detector response, the response is increased. The suppressor lowers the background conductivity (and therefore the baseline noise and drift) and increases the signal. Suppression can also be accomplished without water electrolysis by pumping a dilute sulfuric acid solution (the regenerant) through the suppressor on the side of the membranes opposite the mobile phase.

For ion chromatography of cations, the suppressor membranes are anion exchange polymers. They allow anions to pass freely but exclude cations. Dilute acids such as methanesulfonic acid are used in the mobile phase. In the Cation Self-Regenerating Suppressor (CSRS), methanesulfonate counterions are replaced by hydroxide generated by the electrolysis of water. This neutralizes the acidic mobile phase and provides the highly conductive hydroxide counterion to the analyte cations.

Using a suppressor typically increases signal-to-noise ratios about one order of magnitude for strong acid or base ions. The improvement is somewhat less for ions of weak acids or bases due to decreased ionization at the neutral pH of the mobile phase following suppression. Nonetheless, the benefits from reducing the background, and therefore the noise, almost always yield a net improvement in signal-to-noise ratio compared to nonsuppressed conductivity detection.

Suppressors provide several important advantages. The first three listed below are a direct result of increased signal-to-noise ratio.

- Lower detection limits.
- Dirty samples may be diluted more, extending column life.
- Wider dynamic range.
- More concentrated mobile phases can be used, providing a greater range of elution control and permitting larger sample concentrations or volumes.
- Gradient elution capability.
- Faster equilibration time.
- Elimination of interference from counterions.
- Elimination of system peaks.

6.3.6 Mobile Phases for Conductivity Detection

When choosing a mobile phase, the constraints placed by the separation and detection methods must be considered. To obtain optimum separation, the elution strength of the mobile phase, the separation efficiency, and the resolution of the analytes of interest are the major criteria. For conductivity detection, the criteria for a good mobile phase are the relative conductivity response of the analytes and the magnitude of the background.

Mobile phases can be wholly aqueous containing only water and a strong electrolyte. Or, if an organic solvent compatible column such as a Dionex OmniPac or MPIC column is used, typical reversed phase solvents such as methanol or acetonitrile can be used. Organic solvents are essential components of ion-pair mobile phases and provide important selectivity control during ion exchange separations. Since these solvents are nonconducting, they do not interfere with conductivity detection.

Anion Exchange

When a suppressor is used, the ionic components of the mobile phase must be such that they are removed or converted to weakly conducting compounds by the suppressor. Sodium salts of weak acids are used because they are converted to the neutral free acid form in the suppressor. The higher the acid's pKa, the lower the background conductivity following suppression. Weak acids with pKa's above 6 can be used for isocratic separations. However, for gradient elution, pKa's should be above 8 to minimize baseline shift during the gradient.

Sodium hydroxide solutions make excellent mobile phases for anion exchange because hydroxide is neutralized in the suppressor to water (the free acid form of hydroxide). This is the case regardless of its concentration, making it most useful for gradient elution. Another commonly used

mobile phase is a carbonate/bicarbonate buffer. It is suppressed to carbonic acid (pKa = 6.2) which has conductivity low enough for isocratic but not for gradient elution. Carbonate/bicarbonate buffers are easily prepared and are routinely used for isocratic separations of inorganic anions, as shown in Figure 6-4.

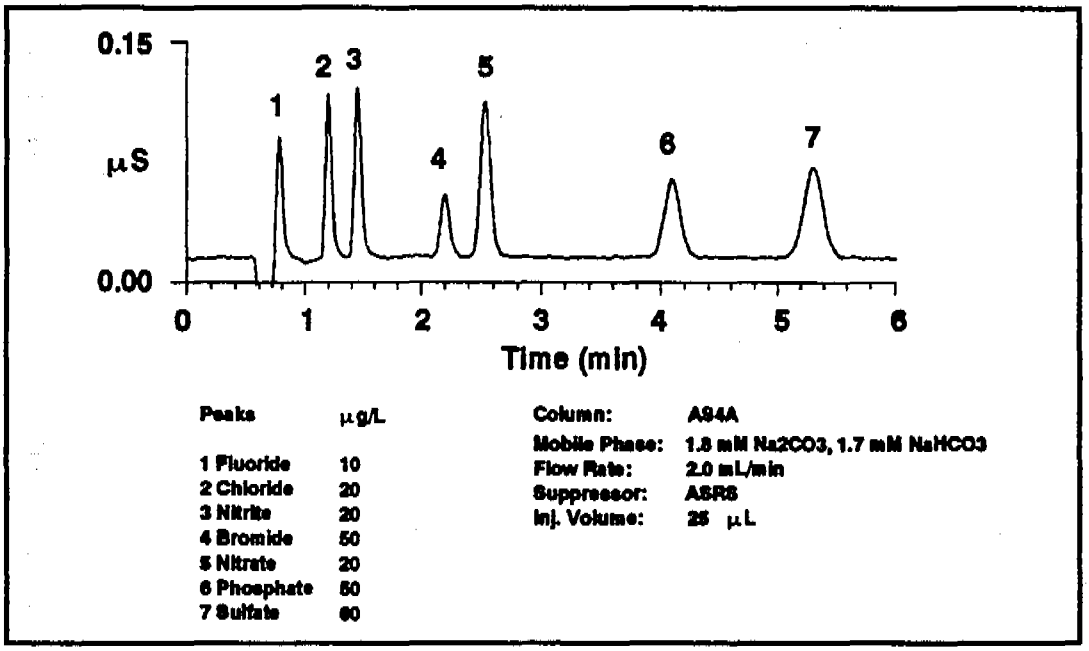


Figure 6-4. Anion Standard

Other mobile phases which may be used in suppressed anion chromatography are the sodium salts of boric acid (borax, tetraborate, pKa = 9.2) and p-cyanophenol (pKa = 8.0). Borate forms weak bonds with hydroxy-organic acids, producing changes in selectivity compared to hydroxide. Because of its high pKa, background conductivity following suppression is very low, making it useful for gradient elution. p-Cyanophenol is a powerful monovalent displacer, useful for eluting strongly retained hydrophobic monovalent anions such as iodide and thiocyanate.

In nonsuppressed (sometimes called single column) ion chromatography, the ionic components in the mobile phase are chosen so that their conductivity is as different as possible from the analyte's. For anion IC, large ions with low equivalent conductivity such as benzoate and phthalate may be used. These produce backgrounds of moderately high conductivity. A buffer composed of a gluconate/borate solution produces somewhat lower backgrounds. Sensitivity and baseline noise are acceptable for analyzing samples containing high concentrations of analytes. However, the advantages provided by a suppresser are not realized.

Cation Exchange

Millimolar concentrations of dilute strong acids, often mixed with organic solvents, are good choices for cation exchange chromatography of both monovalent and divalent cations. Methanesulfonic acid (MSA) is commonly used since it is compatible with the CSRS. A large number of amines and inorganic cations can be eluted in a single run using a gradient of MSA and acetonitrile (see Figure 6-5).

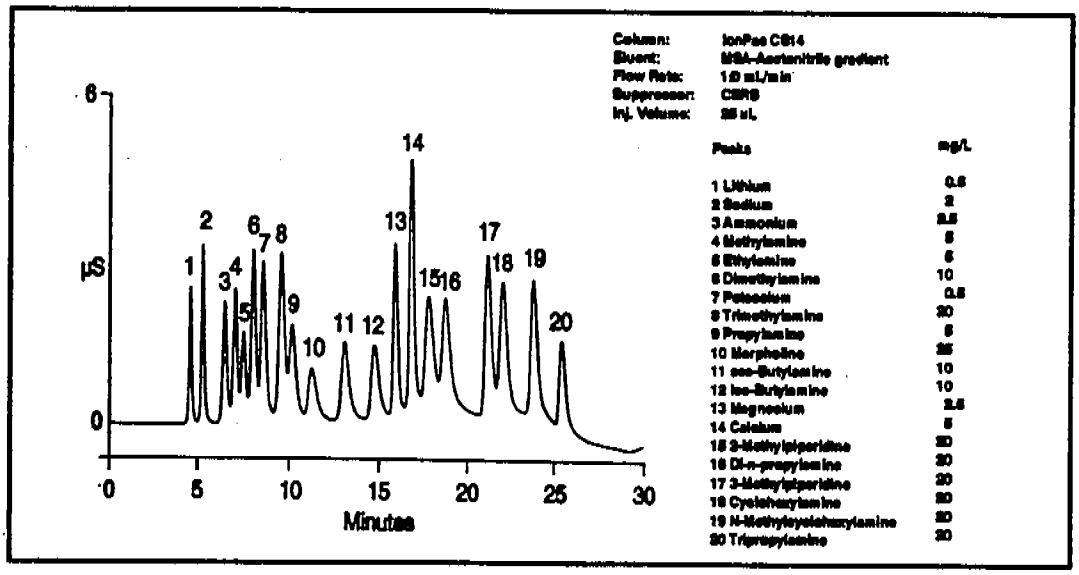


Figure 6-5. Amines and Inorganic Cations

Some columns require a stronger displacing ion than hydrogen ion to elute more strongly retained divalent cations. The zwitterion 2,3-diaminopropionic acid (DAP), mixed with a strong acid to protonate the DAP, is a good choice.

The best mobile phases for nonsuppressed cation IC are dilute strong acids such as 1 mM nitric acid. Backgrounds are very high (around 1 mS), so signal-to-noise ratios are not good enough for low level work. Since the conductivity of the hydrogen ion is greater than that of all other cations, elution of analytes causes decreases in conductivity. Instead of peaks, eluting analytes produce dips.

Ion-Pair

Mobile phases for ion-pair chromatography contain mixes of aqueous and organic solvent solutions with hydrophobic ion-pair reagents as additives. Commonly used reagents are quaternary ammonium salts for anion separations and long-chain sulfonates for cation

separations. For suppressed conductivity detection, these reagents are easily used provided the counterions are either hydroxide (anion-ion pair) or hydrogen ion (cation-ion pair). These are provided by Dionex as IonSep reagents. They are purified solutions of quaternary ammonium hydroxide solutions and sulfonic acid solutions.

6.4 Amperometric Detection

The two main forms of amperometric detection (DC and integrated amperometry) measure the current or charge resulting from oxidation or reduction of analyte molecules at the surface of a working electrode. During oxidation reactions, electrons are transferred from molecules of an electroactive analyte to the working electrode in the amperometry cell. Conversely, during reduction reactions, electrons are transferred from the working electrode to the analyte. For analytes which can be oxidized or reduced, detection is usually sensitive and highly selective, since many potentially interfering species cannot be oxidized or reduced, and are not detected. When a single constant potential is applied to the working electrode, the detection mode is *DC Amperometry*. *Integrated* and *Pulsed Amperometry* employ a repeating sequence of potentials.

6.4.1 Voltammetry

The determination of the optimum potentials to use in amperometry begins with an electrochemical technique called *Voltammetry*. This technique can be performed by continuously moving a solution containing the analyte and supporting electrolyte past the surface of the working electrode. This can be accomplished in a standard beaker-type cell employing a rotated disk electrode, or in the ED40 amperometry cell with the mobile phase and analyte flowing through the cell. The current as a result of oxidation or reduction reactions is measured and plotted vs. applied

potential, which is scanned between preset limits. If the solution is not flowing and the potential is scanned in one direction and then reversed so that the potential at the end of the scan is the same as at the beginning, the technique is called *cyclic voltammetry*. Cyclic voltammetry is performed with the ED40 by programming a triangle wave in the Voltammetry mode. The voltammogram is recorded using an X-Y recorder, storage oscilloscope, or computer.

Consider the following generalized electrochemical reaction.

$$A \rightleftharpoons B + ne^-$$

When the reaction proceeds in the forward direction, species A transfers *n* electrons to the working electrode and is oxidized to species B. The reverse reaction is the reduction of B back to A. The direction of the reaction can be predicted by the Nernst equation:

$$E_{app} = E^\circ + \frac{0.059}{n} \log\frac{[B]}{[A]}$$

where:

- E_{app} is the applied potential.
- [A] and [B] are the equilibrium concentrations of species A and B *at the surface of the working electrode.*
- E° is the potential at which these two concentrations are equal. (For simplicity, concentrations are used instead of activities.)

Each oxidation/reduction reaction has a characteristic E°. Many chemical reference books contain tables of E°'s for various substances listed as reductions vs. an H_2/H^+ reference electrode. When E_{app} = E°, log [B]/[A] must equal zero; thus [B] = [A]. If E_{app} is set positive of E°, then log [B]/[A] must be greater than zero and therefore [B] > [A]. The reaction proceeds in the forward direction with species A being oxidized to species B. The current will be positive. (Positive

currents are called *anodic*.) Conversely, setting E_{app} negative of E° results in the reduction of B to A, generating a negative current (*cathodic*).

Consider a situation in which only species A is present in solution and where E° is +0.4 V vs. an Ag/AgCl reference electrode. Figure 6-6 shows the current as a function of applied potential, the *voltammogram*.

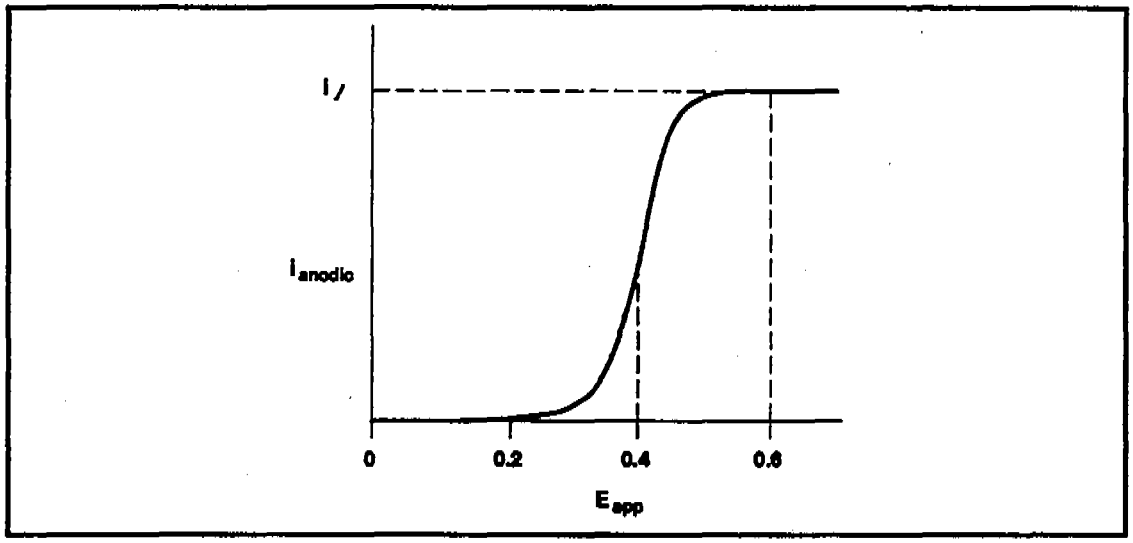


Figure 6-6. Voltammogram

The shape of the voltammogram can be explained by considering the concentration of A at the electrode surface at three different applied potentials. At 0.2 V, E_{app} is negative of E°. The Nernst equation indicates that at 0.2 V, the reduction of B to A is favored. Because the solution contains only substance A, no reaction occurs. As the potential is increased, it approaches a level high enough to cause oxidation of a percentage of analyte molecules, and the current increases. At a higher potential, 100% of the analyte molecules reaching the surface of the working electrode are oxidized, and the current is no longer dependent on potential. Since the current is now limited by the rate at which the analyte molecules are transported to the surface of the working electrode, and since

this rate is largely dependent on diffusion, this maximum current is called the *diffusion limited current.*

The previous discussion used an example analyte A which could be in equilibrium with its oxidized form B at E°. This is called a *reversible* reaction. More often than not, redox reactions are *irreversible*, and a potential considerably in excess of E° is required to oxidize or reduce the molecule. However, the required potential can still be easily determined using voltammetric techniques, as described in the next section.

6.4.2 DC Amperometry

Choosing the Applied Potential

The optimum detection potential for DC amperometry is the lowest which will produce a diffusion limited current. In the above example, the optimum potential would be +0.6 V. Increasing the potential beyond this value will increase only the noise and not the signal, and also decrease selectivity by allowing more species to be oxidized. The optimum potential is most easily determined from a plot of peak height vs. applied potential, which is generated using DC amperometry by making multiple injections of analyte and increasing the potential after each injection. A plot created using this method with serotonin as the analyte is shown in Figure 6-7. From this plot, the optimum applied potential should be about 0.7 V.

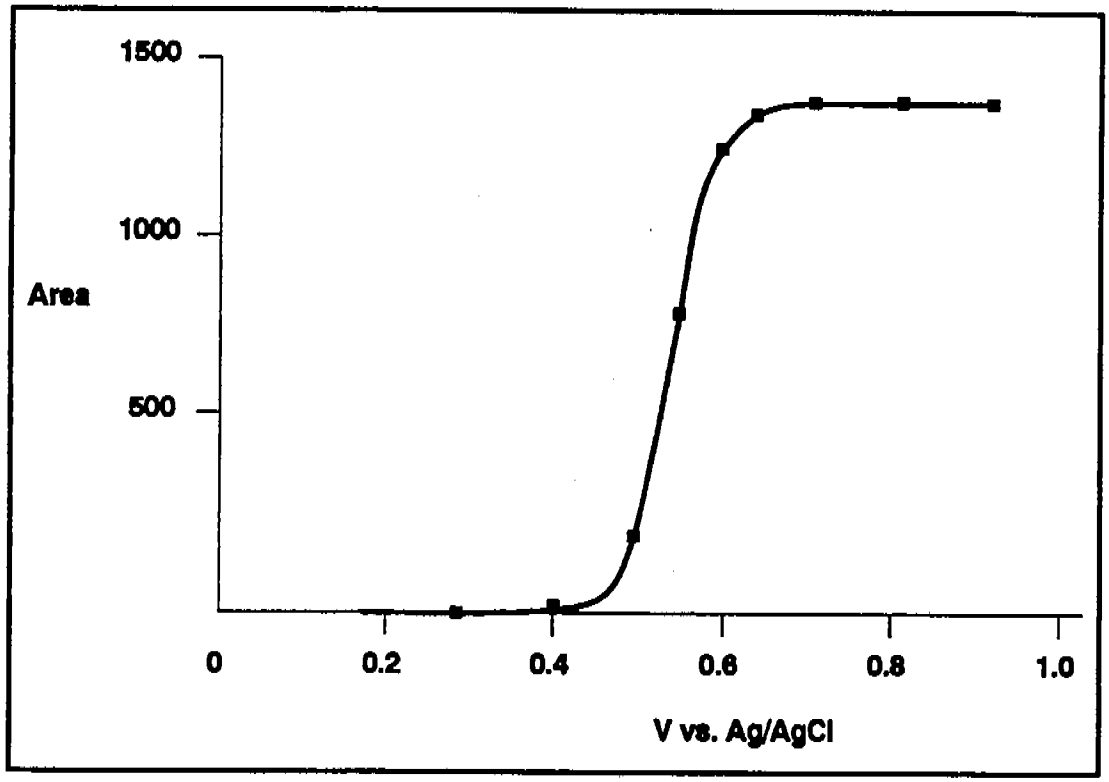


Figure 6-7. Peak Area vs. Potential for Serotonin

The current resulting from oxidation or reduction of analyte molecules is dependent on many factors; the most important of which is the concentration of analyte. Other factors include temperature, the surface area of the working electrode, and the linear velocity of the flowing stream over the surface of the working electrode. The ED40 cell is designed to maximize linear velocity, thus maximizing signal-to-noise ratio.

Species Detected by DC amperometry

The major application is the detection of molecules containing phenol or catechol functional groups. Numerous molecules of interest in pharmaceutical or biochemical analyses are in this category. The most important application is the detection of catecholamines

such as epinephrine and dopamine and other biogenic neurotransmitters, usually in urine or plasma. An example chromatogram of catecholamines in an alumina extract of urine is shown in Figure 6-8. DHBA is added as an internal standard.

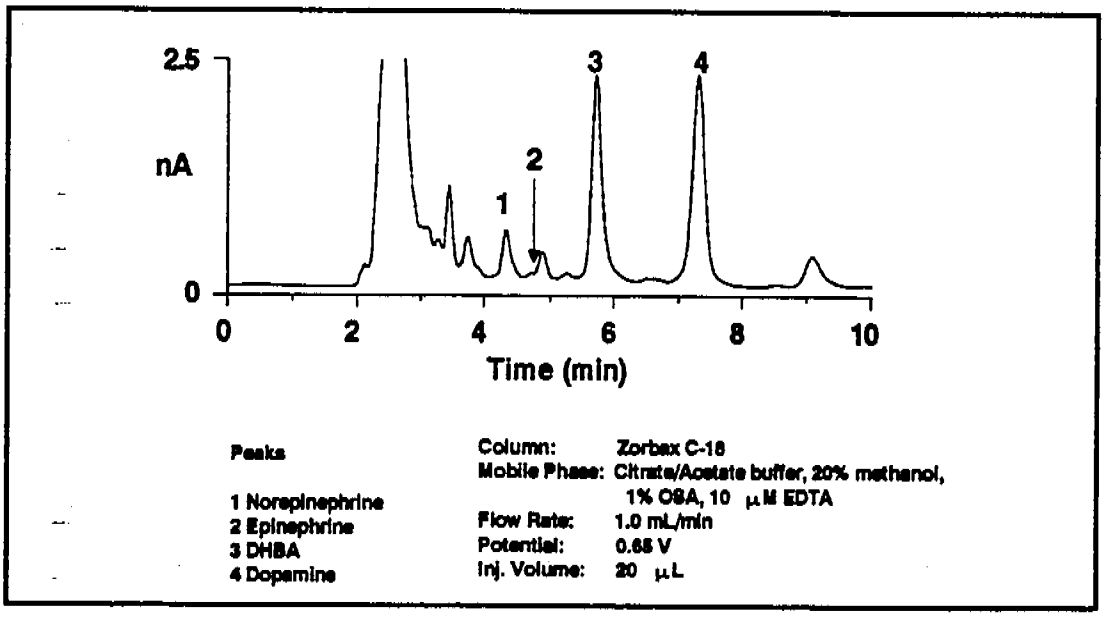


Figure 6-8. Catecholamines in Urine

The analgesic acetaminophen contains a phenol functional group and is easily detected. The amino acid tyrosine also contains a phenol functional group. Not only can this amino acid be detected, but any peptides containing tyrosine also can be detected. The neurotransmitter serotonin is based on the tyrosine structure, and is therefore detected. Some other detectable organic molecules are aromatic amines, thiols, and sulfides. Sulfonamide antibiotics are detected since they are aromatic amines. In addition to these organic molecules, inorganic anions forming complexes with silver such as cyanide, sulfide, and iodide are detected at a silver electrode.

DC Amperometry is a very popular detection method, so articles on applications frequently appear in the literature. Table 6-3 lists species most commonly detected by DC amperometry and the working electrode material used. In addition, species determined by Pulsed Amperometric Detection (PAD) and Integrated Amperometry are listed.

Analyte or Analyte Class	Working Electrode	Method	References†
Alcohols, glycols	Au, Pt	PAD	26
Aldehydes	Pt	PAD	30
Aliphatic amines and amino acids	Au, Pt	Int. Amp	28
Alkanolamines	Au	PAD	25, 29
Aromatic amines	G.C.	DC	13
Aromatic nitro compounds	G.C.	DC	13
Ascorbic acid	Pt	DC	12
Bromide	Ag	DC	19
Carbohydrates	Au	PAD	20-23, 27
Catecholamines and other biogenic amines	G.C.	DC	13-17
Cyanide	Ag	DC	10, 19
Hydroquinones	G.C	DC	13
Iodide	G.C.	DC	18, 19
Phenols	G.C.	DC	13
Sulfide	Ag	DC	19
Sulfite	Pt	DC	11
Thiourea and other sulfur species	Pt	PAD	24
Uric acid	G.C.	DC	13

Table 6-3. Analytes Detected by Amperometry

†References are listed in Appendix F.

6.4.3 Pulsed Amperometry

Pulsed amperometry is a specific application of integrated amperometry, which is described in Section 6.3.4.

The development of pulsed amperometric detection grew from the need to detect carbohydrates. Since most carbohydrates contain no UV chromophore, UV absorbance detection can only be used at very low wavelength. The detection of carbohydrates at 210 nm is insensitive and nonselective. Refractive index detection, also insensitive and nonselective, had been the most commonly used detection method. Pulsed amperometric detection is replacing these optical methods for carbohydrates, and is now being used for other nonchromophoric molecules containing alcohol, aldehyde, amine, or sulfur functional groups.

Although carbohydrates can be oxidized at gold and platinum electrodes, the products of the oxidation reaction poison the surface of the electrode, inhibiting further analyte oxidation. By repeatedly pulsing between high positive and negative potentials, a stable and active electrode surface can be maintained. Pulsed amperometric detection at a gold electrode is a reproducible and sensitive method for all carbohydrates of molecular weight up to approximately ten-thousand.

Carbohydrates can only be detected by pulsed amperometry in high pH solutions (above pH 11). They are also very weak acids with pKa's around 12 and are easily separated on high efficiency anion exchange columns such as Dionex CarboPac™ columns. Mobile phase pH's of 11 to 14 are used (1 mM to 1 M NaOH). Sodium acetate is often added to elute oligo- and polysaccharides by increasing the strength of the mobile phase. The combination of anion exchange separation with pulsed amperometric detection is a powerful method for the determination of carbohydrates. Although there can be some interference from amines and certain sulfur species, the technique is generally very sensitive and selective.

Principles of Pulsed Amperometry

To understand the mechanism of pulsed amperometry, it is first necessary to study the oxidation of an analyte using a conventional electrochemical technique such as voltammetry. The cyclic voltammetry of glucose in 0.1 M sodium hydroxide using a gold working electrode and an Ag/AgCl reference electrode is shown as an example in Figure 6-9.

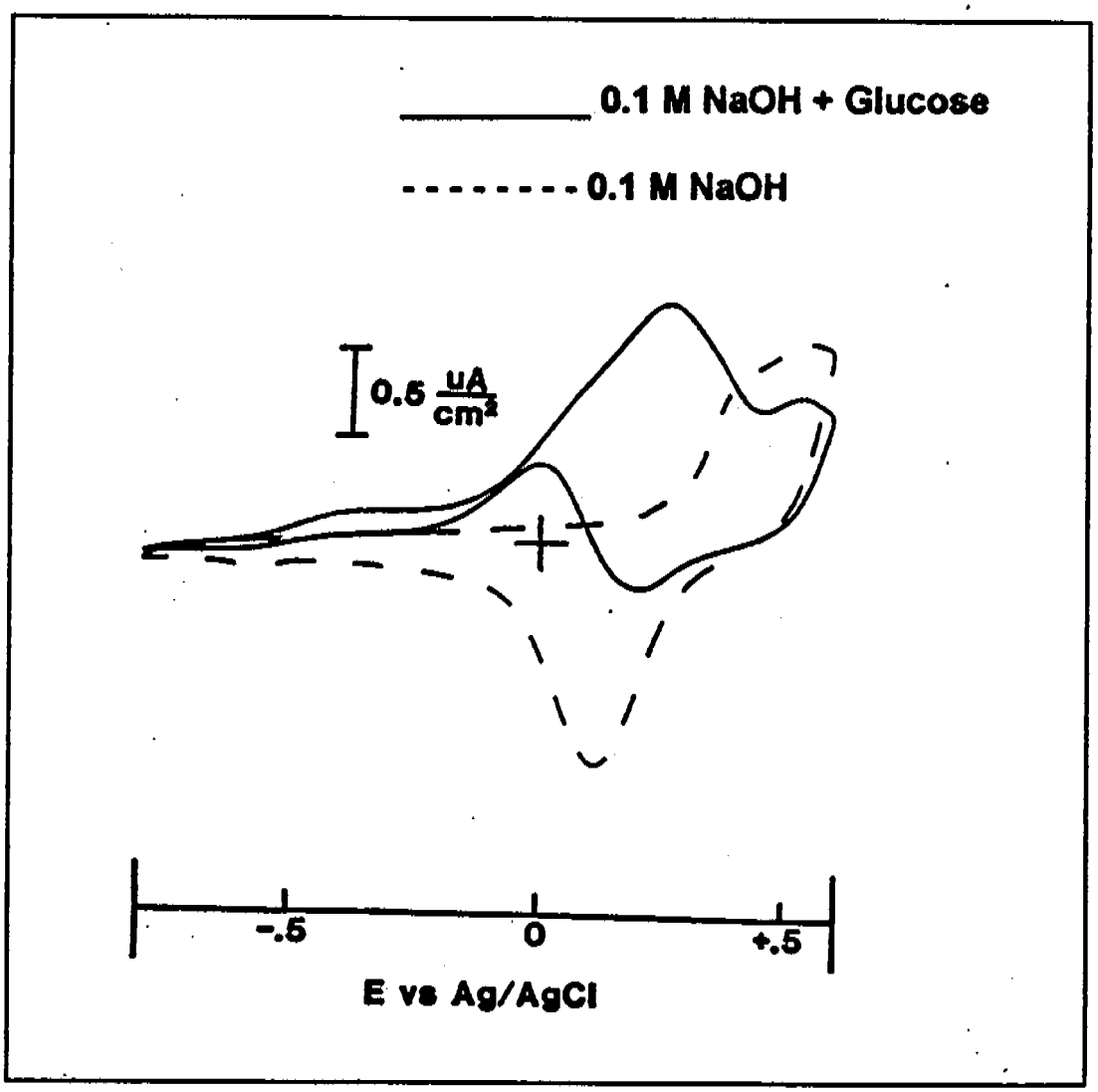


Figure 6-9. Cyclic Voltammetry of Glucose, Gold W.E.

The dashed line in the figure is the current resulting from the 0.1 M NaOH supporting electrolyte in the absence of glucose analyte; that is, the background current. Beginning at -0.8 V and sweeping in a positive direction, the background current is nearly flat until approximately 0.25 V, where oxidation of the surface of the gold electrode to gold oxide begins. Following reversal of the potential sweep direction at 0.6 V, the gold oxide is reduced back to gold, with the negative peak current at 0.1 V.

With glucose added to the solution, the current rises slightly as the potential is swept in a positive direction from -0.8 V and remains unchanged until glucose oxidation begins. This causes the current to rise at -0.15 V towards a peak at about 0.25 V. The current then decreases for two reasons. First, the concentration of glucose at the electrode surface has been depleted because much of it has been oxidized. Second, the formation of gold oxide inhibits further glucose oxidation. On the reverse scan, the current actually reverses from reducing to oxidizing (positive) at the onset of the gold oxide reduction; as soon as the reduction of gold oxide back to gold begins, oxidation of glucose also begins.

If DC amperometric detection were used, the appropriate applied potential would be approximately 0.2 V. This is the potential at which the glucose oxidation current is the highest and the background current the lowest. However, the use of a single potential results in rapidly decreasing sensitivity as an oxide layer forms and products from the oxidation reaction coat and poison the electrode surface. This problem is solved by first measuring the glucose oxidation current near the peak at 0.25 V, pulsing the potential to a high positive value to form gold oxide, and then back to a potential negative of the gold oxide reduction peak. The action of repeatedly forming and removing the metal oxide surface layer cleans the

electrode surface and maintains an active and stable surface. A three-step waveform useful for detecting carbohydrates is shown in Figure 6-10.

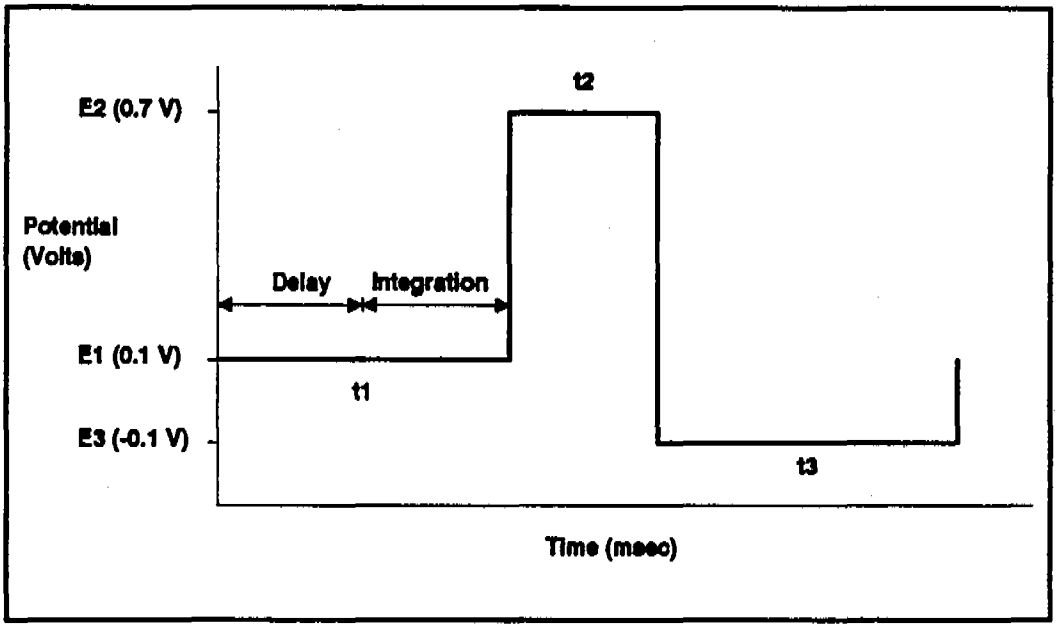


Figure 6-10. Three Potential Pulsed Amperometry Waveform

The potentials are labeled E1, E2, and E3, and are applied for durations of t1, t2, and t3. (E1 is +0.1 V, below the peak current at 0.25 V. This minimizes noise caused by gold oxide formation background current which begins at approximately 0.2 V, and provides a margin of safety in the event of shifts in reference electrode potential.) The signal is measured at E1 by integrating the current for a fixed time and storing the resulting charge in a sample-and-hold amplifier until the next measurement. Current integrated for a fixed time is charge, and the units are coulombs. The ED40 reports the charge directly in coulombs. The step from E3 back to E1 is from -0.1 V to +0.1 V, which charges up the electrode/solution interfacial capacitance.

The carbohydrate oxidation current is integrated after a delay which allows the charging current to decay. Similar triple-potential waveforms are used to detect other species, especially alcohols and aldehydes.

Optimizing the Waveform Parameters

To find the optimum potentials and times for pulsed amperometric detection, begin with a basic waveform and then optimize the parameters. Choose the basic waveform from the voltammogram or from published parameters for similar compounds, such as those listed in Appendix F.

First, E1 is chosen to be the potential providing the largest ratio of analyte oxidation current to background current. A 0.4 sec period for t1 containing a 0.2 sec delay period and a 0.2 sec integration period are good starting values. E2 and E3 are set near the positive and negative potential limits. 0.1 sec durations for both can be used to start. To optimize all the parameters, each one must be varied independently and the effect on reproducibility, signal magnitude, baseline level, and noise determined. For example, the dependence of background current on delay time for carbohydrate determinations using a gold working electrode is shown in Figure 6-11.

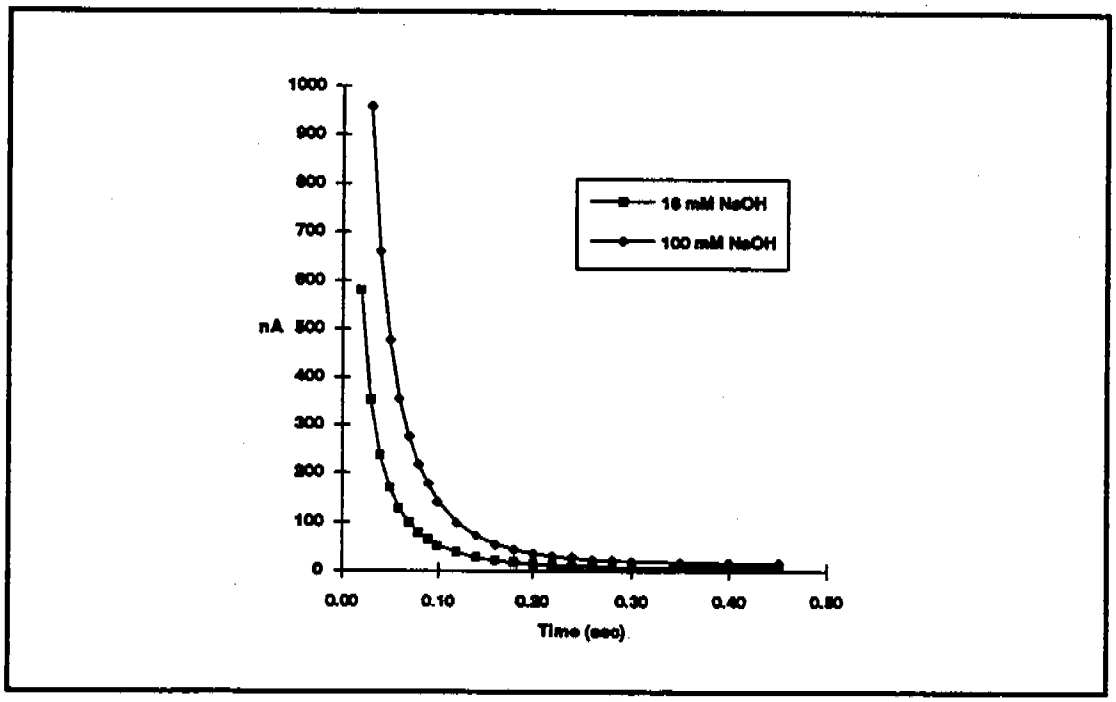


Figure 6-11. Charging Current vs. Delay Time, Au W.E.

This plot was developed by making repeated measurements while moving the integration period to later times. From this plot it can be seen that a delay time of 0.2 sec is sufficient to allow the charging current to decay to near zero. The dependence of analyte peak height on delay time, using a gold working electrode, is shown in Figure 6-12.

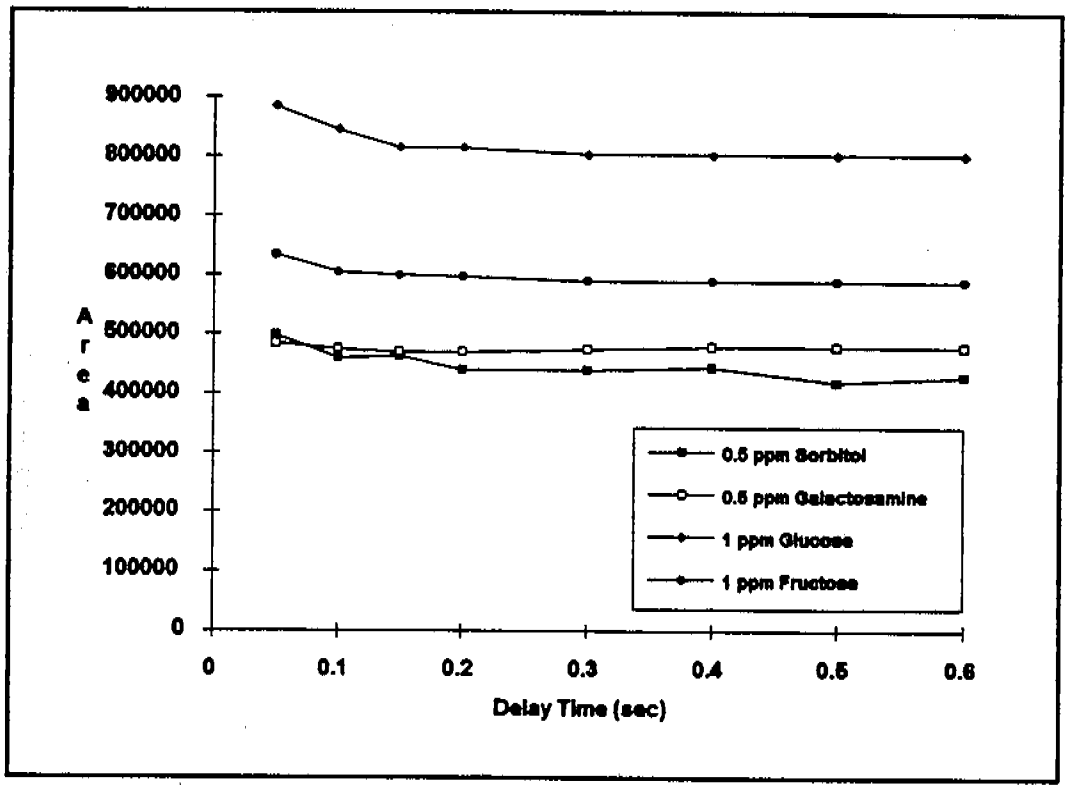


Figure 6-12. Peak Height vs. Delay Time

Since only a minor decrease in response occurs between zero and 0.2 sec, a delay time of at least 0.2 sec provides the optimum ratio of signal to background. Similar plots are then created for E1 and for the positive and negative cleaning times and potentials by making repeated injections while varying their values. The cleaning potentials should be the least positive and negative potentials that produce both maximum detector response and reproducible response. (Reproducible response should be checked with real samples and not just with standards, to ensure that components in the sample which may coat and poison the working electrode do not interfere with electrode cleaning.) To maintain an accurate reproduction of the eluting peak, a rapid sample rate is obtained using entire waveforms that are as short as possible. The resulting waveform is usually a compromise of each of

these goals. For example, doubling the integration period will increase the signal-to-noise ratio, but will decrease reproducibility of early eluting peaks by increasing the total waveform period. The program shown in Figure 6-10 was developed using this optimization method.

Species Detected by Pulsed Amperometry

Pulsed amperometric detection has now emerged as the most sensitive and selective method for the detection of carbohydrates. High-pH anion-exchange with pulsed amperometric detection (HPAE-PAD) is becoming the principal method for analyzing the carbohydrate portions of glycoproteins (Figure 6-13).

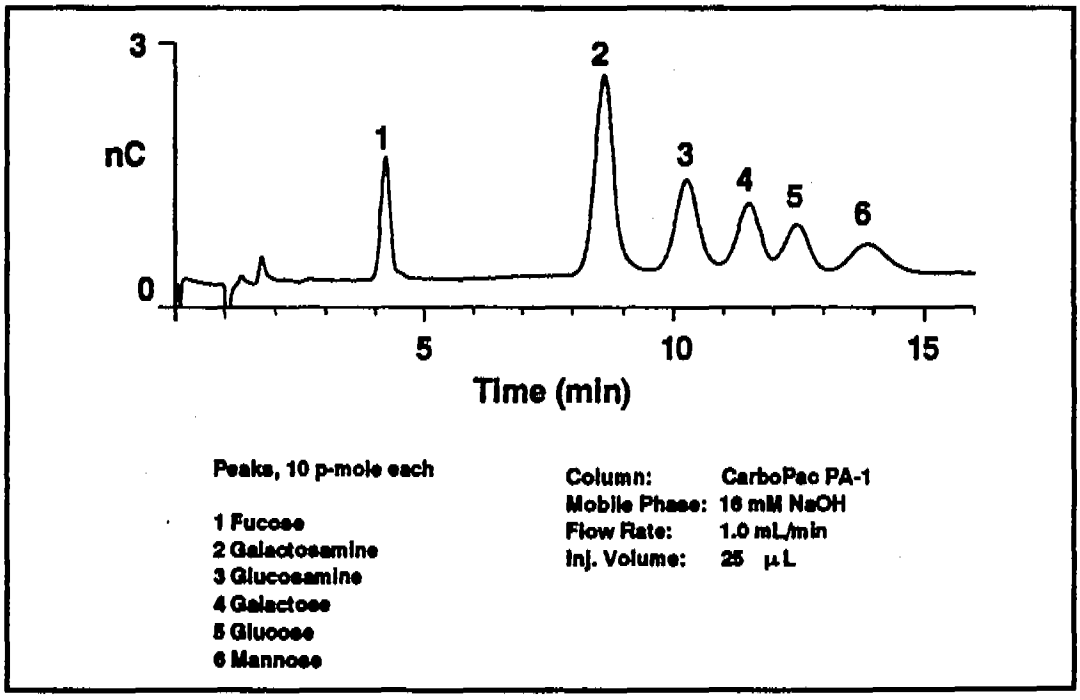


Figure 6-13. Monosaccharides from Glycoproteins Standard

Many new applications are being developed for the determination of carbohydrates in foods and beverages and in biological tissues and fluids.

Other species which can be detected by pulsed amperometry include alcohols, aldehydes, amines (primary, secondary and tertiary, including amino acids), and many organic sulfur species. Thiols, sulfides, and mercaptans can be detected, but fully oxidized sulfur species such as sulfates, sulfonates, and sulfones cannot be detected. Refer to the literature references in Appendix F for articles describing the use of pulsed amperometry to detect these species.

6.4.4 Integrated Amperometry

Integrated amperometric detection employs a repeating potential vs. time waveform. The cell current is integrated during a specific section of the waveform. It is a more general technique than pulsed amperometric detection in that pulsed amperometry employs a repeating sequence of three potentials, while integrated amperometry can be any waveform. This method is useful for amines and sulfur species because their oxidation at metal electrodes is catalyzed by the formation of metal oxide, and an integrated amperometry waveform can be used that minimizes background effects caused by metal oxide formation. Also, integrated amperometry can be used to decrease the effect of changes in pH, allowing moderate pH gradients to be performed without large shifts in the baseline.

The principle of integrated amperometry is illustrated in Figure 6-14. With pulsed amperometry, the current is integrated at a single potential following a pulse. The figure shows a comparison of pulsed vs. integrated amperometry for leucine on a gold working electrode in 100 mM NaOH.

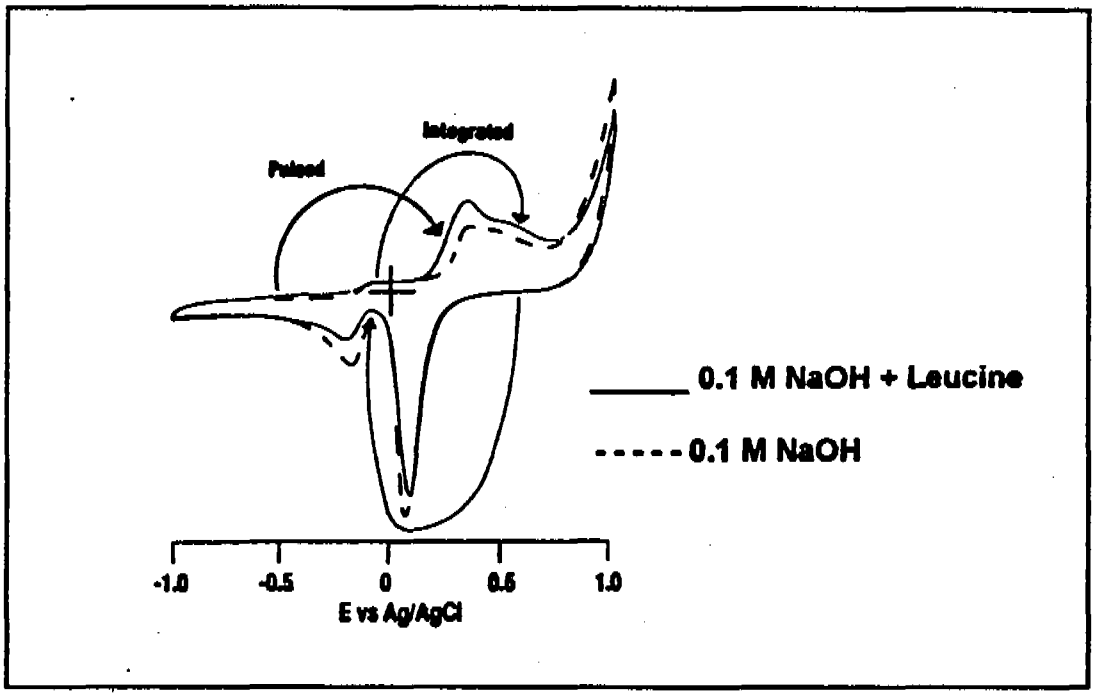


Figure 6-14. Pulsed vs. Integrated Amperometry

With the integrated amperometry waveform shown in Figure 6-15, the current is integrated while the potential is swept across the metal oxide formation wave and also during the reverse sweep across the oxide reduction wave. Without the presence of analyte molecules, the net charge is approximately zero. Positive and negative cleaning pulses are added to the potential vs. time waveform following the integration period. Waveforms are optimized using a technique similar to the method used for pulsed amperometry.

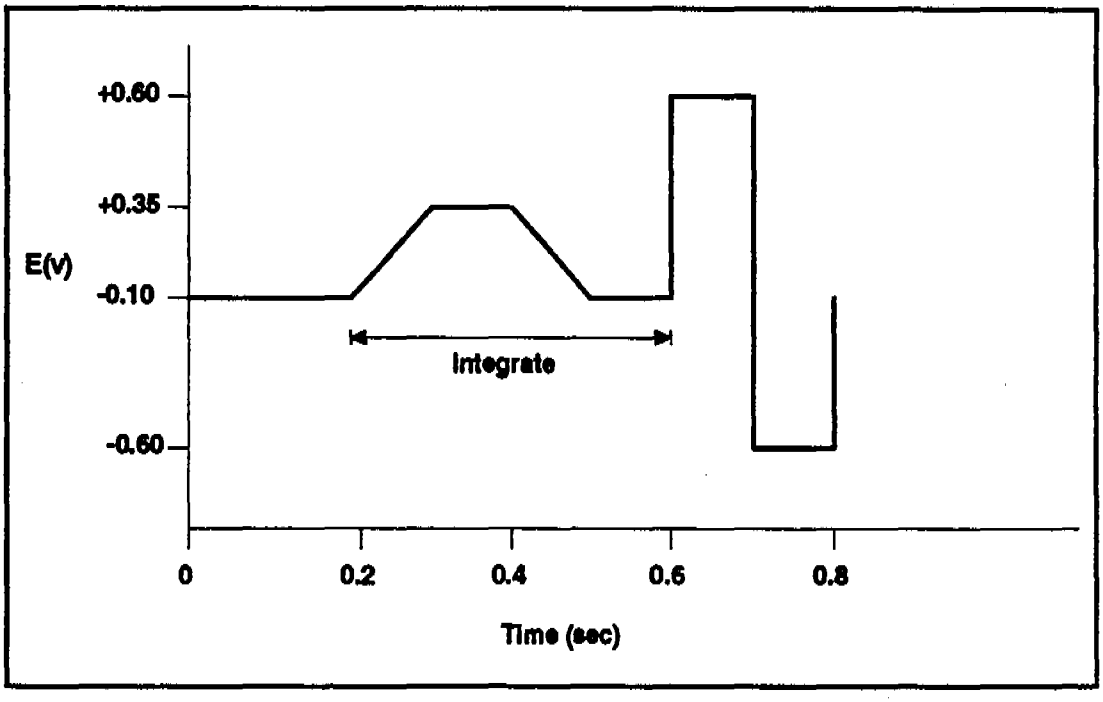


Figure 6-15. Example Integrated Amperometry Waveform

The advantage of integrated amperometry is that by canceling the charge from oxide formation and reduction, the effect on the baseline is greatly minimized. An example of the effect of canceling the working electrode oxidation current is shown in Figure 6-16. The figure shows a comparison of two integration periods, 10 ppm leucine (peak 1) and lactose (peak 2), gradient of 15 to 150 mM NaOH.

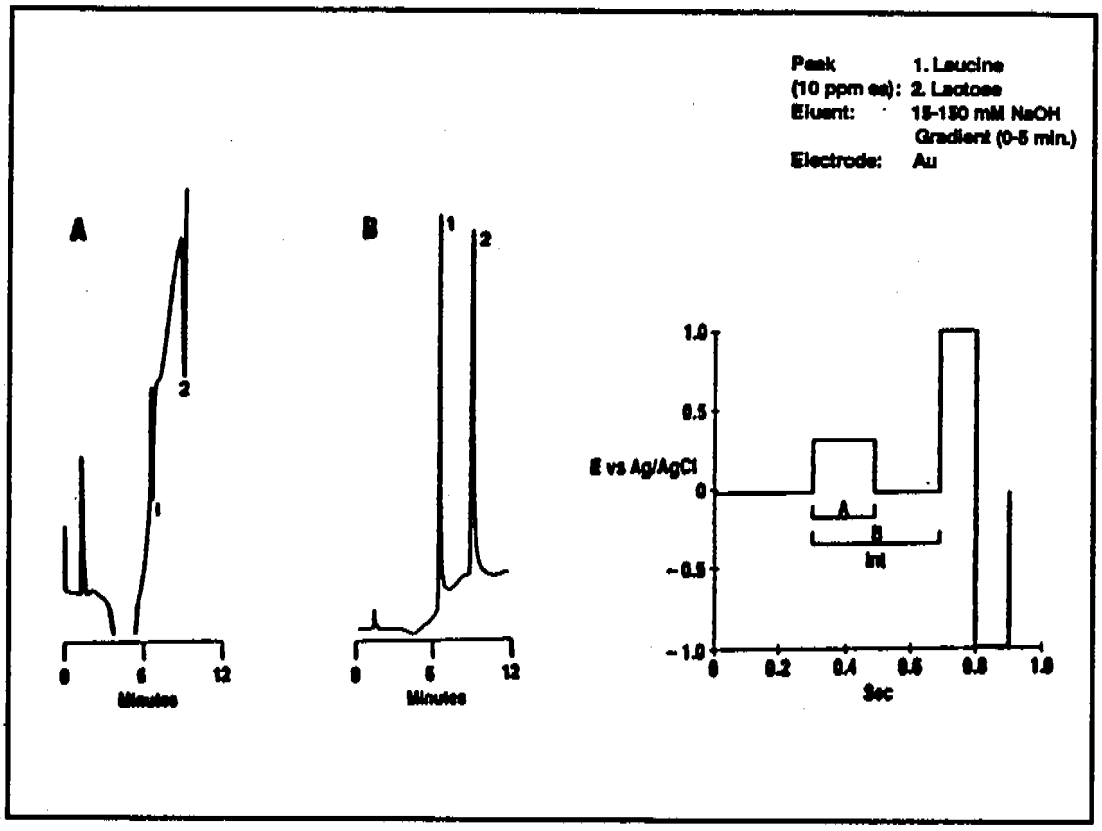


Figure 6-16. Comparison of Integration Periods

When the current is integrated only during the forward step across the metal oxide formation wave, the baseline shift during the gradient is very large (Fig 6-16A). Also, the eluting analytes cause dips instead of peaks because their effect on surface oxide suppression is greater than the detector response from the analytes. Integrating the current for both the forward and reverse steps greatly minimizes the baseline shift and eliminates the dips, resulting in good peaks (Fig 6-16B).

Integrated amperometry is a new technique developed in Professor Dennis Johnson's laboratory at Iowa State University. Dr. Johnson has published several recent papers showing the utility of integrated amperometry. (These papers are listed Appendix F.)

6.4.5 Working Electrodes

The ED40 can be used with four working electrode materials: gold, silver, platinum, and glassy carbon. The precious metal electrodes are very high purity solid metals. Glassy carbon is a hard graphitic substance. The analytes determined using these working electrodes are listed in Table 6-3.

The choice of working electrode material for a given application depends on four factors:

- Potential limits for the working electrode in the mobile phase.
- Involvement of the electrode in the electrochemical reaction.
- Kinetics of the electron transfer reaction.
- Long term stability of the electrode.

Potential Limits

The negative potential limit is the potential at which the mobile phase or supporting electrolyte is reduced. At the positive potential limit, the mobile phase, the supporting electrolyte, or the electrode itself can be oxidized. Because these reactions will produce current far in excess of the analytical redox reaction, the potential used to detect the analyte must be within these limits. Table 6-4 lists the potential limits for the four electrode materials in acidic and basic solutions. The potential limits are strongly affected by the pH of the mobile phase. Negative potential limits are more negative in base and more positive in acid. Conversely, positive limits are more positive in acid and more negative in base. In other words, the usable potential window shifts negative in basic solutions and positive in acidic solutions.

Working Electrode	Solution (0.1 N)	Negative Limit (V)	Positive Limit (V)
Glassy Carbon (GC)†	KOH $HClO_4$	(-1.5) (-0.8)	(+0.6) (+1.3)
Gold (Au)	KOH $HClO_4$	-1.25 -0.35	+0.75 +1.10
Silver (Ag)	KOH $HClO_4$	-1.20 -0.55	+0.10 +0.40
Platinum (Pt)	KOH $HClO_4$	-0.90 -0.20	+0.65 +1.30

†Unlike metallic electrodes, the potential limits for the glassy carbon electrode do not cut off sharply. The noise and background level will differ from application to application and must be determined experimentally.

Table 6-4. Potential Limits vs. Ag/AgCl Electrode

As the applied potential approaches the potential limit, the noise will increase as the background current increases. On metal electrodes, there is a sharp increase in background current as the potential limit is approached. On glassy carbon, the increase in background current is more gradual. Because the maximum applied potential that can be used is determined by the required signal-to-noise ratio, the values listed in Table 6-4 are only a rough guide. For some applications using glassy carbon, it may be necessary to exceed these limits.

The largest positive potential limits are obtained on glassy carbon and platinum. Accordingly, oxidations are often performed using one of these two materials. The largest negative potential limits, listed in order, are obtained on glassy carbon, silver, and gold. Because of the ease of reducing hydrogen ion to hydrogen gas on a platinum electrode, platinum has a poor negative potential limit and is generally not used for reductions.

When potentials are used that are more negative than approximately -0.1 V vs. an Ag/AgCl reference electrode, high background current is caused by the reduction of molecular oxygen dissolved in the mobile phase. This background current can be greatly reduced by degassing the mobile phase.

Involvement of the Electrode in the Redox Reaction

The reaction mechanism for the oxidation of many analytes is the transfer of electrons from the analyte molecules to the electrode. The electrode acts as an inert electron sink and is otherwise not involved in the oxidation reaction. With this reaction mechanism, carbon is often the preferred electrode material. Examples include the detection of catecholamines and aromatic amines. In contrast, silver and gold can be oxidized in the presence of complex or precipitate-forming ions. For the detection of these ions, the working-electrode material is directly involved in the reaction and is actually slowly consumed, although so slowly that no degradation in performance is observed. For example, silver can be oxidized to silver cyanide in the presence of cyanide ion. This reaction takes place at a much lower potential than the oxidation of cyanide to cyanate at a platinum electrode. The ability to use a lower applied potential increases the selectivity of the analysis, as fewer other species will be oxidized. Also, noise caused by the oxidation of trace contaminants in the mobile phase will be decreased at the lower applied potential. A silver electrode can also be used to detect other complex or precipitate-forming ions. These include bromide and iodide, as well as numerous sulfur-containing species such as sulfide, sulfite, thiosulfate, and organic thiols. One disadvantage to the use of silver or gold for oxidations is that the presence of halides in the mobile phase will greatly decrease the positive potential limit. Halides can usually be replaced by nonreacting anions such as acetate, methanesulfonate,

perchlorate, nitrate, phosphate, or sulfate.

Kinetics of the Electron-Transfer Reaction

For a kinetically fast electron-transfer reaction at E°, the ratio of the oxidized to the reduced form of the analyte species will be described by the Nernst equation (page 6-18). The reaction is said to be *reversible*. Note that if E_{app} is set 0.118 V positive of E°, then (for $n = 1$) the ratio of the oxidized to the reduced form of the analyte at the electrode surface will be 100:1. Nearly all of the analyte that reaches the electrode will be oxidized. The limiting current will have been attained, and no advantage will be gained from a further increase in the applied potential. More often than not, redox reactions are *irreversible*, in that the electron transfer reaction rate is slow at E°. For irreversible reactions, a potential considerably in excess of E° is required to drive the reaction at a fast rate. This excess voltage is called *overpotential*. The more irreversible the redox reaction, the greater the applied potential must be. This will result in more noise and less selectivity. The oxidation or reduction of many species is more facile on one electrode material than on another. This is particularly true for small inorganic species, many of which can be oxidized or reduced much more easily on platinum than on carbon. For example, platinum electrodes are used to detect arsenite, iodide, and sulfite.

Long-Term Stability of the Electrode

A major consideration when choosing an electrode material is its ability to maintain an active surface. Electrodes will develop a layer of surface oxide at positive applied potentials. This buildup will inhibit oxidation of the analyte, often resulting in decreasing response with repeated injections. The active surface can be renewed by polishing the electrode. Glassy carbon

electrodes are more resistant to poisoning by oxide formation than are metallic electrodes, and do not need to be polished as often. This is one of the reasons glassy carbon is used far more extensively than any other electrode material for DC amperometry. Pulsed amperometry and integrated amperometry solve this problem for platinum and gold electrodes by pulsing to high positive and negative potentials after each current measurement to clean the electrode.

A • Specifications

A • Specifications

A.1 Electrical

Main Power 85 to 270 Vac, 47/63 Hz; 40 W Max, 25 W typical. The ED40 power supply is auto-sensing and no voltage adjustment is required.

Fuse Two 3.15 amp slow-blow IEC127 fuses (P/N 954745).

Analog Output User-selectable full-scale output of 10, 100, or 1000 mV.

A.2 Environmental

Operating Temperature 4 °C to 40 °C (40 °F to 104 °F)

Operating Humidity 5 to 95% relative humidity (non-condensing)

A.3 Physical

Dimensions 22.5 cm W x 17.0 cm H x 42.0 cm D
(8.8 in W x 6.6 in H x 16.4 in D)
6 cm (2.4 in) clearance required behind the detector.

Weight 8.2 kg (18 lb)

A.4 Display and Keypad

Display A Power-Up screen and eight basic User-Interface screens for method generation and control. The ED40 Diagnostics Program adds eight diagnostic screens. The display is liquid crystal with adjustable backlighting

Keypad 26-key keypad for entering commands and numerical values for screen parameters.

A.5 Detector

Range 0.01 µS to 3000 µS, full scale (Conductivity)

50 pC to 200 µC (Integrated Amperometry)

50 pA to 300 µA (DC Amperometry)

Temperature Compensation 0.0 to 3.0% per °C (Conductivity)

Cell Drive Variable 8 kHz square wave (Conductivity)
±2.04 V (DC and Integrated Amperometry)

Local Operation Front panel controls and display status of all functions

Remote Operation All functions controlled by PeakNet software on a computer. Connection is via the DX LAN. Control of 4 of 7 functions is possible via TTL or Relay contacts.

A.6 Conductivity Cell

Cell Body	PEEK
Active Volume	1.0 µL
Maximum Pressure	2.0 mPa (300 psi)
Electrodes	316 stainless steel

A.7 Amperometry Cell

Cell Body	Titanium (counterelectrode)
Active volume	~ 0.3 µL
Maximum Pressure	0.7 mPa (100 psi)
Working Electrodes	Gold, Silver, Platinum, Glassy Carbon
Reference Electrode	Combination pH — Ag/AgCl

A.8 SRS Power Supply

Supply Current	50, 100, 300, 500 mA @ 1.5 to 7.5 V.
Over-Voltage Alarm	8.5 V
Over-Temperature Alarm	40 °C

A.9 DS3 Detection Stabilizer

Operating Temperature	25 °C to 40 °C (50 °F to 104 °F)
Warm-up Time	10 minutes (typical)
Under/Over Temperature Alarms	Message displayed when not at set temperature.

B • Installation

B • Installation

This appendix describes the installation and connections necessary to place the ED40 Electrochemical Detector into operation. All cables are routed through the front slots and the rear cable chase, and then on through similar ports of entry on each module in the stacked system.

B.1 Facilities Required

The installation site should meet the following requirements.

B.1.1 Bench Space

The ED40 should be installed on a sturdy table or work bench with at least 5 cm (2 in) clearance behind the detector for power connection and ventilation.

B.1.2 Stacking

The ED40 can be stacked on or under any other DX 500 module. A typical installation has the ED40 stacked on top of the GP40 Gradient Pump. Stacking the modules frees up bench space and minimizes plumbing and cable lengths.

B.1.3 Power

The ED40 requires a grounded, single-phase power source. The three-conductor line cord ensures a safety ground. The ED40 meets safety standards IEC 1010 and UL 1262, and is designed for immunity to electromagnetic field interference (EMI) and to be free of harmful EMI emission levels. No user adjustment is required for line voltage selection.

Operation at input levels outside the specified range may damage the detector.

SHOCK HAZARD—A grounded receptacle must be used to avoid electrical shock. Do not operate or connect to AC power mains without an earthed ground connection.

B.2 Installation Instructions

Remove the ED40 carefully from the shipping container. Use the lift strap to lift the detector.

When moving or carrying the ED40, avoid stressing the front panel hinge assembly by lifting on the front panel.

Do not turn on the detector if it is not at room temperature (10 to 40 °C or 50 to 104 °F). If the detector is moved from a cold environment (outside in winter) to a warm environment (heated room), allow at least one hour for condensation to evaporate before turning on the power.

NOTE

Save the shipping container for possible reuse.

B.2.1 Ship Kit Contents

The Ship Kit (P/N 046297) contains items required to install the ED40. The contents are listed on the packing slip. The Ship Kit includes the following electrical parts:

- A line cord (P/N 096708) for the 110/120 Vac power connection.
- A black and red wire assembly (P/N 043598) for the Recorder/Diagnostic connection.
- Two spare fuses.
- Self-Regenerating Suppressor cabling.

NOTE

When necessary, replace the line cord with an appropriate power cord. Modular line cords are available with other plugs from electrical supply distributors in countries where the plug is different than the one supplied with the detector.

The Ship Kit includes various tubing assemblies for plumbing the columns and cell into the LC10, LC20, or LC30. Refer to the appropriate manual for installation instructions.

- *LC10 Chromatography Organizer Operator's Manual,* (Document No. 034858).
- *LC20 Chromatography Enclosure Operator's Manual* (Document No. 034859).
- *LC30 Chromatography Oven Operator's Manual* (Document No. 034860).

The Ship Kit contains a screwdriver for connecting wires to the Recorder/Diagnostic Connector Plug. Place this tool in a convenient, secure place for future use. Also provided are parts specifically for use with the Self-Regenerating Suppressor (SRS) Control. If you are not using an SRS, store the parts so that you will have them if you later install an SRS.

The Ship Kit includes four anti-skid feet which may be positioned in indentations on the bottom of the ED40. If the detector is to be stacked on top of a matching DX 500 instrument, installation of the feet is not recommended. Store them in a convenient, safe place for possible future use.

B.2.2 Shoe and Ties

The Ship Kit contains a shoe and ties that help to secure the ED40 to other Dionex chromatography instruments — providing additional security and organization to the chromatography station.

Shoe

The shoe (P/N 046478) is a rubber, gray-colored rectangle with raised edges. It is designed to be installed on the laboratory bench, under two DX 500 modules located side-by-side. The shoe keeps both modules together and prevents them from sliding apart.

First, decide how you want to arrange the chromatography modules. Then install the shoe under the bottom two modules that are placed next to each other. For example, a typical chromatography installation may have the LC30 Chromatography Oven and the GP40 Gradient Pump installed next to each other on the workbench. Place both modules on their respective sides of the shoe which is installed on the workbench.

Ties

The Ship Kit contains two ties (P/N 046476) that can be used to hold two DX 500 modules together to provide increased stability. The ties are elastic pieces that fit into the slots at the front of the DX500 modules.

For example, a typical chromatography installation will have the ED40 Electrochemical Detector installed on top of the GP40 Gradient Pump. Use the ties to anchor the two modules together.

B.2.3 Conductivity Cell Installation

The conductivity cell is installed in either the DS3 Detection Stabilizer or in an external grounded shield box. A shield box is required, if the DS3 is not used, to prevent reception of electromagnetic interference (EMI). A second detector — such as the AD20 Absorbance Detector — may be installed in-line after the conductivity cell as long as the pressure at the cell inlet is less than 700 kPa (100 psi).

1. Connect the cell cables and DS3 control cable to the detector. The cell cable grounds the shield.
2. To prevent bubble trapping, position the DS3 or shield is positioned so that the output connection is on the top. Observe inlet and outlet labels. This orientation ensures that the flow direction through the cell is upward. (On the DS3, the input is on the top; on the shield, the input is on the bottom.)
3. To further minimize bubble formation, the outlet connection should provide some restriction to generate a small amount of backpressure. A backpressure restrictor consisting of approximately 1 meter (39 in) of 0.25-mm (0.010-in) ID capillary tubing is recommended. This provides 150 kPa (22 psi) for flow rates of approximately 1 mL/min. Avoid flow rates over 5 mL/min with this length of backpressure tubing.

NOTE

If you need more tubing in order to reach the waste container, use 0.5 mm (0.02 in) ID tubing or larger. This size produces virtually no backpressure and can be as long as necessary to reach the waste container or drain.

Route the cell cables through the detector cable passageway to the back, or across the front, using the provided slots.

B.2.4 Self-Regenerating Suppressor Installation

Complete installation and operating instructions are contained in the manual shipped with the Self-Regenerating Suppressor (SRS).

NOTE

The backpressure generated by the DS3, cell, and backpressure tubing is applied to the SRS. This is approximately 200 kPa (30 psi) for the DS3 when 1 meter of 0.25-mm (0.01-in) ID tubing is used at 1 mL/min.

B.2.5 Amperometry Cell Installation

Install the ED40 amperometry cell directly after the column. (A suppressor is not typically used with the amperometry cell.) A second detector such — as the AD20 Absorbance Detector — may be installed in-line after the amperometry cell as long as the pressure at the amperometry cell inlet remains less than 700 kPa (100 psi). Because of the volume within the reference electrode section of the cell, there may be some band broadening at the second detector. However, this is minimized by the precision flat bottomed reference electrode.

1. Inspect the cell gasket for scratches or damage. If scratched or damaged, replace the gasket (P/N 045972).
2. Rinse the gasket with deionized water, and clean the polished gasket surface of the cell with a damp paper towel.
3. Install the gasket over the alignment studs on the cell body. Note that when installed, one end of the gasket extends beyond the cell body. This facilitates easier gasket installation and removal.
4. Polish the working electrode block (see Section 3.12.4) and rinse its surface with deionized water. Wipe it with a damp paper towel.
5. Install the working electrode block over the alignment studs so that the electrode type stamped on the top of the working electrode is facing upwards.
6. Fasten it in place with the wing screws. Note that the electrode material stamped on the block is visible with the cover on.

NOTE

Polishing the electrode is recommended when it is first installed and when it is seriously fouled. Otherwise, it should give superior performance.

7. Remove the pH reference electrode from its box within the amperometry cell shipping container. Remove the pH reference electrode from the soaker bottle by partially unscrewing the lid off the soaker bottle and pulling the electrode out of the O-ring groove within the lid. (See the maintenance section in Chapter 3 for further information.)
8. Rinse the pH reference electrode in deionized water, being sure to rinse off any precipitated salt. Do not discard the soaker bottle and lid as these are used for safe storage of the electrode when the amperometry cell is not in use.
9. Before intalling the pH reference electrode in the cell block, it must be calibrated. See Section 3.12.2.
10. After calibration, install the electrode by removing the pH reference electrode compression nut (P/N 045968) from the cell body.
11. Fill the reference electrode cavity within the cell body with enough deionized water so that the O-ring within the reference electrode cavity is completely wet.
12. Feed the pH reference electrode cable through the slot in the compression nut. Carefully guide the pH reference electrode with the nut into the reference electrode cavity within the cell body. Screw the compression nut into the cell body until it completely bottoms out. As the compression nut is tightened, the pH reference electrode will slip into position past the O-ring.
13. Connect the pH reference electrode cable to Junction J2 on the cell pre-amp PC board.

14. Verify that the white working electrode lead wire is connected to the cell pre-amp PC board.

15. Slide the cell cover back over the cell body and tighten the cell cover thumbscrew.

16. Make sure the detector cell is turned off. Connect the amperometry cell cable to connector #1 on the SP board in the front of the ED40 detector card cage. Depending on your preference, feed the amperometry cable either under the card cage and out the back of the detector, or directly out the side of the detector.

17. If you are using an LC20 Chromatography Enclosure or LC30 Chromatography Oven, the amperometry cell cable may be routed through either the rear or the side of the module, depending on your preference. Connect the amperometry cell cable to the amperometry cell, allowing a sufficient service loop to slide the chromatography component card in and out of the module.

18. If you are using an LC10 Chromatography Organizer, the amperometry cell insulation plate (P/N 046617), cell mounting screws (P/N 045796), and cell mounting washers (P/N 045973) need to be removed from the cell body. Store these components in a safe place, as they are necessary insulation and mounting components for the LC20 and LC30 (if the system is late upgraded). Connect the amperometry cell cable to the amperometry cell.

19. Attach the tubing from the column to the cell inlet.

NOTE

The short length of stainless steel tubing at the cell inlet is an integral part of the cell. DO NOT REMOVE IT. This tube extends the counter electrode, thereby shielding the working electrode from electrical noise.

20. Connect the waste line to the cell outlet.

21. Secure the plumbed amperometry cell to its appropriate mounting location in the chromatography module.

NOTE

When properly mounted, the outlet fitting on the amperometry cell will be positioned on the uppermost surface of the cell. This orientation ensures proper pH reference electrode orientation within the amperometry cell, as well as proper bubble sweepout.

B.2.6 Recorder/Diagnostic Connection

Use the recorder/diagnostic black and red wire assembly provided in the Ship Kit to connect a strip chart recorder or integrator to the SCR card. Several parameters may be recorded or monitored with a voltmeter or chart recorder in addition to the cell analog output, by attaching wires to the connector with a screwdriver. Table E-1 lists the pinouts for the cable.

B.2.7 Relay/TTL Control Connections

Eight 2-pin connectors are provided: 4 input and 4 output. You can attach individual wires, twisted pairs, or coaxial cables to these plugs. Strip the end of the wire(s), insert into the plug, and use a screwdriver (provided in the Ship Kit) to tighten the plug locking screw.

Connections 1 and 2 can be programmed to switch any low-voltage control. Switched current must be less than 200 mA and 42 V peak.

Refer to the label on the back of the front panel for connector locations.

Table E-4 describes the pinouts for the Relay/TTL connectors. TTL inputs 1, 2, 3, and 4 can be used to control the following functions:

- OFFSET Recorder
- HOLD/RUN Program
- SRS OFF/ON
- METHOD NUMBER INCR
- METHOD NUMBER DECR
- MARK Recorder
- Increase Recorder RANGE x10

Use the TIME FUNCTION IN screen to select which four functions will be controlled by TTL 1 through 4.

The relay output, TTL output, and TTL inputs use the same style of connector. Connection of relay loads and their power sources to the TTL outputs will damage the TTL output stage. If the relay load can supply more than 200 mA at 5 V or higher, damage to the CPU module may result.

B.2.8 Remote Network Connection (DX LAN Option)

In order to use the PeakNet software with the ED40, a DX LAN I/O board must be installed. When present, a standard BNC connector will be visible at the upper left on the rear of the detector.

STATIC — To prevent damage to the detector, the installation of a DX LAN card or the handling of the CPU card must be done using static control procedures. Use an anti-static work mat, wrist strap, and proper grounding, or refer servicing to qualified personnel.

To prevent damage to the detector, it must first be turned off. Confirm that the LED on the CPU board is off (not green or red). Then unplug the power cord from the mains. Do not rely on the front panel power switch.

To install the DX LAN I/O card:

1. Remove any TTL/Relay plugs from the connectors on the SP card (slot 4).
2. Disconnect the 60-pin ribbon cable from the front panel. Close the tilt panel to expose the connector and its ejector latches. Remove the cable by opening the ejector latches.
3. Use a screwdriver as a lever to open the white ejector latch at the bottom of the CPU board and remove the CPU board, cable, and Relay board as a single unit.
4. Inserte the DX LAN board into slot 4. Slide it to the rear. Make sure that the round BNC connector is aligned with the hole at the rear and the board is aligned with the connector. Press firmly on the board until it is inserted into the connector on the back panel.
5. Reinstall the CPU/Relay board. Press firmly until the CPU board is inserted into the connector on the back panel.
6. Reconnect the display ribbon cable to the 60-pin connector on the front panel. The header and connector are key polarized near the center. The ejector latches should be partially open to accept the cable connector.
7. If the detector is connected at the end of the DX LAN network, install the terminator resistor plut on the remaining port of the BNC tee connector. If it is not at the end, connect the cable from the next module to the BNC tee.

NOTE

Terminator resistor plugs must be installed at each end of the DX LAN. Verify that both ends of the LAN have resistor plugs installed.

8. Connect the DX LAN cable to the BNC jack on the rear panel of the detector.

C • User Interface

C.1 The User Interface Screens

This appendix describes ED40 Electrochemical Detector screens. The first part describes the User Interface screens. The second part describes the Diagnostics available in the ED40. Use the screens and the keypad to create, edit, and run the methods and waveforms that control the detector operation, to select default parameters, and to access help and diagnostic information.

Screen alternately signifies: (1) the liquid crystal display (LCD) itself and (2) the information that appears in the display.

Menu is a display that offers a selection of additional screens or menus that you can choose for specific functions. Generally, parameters cannot be changed in a menu.

The liquid crystal display has a fluorescent backlight. The backlight intensity is adjustable from the **MODULE SET-UP** screen.

The ED40 has one power-up screen and eight User Interface screens. In addition, the **MENU of SCREENS**, the **MAIN** screen, the **DETAIL** screen, the **METHOD** screen, and the **WAVEFORM** screen are unique to each of the four detection modes. The rest of the screens are common to all detection modes.

You can enter parameter changes only in the fields shown in reverse video on the display, and with the cursor positioned in the field to be changed.

Table C-1 lists the ED40 screens available for/used by each detection mode. The body of the table contains the section numbers where the screens are described.

Screen	Conductivity	Integrated Amperometry	DC Amperometry	Voltammetry
Menu of Screens	C.1.1	C.1.5	C.1.10	C.1.14
Main Screen	C.1.2	C.1.6	C.1.11	C.1.15
Detail Screen	C.1.3	C.1.7	C.1.12	C.1.16
Method	C.1.4	C.1.8	C.1.13	———
Waveform Edit	———	C.1.9	———	C.1.17
Module Set-up	C.1.18			
Analog Out Set-up	C.1.19			
Time Function In	C.1.20			
Diagnostics Menu	C.2.1			

Table C-1. ED40 Screens by Detection Mode

C.1.1 Menu of Screens — Conductivity

The **MENU of SCREENS** provides top level access to the menu structure. Figure C-1 illustrates the **MENU of SCREENS** for the Conductivity mode.

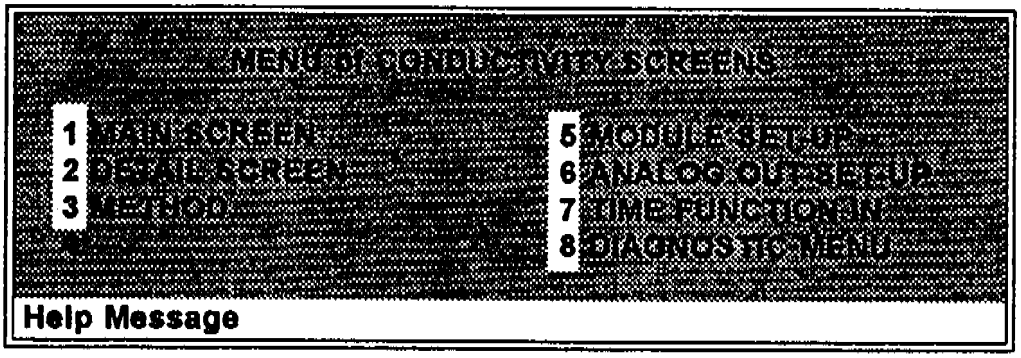


Figure C-1. Menu of Screens — Conductivity

There are two ways to select a screen from this menu:

- Use the arrow keys to move the cursor to the field containing the number of the screen you want. Then press **Enter**.
- Press the number key corresponding to the screen you want on the keypad.

Pressing the **Help** key brings up a brief description of each menu.

C.1.2 Main Screen — Conductivity

Figure C-2 illustrates the **MAIN** screen for the Conductivity mode. The **MAIN** screen provides a large graphic character display of the measured conductivity (siemens) and other primary functions for Conductivity mode.

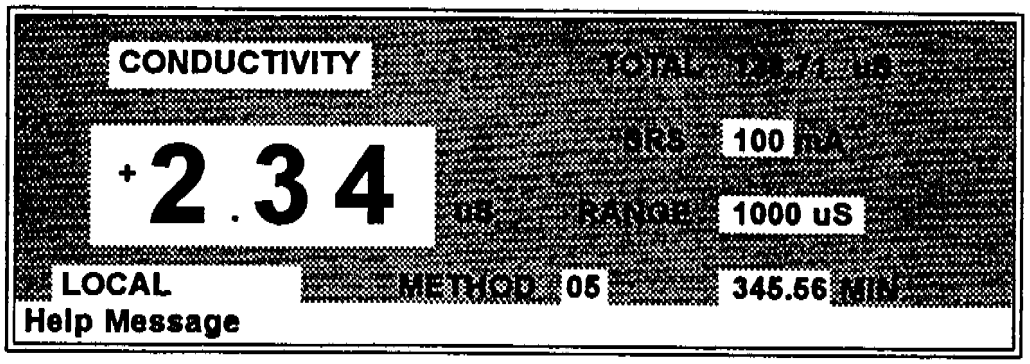


Figure C-2. Main Screen — Conductivity

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, Integrated Amperometry, or Voltammetry.
TOTAL	Displays total conductivity (without an offset).
SRS	Selects the amount of current sent to the suppressor. Current selection depends on the eluent concentration, flow rate, etc. The discrete settings are Off, 50, 100, 300, and 500 mA.
RANGE	Sets the analog output scale factor. Select a range between 0.01 and 3000 µS.
METHOD	Sets the method number. Pressing **Select** and **Enter** sets the detector to Direct control.
Control Mode	Sets the detector to Local, Remote, or Locked Remote control.
MIN	Shows the method clock elapsed time.

C.1.3 Detail Screen — Conductivity

Figure C-3 shows the **DETAIL SCREEN** for Conductivity mode. The **DETAIL SCREEN** contains all of the **MAIN** screen fields. In addition, the **DETAIL SCREEN** contains TTL and Relay fields and other fields to control conductivity.

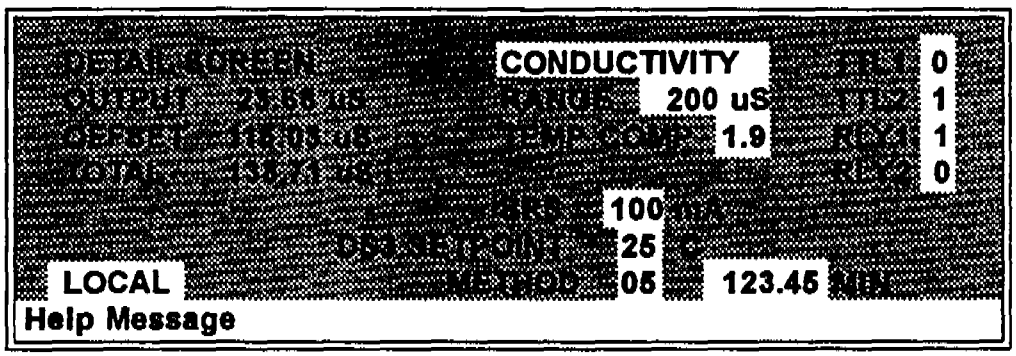


Figure C-3. Detail Screen — Conductivity

The following fields appear on the **DETAIL SCREEN**. Refer to the **MAIN SCREEN** for a description of the other fields.

TEMP COMP — Sets the temperature compensation factor. The range is 0 to 3%. 1.7% is appropriate for most eluents.

DS3 SETPOINT — Sets the temperature of the DS3 Detection Stabilizer.

TTL-1
TTL-2 — Provides TTL control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).

RLY-1
RLY-2 — Provides relay contact closure control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).

C.1.4 Method — Conductivity

Figure C-4 shows the **METHOD** screen for Conductivity mode. A method consists of a series of timed steps. Each step has a set of parameters associated with it.

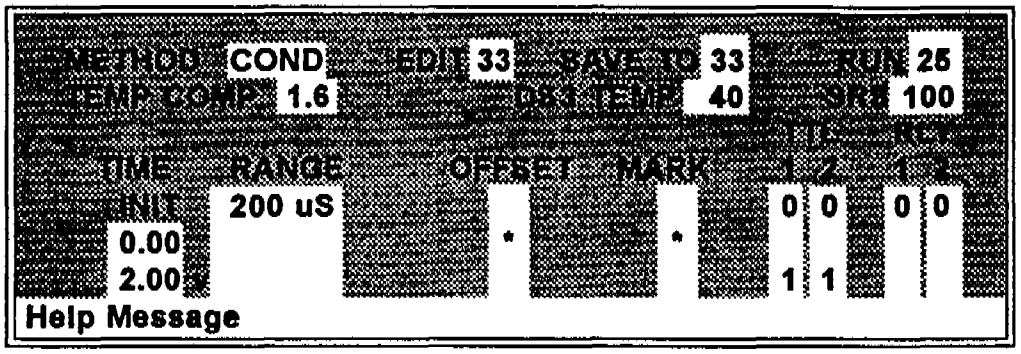


Figure C-4. Method Screen — Conductivity

Initial conditions are applied when a method is selected. A lower case **v** next to the last step on the display indicates that the method contains more steps.

Blank fields denote no change from the previous step. The **Delete** blanks the field.

The **METHOD** screen for Conductivity contains the following fields. Note that **TEMP COMP**, **DS3 TEMP**, and **SRS CURRENT** are not time programmable.

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, or Integrated Amperometry.
EDIT	Specifies the method number (0 - 99) to edit.
SAVE TO	Specifies the method number (0 - 99) to save the current method to.
RUN	Specifies the method number (0 - 99) to run. The **Hold/Run** key controls running the method.

TEMP COMP	Sets the Temperature Compensation factor.
SET TEMP	Sets the temperature for the DS3 Detection Stabilizer.
SRS	Sets the Self-Regenerating Suppressor current.
TIME	Specifies the start time for each step. Times are displayed chronologically.
RANGE	Sets the analog output range.
OFFSET	Stores the offset value. The baseline is set by subtracting the offset measured when this step is executed from all subsequent measurements. An asterisk (*) indicates that OFFSET will occur at this time.
MARK	Sends a positive pulse to the analog output (recorder) as an event marker. An asterisk (*) indicates a MARK will occur at this time.
TTL	Sets TTL-1 and TTL-2 to off (0) or on (1).
RLY	Sets RLY-1 and RLY-2 to off (0) or on (1).

C.1.5 Menu of Screens — Integrated Amperometry

Figure C-5 shows the **MENU of SCREENS** for Integrated Amperometry mode.

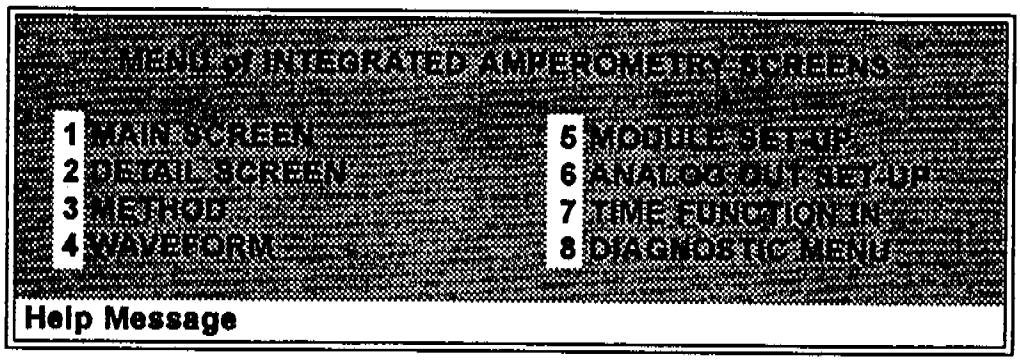


Figure C-5. Menu of Screens — Integrated Amperomety

There are two ways to select a screen from this menu:

- Use the arrow keys to move the cursor to the field containing the number of the screen you want. Then press **Enter**.
- Press the number key corresponding to the screen you want on the keypad.

Pressing the **Help** key brings up a brief description of each menu.

C.1.6 Main Screen — Integrated Amperometry

Figure C-6 illustrates the **MAIN** screen for the Integrated Amperometry mode. The **MAIN** screen provides a large graphic character display of the measured charge (coulombs) and other primary functions for Integrated Amperometry mode.

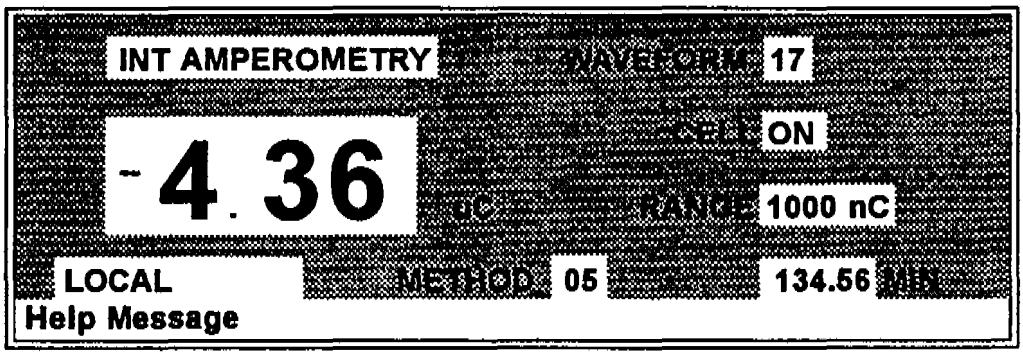


Figure C-6. Main Screen — Integrated Amperometry

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, Integrated Amperometry, or Voltammetry.
WAVEFORM	Sets the waveform number to run. Program the Waveform using screen 4.
CELL	Turns the amperometry cell off and on, disabling or enabling detection.
RANGE	Sets the detector sensitivity between 50 pC and 200 µC.
METHOD	Sets the method number. Pressing **Select** and **Enter** sets the detector to Direct control.
Control Mode	Sets the detector to Local, Remote, or Locked Remote control.
MIN	Shows the waveform clock elapsed time.

C.1.7 Detail Screen — Integrated Amperometry

Figure C-7 shows the **DETAIL SCREEN** for Integrated Amperometry mode. The **DETAIL SCREEN** contains all the fields that the **MAIN SCREEN** contains. In addition, the **DETAIL SCREEN** contains TTL and Relay fields and other fields to control detection.

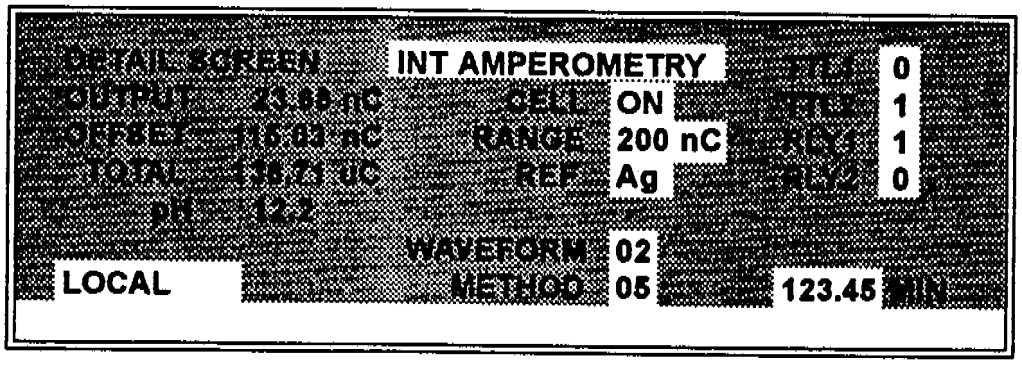


Figure C-7. Detail Screen — Integrated Amperometry

The following fields appear on the **DETAIL SCREEN**. Refer to the **MAIN SCREEN** for a description of the other fields.

REF	Sets the reference electrode to either the pH or Ag/AgCl half cell.
pH	Displays the mobile phase pH.
TTL-1 **TTL-2**	Provides TTL control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).
RLY-1 **RLY-2**	Provides relay control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).

C.1.8 Method — Integrated Amperometry

Figure C-8 shows the **METHOD** screen for Integrated Amperometry mode. A method consists of a series of timed steps. Each step has a set of parameters associated with it.

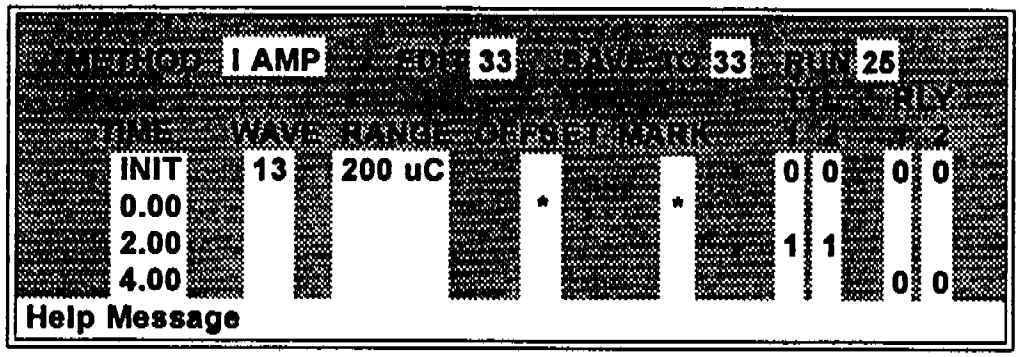


Figure C-8. Method — Integrated Amperometry

Initial conditions are applied when a method is invoked. A lower case **v** next to the last step on the display indicates that the method contains more steps.

Blank fields denote no change from the previous step. The **Delete** blanks the field.

The **METHOD** screen for Integrated Amperometry contains the following fields.

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, or Integrated Amperometry.
EDIT	Specifies the method number (0 - 99) to edit.
SAVE TO	Specifies the method number (0 - 99) to save the current method to.
RUN	Specifies the method number (0 - 99) to run. The **Hold/Run** key controls running the method.

TIME	Specifies the start time for each step.. Times are displayed chronologically.
WAVE	Sets the waveform number (0 - 19) to run.
RANGE	Specifies the detection range.
OFFSET	Stores the offset value. The baseline is set by subtracting the offset measured when this step executes from all subsequent measurements. An asterisk (*) indicates that OFFSET will occur at this time.
MARK	Sends a positive pulse to the analog output (recorder) as an event marker. An asterisk (*) indicates a MARK will occur at this time.
TTL	Sets TTL-1 and TTL-2 to off (0) or on (1).
RLY	Sets RLY-1 and RLY-2 to off (0) or on (1).

C.1.9 Waveform — Integrated Amperometry

Figure C-9 shows the **WAVEFORM** screen for Integrated Amperometry. These entries form points on a plot of Potential vs. Time.

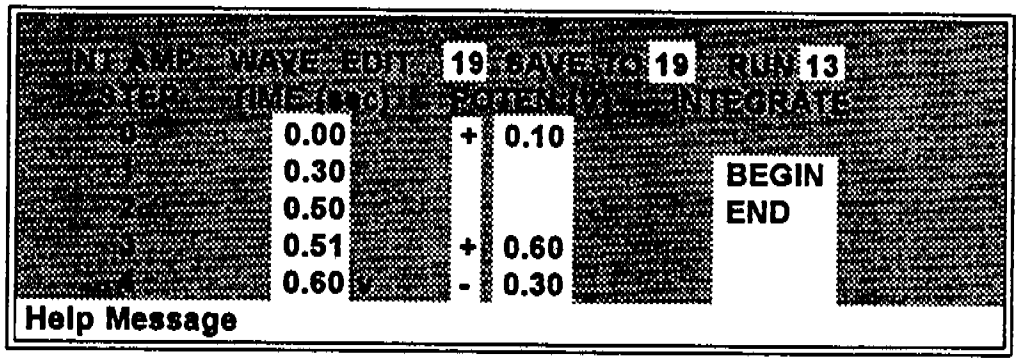


Figure C-9. Waveform — Integrated Amperometry

When the last step displayed is not the last step in the waveform, a lower case **v** displays next to the time digits in the last line.

WAVE EDIT — Specifies the waveform number (0 - 19) to edit.

SAVE TO — Specifies the waveform number (0 - 19) to save the current waveform definition to.

RUN — Specifies the waveform number (0 - 19) to run.

TIME — Specifies the time for this step. Times are displayed chronologically.

POTENTIAL — This is two fields. The first field sets the polarity. The second field is the point in the waveform for this voltage.

INTEGRATE — Sets the time for the integration period to begin and end. Integration cannot begin on the first step nor end on the last step in the waveform.

C.1.10 Menu of Screens — DC Amperometry

Figure C-10 shows the **MENU of SCREENS** for DC Amperometry mode.

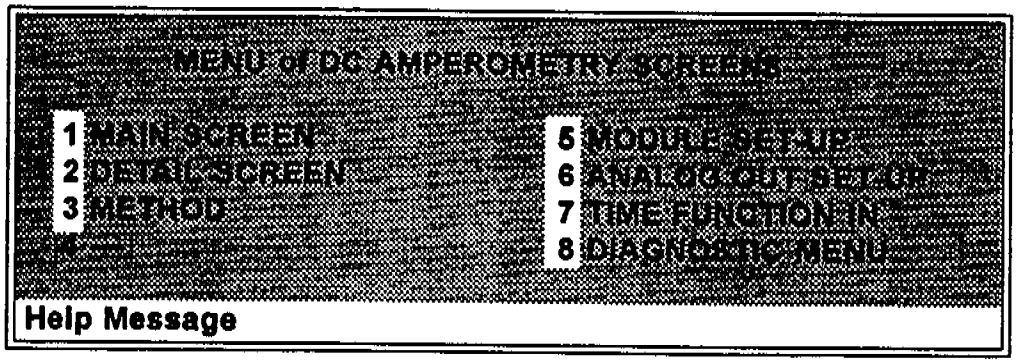


Figure C-10. Menu of Screens — DC Amperometry

There are two ways to select a screen from this menu:

- Use the arrow keys to move the cursor to the field containing the number of the screen you want. Then press **Enter**.
- Press the number key corresponding to the screen you want on the keypad.

Pressing the **Help** key brings up a brief description of each menu.

C.1.11 Main Screen — DC Amperometry

Figure C-11 illustrates the **MAIN** screen for the DC Amperometry mode. The **MAIN** screen provides a large graphic character display of the measured current (Amperes) and other primary functions for DC Amperometry mode.

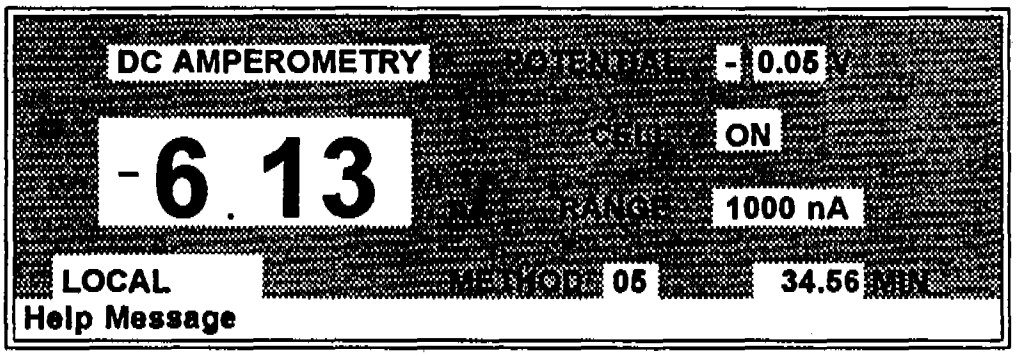


Figure C-11. Main Screen — DC Amperometry

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, Integrated Amperometry, or Voltammetry.
POTENTIAL	This is two fields. The first sets the polarity. The second sets the applied potential.
CELL	Turns the amperometry cell off or on, disabling or enabling detection.
RANGE	Sets the detector sensitivity between 50 pA to 300 μA.
METHOD	Sets the method number. Pressing **Select** and **Enter** sets the detector to Direct control.
Control Mode	Sets the detector to Local, Remote or Locked Remote control.
MIN	Shows the method clock elapsed time.

C.1.12 Detail Screen — DC Amperometry

Figure C-12 shows the **DETAIL SCREEN** for DC Amperometry mode. The **DETAIL SCREEN** contains all the fields that the **MAIN SCREEN** contains. In addition, the **DETAIL SCREEN** contains TTL and Relay fields and other fields to control detection.

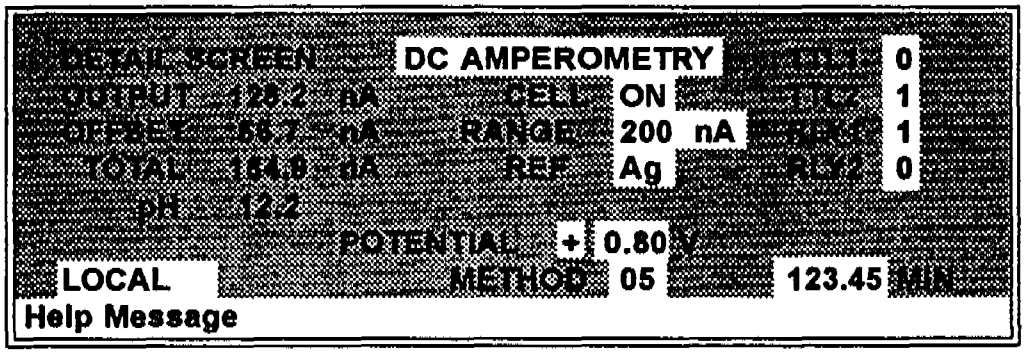


Figure C-12. Detail Screen — DC Amperometry

The following fields appear on the **DETAIL SCREEN**. Refer to the **MAIN SCREEN** for a description of the other fields.

REF	Sets the reference electrode to either pH or Ag/AgCl half cell.
pH	Displays the mobile phase pH.
TTL-1 **TTL-2**	Provides TTL control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).
RLY-1 **RLY-2**	Provides relay contact closure control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).

C.1.13 Method — DC Amperometry

Figure C-13 shows the **METHOD** screen for DC Amperometry mode. A method consists of a series of timed steps. Each step has a set of parameters associated with it.

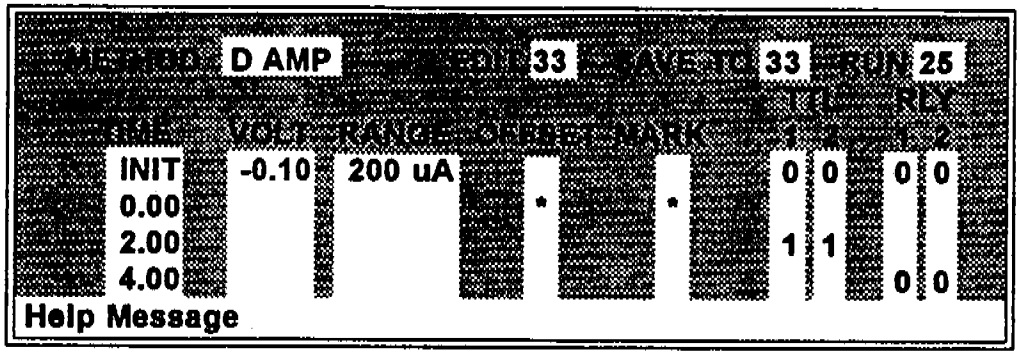


Figure C-13. Method — DC Amperometry

Initial conditions are applied when a method is selected. A lower case **v** next to the last step on the display indicates that the method contains more steps.

Blank fields denote no change from the previous step. The **Delete** blanks the field.

The **METHOD** screen for DC Amperometry contains the following fields.

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, or Integrated Amperometry.
EDIT	Specifies the method number (0 - 99) to edit.
SAVE TO	Specifies the method number (0 - 99) to save the current method to.
RUN	Specifies the method number (0 - 99) to run. The **Hold/Run** key controls running the method.

TIME	Specifies the start time for each step. Times are displayed chronologically.
POTENTIAL	Specifies the voltage applied to the cell.
RANGE	Specifies the detection range.
OFFSET	Stores the offset value. The baseline is set by subtracting the offset measured when this step executes from all subsequent measurements. An asterisk (*) indicates that OFFSET will occur at this time.
MARK	Sends a positive pulse to the analog output (recorder) as an event marker. An asterisk (*) indicates that a MARK will occur at this time.
TTL	Sets TTL1 and TTL2 to off (0) or on (1).
RLY	Sets RLY1 and RLY2 to off (0) or on (1).

C.1.14 Menu of Screens — Voltammetry

Figure C-14 shows the **MENU of SCREENS** for Voltammetry mode.

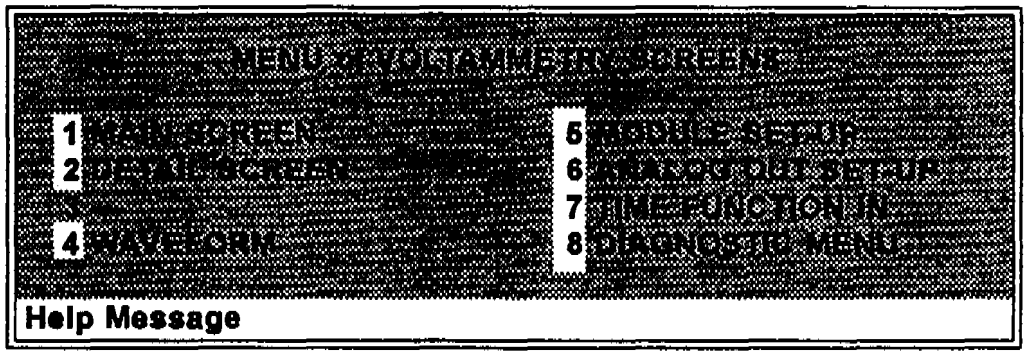


Figure C-14. Menu of Screens — Voltammetry

There are two ways to select a screen from this menu:

- Use the arrow keys to move the cursor to the field containing the number of the screen you want. Then press **Enter**.
- Press the number key corresponding to the screen you want on the keypad.

Pressing the **Help** key brings up a brief description of each menu.

C.1.15 Main Screen — Voltammetry

Figure C-15 illustrates the **MAIN** screen for the Voltammetry mode. The **MAIN** screen provides a large graphic character display of the measured current (Amperes) and other primary functions for Voltammetry mode.

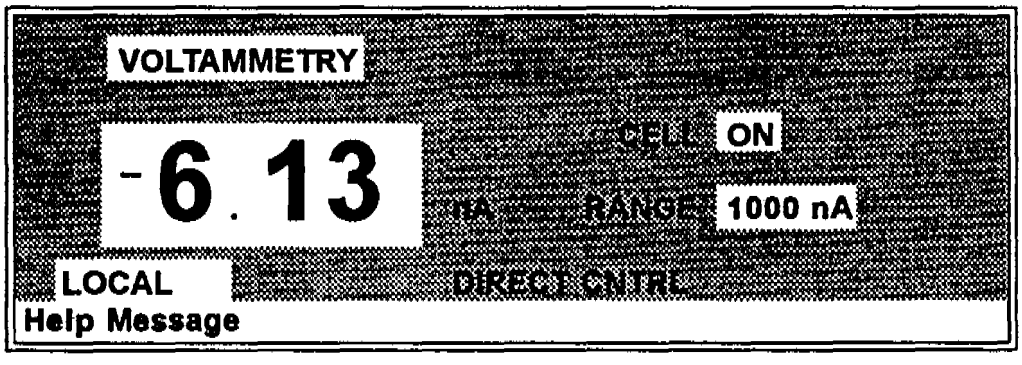


Figure C-15. Main Screen — Voltammetry

Detector Operating Mode	Selects the detector operating mode: Conductivity, DC Amperometry, Integrated Amperometry, or Voltammetry.
CELL	Turns the amperometry cell off or on, disabling or enabling detection.
RANGE	Sets the detector sensitivity between 1 nA to 100 µA.
DIRECT CNTRL	In Voltammetry mode, the detector is always in Direct control mode. Because methods do not apply to Voltammetry, this field cannot be changed.
Control Mode	Sets the detector to Local, Remote, or Locked Remote control.

C.1.16 Detail Screen — Voltammetry

Figure C-16 shows the **DETAIL SCREEN** for Voltammetry mode. The **DETAIL SCREEN** contains all the fields that the **MAIN SCREEN** contains. In addition, the **DETAIL SCREEN** contains TTL and Relay fields and other fields to control detection.

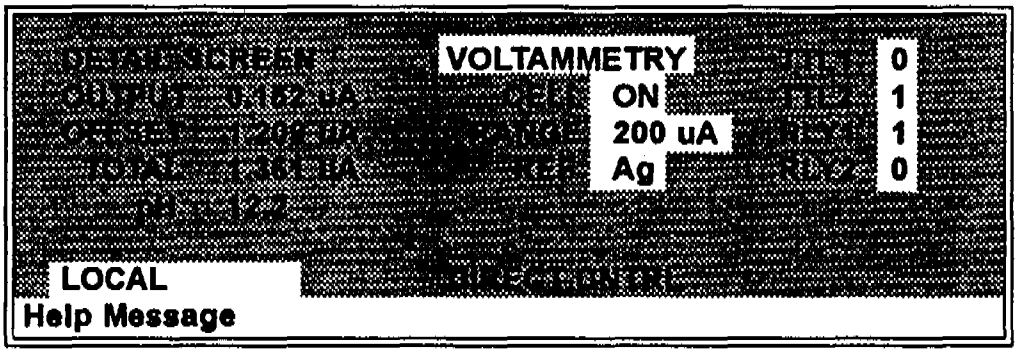


Figure C-16. Detail Screen — Voltammetry

The following fields appear on the **DETAIL SCREEN**. Refer to the **MAIN SCREEN** for a description of the other fields.

REF	Sets the reference electrode to either the pH or Ag/AgCl half cell.
pH	Displays the mobile phase pH.
TTL1 **TTL2**	Provides TTL control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).
RLY1 **RLY2**	Provides relay control of accessories. In a method, these values occur according to the method timing. In Direct control, select off (0) or on (1).

C.1.17 Waveform — Voltammetry

Figure C-17 shows the **WAVEFORM** screen for Voltammetry. These entries form points on a plot of Potential vs. Time.

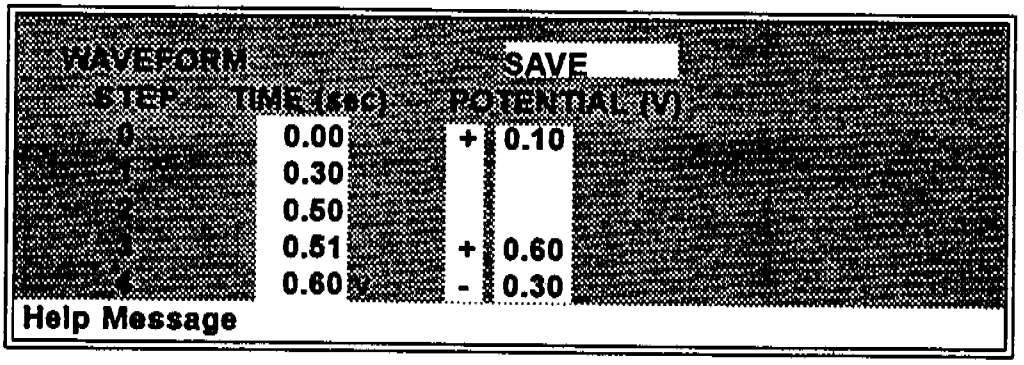


Figure C-17. Waveform — Voltammetry

When the last step displayed is not the last step in the waveform, a lower case **v** displays next to the time digits in the last line.

TIME — Specifies the time for this step to begin. Times must be entered chronologically.

POTENTIAL — This is two fields. The first sets the polarity. The second is the point in the waveform for this voltage.

SAVE — Move the cursor to this field and press **Enter** to save the waveform.

C.1.18 Module Set-up

Figure C-18 illustrates the **MODULE SET-UP** screen. Use this screen to configure the backlight intensity, key-beep, and error-beep.

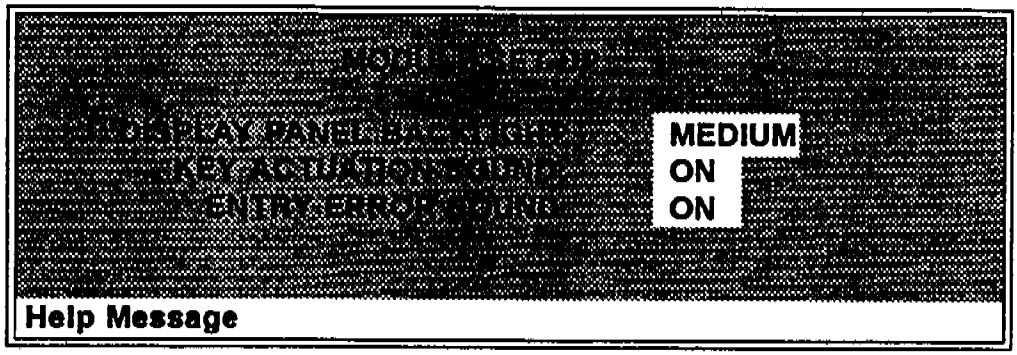


Figure C-18. Module Setup

DISPLAY PANEL BACKLIGHT	Sets the display panel backlight to LOW, MEDIUM, or HIGH.
KEY ACTUATION SOUND	Toggles the keypad touch sound. When on, the detector sounds a beep when a key is pressed.
ENTRY ERROR SOUND	Toggles the error sound. When on, the detector sounds a beep when an invalid entry is made.

C.1.19 Analog Out Setup

Figure C-19 shows the **ANALOG OUT SET-UP** screen. This screen contains parameters for setting the analog output, such as for a recorder or oscilloscope.

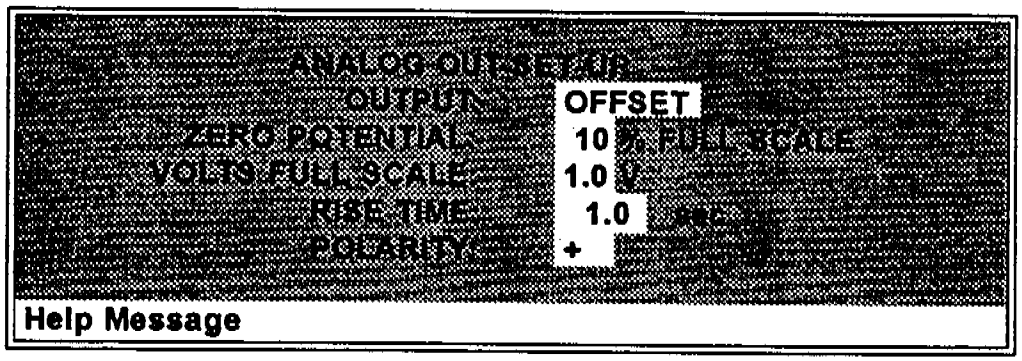


Figure C-19. Analog Out Setup

OUTPUT — Sets the analog output to one of the following:
OFFSET uses the offset level value.
TOTAL sets the detector output to the total cell conductivity, charge or current, disabling the Offset function.
ZERO sets the detector output to zero volts.
FULL SCALE sets the output to the full-scale setting.

OFFSET LEVEL — Sets the percent of full scale that the analog output will go to when Offset is pressed.

VOLTs, FULL SCALE — Sets the full-scale voltage for a signal equal to the range setting. The three choices are 1.0, 0.1, and 0.01 Volts.

RISE TIME — Sets the analog output filter rise time to 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, or 10.0 seconds. Rise time is a measure of how quickly the detector responds to a change in signal. The filter is a Bessel filter for optimum noise rejection and low signal distortion.

POLARITY

Determines the output voltage polarity. Typically, the output is set to positive polarity. Negative polarity is used to reverse peaks from indirect detection.

C.1.20 Time Function In

Figure C-20 shows the **TIME FUNCTION IN** screen. Four input TTL controls may be assigned between seven functions. Control is enabled when Local mode is selected.

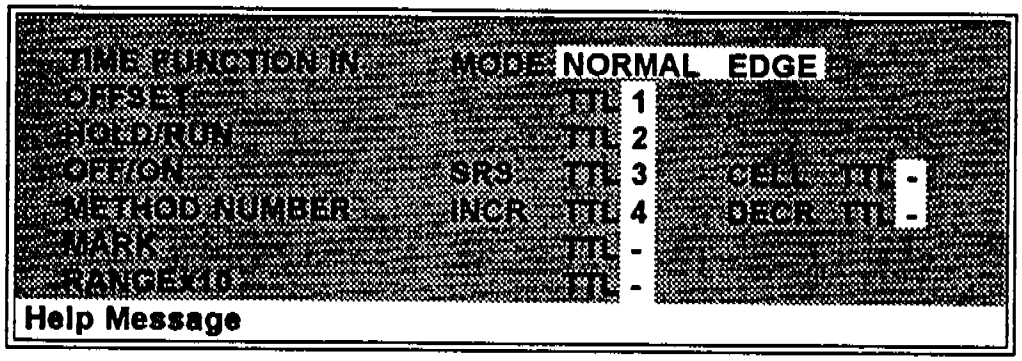


Figure C-20. Time Function In

Use the **Select** keys to assign TTL1 through TTL-4 to any four of the seven time functions. TTL input ports can also be assigned to the **INCR** and **DECR** fields to increase or decrease the method number.

C.2 Diagnostics

The Diagnostic screens for the ED40 Electrochemical Detector are defined in this section. Diagnostics are accessed by selecting the **DIAGNOSTICS MENU** from the **MENU of SCREENS**. While in the diagnostic system, the **Menu** key returns you to the **DIAGNOSTIC MENU**. From here, the **Menu** key returns you to the **MENU of SCREENS**.

C.2.1 Diagnostic Menu

Figure C-21 shows the **DIAGNOSTIC MENU**. It contains ten submenus that comprise the diagnostic system.

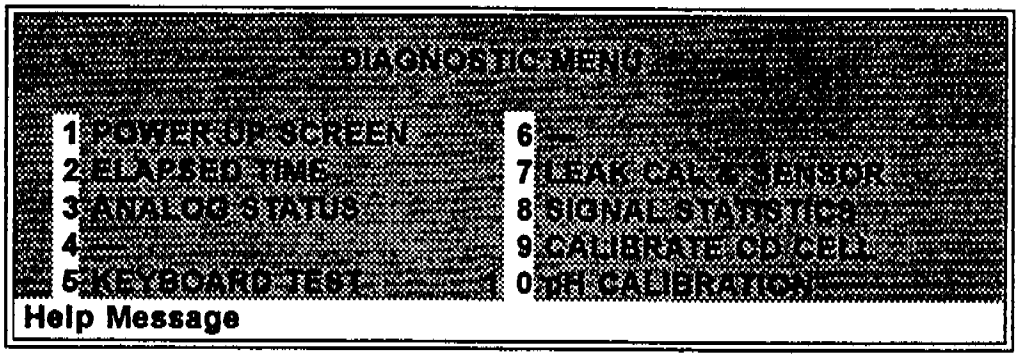


Figure C-21. Diagnostic Menu

Each of these diagnostic screens is explained in detail in the following sections.

Diagnostic screen 7, **LEAK CAL & SENSOR**, is available only when in Conductivity mode and a leak detector is connected.

Diagnostic screen 9, **CALIBRATE CD CELL**, is available only in Conductivity mode.

Diagnostic screen 10, **pH CALIBRATION**, is available only in Integrated Amperometry, DC Amperometry, and Voltammetry modes.

C.2.2 Power-Up Screen

Figure C-22 shows the Power Up screen. This screen displays the Moduleware revision number and the BIOS code revision number. When the ED40 is connected to a PC via the DX LAN, updated Moduleware can be downloaded from the PC to the ED40.

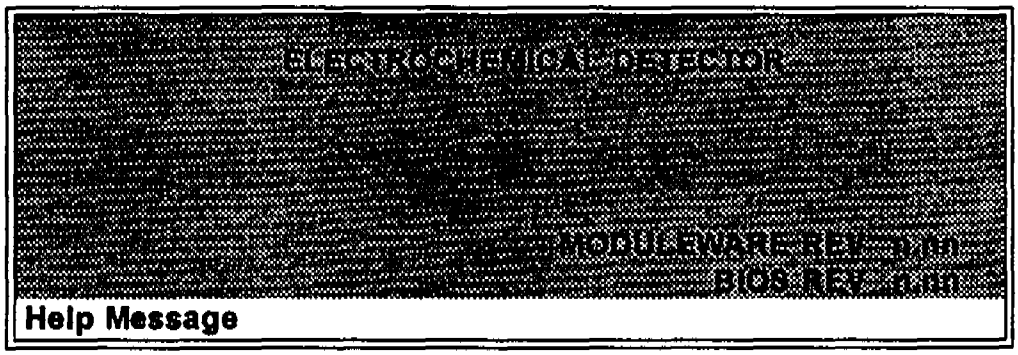


Figure C-22. Power-Up Screen

C.2.3 Elapsed Time

Figure C-23 shows the **ELAPSED TIME** screen. This screen reports the time used (in hours) of various parameters of the ED40. Each status updates in real time.

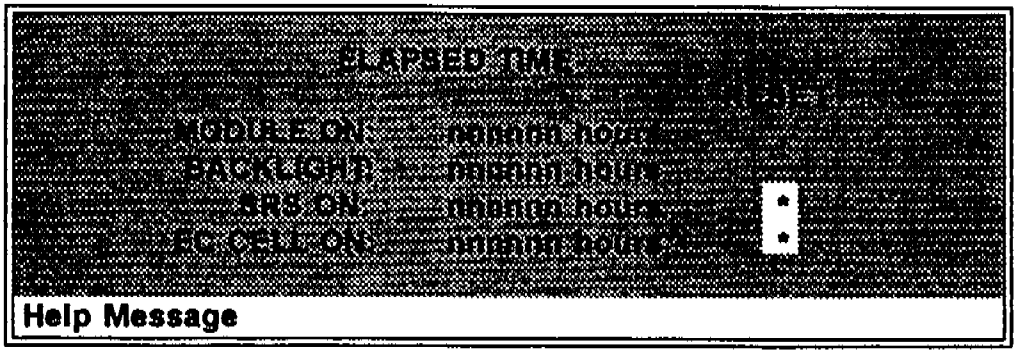


Figure C-23. Elapsed Time

MODULE ON — Reports the total time the module has been powered up in its lifetime.

BACKLIGHT — Reports the total time the LCD display backlight has been on in its lifetime.

SRS ON — Reports the total time the SRS has run. This field can be reset to zero when the SRS is changed.

EC CELL ON — Reports the total time the amperometry cell has run. This field can be reset to zero when the cell is replaced.

RESET — Selection of the reset causes the corresponding timer to be set to zero. The appropriate timer should be reset when a new component is installed.

C.2.4 Analog Status

Figure C-24 shows the **ANALOG STATUS** screen. This screen reports the status of the ED40 dynamic parameters. The status updates in real time.

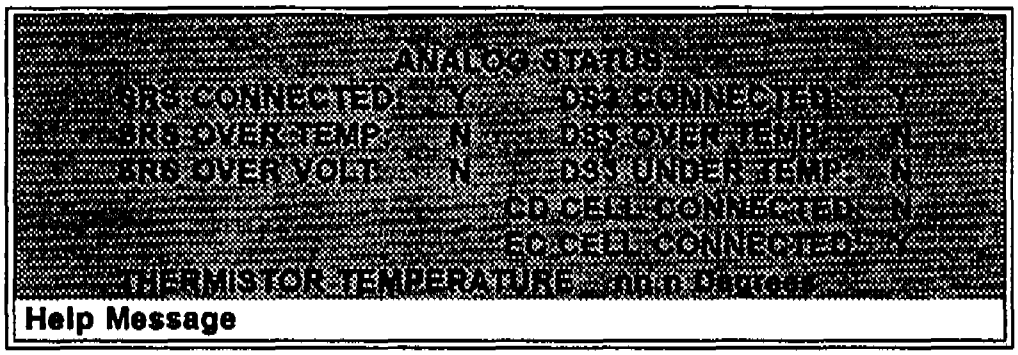


Figure C-24. Analog Status

SRS CONNECTED	Indicates whether an SRS is connected to the detector.
SRS OVER TEMP	Indicates whether the SRS is over the temperature specified.
SRS OVER VOLT	Indicates whether the SRS is over the voltage range specified.
DS CONNECTED	Indicates whether a DS3 is connected to the detector.
DS3 OVER TEMP	Indicates whether the DS3 is over the temperature specified.
DS3 UNDER TEMP	Indicates whether the DS3 is under the temperature specified.
CD CELL CONNECTED	Indicates whether the conductivity cell is connected to the detector.
EC CELL CONNECTED	Indicates whether the amperometry cell is connected to the detector.

THERMISTOR TEMPERATURE	Indicates the temperature recorded from the conductivity cell thermistor.

C.2.5 Keyboard Test

Figure C-25 shows the **KEYBOARD TEST** screen. This screen provides an interactive test of the keypad keys. When you press any key, the corresponding key indicator on the display changes to reverse video. When the key is released, the display returns to normal video.

Press the **Menu** key twice in succession to exit this diagnostic.

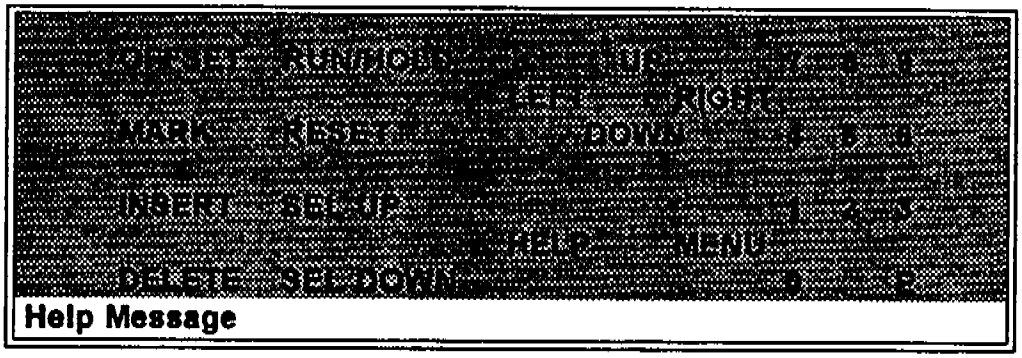


Figure C-25. Keyboard Test

C.2.6 Leak Calibration and Sensor

Figure C-26 shows the **LEAK CALIBRATION AND STATUS** screen.

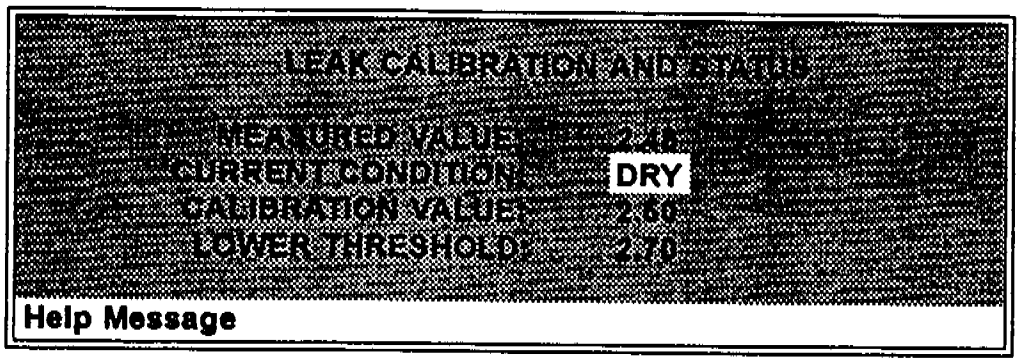


Figure C-26. Leak Calibration and Sensor

MEASURED VALUE	Reports the measured voltage from the leak sensor.
CURRENT CONDITION	Reports the current (error) conduction of the leak sensor: WET, DRY, or ERR. Error indicates an open or short circuit. You can calibrate a leak sensor by selecting **CAL** and pressing **Enter**. After calibration, the field will revert to DRY or ERR.
CALIBRATION VALUE	Reports the value saved when the leak sensor was last calibrated.
UPPER THRESHOLD	Reports the threshold value above which a leak is indicated. This is based on the calibration value.
LOWER THRESHOLD	Reports the threshold value below which a leak is indicated. This is based on the calibration value.

C.2.7 Signal Statistics

Figure C-27 shows the **SIGNAL STATISTICS** screen. This screen monitors the selected input to the A/D circuitry from the time the screen is selected until you exit the screen. Press the **Enter** key to exit.

When you first enter the screen, the **INPUT**, **MAX**, and **MIN** status values will all be equal to the Input value, and **DURATION** will read 0. The status values are reported in A/D volts and update dynamically.

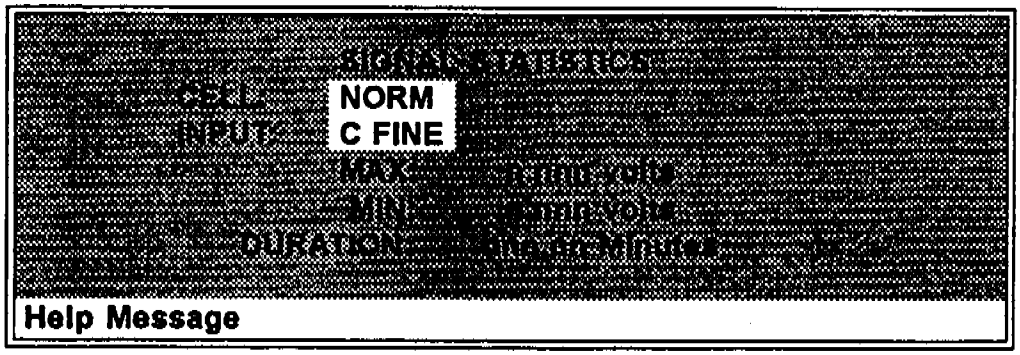


Figure C-27. Signal Statistics

CELL — The mode of the cell for the test:
NORM — Input data is used from the cell.
FIXED — Uses a fixed dummy cell for input.

INPUT — The measured data from the A/D circuit:
C FINE — Conductivity cell fine input
C COARSE — Conductivity cell coarse input
C THER — Conductivity cell thermistor input
E FINE — Amperometry cell fine input
E COARSE —Amperometry cell coarse input
E pH — Amperometry cell pH input
LEAK — Leak detector input
DRIVE — Cell drive circuit input

MAX — The maximum input data value during the duration of the test.

MIN	The minimum input data value during the duration of the test.
DURATION	The duration (in minutes) of the test. The test starts when you enter this screen and terminates when you exit.

C.2.8 Calibrate Conductivity Cell

Figure C-28 shows the **CALIBRATE CONDUCTIVITY CELL** screen. This screen allows the calibration of the conductivity cell with 1 mM KCl.

Figure C-28. Calibrate Conductivity Cell

CONDUCTIVITY — Reports the measured conductivity from the conductivity cell.

Calibrate — Select **CAL** and press **Enter** to calibrate the conductivity cell to the value displayed in the conductivity field. The calibration assumes that the cell is full of 1 mM KCl. The new value replaces the previous calibration value.

C.2.9 pH Calibration

Figure C-29 shows the **pH CALIBRATION** screen. This screen allows calibration of the pH reference electrode in the amperometry cell with either Na correction or linear (no correction).

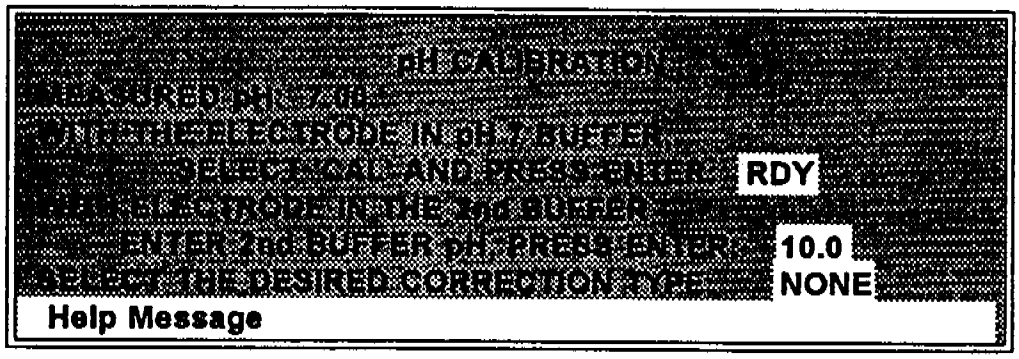


Figure C-29. pH Calibration

The steps in this screen must be performed in sequence. Two calibrations are required.

- The first calibration should be done at pH 7.0. With the electrode in pH 7.0 buffer solution, verify that the measured pH field displays 7.0. If not, press **Select** and then **Enter**.
- The second calibration should be done with another buffer solution of known pH. For example: pH 10.0.

MEASURED pH	Reports the pH measured from the electrode.
SELECT CAL	**RDY** indicates no selection has been made. Calibration will not occur. Select **CAL** and press **Enter** to calibrate the electrode for pH 7.0.

2nd BUFFER	Enter the known pH of the second buffer solution. With the reference electrode in the second buffer solution, press **Enter** to perform the second calibration.
CORRECTION TYPE	Selects whether a correction for sodium will be applied to the calibration.

D • Signal Processor Functions

D • Signal Processor Functions

Table D-1 shows the functions of the Signal Processor (SP) card.

Function	Cond.	DC Amp.	Int. Amp.	Volt-ammetry
Temperature compensation digital-to-analog converter	X			
Cell chopper, driver	X			
Offset digital-to-analog scaling switch	X			
Conductivity signal receiver	X			
Second stage amplifier and gain switch	X			
Synchronous rectifier	X			
5 mS Noise Filter	X	X		X
DC amplifier 100 mS filter	X	X		
Bipolar cell drive analog-to-digital converter		X	X	X
Amperometry cell drive smoothing filter		X	X	X
pH slope and offset corrector		X	X	X
Cell receiver/driver		X	X	X
Fine and coarse integrators			X	
Signal selection (MUX)	X	X	X	X
16-bit analog-to-digital converter	X	X	X	X
Digital interface	X	X	X	X

Table D-1. SP Card Functions

E • Connector Pin-Outs

This appendix contains all connector pinout descriptions.

E.1 Recorder/Diagnostic Signals

This section describes the Recorder/Diagnostic Signal pinouts.

Pin	Signal
1	Recorder Negative
2	Recorder Positive
3	SRS Supply Voltage
4	DS3 Supply Current
5	Conductivity Cell Flow Stream Temperature
6	Amperometry Cell Flow Stream pH
7	Amperometry Cell Voltage, Working to Reference Electrode
8	+10 V Reference from SCR Card
9	Integrated Amperometry Scope Sync. Pulse
10	Common Ground for Signals 3 through 9

Table E-1. Recorder/Diagnostic Cable Pinouts

The connector is supplied plugged into the socket The pins numbered consecutively from 1 to 10 (top to bottom).

E.1.1 Signal Electrical Parameters

Pin 2 Three Full-Scale output ranges may be selected using the **ANALOG OUTPUT** screen.

0 to 0.01 V
0 to 0.1 V
0 to 1.0 V

Output resistance is 1 to 2 kΩ.

Pin 3 Negative voltage is equal to that developed across the SRS. The SRS is driven by a regulated current source.

The output resistance is 10 kΩ.

Pin 4 Voltage is proportional to the DS3 heater current. The maximum heater power produces approximately 1.2 V.

The output resistance is 5 kΩ.

Pin 5 The voltage is related to the inverse exponential of the temperature. Table E-2 lists the Conductivity Flow Stream Temperatures.

°C	Volts	Slope (-mV / °C)
0	2.00	88
5	1.71	75
10	1.42	63
15	1.18	52
20	0.97	43
25	0.80	35
30	0.65	28
35	0.53	23
40	0.45	20
45	0.35	15
50	0.30	13

Table E-2. Conductivity Flow Stream Temperatures

The output resistance is 1 kΩ.

Pin 6 The voltage is proportional to the pH, after calibration, as indicated in Table E-3.

pH	Volts
0	-0.7
1	-0.6
2	-0.5
3	-0.4
4	-0.3
5	-0.2
6	-0.1
7	0.0
8	0.1
9	0.2
10	0.3
11	0.4
12	0.5
13	0.6
14	0.7

Table E-3. Amperometry Cell Flow Stream

The output resistance is 900 Ω.

Pin 7 The voltage is equal to the applied amperometry cell voltage.

The output resistance is 790 Ω.

Pin 8 The signal on this pin is 10.00 ± 0.01 V.

The output resistance is 0 Ω.

The maximum load current capability is 10 mA. Note that this output may be divided with a resistor network to provide an offset to a monitoring device. Avoid shorting or overloading this output or normal operation of the SCR module will be disrupted.

Pin 9 — 0 to 5 V logic pulse of 1 mS duration at the start of each integrated amperometry waveform cycle (time zero on the WAVEFORM screen).

The output resistance is approximately 100 Ω.

The maximum current is approximately 10 mA.

Pin 10 — A signal ground (0 Volts) for monitoring only. Avoid connecting this pin to any grounds or sources of AC or DC current. This ground may be used in common for any of the signals on pins 3 through 9.

E.2 TTL/Relay Pinouts

The TTL and Relay connectors are on the LAN/Relay card. Table E-4 lists the TTL/Relay connector pinouts. The TTL and Relay connectors all have the same pinout configuration. Be careful to use the correct connector.

Connector Number	Pin Number	Description
Relay 1	1 and 2	Solid State Relay Contacts Out
Relay 2	1 and 2	Solid State Relay Contacts Out
Relay 3	1 2	TTL Out (1 kΩ pull up to +5, 100 mA sink) Ground
Relay 4	1 2	TTL Out (1 kΩ pull up to +5, 100 mA sink) Ground
Relay 5	1 2	Input TTL 1 Ground
Relay 6	1 2	Input TTL 2 Ground
Relay 7	1 2	Input TTL 3 Ground
Relay 8	1 2	Input TTL 4 Ground

Table E-4. TTL/Relay Pinouts

E.3 DS3 Connector Pinouts — SCR

The DS3 connects to the SCR card. Table E-5 lists the SCR connector pinouts. The connector is a double row, 1.6 cm (0.63 in) latching displacement connector.

Pin Number	Description
1	DS3 Ground (body)
2	+ 24 V
3	Base Drive
4	Emitter
5	Emitter
6	Thermistor Ground
7	Thermistor
8	Leak +5 V
9	Leak
10	Lead Ground
11	Disconnect
12	Disconnect Ground (24 gauge)

Table E-5. DS3 Connector Pinouts

E.4 SRS Connector Pinouts — SCR

The SRS connects to the SCR card. Table E-6 lists the SCR connector pinouts. The connector is a double row, 0.84 cm (0.33 in) latching displacement connector.

Pin Number	Description
1	Ground
2	Thermistor
3	SRS Positive
4	SRS Negative
5	Disconnect
6	Disconnect (Ground)

Table E-6. SRS Connector Pinouts

E.5 Amperometry Cell Connector Pinouts — SP

The amperometry cell connects to the SP card. Table E-7 lists the pinouts for the amperometry cell connector. The amperometry cell connector is a single row, shielded BERG-type latching connector.

Pin Number	Description	Color (inside cable)
1	Ground, Counterelectrode	Black
2	Working Electrode	Red
3	pH Reference Electrode	Brown
4	Ag/AgCl Reference Electrode	Orange
5	+ 15 V	Yellow
6	- 15 V	Blue
7	Amperometry Cell Disconnect	Green
8	Spare	Purple

Table E-7. Amperometry Cell Connector Pinouts

E.6 Conductivity Cell Connector Pinouts — SP

The conductivity cell connects to the SP card. Table E-8 lists the conductivity cell connector pinouts. The connector is a single row, shielded, BERG-type, latching connector.

Pin Number	Description	Color (inside cable)
1	Cell Drive	Red COAX
2	Ground (Thermistor & Shield)	All COAX
3	Thermistor	Black COAX
4	Cell Return	Red COAX
5 - 8	Grounded (Plug Body Shield)	On Receptacle Only, Not on Plug

Table E-8. Conductivity Cell Connector Pinouts

F • Further Reading

F • Further Reading

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