Instruction Manual

HI 84500
FREE & TOTAL SULFUR DIOXIDE
MINITITRATOR
for wine analysis
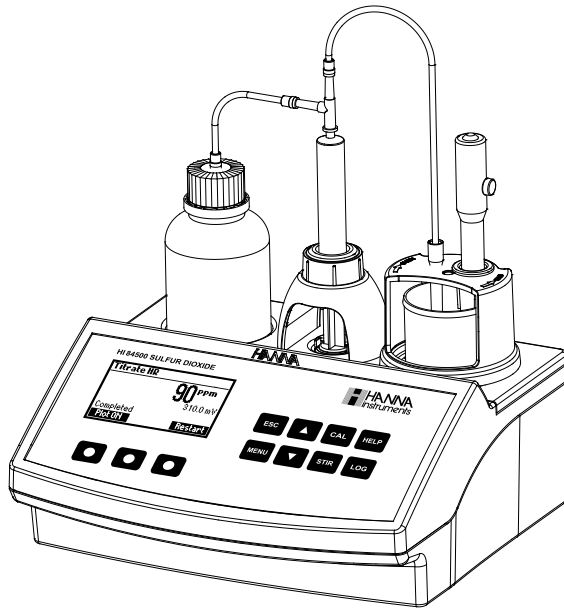
HANNA®
instruments

www.hannainst.com

Dear Customer,

Thank you for choosing a Hanna Instruments product.

Please read this instruction manual carefully before using this instrument. This manual will provide you with the necessary information for correct use of this instrument, as well as a precise idea of its versatility.

If you need additional technical information, do not hesitate to e-mail us at tech@hannainst.com or view our worldwide contact list at www.hannainst.com.

TABLE OF CONTENTS

PRELIMINARY EXAMINATION

Please examine this product carefully. Make sure that the instrument is not damaged. If any damage occurred during shipment, please notify your Dealer.

Each **HI 84500** minititrator is supplied complete with:

- **HI 84500-70** Reagent Kit for SO_2 determination
- **HI 3148B** ORP electrode
- **HI 7082** Electrode Fill Solution (30 mL)
- Two 100 mL beakers
- Two 20 mL beakers
- Scissors
- Dosing Pump Valve
- 5 mL Syringe
- 1 mL Plastic Pipette
- Tube set (aspiration tube with titrant bottle cap and dispensing tube with tip)
- Stir bar
- Power Adapter
- Two sachets of cleaning solution for wine deposits
- Two sachets of cleaning solution for wine stains
- Instruction manual

Note: Save all packing material until you are sure that the instrument works correctly. Any defective item must be returned in its original packing.

GENERAL DESCRIPTION

The **HI 84500** is a low-cost, easy to use, microprocessor-based automatic titrator that benefits from Hanna's years of experience as a manufacturer of analytical instrumentation.

The instrument incorporates a simple and reliable dosing pump which ensures high dosing reproducibility. Pump calibrations, performed with the provided Hanna reagents, assure the accuracy of the instrument.

The instrument comes with a preprogrammed method for Free and Total Sulfur Dioxide measurements in wine. The instrument uses a powerful algorithm which analyzes the shape of the electrode response in order to determine when the titration has reached completion.

The **HI 84500** provides a simple user interface. By simply pressing the **Start** key in Titration mode, the instrument will automatically titrate the sample to the equivalence point and the results are immediately displayed in ppm. Another titration can be started immediately by pressing **Restart**.

A dedicated **HELP** key aids in setup, calibration, status and troubleshooting.
Other features:
- ORP meter
- Stirrer speed control
- Graphic mode to display the titration data
- Data can be stored using the log feature and then exported to a USB stick or transferred to a PC using the USB connection
- Log on demand for up to 400 samples (200 for mV measurements; 200 for titration results)
- GLP feature, to view calibration data for the pump

SIGNIFICANCE OF USE

Wine makers add sulfur dioxide to wine in order to inhibit bacteria and wild yeast growth and to serve as an antioxidant to prevent browning.

When SO_2 is added to wine, a portion of it becomes immediately bound while a remaining portion is unbound SO_2. The portion that is unbound is also called free; it is responsible for protecting the wine. The bound and unbound SO_2 together are referred to as total SO_2.

The relationship between the amount of SO_2 added and the amount of free SO_2 is complex. This relationship is governed by the total amount of SO_2 in the wine. The exact relationship between free and bound will vary wine to wine. The amount of free SO_2 depends on how much is added, how much was present before the addition and how much was immediately bound.

Free SO_2 exists in two forms. Bisulfite (HSO_3^-) is the predominante form but is relatively ineffective. Molecular SO_2 is the minor form and is responsible for protecting the wine.

The amount of molecular SO_2 available in wine is depended on the amount of free SO_2 present and the pH. Typically 0.8 ppm of molecular SO_2 provides adequate protection against bacteria growth and oxidation. In order to obtain this value for a wine sample that has a pH of 3.2 you would need 22 ppm of free SO_2, if the pH was at 3.5 you would need double, 44 ppm.

Molecular SO_2 can be detected by human senses at about 2.0 ppm. This level is needed for maximum protection of wine. Higher levels are needed for sweet and most notable, botrytised wine.

The **HI 84500** can be used to test for free and total SO_2 in all wines, including red, which are difficult to test using traditional methods associated with a distinctive color change to determine the end point.

pH	3.0	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9
Free SO_2	14	18	22	28	35	44	55	69	87	109

SPECIFICATIONS

| Titrator	Range	Low Range: 1.0 to 40.0 ppm of SO_2
		High Range: 30 to 400 ppm of SO_2
	Resolution	Low Range: 0.1 ppm
		High Range: 1 ppm
	Accuracy	Low Range: 3% of reading or ± 0.5 ppm @ 25 °C, whichever is greater
		High Range: 3% of reading or ± 1 ppm @ 25 °C, whichever is greater
		Sample volume 50 mL
	Titration method	Ripper method
	Principle	Equivalence point redox titration
	Pump speed	10 mL/min
	Stirring speed	700 rpm
		Log data Up to 200 samples
ORP meter	ORP meter	-2000.0 to 2000.0 mV
	ORP Resolution	0.1 mV
	ORP Accuracy	± 1 mV
	Log data	Up to 200 samples
ORP Electrode	**HI 3148B**	
Environment	0 to 50 °C (32 to 122 °F); max 95% RH non-condensing	
Power supply	12 Vdc power adapter	
Dimensions	235 x 200 x 150 mm (9.2 x 7.9 x 5.9")	
Weight	1.9 kg (67.0 oz.)	

REQUIRED REAGENTS

Code	Description
HI 84500-50	Low Range Titrant
HI 84500-51	High Range Titrant
HI 84500-55	Calibration Standard
HI 84500-60	Acid Reagent
HI 84500-61	Alkaline Reagent (Total SO_2)
HI 84500-62	Stabilizer Packet

PRINCIPLE OF OPERATION

The **HI 84500** determines the free and total sulfur dioxide concentration in wine using the Ripper method. Excess iodide added to the wine sample reacts with iodate introduced by the titrant to produce iodine.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
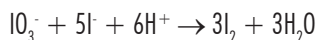
The iodine produced in the sample then reacts with sulfur dioxide in the wine according to the redox reaction below:

$$H_2SO_3 + I_2 \rightarrow H_2SO_4 + 2HI$$
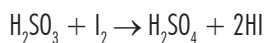
The **HI 84500** utilizes an ORP electrode to monitor the redox titration. The integrated algorithm detects when the reaction is complete (equivalence point). The volume of titrant required to reach the equivalence point, the titrant concentration and the sample size are used to calculate the sulfur dioxide concentration in the wine sample.

FUNCTIONAL DESCRIPTION

OVERHEAD VIEW

1) Titrant bottle
2) Liquid Crystal Display (LCD)
3) Keypad
4) Electrode holder
5) Dispensing tube
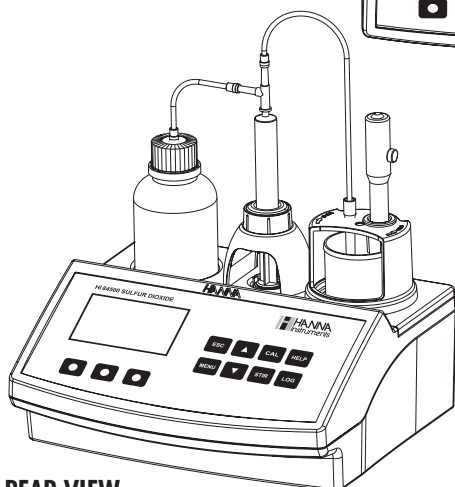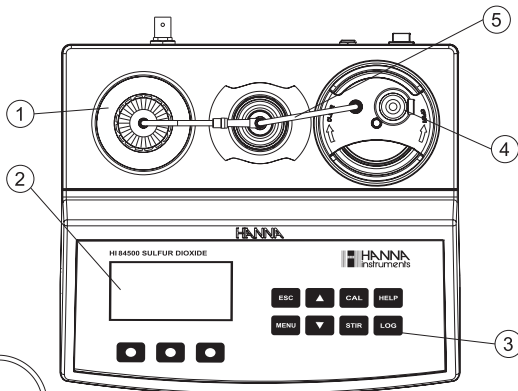
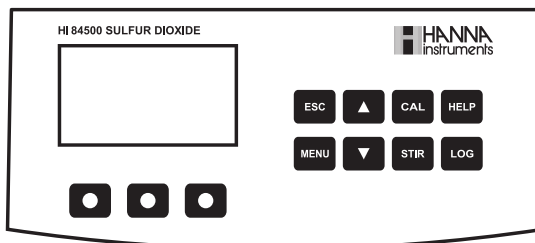**FRONT VIEW**

REAR VIEW

6) ORP Electrode
7) Beaker
8) Dosing pump
9) Power switch
10) Power adapter
11) USB connector (PC interface)
12) USB connector (Storage interface)
13) BNC electrode connector
14) Titrant bottle
15) Syringe
16) Aspiration tube
17) Dosing Pump Valve
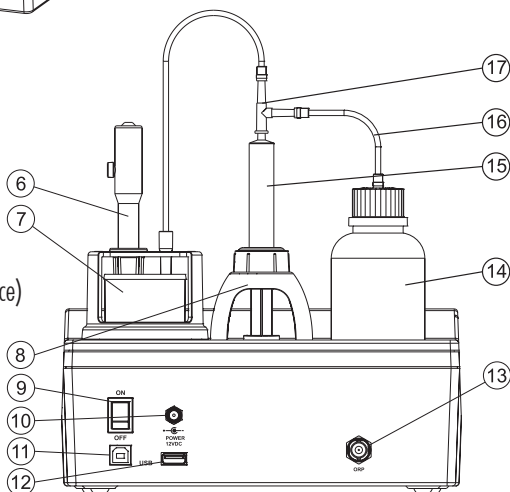
KEYPAD FUNCTION

ESC - used to leave the current screen and to return either to the previous screen or to the main screen. In Setup menu, exits a parameter without changing the value.

▼/▲ - used to modify the parameter values, to scroll the information displayed while viewing a help screen or to move between the options from the instrument's Setup menu

CAL - used to access the Pump calibration

HELP - used to access/exit the instrument's contextual help

LOG - used to save the current mV-ORP reading in ORP meter mode and the titration result

MENU - used to enter **Setup**, **Recall** or **GLP** selection menu, while instrument is in **ORP** or **Titration** mode

STIR - used to start/stop the stirrer

    Note: The stirrer starts automatically during pump calibration and titration, it cannot be stopped by pressing **STIR** key.

GUIDE TO INDICATORS

During the instrument's operation information is displayed on the LCD.
Displayed icons:

⊥ Stirrer on.	Pump running.	Unstable reading.
Stirrer is not working properly.		◆ Parameter can be modified.
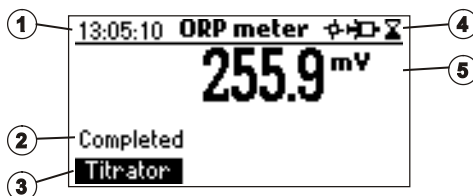
1) Current time and instrument mode information (ORP meter or Titrator)
2) Instrument status
3) Virtual option keys
4) Stirrer and reading status
5) Main reading information

DOSING PUMP

The dosing pump is based on a valve that automatically moves the titrant between the titrant bottle and syringe when filling the syringe and between the syringe and sample when dispensing. A replaceable 5 mL plastic syringe is used to limit the amount of titrant used per test to ensure the highest possible accuracy. Before a set of titrations, it is necessary to prime the dosing system.

Note: Once titrations have been completed, the dosing system should be cleaned with deionized water using the prime feature.

TITRATOR STARTUP

This is a general outline of the steps required to perform a titration. The following topics are expanded upon in each section that follows.

- Place the instrument on a flat table. Do not place the instrument in direct sun light.
- Connect the power adapter to the instrument.
- Turn the instrument ON using the power switch from the rear panel of the instrument.
- Set up the instrument. See the "Setup Menu" section for details.
- Connect the ORP sensor to the instrument.
- Connect the tubes and the valve. See the "Dosing Pump Installation" section for the procedure.
- Remove the titrant bottle cap and replace it with the bottle cap with tubes. Place the titrant bottle in the appropriate place on the titrator top.

Note: Different titrants are required based on the concentration. See "Pump Calibration Procedure" for details.

- Prime the syringe. To assure high accuracy, verify there are no air bubbles in the syringe or tubing.
- Calibrate the pump.

Note: Different volumes of standard are required based on the concentration. See "Pump Calibration Procedure" for details.

- Prepare the sample.
- Run a titration and log sample results.

SETUP MENU

The titrator's setup menu may be accessed from the main screen (meter or titrator mode) by pressing the **MENU** key, then **Setup**.

A list of setup parameters will be displayed with currently configured setting.

While in the setup menu it is possible to modify the instrument's operation parameters. The **ARROW** keys permit the user to scroll the setup parameters.

Press **HELP** to view the contextual help.

Press **ESC** to return to the main screen.

Range Setup

Meter setup	
Meas. Range	**Low**
Derivative Filter	☑
Threshold HR	450
Threshold LR	550
	High

Use **Low** measurement range for 1.0 - 40.0 ppm.

Use **High** measurement range for 30 - 400 ppm.

Use the appropriate titrant for each range.

To ensure a high accuracy, it is recommended to recalibrate the pump after the valve, titrant or electrode has been changed.

Derivative Filter

Meter setup	
Meas. Range	**Low**
Derivative Filter	☑
Threshold HR	450
Threshold LR	550
	Disable

Select **Enable** to activate or **Disable** to deactivate the derivative filter function.

If enabled, a filtering procedure of first derivate is applied that reduces the influence of mV noise that can appear due to chemical system properties, such as slow reaction or unbuffered wine sample, electrode response.

Threshold HR

Meter setup	
Meas. Range	**Low**
Derivative Filter	☑
Threshold HR	450
Threshold LR	550
	Modify

Threshold HR	
10	10000
	450
←	Accept	→

Press Modify to change the value.

The threshold value must be set by user in acording with wine sample analysis. It represents the absolute value of the first derivative expressed in mV/mL below which the detection algorithm does not search to equivalance point. Range between 10 and 10000 mV/mL. The recommended value for the threshold is around 40% of the estimated maximum absolute value of the first derivate.

Use the ARROW keys or ← / → to increase/decrease the value. Press Accept to confirm the value or ESC to return to the setup menu.

Threshold LR

Meter setup
Derivative Filter	☑
Threshold HR	**450**
Threshold LR	**550**
Time	**13:37:17**
	Modify

Threshold LR

10   10000

550

← | Accept | →

Time

Meter setup
Threshold HR	**450**
Threshold LR	**550**
Time	**13:37:33**
Date	**2015/02/03**
	Modify

Time

13:37:36

hh:mm:ss 24 Hours

Format | → | Accept

Date

Meter setup
Threshold LR	**550**
Time	**13:37:44**
Date	**2015/02/03**
Key Beep	☐
	Modify

Date

2015/02/03

yyyy/mm/dd

Format | → | Accept

Press **Modify** to change the value.
Note: To find the optimal threshold value follow the next steps:
- Set the maximum threshold value for selected range.
- Run the titration to reach the maximum titration volume.
- Use the dmV/dmL value displayed on the screen to estimate the optimal threshold (recommended value is 40% of this value).

Titrate LR
40.0 ppm
168.8 mV
Max. dmV/dmL value is 220
Plot ON   Restart
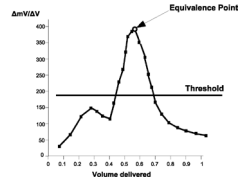
Press the **Modify** key to change the time and time format.

Press **Format** to switch between 12 hour (am/pm) and 24 hour mode.
Press → to highlight the value to be modified. Use the ARROW keys to change the value. Press Accept to confirm the new value or ESC to return to the setup.

Press the **Modify** key to change the date and date format.

Press **Format** to cycle between the available date formats.
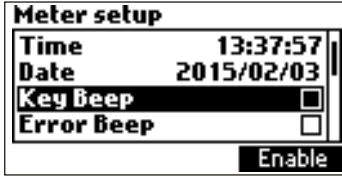Press → to highlight the value to be modified. Use the ARROW keys to change the value. Press Accept to confirm the new value or ESC to return to the setup.
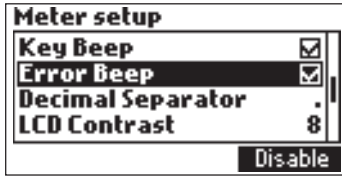
Key Beep

```
Meter setup
Time            13:37:57
Date          2015/02/03
Key Beep             □
Error Beep           □
                Enable
```

Select **Enable** to activate or **Disable** to deactivate the Key Beep function.

If enabled, a short beep will be heard every time a key is pressed.

Error Beep

```
Meter setup
Key Beep             ☑
Error Beep           ☑
Decimal Separator    .
LCD Contrast         8
               Disable
```

Select **Enable** to activate or **Disable** to deactivate the Error Beep function.

If enabled, a beep will be heard when an error condition occurs.

Decimal Separator

```
Meter setup
Key Beep             ☑
Error Beep           ☑
Decimal Separator    .
LCD Contrast         8

```
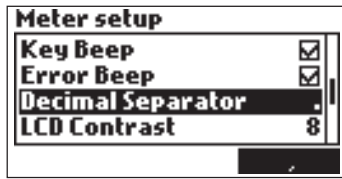
This option allows the user to select the symbol used for a decimal separator.

LCD Contrast

```
Meter setup
Error Beep           ☑
Decimal Separator    .
LCD Contrast         8
LCD Backlight        3
                Modify
```
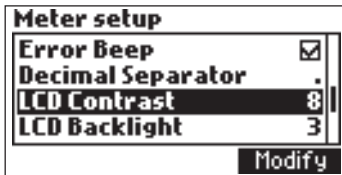
This option is used to set the display's contrast.
Press Modify to change the display's contrast.
The default value is 8.
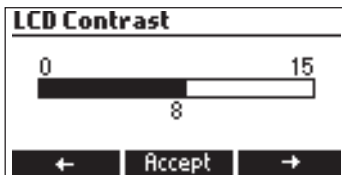
```
LCD Contrast

0                   15
        ▬▬▬
         8

    ←    Accept    →
```

Use the ARROW keys or ← / → to increase/decrease the value. Press Accept to confirm the value or ESC to return to the setup menu.

LCD Backlight

```
Meter setup
Decimal Separator    .
LCD Contrast         8
LCD Backlight        3
Language       English
                Modify
```
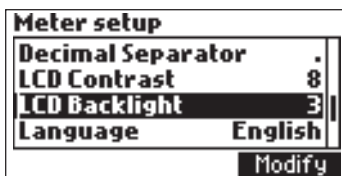
Press **Modify** to change the backlight level.
The default value is 3.

```
┌─────────────────────────┐
│ **LCD Backlight**       │
│                         │
│  0                  15  │
│  �█████████▌             │
│          7              │
│                         │
│  ←   │ Accept │   →    │
└─────────────────────────┘
```

Use the **ARROW** keys or ← / → to increase/decrease the backlight level.

Press **Accept** to confirm or **ESC** to return to the setup menu.

Language

```
┌─────────────────────────┐
│ **Meter setup**         │
│ **LCD Backlight**     3 │
│ **Language**    English │
│ **Tutorial**         ☑ │
│ **Meter Information**   │
│ Spanish │ Italiano      │
└─────────────────────────┘
```
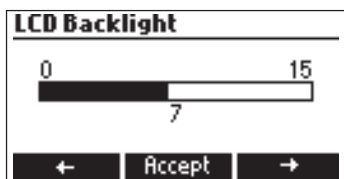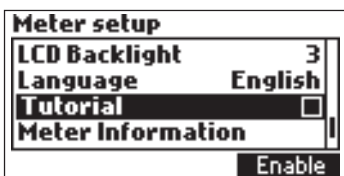
Press the corresponding virtual option key to change the language.

If the selected language cannot be loaded, the previously selected language will be reloaded.
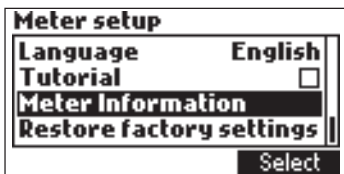
If no language can be loaded at startup the instrument will work in "safe mode". In "safe mode" all messages are displayed in English. Tutorial and help information are not available.
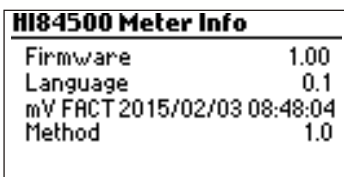
Tutorial

```
┌─────────────────────────┐
│ **Meter setup**         │
│ **LCD Backlight**     3 │
│ **Language**    English │
│ **Tutorial**         ☐ │
│ **Meter Information**   │
│                 Enable  │
└─────────────────────────┘
```

Enable or **Disable** the Tutorial. This helpful tool offers additional information during calibration and titration.

Meter Information

```
┌─────────────────────────┐
│ **Meter setup**         │
│ **Language**    English │
│ **Tutorial**         ☐ │
│ **Meter Information**   │
│ **Restore factory settings**│
│                 Select  │
└─────────────────────────┘
```
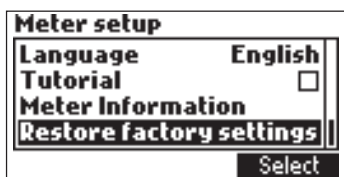
Press **Select** to view the firmware version, language version, mV factory calibration date and time, method version.

```
┌─────────────────────────┐
│ **HI84500 Meter Info**  │
│                         │
│ Firmware          1.00  │
│ Language           0.1  │
│ mV FACT 2015/02/03 08:48:04│
│ Method             1.0  │
│                         │
└─────────────────────────┘
```

Press **ESC** to return to the setup menu.

Restore Factory Settings

```
┌─────────────────────────┐
│ **Meter setup**         │
│ **Language**    English │
│ **Tutorial**         ☐ │
│ **Meter Information**   │
│ **Restore factory settings**│
│                 Select  │
└─────────────────────────┘
```

Press **Select** to restore the factory settings.

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Restore factory settings

Do you want to perform the current operation?

Yes　　　No
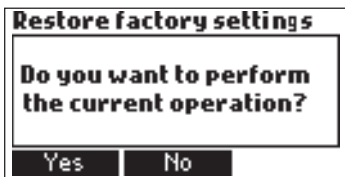
Press **Yes** to confirm the restore process or **No** to return without restoring.
Press **ESC** to return to the setup menu.

GUIDE TO DISPLAY CODES
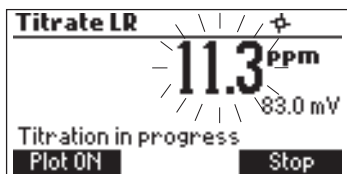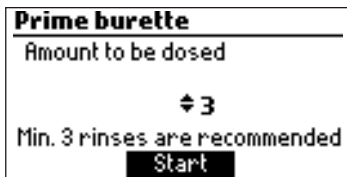
HANNA instruments

HI84500 v1.xx

This screen appears when the instrument is turned on during the initialization process.

Titrate LR

– – – –

Meter　　Start　　Prime

Titration screen display.

Titrate LR

11.3 ppm

83.0 mV

Titration in progress

Plot ON　　　　Stop

Titration screen when a titration is in progress.

Prime burette

Amount to be dosed

＄ 3

Min. 3 rinses are recommended

Start

Prime burette screen.

Prime burette

2 rinses left

Dispensing, wait...

Pause　　Stop

Prime burette screen when the dosing system is running.

15

Prime burette

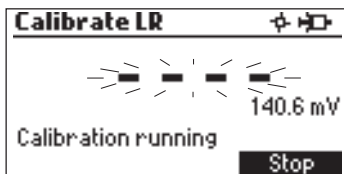**3 rinses left**

Pump Error
Restart

This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.

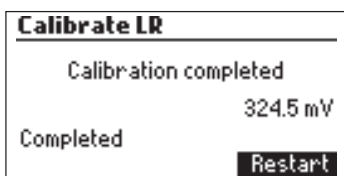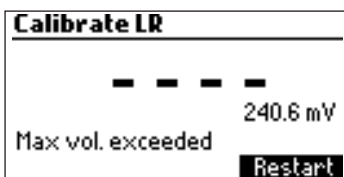## PUMP CALIBRATION MESSAGES

Calibrate LR

— — — —

Start   Prime
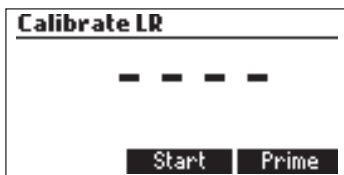
Pump calibration is initiated by pressing the **Start** key.
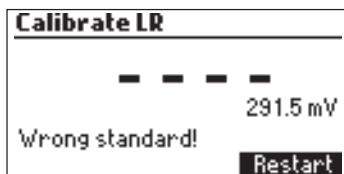
Calibrate LR

— — — —
140.6 mV

Calibration running
Stop

This screen appears while pump calibration is in progress. Press **ESC** or **Stop** key to return to the Pump Calibration screen.

Calibrate LR

Calibration completed
324.5 mV

Completed
Restart

This screen appears when pump calibration is complete.

Calibrate LR

— — — —
240.6 mV

Max vol. exceeded
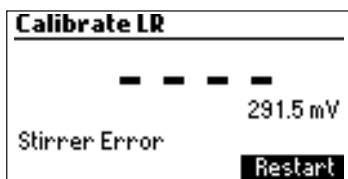Restart

This error message appears during pump calibration when the end point can not be reached and the maximum amount of titrant is exceeded. Check standard, electrode and/or dosing system and try again.

Calibrate LR

— — — —
291.5 mV

Wrong standard!
Restart

The calibration was outside the acceptable limits. Prepare a new standard and try again.
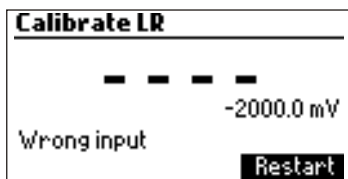
Calibrate LR

― ― ― ―

-2000.0 mV

Wrong input

Restart

This error message appears when the input reading (mV) exceeds the input limits ($\pm$ 2000.0 mV).

Calibrate LR

― ― ― ―

291.5 mV

Stirrer Error

Restart

This screen appears when the stirrer is not working properly. Check the stir bar and beaker content. Press **Restart** to try again.

Calibrate LR

― ― ― ―

291.5 mV

Pump Error
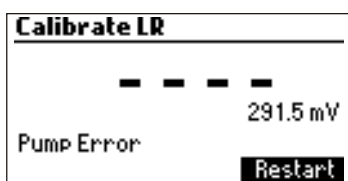
Restart

This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.

TITRATION MESSAGES

Titrate LR

― ― ― ―

Meter   Start   Prime
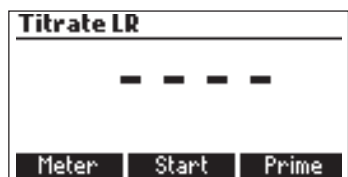
This screen is displayed when the instrument is in titration mode. Press **Start** to begin a titration, **Meter** to enter ORP meter mode or **Prime** to enter into the prime function.

Titrate LR

2.3 ppm
218.4 mV

Completed

Plot ON   Restart

The titration result, expressed as the concentration of sulfur dioxide in ppm (mg/L), is displayed automatically at the end of the titration. Press **Restart** to start another titration or **ESC** to return to the main screen.

Titrate LR

1.0 ppm
2000.0 mV

Wrong input

Plot ON   Restart

This error message appears when the input reading ($\pm$ 2000 mV) exceeds the input limits during a titration.

This screen appears when the sample concentration is out of range.

This screen appears when the first derivative is under the threshold value. Check the sample and threshold settings.
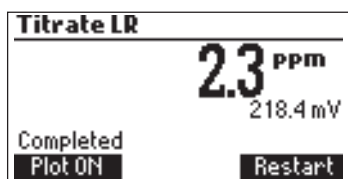

This screen appears when the stirrer is not working properly. Check the stir bar and beaker content. Press **Restart** to try again.
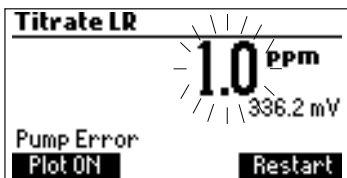
This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.
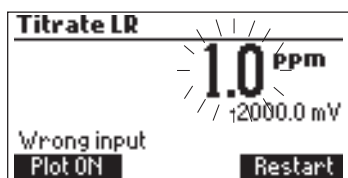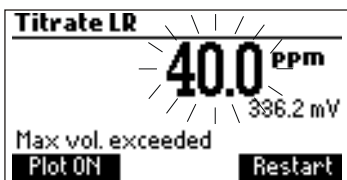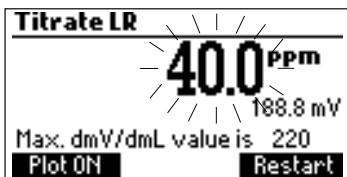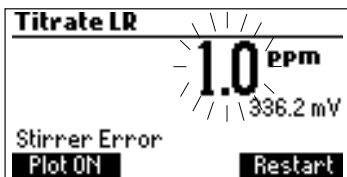
ELECTRODE PREPARATION

PREPARATION PROCEDURE

Remove the electrode protective cap.

DO NOT BE ALARMED IF ANY SALT DEPOSITS ARE PRESENT. This is normal with electrodes and they will disappear when rinsed with distilled/deionized water.

During transport tiny bubbles of air may have formed inside the glass bulb. The electrode cannot function properly under these conditions. These bubbles can be removed by "shaking down" the electrode as you would do with a glass thermometer.

If the bulb is dry, soak the electrode in **HI 70300** Storage Solution for at least one hour.

DOSING PUMP INSTALLATION

To install the dosing pump follow the procedure below:

- Extend the plunger on the 5 mL syringe to its maximum volume.
- Place the syringe in the dedicated spot on the top of the meter (1).
- Arrange the bottom of the syringe into the holder on the pump (2). Once the syringe is in place lower the barrel until it sits flush on the holder.
- Put the o-ring and syringe-fixing nut over the syringe (3) and turn clockwise to secure it in place (4).
- Place the valve on the top of the syringe (5). Ensure it fits securely.
- Insert the aspiration tube into the left side of the valve (6) and replace the titrant bottle cap with the attached cap (7).
- Insert the dispensing tube into the top of the valve (8).

Back side view
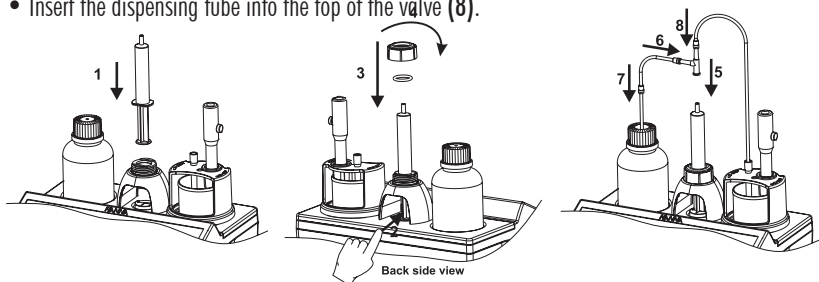
DOSING PUMP PRIME PROCEDURE

Prime cycle should be performed:

- if you notice there is no titrant in the tip
- whenever the dosing system tubes are replaced
- whenever a new bottle of titrant is used
- before starting a pump calibration
- before starting a series of titrations

The prime cycle is used to fill the syringe before starting a set of titrations.

Two rinse cycles of the syringe are shown in the figure below. The dispensing tube is connected to the top of the valve and the aspiration tube on the left side.
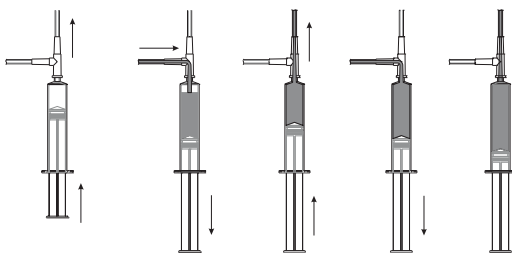
Note: • The aspiration tube must be inserted in the titrant bottle. The dosing tip must be placed over a rinse beaker.
• Before starting the prime procedure, make sure you are using the appropriate titrant solution for the selected range.

```
┌────────────────────────────────┐
│ Titrate LR                     │
│ ───────────────────────────────│
│                                │
│       ━   ━   ━   ━            │
│                                │
│                                │
│  Meter  │  Start  │  Prime     │
└────────────────────────────────┘
```
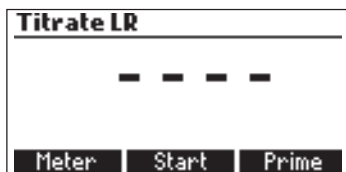
• To prime the burette, select **Prime** option from **Titration** mode.
• Adjust the rinses number by pressing the ▼ and ▲ keys and press **Start**.
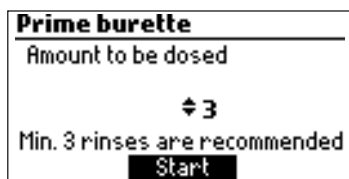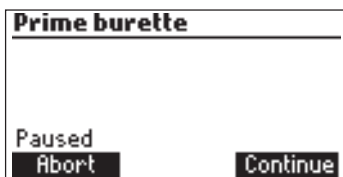
```
┌────────────────────────────────┐
│ Prime burette                  │
│ Amount to be dosed             │
│                                │
│              ⬍ 3               │
│ Min. 3 rinses are recommended  │
│            Start               │
└────────────────────────────────┘
```

• The number of syringe rinses can be set between 1 and 5 (at least three rinses are recommended

```
┌────────────────────────────┐   ┌────────────────────────────┐
│ Prime burette              │   │ Prime burette         ⊫⊐   │
│ ───────────────────────────│   │ ───────────────────────────│
│                            │   │                            │
│     3 rinses left          │   │     2 rinses left          │
│                            │   │                            │
│ Filling, wait...           │   │ Dispensing, wait...        │
│       Pause  │  Stop        │   │       Pause  │  Stop        │
└────────────────────────────┘   └────────────────────────────┘
```

to ensure that the air bubbles are completely removed).
• To pause the prime process press the **Pause** key; to continue press the **Continue** key. To stop the

```
┌────────────────────────────────┐
│ Prime burette                  │
│ ───────────────────────────────│
│                                │
│                                │
│ Paused                         │
│  Abort              Continue   │
└────────────────────────────────┘
```

prime process press the **Stop** key.

Note: This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.

```
┌────────────────────────────────┐
│ Prime burette                  │
│ ───────────────────────────────│
│                                │
│     3 rinses left              │
│                                │
│ Pump Error                     │
│          Restart               │
└────────────────────────────────┘
```

ELECTRODE CHECK PROCEDURE

Before taking any measurements with the **HI 84500** minititrator, it is recommended to check the **HI 3148B** ORP electrode using the following steps:

- Press **Meter** to enter mV mode.
- Pour roughly 15 mL of **HI 7021** into a 20 mL beaker. This does not need to be exact, as long as the PTFE junction is covered by the solution.
- Place the electrode in the solution, stir gently for a few seconds and verify the mV reading. If the mV reading is 240 ± 20 mV this indicates the electrode is in good condition and can be used for titrations. A mV reading of 240 ± 30 mV indicates the electrode is beginning to drift. Follow the "Electrode Conditioning and Maintenance", Probe Maintenance section on page 32. If the mV reading is greater than 240 ± 40 mV replace the electrode.
- Remove the electrode from the solution and rinse thoroughly with deionized or distilled water.

PUMP CALIBRATION PROCEDURE

Pump calibration must be performed every time the syringe, pump tube, the titrant bottle or the ORP electrode is changed. A pump calibration is recommended before each set of titrations or after the titrator is left idle for several hours.

- Press **MENU**, select **Setup** and select the corresponding range according to the table below:
- Ensure the pump is primed with the correct titrant for the selected range (**HI 84500-50** Low Range Titrant or **HI 84500-51** High Range Titrant).

Sample preparation: Use a clean pipette to precisely add the appropriate amount of **HI 84500-55 Calibration Standard** to a clean beaker as indicated below:

Low Range	High Range
1.0 to 40.0 ppm	30 to 400 ppm

Low Range (Free & Total SO_2) - 1 mL
High Range (Free & Total SO_2) - 10 mL

Note: Failure to use a clean pipette will result in erroneous readings.

- Fill the beaker up to the 50 mL mark with the distilled or deionized water.
- Fill the 20 mL beaker up to the 5 mL mark with the **HI 84500-60 Acid Reagent** and add the contents to the 100 mL beaker.
- Add the contents of one packet of **HI 84500-62 Stabilizer Packet** to the sample beaker.
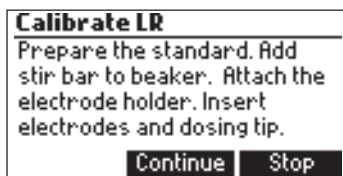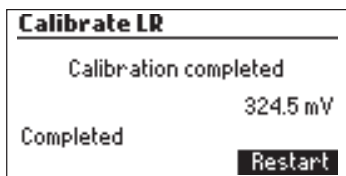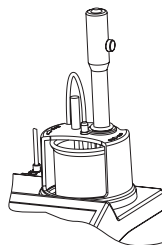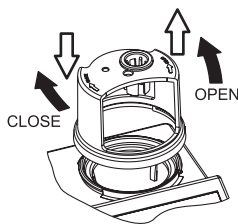

50 mL

HI 84500-60
Acid Reagent

HI 84500-62
Stabilizer

21
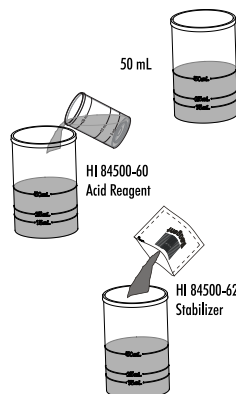
- Press **CAL** key.

Note: DO NOT PLACE THE TIP INTO THE CALIBRATION BEAKER, PLACE THE TIP OVER A WASTE BEAKER. A SMALL AMOUNT OF TITRANT IS DISPENSED WHEN THE PUMP RESETS.
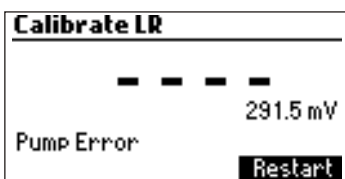
```
Calibrate LR
─────────────────────

      ▬   ▬   ▬   ▬

          Start   Prime
```
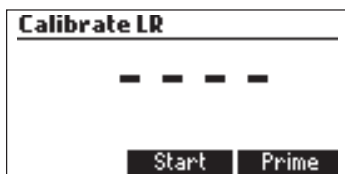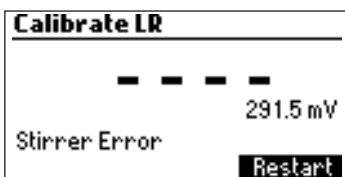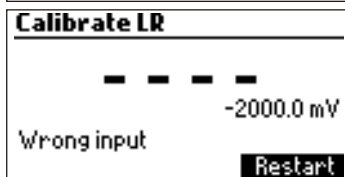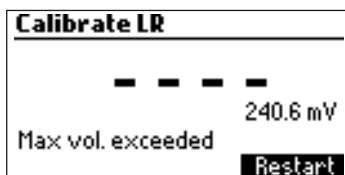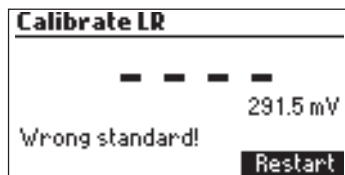
- Press **Start**, wait for the syringe to refill.
- Place the stir bar in the beaker and put the beaker in the minititrator top.
- Place the probe holder on the top of the beaker and secure it by turning clockwise.
- Rinse the ORP electrode with deionized water and immerse into the sample until the PTFE reference junction is completely submerged. Be sure that the tip of the electrode is not hitting the stir bar. If necessary additional distilled or deionized water can be added.
- Insert the dosing tip into the titrant tube sleeve. IT IS CRITICAL THAT THE TIP BE IMMERSED APPROXIMATELY 0.25 CM (0.1") INTO THE SOLUTION BEING TITRATED.
- Press **Continue** to begin the calibration and **Stop** to abort it.
- At the end of the calibration, "**Calibration Completed**" appears on display. To repeat the calibration press **Restart** and **ESC** to return to the main screen.

```
Calibrate LR
─────────────────────
    Calibration completed

                324.5 mV
Completed
                 Restart
```

```
Calibrate LR
─────────────────────
Prepare the standard. Add
stir bar to beaker. Attach the
electrode holder. Insert
electrodes and dosing tip.
       Continue   Stop
```

Note:

- If an erroneous situation is encountered during the calibration, an error message is displayed and the calibration can be restarted by pressing **Restart**. Prepare a new standard, rinse electrode and dosing tip and try again.

- If the calibration doesn't complete and the max titrant volume of titrant is reached, an error message will be displayed. The calibration can be restarted by pressing **Restart**. Prepare a new standard, rinse the electrode and dosing tip and try again.

- This error message appears when the input reading (mV) exceeds the input limits ($\pm$ 2000.0 mV).

- This screen appears when the stirrer is not working properly. Check the stir bar and beaker content. Press **Restart** to try again.

- This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.

Calibrate LR

— — — —

291.5 mV

Wrong standard!

Restart

Calibrate LR

— — — —

240.6 mV

Max vol. exceeded

Restart

Calibrate LR

— — — —

-2000.0 mV

Wrong input

Restart

Calibrate LR

— — — —

291.5 mV

Stirrer Error

Restart

Calibrate LR

— — — —

291.5 mV

Pump Error

Restart

FREE SO₂ MEASUREMENT PROCEDURE

- Refer to "Setup Menu" (see page 10) to set up the instrument for your measurement.
- For best accuracy, before taking any measurement, ensure that the pump is calibrated on the selected range following the "Pump Calibration Procedure" (see page 19).
- Select the corresponding range according to the table below:
- Ensure the pump is primed with the correct titrant for the selected range (**HI 84500-50** Low Range Titrant or **HI 84500-51** High Range Titrant).

Sample preparation: Use a clean pipette to precisely add the appropriate amount of wine sample to a clean 100 mL beaker as indicated below:

Low Range (50 mL sample)	High Range (50 mL sample)
1.0 to 40.0 ppm	30 to 400 ppm

Low Range (Free & Total SO₂) - 50 mL
High Range (Free & Total SO₂) - 50 mL

Note:
- The volume of wine added is critical to the measurement accuracy. Pipettes are recommended.
- Failure to use a clean pipette will result in erroneous readings.

- Fill the 20 mL beaker up to the 5 mL mark with the **HI 84500-60 Acid Reagent** and add the contents to the 100 mL beaker.
- Add the contents of one packet of **HI 84500-62 Stabilizer Packet** to the 100 mL beaker.
- Press **Titrator**.
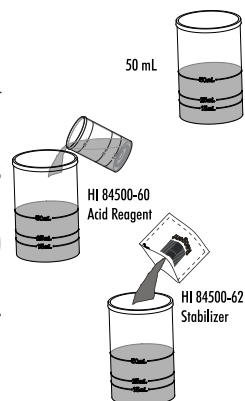
50 mL

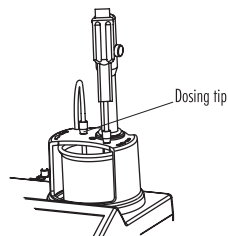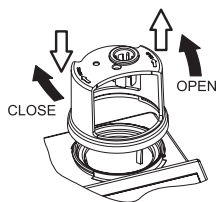HI 84500-60 Acid Reagent

HI 84500-62 Stabilizer

Note: DO NOT PLACE THE TIP INTO THE SAMPLE BEAKER. PLACE THE TIP OVER A WASTE BEAKER. A SMALL AMOUNT OF TITRANT IS DISPENSED WHEN THE PUMP RESETS.
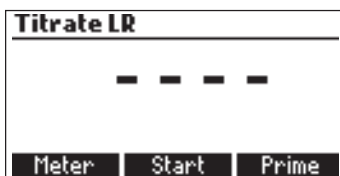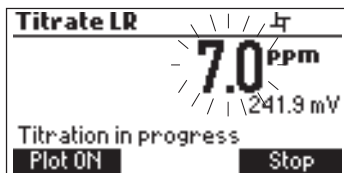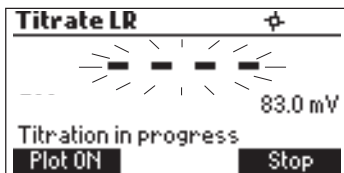
- Press **Start** to begin a titration.
- Wait for the syringe to refill.
- Place the stir bar in the beaker and put the beaker into the beaker holder.

- Place the probe holder on the top of the beaker and secure it by turning clockwise.
- Rinse the ORP electrode with deionized water and immerse into the sample until the PTFE reference junction is completely submerged. Be sure that the tip of the electrode is not hitting the stir bar.
- Insert the dosing tip into the titrant tube sleeve. IT IS CRITICAL THAT THE TIP BE IMMERSED APPROXIMATELY 0.25 CM (0.1″) INTO THE SOLUTION BEING TITRATED.
- Press **Continue** to begin the titration and **Stop** to abort it.

Titrate LR
Prepare the sample. Add stir bar to beaker. Attach the electrode holder. Insert electrodes and dosing tip.
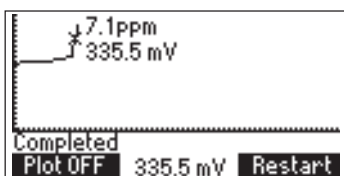
Continue   Stop

- The instrument will continuously update the concentration on the display. The value will be displayed blinking. When the reading is under range "----" symbol appears blinking.

Titrate LR
- - - -
83.0 mV
Titration in progress
Plot ON   Stop

Titrate LR
7.0 ppm
241.9 mV
Titration in progress
Plot ON   Stop

- The titration curve can be visualized during a titration by pressing **Plot ON**. Press **Plot OFF** to exit this mode.
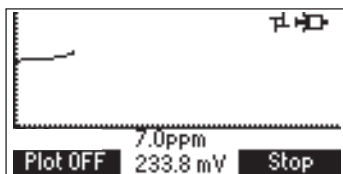
7.0ppm
Plot OFF   233.8 mV   Stop

- At the end of the titration the instrument displays the concentration in ppm of SO_2. The titration curve can be viewed by pressing **Plot ON**. Press **Plot OFF** to exit this mode.

Titrate LR
7.1 ppm
332.3 mV
Completed
Plot ON   Restart

7.1ppm
335.5 mV
Completed
Plot OFF   335.5 mV   Restart

25

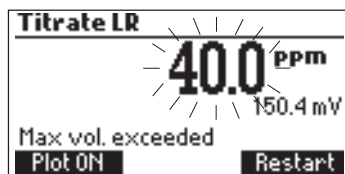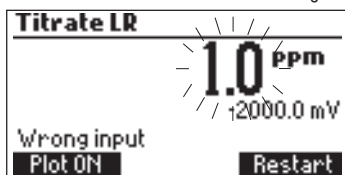- Press **LOG** to record the concentration value and the titration curve into the instrument's memory. A message will be displayed for a few seconds indicating the amount of free log space. Up to 200 log samples can be recorded in the instrument's memory.

```
┌─────────────────────────────────┐
│ Titrate LR                      │
│                                 │
│              7.1  ppm           │
│                  332.3 mV       │
│ Free Log space: 86%             │
│ ▌Plot ON         ▐   Restart▌   │
└─────────────────────────────────┘
```
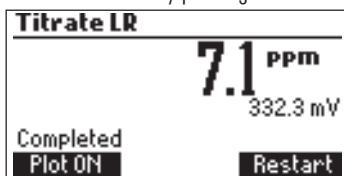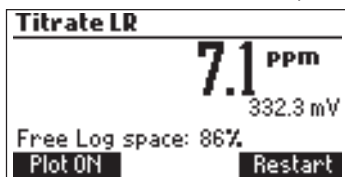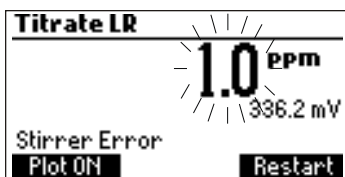
- Press **Restart** to begin a new titration or **ESC** to return to the titration menu.
- If the concentration exceeds the range limits (>40.0 ppm for **Low Range**, >400 ppm for **High Range**), the exceeded range limit will be displayed blinking. Another titration can be started by pressing **Restart**.
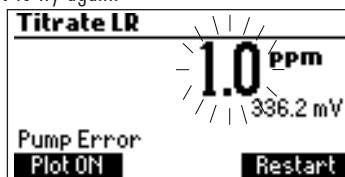
```
┌─────────────────────────────────┐
│ Titrate LR      \ | /           │
│              40.0  ppm          │
│                / | \ 150.4 mV   │
│ Max vol. exceeded               │
│ ▌Plot ON         ▐   Restart▌   │
└─────────────────────────────────┘
```

- "**Wrong input**" error message appears when the input reading (mV) exceeds the specified limits. The mV value and the concentration will blink indicating an error.

```
┌─────────────────────────────────┐
│ Titrate LR      \ | /           │
│               1.0  ppm          │
│              / / 2000.0 mV      │
│ Wrong input                     │
│ ▌Plot ON         ▐   Restart▌   │
└─────────────────────────────────┘
```

- This screen appears when the stirrer is not working properly. Check the stir bar and beaker content. Press **Restart** to try again.

```
┌─────────────────────────────────┐
│ Titrate LR      \ | /           │
│               1.0  ppm          │
│              / | \ 336.2 mV     │
│ Stirrer Error                   │
│ ▌Plot ON         ▐   Restart▌   │
└─────────────────────────────────┘
```

- This error message appears when the pump is not working properly. Check the tubing, valve and syringe. Press **Restart** to try again.

```
┌─────────────────────────────────┐
│ Titrate LR      \ | /           │
│               1.0  ppm          │
│              / | \ 336.2 mV     │
│ Pump Error                      │
│ ▌Plot ON         ▐   Restart▌   │
└─────────────────────────────────┘
```

TOTAL SO$_2$ MEASUREMENT PROCEDURE

- For best accuracy, before taking any measurement, ensure that the pump is calibrated on the selected range following the "Pump Calibration Procedure" (see page 19).

- Select the corresponding range according to the table below:

Low Range (50 mL sample)	High Range (50 mL sample)
1.0 to 40.0 ppm	30 to 400 ppm

Menu

Setup | GLP | Recall

- Ensure the pump is primed with the correct titrant for the selected range (**HI 84500-50** Low Range Titrant or **HI 84500-51** High Range Titrant).

Sample preparation: Use a clean pipette to precisely add the appropriate amount of wine sample to a clean 100 mL beaker as indicated below:

> Low Range (Free & Total SO$_2$) - 50 mL
> High Range (Free & Total SO$_2$) - 50 mL

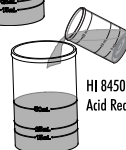Note: • The volume of wine added is critical to the measurement accuracy. Pipettes are recommended.

　　　• Failure to use a clean pipette will result in erroneous readings.

Wine sample

- Fill the 20 mL beaker up to the 5 mL mark with the **HI 84500-61 Alkaline Reagent**, add the contents to the 100 mL beaker containing the sample.

HI 84500-61 Alkaline Reagent

- Cover the beaker, swirl and wait for 10 minutes.

- Fill the 20 mL beaker up to the 5 mL mark with the **HI 84500-60 Acid Reagent**, add the contents to the 100 mL beaker containing the sample.

HI 84500-60 Acid Reagent

- Add the contents of one packet of **HI 84500-62 Stabilizer Packet** to the 100 mL beaker.

HI 84500-62 Stabilizer

- Place the beaker into the beaker holder.

- Press **Titrator**.
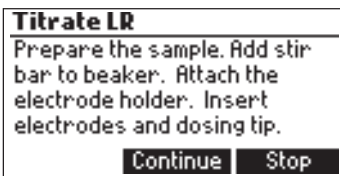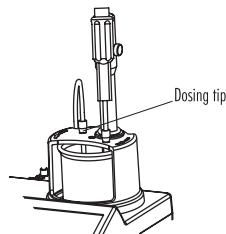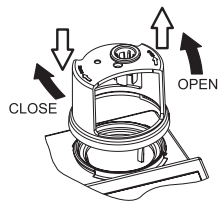
Note: DO NOT PLACE THE TIP INTO THE SAMPLE BEAKER. PLACE THE TIP OVER A WASTE BEAKER. A SMALL AMOUNT OF TITRANT IS DISPENSED WHEN THE PUMP RE-SETS.

Titrate LR

— — — —

Meter | Start | Prime

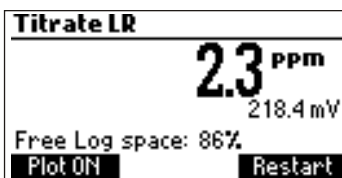- Press **Start** to begin a titration.

27

- Wait for the syringe to refill.
- Place the stir bar in the beaker and put the beaker into the beaker holder.
- Place the probe holder on the top of the beaker and secure it by turning clockwise.
- Rinse the ORP electrode with deionized water and immerse into the sample until the PTFE reference junction is completely submerged. Be sure that the tip of the electrode is not hitting the stir bar.
- Insert the dosing tip into the titrant tube sleeve. IT IS CRITICAL THAT THE TIP BE IMMERSED APPROXIMATELY 0.25 CM (0.1") INTO THE SOLUTION BEING TITRATED.
- Press **Continue** to begin the titration and **Stop** to abort it.

OPEN
CLOSE
Dosing tip

Titrate LR

Prepare the sample. Add stir bar to beaker. Attach the electrode holder. Insert electrodes and dosing tip.

Continue | Stop

- At the end of the titration the instrument displays the concentration in ppm of SO_2. The titration curve can be viewed by pressing **Plot ON**. Press **Plot OFF** to exit this mode. For more information about this feature, see page 22.
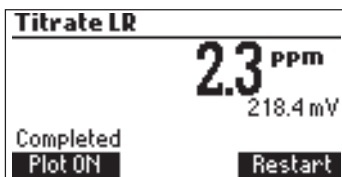
Titrate LR

2.3 PPM
218.4 mV

Completed
Plot ON | Restart

- Press **LOG** to record the concentration value and the titration curve into the instrument's memory. A message will be displayed for a few seconds indicating the amount of free log space. Up to 200 log samples can be recorded in the instrument's memory.

Titrate LR

2.3 PPM
218.4 mV

Free Log space: 86%
Plot ON | Restart

- Press **Restart** to begin a new titration or **ESC** to return to the titration menu.

<u>TIPS FOR AN ACCURATE MEASUREMENT</u>

The instructions listed below should be followed carefully to ensure measurements are conducted with the highest possible accuracy and precision.

- IT IS CRITICAL THAT THE TIP BE IMMERSED IN THE SOLUTION BEING TITRATED (APPROXIMATELY 0.25 CM).
- Use a clean, volumetric pipette to measure and transfer the wine sample into the titration beaker.
- Calibrate the pump prior to each series of titrations.
- Calibrate the pump if the meter is left idle for several hours.
- Analyze the wine sample immediately after it is obtained.
- Clean the electrode with **HI 700635** or **HI 700636** cleaning solutions specially designed for the wine industry.

VIEW/DELETE TITRATOR RECORDED DATA

Press **MENU** then **Recall** to access the **Titrator** logs.
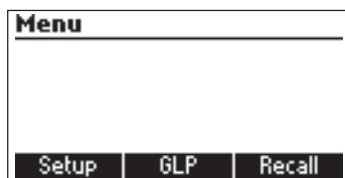
When an external USB storage device is connected, the **Export** key is displayed. It saves the meter and titrator logs in two text format files on the storage device.

Press **Meter** or **Titrator** to view the respective logs.

The instrument will display a list of all the records stored in the log.

Use the **ARROW** keys to scroll the stored records list.

If the saved concentration was out of range, the "<" or ">" symbols are displayed in front of the reading.
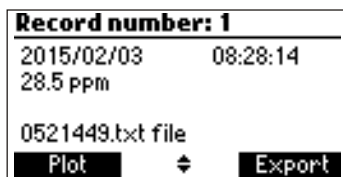

Press **Delete** to delete the selected log from the memory.

Press **Del.All** to delete all records.

Press **Info** to see detailed information about the highlighted record.

Record number: 1

2015/02/03   08:28:14
28.5 ppm

0521449.txt file

| Plot | ⬍ | Export |

The selected record data and the titration curve data file name are displayed.

When a USB storage device is connected, the **Export** key is displayed. It saves the titration curve data as a text file on the storage device using the displayed file name.

Use the **ARROW** keys when ⬍ is displayed to scroll between the log records.

Press **ESC** to return to the previous screen.

Record number: 1

2015/02/03   08:28:14
28.5 ppm

0521449.txt file
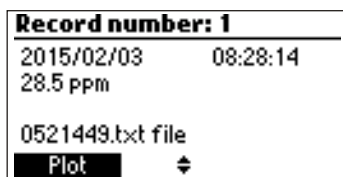
| Plot | ⬍ |

Press **Plot** to visualize the titration curve or **ESC** to return to the previous screen. On the titration curve, the end point volume and mV are displayed. The titration data (Total Titrant Volume on the x-axis and mV on the y-axis) can be scanned through with the dotted line by using the **ARROW** keys.

To zoom on the titration curve press **Zoom**.

2015/02/03 11:34:32

2.651mL
229.5mV

| 7.1ppm | ⬍ | Zoom |
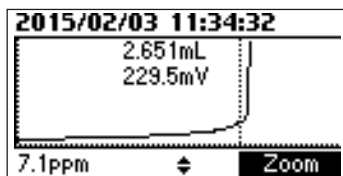
If **Delete** or **Del.All** is pressed the instrument will ask for confirmation.

Press **Yes** to delete the record or **No** to return to the previous screen.

Deleting a single record will renumber the list of records.

Delete Titrator log

Do you want to perform
the current operation?

| Yes | No |

Delete Titrator logs

Do you want to perform
the current operation?

| Yes | No |

If the titrator log is empty, the message **"No records available!"** will be displayed.

```
Titrator
─────────────────────────

    No records available!


```
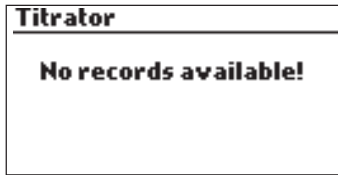
TITRATOR GLP INFORMATION

Press MENU then GLP.

```
Menu
─────────────────────────




│ Setup │ GLP │ Recall │
```
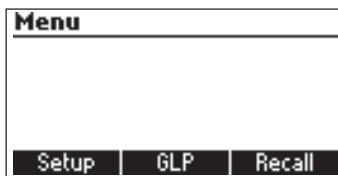
The **pump's last calibration** time, date and slope is displayed.

```
Last pump calibration LR
─────────────────────────
Date: 2015/02/03
Time: 15:51:33
Slope: 101.44%


```
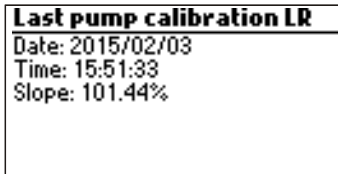
If a calibration hasn't been performed, the message **"Not Calibrated"** will be displayed.

```
Last pump calibration LR
─────────────────────────

    Not Calibrated


```
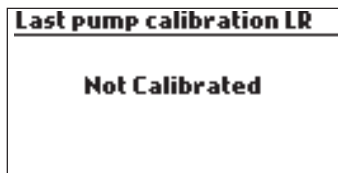
ORP MEASUREMENT

The **HI 84500** can be used as an ORP meter for direct measurements.

Set the instrument to **ORP meter**. From titrator mode press **Meter** until mV units are displayed.

Rinse the ORP tip with distilled or deionized water.

Place ORP electrode into electrode holder.

For a faster response and to avoid cross-contamination of the samples, rinse the electrode tip with a few drops of the solution to be tested before taking measurements.

Immerse the ORP sensor in the sample until the PTFE reference junction is completely submerged and stir gently for a few seconds.

When the reading becomes stable the Σ (unstable measurement) symbol will disappear.

If the potential reading is less than -2000.0 mV or greater than 2000.0 mV the closest full-scale value will be displayed blinking.
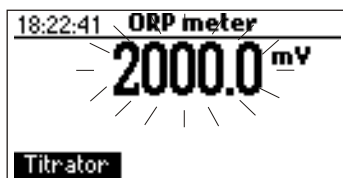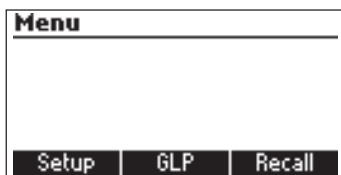

Press **LOG** to save the current reading.

During ORP measurements with stirrer on, the stirrer icon will be displayed. In case of a stirrer malfunction, the stirrer will stop and the stirrer icon will start blinking.
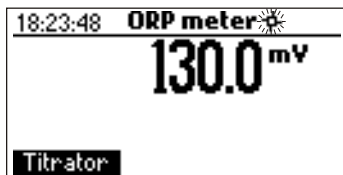
VIEW/DELETE RECORDED ORP DATA

To view or delete previously logged ORP records, press **MENU** then **Recall** to access meter logs.

When an external USB storage device is connected, the **Export** key is displayed. It saves the meter and titrator logs in two text format files on the storage device.

Press **Meter** or **Titrator** to view the respective logs.

The instrument will display a list of all the records stored in the log.

Use the **ARROW** keys to scroll the list of records.

If the saved ORP measurements are out of range, the "<" or ">" symbols are displayed in front of the reading.

```
    mV          Date
1   >2000.0     2015-02-03
2   122.4       2015-02-03
3   <-2000.0    2015-02-03
4   -100.0      2015-02-03
  Delete    Del.All    Info
```

Press **Delete** to delete the selected log from the memory.
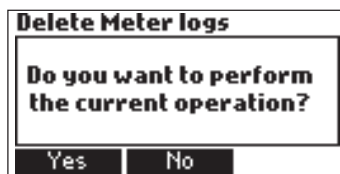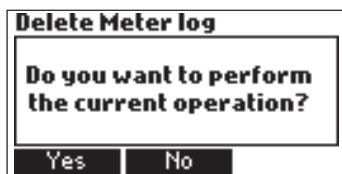
Press **Del.All** to delete all records.

Press **Info** to see detailed information about the highlighted record.

Use **ARROW** keys when ↕ is displayed to scroll between the records.

```
Record number: 4
2015/02/03          15:23:53
27.4 mV


              ↕
```

If **Delete** or **Del.All** is pressed the instrument will ask for confirmation.

```
Delete Meter log

Do you want to perform
the current operation?

  Yes        No
```

```
Delete Meter logs

Do you want to perform
the current operation?

  Yes        No
```

Press **Yes** to delete the record or **No** to return to the previous screen without deleting.

Deleting a single record will renumber the list of records.

If the ORP log is empty, the message "**No records available!**" will be displayed.

```
ORP meter

   No records available!


```

PC INTERFACE AND DATA TRANSFER

Data stored on the meter with the **LOG** function during mV measurement and titrations can be transferred from the meter to a **USB stick** using the **Export** function from the log recall menu. Two text files are transferred on the USB stick. These files can be used for further analysis on a PC.

The logged data can also be transferred from the instrument to the PC using a USB cable. Connect the USB cable and the following screen will be displayed.

Press **Meter** to generate the text file with Meter log data.

Press **Titrator** to generate the text file with Titrator log data.

Press **Plot** to generate the text files with Titration Plots.

Generate log text files

Select the logging data to be converted in text file

| Meter | Titrator | Plot |

The generated files are now visible and can be used fot further analysis.

If the instrument has no logged Meter or Titrator records, the PC connected screen is displayed.

PC connected...
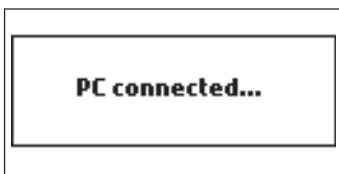
TROUBLESHOOTING GUIDE

SYMPTOMS	PROBLEM	SOLUTION
Slow response/excessive drift.	Dirty ORP electrode.	Soak the electrode tip in **HI 7061** cleaning solution for 30 minutes. Refill with fresh fill solution.
Reading fluctuates up and down (noise).	Cable connection.	Soak the electrode tip in **HI 7061** cleaning solution for 30 minutes. Refill with fresh fill solution. Check cable connection to meter and verify protective cap is off
While in ORP meter mode, -2000 or +2000 mV is displayed blinking.	Reading out of range.	Check cable connection to meter and verify protective cap is off. Check the quality of the sample. Clean the electrodes. Refill with fresh fill solution.
The pump calibration can't be performed	Valve, tubing, or syringe issue. Wrong or contaminated pump calibration solution. Broken ORP electrode.	Verify tubing, valve, syringe are intact and solution passes when pump is primed and no air bubbles are present. Check the pump calibration solution. Prepare another standard, prime the pump and restart the calibration.
After a titration, the instrument displays 40.0 mg/L - LR, 400 mg/L - HR blinking.	Broken electrode. Concentration out of range. Wrong range selected.	Check/clean the electrode. Recalibrate the pump. Select the correct range, recalibrate the pump.
At startup the meter displays the HANNA logo permanently.	One of the keys is stuck.	Check the keyboard or contact the vendor.
"Error xx" message is displayed.	Internal error.	Power off the meter and then power it on again. If the error persists, contact the vendor.

SYMPTOMS	PROBLEM	SOLUTION
"Stirrer error" message is displayed at the end of pump calibration or titration.	Check the stir bar and beaker content.	If the error persists, contact the vendor.
Non-spinning stirrer icon blinking in ORP meter mode.	Check the stir bar and beaker content.	If the error persists, contact the vendor.
"Pump error" message is displayed.	Check the tubing, valve and syringe.	If the error persists, contact the vendor.
At startup the meter displays "Methods corrupted".	The method file was corrupted.	Contact the vendor.

ELECTRODE CONDITIONING AND MAINTENANCE
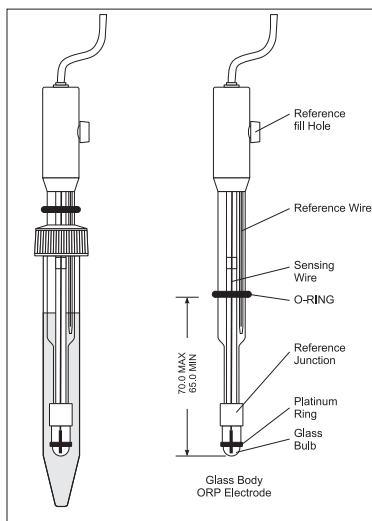
PREPARATION PROCEDURE

Remove the protective cap of the ORP electrode (**HI 3148B**).

DO NOT BE ALARMED IF SALT DEPOSITS ARE PRESENT. This is normal with electrodes. They will disappear when rinsed with distilled/deionized water.

During transport, tiny bubbles of air may have formed inside the glass bulb, affecting proper functioning of the electrode. These bubbles can be removed by "shaking down" the electrode as you would do with a glass thermometer.

If the bulb and/or junction is dry, soak the electrode in **HI 70300L** Storage Solution for at least one hour.

If the fill solution (electrolyte) is more than 2½ cm (1") below the fill hole, add **HI 7082** 3.5M KCl Electrolyte Solution.

For faster response, unscrew the fill hole screw during measurements.

STORAGE PROCEDURE

To minimize clogging and assure a quick response time, the glass bulb and junction of the electrode should be kept moist and not allowed to dry out.

Replace the solution in the protective cap with a few drops of **HI 70300L** Storage Solution or, in its absence, **HI 7082** Fill Solution. Follow the Preparation Procedure before taking measurements.

Note: NEVER STORE THE ELECTRODE IN DISTILLED OR DEIONIZED WATER.

PERIODIC MAINTENANCE

Inspect the electrode and the cable. The cable used for connection to the instrument must be intact and there must be no points of broken insulation on the cable or cracks on the electrode stem or bulb. Connectors must be perfectly clean and dry. If any scratches or cracks are present, replace the electrode. Rinse off any salt deposits with water.

PROBE MAINTENANCE

Refill the reference chamber with fresh electrolyte (**HI 7082**). Allow the electrode to stand upright for 1 hour. Follow the Storage Procedure above.

CLEANING PROCEDURE

- *Wine deposits*   Soak in Hanna **HI 70635** cleaning solution for 15 minutes
- *Wine stains*   Soak in Hanna **HI 70636** cleaning solution for 15 minutes

IMPORTANT: After performing any of the cleaning procedures, rinse the electrode thoroughly with distilled water, refill the reference chamber with fresh electrolyte and soak the electrode in **HI 70300** Storage Solution for at least 1 hour before taking measurements.

ACCESSORIES

REAGENTS

HI 84500-50	Low Range Titrant (230 mL)
HI 84500-51	High Range Titrant (230 mL)
HI 84500-55	Calibration Standard (120 mL)
HI 84500-60	Acid Reagent (230 mL)
HI 84500-61	Alkaline Reagent (120 mL)
HI 84500-62	Stabilizer Packet (100 pcs.)

ELECTRODE TEST SOLUTION

HI 7021M	ORP Test Solution (230 mL)
HI 7021L	ORP Test Solution (500 mL)

ELECTRODE

HI 3148B	ORP Electrode

ELECTRODE FILL SOLUTION

HI 7082	Electrode fill solution (4 x 30 mL)

ELECTRODE STORAGE SOLUTION

HI 70300L	Electrode storage solution (500 mL)

CLEANING SOLUTION

HI 70635L	Cleaning solution for wine deposits (500 mL)
HI 70636L	Cleaning solution for wine stains (500 mL)

OTHER ACCESSORIES

HI 70500	Tube set with cap for titrant bottle, tip and valve
HI 71005/8	115 Vac to 12 Vdc, 800 mA
HI 71006/8	230 Vac to 12 Vdc, 800 mA
HI 731319	Stir bar (10 pcs., 25 x 7 mm)
HI 740036P	Beaker 100 mL (10 pcs.)
HI 740037P	Beaker 20 mL (10 pcs.)
HI 740236	5 mL Syringe for minititrator
HI 920013	PC Connection Cable

WARRANTY

HI 84500 is guaranteed for two years against defects in workmanship and materials when used for it's intended purpose and maintained according to instructions. Electrodes and probes are guaranteed for six months. This warranty is limited to repair or replacement free of charge.

Damage due to accidents, misuse, tampering or lack of prescribed maintenance is not covered.

If service is required, contact your dealer from whom you purchased the instrument. If under warranty, report the model number, date of purchase, serial number and the nature of the problem. If the repair is not covered by the warranty, you will be notified of the charges incurred.

If the instrument is to be returned to Hanna Instruments, first obtain a Returned Goods Authorization number from the Technical Service department and then send it with shipping costs prepaid. When shipping any instrument, make sure it is properly packed for complete protection.

To validate your warranty, fill out and return the enclosed warranty card within 14 days from the date of purchase.

RECOMMENDATION FOR USERS

Before using this product, make sure that it is entirely suitable for your specific application and for the environment in which it is used.

Operation of this instrument may cause unacceptable interferences to other electronic equipment, this requiring the operator to take all necessary steps to correct interferences.

Any variation introduced by the user to the supplied equipment may degrade the instrument's EMC performance.

To avoid damages or burns, do not put the instrument in microwave ovens. For your's and the instrument's safety do not use or store the instrument in hazardous environments.