



Chlorine Amperometric Titrator

***AutoCAT*[™] 9000**

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Safety Information

Please read this entire manual before unpacking, setting up, or operating this instrument. Pay particular attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure that the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that which is specified in this manual.

Hazard Information

If multiple hazards exist, this manual will use the signal word (Danger, Caution, Note) corresponding to the greatest hazard.

DANGER

Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury.

CAUTION

Indicates a potentially hazardous situation that may result in minor or moderate injury.

NOTE

Information that requires special emphasis.

Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.



This symbol, when noted on the instrument, references this instruction manual for operational and/or safety information.



This symbol, when noted on the product, identifies the location of a fuse or current limiting device.

Specifications

Specifications are subject to change without notice.

Methods	
Titration methods	7 embedded methods
Titration stops	Automatic and manual titration termination
Titrant addition technique	Incremental
Titrant calibration	4 embedded procedures
Back titration with manual reductant addition	
Measuring Ranges	
Current ranges	2 μ A, 20 μ A, 200 μ A, 1 mAmp
Temperature range	-10 to +100 °C (14 to 212 °F)
Temperature resolution	0.1 °C (0.18 °F)
Printout	
Automatic, GLP compliant	
Selectable; OFF or 80 columns	
Detailed or condensed	
Graphic or no graphic	
Results	
QC check on results with visual warning	
Statistical calculations	
Units	
All standard units for samples/results	
Titration Curve	
Up to 2000 points can be stored	
Storage Capacity	
Global password protection for programming access	
Non-volatile memory	
Storage of 200 titration results	
Stored parameters characterized by own ID, location, and calibration data	
Embedded operating procedures for electrode and reagent exchange	
Automatic electrode, titrant calibration, and QC prompt	
Sample List	
Up to 126 data with alphanumeric ID	
QC sample definition	
Stirrer Platform	
Magnetic stirrer	22 reproducible speeds (0 to 1100 rpm) in 50-rpm increments
Beaker volumes	5- to 400-mL

Specifications

Burette	
Embedded burette stand	1
Burette volume	5- or 10-mL
ISO/FDIS 8655-3 compliant	
Burette step motor	18,000 steps
UV-protected encapsulated glass syringe	
Embedded operating procedures	Burette exchange, air bubble removal (Flush), Rinse, Fill, and Empty functions
Inputs/Outputs	
Electrode input	
Temperature input	
Serial connections for printer/PC	
PS/2 port for PC keyboard	
Language Options	
English and Spanish	
General Specifications	
Casing	Splashproof ABS plastic. Graphic 128 x 128-dot LCD and alphanumeric keypad
Dimensions (H x W x D)	380 x 230 x 450 mm (15 x 9 x 17¾ inch) excluding tubing
Weight	5 kg (11 lb) excluding reagent bottles
CE marking	EMC directive 89/336/EED Compliant LV directive 73/23/EEC Compliant
Power requirements	50/60 Hz (±3 Hz) 100/240 V ac (±10%) Pollution Degree II Overvoltage Category II
Fuses	Primary, User-serviceable. Slow-blow 1.0 A, 250 V Secondary, factory-serviceable only.
Environmental operating conditions	5 to 40 °C (41 to 104 °F) temperature range 20 to 80% relative humidity range

Section 1 Introduction

1.1 General Information

The AutoCAT 9000™ is an automated chlorine amperometric end point titration instrument. Its biamperometric system uses a dual platinum electrode (DPE) probe.

Hach offers amperometric methods for determining total chlorine*, free chlorine, sulfite, and chlorine dioxide in water. The chlorine dioxide procedure also provides a measurement of chlorite concentration.

Follow the steps listed in *Section 1.2, Instrument Startup Summary*, on page 9. After completing these steps, refer to the method calibrations and method procedures for instructions on specific analyses.

Amperometric titration theory and interferences are detailed in *Amperometric Titration Theory* on page 145.

1.2 Instrument Startup Summary

When you receive your AutoCAT 9000, proceed in the following order:

1. Unpack the instrument and inspect all parts for any damage that occurred during shipment. Refer to *Table 1* and *Figure 1* and *Figure 2* on page 24.
2. Assemble the instrument following the instructions in *Section 2* on page 13
3. Review *Basic Operation* on page 23 to familiarize yourself with the user interface and the keypad, navigation, and command keys.
4. Set the software parameters and configure the interface following the instructions given in *Section 4 Software Setup*.
5. Clean and condition the electrode according to section 9.1.4 on page 139.
6. The instrument is set up and ready to perform analyses. The default titrant concentration is adequate when using a fresh bottle of titrant but you may choose to calibrate the titrant using the procedures given in *Calibration Procedures* on page 49 or you can download the exact concentration of your titrant, see *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
7. At this time you may wish to run a few test samples to familiarize yourself with the instrument. We recommend that you use tap water to perform the Total Chlorine procedure in *Titration Procedures* on page 65.
8. If desired, you may choose to perform certain setup or configuration steps in *Basic Operation* on page 23 but they are not essential for using the instrument.

*Forward and Back titration methods are offered for the determination of Total Chlorine.

1.3 Unpacking

Remove the instrument and accessories from the shipping cartons and inspect each item for damage that may have occurred during shipment. Refer to *Table 1* and *Figure 1* on page 23 to verify that your order is complete.

Table 1 Packing List

Illustration Item Number	Catalog Number	Qty.	Product Description
Not shown	50083-00	1	AutoCAT 9000 Amperometric Titration Workstation
Not shown	18010-00	1	125 V ac power cord
1	—	1	Titration pick-up tubing
2	50082-40	1	Delivery tubing with plastic anti-diffusion tip
3	—	1	Desiccant column
4	50087-00	1	Temperature sensor, glass, 103-mm, CINCH plug
5	50086-00	1	Metal electrode, dual platinum wire, BNC plug
6	50082-10	1	Burette stand, 5-mL, red cover
7	50082-50	1	Bottle stopper for 500 mL and 1000 mL plastic titrant bottles
8	50085-00	1	Magnetic stir bar
9	50082-60	1	Bottle stopper for 1-L glass titrant bottle
10	50088-00	1	Bottle holder
11	—	1	Stop ring for electrode head (may be pre-assembled)
12	—	1	Metal key for burette plunger adjustment
13	50082-30	1	Metal rod for electrode head support, 20-mm, with stop ring
14	50082-80	1	Bayonet electrode head macro, with support
15	50082-70	1	Fuse, slow-blow 1.0 A, (5 x 20 mm)
16	A25B600	1	Tubing from stopcock to glass cylinder
Not shown	500-46H	1	Beaker, 250-mL
Not shown	1999-53	1	Titration, PAO standard solution, 0.00564 N, 1000-mL
Not shown	28341-00	1	KI SwifTest Dispenser
Not shown	1077-60	1	Refill vial for KI SwifTest Dispenser
Not shown	14909-32	1	Buffer, pH 4, 100-mL MDB
Not shown	21553-32	1	Buffer, pH 7, 100-mL MDB
Not shown	50081-18	1	User manual

If any items are missing or damaged, please contact Hach Company or your sales representative immediately.

1.4 User Access Levels

The AutoCAT offers two user access levels:

Supervisor allows users to edit titration and analysis parameters to fit specific needs. A Supervisor-level user can also assign a password to protect the data and customized settings from inadvertent changes.

Routine allows users to access only the routine functions when performing the embedded analyses.

Section 2 Instrument Assembly

2.1 Operating Environment

Maintain an ambient temperature of 5–40 °C (40–104 °F) for proper instrument operation. The relative humidity should be between 20 and 80%; do not allow moisture to condense on the instrument.

Note: Retain the original packaging material. Instruments returned for service should be shipped in the original packaging material to protect against damage during transportation.

Figure 1 Individual Parts (Refer to Table 1 for Part Descriptions)

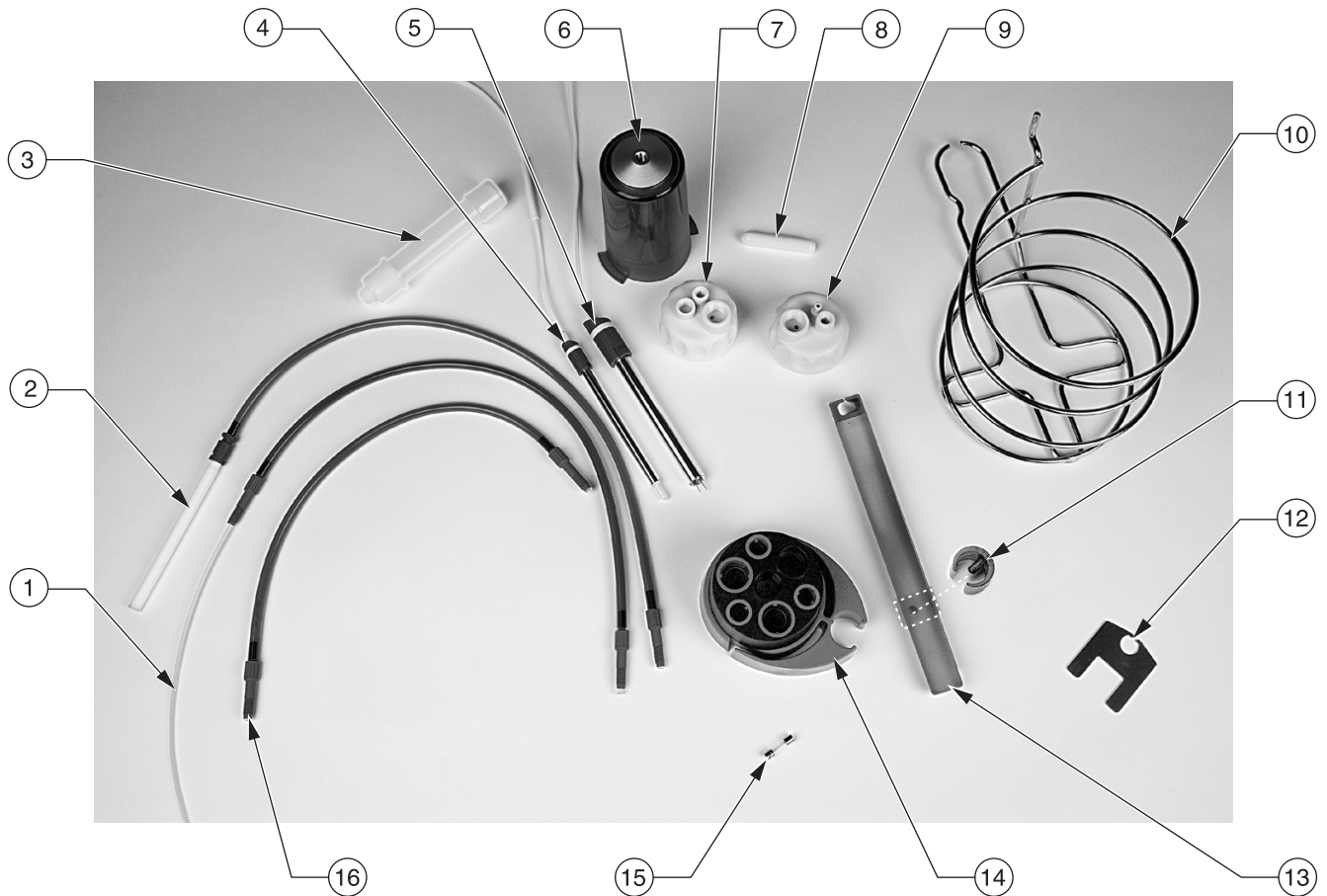
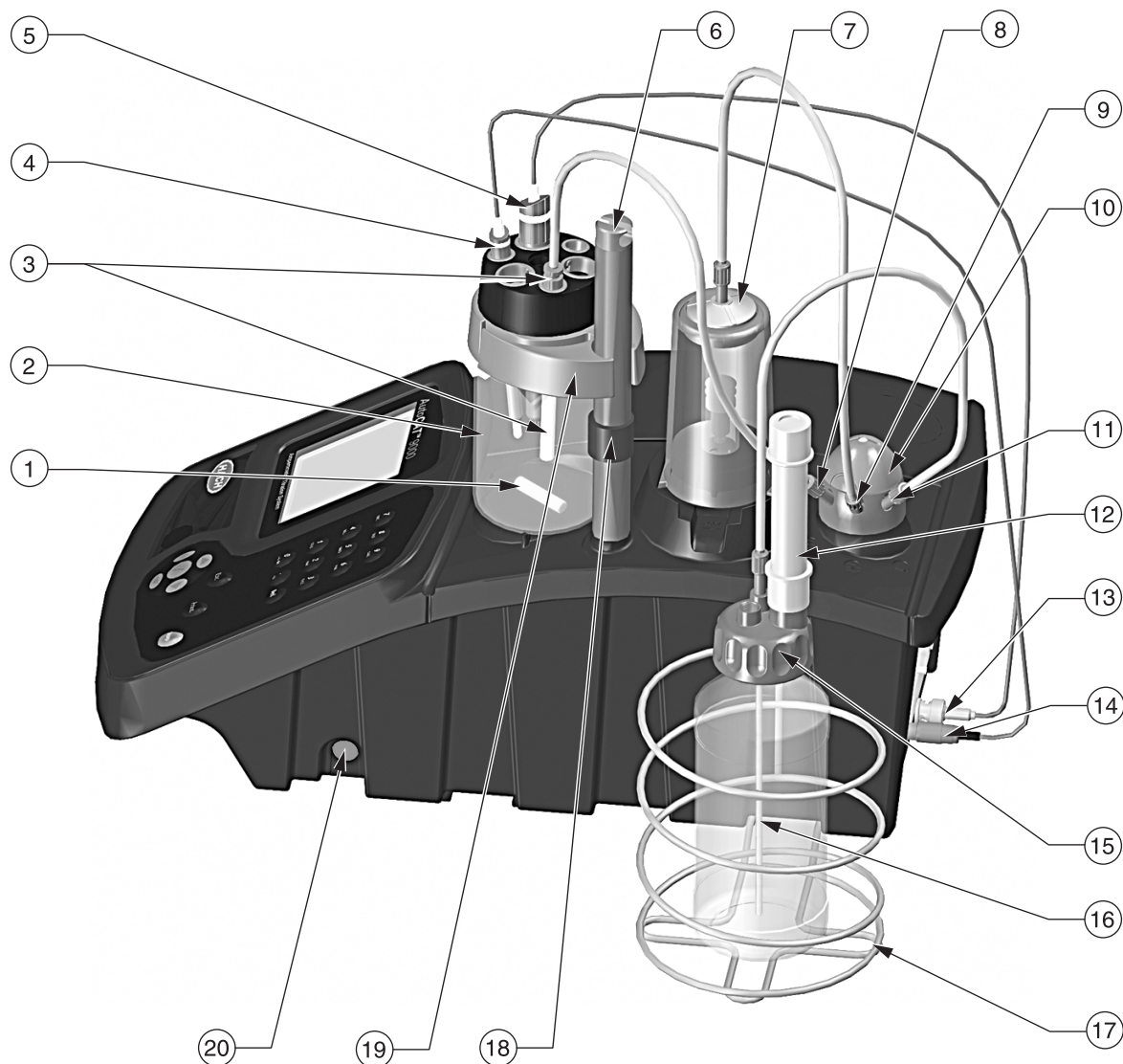


Figure 2 Assembled AutoCAT 9000



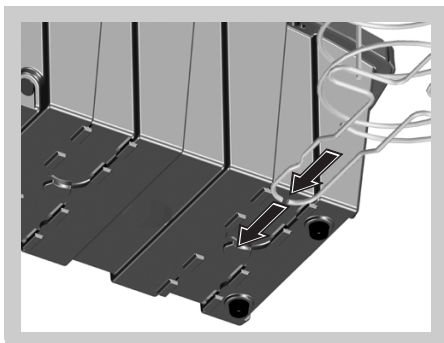
Legend

Number	Item Name	Number	Item Name
1	Magnetic Stir Bar	11	Titrant Pick-up Tubing Connection
2	250-mL Beaker	12	Desiccant Column
3	Plastic Anti-diffusion Tip	13	Electrode (BNC Connector)
4	Temperature Sensor	14	Temperature Sensor (CINCH Connector)
5	Dual Platinum Electrode	15	Bottle Stopper for Plastic Titrant Bottle
6	Support Rod for Electrode Head	16	Pick-up Tubing
7	Burette	17	Bottle Holder
8	Plastic Anti-diffusion Tip Tubing Connection	18	Stop Ring for Electrode Head
9	Burette Tubing Connection	19	Electrode Head
10	Rotating Valve	20	Keyboard PS/2 Connector

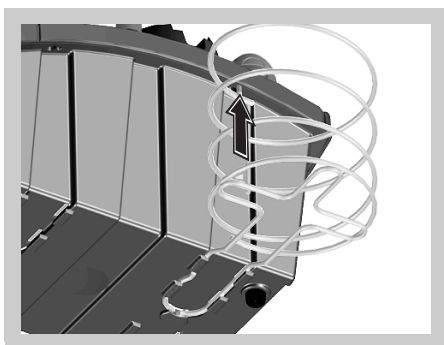
2.2 Instrument Assembly

Perform the assembly procedures in this section and then complete the steps in Section 3 on page 23 to enter basic user information in preparation for performing analyses to comply with Good Laboratory Practices (GLP). Refer to **Section 4** on **page 33** for the software setup required prior to performing analyses. The software setup in **Section 4** must be completed before any analyses can be performed.

2.2.1 Attaching the Titrant Bottle Holder



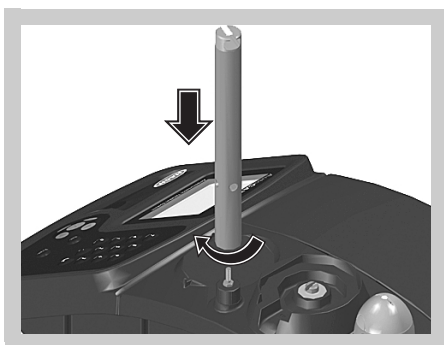
1. Slide the titrant bottle holder into the mounting slot located on the bottom of the instrument housing.



2. Affix holder into position by compressing the bottle holder slightly and inserting the tip into the hole located under the rim of the instrument housing.

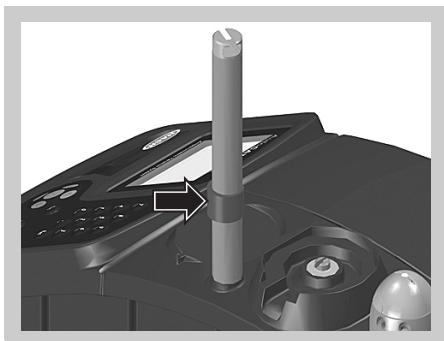
Note: Never pick up or carry the titrator by the bottle holder.

2.2.2 Connecting the Electrode Head and Accessories



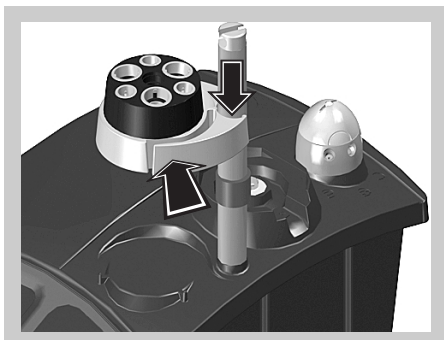
1. Thread the support rod onto the threaded stud of the stirrer platform.

Note: Never pick up or carry the titrator by the support rod.

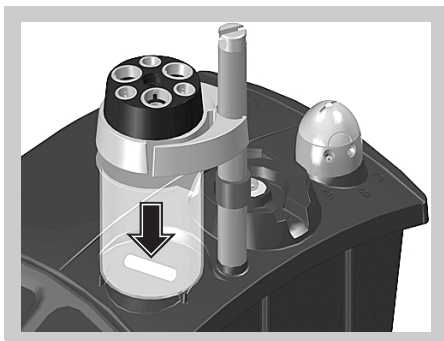


2. Clip the stop ring into the locating hole on the support rod.

Note: The stop ring may be pre-assembled on the support rod.



3. Compress the clips on each side of the electrode head and slide the head onto the metal rod. Release the two clips to secure the head in place.



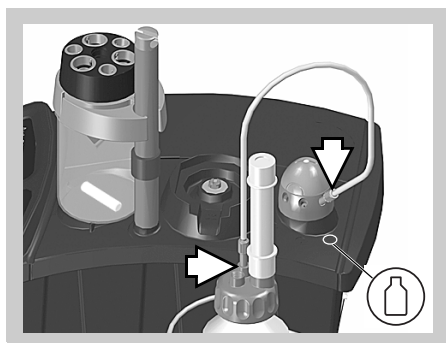
4. Drop the supplied magnetic stir bar into the titration beaker and place the beaker on the titration platform.

Note: The provided stir bar has been specifically selected for use with the AutoCAT 9000. A different stir bar may spin erratically and produce unwanted turbulence and added noise in the titration curve.

2.2.3 Connecting the Titrant Bottle

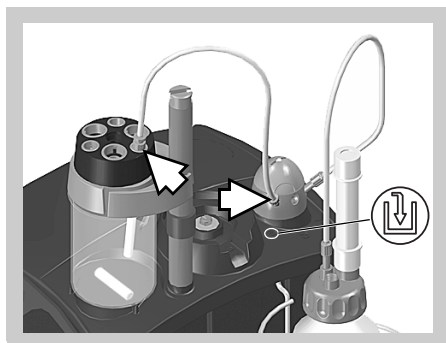


1. Place the titrant bottle into the bottle holder.
2. Thread the desiccant column onto the supplied bottle stopper.
3. Thread the appropriate bottle stopper (for 500 mL or 1000 mL titrant bottle) onto the new titrant bottle and place it into the holder.



4. Push the long section of exposed titrant pick-up tubing through the remaining connection point on the bottle stopper and into the titrant bottle. Thread the tubing connector into the bottle stopper.
5. Thread the opposite connector into the corresponding receptacle on the rotating valve.

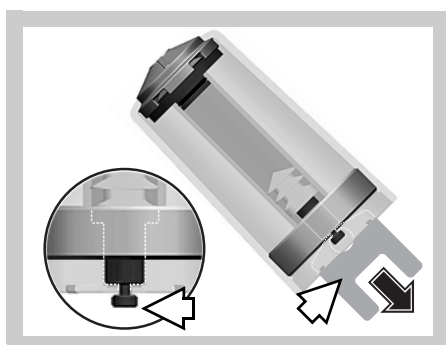
Note: Make sure that the tubing is connected to the correct point on the rotating valve as indicated by the "bottle" icon.



6. The plastic anti-diffusion tip is pre-assembled onto the beaker supply tubing. Thread the tubing connector into the corresponding receptacle on the rotating valve.
7. Insert the plastic anti-diffusion tip into a small hole on the electrode head. Turn the locking collar 1/4-turn clockwise to lock it in place.

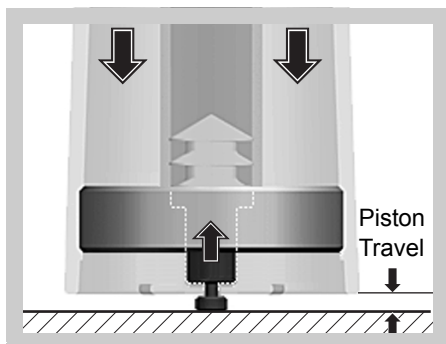
Note: Make sure that the tubing is connected to the correct point on the rotating valve, indicated by the "beaker" icon.

2.2.4 Assembling the Burette



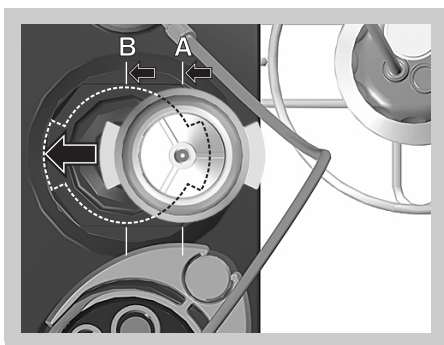
1. Use the metal key to gently pull the piston plunger downward until it protrudes slightly below the bottom of the burette.

Note: The bottom lip of the cylinder will offer only SLIGHT resistance. Do not pull the plunger out completely. If it is inadvertently removed it may be carefully pushed back into the cylinder. After reinsertion, closely monitor the integrity of the seals after titrant is installed.



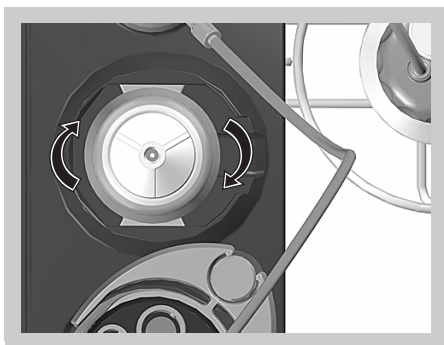
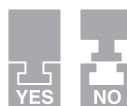
2. Place the burette on a flat surface and press the burette downward until the piston shaft is flush with the bottom of the burette.

Note: Piston position is essential to proper instrument operation. Refer to the illustration (left) for the correct position.

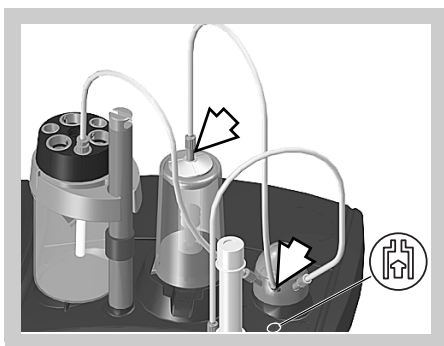


3. Place the burette on the burette stand in position A then slide the burette from position A to position B.

Note: *Inspect the alignment of the piston with the plunger shaft. Ensure that they are properly engaged as displayed in the illustration to the right.*



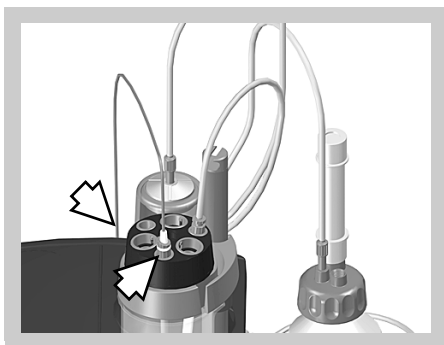
4. Turn the burette $\frac{1}{4}$ -turn clockwise to engage the locking tabs with the burette stand and lock the burette into position.



5. Thread the connectors of the remaining section of tubing into the top of the burette and into the corresponding receptacle on the rotating valve.

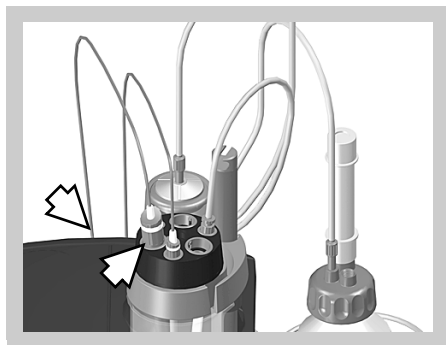
Note: *Ensure that the tubing is connected to the correct point on the rotating valve as indicated by the "burette" icon.*

2.2.5 Connecting the Temperature Sensor



1. Remove the protective cap from the temperature sensor.
2. Insert the temperature sensor into a remaining small hole on the electrode head.
3. Turn the sensor $\frac{1}{4}$ -turn clockwise to lock the collar in place.
4. Connect the cable to the CINCH connector on the back of the instrument (see *Figure 3 on page 19*).

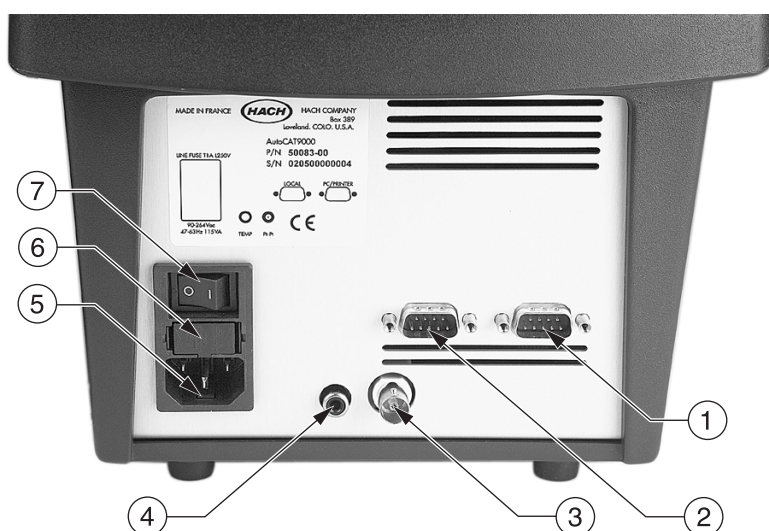
2.2.6 Installing the Electrode



1. Remove the protective cap from the electrode.
2. Insert the electrode into a large hole (opposite the plastic anti-diffusion tip) on the electrode head.
3. Turn the electrode 1/4-turn clockwise to lock the collar in place.
4. Connect the cable to the BNC connector on the back of the instrument (see Figure 3 on page 19).

Note: The electrode **must** be installed opposite the plastic anti-diffusion tip to allow maximum mixing of the titrant before the reaction is sensed by the electrode.

Figure 3 AutoCAT 9000 Workstation Cable Connections



Legend

Number	Item Name
1	PC/Printer
2	Local
3	Electrode
4	Temperature Sensor
5	Power
6	Fuse Access
7	ON/OFF Switch

2.2.7 Power Connection

A UL/CSA-approved 125-V ac power cord (Cat. No. 18010-00) is supplied with the North American AutoCAT 9000 models.

To power North American AutoCAT 9000 models with 230 V ac, replace the supplied 125-V ac power cord with a UL/CSA approved 230-V ac power cord. See section *Section 3.3.6 Selecting the ac Power Frequency* on page 28 for configuration settings.

Plug the power cord into the back panel of the instrument and connect the power cord to the proper outlet. See *Figure 3*.

After assembly is complete, perform the steps in Section 3 on page 23 to enter basic user information in preparation for performing analyses to comply with Good Laboratory Practices. Refer to Section 4 on page 33 for the software setup required prior to performing analyses. The software setup in Section 4 must be completed before any analyses can be performed.

2.2.8 Serial Printer and PC Connections

***Note:** Use of the specified or equivalent shielded cable is mandatory for proper protection from electromagnetic interferences.*

Connect the AutoCAT 9000 Workstation to a personal computer (PC) using the optional computer interface serial cable (Cat. No. A95P201). The cable provides a direct connection between the AutoCAT 9000 Workstation and the 9-pin “D” connector used for the serial port found on most personal computers. If your computer has a 25-pin D connector, use a 9-pin to 25-pin adapter (available at many computer supply stores).

Connect the AutoCAT 9000 to an existing printer using the optional printer interface serial cable (Cat. No. A95P201). The printer must have the following characteristics:

- 80 characters
- RS232C: 9600 baud, 8 data bits, no parity, 1 stop bit
- Must allow printing of tables

Hach offers an optional printer (Cat. No. A70P021) for use with the AutoCAT 9000. See *Appendix B Printer Installation and Setup on page 153*.



Be Right™

Operation

Operation

DANGER

Handling chemical samples, standards, and reagents can be dangerous. Review the necessary Material Safety Data Sheets and become familiar with all safety procedures before handling any chemicals.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les Fiches de Données de Sécurité des Produits (FDSP) et se familiariser avec toutes les procédures de sécurité avant de manipuler tous les produits chimiques.

PELIGRO

La manipulación de muestras químicas, estándares y reactivos puede ser peligrosa. Revise las fichas de seguridad de materiales y familiarícese con los procedimientos de seguridad antes de manipular productos químicos.

GEFAHR

Das Arbeiten mit chemischen Proben, Standards und Reagenzien ist mit Gefahren verbunden. Es wird dem Benutzer dieser Produkte empfohlen, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

PERICOLO

La manipolazione di campioni, standard e reattivi chimici può essere pericolosa. La preghiamo di prendere conoscenza delle Schede Tecniche necessarie legate alla

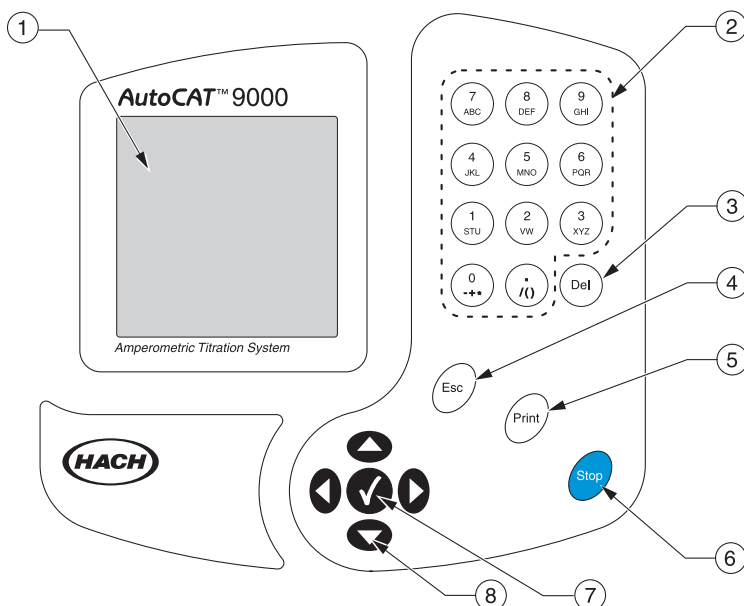
Section 3 Basic Operation

3.1 Instrument Display and Keypad

The instrument display and keypad form an interactive user interface for the AutoCAT 9000 allowing the user to view data, select options, and enter commands.

Individual screens define certain keystrokes at the bottom of the display. The horizontal scroll bar indicates the relative status of the page being displayed. Use the **RIGHT** and **LEFT** keys to scroll the screens.

Figure 1 Display and Keys



Legend

Number	Item Name	Number	Item Name
1	Display	5	Print Key
2	Keypad	6	Stop Key
3	Delete Key	7	Check Mark Key
4	Escape Key	8	Navigation Keys (LEFT, RIGHT, UP, DOWN)

- The keypad is used to enter alpha and numeric characters and punctuation. Press and hold a key to cycle through the series of characters assigned to it. Choose a character by pressing and holding the key until the desired character is displayed, then release the key. Press and hold to scroll from uppercase to lowercase letters. Delete the character displayed above the screen cursor by pressing the **DEL** key.
- The navigation keys include a **CHECK MARK** and four directional keys (**LEFT**, **RIGHT**, **UP**, **DOWN**). Use these keys to navigate within menus, move cursors, and select between options. The **CHECK MARK** key is generally used to select an option or confirm displayed information. The **CHECK MARK** key is also used to stop the data collection process during titration.
- The remaining keys on the keypad are labeled **ESC**, **PRINT**, and **STOP**.
 - The **ESC** key is generally used to exit the currently displayed screen and return to the previously displayed screen.

Basic Operation

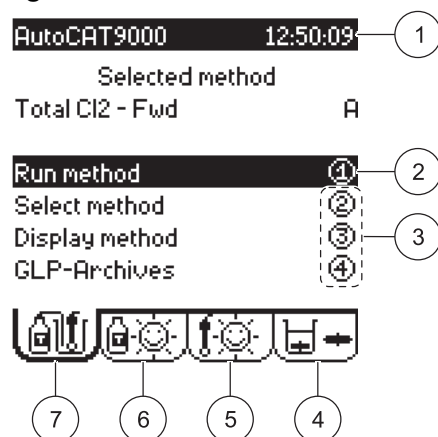
- The **PRINT** key sends titration and calibration analysis results to the printer. Results can be printed either during the method procedure or later from the GLP archives.

Note: Curve and Line Fit printer parameters can only be utilized when printing during a method procedure—not from the GLP archives.

- The **STOP** key is an emergency stop and is used to interrupt the current operation or exit an embedded method. If an analysis is interrupted, the AutoCAT 9000 will prompt the user to resume or end the analysis. All data for the analysis will be lost if it is ended prior to completion.
the **STOP** key is also used to access the Setup menu from the Methods menu (press and hold for approximately three seconds).

3.2 AutoCAT Main Menus

Figure 2 Main Menu



Legend

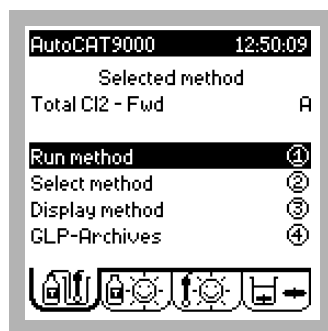
Number	Item Name
1	Title Bar
2	Selected Menu Item
3	Available Menu Items
4	Cell Tab
5	Electrode Tab
6	Reagents Tab
7	Methods Tab

3.2.1 How to Access the Menus

- Press **UP** or **DOWN** key to scroll vertically and highlight various items within currently displayed menus. To select, highlight the desired item and press the **CHECK MARK** to confirm. Selections can also be made by pressing the corresponding number (1 – 6, if available), to the right of the selection; this feature provides quick, one-step access.
- Individual menus define certain keystrokes at the bottom of the display. The horizontal scroll bar indicates the relative status of the screen(s) being displayed.

Note: Press the **RIGHT** or **LEFT** key to tab horizontally between Methods, Titrants, Electrodes, and Cell menus.

3.2.2 Methods Menu



The Methods menu provides access to the embedded procedures, adjustable parameters, and stored titration analyses results. Major components are explained below.

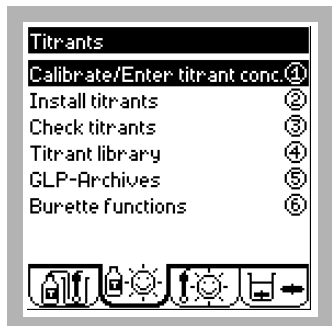
- Title bar**—displays the instrument name, current time, and current "method" name, along with the Sub-ID.
- Run method**—initiates the method currently selected.
- Select method**—allows selection of the method(s) for analyses.
- Display method**—(available in Routine Mode) allows the user to change the Method or Sub-ID.



- **Method library**—(available in Supervisor Mode) contains all of the adjustable method parameters. Those with supervisor access can edit, reset, and delete method parameters to suit specific needs.
- **GLP-Archives**—provides access to the Good Laboratory Practice (GLP) tables, the stored method analysis results, and global variables.
- **Method Tab**—is an animated icon that becomes active when a titration/calibration is being performed.

Note: From the Methods menu, adjust the contrast of the display by pressing **7** to lighten, and **0** to darken.

3.2.3 Titrants Menu



The Titrants menu provides access to the embedded calibration procedures, adjustable parameters, stored calibration results, and burette functions.

- **Title bar**—displays Titrants
- **Calibrate/Enter titrant conc.**—determines the concentration of the titrant by running a calibration or calibration sequence. Alternatively, the concentration can be input manually on the alphanumeric keypad.
- **Install titrants**—allows the user to install or replace the titrants in the selected method.
- **Check titrants**—allows the user to verify the parameters of the titrant used in the selected method.
- **Titrant library**—contains all of the adjustable calibration parameters. Supervisors can choose to have the titrant concentration input manually or determined through embedded calibration.
- **GLP-Archives**—provides access to the Good Laboratory Practice (GLP) tables and display the stored titrant calibration results.
- **Burette functions**—allows the user to fill, empty, flush, rinse, and replace the burette.
- **Titrants tab**—displays one of four titrant status icons, see *Table 1*.

Table 1 Titrant Status Icons

	Sunny Icon—the titrant calibration or manual entry of the titrant concentration has been performed satisfactorily for the current titrant.
	Cloudy Icon—either the titrant calibration should be performed within 24 hours, or the titrant will expire in less than one week.
	Stormy Icon—the titrant calibration or the titrant in the system has expired, the calibration has failed to satisfy the user-programmed acceptance limits, or the installed titrant and selected method are incompatible.
	Question Mark—a problem exists within the method parameters for the titrant. Supervisory level access is required.

3.2.3.1 Changing Titrants

The auto-flush routine takes 60 seconds and uses 10–12 mL of titrant. This function provides a thorough flush and should be used when changing to a different titrant.

1. From the Titrant menu, press **6** to access Burette Functions.
2. Press **3** to begin the flush cycle. Allow the cycle to run to completion.

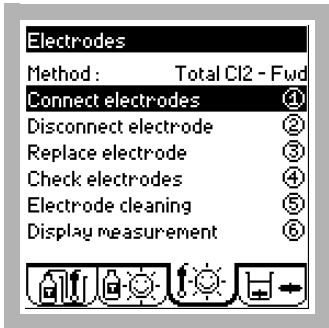
3.2.3.2 Daily Start-up

Even though the delivery tube has an anti-diffusion tip, titrant in the delivery line can be slightly diluted or contaminated when electrodes are in storage solution (tap water, or water with weak bleach solution). Bubbles may form due to titrant outgassing. Diluted titrant and air bubbles can be purged with a manual empty/fill cycle prior to first run on a daily basis, or after a lengthy idle period.

A manual flush cycle uses only 5 mL of titrant.

- 1. From the Titrant menu, press **6** to access Burette Functions.
- 2. Press **2** to empty the burette.
- 3. When the burette empties at least half of its contents, press **STOP**, then press **1** to refill the burette.

3.2.4 Electrodes Menu



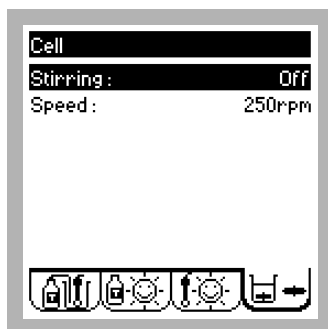
The Electrodes menu provides access to the electrode cleaning and conditioning procedure, adjustable parameters, direct measurement, and electrode/temperature sensor functions.

- **Title bar**—displays Electrodes.
- **Method**—indicates the method currently selected.
- **Connect electrodes**—allow the user to connect the electrode.
- **Disconnect electrode**—allows the user to disconnect the electrode.
- **Replace electrode**—allows the user to replace the electrode.
- **Check electrodes**—identifies and displays the parameters of the electrode used in a method.
- **Electrode cleaning**—guides the user through the electrode cleaning and conditioning procedure.
- **Display measurement**—performs current measurement or displays the temperature, based on the selected electrode.
- **Electrodes tab**—displays one of three electrode status icons, see *Table 2*.

Table 2 Electrode Status Icons

	Sunny Icon—the electrode has been correctly installed.
	Stormy Icon—there is a problem with the electrode installation.
	Question Mark—a supervisory level problem exists within the method parameters for the installed electrode.

3.2.5 Cell Menu



The Cell menu provides access to stirrer function and speed increment adjustment.

- **Title bar**—displays Cell.
- **Stirring**—allows the user to switch the stirrer On or Off.
- **Speed**—allows the user to adjust the internal stirring speed from 100 to 1100 revolutions per minute (rpm) in 50-rpm increments.

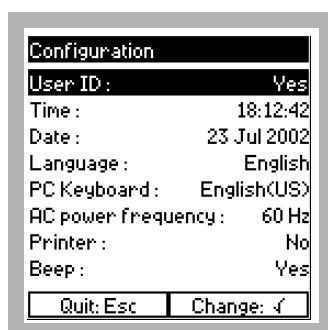
Note: The default stir speed is 250 rpm.

- **Cell tab**—displays an animated icon that indicates the stirrer status.

3.3 System Configuration

3.3.1 Entering the Supervisor Code

Note: There is no factory default code. To proceed in supervisory mode, a user-defined code must be entered.



1. Turn the instrument ON. From the Methods Menu, press and hold the **STOP** key for approximately three seconds to enter the Setup Menu.
2. Input the Supervisor Code input up to 10 digits consisting of any combination of numbers, upper- and lower-case letters, or symbols. Press the **CHECK MARK** to record this code. All future access to the Setup menu will require the input of this case-sensitive code.

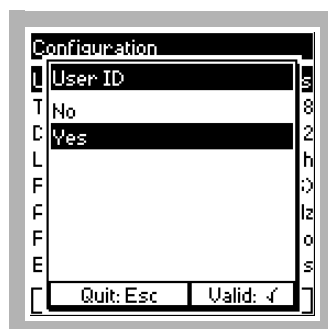
Note: To establish the Supervisor code, see *Accessing Supervisor Mode* on page 33.

3. Press the **CHECK MARK** to confirm.

Note: If already operating in Supervisor mode, the AutoCAT 9000 will not request the supervisor code to access the Setup menu.

4. Select the Configuration Menu and proceed to Section 3.3.2.

3.3.2 Setting a User ID



Select whether or not a User ID will be required:

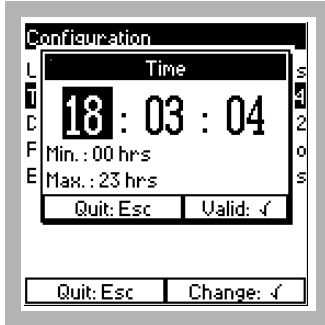
1. Highlight User ID.
2. Press the **CHECK MARK** to confirm. The title bar will display User ID.
3. Press the **UP** or **DOWN** key to toggle between Yes (to enable the User ID function) and No (to disable the User ID function).
4. Press the **CHECK MARK** to validate the highlighted selection and return to the Configuration Menu.

3.3.3 Choose a Language



1. Highlight Language.
2. Press the **CHECK MARK** to confirm. The title bar will display Language.
3. Press the **UP** or **DOWN** key to highlight one of the available languages (English, French, or Spanish).
4. Press the **CHECK MARK** to accept the highlighted selection and return to the Configuration Menu.

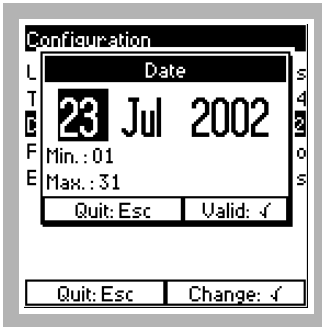
3.3.4 Set the Time



1. Highlight Time.
2. Press the **CHECK MARK** to confirm the selection.
3. Input the hour (00 to 23). Press the **RIGHT** key to scroll to minutes.
4. Input the minutes (00 to 59). Press the **RIGHT** key to scroll to seconds.
5. Input the seconds (00 to 59). Press the **CHECK MARK** to validate and return to the Configuration Menu.

Note: Press the **LEFT** arrow to access a previous field.

3.3.5 Set the Date



1. Highlight Date.
2. Press the **CHECK MARK** to confirm the selection.
3. Input the day (1 to 31). Press the **RIGHT** key to scroll to Month.
4. Select the month using the **UP** or **DOWN** key. Press the **RIGHT** key to scroll to Year.
5. Input the year (2000 to 2069). Press the **CHECK MARK** to validate and return to the Configuration Menu.

Note: Press **◀** to access a previous field.

3.3.5.1 Select Optional PC Keyboard

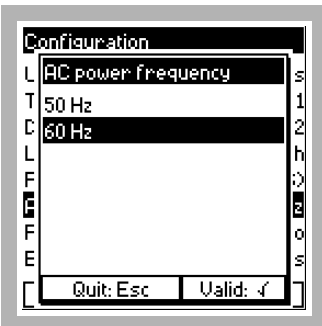


Select an optional, external keyboard to connect to the 6-pin PS/2 receptacle located on the right hand side, bottom edge of the instrument.

1. Scroll to highlight PC Keyboard.
2. Press the **CHECK MARK** to confirm the selection.
3. Press the **UP** or **DOWN** key Highlight English (US) for a standard, QWERTY-type keyboard.
4. Press the **CHECK MARK** to validate and return to the Configuration Menu.

Note: When using the optional keyboard, press F12 to enter the Setup menu. This is done by pressing the Fn and F2 keys simultaneously.

3.3.6 Selecting the ac Power Frequency



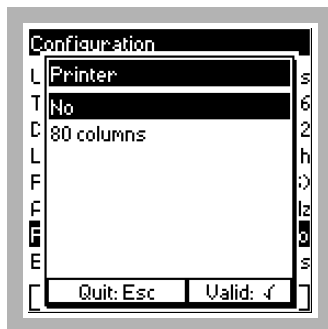
Select the ac power supply frequency (50 Hz/230 V ac or 60 Hz/115 V ac) to optimize instrument operation for regional power.

1. Highlight AC Power Frequency.
2. Press the **CHECK MARK** to confirm the selection.
3. Press the **UP** or **DOWN** key to highlight the desired setting.

Note: The default, 60-Hz /125-V ac setting is required for operation in the U.S. and Canada.

4. Press the **CHECK MARK** to validate and return to the Configuration Menu.

3.3.7 Printer Status

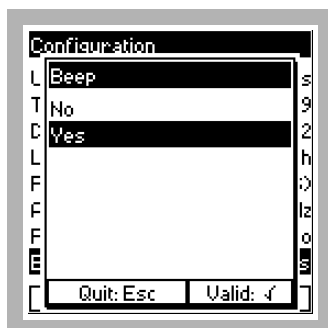


See *Printer Installation and Setup* on page 153 for the printer installation procedure.

1. Select the printer status using the **DOWN** key to highlight Printer. Press the **CHECK MARK** to confirm the selection.
2. Press the **UP** or **DOWN** key. With the desired setting highlighted, press the **CHECK MARK** to validate and return to the Configuration Menu.

Note: If the printer option is enabled, a printer **must** be connected to the instrument. If no printer is connected, an error message will be displayed and the instrument will try to detect a printer for extended periods of time.

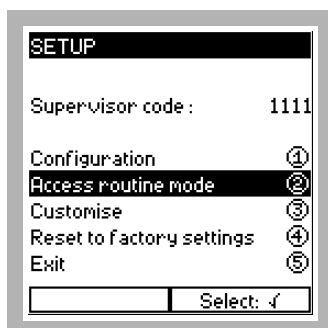
3.3.8 Beep ON/OFF



This selection toggles the ON/OFF status of the alarm beeper. If enabled, the AutoCAT will emit an audible beep to alert the user to analysis completion, titrant expiration, etc.

1. Highlight Beep.
2. Press the **CHECK MARK** to confirm the selection.
3. Press the **UP** or **DOWN** key
4. Press the **CHECK MARK** to validate and return to the Configuration Menu.

3.3.9 Rules for Routine Access Users



1. Access the Setup menu.
2. Select Access Routine Mode.

The Supervisor defines which operations can be ignored in routine mode. Configure Demand and Alarm parameters for Titrant calibration by highlighting the desired selection then pressing The configuration options are as follows:

Demand: Unlocked

The routine user can ignore the demand for titrant calibration and continue the measurements.

Demand: Locked

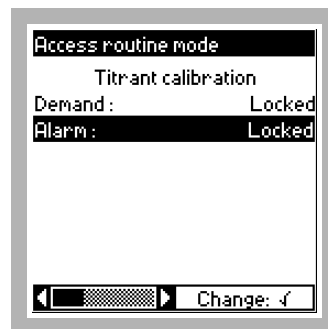
The routine user must either calibrate the titrant or input a new titrant concentration before continuing the measurements.

Alarm: Unlocked

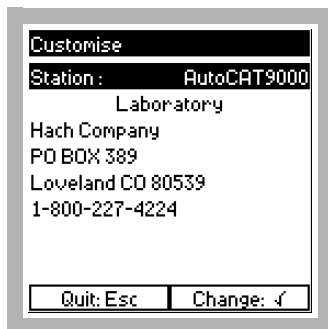
The routine user can accept a titrant calibration even if the analysis result lies outside the acceptance range specified by the method.

Alarm: Locked

The routine user must repeat the titrant calibration when the analysis result lies outside the acceptance range specified by the method.



3.3.10 Customizing the Station



From the Setup menu, select Customize.

1. Highlight Station.
2. Input the desired station information.
3. Press the **CHECK MARK** to confirm.
4. Individually highlight text lines 1–4 (below Laboratory).
5. Input text (up to 32 characters x 4 lines). After the entry of each line, press the **CHECK MARK** to validate and move to the next line.
6. Press **ESC** to return to the Setup menu.

Note: A typical workstation is defined with a name, user(s) name(s), address, contact information, etc.

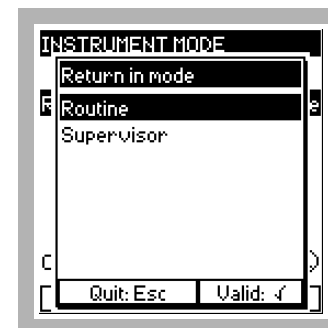
3.3.11 Reset to Factory Settings



This option will return the AutoCAT parameters to factory defaults. All user-installed information, archived analysis results, method/titrant library changes, etc., will be erased. Only the burette parameters will remain in memory.

1. From the Setup menu, select Reset to Factory Settings.
2. Press the **CHECK MARK** or Press **1** to confirm the selection and return to the Setup menu.

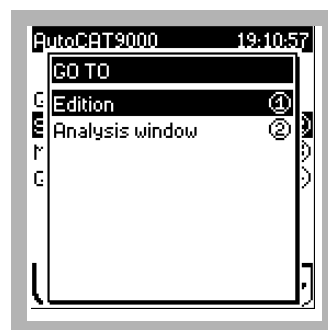
3.3.12 Exit



This selection allows the user to exit the Setup menu and return to the main menus with either supervisor or routine access.

1. From the Setup menu, select Exit.
2. Highlight Return In Mode. Press the **CHECK MARK** to confirm the selection.
3. Press the **UP** or **DOWN** key. Press the **CHECK MARK** to validate.
4. Select Confirm. The Methods menu will be displayed.

3.4 Edition Mode



The AutoCAT 9000 edition feature allows the user to multi-task by viewing/editing parameters during embedded procedure timer and data collection periods. This can only be accessed during data collection, timers, and on screens where Esc is not defined.

1. To access the Edition feature (during a titration/calibration):
 - a. Press **ESC**.
 - b. Select Edition.The user can now access parameters and make any desired changes.
2. To return to the embedded procedure:
 - a. Press **ESC**.
 - b. Select Analysis Window.

Note: Access to parameters is governed by the access mode (Supervisor/Routine).

Note: Any changes made with the Edition feature will take effect on subsequent procedures— not on the current sample titration.

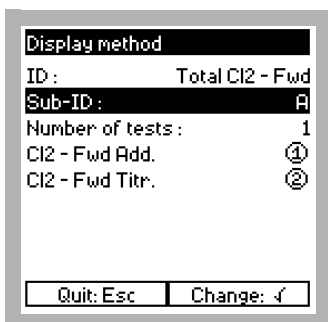
3.5 Using Sub-ID's



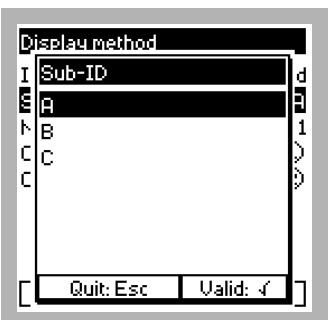
The AutoCAT 9000 allows the user to store optimized parameters for up to three Sub-IDs for each method. The user can create these Sub-IDs with parameters optimized for a specific point of the process they need to monitor.

This eliminates the need for operators to change the titration parameters for samples from different points of their process: they need only to select an appropriate Sub-ID.

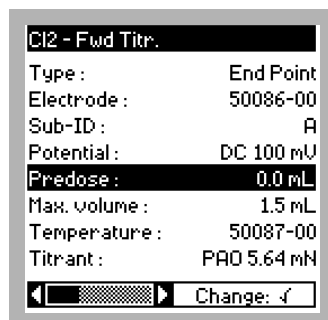
1. To change the Sub-ID in Routine Mode, select Display Method on the Main Menu screen. In Supervisor Mode, select Method Library on the Main Menu screen.



2. From this screen, both the Method and the Sub-ID can be changed. To change the Method or the Sub-ID select ID or Sub-ID respectively.

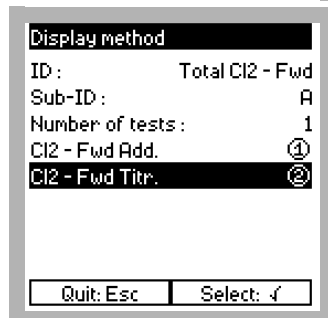


3. Initially these Sub-IDs have identical default parameters, and are simply named A, B, C. The user can assign names to these Sub-IDs, such as Influent, Effluent, Low, Medium, High, Tap 1, Tap 2, Pre-Dechlor, etc.



4. The individual parameters for a Sub-ID (Predose, Max. Volume, Increment, and Current Range) can be changed by selecting any of the titrations listed for the method.

Note: More information on the effects of changing these parameters can be found in *Collecting and Accessing Data* (page 43).



5. To return to the Main Menu press **ESC**.

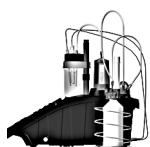
Section 4 Software Setup

The AutoCAT 9000 requires both assembly and software setup before any calibration or titration analyses may be performed. The software setup labels the installed hardware/titrant for use with the embedded procedures. In this section the supervisor-level user will perform, in order, the following setup tasks:

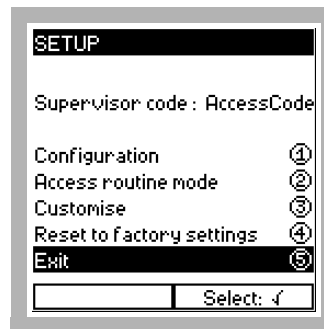
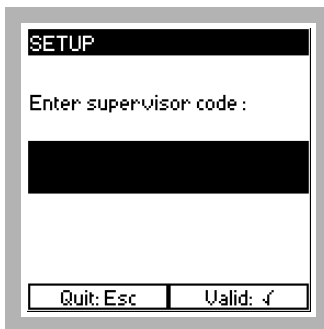
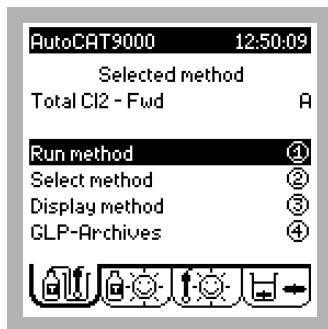
1. Input the supervisor code and operate in supervisor mode.
2. Software setup for installing the electrode and temperature sensor.
3. Software setup for installing the burette.
4. Software setup for installing the titrant.
5. Input the titrant concentration value.

After the initial software setup, the user will seldom need to install the burette, electrode, or temperature sensor. The titrant will need to be installed only when replacing the titrant bottle or switching to a method requiring a different titrant.

Use the following procedures to set up the AutoCAT 9000 titrator software.



4.1 Accessing Supervisor Mode



1. Turn the instrument ON or, if already in operation, access the Methods menu (see Section 3.2.1 on page 24).

Press and hold the **STOP** key for approximately 3 seconds to enter the Setup menu.

Note: The Total Cl2 - Fwd. procedure has been chosen for demonstration purposes because it utilizes the provided PAO titrant.

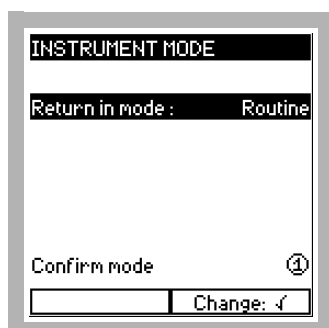
2. Enter or set the supervisor code by using the key pad to input any combination of numbers, upper- and lower-case letters, or symbols (up to 10 digits).

Note: There is no factory default code. To proceed in supervisory mode, a user-defined code must be entered.

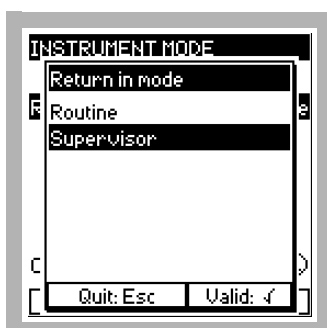
Note: To initially set the Supervisor Code, refer to the instructions in Section 3.3.1 on page 27. All future access to the Setup menu will require the user to input this case-sensitive code.

3. Press the **CHECK MARK** to validate, and enter the Setup menu.

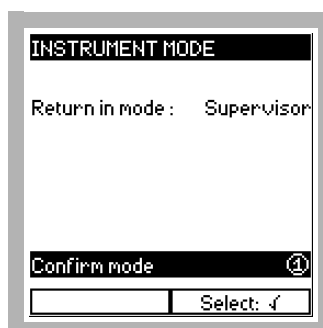
4. Press **5** to Exit.



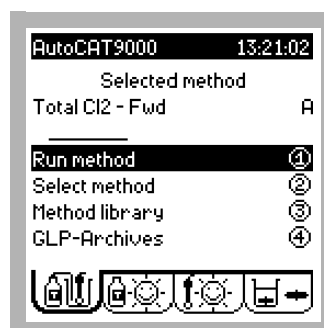
5. Press the **CHECK MARK** to change the Return In Mode.



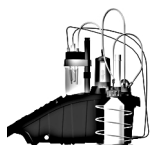
6. Highlight Supervisor.
Press the **CHECK MARK** to validate.



7. Press 1 to select Confirm Mode.



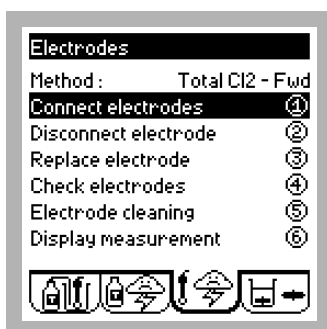
8. The AutoCAT is now operating in Supervisor mode. The Methods menu will be displayed. Proceed to *Software Setup for Electrode and Temperature Sensor Installation*.



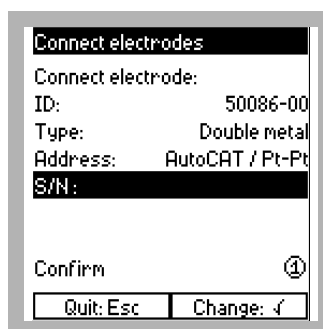
4.2 Software Setup for Electrode and Temperature Sensor Installation



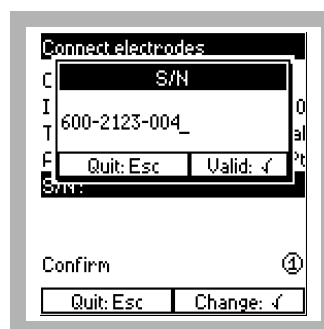
1. From the Methods menu (see *How to Access the Menus* on page 24), use the **RIGHT** and **LEFT** keys to tab to the Electrodes menu.



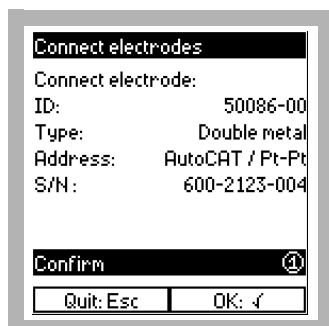
2. Press 1 to select Connect Electrodes.



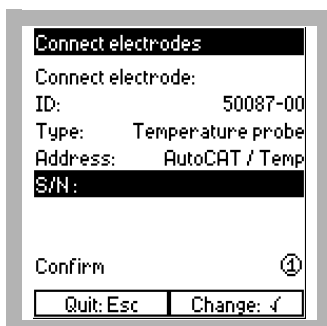
3. Highlight S/N.
Press the **CHECK MARK** to input or change.



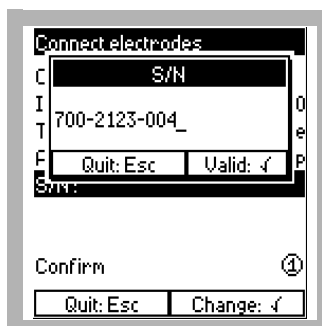
4. Use the alphanumeric keypad to input the last 10 digits of the electrode serial number (located on the electrode cable).
Press the **CHECK MARK** to validate.



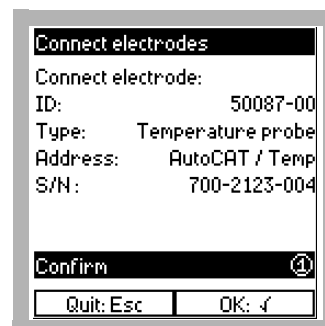
5. Press **1** to select confirm and proceed to temperature sensor installation.



6. Highlight S/N.
Press the **CHECK MARK** to input or change.



7. Use the alphanumeric keypad to input the last 10 digits of the sensor serial number (located on the electrode cable).
Press the **CHECK MARK** to validate.



8. Press **1** to select Confirm and complete the installation and return to the Electrodes menu.
Proceed to *Software Setup for Burette Installation* on page 36.

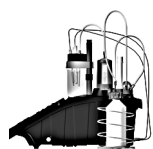
4.2.1 Software Setup for Disconnecting or Replacing Electrodes

To disconnect the temperature sensor and electrode:

1. Press **2** to select Disconnect Electrode.
2. Confirm by pressing the **CHECK MARK** (for each probe).
3. Remove the probes.

To replace the temperature sensor and/or electrode:

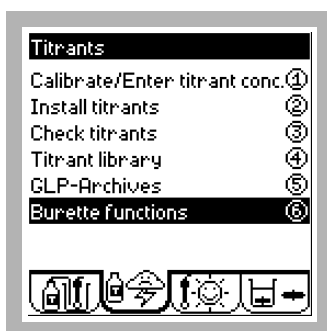
1. Press **3** to select Replace Electrode.
2. Highlight ID, press the **CHECK MARK** to confirm.
3. Highlight either 50086-00 (electrode), or 50087-00 (temperature sensor).
4. Press the **CHECK MARK** to validate.
5. Press **1** to confirm.
6. Remove the probe.
7. Install the replacement probe.
8. Input the serial number of the replacement probe.
9. Press **1** to confirm.



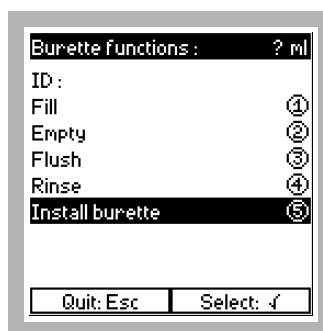
4.3 Software Setup for Burette Installation



1. Use navigation keys to tab to the Titrants menu.



2. Press 6 to select Burette Functions.



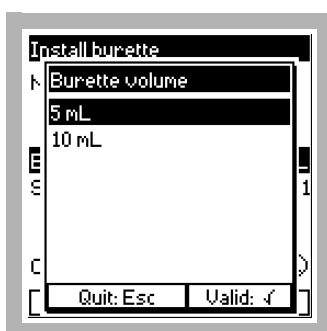
3. Press 5 to select Install Burette.



4. The burette will automatically move to the install position.



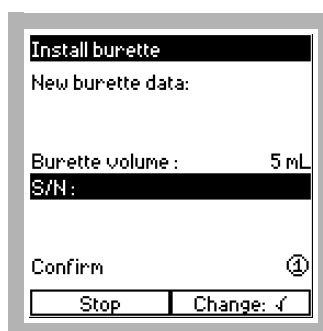
5. Highlight Burette Volume. Press the **CHECK MARK** to input or change.



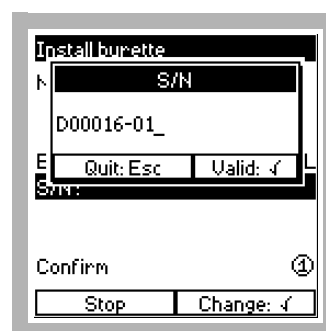
6. Highlight the desired burette.

Note: The default software setting is 5-mL.

Press the **CHECK MARK** to validate.



7. Highlight S/N. Press the **CHECK MARK** to input or change.



8. Use the alphanumeric keypad to input the burette serial number (located on the bottom edge of the burette).

Press the **CHECK MARK** to validate.



9. Verify the burette information.

Press **1** to confirm.

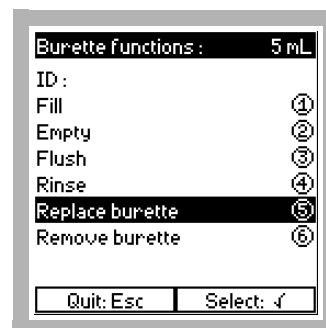


10. Install the burette if not already installed. See *Section 2.2.4 Assembling the Burette* on page 17 for complete instructions.

Press the **CHECK MARK** to validate.



11. The burette will automatically reposition after the install.



12. Press **Esc** to return to the Titrants menu. Proceed to *Section 4.4* on page 38.

Note: When the burette installation is complete the *Replace Burette* and *Remove Burette* options will be displayed.

4.3.1 Software Setup for Removing or Replacing the Burette

To remove the burette:

1. Press **6** to select Remove Burette.
2. Press the **CHECK MARK** to confirm.
3. Follow the embedded procedure (including the purge and rinse cycles).
4. Remove the burette.

To replace the burette:

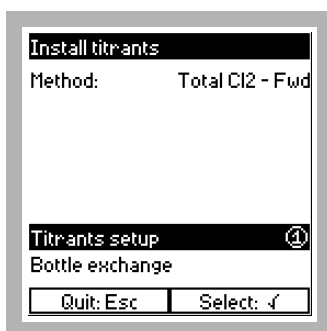
1. Press **5** to select Replace Burette.
2. Press **1** to confirm.
3. Highlight Burette Volume and press the **CHECK MARK** to confirm.
4. Input the replacement burette volume and press the **CHECK MARK** to validate.
5. Highlight Serial Number and press the **CHECK MARK** to confirm.
6. Input the replacement burette serial number and press the **CHECK MARK** to validate.
7. Press **1** to confirm.
8. Remove the burette and press the **CHECK MARK** to confirm.
9. Install the replacement burette and press the **CHECK MARK** to confirm.



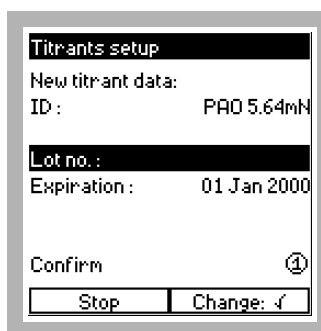
4.4 Software Setup for Titrant Installation



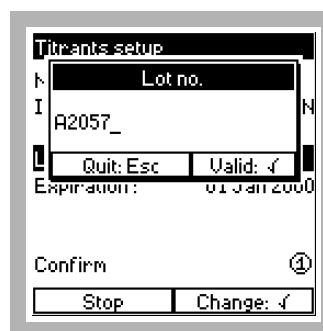
1. From the Titrants menu, press 2 to select Install Titrants.



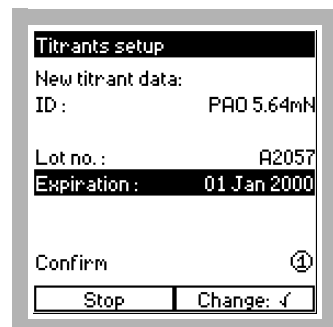
2. Press 1 to select Titrants Setup.



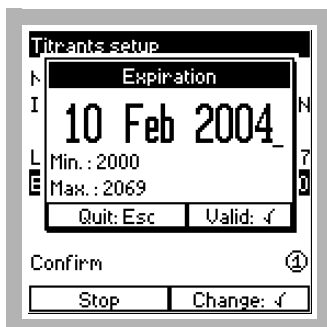
3. Highlight Lot no. Press the **CHECK MARK** to input or change.



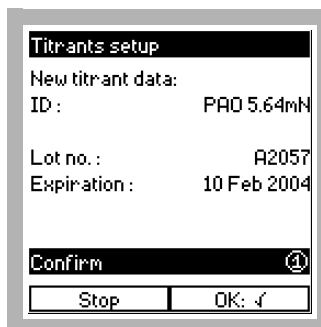
4. Use the alphanumeric keypad to input or change the titrant lot number—located next to the barcode on the titrant bottle. Press the **CHECK MARK** to validate.



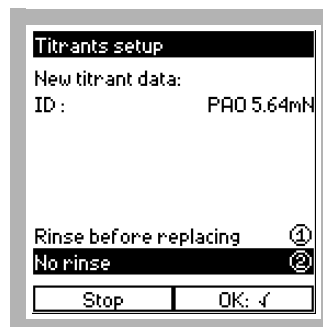
5. Highlight Expiration. Press the **CHECK MARK** to input or change.



6. Use the alphanumeric keypad to input the month and year of the titrant expiration date (located next to the barcode on the titrant bottle). Press the **CHECK MARK** to validate.

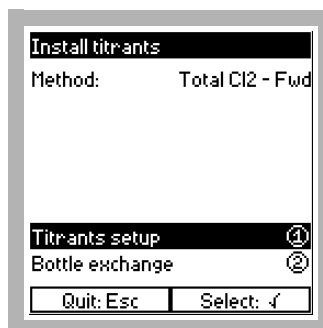
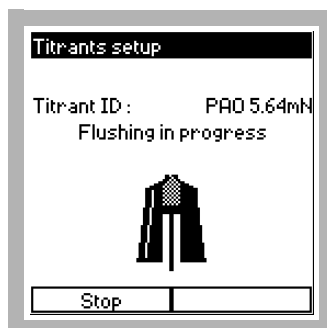


7. Verify the titrant information. Press 1 to confirm.



8. Press 2 to select No Rinse.

Note: Initial installation does not require a burette rinse; however, it is highly recommended for titrant replacement or exchange.



9. Connect the tubing and install the titrant bottle if it is not already installed. See *Section 2.2.3 Connecting the Titrant Bottle* on page 16 for complete instructions.

Place the 250-mL beaker onto the stirrer platform.

Press the **CHECK MARK** to confirm.

10. The burette will complete several cycles to purge air bubbles in the system.

Verify that connections are not leaking and that air is not present in the delivery tubing.

Lightly tap the tubing during the flush to dislodge and displace any trapped bubbles.

Note: *DO NOT stop the flushing process before it is complete or the titrant installation procedure will not be completed. Flushing will take approximately 60 seconds.*

11. The titrant has been successfully installed. Discard the waste titrant and clean and pretreat the beaker before performing another titration.

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

Proceed to *Setting Titrant Concentration* on page 40.

4.4.1 Software Setup for Switching or Replacing Titrants

Note: *AutoCAT will display an error message if the method and titrant are incompatible. If this message appears, the user must switch titrants to accommodate the method.*

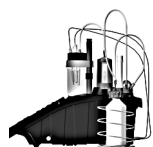
1. Access the Methods menu (see *Section 3.2.1* on page 24)
2. Press **2** choose Select Method.
3. Highlight the desired method, press the **CHECK MARK** to validate.
4. Use the **RIGHT** and **LEFT** keys to move to the Titrants menu.
5. Press **2** to select Install Titrants.
6. Press **1** to select Titrants Setup to replace titrants (for a new method), or press **2** to select Bottle Exchange to replace depleted titrant with a new bottle.
7. Press **1** to confirm.
8. Highlight Lot No. and press the **CHECK MARK** to confirm.
9. Input the lot number for the required titrant, press the **CHECK MARK** to validate.
10. Highlight Expiration, press the **CHECK MARK** to confirm.
11. Input the Expiration date for the required titrant, press the **CHECK MARK** to validate.

Note: *If replacing depleted titrant, the embedded procedure will automatically begin here.*

12. Press **1** to confirm.
13. Ensure that the correct change will be made.

14. Press **1** to confirm.

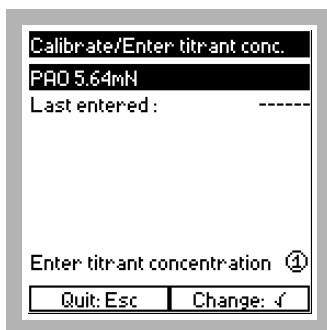
15. Select Rinse Before Replacing and follow the embedded method procedure.



4.5 Setting Titrant Concentration

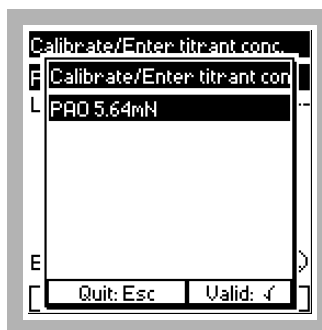


1. From Titrants menu, press **1** to select Calibrate/Enter Titrant Conc.



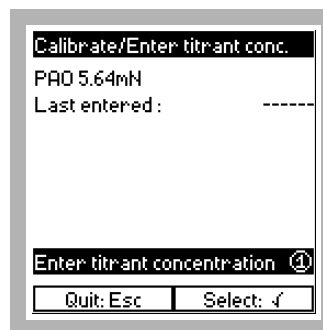
2. Highlight PAO 5.64mN (or another method) and press the **CHECK MARK** to view the list of available titrants for the chosen procedure.

Note: 5.64 mN is equivalent to 0.00564 N.

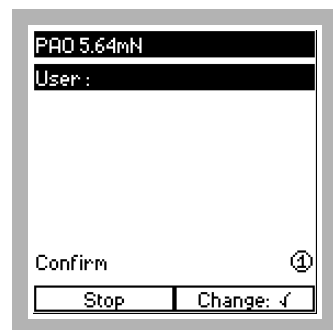


3. Highlight the titrant identifier (PAO 5.64mN in this example) and press the **CHECK MARK** to validate.

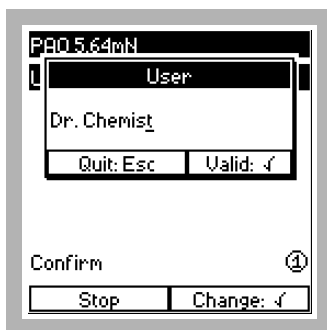
Note: The AutoCAT 9000 automatically stores installed titrants for later concentration updates or calibrations.



4. Press **1** to select Enter Titrant Concentration.

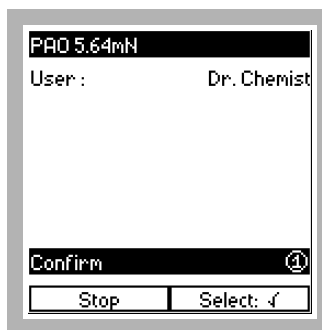


5. Highlight User and press the **CHECK MARK** to input or change the user ID.



6. Use the alphanumeric keypad to input the user ID. Press the **CHECK MARK** to validate.

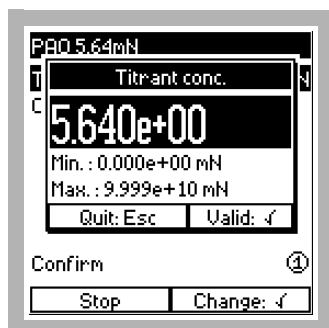
Note: The user ID may be any combination of alphanumeric characters up to 16 characters in length.



7. Verify the user ID and press **1** to confirm.



8. Highlight Titrant Conc. and press the **CHECK MARK** to input or change the concentration.



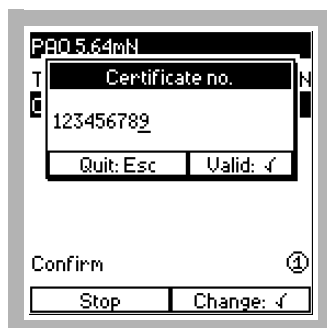
9. Use the alphanumeric keypad and navigation keys to input or change the titrant concentration.

Press the **CHECK MARK** to validate.

Note: Product lots differ slightly in concentration. See Section 4.6 Obtaining the Certificate of Analysis for Hach Reagents.



10. Highlight Certificate No. and press the **CHECK MARK** to input/change.



11. Use the alphanumeric keypad to input the titrant certificate number.

Press the **CHECK MARK** to validate.

Note: This supports the GLP archives for titrant install/calibration, but is not required for operation.



12. Verify the titrant concentration and certificate number.

Press **1** to confirm and return to the Titrants menu.

Initial software setup is now complete for the Total Cl2 - Fwd. method.

4.6 Obtaining the Certificate of Analysis for Hach Reagents

Using an internet connection, download the “Certificate of Analysis” (COA) for any Hach Company reagent or titrant to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution.

1. Go to www.hach.com.
2. Click on “Information Central”.
3. Click on “Certificate of Analysis Download”.

The Catalog Number and Lot Number, located on the label of your Hach reagent bottle, will be requested.

Section 5 Collecting and Accessing Data

5.1 Using the AutoCAT 9000 for Amperometric Methods

The following analysis procedures, based on Standard Methods, are embedded directly in the instrument software:

- Forward titration for free chlorine
- Forward titration for total chlorine
- Back titration for total chlorine
- Forward titration for chlorine dioxide

Hach sells pre-standardized titrants, prepared according to Standard Methods, for both forward and back titrations. The 0.00564 N phenylarsine oxide titrant (Cat. No. 1999-53) has a shelf life of >1 year in the unopened bottle. The unopened 0.0282 N Iodine Standard Solution titrant (Cat. No. 23333-53) is stable for 6 to 12 months.

Periodically recalibrate the titrants after opening to ensure accuracy. Dispense reagents directly from the product bottle to eliminate contamination from transferring them to separate containers.

5.2 AutoCAT Titration

AutoCAT 9000 functions can be separated into three categories: (1) data collection, (2) end point determination, and (3) calculation. Each category is described in the sections below.

5.2.1 Data Collection

The AutoCAT displays the titration curve (current (μA) vs. titrant volume (mL)) graphically in real time, as it dispenses titrant and measures the current. After the titration is complete, the user can choose between a fully automated or manual routine to determine the end point. Following end point determination, the AutoCAT 9000 automatically calculates the analyte concentration.

The titration curve is constructed by plotting the measured current as a function of the volume of titrant added. Several parameters, which must be set prior to data collection, are available to control the data collection process. These parameters include the (1) current range, (2) volume increment, (3) predose volume, and (4) Auto-scaling.

5.2.1.1 Current Range

Current Range allows the user to set the maximum current (in μA) expected for a particular titration. The AutoCAT 9000 allows four possible settings (2 μA , 20 μA , 200 μA , and 1 mA) for the current range. The default setting (20 μA) setting is adequate for most purposes. The 2 μA setting is recommended when analyzing samples with concentration less than 0.600 mg/L Total Chlorine.

Note: The 200- μA and 1-mA settings are available for experimental use, and are not recommended for most titrations.

5.2.1.2 Volume Increment

The AutoCAT 9000 delivers titrant to the sample solution in discrete volume increments. During data collection, the AutoCAT 9000 injects one volume increment of titrant solution into the sample once every 3 seconds. The volume increment is an adjustable parameter that controls the volume (mL) of titrant dispensed for each addition. The smallest increment setting is 0.0003 mL.

In general, for forward titrations, a reasonable volume increment can be calculated based on the estimated analyte concentration (in mg/L) by dividing the end point volume in milliliters (numerically equivalent to the chlorine concentration when using 0.00564 N PAO as a titrant) by the number of points to be collected before the end point.

For example, if you wish to collect 50 points before the end point then the appropriate volume increment would be given by the following equation:

$$\text{Volume Increment (mL)} = \frac{\text{Estimated Chlorine Concentration (mg/L)}}{50}$$

A table is provided in each embedded method procedure to help determine the appropriate volume increment to use for data collection.

5.2.1.3 Predose Volume

Predose defines a volume of titrant added to the sample prior to data collection.

If 1.50 mL of titrant is required to reach the end point, the entire titration can be run using a 0.03 mL volume increment and no predose. Alternatively, a titration can run using a 0.01 mL volume increment and a 1.00 mL predose. In this case 1.00 mL of titrant is added prior to data collection and the final 0.50 mL is delivered during data collection. The same number of points will be collected and the same amount of time will be required. In the first titration a 20 μ A current range will be required to avoid “clipping” the top of the titration curve. A 2 μ A current range may be used in the second case.

5.2.1.4 Auto-scaling

The AutoCAT 9000 has an auto-scaling feature. When Auto-scaling is enabled the AutoCAT 9000 will attempt to set the current range and volume increment automatically. This feature is useful for titration of samples containing over 25 ppb total chlorine. Auto-scaling is less useful for free chlorine titrations and cannot be used with back titrations. Auto-scaling can be used with or without a titration predose.

Two associated parameters, No. points before EP and Fraction before EP, become available when Auto-scaling is activated.

The No. points before EP sets the approximate number of points desired before the end point.

The Fraction before EP sets the fraction of the total number of points collected. For example if the fraction is set to “0.50” then approximately 50% of the data points are collected before the end point and 50% afterwards.

5.2.2 End Point Determination

The AutoCAT9000 incorporates two routines for end point determination. Both routines (described in Section 5.2.2.1 and 5.2.2.2) attempt to determine the volume of titrant needed to reach the break in the titration curve.

5.2.2.1 Manual End Point Determination (MEPD)

MEPD requires the user to manually position the cursors on the instrument display to define separate linear regions of the titration curve on each side of the end point (i.e., the break in the titration curve). When selecting line segments, it is generally advisable to select points closer to the end point of the titration, and to avoid, as much as possible, “noisy” sections of the curve. Select a pair of lines that intersect as near as possible to the break in the titration curve. After the linear regions have been selected, the linear least squares regression lines are fit through all the points between each pair of cursors. The intersection of the two regression lines determines the end point. More guidelines for Manual End Point Determination can be found on page 135.

5.2.2.2 Automatic End Point Determination (AEPD)

AEPD allows the AutoCAT 9000 to search for a pair of intersecting lines that best fit the titration curve. The end point is determined from the intersection of the two best-fit lines.

5.2.2.3 Auto Detection

Normally, when a user runs an analysis on the AutoCAT 9000, the instrument will go directly from data collection to the zoom window. The instrument will stop in the zoom window, allowing the user to select the desired range of data points and the mode (AEPD or MEPD) to be used for end point determination.

If the auto-detection feature is enabled (set to Yes), then the instrument will proceed directly from data collection to AEPD without the usual intervening zoom window. Following AEPD, the results are displayed and the user can accept the results or reprocess the data using either AEPD or MEPD.

5.2.3 Parameters Used in the Calculation of the Analyte Concentration

After the end point has been determined, the AutoCAT 9000 automatically calculates the corresponding analyte concentration. The titrant concentration, sample volume, and dilution factors are used to calculate the analyte concentration, regardless of the method. In addition, the back titration method uses the concentration and volume of the reductant solution used to fix the sample. Each parameter must be properly set prior to running an analysis.

A Number of Decimals parameter is available in supervisor-level mode to set the number of decimal places used to report the analysis. For example, if Number of decimals is set to “4”, the experimental results will be reported as 0.3296 mg/L. If it is set to “2”, the result would be displayed as 0.33 mg/L.

5.2.3.1 Titrant Concentration

The titrant concentration (mN) can be entered manually or determined experimentally using the appropriate embedded titrant calibration routine. The exact concentration of the titrant is needed when entering the titrant concentration. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.

5.2.3.2 Sample Volume

The sample volume (mL) is the volume of the sample solution actually placed on the instrument. This is a run-time parameter, allowing it to be changed each time a sample analysis is performed. The default sample volume is 200 mL. If the sample volume is changed, the new value is used as a default until the method defaults are reset or the value changed again.

5.2.3.3 Dilution

If a sample solution is diluted prior to analysis, the sample parameter Dilution should be enabled (set to Yes), allowing access to three other parameters (Predilution vol., Final dilution vol., and Sample vol.). These parameters allow the calculated analyte concentration to be corrected for dilution and are only applicable when dilution is enabled.

This is generally done to bring the analyte concentration into the proper range for analysis. The AutoCAT 9000 can automatically correct any measured analyte concentration for sample dilution and three parameters are used to calculate analyte concentration:

- Predilution volume is the volume of the original sample
- Final dilution vol. is the volume of the sample after dilution
- Volume for Test is the volume of solution taken from the diluted sample and analyzed.

Normally, AutoCAT returns the concentration of the sample actually presented to it (i.e., the concentration of the sample placed in the analysis beaker and analyzed by the instrument). Using the dilution information, the AutoCAT can automatically convert the concentration measured for the diluted sample into the concentration of the undiluted sample.

5.2.3.4 Reductant Concentration

When performing a back titration the sample is fixed by spiking it with reductant (either PAO or sodium thiosulfate) solution. Reductant concentration is the concentration (mN) of the solution used to fix the sample. The exact concentration of a Hach reductant solution can be obtained. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.

5.2.3.5 Reductant Volume

In a back titration the sample is fixed by spiking it with reductant (either PAO or sodium thiosulfate) solution. Reductant Volume is the volume (mL) of the reductant solution used to fix the sample.

5.2.4 Analysis Calculations

When two or more consecutive new tests (as opposed to new samples) are run, the AutoCAT 9000 automatically calculates the mean and the standard deviation of the mean for the results obtained from the individual tests. This is equivalent to making several replicate measurements starting with identical samples for each measurement. The standard deviation of the mean is different than the standard deviation of the replicate measurements.

5.2.4.1 Calculation of Mean

The mean is calculated using the following equation:

$$\text{Mean} = \frac{\sum_{i=1}^N R_i}{N}$$

Where:

R_i is the result from the i^{th} replicate measurement (i.e., Test)

N is the number of replicate measurements.

5.2.4.2 Calculation of Standard Deviation (<5 replicate analyses)

When the number of replicate measurements is between 2 and 5, the standard deviation of the mean, S_{Mean} is estimated using the following formula:

$$S_{\text{Mean}} = \sqrt{\frac{\left(\frac{R_{\text{max}} - R_{\text{min}}}{Q}\right)^2}{N}}$$

Where:

R_{max} is the maximum value obtained from the replicate measurements

R_{min} is the minimum value obtained from the replicate measurements

Q is taken from the following table:

N	Q
2	1.128
3	1.693
4	2.059
5	2.326

5.2.4.3 Calculation of Standard Deviation (>5 replicate analyses)

If more than five replicate measurements (i.e., Tests) are made, the standard deviation of the mean, S_{Mean} is calculated using the following formula:

$$S_{\text{Mean}} = \sqrt{\frac{\sum_{i=1}^N R_i^2 - \frac{\left(\sum_{i=1}^N R_i\right)^2}{N}}{(N-1)N}}$$

The final average is reported as: Mean ($\pm S_{\text{Mean}}$)

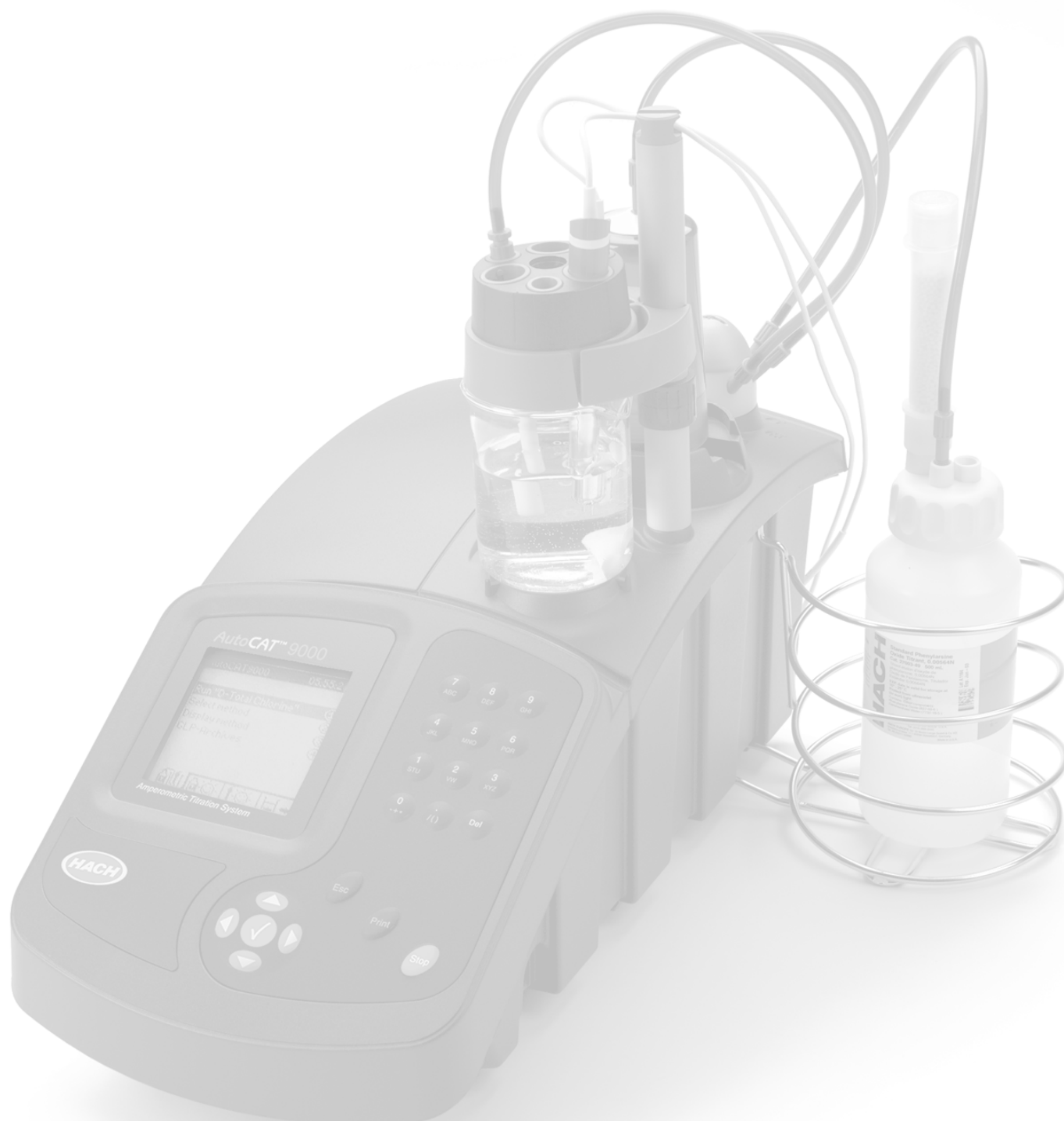
5.2.5 Retrieving Analysis Results from Archives

As part of the Good Laboratory Practices (GLP) capability incorporated into the AutoCAT 9000, all analysis results are automatically stored in the archive and organized according to method. For example, all results obtained using the free chlorine method are listed together. Before a particular result can be viewed the associated method must first be selected. The most recent result is always assigned to position “1” in the archive.

For example, if the user performs a series of 10 separate chlorine analyses, then the results for the most recent analysis will be stored in position “1” of the archive while the results of the least-recent analysis will be stored in position “10” of the archive. Each time a new analysis is performed, the results are pushed to the next (higher number) position in the archive. The AutoCAT 9000 can archive the results from 200 individual analyses; if more than 200 results are archived, the oldest analysis result is displaced in favor of the most recent result.

Important Note: All archived results are deleted when the system defaults are reset.

Section 6 Calibration Procedures



Amperometric Forward Titrant Calibration

Titration Workstation

Scope and Application: The following sequence guides the user through the calibration procedure for the 0.00564 N (5.64 mN) Phenylarsine Oxide titrants.



Sample Tips and Techniques

- Sample glassware must be cleaned and pretreated to satisfy any chlorine demand. See *Section 7.2 Container Pretreatment* on page 63 for additional information.
- Always use organic-free reagent water for sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



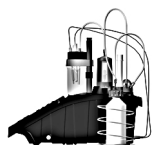
Reagent Tips and Techniques

- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Download the "Certificate of Analysis" (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.
- It is recommended that titrations for titrant calibration be performed in triplicate.



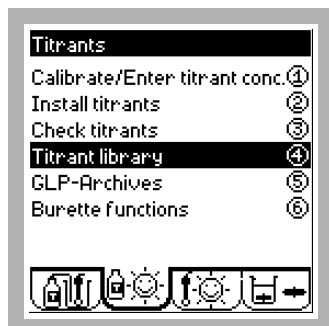
Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu, and then pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current or previous sample analysis. The AutoCAT automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT calculates concentration based on the sample volume. Make sure that the sample volume is correct.
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water between calibrations.
- The data for any individual sample calibration may be repeatedly analyzed in manual or automatic mode. The results are not stored in the archives until they are accepted.
- Press the **STOP** key any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit completely.
- Press **CHECK MARK** key any time during data acquisition to halt data collection.
- Press the **DEL** key during any timer period (except the Start Timer) to immediately exit the timer and proceed to the next step in the procedure.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.



AutoCAT Calibration Method

PAO/5.64 mN Titrant



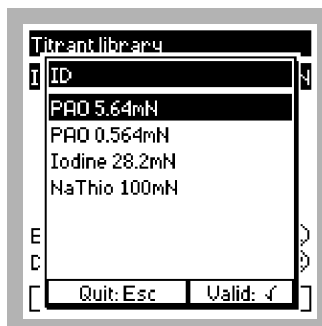
1. Turn the instrument on if necessary and access the Titrants menu.

Press 4 to select Titrant Library.

Note: Supervisor-mode is required to access calibrations. See Accessing Supervisor Mode on page 33.



2. Highlight ID.
Press the **CHECK MARK** to change.

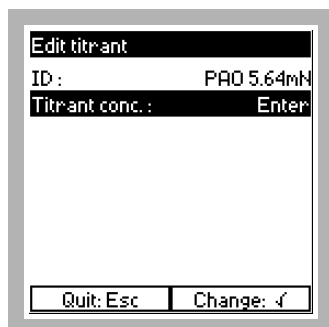


3. Highlight PAO 5.64mN.
Press the **CHECK MARK** to validate.

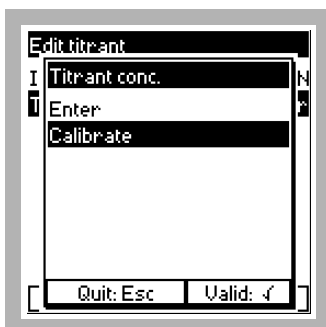
Note: PAO 5.64mN has been chosen for demonstration purposes only.



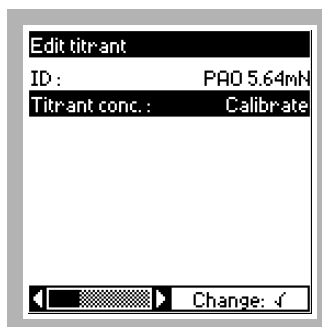
4. Press 1 to select Edit titrant.



5. Press the **CHECK MARK** to change the titrant concentration input mode.



6. Highlight Calibrate.
Press the **CHECK MARK** to validate.



7. The titrant concentration input mode is now set to Calibrate and calibration parameters are available by scrolling this screen. Press **ESC** twice to return to the Titrants menu.



8. Press 1 to select Calibrate/Enter titrant conc.

Note: Titrant calibration is required before further analyses may be run, as indicated by the "Stormy" icon.

9. Press **1** to select.

Run calibration to start the calibration sequence.

Note: Last Calibration will indicate the date of the previous calibration.

10. Press the **CHECK MARK** to change the User or press **1** to confirm.

Note: The user ID will be stored in the GLP archives for any future reference to this calibration.

Note: This screen will be skipped if User ID is disabled. See Section 3.3.2 Setting a User ID on page 27.

11. Highlight Concentration.

Press the **CHECK MARK** to change the concentration or proceed to step 12.

Note: Use a recent lot of 0.0282 N Iodine Standard Solution for calibration.

Note: The default concentration may be changed to reflect standardization or the "Certificate of Analysis" value for a new bottle of titrant.

12. Highlight Lot No.

Press the **CHECK MARK** to change the titrant lot number or proceed to step 13.

13. Highlight Volume for Test 1.

Press the **CHECK MARK** to change the calibration volume or proceed to step 14.

Note: The default volume for the standard solution has been optimized for this embedded calibration.

14. Prepare a calibration sample.

- Add 200 mL of DI-water to a 250-mL glass beaker.
- Using a Class A pipet, add 0.50 mL of recently standardized iodine solution.
- Add 1 SwifTest dispensation (0.1 g) of potassium iodide (KI), and 1.0 mL of pH 4 acetate buffer.

Press **1** to confirm.

15. Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water.

Insert the specified magnetic stir bar into the calibration sample and place it onto the stirrer platform.

Lower the electrode head onto the beaker rim.

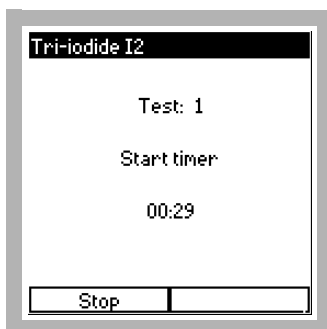
Press **1** to confirm.

16. Press **1** to confirm the displayed increment or press the **CHECK MARK** to change the Increment.

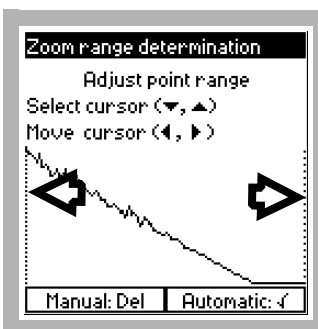
Note: The default volume increment has been optimized for this embedded calibration; it may be changed to suit specific needs.



17. The calibration titration starts by filling the burette with titrant and subsequently dispensing a 2.2-mL predose of PAO into the calibration sample. This will bring the electrical signal into measurable range.



18. The Start Timer will begin. This allows the electrode to stabilize before data is collected. Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve in real time.

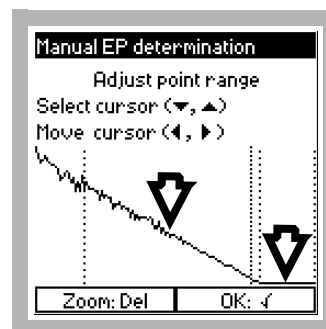


19. The Zoom range determination window will display the titration curve. Use the navigation keys to select and move the cursor (vertical lines) to define the range of data points for analysis.

Note: Defining the range of data points eliminates undesirable portions of the titration curve.

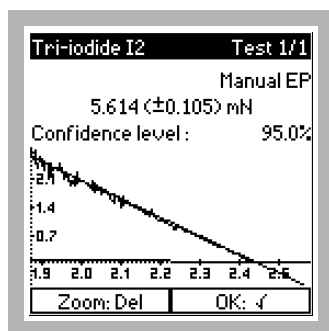
Select type of end point determination.

Press the **CHECK MARK** for Automatic. Proceed to step 22 or press **DEL** for Manual and proceed to step 20.



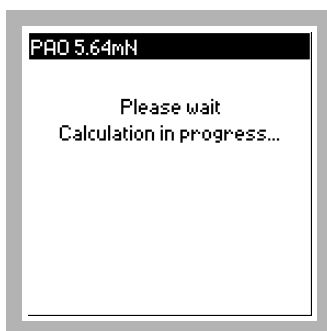
20. Select two line segments, one on each side of the titration end point, by positioning cursors at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes, press **DEL** to return to the previous window.



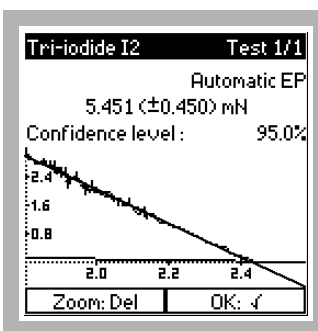
21. Press the **CHECK MARK** to accept the analysis. Proceed to step 24.

Press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.



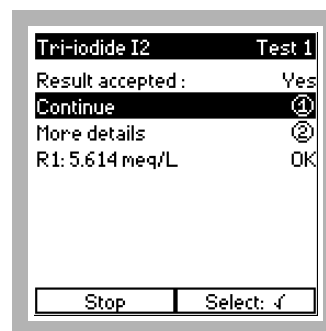
22. The AutoCAT will run the analysis based on the automatic selection of linear segments.

Note: This algorithm requires approximately 60 seconds to complete.



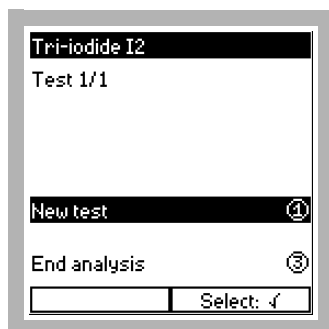
23. Press the **CHECK MARK** to accept the analysis.

Press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.



24. Press 1 continue.

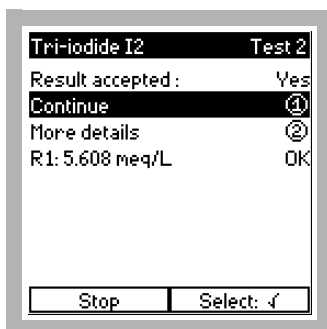
Press 2 to select More details to view analysis statistics specific to the current calibration.



25. Press **1** to select New Test and run a replicate calibration. Proceed to *step 26*.

Press **3** to select End Analysis and store the titrant calibration value and return to the Methods menu.

Note: If subsequent replicate calibrations are run, the final titrant concentration will automatically be stored as the mean value from all the replicate titrant calibrations.

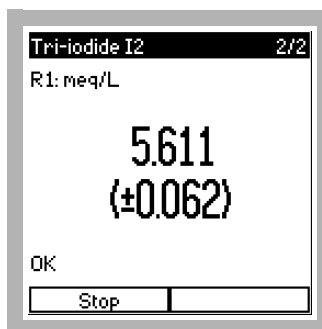


26. The replicate analysis is identical to the first calibration.

Upon completion of the analysis, and acceptance of the data, subsequent replicate analyses can be performed if desired.

Press **1** to continue.

Press **2** to select More Details to view analysis statistics specific to the current calibration.



27. The mean and standard deviation are calculated from the replicate analyses.

Press the **CHECK MARK** to accept the calibration value and return to the Titrants menu.



In the Titrants menu, the accepted calibration has caused the **Titrant** tab icon to become sunny. This indicates that the titrant concentration has been properly calibrated and analyses may resume.

Safety

Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

Summary of Method

The 0.00564 N reductant titrants, phenylarsine oxide (PAO) and sodium thiosulfate (NaThio), are standardized by titrating them against a known volume of 0.0282 N Iodine Standard Solution. The PAO/NaThio calibration procedure embedded in the AutoCAT 9000 is adapted from procedure 4500-Cl C. *a.* in “Standard Methods for Examination of Water and Wastewater” (20th Edition).

A calibration sample is prepared by adding 0.50 mL of 0.0282 N Iodine Standard Solution to 200 mL of chlorine-free deionized water. Potassium iodide (KI) and pH 4 acetate buffer are then added to the calibration sample. The calibration sample is then titrated using the desired reductant titrant. The embedded procedure calls for a 2.2-mL predose prior to titration. The titration end point is around 2.5 mL using the embedded method as defined. If the concentration of the Iodine Standard Solution is significantly less than 0.0282 N, it may be necessary to reduce the predose volume prior to titration. Titrate to an amperometric end point.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Acetate Buffer Solution, pH 4, w/dropper.....	1 mL.....	100 mL	14909-32
Iodine Standard Solution, 0.0282 N	varies.....	1000 mL	23333-53
Phenylarsine Oxide (PAO) Titrant, 0.00564 N*	varies.....	1000 mL	1999-53
Potassium Iodide, SwifTest refill	0.10 g	50 g.....	1077-60
Sodium Thiosulfate Standard Solution, stabilized, 0.00564 N*	varies.....	1 L	24088-53

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®† coated.....	1	each.....	50085-00
Pipet, Volumetric, Class A, 0.50 mL	1	each.....	14515-34
SwifTest dispenser.....	1	each.....	28341-00

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
Potassium Iodide, Powder Pillows	1	100/pkg.....	1077-99

Optional Apparatus

Mini-printer, thermal, w/cable.....	each.....	A70P021
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*Either titrant may be calibrated with this procedure.

†Teflon is a Registered Trademark of EI DuPont Company.



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FAX: (970) 669-2932

Amperometric Back Titrant Calibration

Titration Workstation

Scope and Application: The following sequence guides the user through the calibration procedure for the 0.0282 N (28.2 mN) Iodine Standard Solution titrant.



Sample Tips and Techniques

- Sample glassware must be cleaned and pretreated to satisfy any chlorine demand. See *Section 7.2 Container Pretreatment* on page 63 for additional information.
- Always use organic-free reagent water for sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every calibration.



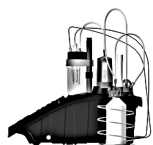
Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.
- It is recommended that titrations for titrant calibration be performed in triplicate.



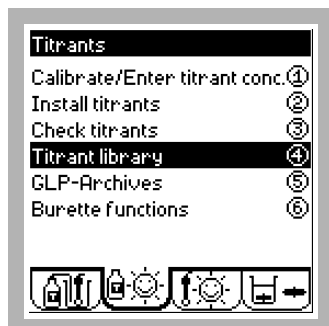
Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten, and **0** to darken.
- A distinction is drawn between running a new test and a new sample on the AutoCAT. Each test is a replicate run of the current or previous sample analysis. The AutoCAT automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water between calibrations.
- The AutoCAT 9000 can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates concentration based on the sample volume. Make sure that the sample volume is correct.
- The data for any sample calibration may be analyzed repeatedly in manual or automatic mode. The results are not stored in the archives until they are accepted.
- Press the **STOP** key any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit.
- Press the **CHECK MARK** key any time during data acquisition to halt data collection.
- Press the **DEL** key during any timer period (except the Start Timer) to immediately exit the timer and proceed to the next step in the procedure.
- Flush the burette each day before the first sample test or calibration is performed. See Daily Start-up on page 26.
- Flush the burette when changing titrants. See Changing Titrants on page 25.



AutoCAT Calibration Method

Iodine Titrant Calibration



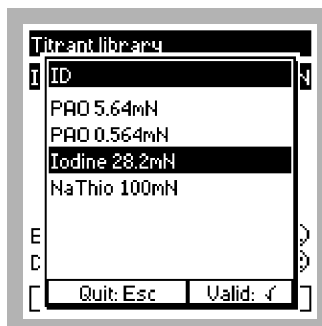
1. Turn the instrument on if necessary and access the Titrants menu.

Press 4 to select Titrant Library.

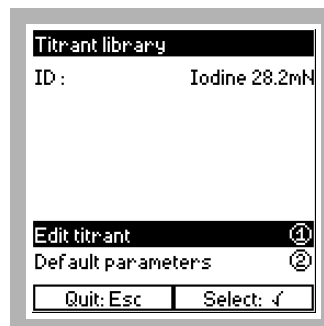
Note: Supervisor-mode is required to access calibrations. See Accessing Supervisor Mode on page 33.



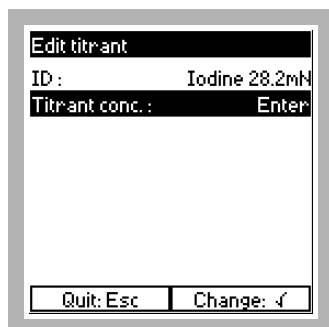
2. Highlight ID.
Press the **CHECK MARK** to change.



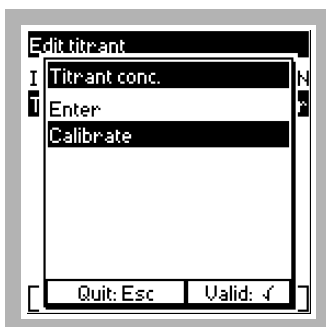
3. Highlight Iodine 28.2mN.
Press the **CHECK MARK** to validate.



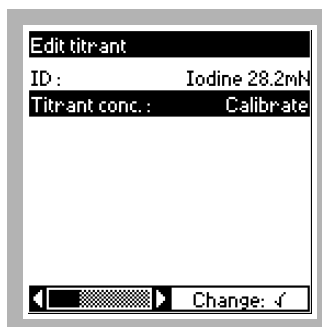
4. Press 1 to select Edit Titrant.



5. Press the **CHECK MARK** to change the titrant concentration input mode.



6. Highlight Calibrate.
Press the **CHECK MARK** to validate.



7. The titrant concentration input mode is now set to calibrate and the calibration parameters are now available by scrolling this screen.
Press **ESC** twice to return to the Titrants menu.



8. Press 1 to select Calibrate/Enter titrant conc.
Note: Titrant calibration is now required before analyses may be run as indicated by the "Stormy" icon.

9. Press **1** to select. Run Calibration to start the embedded calibration sequence.

Note: Last Calibration will indicate the date of the previous calibration.

10. Press the **CHECK MARK** to change the User.

Press **1** to confirm.

Note: The user ID will be stored in the GLP archives for future reference.

Note: This screen is skipped if User ID is disabled. See Section 3.3.2 Setting a User ID on page 27.

11. Highlight Concentration.

Press the **CHECK MARK** to change the concentration or proceed to step 12.

Note: The default concentration may be changed to reflect standardization or the "Certificate of Analysis" value for a new bottle.

12. Highlight Lot No.

Press the **CHECK MARK** to change the titrant lot number or proceed to step 13.

13. Highlight Volume for Test 1.

Press the **CHECK MARK** to change the calibration volume or proceed to step 14.

14. Prepare a calibration sample.

- Add 200 mL of DI-water to a 250-mL glass beaker.
- Add 1.00 mL of Arsenite Standard Solution.
- Add 4 g of sodium bicarbonate.

Press **1** to confirm.

15. Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water.

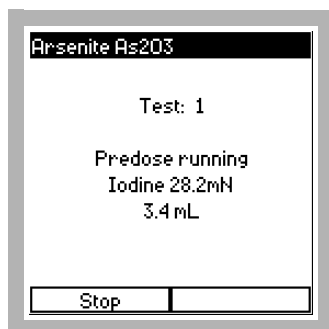
Insert the magnetic stir bar into the calibration sample and place it on the stirrer platform.

Lower the electrode head onto the beaker rim.

Press **1** to confirm.

16. Press **1** to confirm.

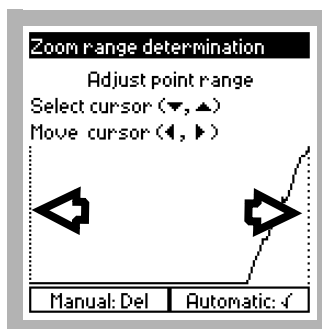
Press the **CHECK MARK** to change the increment.



17. The calibration titration starts by filling the burette with titrant and subsequently dispensing a 3.4-mL predose of Iodine into the calibration sample. This will bring the electrical signal into measurable range.



18. The Start Timer will begin to allow the electrode to stabilize before data is collected. After the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve in real time.

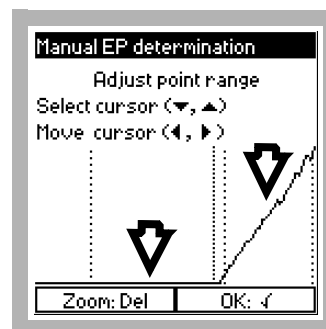


19. The Zoom Range Determination window will display the titration curve. Select and move the vertical lines (cursor) to define the range of data points for analysis.

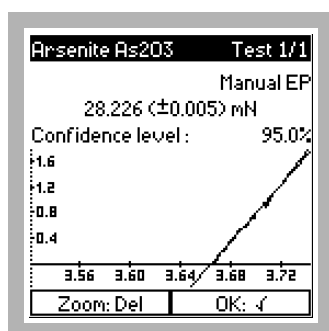
Note: Defining the range of data points eliminates undesirable portions of the titration curve.

Select type of end point determination:

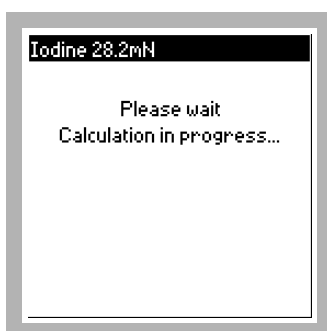
Press the **CHECK MARK** for Automatic and proceed to step 22 or press **DEL** for Manual and proceed to step 20.



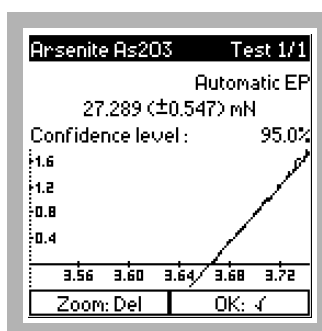
20. Select two line segments, one on each side of the titration end point, by positioning the cursors at the beginning and end of each segment. Press the **CHECK MARK** to confirm changes. Press **DEL** to return to the previous window.



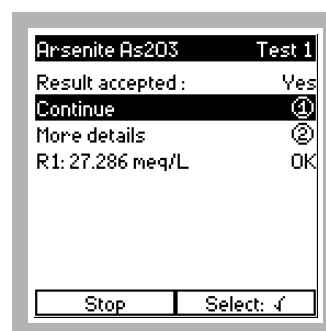
21. Press the **CHECK MARK** to accept the analysis. Proceed to step 24. Press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.



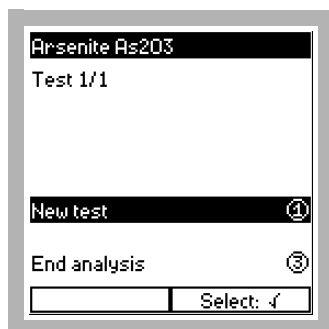
22. The AutoCAT will run the analysis based on the automatic selection of linear segments. **Note:** This algorithm requires approximately 60 seconds to complete the analysis.



23. Press the **CHECK MARK** to accept the analysis. Press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.

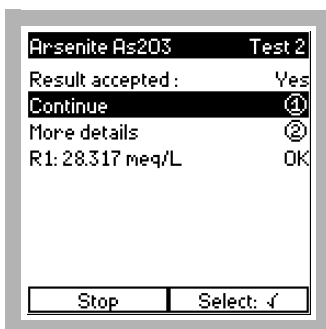


24. Press **1** to select Continue. Press **2** to select More Details and view analysis statistics specific to the current calibration.



25. Press **1** to select New Test to run a replicate calibration. Proceed to *step 26* or select Press **2** to select End Analysis and store the titrant calibration value and return to the Methods menu.

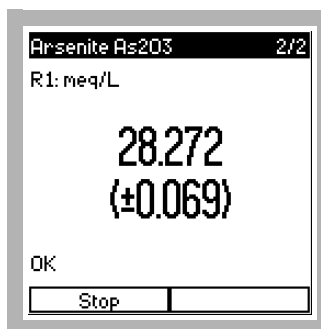
Note: If subsequent replicate calibrations are run, the final titrant concentration will automatically be stored as the mean value from all the replicate titrant calibrations.



26. The replicate analysis is identical to the first calibration.

Upon completion of the analysis, and acceptance of the data, subsequent replicate analyses can be performed if desired.

Press **1** to select Continue and perform additional tests and/or samples, or press **2** to select More Details to view analysis statistics for the current calibration.



27. The arithmetic mean is calculated from the replicate analyses.

Press the **CHECK MARK** to accept the calibration value and return to the Titrants menu.



In the Titrants menu, the accepted calibration has caused the **Titrant** tab icon to become sunny. This indicates that the titrant concentration has been properly calibrated and analyses may resume.

Safety

Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

Summary of Method

The 0.0282 N Iodine solution is standardized by titrating it against 0.1000 N Arsenite Standard Solution. The Iodine calibration procedure embedded in the AutoCAT 9000 is adapted from procedure 4500-Cl C. g. in “Standard Methods for Examination of Water and Wastewater” (20th Edition).

A calibration sample is prepared by adding 1.00 mL of standard 0.1000 N Arsenite solution and 4.0 g sodium bicarbonate (NaHCO_3) to 200 mL of chlorine free deionized water. The calibration sample is then titrated against the Iodine titrant. The embedded procedure calls for a 3.4-mL predose prior to titration. The titration end point is around 3.5 mL using the embedded method as defined. Perform a back titration to an amperometric end point.

Iodine

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Arsenite Standard Solution, 0.1000 N	1.00 mL.....	100 mL	28435-42
Sodium Bicarbonate	4 g	454 g.....	776-01
Iodine Standard Solution, 0.0282 N	varies.....	1000 mL	23333-53

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Pipet, Volumetric, Class A, 1.00 mL	1	each.....	14515-35

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
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Optional Apparatus

Mini-printer, thermal, w/cable.....	each.....	A70P021
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7.1 Chlorine

A common source of error when testing water samples for chlorine is the failure to obtain a representative sample. Free chlorine is a strong oxidizing agent and is very unstable in natural waters. It reacts readily with certain inorganic compounds and oxidizes organic compounds more slowly. Various factors, including reactant concentrations, pH, temperature, salinity, and sunlight influence the decomposition of free chlorine in water. Monochloramine, on the other hand, is much more persistent in the environment. Typically, the decay rate of monochloramine is tenfold slower than the decay of free chlorine in natural waters*.

Ideally, samples should be analyzed for chlorine on site. Because the amperometric method is usually performed in the laboratory, the delay between sample collection and analysis should be minimized. If sampling from a tap, allow water to flow 4–5 minutes to ensure a representative sample.

7.2 Container Pretreatment

Avoid plastic sample containers with a high chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach solution to 1 liter of water) for at least one hour. After soaking, rinse thoroughly with deionized/distilled water. Rinse sample containers thoroughly with deionized/distilled water after use to reduce the need for pretreatment.

7.3 Handling

Use separate, dedicated sample containers that are labelled for free and total chlorine determinations. Do not use the same sample containers for free and total chlorine analysis. Store your labelled sample containers for later use.

Avoid excess agitation and exposure to sunlight when sampling. Allow several volumes of the container to overflow and cap the sample container to eliminate headspace above the sample.

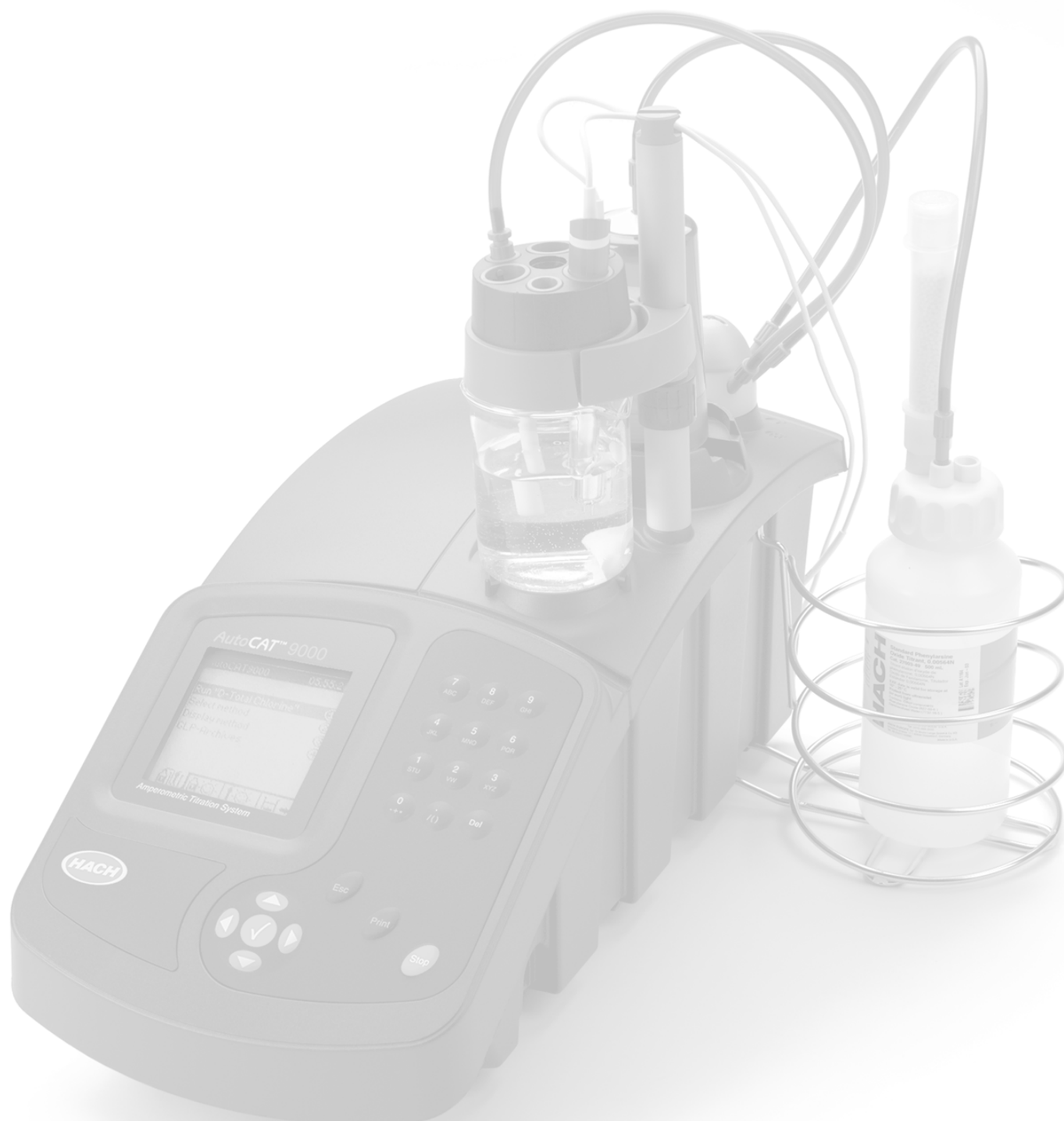
7.4 Samples for Back Titration

If the back-titration method is used for total chlorine determinations, preserve the sample on site. Add 1.00 mL of 0.00564 N phenylarsine oxide (PAO) and 1.0 mL of pH 4 acetate buffer to a clean, dry glass container with at least 250 mL capacity (such as a BOD bottle). At the sampling site, measure 200 mL of sample and carefully transfer it to the sample container. Swirl to mix. Do not overflow the sample container with preservative in it. Headspace will remain above the sample.

The delay between sample fixing and analysis should be minimized (usually less than 1 hour) to prevent bacterial decomposition of excess PAO in the sample. It is important that the entire contents of the sample container be transferred to the beaker used in the titration. See 5.2.3.4 *Reductant Concentration* and Section 5.2.3.5 *Reductant Volume* on page 46.

* *Water Chlorination: Environmental Impact and Health Effects*, Vol. 4, Book 1: *Chemistry and Water Treatment*, page 33.

Section 8 Titration Procedures





Amperometric Forward Titration

Titration Workstation

Chlorine Dioxide
Chlorite
Free Chlorine

100–5000 mg/L as ClO₂
100–5000 mg/L as ClO₂⁻
100–2000 mg/L as Cl₂

Scope and Application: For yield calculation of a chlorine dioxide generator*

* Procedure equivalent to *Standard Methods* 4500-ClO₂ E.



Sample Tips and Techniques

- Soak all glassware in a strong chlorine dioxide (ClO₂) solution (300–500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Use the glassware for this method only.
- Chlorine dioxide and its by-products are volatile and can be easily lost from aqueous solution. Minimize air contact by collecting the effluent sample into an amber glass bottle with minimum headspace.
- Minimize agitation when measuring sample volumes. Remove sample portions with a volumetric pipet. Always place the tip at the bottom of the sample container.
- Always use organic-free water for effluent sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



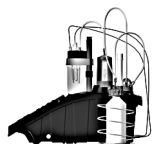
Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. The default volume for this method is 5.0 mL and can be adjusted to expand the test range.
- The AutoCAT 9000 calculates concentration based on the sample volume. Ensure that the sample volume is correct.
- Press **STOP** at any time to interrupt instrument operation; the user can resume, restart, or quit completely.
- Press the **CHECK MARK** at any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except Start Timer) to immediately exit the timer and proceed to the next step.
- Press **ESC** during any titration/calibration data collection period or timer to access **Edition** mode. See *Edition Mode* on page 30.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.



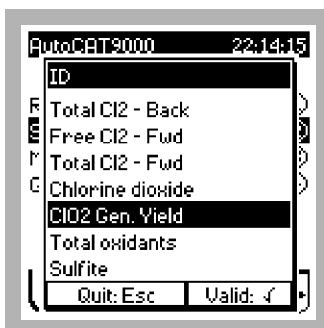
AutoCAT Titration Method

ClO₂ Yield Titration 1



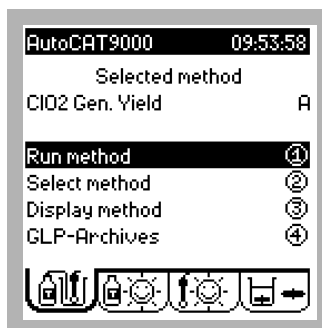
1. Turn the instrument on and access the Methods menu.

Press **2** to choose Select Method.



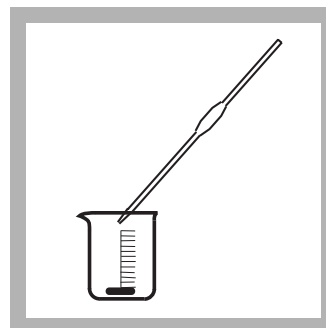
2. Highlight ClO₂ Gen. Yield

Press the **CHECK MARK** to validate.



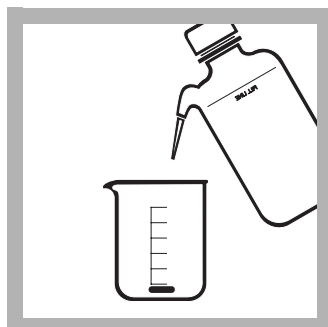
3. Press **1** to select Run method.

This method uses the 0.10 N Sodium Thiosulfate titrant. See *Software Setup for Titrant Installation* on page 38.

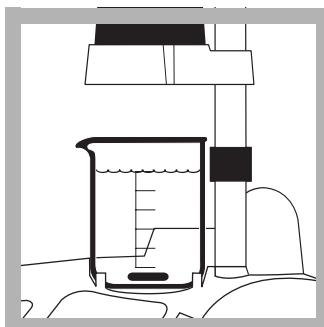


4. Measure 1–5 mL of generator effluent sample with a pipet and transfer to a 250-mL beaker containing the magnetic bar.

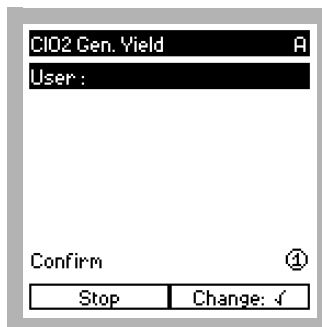
Note: All containers must be pretreated for chlorine demand, see *Container Pretreatment* on page 63.



5. Dilute the sample to approximately 200-mL with Organic Free water.



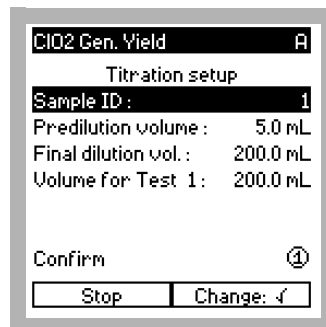
6. Place the sample onto the AutoCAT 9000 stirrer platform.



7. Verify User.

Press the **CHECK MARK** to enter a new user or press **1** to confirm.

Note: This screen will be skipped if the User ID is disabled. See *Setting a User ID* on page 27.



8. Highlight Sample ID.

Press the **CHECK MARK** to enter a new sample ID or proceed to *step 9*.

ClO ₂ Gen. Yield		A
Titration setup		
Sample ID :	1	
Predilution volume :	5.0 mL	
Final dilution vol. :	200.0 mL	
Volume for Test 1 :	200.0 mL	
Confirm Ⓢ		
Stop	Change: ✓	

9. Highlight Predilution volume.

Press the **CHECK MARK** and enter the volume pipetted in Step 4.

Press **1** to confirm.

Note: Final dilution volume and Volume for Test default values need not be changed.

ClO ₂ yield Add.1		A
Add reagent 1		
Phosphate buffer, 1 dose		
Stop	OK: ✓	

10. Add 1 dose of pH 7.0 Phosphate Buffer.

Press the **CHECK MARK** to confirm.

Note: Phosphate buffer is added to adjust the sample pH. The precise amount added is not crucial for the accuracy or precision of the analysis.

ClO ₂ yield Add.1		A
Add reagent 2		
Potassium iodide (KI), 1 dose		
Stop	OK: ✓	

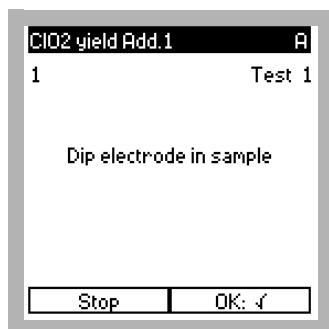
11. Use the measuring spoon to add 1.0 g of potassium iodide (KI).

Press the **CHECK MARK** to confirm.

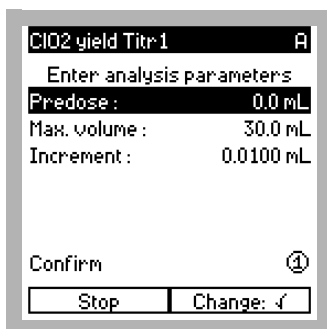
Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.

ClO ₂ yield Add.1		A
Reagents mixing		
Please wait...		
Timer : 00:02		
Stop	Skip: Del	

12. The timer will start, allowing the reagents to mix before starting the titration.



13. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



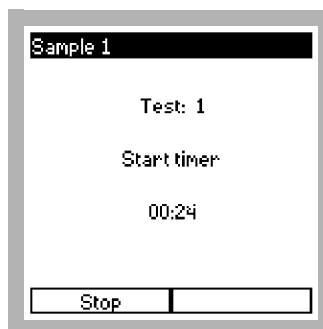
14. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

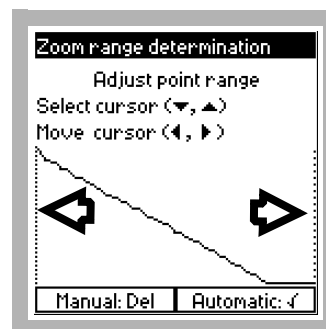
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if auto-scaling software is enabled.



15. The Start Timer will start to allow the electrode to stabilize before data collection.

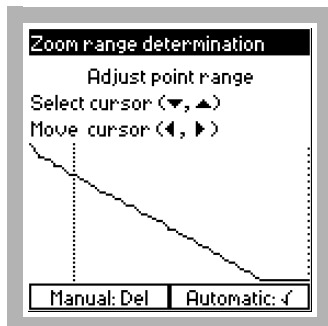
Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



16. The Zoom Range Determination window will display the titration curve.

Use the navigation buttons to select and move the cursors to define the range of data points for analysis.

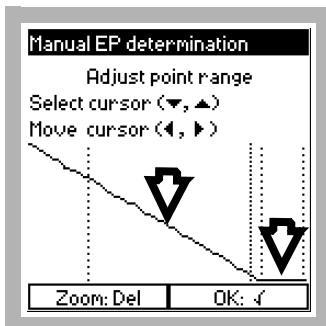
Note: Defining the range of data points excludes undesirable portions of the titration curve from the analysis.



17. Select type of end point determination.

Press **DEL** for Manual.

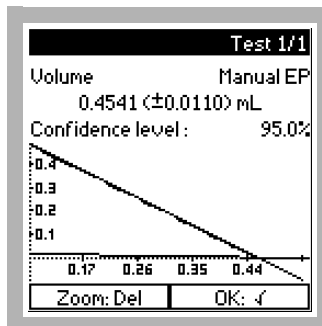
Note: Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.



18. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

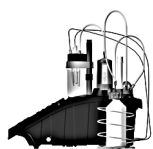
Note: For more information on manual EP determination, see page 135.



19. Press the **CHECK MARK** to accept the analysis and proceed to *Titration 2* or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

Note: The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual and/or automatic modes. The results are not stored until accepted.

Note: The AutoCAT 9000 stores all titration results and then automatically calculates each analyte value after the procedure is complete.



AutoCAT Titration Method

ClO₂ Yield Titration 2

ClO₂ yield Add.2 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of
2.5 N Hydrochloric acid and
stir for several seconds.
Carefully remove the sample
from the stirrer platform and
place in the dark.
Press the **CHECK MARK**
to confirm.

ClO₂ yield Add.2 A

Dark reaction in progress
Please wait...

Timer : 04:54

Stop Skip: Del

2. The timer will start.
This timer allows a 5-minute
reaction period before
starting the titration.

ClO₂ yield Add.2 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample
from the dark and carefully
place onto the AutoCAT
stirrer platform.
Lower the electrode head
onto the beaker rim.
Press the **CHECK MARK**
to confirm.

ClO₂ yield Titr2 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 30.0 mL

Increment : 0.0150 mL

Confirm ①

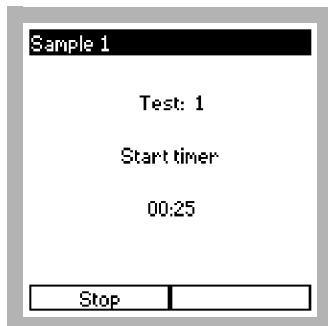
Stop Change: ✓

4. The analysis parameters
that have been stored for the
current Sub-ID may be
edited at this time.
Highlight the appropriate
line and press CHECK
MARK to change one of the
analysis parameters or press
1 to confirm.

Note: Any changes made will
become the new default
parameters for this method
Sub-ID.

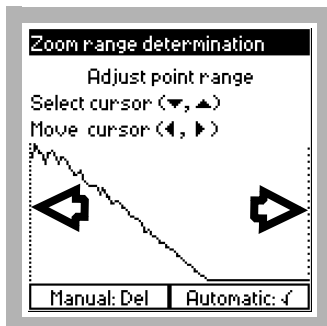
Note: These Sub-ID
parameters can be edited here
as 'run-time' settings, or from
the Main Menu as described in
Section 3.5.

Note: This step will be skipped
if autoscaling software is
enabled.

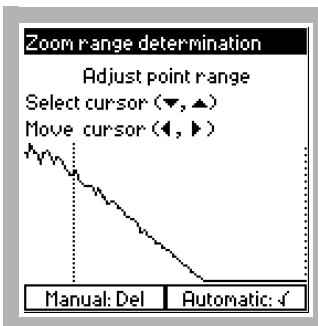


5. The Start Timer will begin, allowing the electrode to stabilize before data is collected.

Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.

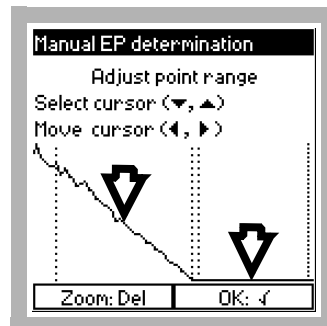


6. The Zoom Range Determination window will display the titration curve. Select and move the cursors to define the range of data points for analysis.



7. Select the type of end point determination. Press **DEL** for Manual.

Note: Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.

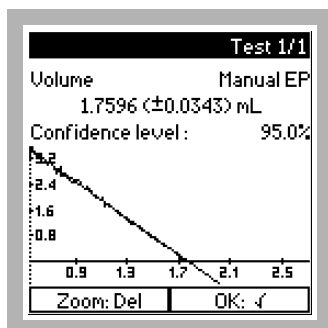


8. Using the navigation keys, select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

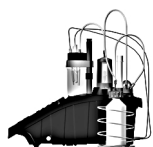
Press the **CHECK MARK** to confirm changes.

Press **DEL** to return to the Zoom window.

Note: For more information on manual EP determination, see page 135.

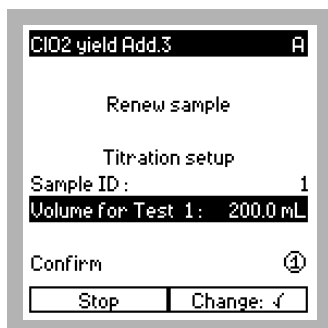


9. Press the **CHECK MARK** to accept the analysis and proceed to Titration 3 or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

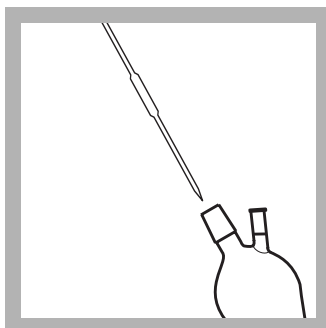


AutoCAT Titration Method

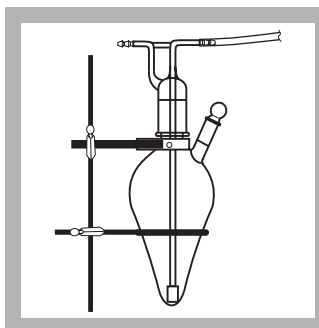
ClO₂ Yield Titration 3



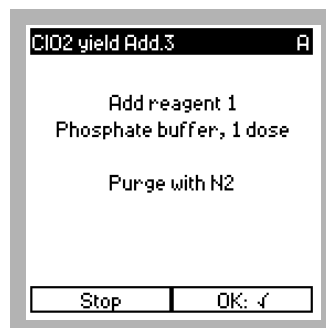
1. Press the **CHECK MARK** to enter a new volume. Press **1** to confirm.



2. Transfer 200 mL of organic-free DI water to a Gas Washing Bottle (GWB). Add identical volume of sample pipetted in Titration 1, Step 4. Add 1 dose of pH 7.0 phosphate buffer, and swirl to mix.



3. Insert the purge tube and dispersion tip into the GWB. Connect the GWB inlet to a tank of purified nitrogen.

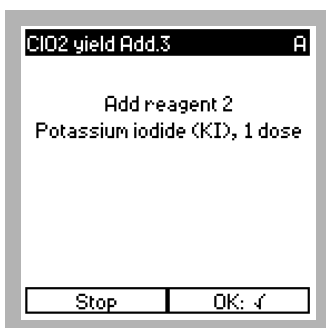


4. Use a needle valve to adjust the flow of nitrogen to provide a steady stream of bubbles through the sample. Press the **CHECK MARK** to continue.



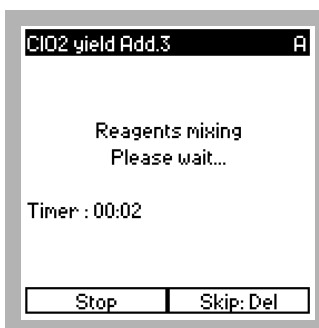
5. Purge nitrogen gas through the sample for 15 minutes. When the timer beeps, transfer the purged sample into a 250-mL beaker. Add the magnetic stir bar.

Note: If the nitrogen purge has already been performed, press **DEL** to skip this timer and proceed to the next step.

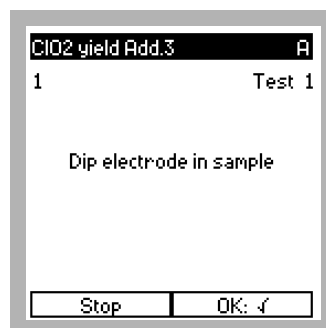


6. Use the measuring spoon to add 1.0 g of potassium iodide (KI). Place the sample onto the stirrer platform. Press the **CHECK MARK** to confirm.

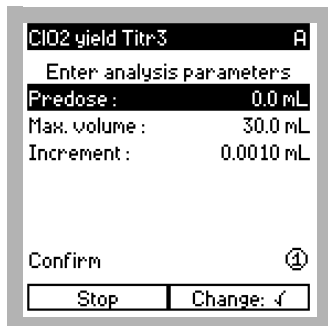
Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.



7. The timer will begin, allowing the reagents to mix before starting the titration.



8. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



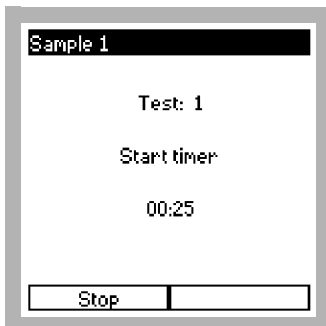
9. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

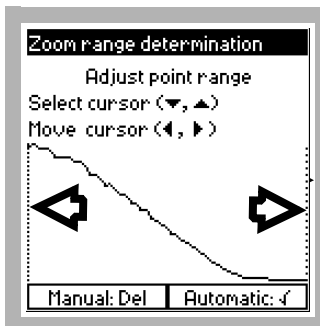
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.

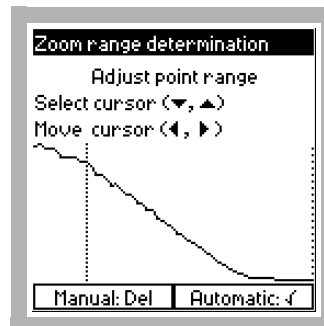


10. The Start Timer will begin, allowing the electrode to stabilize before data is collected.

After the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve in real time.



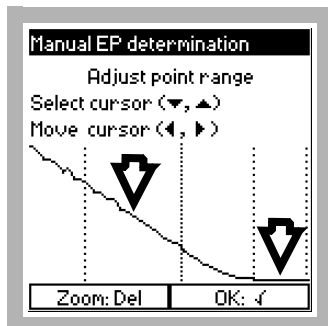
11. The Zoom range determination window will display the titration curve. Select and move the cursors to define the range of data points for analysis. Proceed to *step 12*.



12. Select type of end point determination.

Press **DEL** for Manual.

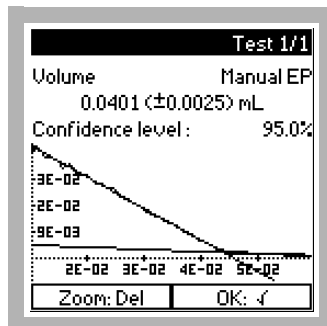
Note: Automatic determination attempts to identify linear segments without user input but is **not** recommended for this method.



13. Use the navigation buttons to select two line segments, one on each side of the titration end point, by positioning the cursors at the beginning and end of each segment (indicated by arrows).

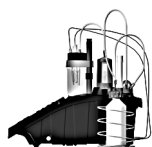
Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.



14. Press the **CHECK MARK** to accept the analysis and proceed to Titration 4.

Press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.



AutoCAT Titration Method

ClO₂ Yield Titration 4

ClO₂ yield Add.4 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of 2.5 N Hydrochloric acid and stir for several seconds.
Carefully remove the sample from the stirrer platform and place in the dark.
Press the **CHECK MARK** to confirm.

ClO₂ yield Add.4 A

Dark reaction in progress
Please wait...

Timer : 04:55

Stop Skip: Del

2. The timer will start.
This timer allows a 5-minute reaction period before starting the titration.

ClO₂ yield Add.4 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample from the dark and place onto the AutoCAT titration platform.
Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.

ClO₂ yield Titr.4 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 30.0 mL

Increment : 0.0100 mL

Confirm ①

Stop Change: ✓

4. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

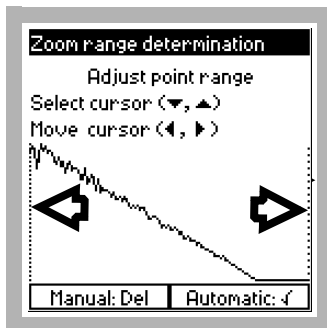
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.



5. The Start Timer will begin, allowing the electrode to stabilize before data is collected.

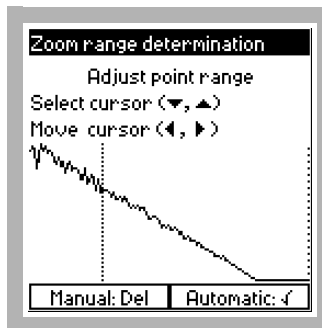
Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve in real time.



6. The Zoom Range Determination window will display the titration curve.

Select and move the cursors to define the range of data points for analysis.

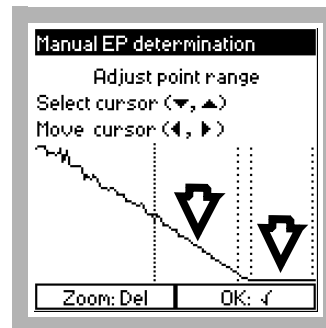
Proceed to step 7.



7. Select type of end point determination.

Press **DEL** for Manual.

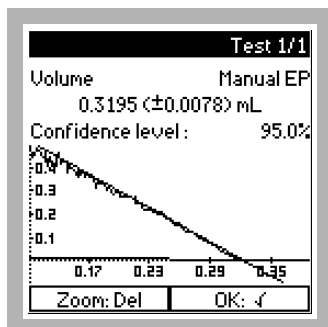
Note: Automatic determination attempts to identify linear segments without user input but is **not recommended** for this method.



8. Use the navigation buttons to select two line segments, one on each side of the titration end point, by positioning the cursors at the beginning and end of each segment.

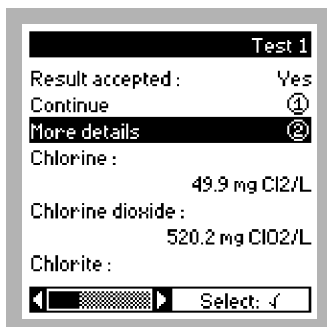
Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.



9. Press the **CHECK MARK** to accept the analysis.

Press **DEL** to return to the previous window. Adjust the linear segments and reanalyze the data.

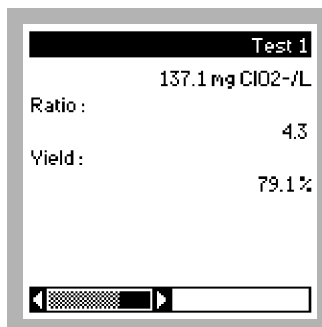


10. The analysis for this test is complete.

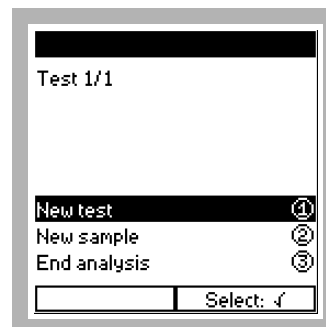
Use the **RIGHT** key to view the second page of results, or:

Press **1** to select Continue and analyze additional samples, perform more tests, or finish analyses.

Press **2** to select More Details and view analysis statistics specific to the current sample ID.



11. View Yield and Ratio on this screen, and then press the **LEFT** key to return to main results screen.



12. Press **1** to select New Test to run a replicate sample.

Press **2** to select New Sample to initiate analysis of a new sample with a new Sample ID. See *Instrument Tips and Techniques* on page 67.

Press **3** to select End Analysis and return to the Methods menu.

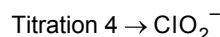
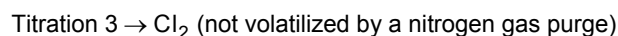
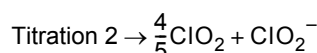
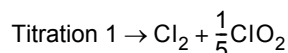
Summary of Method

This method is used to determine the yield from a chlorine dioxide generator system and to optimize the generator performance. Yield is defined as the ratio of chlorine dioxide produced to the theoretical maximum. The percent yield is calculated as follows:

$$\frac{\text{chlorine dioxide concentration}}{\text{sum of the total chlor-oxy species concentration}} \times 100 = \% \text{ yield}$$

Most modern generators will have yields of 95% or better.

The AutoCAT gives results for chlorine dioxide (ClO_2), chlorite (ClO_2^-), and free chlorine (Cl_2). Four successive titrations are required:



The AutoCAT 9000 stores all titration results and, after completion, calculates each analyte value.

This method can be greatly accelerated by purging a sample portion (used for Titrations 3 and 4) with nitrogen while performing Titrations 1 and 2.

Another measurement used to gauge ClO_2 generator production is the ratio of Titration 2 to Titration 1 results. This provides an estimate of any untreated chlorite or chlorine feedstock in the generator effluent. This method is only applicable to those generators using chlorite and gaseous chlorine feeds. Ideally, the optimum ratio of Titration 2/Titration 1 results should lie between 3.9 and 4.05. See *Table 1*.

Table 1 Generator Effluent Condition

Titr 2/Titr 1 Ratio	Effluent Condition
Less than 3.9	Unreacted chlorine, possible chlorate contamination
3.9–4.05	Optimum
Greater than 4.05	Unreacted chlorite

Typically, a ratio of less than 3.75 indicates a generator yield of less than 95%.

Chlorine Dioxide Generator Yield

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Hydrochloric Acid Standard Solution, 2.5 N	4 mL.....	100 mL	1418-32
Phosphate Buffer pH 7, w/dropper	2 mL.....	100 mL	21553-32
Potassium Iodide, ACS.....	1.0 g	100 g.....	167-26H
Sodium Thiosulfate Solution, 0.10 N	varies.....	1000 mL	323-53

Required Apparatus

Description	Qty. required per test	Unit	Cat. No.
Beaker, Glass, 250-mL	1	each.....	500-46H
Gas Washing Bottle	1	each.....	26622-00
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Measuring Spoon, 1.0-g (NaCl weight), molded plastic	1	each.....	510-00
Pipet, Volumetric, Class A, 5.00-mL.....	1	each.....	14515-37
Support, Ring Stand.....	1	each.....	563-00
Support Ring, for GWB.....	1	each.....	26563-00

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
------------------------------------	-------------	--------------	----------

Optional Apparatus

Cylinder, Graduated, 250 mL	1	each.....	508-46
Mini-printer, thermal, w/cable.....		each.....	A70P021
Pipet, Volumetric, Class A, 1.00 mL	1	each.....	14515-35
Pipet, Volumetric, Class A, 2.00 mL	1	each.....	14515-36
Pipet, Volumetric, Class A, 3.00 mL	1	each.....	14515-03
Pipet, Volumetric, Class A, 4.00 mL	1	each.....	14515-04

*Teflon is a Registered Trademark of EI DuPont Company.



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FAX: (970) 669-2932



w/ Chlorite and Free Chlorine

Amperometric Forward Titration

Titration Workstation

Chlorine Dioxide
Chlorite
Free Chlorine

0.10–5.00 mg/L as ClO₂*
0.10–5.00 mg/L as ClO₂⁻
0.10–2.00 mg/L as Cl₂

Scope and Application: For water and wastewater**

* Higher ranges can be determined through sample dilution. See *Section 5.2.3.3 Dilution* on page 46.

**Procedure equivalent to *Standard Methods 4500-ClO₂ E*.



Sample Tips and Techniques

- Soak all glassware in a strong chlorine dioxide (ClO₂) solution (300–500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Use the glassware for this method only.
- Chlorine dioxide and its by-products are volatile and can be easily lost from aqueous solution. Minimize air contact by attaching a flexible hose to a tap and placing the end at the bottom of a 1-L amber glass bottle. Turn on the tap and allow several volumes to overflow, then slowly remove the sample line and cap the container with minimum headspace.
- Minimize agitation when measuring sample volumes. Remove sample portions with a volumetric pipet. Always place the tip at the bottom of the sample container. If using 200-mL sample increments, use a 100-mL pipet to withdraw two portions of sample.
- Always use organic-free water for sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



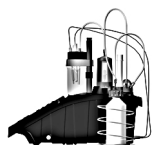
Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



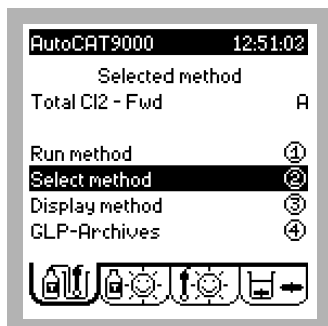
Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates concentration based on the sample volume. Make sure that the sample volume is correct.
- Press **STOP** any time to interrupt instrument operation; the user can resume, restart, or quit completely.
- Press the **CHECK MARK** any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except Start Timer) to immediately exit the timer and proceed to the next step.
- Press **ESC** during any titration/calibration data collection period or timer to access *Edition* mode. See *Edition Mode* on page 30.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.



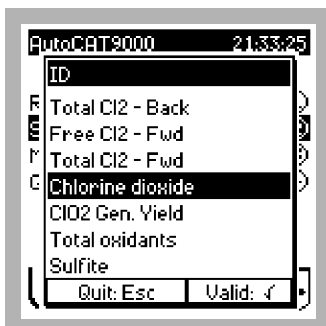
AutoCAT Titration Method

Chlorine Dioxide Titr. 1



1. Turn the instrument on if necessary and access the Methods menu.

Press 2 to choose Select Method.



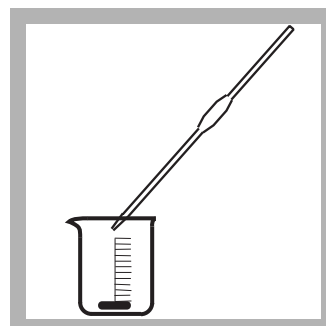
2. Highlight Chlorine dioxide.

Press the **CHECK MARK** to validate.



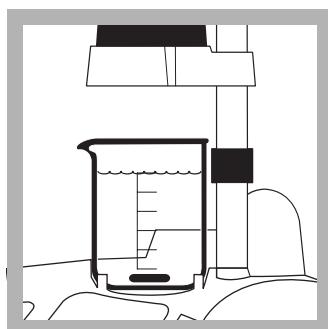
3. Press 1 to select Run method.

This method used the 5.64mN PAO titrant. See *Software Setup for Titrant Installation* on page 38.

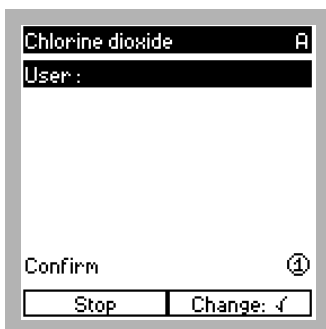


4. Measure 200 mL of sample solution with a pipet and transfer to a 250-mL beaker with the specified magnetic stir bar.

All containers must be pretreated for chlorine demand, see *Container Pretreatment* on page 63.



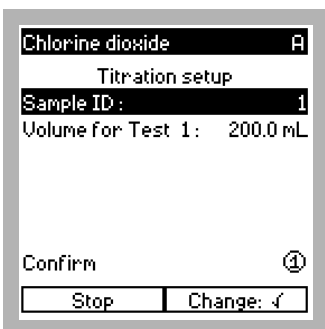
5. Place the sample onto the AutoCAT 9000 stirrer platform.



6. Verify User.

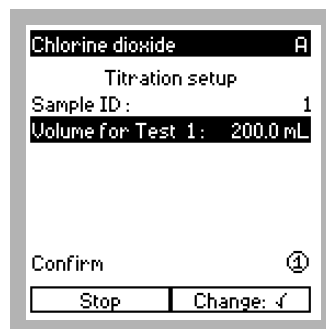
Press the **CHECK MARK** to enter a new user or press 1 to confirm.

Note: This screen will be skipped if the User ID is disabled. See *Setting a User ID* on page 27.



7. Highlight Sample ID.

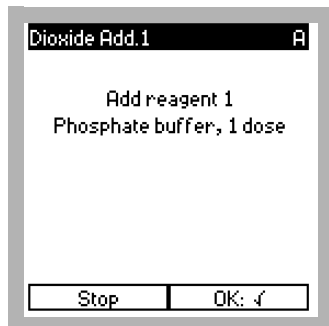
Press the **CHECK MARK** to enter a new sample ID or proceed to step 8.



8. Highlight Volume for Test 1.

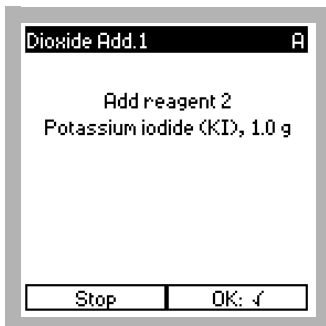
Press the **CHECK MARK** to enter a new volume.

Press 1 to confirm.



9. Add 1.0 mL of pH 7.0 Phosphate Buffer Solution. Press the **CHECK MARK** to confirm.

Note: Phosphate buffer is added to adjust the sample pH. The precise amount added is not crucial for the accuracy or precision of the analysis.

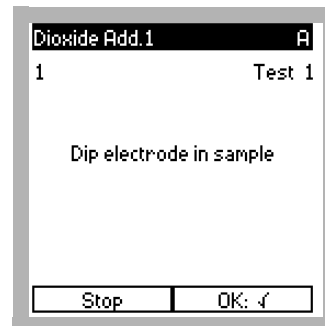


10. Use the measuring spoon to add 1.0 g of potassium iodide (KI). Press the **CHECK MARK** to confirm.

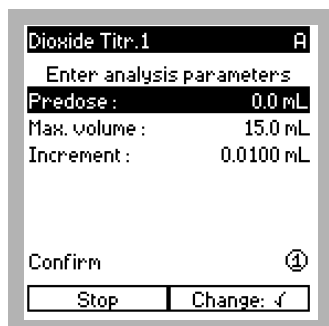
Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.



11. The timer will start. This allows a short period of time for the reagents to mix before starting the titration.



12. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



13. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press **1** to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

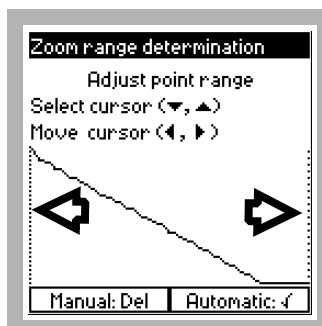
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if auto-scaling software is enabled.



14. The Start Timer will start to allow the electrode to stabilize before data collection.

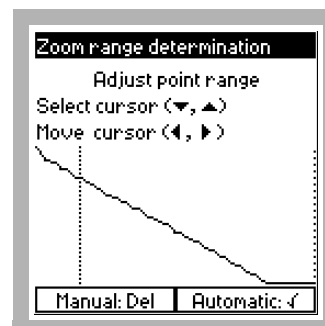
Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



15. The Zoom Range Determination window will display the titration curve.

Use the navigation buttons to select and move the cursors to define the range of data points for analysis.

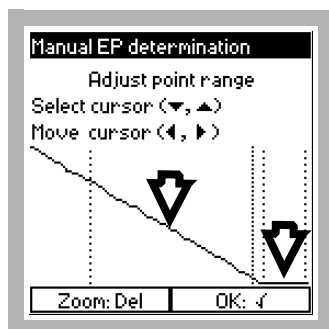
Note: Defining the range of data points excludes undesirable portions of the titration curve from the analysis.



16. Select type of end point determination.

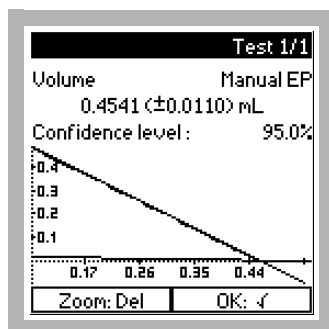
Press **DEL** for Manual.

Note: Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.



17. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment. Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

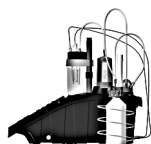
Note: For more information on manual EP determination, see page 135.



18. Press the **CHECK MARK** to accept the analysis and proceed to *Titr. 2* or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

Note: The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual and/or automatic modes. The results are not stored until accepted.

Note: The AutoCAT 9000 stores all titration results and then automatically calculates each analyte value after the procedure is complete.



AutoCAT Titration Method

Chlorine Dioxide Titr. 2

Dioxide Add.2 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of 2.5 N Hydrochloric acid and stir for several seconds.
Carefully remove the sample from the stirrer platform and place in the dark.
Press the **CHECK MARK** to confirm.

Dioxide Add.2 A

Dark reaction in progress
Please wait...

Timer : 02:49

Stop Skip: Del

2. The timer will start.
This timer allows a 5-minute reaction period before starting the titration.

Dioxide Add.2 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample from the dark and carefully place onto the AutoCAT stirrer platform.
Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.

Dioxide Titr.2 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 5.0 mL

Increment : 0.0150 mL

Confirm ①

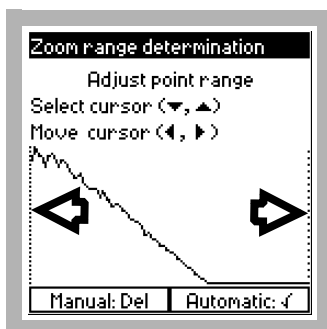
Stop Change: ✓

4. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.
Note: Any changes made will become the new default parameters for this method Sub-ID.
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.
Note: This step will be skipped if autoscaling software is enabled.



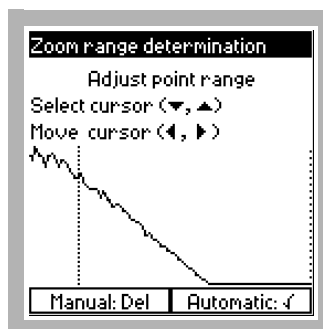
5. The Start Timer will begin to allow the electrode to stabilize before data is collected.

Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



6. The Zoom Range Determination window will display the titration curve.

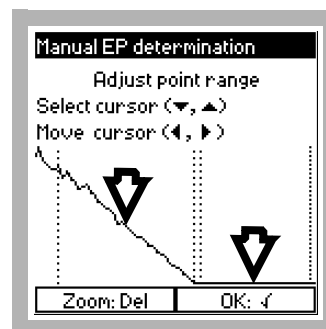
Note: Select and move the cursors to define the range of data points for analysis.



7. Select the type of end point determination.

Press **DEL** for Manual.

*Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.*

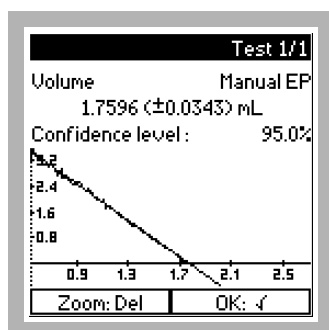


8. Using the navigation keys, select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes.

Press **DEL** to return to the Zoom window.

Note: For more information on manual EP determination, see page 135.



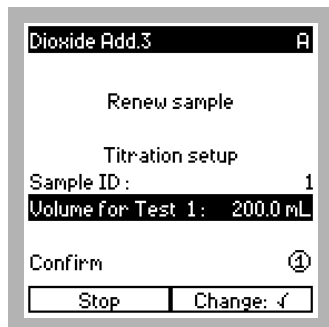
9. Press the **CHECK MARK** to accept the analysis and proceed to *Titration 3* or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

Note: For more information on manual EP determination, see page 135.

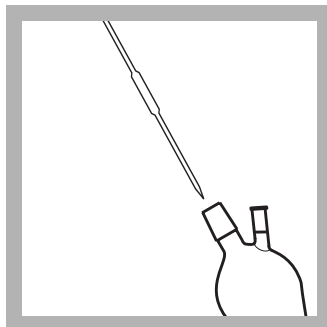


AutoCAT Titration Method

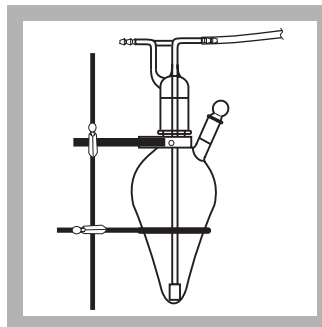
Chlorine Dioxide Titr. 3



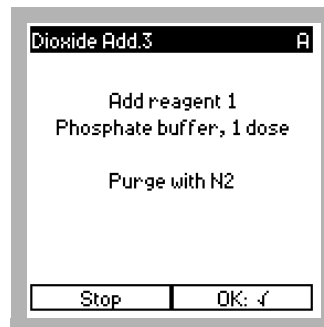
1. Press the **CHECK MARK** to enter a new volume. Press **1** to confirm.



2. Pipet 200 mL sample into a Gas Washing Bottle (GWB).
Add 1 mL of pH 7 Phosphate buffer.
Swirl to mix.



3. Insert the purge tube and dispersion tip into the GWB. Connect the GWB inlet to a tank of purified nitrogen.

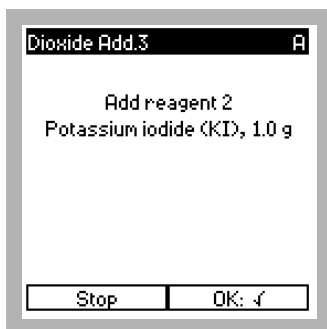


4. Use a needle valve to adjust the flow of nitrogen to provide a steady stream of bubbles through the sample.
Press the **CHECK MARK** to continue.



5. Purge nitrogen gas through the sample for 15 minutes.
When the timer beeps, transfer the purged sample into a 250-mL beaker. Add the specified magnetic stir bar.

Note: If the nitrogen purge has already been performed, press **DEL** to skip this timer and proceed to the next step.

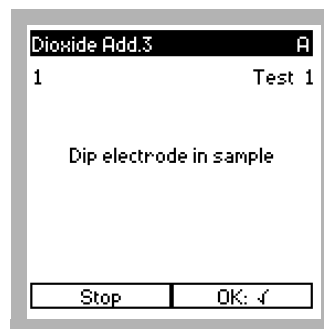


6. Use the measuring spoon to add 1.0 g of potassium iodide (KI). Place the sample onto the stirrer platform.
Press the **CHECK MARK** to confirm.

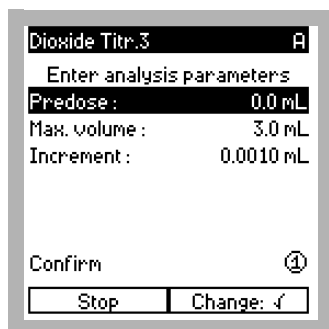
Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.



7. The timer will start to allow a short period of time for the reagents to mix before starting the titration.



8. Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.



9. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

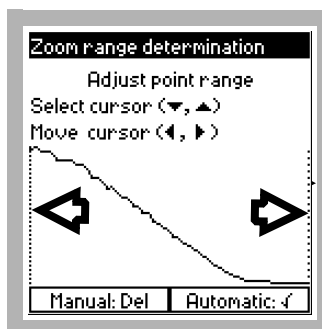
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.



10. The Start Timer will begin to allow the electrode to stabilize before data is collected.

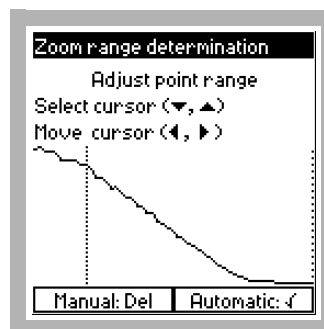
After the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve in real time.



11. The Zoom range determination window will display the titration curve.

Select and move the cursors to define the range of data points for analysis.

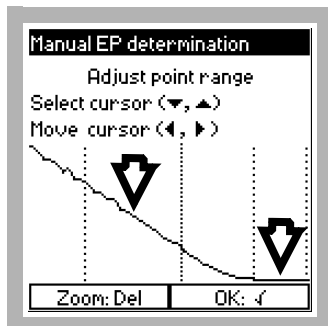
Proceed to *step 12*.



12. Select type of end point determination.

Press **DEL** for Manual.

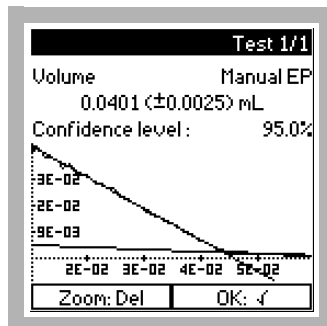
Note: Automatic determination attempts to identify linear segments without user input but is **not** recommended for this method.



13. Use the navigation buttons to select two line segments, one on each side of the titration end point, by positioning the cursors at the beginning and end of each segment (indicated by arrows).

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

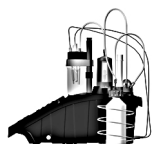
Note: For more information on manual EP determination, see page 135.



14. Press the **CHECK MARK** to accept the analysis and proceed to *Titration 4*.

Press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

Note: For more information on manual EP determination, see page 135.



Dioxide Add.4 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of 2.5 N Hydrochloric acid and stir for several seconds.
Carefully remove the sample from the stirrer platform and place in the dark.
Press the **CHECK MARK** to confirm.

Dioxide Add.4 A

Dark reaction in progress
Please wait...

Timer : 04:52

Stop Skip: Del

2. The timer will start.
This timer allows a 5-minute reaction period before starting the titration.

Dioxide Add.4 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample from the dark and place onto the AutoCAT titration platform.
Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.

Dioxide Titr.4 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 3.0 mL

Increment : 0.0100 mL

Confirm ①

Stop Change: ✓

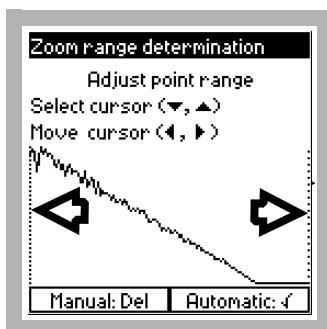
4. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.
Note: Any changes made will become the new default parameters for this method Sub-ID.
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.
Note: This step will be skipped if autoscaling software is enabled.



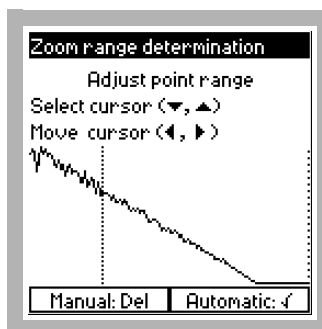
5. The Start Timer will begin.

This allows the electrode to stabilize before data is collected.

Once the electrode has stabilized, the AutoCAT 9000 will begin data acquisition and plot the titration curve in real time.



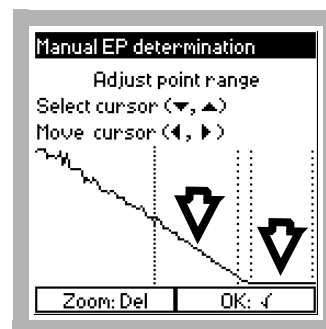
6. The Zoom Range Determination window will display the titration curve. Select and move the cursors to define the range of data points for analysis. Proceed to step 7.



7. Select type of end point determination.

Press **DEL** for Manual.

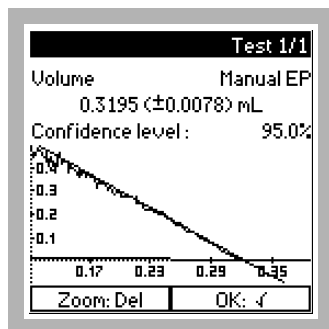
Note: Automatic determination attempts to identify linear segments without user input but is **not recommended** for this method.



8. Use the navigation buttons to select two line segments, one on each side of the titration end point, by positioning the cursors at the beginning and end of each segment.

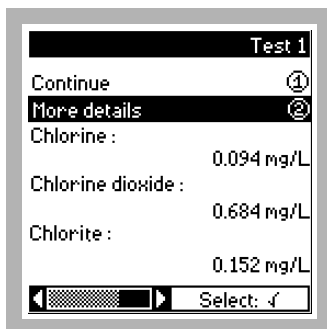
Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.



9. Press the **CHECK MARK** to accept the analysis.

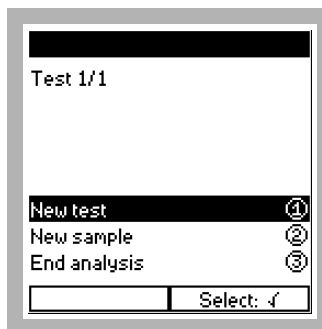
Press **DEL** to return to the previous window. Adjust the linear segments and reanalyze the data.



10. The analysis for this test is complete.

Press **1** to select Continue to perform additional tests and/or samples, or to finish analyses.

Press **2** to select More Details to view analysis statistics specific to the current sample ID.



11. Press **1** to select New Test to run a replicate sample.

Press **2** to select New Sample to initiate analysis of a new sample with a new Sample ID. See *Instrument Tips and Techniques* on page 81.

Press **3** to select End Analysis to return to the Methods menu.

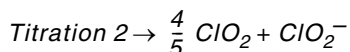
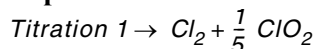
Chlorine Dioxide

Summary of Method

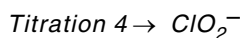
This procedure permits the determination of chlorine dioxide (ClO_2), chlorite (ClO_2^-), and chlorine (Cl_2) in the sample.

This is a multi-step procedure involving four amperometric titrations and two titration samples. These titrations are as follows:

Sample 1



Sample 2



The AutoCAT 9000 stores all titration results and, after completion, calculates each analyte value.

This method can be greatly accelerated by purging a sample portion (used for Titrations 3 and 4) with nitrogen while performing titrations 1 and 2.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1000 mL	1999-53
Hydrochloric Acid Standard Solution, 2.5 N	4 mL.....	100 mL	1418-32
Phosphate Buffer pH 7, w/dropper	2 mL.....	100 mL	21553-32
Potassium Iodide, ACS.....	2.0 g	100 g.....	167-26H

Required Apparatus

Description	Qty. required per test	Unit	Cat. No.
Beaker, Glass, 250-mL	1	each.....	500-46H
Gas Washing Bottle	1	each.....	26622-00
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Measuring Spoon, 1.0-g (NaCl weight), molded plastic	1	each.....	510-00
Pipet, Volumetric, Class A, 100-mL.....	1	each.....	14515-42
Support, Ring Stand.....	1	each.....	563-00
Support Ring, for GWB.....	1	each.....	26563-00

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
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Optional Apparatus

Mini-printer, thermal, w/cable.....	each.....	A70P021
Cylinder, Graduated, 250 mL	1	each.....508-46

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FAX: (970) 669-2932



Titration Workstation

Amperometric Forward Titration

0.100–5.000 mg/L as Cl₂***Scope and Application:** For drinking water; USEPA accepted for reporting*** Higher ranges can be determined through sample dilution. See *Section 5.2.3.3 Dilution* on page 46.**Procedure equivalent to USEPA method 330.2 and *Standard Methods* 4500-Cl.D. for drinking water.

Sample Tips and Techniques

- To avoid loss of chlorine, be careful not to agitate the sample when measuring or pouring.
- Sample glassware must be cleaned and pretreated to satisfy any chlorine demand before the sample is introduced. See *Section 7.2 Container Pretreatment* on page 63 for additional information.
- Always use organic-free water for sample dilution (Cat. No. 26415-49).
- When sampling tap water, let the faucet run for at least 4–5 minutes prior to collecting the sample.
- A convenient test sample can be prepared by diluting Chlorine Standard Solution (Cat. No. 14268-10) with deionized (DI) water.
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



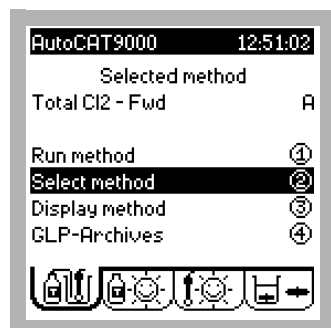
Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and then pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current or previous sample analysis. The AutoCAT automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The analysis data may be analyzed repeatedly from the Zoom Range Determination window, in manual (MEPD) and/or automatic (AEPD) modes. The results are not stored until accepted.
- The AutoCAT calculates the chlorine concentration based on the sample volume. Make sure that the sample volume is correct.
- Press the **STOP** key any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit.
- Press the **CHECK MARK** any time during data acquisition to halt data collection.
- Press the **DEL** key during any timer period (except Start Timer) to immediately exit the timer and proceed to the next step in the procedure.
- Flush the burette each day before the first sample test or calibration is performed. See Daily Start-up on page 26.
- Flush the burette when changing titrants. See Changing Titrants on page 25.

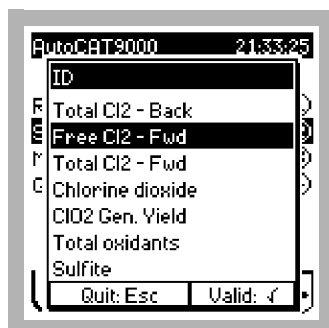


Amperometric Titration

Free Cl₂ - Fwd



1. Access the methods menu.
Press 2 to choose Select Method.



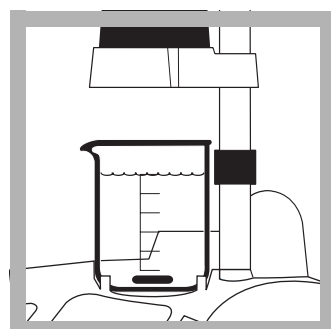
2. Highlight Free Cl₂-Forward.
Press the **CHECK MARK** to validate.



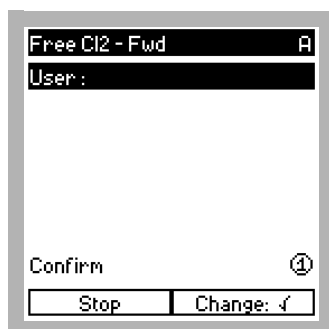
3. Press 1 to select Run method.



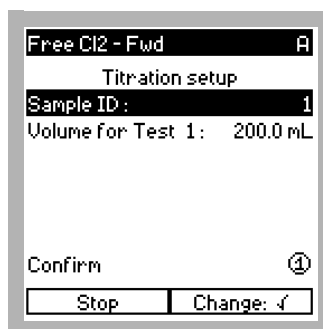
4. Measure 200 mL of sample solution into a clean 250 mL beaker.
Insert the specified magnetic stir bar into the sample beaker.
Note: Use only the provided stir bar to minimize loss of chlorine.



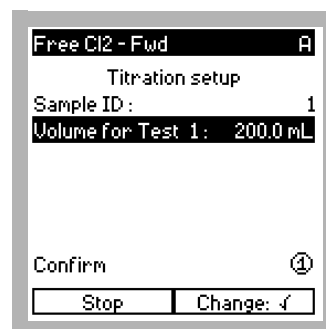
5. Place the sample onto the AutoCAT 9000 stirrer platform.



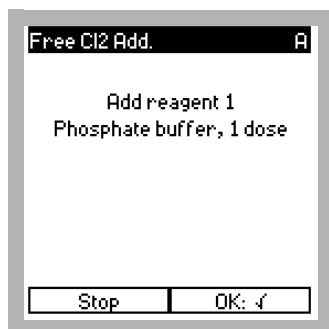
6. Verify User.
Press the **CHECK MARK** to enter a new user or press 1 to confirm.
Note: This screen will be skipped if the User ID is disabled. See Setting a User ID on page 27.



7. Highlight Sample ID.
Press the **CHECK MARK** to enter a new sample ID or proceed to step 8.



8. Highlight Volume for Test 1.
Press 1 to confirm or press the **CHECK MARK** to enter a new volume.



9. Add 1.0 mL of pH 7.0 Phosphate Buffer Solution. Press the **CHECK MARK** to confirm and start the timer.

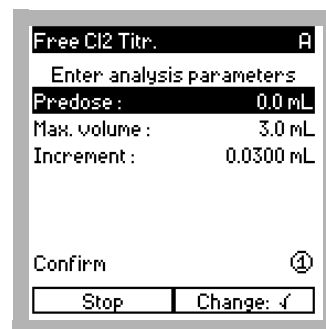
Note: The Phosphate buffer is added to adjust the sample pH. The precise amount added is not crucial for the accuracy or precision of the analysis.



10. The timer will start and the reagents will mix for a short period before titration begins.



11. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



12. The analysis parameters that have been stored for the current Sub-ID may be edited at this time. (Verify Increment from Table 1, “Generator Effluent Condition,” on page 79).

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

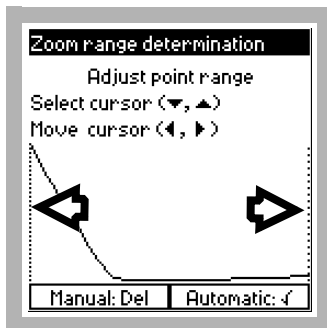
Note: Any changes made will become the new default parameters for this method Sub-ID.

Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.

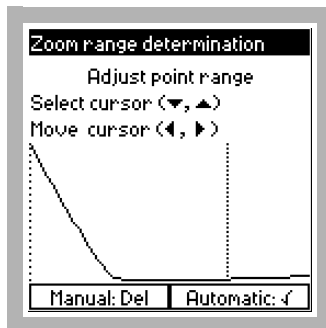


13. The Start Timer will start.
The electrode will stabilize before data collection.



14. The Zoom Range Determination window will display the titration curve. Select and move the cursors to define the range of data points for analysis.

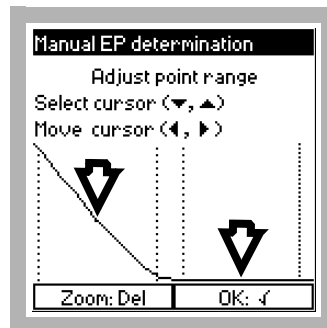
Note: Defining the range of data points allows the user to exclude undesirable portions of the titration curve from the analysis.



15. Select the type of end point determination. Press **CHECK MARK** for Automatic. and proceed to *step 18* or press **DEL** for Manual.

Note: Automatic determination attempts to identify linear segments without user input.

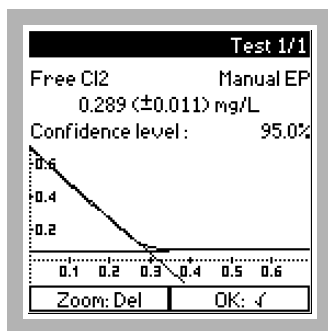
Note: This screen is not displayed if the Auto-detection software is enabled.



16. Use the navigation keys to select two line segments, one on each side of the titration end point, at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.

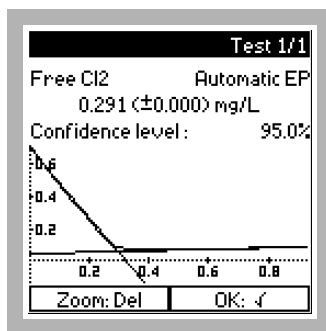


17. Press the **CHECK MARK** to accept the analysis. Proceed to *step 19* or press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.

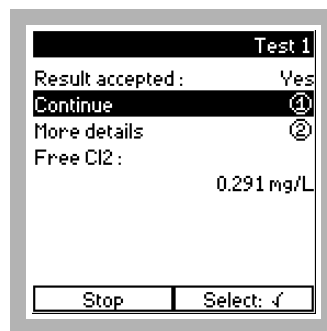


18. The AutoCAT will perform the analysis based on the automatic selection of linear segments.

Note: The automated analysis requires approximately 60 seconds to complete.

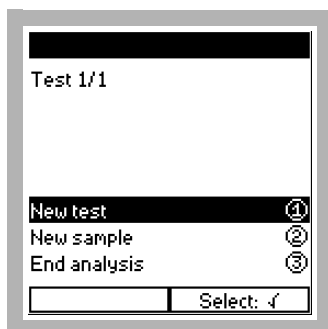


19. Press the **CHECK MARK** to accept the analysis or press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.



20. The analysis for this test is complete.

Press **1** to select Continue or press **2** to select More Details to view analysis statistics specific to the current Sample ID.



21. Press **1** to select
New Test to perform a
replicate sample.

Press **2** to select New Sample
to analyze a new sample with
a new ID.

Press **3** to select
End Analysis to return to the
Methods menu.

Table 1 Recommended Volume Increment Settings for Free Chlorine

Estimated Chlorine Conc. (mg/L)	Suggested Volume Increment (mL)
0.10–0.30	0.0010
0.30–0.50	0.0100
0.50–1.00	0.0300
1.00–1.50	0.0600
1.50–2.00	0.0900
> 2.000	0.1500

Note: These recommendations apply to Free Chlorine titrations, correspond to data collection times typically under 5 minutes, and provide adequate data points on both sides of the titration end point for proper analysis. Adjusting the volume increment will reduce the data collection times and number of data points collected. For example, doubling the volume increment will cut the data collection time and the number of points collected in half.

Method Performance

Table 2 Precision Statements

At Concentration	95% Confidence Limits
0.277 mg/L Cl ₂	0.251–0.303 mg/L Cl ₂
1.924 mg/L Cl ₂	1.778–2.070 mg/L Cl ₂
4.942 mg/L Cl ₂	4.650–5.234 mg/L Cl ₂

Table 3 Accuracy Assessments

Sample	Spike Addition	Average % Recovery	% Range of Recovery
Drinking Water	Free Cl ₂ at 0.060 mg/L	92.6 (n=4)	87.5–98.0
	Free Cl ₂ at 0.220 mg/L	89.7 (n=6)	89.2–92.7
	Free Cl ₂ at 0.530 mg/L	91.0 (n=4)	85.4–93.5

Lower Limit

Titration curve end points are not as sharp as those for Total Chlorine. Therefore, the determination of Free Chlorine concentrations below 0.1 mg/L becomes problematic. As a result, the lower limit for the AutoCAT 9000 has been arbitrarily set to 0.1 mg/L for experimental reasons.

Safety

Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

Summary of Method

This procedure follows method number 4500-Cl D. *b.* in “Standard Methods for the Examination of Water and Wastewater” (20th Edition). This procedure permits determination of the Free Chlorine concentration in a water sample. Free chlorine corresponds to that portion of chlorine existing either as elemental chlorine (Cl₂), hypochlorous acid (HOCl), or hypochlorite (OCl⁻) ion.

In the procedure, the sample pH is adjusted to pH 7 by addition of Phosphate buffer. The sample solution is then titrated amperometrically with standard phenylarsine oxide solution.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1000 mL	1999-53
Phosphate Buffer, pH 7, w/dropper	1 mL.....	100 mL	21553-32

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00

Optional Reagents

Chlorine Standard Solution, Voluette® Ampules, 10-mL	varies.....	16/pkg.....	14268-10
Dilution water, organic-free	varies.....	500 mL	26415-49

Optional Apparatus

Mini-printer, thermal, w/cable.....	each.....	A70P021
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Amperometric Back Titration

0.0051–5.000 mg/L as Cl₂*

Titration Workstation

Scope and Application: For water and wastewater; USEPA accepted for reporting*** Higher ranges can be determined through sample dilution. See *Section 5.2.3.3 Dilution* on page 46.**Procedure equivalent to USEPA method 330.2 and *Standard Methods* 4500-Cl C. for wastewater

Sample Tips and Techniques

- To avoid loss of chlorine, be careful not to agitate the sample when measuring or pouring.
- Sample glassware must be cleaned and pretreated to satisfy any chlorine demand before the sample is introduced. See *Section 7.2 Container Pretreatment* on page 63 for additional information.
- Always use organic-free reagent water for sample dilution (Cat. No. 26415-49).
- When sampling tap water, let the faucet run for at least 4–5 minutes prior to collecting the sample.
- Prepare a test sample by diluting Chlorine Standard Solution (Cat. No. 14268-10) with deionized (DI) water.
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten, and **0** to darken.
- A distinction is drawn between running a new test and a new sample on the AutoCAT 9000. Each test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When a new sample starts, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates the chlorine concentration based on the sample volume. Make sure that the sample volume is correct.
- The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual (MEPD) and/or automatic (AEPD) modes. The results are not stored until accepted by the user.
- The **STOP** key can be pressed at any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit.
- Press the **CHECK MARK** key any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except the Start Timer) to immediately exit the timer and proceed to the next step in the procedure.
- The Predose feature allows the adjustment of titrant addition prior to starting the titration. Make sure that predose does not overshoot the end point by completely titrating the sample.
- Flush the burette each day before the first sample test or calibration is performed. See Daily Start-up on page 26.
- Flush the burette when changing titrants. See Changing Titrants on page 25.



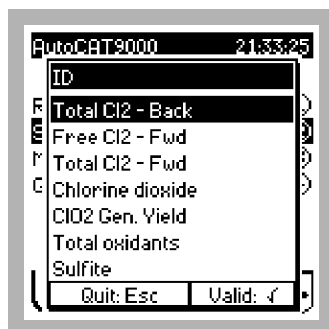
AutoCAT Titration Method

Total Cl₂ - Back



1. Turn the instrument on if necessary and access the Methods menu.

Press 2 to choose Select Method.



2. Highlight Total Cl₂ - Back.

Press the **CHECK MARK** to validate.



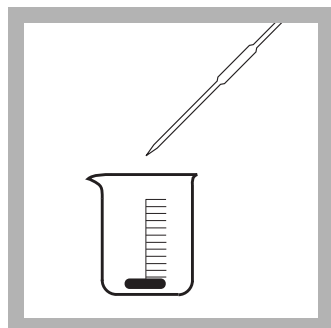
3. Press 1 to select Run method.

Note: This method utilizes the 28.2 mN iodine titrant. See *Software Setup for Titrant Installation* on page 38 to install this titrant.



4. Measure 200 mL of sample solution with a 250-mL graduated cylinder and transfer to a 250-mL beaker with the specified magnetic stir bar.

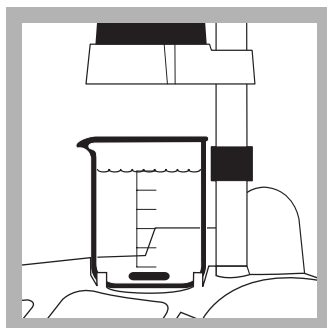
Note: Use the provided stir bar to minimize iodine loss.



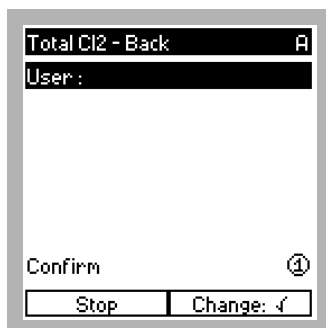
5. Pipet 1.00 mL of reductant (0.00564 N PAO or sodium thiosulfate) and swirl to mix.

Note: The amount of PAO required will vary for different concentrations of chlorine. The recommended amount of 1.00 mL is sufficient for about 1 mg/L of total chlorine. For higher concentrations, a larger amount of PAO should be added.

Note: For total chlorine concentrations below 0.1 mg/L, dispense 800 digits of 0.00564 N PAO with a Digital Titrator. See *Optional Reagents and Optional Apparatus* on page 104.



6. Place the sample onto the AutoCAT 9000 stirrer platform.

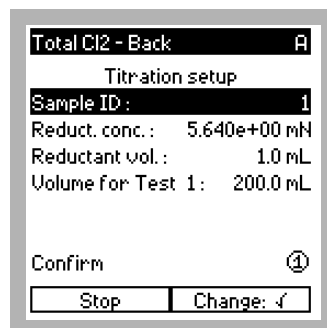


7. Verify User.

Press 1 to confirm.

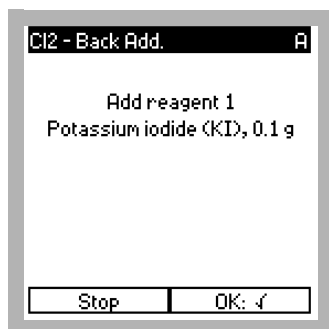
Press the **CHECK MARK** to enter a new user.

Note: This screen will be skipped if the User ID has been disabled in the Configuration menu. See *Setting a User ID* on page 27.



8. To enter a new sample ID, reductant concentration, reductant volume, or sample volume, highlight the appropriate selection and press the **CHECK MARK**. Press 1 to confirm the values.

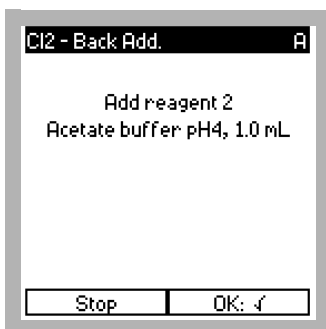
Note: If the sample has not been fixed, this procedure requires the addition of reductant prior to analysis.



9. Add 1 SwiftTest dispensation (0.1 g) of potassium iodide (KI).

Press the **CHECK MARK** to confirm.

Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.



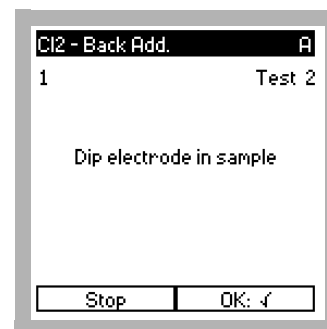
10. Add 1.0 mL of pH 4 acetate buffer.

Press the **CHECK MARK** to confirm.

Note: Acetate buffer is added to adjust the sample pH. The amount used is not crucial for the accuracy or precision of the analysis.

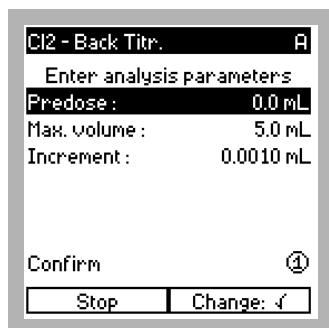


11. The timer will start and the reagents will mix for a short period of time before titration begins.



12. Lower the electrode head onto the beaker rim.

Press the **CHECK MARK** to confirm.



13. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press **1** to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

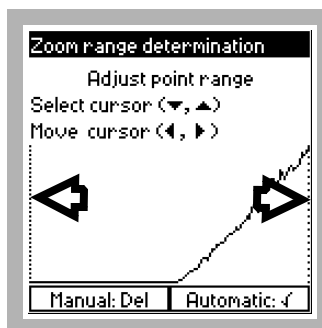
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.



14. The Start Timer will begin to allow the electrode to stabilize before data collection.

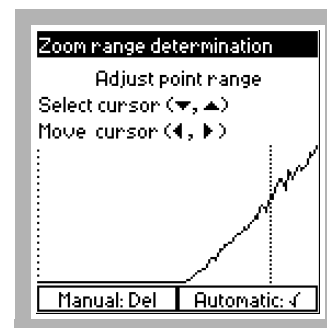
After the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



15. The Zoom Range Determination window will display the titration curve. Use the navigation keys to select and move the cursors (vertical lines) to define the range of data points for analysis.

Proceed to step 16.

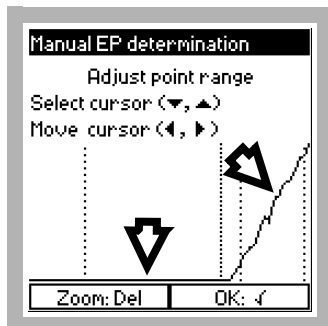
Note: Defining the range of data points allows the user to eliminate undesirable portions of the titration curve from the analysis.



16. Select the type of end point determination. Press the **CHECK MARK** for Automatic and proceed to step 19 or press **DEL** for Manual.

Note: Automatic determination attempts to identify linear segments without user input.

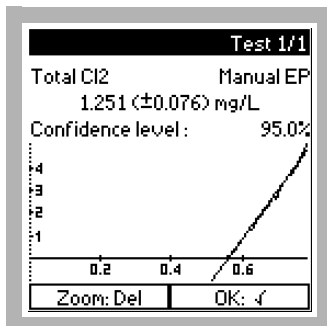
Note: This screen is not displayed if the Auto-detection software is enabled.



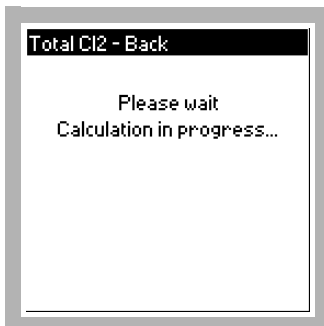
17. Select two line segments, one on each side of the titration end point, by positioning the cursors (vertical lines) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.

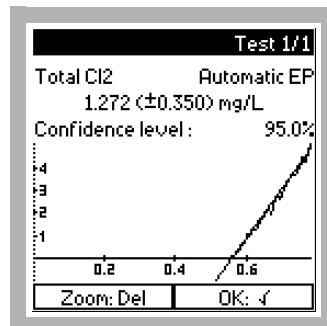


18. Press the **CHECK MARK** to accept the analysis. Proceed to *step 20* or press **DEL** to return to the previous window (Zoom range determination). Adjust the linear segments and reanalyze the data.

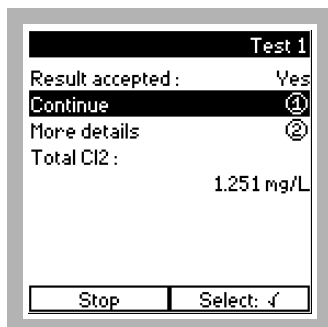


19. The AutoCAT 9000 will run the analysis based on the automatic selection of linear segments.

Note: The automated analysis requires approximately 1 minute to complete.

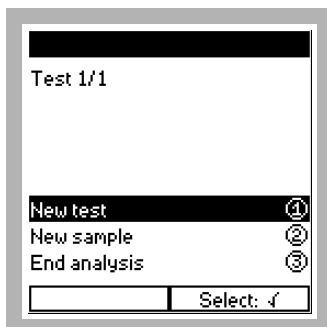


20. Press the **CHECK MARK** to accept the analysis. or press **DEL** to return to the previous window (Zoom range determination) to adjust the linear segments and reanalyze the data.



21. The analysis for this test is complete.

Press **1** to select Continue to perform additional tests or finish analyses. Press **2** to select More Details to view analysis statistics specific to the current Sample ID.



22. Press **1** to select New Test to run a replicate sample.

Press **2** to select New Sample to initiate analysis of a new sample with a new Sample ID.

Press **3** to select End Analysis to return to the Methods menu.

Table 1 Recommended Volume Increment Settings for Total Chlorine (Back)

Estimated Chlorine Conc. (mg/L)	Suggested Volume Increment (mL)
<0.10	0.0010*
0.10–0.90	0.0030
0.90–1.00	0.0010

* with pre-dose

Note: These recommendations apply to Total Chlorine back titrations, correspond to data collection times typically under 5 minutes, and provide adequate data points on both sides of the titration end point for proper analysis. Adjusting the volume increment will reduce the data collection times and number of data points collected. For example, doubling the volume increment will cut the data collection time and the number of points collected in half.

Method Performance

Table 2 Precision Statements

At Concentration	95% Confidence Limits
0.023 mg/L Cl ₂	0.020–0.026 mg/L Cl ₂
0.398 mg/L Cl ₂	0.370–0.426 mg/L Cl ₂
1.313 mg/L Cl ₂	1.287–1.339 mg/L Cl ₂
4.751 mg/L Cl ₂	4.689–4.813 mg/L Cl ₂

Table 3 Accuracy Assessments

Sample	Spike Addition	Average % Recovery	% Range of Recovery
Drinking Water	Free Cl ₂ at 0.465 mg/L	97.3 (n=4)	95.8–99.1
Denitrified Wastewater Effluent (Source #1)	NH ₂ Cl at 0.423 mg/L	87.23 (n=3)	73.5–94.8
	NH ₂ Cl at 0.844 mg/L	93.07 (n=3)	91.8–93.8
	NH ₂ Cl at 1.262 mg/L	88.56 (n=3)	85.3–91.9
Denitrified Wastewater Effluent (Source #2)	NH ₂ Cl at 0.423 mg/L	92.59 (n=3)	88.9–97.2
	NH ₂ Cl at 0.844 mg/L	98.06 (n=3)	96.8–98.8
	NH ₂ Cl at 1.262 mg/L	95.01 (n=3)	89.9–98.0

Estimated Detection Limit

Based on the USEPA procedure of estimating the method detection limit (40 CFR Pt.136, App. B, 7-1-95), the estimated detection limit, using the procedure as written, is 5.1 µg/L (0.0051 mg/L) chlorine.

Safety

Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

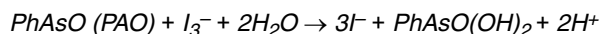
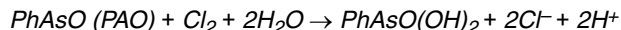
Total Chlorine

Summary of Method

This procedure follows method number 4500-Cl *c.* in “Standard Methods for the Examination of Water and Wastewater” (20th Edition). In the amperometric back titration, a measured volume of reductant (phenylarsine oxide or sodium thiosulfate solution) is added directly to a measured volume of the sample at collection time. This “fixes” the chlorine concentration, allowing the sample to be stored for later analysis.

At analysis time, the sample is adjusted to pH 4 with acetate buffer, and excess potassium iodide is added. The unreacted reductant is then titrated with standard tri-iodide solution. The chlorine concentration is derived from the difference in the amount of reductant originally added to the sample and the amount remaining prior to titration.

The chemical reactions are:



(Ph=phenyl)

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Acetate Buffer Solution, pH 4, w/dropper.....	1 mL.....	100 mL	14909-32
Iodine Standard Solution, 0.0282 N	varies.....	1000 mL	23333-53
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1 L	1999-53
Potassium Iodide, SwifTest refill	0.10 g	25 g.....	1077-60

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Pipet, Volumetric, Class A, 1.00 mL	1	each.....	14515-35
SwifTest Dispenser	1	each.....	28341-00

Optional Reagents

Chlorine Standard Solution, Voluette® Ampules	varies.....	16/pkg.....	14268-10
Dilution Water, organic-free	varies.....	500 mL	26415-49
Phenylarsine Oxide (PAO) Titrant, 0.00564 N, cartridge	varies.....	each.....	1949-01
Sodium Thiosulfate Standard Solution, stabilized, 0.00564 N	varies.....	1 L	24088-53

Optional Apparatus

Digital Titrator	each.....	16900-01
Delivery Tubes, straight w/”J” hook	5/pkg.....	17205-00
Mini-printer, thermal, w/cable.....	each.....	A70P021

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Amperometric Forward Titration

0.0012–5.000 mg/L as Cl₂*

Titration Workstation

Scope and Application: For water and wastewater; USEPA accepted for reporting*** Higher ranges can be determined through sample dilution. See *Section 5.2.3.3 Dilution* on page 46.**Procedure equivalent to USEPA methods 330.1 and 330.3, and *Standard Methods* 4500-Cl D. for wastewater.

Sample Tips and Techniques

- To avoid loss of chlorine, be careful not to agitate the sample when measuring or pouring.
- Sample glassware must be cleaned and pretreated to satisfy any chlorine demand before sample is introduced. See *Section 7.2 Container Pretreatment* on page 63 for additional information.
- Always use organic-free reagent water for sample dilution (Cat. No. 26415-49).
- When sampling tap water, let the faucet run for at least 4–5 minutes prior to collecting the sample.
- Prepare a test sample diluting Chlorine Standard Solution (Cat. No. 14268-10) with deionized (DI) water.
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



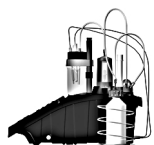
Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



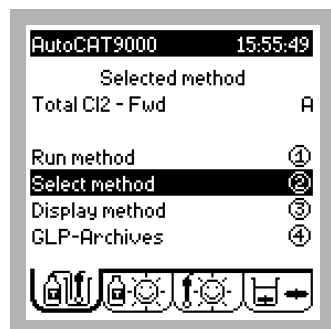
Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu, then pressing **7** to lighten, **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current, or previous, sample analysis. The AutoCAT automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT can accommodate any sample size. The default sample volume of 200 mL is recommended in *Standard Methods*, and can be adjusted to expand the test range.
- The AutoCAT calculates the chlorine concentration based on the sample volume. Make sure that the sample volume is correct.
- The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual (MEPD) and/or automatic (AEPD) modes. The results are not stored until accepted by the user.
- The **STOP** key can be pressed at any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit completely.
- Press the **CHECK MARK** key at any time during data acquisition to halt data collection.
- Press the **DEL** button during any timer period except the Start Timer to immediately exit the timer and proceed to the next step in the procedure.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.



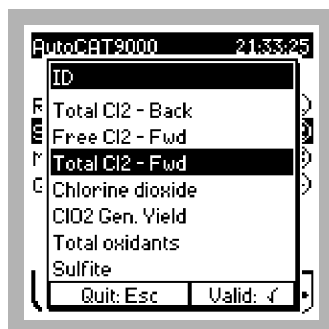
AutoCAT Titration Method

Total Cl₂ - Fwd

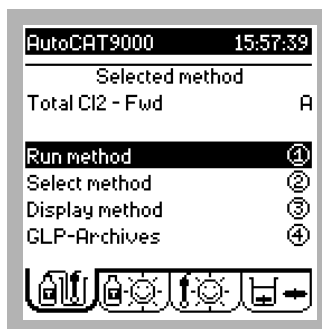


1. Turn the instrument on if necessary and access the Methods menu.

Press 2 to choose Select Method.



2. Highlight Total Cl₂ - Fwd and press the **CHECK MARK** to validate.



3. Press 1 to select Run method.

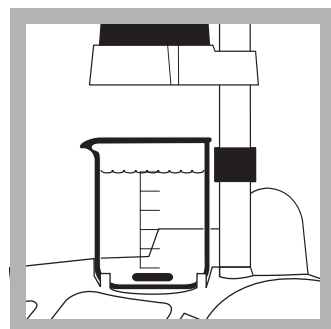
Note: This method utilizes the 5.64mN PAO titrant. To install this titrant, see Software Setup for Titrant Installation on page 38.



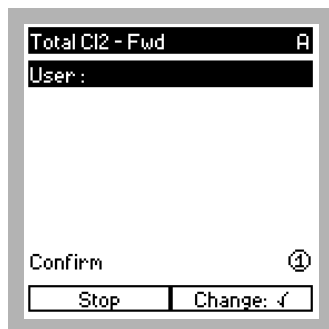
4. Measure 200 mL of sample solution into a clean 250-mL beaker.

Insert the magnetic stir-bar into the beaker.

Note: Use only the provided magnetic stir-bar to minimize loss of chlorine or iodine.

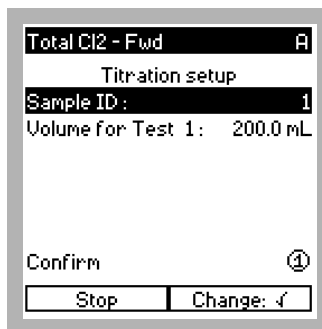


5. Place the sample onto the AutoCAT stirrer platform.



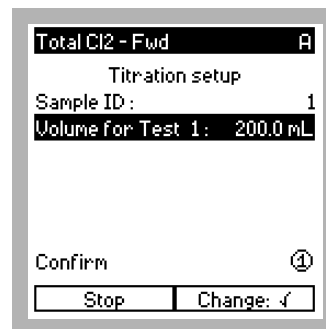
6. Highlight User and verify the user ID. Press 1 to confirm and accept the displayed ID. To change the user ID, press the **CHECK MARK**.

Note: If the User ID parameter has been disabled in the **Configuration** menu, this screen will be skipped. See Section 3.3.2 on page 27 for more information.



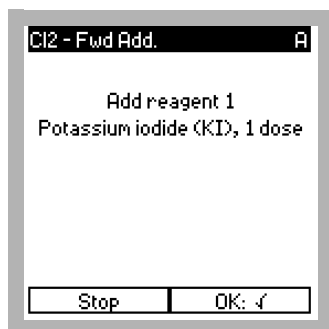
7. Highlight Sample ID. Press the **CHECK MARK** to enter a new sample ID or proceed to the next step.

Note: The Sample ID is used to identify individual samples within the GLP archives.



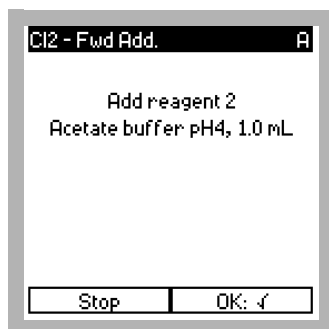
8. Highlight Volume for Test 1.

Press the **CHECK MARK** to enter a new sample volume or press 1 to confirm and accept the current volume and start the stirrer.



9. Add 1 SwiftTest dispensation (0.1 g) of potassium iodide (KI). Press the **CHECK MARK** to confirm.

Note: KI is added in excess; the precise amount added is not crucial for the accuracy or precision of the analysis.

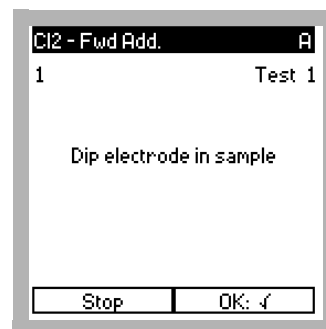


10. Add 1.0 mL of pH 4 acetate buffer. Press the **CHECK MARK** to confirm.

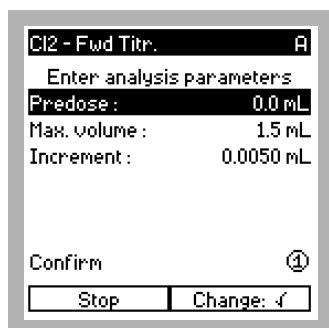
Note: Acetate buffer is added to adjust the sample pH; the precise amount added is not crucial for the accuracy or precision of the analysis.



11. The timer will start. The reagents will mix for a brief period before starting the titration.



12. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



13. The analysis parameters that have been stored for the current Sub-ID may be edited at this time. Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

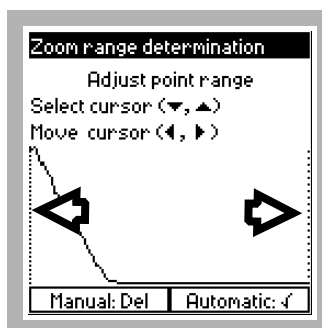
Note: Any changes made will become the new default parameters for this method Sub-ID.

Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.



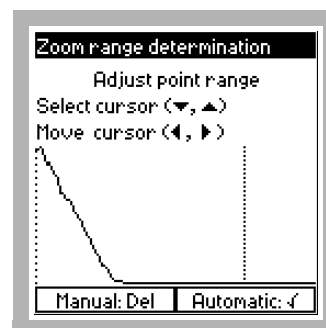
14. The Start Timer will begin and allow the electrode to stabilize before data collection and titration curve generation.



15. The Zoom Range Determination window will display the titration curve. Use the navigation keys to select and move the cursors (vertical lines) to define the range of data points for analysis.

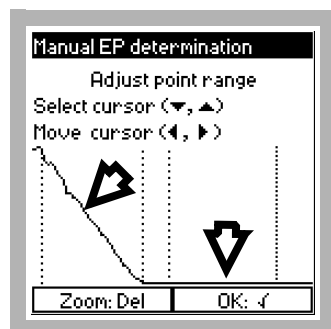
Proceed to step 16.

Note: Defining the range of data points excludes undesirable portions of the titration curve from the analysis.



16. Select the type of end point determination. Press the **CHECK MARK** for Automatic then proceed to step 19 or press **DEL** for Manual.

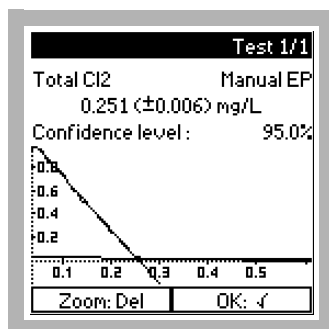
Note: Automatic determination attempts to identify optimal linear segments without user input.



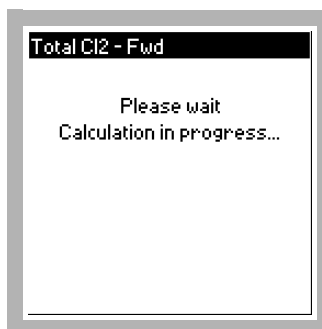
17. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning cursors at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.

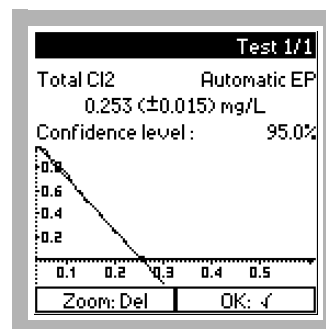


18. Press the **CHECK MARK** to accept the analysis. Proceed to *step 21*. Press **DEL** to return to the previous window (Zoom Range Determination) to adjust the linear segments and reanalyze the data.

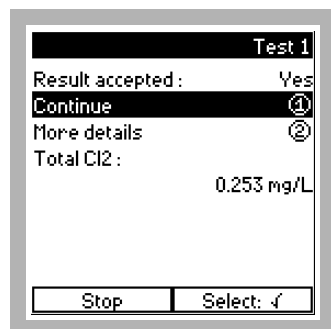


19. The AutoCAT will run the analysis based on the automatic selection of linear segments.

Note: The automated analysis requires approximately 1 minute to complete.

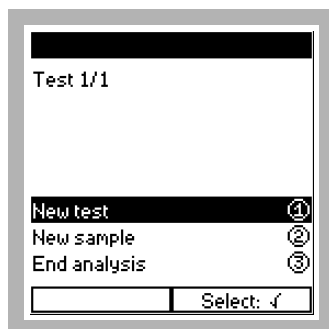


20. Press the **CHECK MARK** to accept the analysis, or press **DEL** to return to the previous window (Zoom Range Determination) to adjust the linear segments and reanalyze the data.



21. Press **1** to select Continue for additional tests and/or samples.

Press **2** to select More Details to view analysis statistics for the current Sample ID.



22. Press **1** to select New Test to run a replicate sample.

Press **2** to select New Sample to analyze a new sample, see *Sample Tips and Techniques* on page 105.

Press **3** to select End Analysis to return to the Methods menu.

Table 1 Recommended Volume Increment Settings for Total Chlorine

Estimated Chlorine Conc. (mg/L)	Suggested Volume Increment (mL)
< 0.010	0.0003
0.010–0.050	0.0010
0.050–0.200	0.0030
0.200–0.400	0.0070
0.400–0.600	0.0110
0.600–0.800	0.0150
0.800–1.000	0.0200
> 1.000	0.0500

Note: These recommendations apply to Total Chlorine forward titrations, correspond to data collection times typically under 5 minutes, and provide adequate data points on both sides of the titration end point for proper analysis. Adjusting the volume increment will proportionately adjust the data collection times and number of data points collected. For example, doubling the volume increment will cut the data collection time, and the number of points collected, in half.

Method Performance

Table 2 Precision Statements

At Concentration	95% Confidence Limits
0.0090 mg/L Cl ₂	0.0084–0.0096 mg/L Cl ₂
0.423 mg/L Cl ₂	0.413–0.433 mg/L Cl ₂
4.241 mg/L Cl ₂	4.165–4.317 mg/L Cl ₂

Table 3 Accuracy Assessments

Sample	Spike Addition	Average % Recovery	% Range of Recovery
Drinking Water	Free Cl ₂ at 0.196 mg/L	101.2 (n=4)	100.3–101.9
	Free Cl ₂ at 0.391 mg/L	99.8 (n=4)	99.0–100.4
	NH ₂ Cl at 0.196 mg/L	93.4 (n=4)	93.0–93.9
	NH ₂ Cl at 0.391mg/L	93.4 (n=3)	93.0–94.0
Denitrified Wastewater Effluent (Source #1)	NH ₂ Cl at 0.489 mg/L	87.3 (n=6)	82.2–90.7
	NH ₂ Cl at 0.975 mg/L		
	NH ₂ Cl at 1.459 mg/L		
Denitrified Wastewater Effluent (Source #2)	NH ₂ Cl at 0.489 mg/L	93.6 (n=6)	88.8–95.8
	NH ₂ Cl at 0.975 mg/L		
	NH ₂ Cl at 1.465mg/L		

Estimated Detection Limit

Based on the USEPA procedure of estimating the method detection limit (40 CFR 136, App. B, 7-1-95), the estimated detection limit, using the procedure as written, is 1.2 µg/L (0.0012 mg/L) chlorine.

Total Chlorine

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagent(s) used.

Summary of Method

This procedure follows method number 4500-Cl D. in “Standard Methods for the Examination of Water and Wastewater” (20th Edition). This procedure permits determination of the total chlorine concentration (= Free Chlorine Conc. + Combined Chlorine Conc.) in a water sample. Total chlorine corresponds to the chlorine derived from all its possible forms in solution including free elemental chlorine (Cl_2), hypochlorous acid (HOCl), hypochlorite (OCl^-) ion, and chloramines (NH_2Cl , NHCl_2 , etc.) among other species.

In the procedure an excess of potassium iodide is added to a water sample. Sample pH is adjusted to pH 4 by addition of acetate buffer. The sample solution is then titrated amperometrically with standard phenylarsine oxide solution.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Acetate Buffer Solution, pH 4, w/dropper.....	1 mL.....	100 mL	14909-32
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1000 mL	1999-53
Potassium Iodide, SwifTest refill	0.10 g	25 g.....	1077-60

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
SwifTest dispenser.....	1	each.....	28341-00

Optional Reagents

Chlorine Standard Solution, Voluette Ampules.....	varies.....	16/pkg.....	14268-10
Dilution water, organic-free	varies.....	500 mL	26415-49
Potassium Iodide, Powder Pillows	1	100/pkg.....	1077-99
Sodium Thiosulfate Standard Solution, stabilized, 0.00564 N	varies.....	1 L	24088-53

Optional Apparatus

Mini-printer, thermal, w/cable.....	each.....	A70P021
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Amperometric Back Titration

0.00–20.00 mg/L as SO_3^{2-} *

Titration Workstation

Scope and Application: For treated wastewater

* Higher ranges can be determined through sample dilution. See *Section 5.2.3.3 Dilution* on page 46.



Sample Tips and Techniques

- To avoid loss of sulfite, be careful not to agitate the sample when measuring or pouring.
- Always use organic-free reagent water for sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



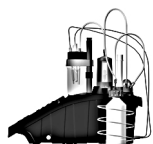
Reagent Tips and Techniques

- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten, and **0** to darken.
- A distinction is drawn between running a new test and a new sample on the AutoCAT 9000. Each test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When a new sample starts, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates the chlorine concentration based on the sample volume. Ensure that the sample volume is correct.
- The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual (MEPD) and/or automatic (AEPD) modes. The results are not stored until accepted by the user.
- Press the **STOP** key at any time to interrupt instrument operation. The user will be given the option to resume, restart, or quit.
- Press **CHECK MARK** at any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except the Start Timer) to immediately exit the timer and proceed to the next step in the procedure.
- The Predose feature allows the adjustment of titrant addition prior to starting the titration. Ensure that predose does not overshoot the end point by completely titrating the sample.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.



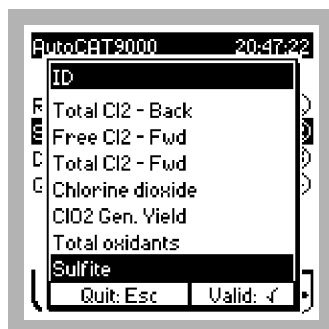
AutoCAT Titration Method

Sulfite - Back



1. Turn the instrument on if necessary and access the Methods menu.

Press **2** to choose Select Method.



2. Highlight Sulfite. Press **CHECK MARK** to validate.

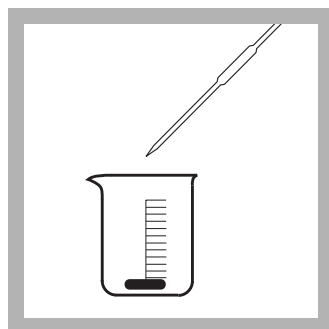


3. Press **1** to select Run method.

Note: This method uses the 5.64 mN PAO titrant. See *Software Setup for Titrant Installation* on page 38.



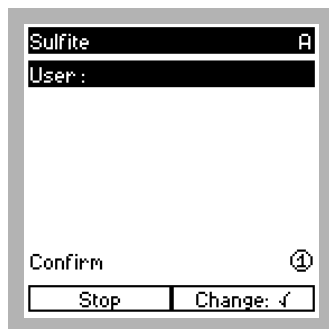
4. Measure 200 mL of sample solution with a 250-mL graduated cylinder and transfer to a 250-mL beaker with the specified magnetic stir bar.



5. Pipet 5.00 mL of oxidant (0.0282 N iodine) and swirl to mix.

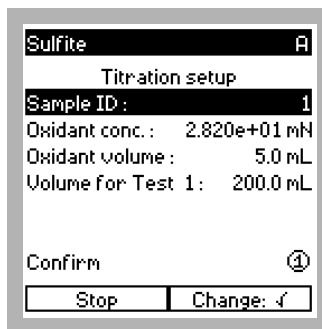
Place the sample onto the AutoCAT 9000 stirrer platform.

Note: Depending on sulfite concentration, the titration may yield higher results for sulfite due to iodine demand. See Table 1 on page 116 for suggested spike volumes.

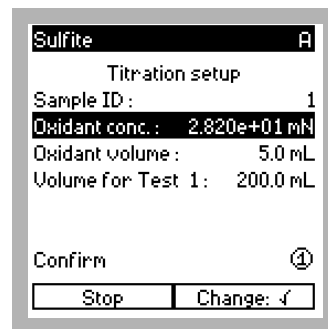


6. Verify User. Press **1** to confirm. Press the **CHECK MARK** to enter a new user.

Note: This screen will be skipped if the User ID has been disabled in the Configuration menu. See *Setting a User ID* on page 27.



7. Highlight Sample ID. Press the **CHECK MARK** to enter a new sample ID or proceed to step 8.



8. Highlight Oxidant conc. Press the **CHECK MARK** to enter a new oxidant concentration or proceed to step 9.

Sulfite		A
Titration setup		
Sample ID :	1	
Oxidant conc. :	2.820e+01 mN	
Oxidant volume :	5.0 mL	
Volume for Test 1 :	200.0 mL	
Confirm ①		
Stop	Change: ✓	

9. Highlight Oxidant vol.
Press the **CHECK MARK** to enter a new oxidant volume (see Table 1), or proceed to *step 10*.

Note: If the sample has not been fixed this procedure requires the addition of oxidant prior to analysis.

Sulfite		A
Titration setup		
Sample ID :	1	
Oxidant conc. :	2.820e+01 mN	
Oxidant volume :	5.0 mL	
Volume for Test 1 :	200.0 mL	
Confirm ①		
Stop	Change: ✓	

10. Highlight Volume for Test 1.
Press **1** to confirm.
Press the **CHECK MARK** to enter a new sample volume.

Sulfite Add.		A
Add reagent 1		
Potassium iodide (KI), 0.1 g		
Stop OK: ✓		

11. Add 1 SwifTest dispensation (0.1 g) of potassium iodide (KI).
Press the **CHECK MARK** to confirm.

Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.

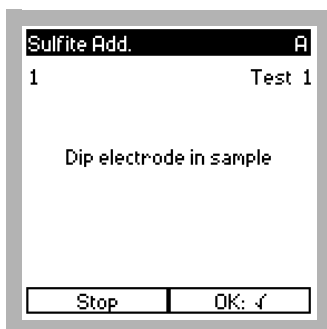
Sulfite Add.		A
Add reagent 2		
Phosphate buffer pH7, 1 dose		
Stop OK: ✓		

12. Add one dose of pH 7.0 Phosphate Buffer.
Press the **CHECK MARK** to confirm.

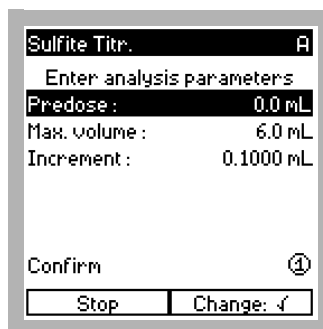
Note: Phosphate buffer is added to adjust the sample pH. The amount used is not crucial for the accuracy or precision of the analysis.



13. The timer will start and the reagents will mix for a short period of time before titration begins.



14. Lower the electrode head onto the beaker rim. Press **CHECK MARK** to confirm.



15. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

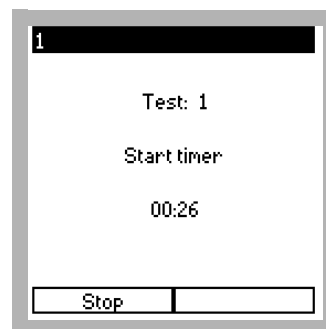
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press **1** to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

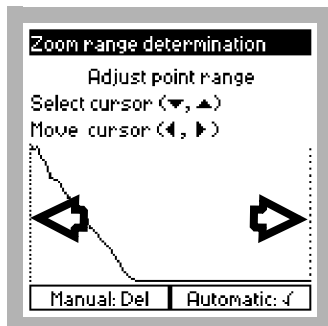
Note: This step will be skipped if autoscaling software is enabled.

Note: Increment volume adjustment is not necessary if the correct oxidant volume is selected.



16. The Start Timer will begin, allowing the electrode to stabilize before data collection.

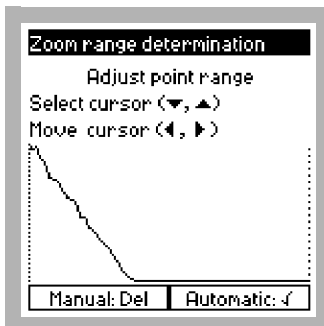
After the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



17. The Zoom Range Determination window will display the titration curve. Use the navigation keys to select and move the cursors (vertical lines) to define the range of data points for analysis.

Proceed to *step 18*.

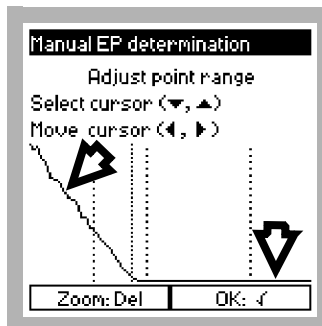
Note: Defining the range of data points allows the user to eliminate undesirable portions of the titration curve from the analysis.



18. Select the type of end point determination. Press the **CHECK MARK** for “Automatic” and proceed to *step 21* or press **DEL** for “Manual”.

Note: Automatic determination attempts to identify linear segments without user input.

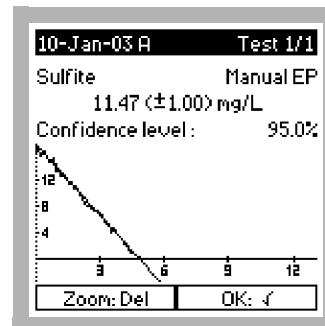
Note: This screen is not displayed if the Auto-detection software is enabled.



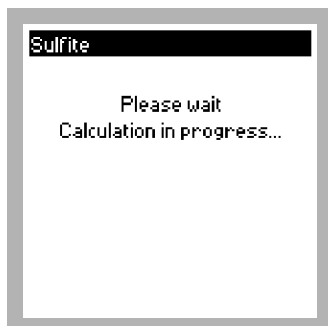
19. Select two line segments, one on each side of the titration end point, by positioning the cursors (vertical lines) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the previous window.

Note: For more information on manual EP determination, see page 135.

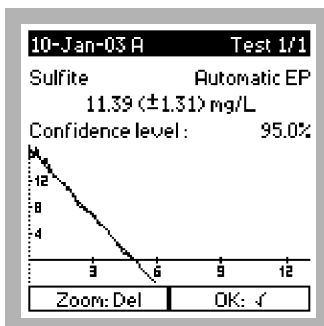


20. Press the **CHECK MARK** to accept the analysis. Proceed to *step 22* or press **DEL** to return to the previous window (Zoom Range Determination). Adjust the linear segments and reanalyze the data.

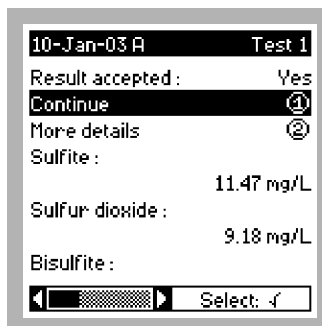


21. The AutoCAT 9000 will run the analysis based on the automatic selection of linear segments.

Note: The automated analysis requires approximately 1 minute to complete.



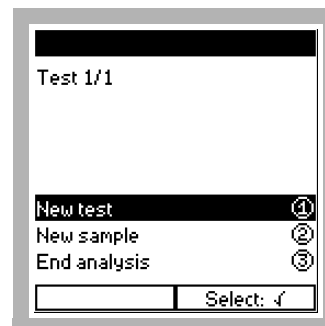
22. Press the **CHECK MARK** to accept the analysis. Press **DEL** to return to the previous window (Zoom Range Determination) to adjust the linear segments and reanalyze the data.



23. The analysis for this test is complete.

Press **1** to select Continue and perform additional tests or finish analyses. Press **2** to select More Details and view analysis statistics for the current Sample ID.

Note: The results show the concentration of one of these analytes, depending on what form of the test is being performed. The results given do not indicate the presence of all compounds listed.



24. Press **1** to select New Test and run a replicate sample.

Press **2** to select New Sample and initiate analysis of a new sample with a new Sample ID.

Press **3** to select End Analysis and return to the Methods menu.

Oxidant Volume Adjustment

Deviations can occur in the sulfite method due to loss of iodine through the iodine demand of the sample. Minimizing the total amount of free iodine to be titrated in the solution can reduce this phenomenon.

By increasing the oxidant volume to slightly more than is needed to react with the sulfite, the amount of free titratable iodine will be minimized. Data acquisition will be optimized and error due to iodine loss will be minimized.

Table 1 Recommended Iodine Spike Volume for Sulfite

Estimated Sulfite Conc. (mg/L as SO ₃)	Volume of 0.0282 N Iodine (mL)
0–5	1.00
5–10	2.00
10–15	3.00
15–20	4.00
20–25	5.00

Method Performance

Table 2 Precision

At Concentration	95% Confidence Limits
19.05 mg/L	18.77 mg/L–19.33 mg/L

Table 3 Accuracy Assessments

Sample	Spike Addition (mg/L)	% Recovery*
Deionized Water	18.75	103.77
	12.50	104.31
	6.25	101.93
Wastewater Effluent (Source #1)	18.75	102.05
	12.50	100.95
	6.25	100.56
Wastewater Effluent (Source #2)	18.75	103.42
	12.50	102.63
	6.25	106.46

* Percent recovery does not reflect correction for sample iodine demand.

Safety

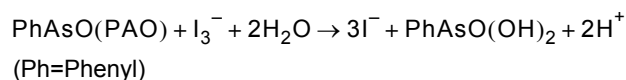
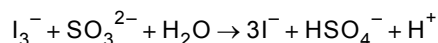
Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

Summary of Method

This procedure follows method number 4500-SO₃²⁻ B in *Standard Methods for the Examination of Water and Wastewater*. In the amperometric back titration, a measured volume of oxidant (iodine) is added directly to a measured volume of the sample at collection time. This “fixes” the sulfite concentration and decreases the amount of sample loss throughout the titration. The method is performed at neutral pH to minimize interference from dissolved oxygen and organic chloramines.

At the time of analysis, the sample is adjusted to pH 7 with phosphate buffer, and excess potassium iodide is added. The unreacted oxidant is then titrated with standard PAO solution. The sulfite concentration is derived from the difference in the amount of oxidant originally added to the sample and the amount remaining prior to titration.

The chemical reactions are:



Accounting for Sample Iodine Demand

Iodine demand in the sample can occasionally have a significant impact on the accuracy of a titration. This can be accounted for by titrating the sample matrix prior to sulfite (or sulfur dioxide) addition. For best results, chlorine should be eliminated from the sample by UV irradiation. The resulting value from the titration is the blank value, and should be performed at least once daily when sulfite titrations are run. The blank value is subtracted from the result of each sulfite titration for maximum accuracy.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Iodine Standard Solution, 0.0282 N	varies.....	1000 mL	23333-53
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1 L	1999-53
Phosphate Buffer, pH 7, w/dropper	1 mL.....	100 mL	21553-32
Potassium Iodide, SwifTest refill	0.10 g	25 g.....	1077-60

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Cylinder, Graduated, 250 mL	1	each.....	508-46
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
SwifTest dispenser.....	1	each.....	28341-00

Optional Reagents

Chlorine Standard Solution, Voluette® Ampules	varies.....	16/pkg.....	14268-10
Dilution Water, organic-free	varies.....	500 mL	26415-49
Phenylarsine Oxide (PAO) Titrant, 0.00564 N, cartridge	varies.....	each.....	1949-01
Sodium Thiosulfate Standard Solution, stabilized, 0.00564 N	varies.....	1 L	24088-53

*Teflon is a Registered Trademark of EI DuPont Company.

Optional Apparatus

Digital Titrator.....	each.....	16900-01
Delivery Tubes, straight w/"J" hook	5/pkg.....	17205-00
Mini-printer, thermal, w/cable.....	each.....	A70P021
Pipet, Volumetric, Class A, 1-mL.....	each.....	14515-35
Pipet, Volumetric, Class A, 2-mL.....	each.....	14515-36
Pipet, Volumetric, Class A, 3-mL.....	each.....	14515-03
Pipet, Volumetric, Class A, 4-mL.....	each.....	14515-04
Pipet, Volumetric, Class A, 5-mL.....	each.....	14515-37



FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

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Outside the U.S.A. – Contact the HACH office or distributor serving you.

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HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932



Chlorite + Chlorine Dioxide

“Quick” Two Step Amperometric Titration

0.1–5.0 mg/L as $\text{ClO}_2 + \text{ClO}_2^-$

Titration Workstation

Scope and Application: For drinking water

Sample Tips and Techniques

- Soak all glassware in a strong chlorine dioxide (ClO_2) solution (300–500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Use the glassware for this method only.
- Chlorine dioxide and its by-products are volatile and can be easily lost from aqueous solution. Minimize air contact by attaching a flexible hose to a tap and placing the end at the bottom of a 1-L amber glass bottle. Turn on the tap and allow several volumes to overflow, then slowly remove the sample line and cap the container with minimum headspace.
- Minimize agitation when measuring sample volumes. Remove sample portions with a volumetric pipet. Always place the tip at the bottom of the sample container. If using 200-mL sample increments, use a 100-mL pipet to withdraw two portions of sample.
- Always use organic-free water for sample dilution (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



Reagent Tips and Techniques

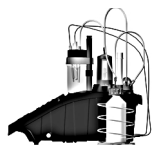
- Download the “Certificate of Analysis” (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



Instrument Tips and Techniques

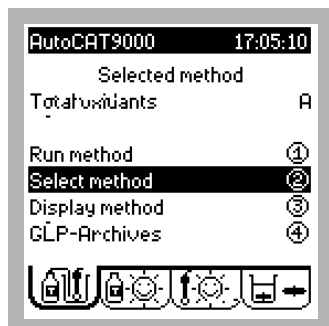
- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new Test and a new Sample. Each Test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each Test is given a different number, all of which are listed under the same Sample ID. When starting a new Sample, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates concentration based on the sample volume. Make sure that the sample volume is correct.
- Press **STOP** at any time to interrupt instrument operation; the user can resume, restart, or quit completely.
- Press the **CHECK MARK** key at any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except Start Timer) to immediately exit the timer and proceed to the next step.
- Press **ESC** during any titration/calibration data collection period or timer to access Edition mode. See *Edition Mode* on page 30.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.

* Adapted from Gates, “The Chlorine Dioxide Handbook”, AWWA, 1998. Not suitable for compliance testing.

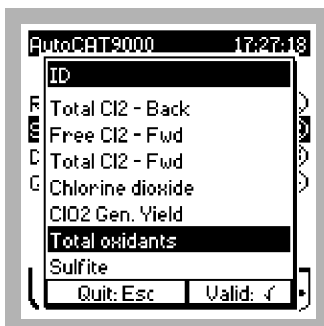


AutoCAT Titration Method

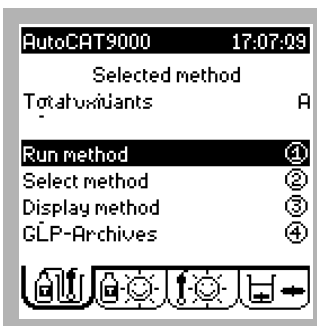
Total Oxidants Titration 1



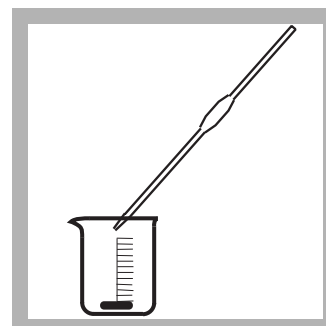
1. Turn the instrument on and access the Methods menu.
Press 2 to choose Select Method.



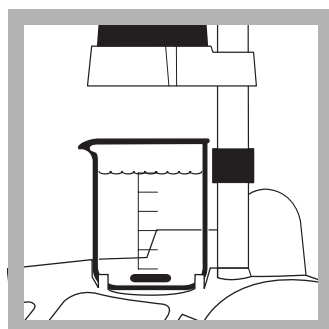
2. Highlight Total Oxidants
Press the **CHECK MARK** to validate.



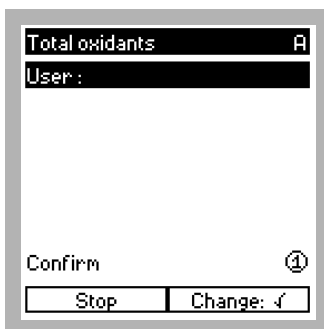
3. Press 1 to select Run method.
This method uses the 5.64 mN PAO titrant. See *Software Setup for Titrant Installation* on page 38.



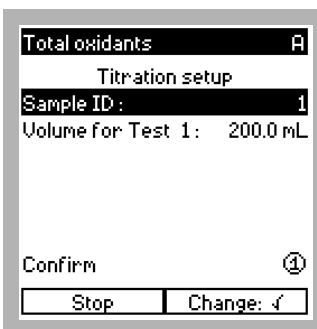
4. Measure 200 mL of sample solution with a pipet and transfer to a 250-mL beaker with the specified magnetic stir bar.
All containers must be pretreated for chlorine demand, see *Container Pretreatment* on page 63.



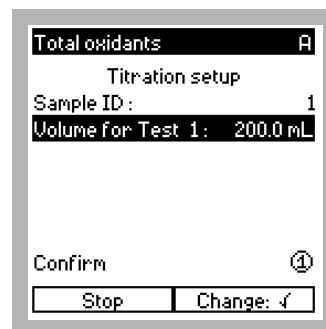
5. Place the sample onto the AutoCAT 9000 stirrer platform.



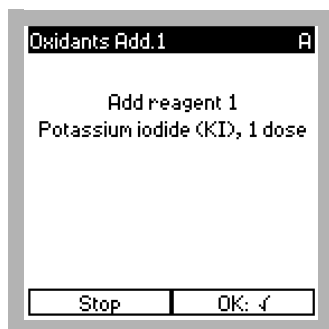
6. Verify User.
Press the **CHECK MARK** to enter a new user or press 1 to confirm.
Note: This screen will be skipped if the User ID is disabled. See *Setting a User ID* on page 27.



7. Highlight Sample ID.
Press the **CHECK MARK** to enter a new sample ID or proceed to step 8.



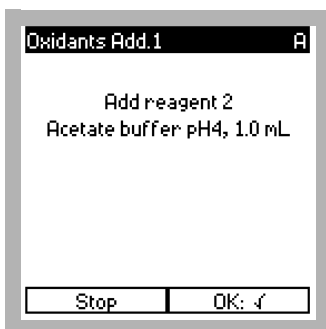
8. Highlight Volume for Test 1.
Press the **CHECK MARK** to enter a new volume.
Press 1 to confirm.



9. Add 1.0 g of potassium iodide (KI).

Press the **CHECK MARK** to confirm.

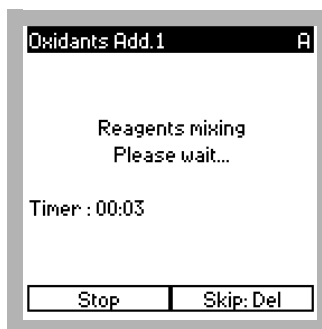
Note: KI is added in excess; the precise amount added is not crucial to the accuracy or precision of the analysis.



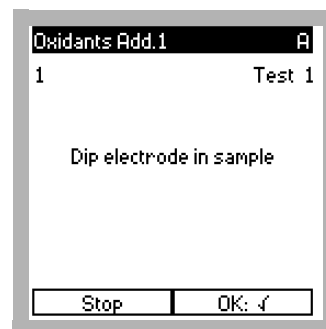
10. Add 1.0 mL of pH 4 acetate buffer.

Press the **CHECK MARK** to confirm.

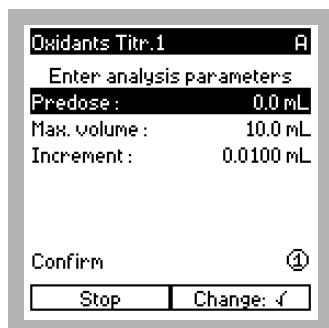
Note: Acetate buffer is added to adjust the sample pH; the precise amount added is not crucial to the accuracy or precision of the analysis.



11. The timer will start. This allows a short period of time for the reagents to mix before starting the titration.



12. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.



13. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

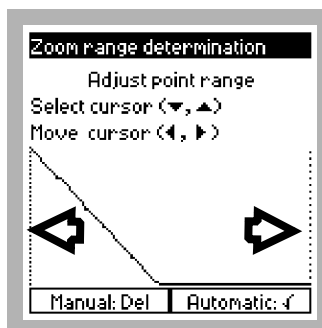
Note: Any changes made will become the new default parameters for this method Sub-ID.

Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.

Note: This step will be skipped if autoscaling software is enabled.

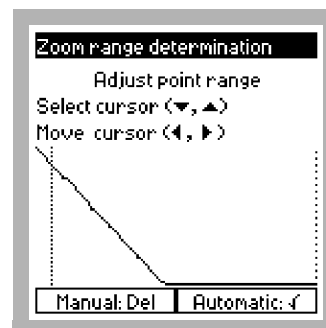


14. The timer will start, allowing the electrode to stabilize before data collection. Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



15. The Zoom Range Determination window will display the titration curve. Use the navigation buttons to select and move the cursors to define the range of data points for analysis.

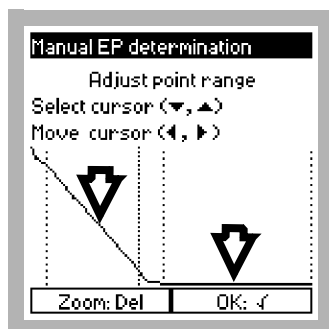
Note: Defining the range of data points excludes undesirable portions of the titration curve from the analysis.



16. Select type of end point determination.

Press **DEL** for Manual.

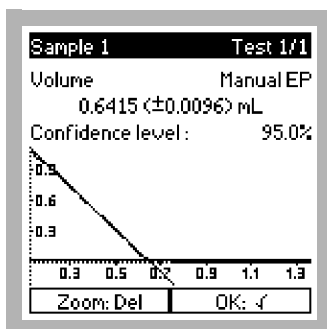
Note: Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.



17. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

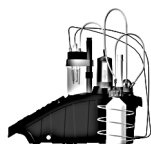
Note: For more information on manual EP determination, see page 135.



18. Press the **CHECK MARK** to accept the analysis and proceed to Titration 2, or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.

Note: The analysis data may be analyzed as many times as needed from the Zoom Range Determination window, in manual and/or automatic modes. The results are not stored until accepted.

The AutoCAT stores all titration results and then automatically calculates each analyte value after the procedure is complete.



AutoCAT Titration Method

Total Oxidants Titration 2

Oxidants Add.2 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of 2.5 N Hydrochloric acid and stir for several seconds.
Carefully remove the sample from the stirrer platform and place in the dark.
Press the **CHECK MARK** to confirm.

Oxidants Add.2 A

Dark reaction in progress
Please wait...

Timer : 04:53

Stop Skip: Del

2. The timer will start.
This timer allows a 5-minute reaction period before starting the titration.

Oxidants Add.2 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample from the dark and carefully place onto the AutoCAT stirrer platform.
Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.

Oxidants Titr.2 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 10.0 mL

Increment : 0.0150 mL

Confirm ①

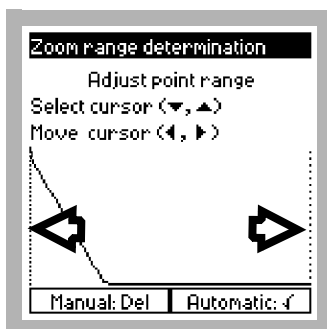
Stop Change: ✓

4. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.
Note: Any changes made will become the new default parameters for this method Sub-ID.
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section step 3.5.
Note: This step will be skipped if autoscaling software is enabled.

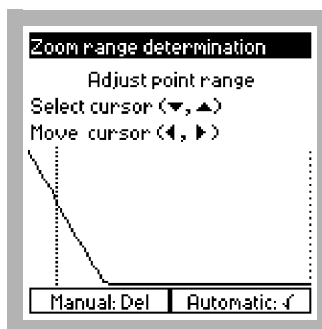


5. The timer will begin, allowing the electrode to stabilize before data is collected.

Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.

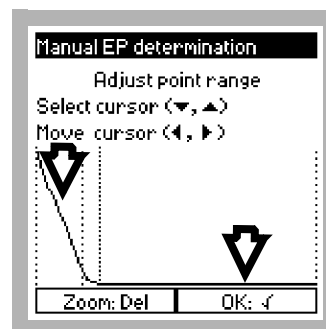


6. The Zoom Range Determination window will display the titration curve. Select and move the cursors to define the range of data points for analysis.



7. Select the type of end point determination. Press **DEL** for Manual.

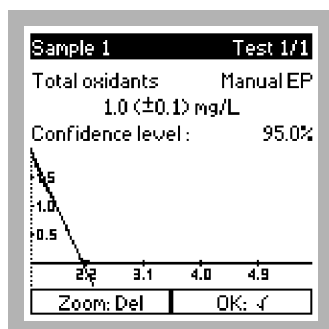
Note: Automatic determination attempts to identify linear segments without user input and is **not recommended** for this method.



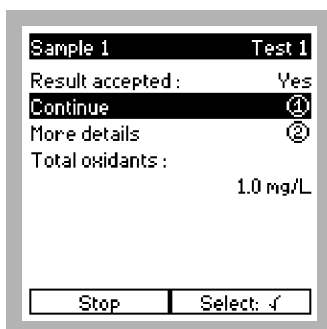
8. Using the navigation keys, select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

Note: For more information on manual EP determination, see page 135.



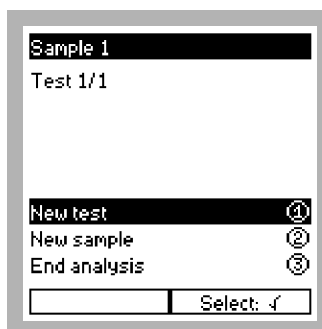
9. Press the **CHECK MARK** to accept the analysis. Press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.



10. The analysis for this test is complete.

Press **1** to select Continue to perform additional tests and/or samples, or to finish analyses.

Press **2** to select More Details to view analysis statistics specific to the current sample ID.



11. Press **1** to select New Test and run a replicate sample.

Press **2** to select New Sample to initiate analysis of a new sample with a new Sample ID. See *Instrument Tips and Techniques* on page 119.

Press **3** to select End Analysis and return to the Methods menu.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagents used in this procedure.

Summary of Method

This method gives results as “total oxidants”, which includes total chlorine (Cl_2), chlorine dioxide (ClO_2), and chlorite (ClO_2^-). The first titration yields total chlorine (includes any chloramines and free chlorine) plus a portion of the chlorine dioxide. The second titration (pH 2) yields chlorite plus a smaller portion of chlorine dioxide not titrated at pH 4.

The AutoCAT stores all titration results and calculates the results for total oxidants. The total oxidant value represents the sum of chlorite plus chlorine dioxide. Since chlorine dioxide has a short residence time in most drinking water, the total oxidant result mainly consists of the chlorite ion. This method can therefore be employed as an acceptable surrogate operational control for monitoring chlorite, which must be less than 1 mg/L. This method is not acceptable for regulatory testing.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Acetate Buffer Solution, pH 4, with dropper	1 mL.....	100 mL	14909-32
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1000 mL	1999-53
Hydrochloric Acid Standard Solution, 2.5 N	4 mL.....	100 mL	1418-32
Potassium Iodide	1.0 g.....	100 g.....	167-26H

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Measuring spoon, 1.0 g	1	each.....	510-10
Pipet, Volumetric, Class A, 100-mL.....	1	each.....	14515-42

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
------------------------------------	-------------	--------------	----------

Optional Apparatus

Mini-printer, thermal, w/cable.....		each.....	A70P021
Cylinder, Graduated, 250 mL	1	each.....	508-46

*Teflon is a Registered Trademark of EI DuPont Company.



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FAX: (970) 669-2932



“Quick” Two Step Amperometric Titration

0.1–5.0 mg/L as ClO_2^-

Titration Workstation

Scope and Application: For water and wastewater*.*Procedure equivalent to Standard Methods 4500- ClO_2 E.

Sample Tips and Techniques

- Soak all glassware in a strong chlorine dioxide (ClO_2) or chlorite (ClO_2^-) solution (300–500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Use the glassware for this method only.
- Remove sample portions with a volumetric pipet. Always place the tip at the bottom of the sample container. If using 200-mL sample increments, use a 100-mL pipet to withdraw two portions of sample.
- Always use organic-free water for sample dilution. (Cat. No. 26415-49).
- Rinse the electrode, temperature probe, and anti-diffusion tip with deionized water before every titration.



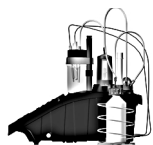
Reagent Tips and Techniques

- Download the Certificate of Analysis (COA) to obtain the exact concentration of any unopened bottle of Hach titrant or standard solution. See *Obtaining the Certificate of Analysis for Hach Reagents* on page 41.
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis.
- Never substitute buffers designed for calibrating pH meters. They may contain dyes that interfere with amperometric titration.
- Never use buffers contaminated with mold or bacteria.



Instrument Tips and Techniques

- Adjust the contrast of the display by accessing the Methods menu and pressing **7** to lighten or **0** to darken.
- A distinction is drawn between running a new test and a new sample. Each test is a replicate run of the current or previous sample analysis. The AutoCAT 9000 automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results. Each test is given a different number, all of which are listed under the same Sample ID. When starting a new sample, a new ID is assigned.
- The AutoCAT 9000 can accommodate any sample size. Standard Methods recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The AutoCAT 9000 calculates concentration based on the sample volume. Make sure that the sample volume is correct.
- Press **STOP** at any time to interrupt instrument operation; the user can resume, restart, or quit completely.
- Press the **CHECK MARK** at any time during data acquisition to halt data collection.
- Press **DEL** during any timer period (except Start Timer) to immediately exit the timer and proceed to the next step.
- Press **ESC** during any titration/calibration data collection period or timer to access Edition mode. See *Edition Mode* on page 30.
- Flush the burette each day before the first sample test or calibration is performed. See *Daily Start-up* on page 26.
- Flush the burette when changing titrants. See *Changing Titrants* on page 25.
- A distinction is drawn between running a new Test and a new Sample. Each Test is a replicate run of the current or previous.



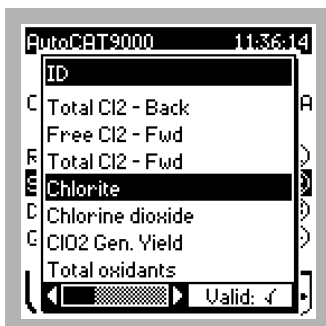
AutoCAT Titration Method

Chlorite Titration 1



1. Turn the instrument on and access the Methods menu.

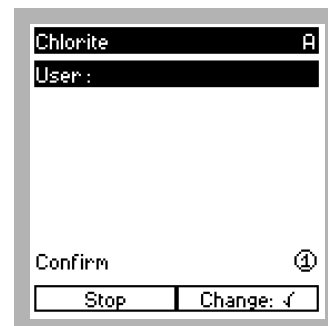
Press 2 to choose Select Method.



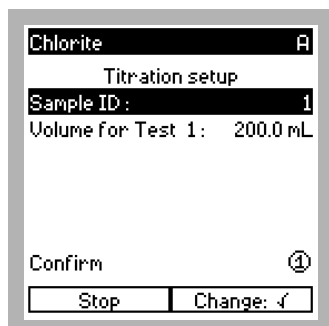
2. Highlight Chlorite. Press the **CHECK MARK** to validate.



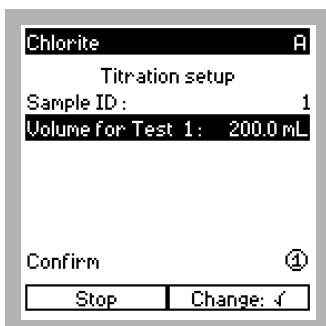
3. Press 1 to select Run method. This method uses the 5.64 mN PAO titrant. See *Software Setup for Titrant Installation* on page 38.



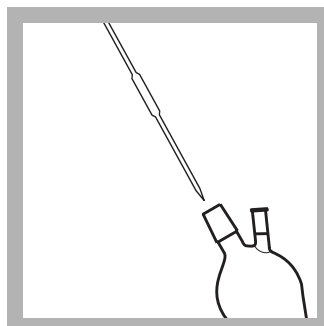
4. Verify User. Press the **CHECK MARK** to enter a new user or press 1 to confirm. **Note:** This screen will be skipped if the User ID is disabled. See *Setting a User ID* on page 27.



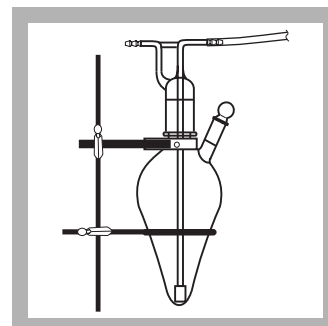
5. Highlight Sample ID. Press the **CHECK MARK** to enter a new sample ID or proceed to step 6.



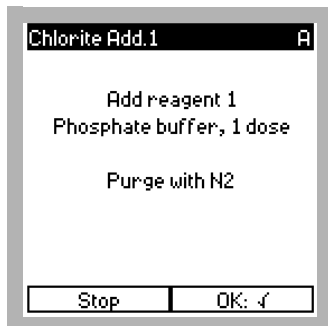
6. Highlight Volume for Test 1. Press the **CHECK MARK** to enter a new volume. Press 1 to confirm.



7. Pipet 200 mL of sample into a Gas Washing Bottle (GWB). Add 1 mL of pH 7 Phosphate buffer. Swirl to mix.



8. Insert the purge tube and dispersion tip into the GWB. Connect the GWB inlet to a tank of high purity nitrogen.



9. Use a needle valve to adjust the flow of nitrogen to provide a steady stream of bubbles through the sample.

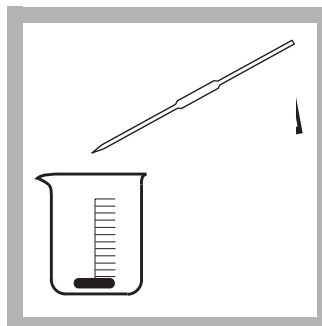
Press the **CHECK MARK** to continue.



10. Purge nitrogen gas through the sample for 15 minutes.

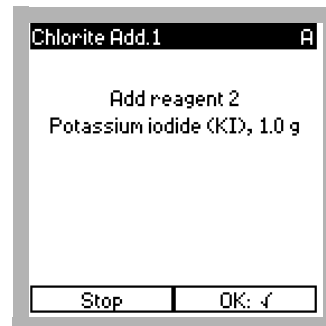
When the timer beeps, move to step 11.

Note: If the nitrogen purge has already been performed, press **DEL** to skip this timer and proceed to the next step.



11. Transfer the purged sample into a 250-mL beaker. Add the specified magnetic stir bar.

All containers must be pretreated for chlorine demand, see Container Pretreatment on page 61.



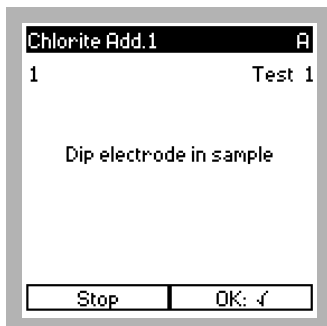
12. Use the measuring spoon to add 1.0 g of potassium iodide (KI). Place the sample onto the stirrer platform.

Press the **CHECK MARK** to confirm.

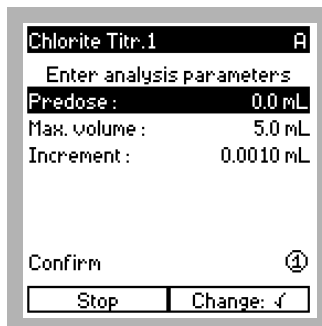
Note: KI is added in excess. The precise amount added is not crucial for the accuracy or precision of the analysis.



13. The timer will start. This allows a short period of time for the reagents to mix before starting the titration.



14. Lower the electrode head onto the beaker rim. Press the **CHECK MARK** to confirm.

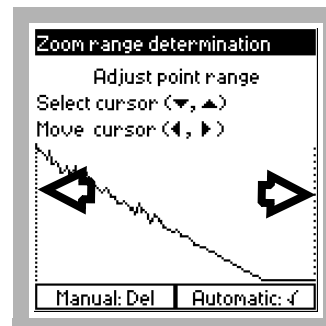


15. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.

Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press **1** to confirm.

Note: Any changes made will become the new default parameters for this method Sub-ID.

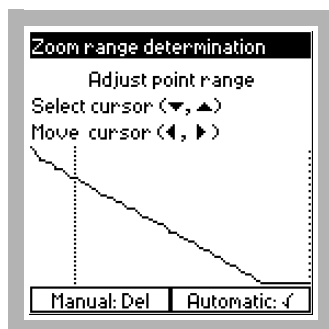
Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.



16. The Zoom Range Determination window will display the titration curve.

Use the navigation buttons to select and move the cursors to define the range of data points for the analysis.

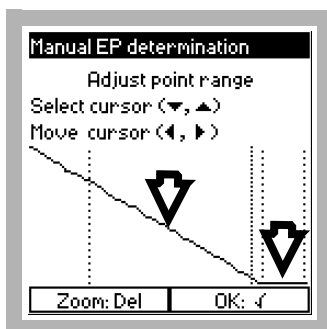
Note: Defining the range of data points excludes undesirable portions of the titration curve from the analysis.



17. Select type of end point determination.

Press **DEL** for Manual.

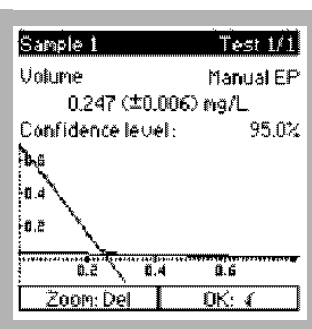
Note: Automatic determination attempts to identify linear segments without user input is **not recommended** for this method.



18. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

Note: For more information on manual EP determination, see page 135.



19. Press the **CHECK MARK** to accept the analysis and proceed to Titration 2, or press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.



AutoCAT Titration Method

Chlorite Titration 2

Chlorite Add.2 A

Add reagent 1
HCl 2.5N, 2.0 mL

Stir

Place the solution in the dark

Stop OK: ✓

1. Raise the electrode head.
Add 2.0 mL of 2.5 N Hydrochloric acid and stir for several seconds.
Press the **CHECK MARK** to confirm.

Chlorite Add.2 A

Dark reaction in progress
Please wait...

Timer : 04:56

Stop Skip: Del

2. Carefully remove the sample from the stirrer platform and place in the dark.
The timer will start to allow a 5-minute reaction period before starting the titration.

Chlorite Add.2 A

1 Test 1

Place the sample
on the instrument

Dip electrode in sample

Stop OK: ✓

3. Remove the sample from the dark and carefully place onto the AutoCAT stirrer platform.
Lower the electrode head onto the beaker rim.
Press the **CHECK MARK** to confirm.

Chlorite Titr.1 A

Enter analysis parameters

Predose : 0.0 mL

Max. volume : 5.0 mL

Increment : 0.0010 mL

Confirm ①

Stop Change: ✓

4. The analysis parameters that have been stored for the current Sub-ID may be edited at this time.
Highlight the appropriate line and press the **CHECK MARK** to change one of the analysis parameters or press 1 to confirm.

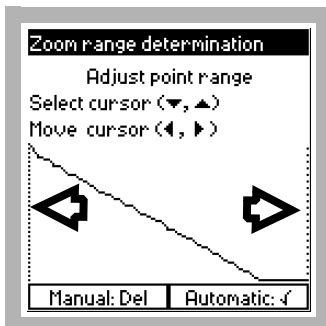
Note: Any changes made will become the new default parameters for this method Sub-ID.

Note: These Sub-ID parameters can be edited here as 'run-time' settings, or from the Main Menu as described in Section 3.5.



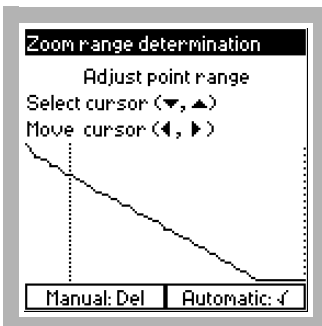
5. The timer will begin, allowing the electrode to stabilize before data is collected.

Once the electrode has stabilized, the AutoCAT will begin data acquisition and plot the titration curve.



6. The Zoom Range Determination window will display the titration curve.

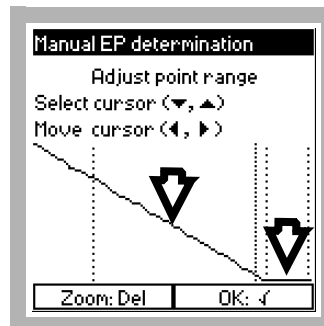
Use the navigation buttons to select and move the cursors to define the range of data points for analysis.



7. Select the type of end point determination.

Press **DEL** for Manual.

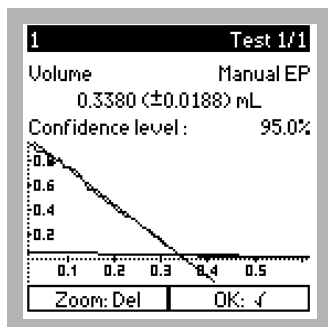
Note: Automatic determination attempts to identify linear segments without user input is **not recommended** for this method.



8. Use the navigation keys to select two line segments, one on each side of the titration end point, by positioning vertical lines (cursors) at the beginning and end of each segment.

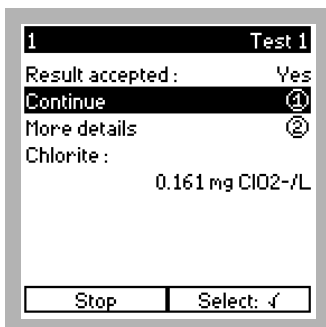
Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.

Note: For more information on manual EP determination, see page 135.



9. Press the **CHECK MARK** to accept the analysis.

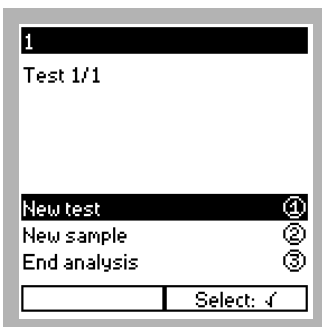
Press **DEL** to return to the previous window to adjust the linear segments and reanalyze the data.



10. The analysis for this test is complete.

Press **1** to select Continue to perform additional tests and/or samples, or to finish analyses.

Press **2** to select More details to view analysis statistics specific to the current sample ID.



11. Press **1** to select New Test and run a replicate sample.

Press **2** to select New Sample to initiate analysis of a new sample with a new Sample ID. See *Instrument Tips and Techniques* on page 127.

Press **3** to select End Analysis and return to the Methods menu.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagents used in this procedure.

Summary of Method

This procedure permits the determination of chlorite (ClO_2^-) in the sample.

This procedure involves two amperometric titrations. These titrations are as follows:

- Titration 1 — Cl_2 (not volatilized by a nitrogen gas purge)
- Titration 2 — ClO_2^-

The AutoCAT 9000 stores all titration results and, after completion, calculates the analyte value.

Required Reagents

Description	Qty. required per test	Unit	Cat. No.
Phenylarsine Oxide (PAO) Titrant, 0.00564 N.....	varies.....	1000 mL	1999-53
Hydrochloric Acid Standard Solution, 2.5 N	4 mL.....	100 mL	1418-32
Phosphate Buffer, pH 7, with dropper.....	1 mL.....	100 mL	21553-32
Potassium Iodide, ACS.....	1.0 g.....	100 g.....	167-26H

Required Apparatus

Beaker, Glass, 250-mL	1	each.....	500-46H
Gas Washing Bottle (GWB)	1	each.....	26622-00
Magnetic Stir Bar, Teflon®* coated.....	1	each.....	50085-00
Measuring Spoon, 1.0 g (NaCl weight), molded plastic	1	each.....	510-00
Pipet, Volumetric, Class A, 100-mL.....	1	each.....	14515-42
Stand, Support Ring.....	1	each.....	563-00
Support Ring, for GWB.....	1	each.....	26563-00

Optional Reagents

Dilution water, organic-free	varies.....	500 mL	26415-49
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Optional Apparatus

Mini-printer, thermal, w/cable.....		each.....	A70P021
Cylinder, Graduated, 250 mL	1	each.....	508-46

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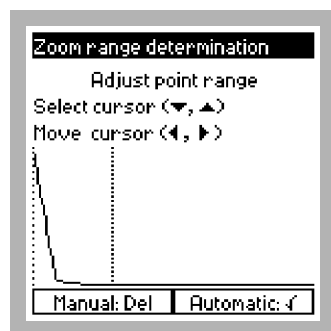
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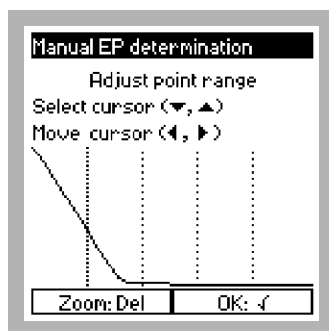
FAX: (970) 669-2932

Manual Endpoint Determination

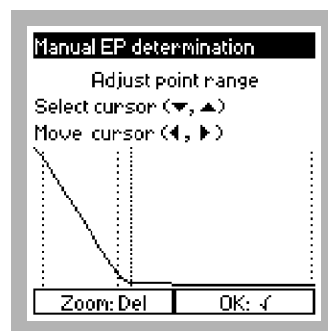
General Guidelines for Manual Endpoint Determination



1. In the Zoom screen, move the right and left cursors as necessary, to exclude any non-linear portions at the beginning or end of the curve, and if necessary, move the cursors so that the endpoint will be roughly centered within the selected region.

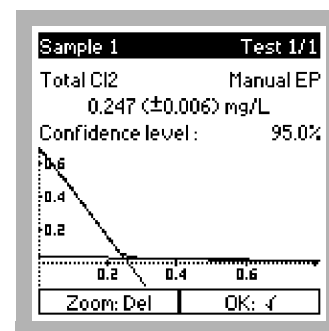


2. Press **DEL** to enter the manual endpoint determination screen.

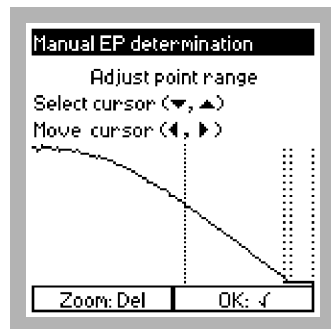


3. Move the four cursors to select one linear region before, and one linear region after the endpoint. Make these linear segment selections as large as possible in order to obtain the most accurate endpoint determination.

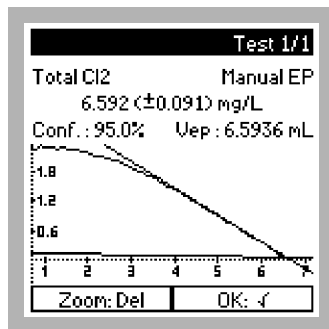
Note: The AutoCAT will draw a best fit regression line through the data points between the two cursors on the left side of the end point, and a best fit regression line through the data points between the two cursors on the right side of the end point. The AutoCAT will use the intersection point of these two lines as the end point in calculations.



4. Press the **CHECK MARK** to calculate the result.



5. When the sample oxidant concentration is high and a predose has not been selected, the initial current change may be flat.



6. By selecting a linear segment just before the endpoint, the lines will intersect at the obvious endpoint, yielding a correct Vep.

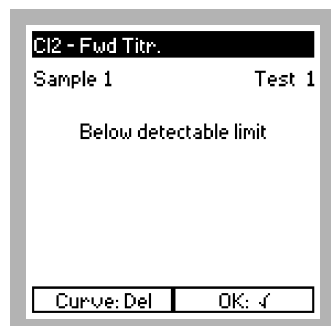
Below Detectable Limit

Method Limits

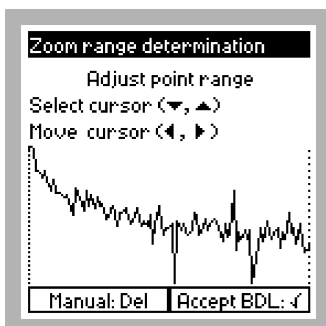
When a titration result is below the limits of the Hach method in use, the instrument will return a result of “Below Detectable Limit” (BDL). During normal operation, drift can occur. Even when a result reads below the method threshold, a real endpoint with low noise level is possible.

The BDL feature allows for review of the titration curve for a usable endpoint. Example 1 shows a BDL result with a high level of noise and no clear endpoint. Example 2 shows a BDL result with usable data (low noise and a sharp endpoint).

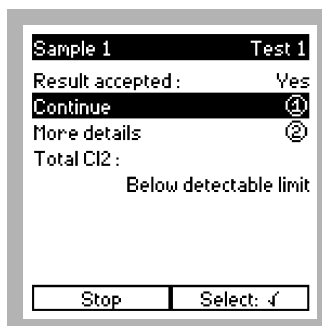
Example 1



1. Press **DEL** to view the titration curve.

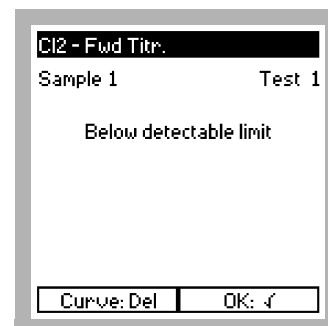


2. Press the **CHECK MARK** to accept BDL as the result.



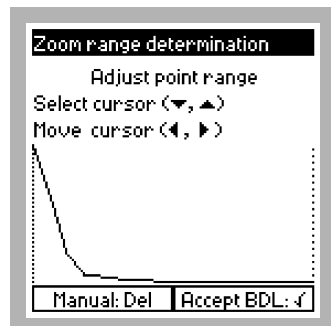
3. In this example, “Below Detectable Limit” is stored with Test 1 for Sample 1.

Example 2

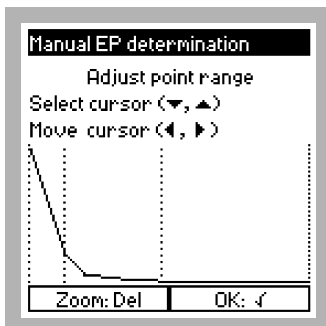


1. Press **DEL** to view the titration curve.

Example 2, continued

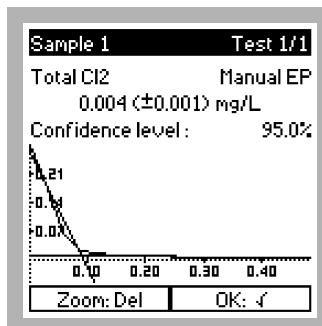


2. Press **DEL** to perform manual endpoint determination.

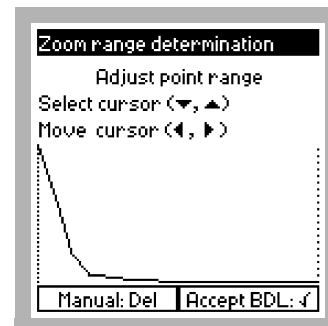


3. Use the navigation keys to select two line segments, one on each side of the titration end point. Position the vertical lines (cursors) at the beginning and end of each segment.

Press the **CHECK MARK** to confirm changes or press **DEL** to return to the Zoom window.



4. Press the **CHECK MARK** to accept this calculated result, press **DEL** to return to the previous window to adjust the linear segments and analyze the data again.



5. If the results are not usable, press **DEL** twice to return to the initial Zoom Range Determination screen. Press the **CHECK MARK** to accept BDL.

Section 9 Maintenance

9.1 Instrument Maintenance

9.1.1 General

Protect the instrument from temperature extremes including direct sunlight, heaters, and other heat sources. Do not store or use the instrument in a dusty, damp, or wet location.

9.1.2 Display

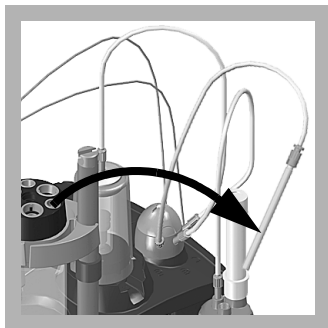
Do not scratch the display screen. Never use a pen, pencil, or other sharp object on the display surface. The display is water-resistant, but should not be exposed to direct rain or moisture. The display screen contains a glass element. Protect the screen against strong impacts.

9.1.3 Cleaning the Instrument

Use a soft, damp cotton cloth to wipe the instrument and the display screen. If the surface of the screen becomes soiled, cleaned it with a soft cloth and diluted window cleaning solution. Do not use strong solvents.

9.1.4 Cleaning and Conditioning the Electrode

Clean and condition the AutoCAT 9000™ dual platinum electrodes (DPE) as shown in the procedure below, to make them more responsive. The frequency of use and the type of samples analyzed will dictate the frequency for electrode cleaning and conditioning. Excess “noise” in the titration curve and/or poor curve shapes can indicate that the electrode is dirty.

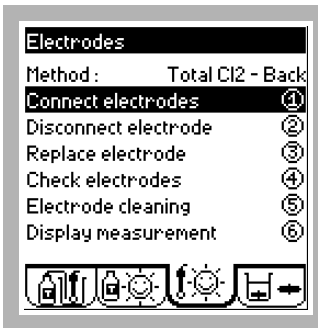


1. Remove the plastic anti-diffusion dispenser tip from the electrode head and set aside. See *Instrument Assembly 6.* on page 17 for more information.



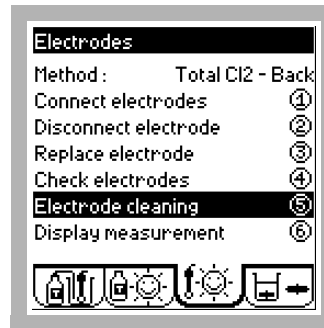
2. Prepare a dilute nitric acid solution. Measure approximately 200 mL of solution into a clean 250-mL beaker.

Note: Hach offers 1:1 (v/v) Nitric Acid (Cat. No. 2540-49) for electrode cleaning.



3. Turn the instrument ON or, if already in operation, access the **Electrodes** menu.

Note: The electrode cleaning routine is identical for all methods.



4. Press **5** to select Electrode Cleaning, and follow the embedded procedure.

After electrode cleaning is complete, replace the plastic anti-diffusion tip to the electrode head.

Note: Electrodes should be conditioned prior to first running a titration. To condition the electrode, soak in a dilute chlorine solution.

9.2 Maintenance Intervals

Table 4 Maintenance Tasks and Schedule

Maintenance Task	Frequency
Check the level of titrant in the titrant bottle and refill or replace if necessary.	Daily
Remove any air bubbles from the burette by performing the flush procedure (Titrants menu>Burette functions>Flush).	Daily
Check electrode and titrant status. Recalibrate the titrant if necessary.	Daily
Rinse the electrode, temperature probe, and plastic anti-diffusion tip with deionized water before and after each use.	Daily
Check the piston plunger in the burette for leakage.	Weekly
Check to see if burette leaks. Replace burette if leaks are present.	Weekly
Replace the burette.	Annually
Replace the delivery tubing and plastic anti-diffusion tip assembly.	Annually
Contact your Hach representative for instrument software updates.	Annually

9.3 Replacing the Fuse

The AutoCAT 9000 is protected by both primary (user-serviceable) and secondary (factory-serviceable only) fuses.

The primary fuse is installed in a holder located above the instrument power cord receptacle (see *Section 2 Instrument Assembly, Figure 3 on page 19*). To inspect or replace the primary fuse, perform the following steps:

1. Disconnect the power cord from the instrument.
2. Use an object with a fine point (e.g., a ball-point pen) to push inward on the retaining tabs located on the sides of the fuse holder. The fuse holder will be pushed outward slightly once the tabs have been disengaged.
3. Pull the holder outward and remove it from the instrument.
4. Inspect the fuses. If either fuse is no longer serviceable, replace with the provided spare (part no. 50082-70), or with one of the same type and rating (Time delay, 1 A, 250 V).
5. Replace the fuse holder. Ensure that it is oriented correctly, and that the retaining tabs are engaged.

Note: Replacement of the circuit board-mounted secondary fuses requires the instrument to be returned to the manufacturer for service.

Section 10 Troubleshooting

The following table is designed to help identify and solve various problems that may be encountered while running the AutoCAT.

Problem Category	Symptom	Probable Cause	Corrective Action
Electrical	Display does not show up or is too dark	No operating power	- Confirm that the power switch on the back of the instrument has been turned ON. - Confirm that the power cord is fully inserted into the back of the instrument and that it is properly plugged into the wall outlet. - Confirm that there is power to the wall outlet. - Verify the integrity of the fuses; change if necessary. See <i>Section 9.3 Replacing the Fuse</i> on page 140.
		The screen contrast or intensity is too low.	While in the Methods menu, press the 0 to darken, and/or 7 to lighten until the desired screen intensity and contrast is obtained.
Mechanical	Air bubbles trapped in the lines	Air bubbles have inadvertently been trapped while trying to install the titrant or air is being sucked into the system where the tubing is connected to the instrument.	- Verify that the inlet tube for the titrant is secure and below the surface of the titrant solution inside the titrant bottle. - Verify that the all the tubing connections are tight. If the threads of tubing connection are damaged or stripped, and cannot be properly tightened, they must be replaced. - Select Titrants>Burette functions>Flush. Lightly tap the tubing while the instrument is flushing to purge air bubbles from the system.
	Titrant leaks	Titrant leaks can also occur when the burette seals become faulty. Titrant leaks generally indicate that a tubing connector has not been properly tightened.	- Tighten the leaking tube connection. If the tube connection has been damaged, replace the tubing. - Verify the integrity of the burette seals. If the burette seals are leaking, replace the burette.
	Titrant doesn't flow through tubing	Loose tubing connection	- Verify that the inlet tube for the titrant is secure and below the surface of the titrant solution inside the titrant bottle. - Verify that the all the tubing connections are tight. If the threads of tubing connection are damaged or stripped, and cannot be properly tightened, they must be replaced.
		Tubing is connected to the wrong ports on the rotary valve.	Verify that the tubing sections are connected to the correct ports on the rotary valve, respectively. Observe the icons. See <i>Section 2.2 Instrument Assembly</i> on page 15.
Data Collection (w/o Auto-scaling)	The titration is very quick and the resolution of the titration curve is too low. The titration curve is too noisy.	The selected volume increment is too large.	Decrease the volume increment. The volume increment is user adjustable during the titration procedure.
	The titration is very slow and there are too many points before the end point.	The volume increment is too small.	Increase the volume increment. The volume increment is user adjustable during the titration procedure.

Troubleshooting

Problem Category	Symptom	Probable Cause	Corrective Action
Data Collection (w/ Auto-scaling)	Not enough points in the titration curve.	The number of points before the end point is too small.	• Increase the number of points before the end point (Methods>Method library> "method" Titr.>Auto-scaling Yes> No. of points before EP).
	Too many points in the titration curve.	The number of points before the end point is too large.	• Decrease the number of points before the end point (Methods>Method library> "method" Titr.>Auto-scaling Yes> No. of points before EP).
	The titration curve stops too soon after the end point.	The fraction of points before the end point is too large.	• Decrease the fraction of points before the end point (Methods>Method library> "method" Titr.>Auto-scaling Yes> Fraction before EP).
Data Collection (w/ Auto-scaling)	The titration curve stops too late after the end point.	The fraction of points before the end point is too small.	• Increase the fraction of points before the end point (Methods>Method library> "method" Titr.>Auto-scaling Yes> Fraction before EP).
	Auto-scaling is unable to set the current range or the volume increment for the titration.	Auto-scaling relies on the measurement of the initial current and an estimate of the initial slope of the titration curve to predict the approximate end point for the titration. If the signal is very low or the noise level is very high it may not be able to estimate the end point accurately enough to set the current range or volume increment.	• Re-run the analysis. Auto-scaling is often successful on a second attempt. • Turn Auto-scaling off, set the current range and volume increment manually, and re-run the analysis.
Automated end point Determination	The fitted end points are poor.	The titration curve is very poorly shaped or very noisy.	• Use the manual end point determination.
		The ends of the titration curve are very noisy or distorted in some way but the region around the end point looks good.	• Use the zoom window cursors to restrict the end point determination to a symmetrical region about the end point.
	The titration curves are fairly asymmetrical.	AEPD works best when the titration curve is symmetrical about the end point. Symmetrical titration curves generally mean that the data collection parameters have been fully optimized.	• Adjust the data collection parameters to promote collection of a symmetrical titration curve. • Use the zoom window cursors to restrict the end point determination to a symmetrical region about the end point.
	The instrument displays a message asking the user to change the data point range.	AEPD requires that a minimum of six points on each side of the end point be assigned to linear segments for regression analysis. If AEPD cannot identify six points on each side it stops.	• Use the manual end point determination routine (MEPD) to determine the end point. • Use the zoom window cursors to select a wider symmetrical region about the end point for analysis. • Reduce the volume increment used to collect data. This will give more points on each side of the end point. The other data collection parameters may also need to be adjusted to promote collection of a symmetrical titration curve.

Problem Category	Symptom	Probable Cause	Corrective Action
General quality of the Titration Curve	The end point is not sharp.	If the electrode hasn't been used for some time it may need to be reconditioned.	• Clean and recondition the electrode. See <i>Cleaning and Conditioning the Electrode</i> on page 139.
	The titration curve is unusually noisy.	Mechanical vibrations of the sample cell or instrument increases the noise in the collected titration curve.	• Remove any source of vibration. This includes repositioning the sample beaker to avoid having the magnetic stir bar strike it's side. • Ensure that the plastic anti-diffusion tip and electrode are properly installed into the electrode head. See <i>Section 2 Instrument Assembly Figure 2</i> on page 14.
	Sharp spikes are observed in the titration curve.	This is generally not a major problem but electrical spikes may be observed when the AutoCAT shares an electrical circuit with other devices or relays during the data collection process. Even if there are electrical spikes in the titration curve, they generally don't prevent the analysis of the data.	• Install a surge protector between the AutoCAT 9000 and the wall outlet. • Turn OFF all other devices on the same circuit. • Use only a dedicated electrical circuit for the AutoCAT 9000.
	Erratic operation	The AutoCAT 9000 is sensitive to static electricity.	• Surround the AutoCAT 9000 with a Faraday cage. • Move the instrument to a location free of strong electrical fields or static discharges if performance is adversely affected.
	Irregular distortions or flat regions in the middle of the titration curves.	Occasionally air bubbles get trapped in the system and pass through burette tip. If air bubbles pass through the burette tip before the titration has reached the end point then the apparent titrant volume will be larger than it really should be. Air bubbles may also develop when the titrant degasses due to temperature changes and/or pressure drops within the system.	• Inspect the tubing and remove or purge any air bubbles that might be trapped in the system; also check to be sure all the tubing connections are tight and not leaking. Loose connections are the primary source for recurring air bubbles to enter the system.
	The titration curve starts or ends with a high, perfectly flat region.	The current range for the A/D converter has been exceeded.	• Increase the current range. • Predose the sample with enough titrant to bring the signal into the appropriate current range. • Use a proportionately smaller sample size to bring the signal into the appropriate current range.

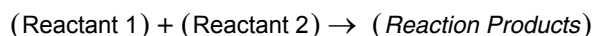
Troubleshooting

Problem Category	Symptom	Probable Cause	Corrective Action
Accuracy of Analysis Results	The concentration for a known standard solution obtained using the AutoCAT 9000 does not match its actual value.	If the measured concentration does not match actual value (within an acceptable uncertainty range) then the concentration of the titrant currently installed on the instrument is probably wrong or the wrong sample volume has been entered.	• Confirm that the correct titrant concentration has been entered into the instrument. • Confirm that the titrant concentration has the correct units. • Confirm that the correct sample volume has been entered. • Restandardize the titrant using the embedded calibration procedure. • Replace the current bottle of titrant with a fresh bottle of titrant and enter the proper titrant concentration for the new titrant.
Warning Signs	"Stormy" icon on <i>Titrant Tab</i>	Indicates that there is a problem with the titrant or burette.	• The stormy icon may appear due to many related causes. To correct the problem complete the following sequence: 1. Verify that the desired method has been selected. 2. Verify that the burette has been properly installed in the software. 3. Verify that the correct titrant has been installed. 4. Verify that the titrant concentration has been properly set by either entering the value manually or by running the appropriate calibration routine.
		If the stormy icon appears immediately after selecting a new method, then it indicates the currently installed titrant is not appropriate for the newly selected method.	• Install the appropriate titrant and then enter the titrant concentration, or run the titrant calibration routine. See <i>Setting Titrant Concentration</i> on page 40.
	"Stormy" icon on <i>Electrodes Tab</i>	Indicates that the electrode and/or the temperature sensor have not been properly installed in the software.	• Install (connect) the electrode and temperature probe in the software. See <i>Software Setup for Electrode and Temperature Sensor Installation</i> on page 34.
	Question Mark on <i>Titrant Tab</i>	Indicates that the titrant calibration is about to expire.	• Recalibrate the titrant or reset the titrant concentration to the correct value.

Appendix A Amperometric Titration Theory

1.1 General Titration Theory

All titrations are carefully regulated and monitored chemical reactions. Any chemical reaction involves adding one reactant to another to form one or more reaction products.



1.1.1 Redox Reactions

Oxidation-reduction reactions (Redox reactions) are a special class of chemical reactions where electrons are transferred from one species to another to form new chemical species. Species gaining electrons are said to be reduced while species releasing electrons are said to be oxidized. Species accepting electrons are called oxidizing agents (or oxidants) and those releasing electrons are called reducing agents (or reductants). Chlorine (Cl_2) is a common oxidizing reagent because it can break into separate chlorine atoms (Cl) that readily accept electrons from other species. Another common oxidizing agent is iodine (I_2). phenylarsine oxide (abbreviated PAO representing PhAsO , where $\text{Ph} = \text{C}_6\text{H}_5^-$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) are examples of common reductants.

1.1.2 Reaction Measurement

The progress of an oxidation-reduction reaction can be monitored by measuring the electrical current passing through a solution under an imposed potential when electrons are transferred from the reductant to the oxidant. Current stops flowing if either the oxidant or reductant is consumed or is otherwise removed from the solution.

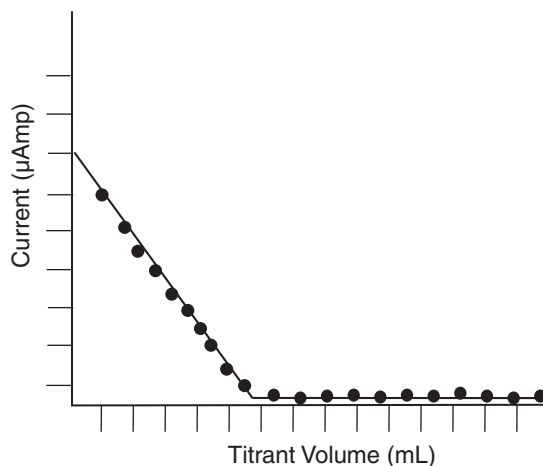
In an amperometric titration a titrant solution containing a reductant is added to a sample containing an oxidant (or a oxidant is added to a sample containing an reductant) while the electrical current passing between two platinum electrodes is monitored. The species being analyzed is called the analyte. The point at which equal amounts of oxidant and reductant are brought together is called the end point. The end point in an amperometric titration curve is identified as that point in the titration curve (electrical current vs. titrant volume) where a sharp break (i.e., change in slope) occurs in the titration curve.

Depending on the oxidation-reduction reaction, the titration can be either a forward or back titration.

1.1.2.1 Forward vs. Back

In a forward titration (*Figure 1*), the measured current starts at a high initial value. It drops continuously as titrant is added until the end point is reached and the current levels off. In a back titration (*Figure 2*) the measured current starts at a low initial value and remains level as titrant is added. When the end point is reached the current increases continuously as titrant is added.

Figure 1 Total Chlorine Forward Titration



1.1.3 Determining Concentration

Experimentally the concentration of the titrant is known very accurately, as is the volume of titrant that must be added to reach the titration end point. Use the following formula to calculate the concentration of the analyte in an unknown sample:

$$N_{\text{Sample}} = \frac{V_{\text{Titrant}} N_{\text{Titrant}}}{V_{\text{Sample}}}$$

Where:

V_{Sample} is the sample volume

V_{Titrant} is the volume of titrant solution that must be added to reach the end point

N_{Titrant} is the concentration (normality) of the titrant solution

N_{Sample} is the concentration (normality) of the analyte in the sample solution

1.1.3.1 Conversion Factor

Use a conversion factor to convert normality to more tangible units such as mg/L or ppm. The precise conversion factor depends on the particular analyte and concentration units involved. For example, one equivalent weight of chlorine (Cl_2) is 35.453 g. Consequently, a 0.100 N chlorine solution contains 3.5453 grams of Chlorine per liter of solution. The following conversion factors can be used to convert from normality to the more common concentration units.

$$\text{Chlorine Concentration: (mg/L) = (ppm) = } N_{\text{chlorine}} \times 35453 \text{ mg/eq wt.}$$

Inserting the conversion factor into the equation permits the chlorine concentration to be expressed in (mg/L), as shown below:

$$C_{\text{sample}} = \frac{N_{\text{Reductant Spike}} V_{\text{Reductant Spike}}}{V_{\text{Sample}}} \times 35453 \text{ mg/equ wt.}$$

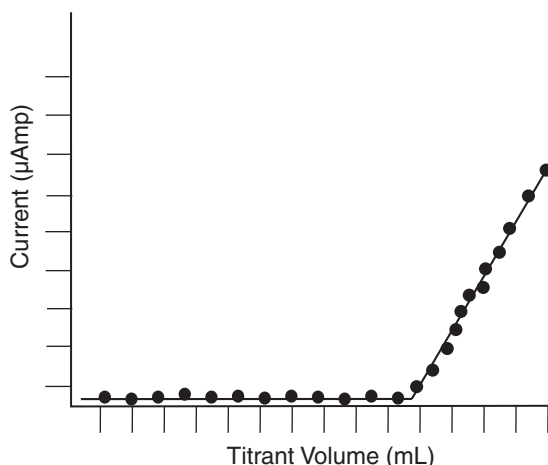
The above equation applies to *forward* titrations only. A slightly different calculation, shown below, is used for *back* titrations.

$$C_{\text{sample}} = \frac{N_{\text{Reductant Spike}} V_{\text{Reductant Spike}} - N_{\text{Titrant}} V_{\text{Titrant}}}{V_{\text{Sample}}} \times 35453 \text{ mg/equ wt.}$$

1.1.3.2 Sample Spike

In a back titration (*Figure 2*), the sample solution is spiked with a measured volume of standard reductant solution (e.g., phenylarsine oxide or sodium thiosulfate). This fixes the chlorine concentration, allowing the sample to be stored for later analysis. The chlorine concentration is derived from the difference between the amounts of reductant originally added to the sample ($N_{\text{Reductant Spike}} V_{\text{Reductant Spike}}$) and that remaining after reacting with the Chlorine in the sample ($N_{\text{Titrant}} V_{\text{Titrant}}$). The amount of unreacted reductant is determined by titration with a standard iodine solution.

Figure 2 Total Chlorine Back Titration



1.2 Errors and Interferences

1.2.1 Overview

According to *Standard Methods*, “the amperometric method is the method of choice because it is not subject to interference from color, turbidity, iron, manganese, or nitrite-nitrogen”. However, several of these factors may affect the determination of chlorine species when using amperometric methods. This is a brief review of common sources of error encountered with actual samples.

The common chlorine methods will detect other disinfectants such as chlorine dioxide (ClO_2), ozone (O_3), bromine (Br_2), hydrogen peroxide (H_2O_2) and disinfectant by-products such as chlorite and chlorate. In the free chlorine determinations, these oxidants will be reduced to varying degrees by PAO or thiosulfate in the titration method. Each of these oxidants will oxidize iodide to iodine, interfering in the total chlorine determination.

1.2.2 Deposition on Electrode Surfaces

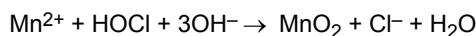
The AutoCAT 9000 is designed with self-cleaning platinum electrodes. Occasionally, it may be necessary to perform the embedded clean/condition procedure to maintain optimal performance. Sharp amperometric titration end points require clean, well-

Amperometric Titration Theory

conditioned electrodes. Since the electrodes contact the sample, certain species in the sample may plate out or coat the electrode's metallic surface. Metal ions such as copper (+2), silver (+1) and iron (+3) have been reported to interfere with amperometric titrations. In some waters, foaming or surface-active agents will coat the metallic electrodes, decreasing sensitivity.

1.2.3 Manganese Compounds

Manganese (Mn) exists in oxidation states of +2 through +7. The higher oxidation states, typically +3 to +7, will interfere with all the common chlorine methods. Free chlorine reacts to oxidize soluble manganese compounds, for example:

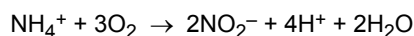


If present, oxidized forms of manganese (+4 to +7) will titrate with PAO in the forward titration procedure for free chlorine. This will cause the measured chlorine concentration to be artificially high.

Iodide (I^-) can be oxidized by Mn (+4 to +7) to I_2 , which also interferes with the titrimetric methods for total chlorine. Oxidized forms of manganese will react with iodide at pH 4 producing iodine, which then titrates with PAO causing an interference. The interference of oxidized manganese in the back titration method appears to be a function of iodide concentration and the test pH*.

1.2.4 Nitrite Interference

Nitrite (NO_2^-) can exist as a transitory compound found in certain waters due to the biological oxidation of ammonia:



There is conflicting information about the interference of nitrites in forward or backward amperometric methods for total chlorine. *Standard Methods*, section 4500-Cl D.1.b, states that nitrites do not interfere in the forward titration methods. Section 4500-Cl C.1.b, the Iodometric Method II, states that nitrite interference can be minimized by buffering to pH 4.0 before addition of iodide. It also states that interference from more than 0.2 mg/L nitrites can be controlled by the use of a phosphoric acid-sulfamic acid reagent. This reagent is used with iodate (IO_3^-) as titrant, since a higher acidity is required to liberate free iodine.

Research scientists at Hach have confirmed that nitrites can oxidize KI to iodine at low pH values, similar to the reaction of KI with chlorine or chloramines. The reaction of KI with nitrite is dependent on the titration pH and the order of reagent addition.

In the forward titration for total chlorine, nitrites appear to cause positive and negative interferences, depending on the order of reagent addition. If iodide is added to the sample before the pH 4 buffer, the error increases as a function of nitrite concentration. If buffer is added before the iodide, a large negative error occurs, which is independent of the nitrite level.

In the back titration using iodate (*Standard Methods* 4500-Cl C), a lower solution pH occurs due to the addition of the phosphoric acid-sulfamic acid mixture. In this case, nitrites as low as 1 mg/L will react quickly with the added iodide, liberating free iodine.

The preferred procedure, which shows little interference from nitrites, is the back titration at pH 4 using standard iodine titrant. The iodometric procedure in which KI is added first, then buffered, is least affected with increasing amounts of nitrites. The back

*. *EPA Report 600/7-77-053*, U.S. Environmental Protection Agency, 1977.

titration procedure buffered at pH 4 is recommended for the amperometric titration of total chlorine in treated wastewaters, and agricultural and industrial discharges.

1.2.5 Choice of Reductant

In the forward amperometric titration method, use only phenylarsine oxide (PAO) as the titrant when measuring total chlorine. PAO gives a sharper end point than standard thiosulfate at pH 4. This is shown comparatively in *Figure 3 on page 150*. The titration plots compare the titration curves obtained for 82 µg/L monochloramine standard using a continuous addition of standard thiosulfate and standard PAO titrants. The rate at which triiodide is generated with thiosulfate evidently changes as the end point is approached. This leads to uncertainty when determining the end point graphically, see (a) in *Figure 3 on page 150*. The use of PAO gives a relatively sharper end point, see (b) in *Figure 3 on page 150*.

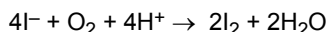
In the case of the amperometric *back* titration method, the addition of excess PAO or thiosulfate is acceptable. The titration end points for both reductants are equivalent when standard iodine is the titrant.

1.3 Errors Common to Total Chlorine Determinations

Most of the common total chlorine methods are based on the oxidation of iodide to triiodide (I_3^-) ion. Several sources of errors related to the iodide/triiodide reaction are discussed here:

- oxidation of the iodide (I^-) reagent
- volatilization of elemental iodine
- iodine or iodate (IO_3^-) contamination in the iodide reagent
- consumption of triiodide by sample components

Potassium iodide reagent may be oxidized by the following reaction:



The reaction is accelerated by low pH, light, and trace metal ions. Iodide reagent solutions are quite susceptible to oxidation from exposure to light and oxygen.

Work conducted at the Electric Power Research Institute (EPRI)* indicates that oxidants equivalent to 1 mg/L chlorine can be generated in one day in a 0.1 M KI stock solution.

Potassium iodide purity is critical in trace total chlorine determinations. The iodide should be free of iodine or iodate which can react directly with chlorine or chloramines in the sample. Even solid potassium iodide can be oxidized with enough exposure to oxygen and ultraviolet light. Hach controls its KI reagent for iodine and trace oxidant contamination before packaging.

Volatilization of free iodine from the reaction of oxidant with iodide is decreased somewhat because excess iodide is present in the sample. Excess iodide causes formation of the less volatile triiodide species. EPRI† reported the error due to iodine volatilization is probably a small percent. Quick analysis will also minimize iodine loss by volatilization.

Adsorption of the produced iodine on suspended particles can be a serious problem in the case of muddy or highly organic-rich waters. A good example is the blue complex formed between I_2 and starch, which is the visual indicator for the starch iodine test. In

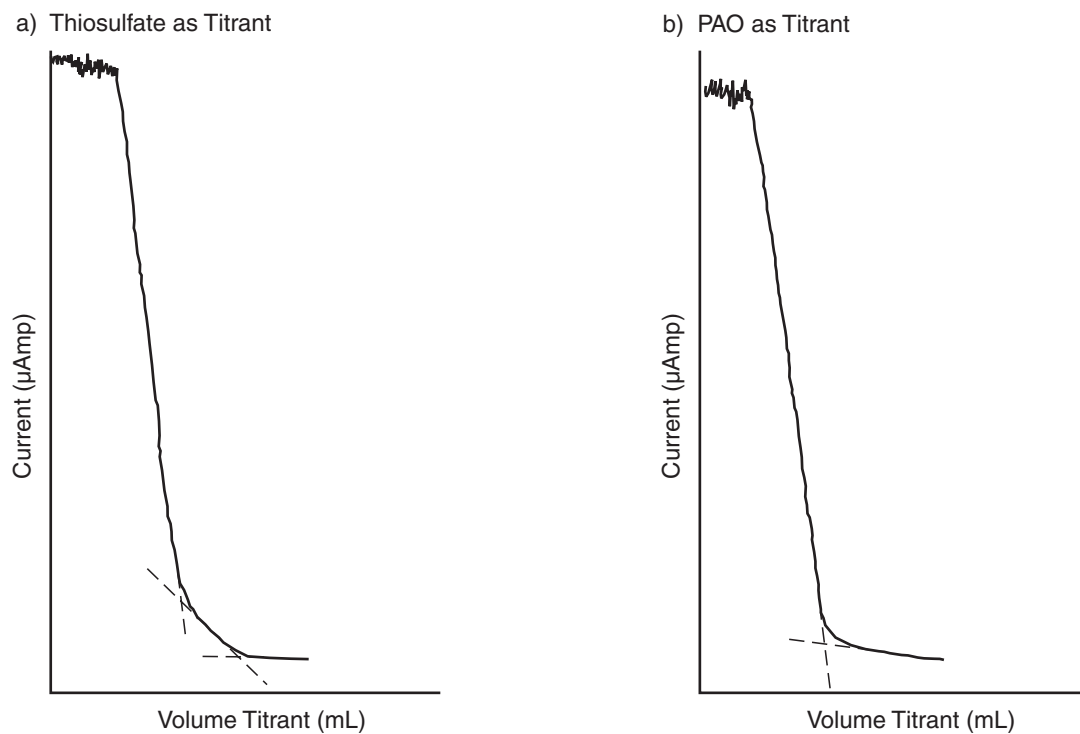
*. EPRI Report EA-929, Project 879-1, October 1978.

†. EPRI Report EA-929, Project 879-1, October 1978.

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addition to adsorption, iodine can react with organic matter, forming carbon-iodine bonds. This is one reason for the traditional preference of the back titration methods for total chlorine in sewage treatment plant effluents.

Figure 3 Titration Curves Using Thiosulfate vs. PAO Titrants



1.4 Shift of Endpoints Due to Sample Iodine Demand

Certain organic compounds exert an “iodine demand” which shifts the titration end point, even if the back titration procedure is used. An example of this effect is shown in *Figure 4*. If the sample contains suspended particles, generated iodine readily adsorbs into the particles, shifting the measured current readings. In addition to adsorption, iodine can react with dissolved organic matter in the sample.

For samples with a high iodine demand, it may be difficult to determine the end point. Continuing the titration past the end point helps determine the end point more accurately. Also, a rapid titration will minimize iodine demand. Sample dilution with chlorine demand-free water also minimizes iodine demand, although this may cause chlorine loss and decreases sensitivity.

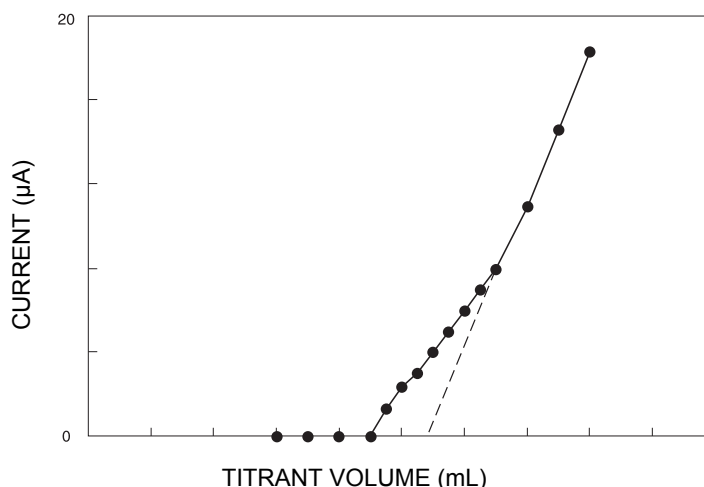
1.5 Order of Reagent Addition

Measuring chlorine in saline, estuary, or seawater is very difficult with any of the available methods. The literature concerning the amperometric determination of total chlorine in salt water is somewhat confusing. Several studies indicate the order of reagent addition (KI and buffer) may underestimate the total chlorine concentration when determined amperometrically.

The chemistry of chlorine in sea water is extremely complex. Saline waters usually contain an appreciable chlorine demand, due in part to oxidation of carbon and nitrogen-containing compounds. Bromide, usually present in seawater, oxidizes to bromine when chlorine is added. Also, the concentration of chlorine-containing and secondary oxidants produced by chlorination depends on the characteristics of the water being chlorinated. Salinity, organic load, water temperature, and incident sunlight influence the level of chlorine-containing compounds and oxidants.

There is general agreement that in the amperometric determination for total chlorine in saline waters, iodide reagent should be added before, or simultaneously with, the pH 4 buffer. If the saline sample is buffered prior to addition of the iodide, the total oxidant concentration may be underestimated.

Figure 4 Iodine Demand (back titration curve)



Appendix B Printer Installation and Setup

The AutoCAT 9000™ can be connected to an optional printer to generate analysis reports. Supervisor-level access is required to modify these parameters (see *Entering the Supervisor Code* on page 27).

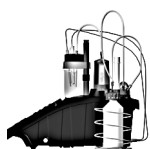
The Kyoline printer requires the correct switch orientation. The printer has 8 DIP switches located under the paper roll. To access the switches, remove the top cover and the paper roll. Use an object with a fine point (e.g., a ball-point pen) to set the switches.

Switch	1	2	3	4	5	6	7	8
Setting	ON	ON	OFF	OFF	ON	OFF	ON	OFF

Insert the round 6-pin plug (index arrow on top) into the back of the printer. Insert the other end of the printer cable into the serial PC/Printer port located on the back panel of the AutoCAT 9000 (see *Figure 3* on page 19). Plug one end of the printer power adapter into a 110-V ac outlet and the other end to the printer.

Note: The AutoCAT 9000 must be in operation before the printer is connected and turned ON in order for the software to detect the printer.

The Titrants menu and Methods menu have identical printer set ups. The following software setup uses the Methods menu as an example.

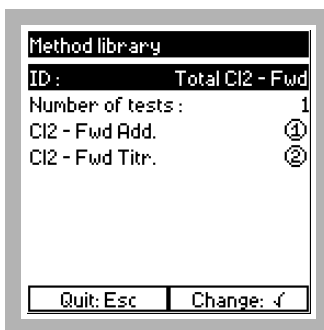


Software Setup

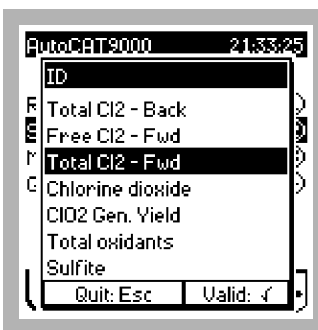
Method Parameters



1. From the Methods menu, press **3** to select Method Library.

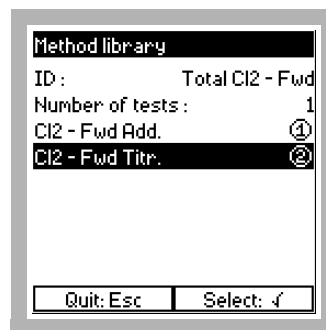


2. Highlight ID.
Press the **CHECK MARK** to validate.



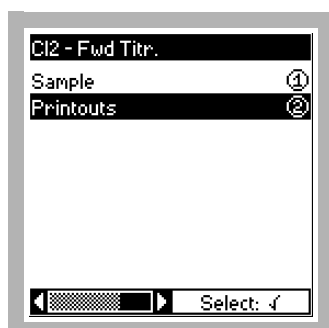
3. Highlight the desired method.
Press the **CHECK MARK** to validate.

Note: Total Cl2 - Fwd is chosen for demonstration purposes only. The printer parameters are identical for all embedded methods.

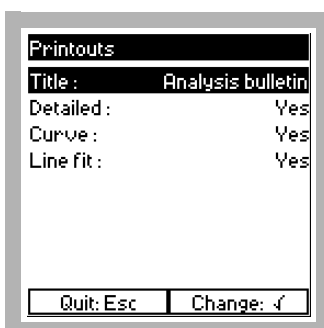


4. Press **2** to select Cl2 - Fwd Titr.

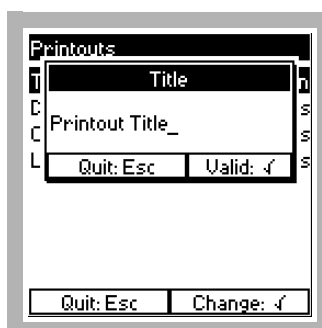
Printer Installation and Setup



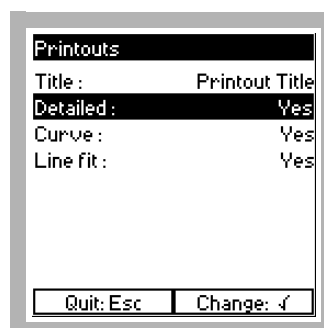
5. Scroll through the method parameters. Press **2** to select Printouts.



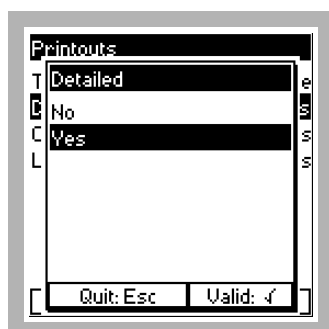
6. Highlight Title.
Press the **CHECK MARK** to change.



7. Use the keypad to enter a printout title.
Press the **CHECK MARK** to validate.

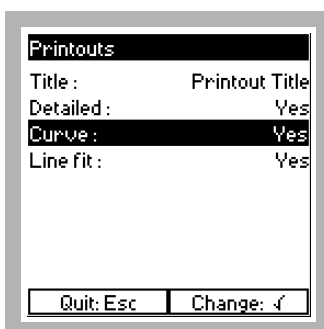


8. Highlight Detailed.
Press the **CHECK MARK** to change.

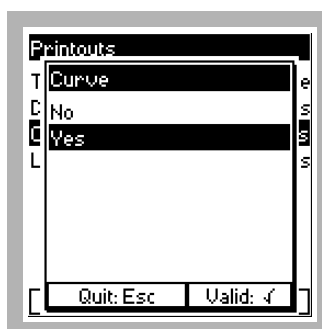


9. Enable or Disable Detail.
Press the **CHECK MARK** to validate.

Note: If Detailed is enabled, the printout will include the titrant certificate number, concentration and install date, and the electrode used.

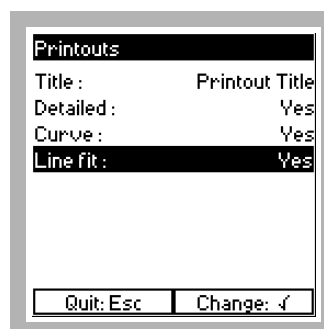


10. Highlight Curve.
Press the **CHECK MARK** to change.

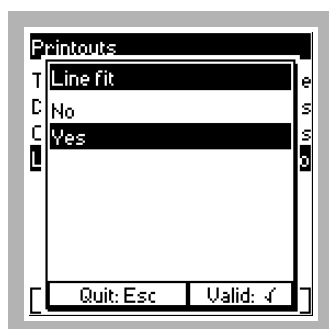


11. Enable or Disable Curve.
Press the **CHECK MARK** to validate.

Note: If Curve is enabled the the calibration curve will printout. The Curve option can also customize the Line fit.



12. Highlight Line Fit.
Press the **CHECK MARK** to change.

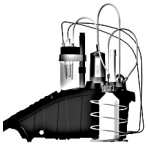


13. Enable or Disable Line Fit.
Press the **CHECK MARK** to validate.

Note: If Line Fit is enabled, the printout will plot the line that was fit to the analysis curve.



14. Press **ESC** three times to return to the Methods menu.



Software Setup

Sample Printout

Hach Company		15 Aug 2002 - 00:04:04	
PO BOX 389		AutoCAT9000 - 689R002N002	
Loveland CO 80539			
1-800-227-4224		Printout Title : Total Cl2 - Fwd	
Sample ID : Sample for Print			
Titrant	: PAO 5.64mN	Certificate no.	:
Titrant conc.	: 5.640e+00 meq/L	Entered the	: 26 Jul 2002
Electrode	: 50086-00	DETAIL	
Test no. 1 : 200.0 mL			
Cl2 - Fwd Titr.			
RESULT		Time : 00h19	Duration : 07min16s
Temperature	: 24.2 °C		
Total Cl2	: 2.514 mg/L	(2.515 mL)	OK
Result accepted			

Hach Company

www.hach.com

Appendix C Replacement Parts & Accessories

Replacement Parts

Burette, 5-mL replacement, with protective UV plastic housing, see <i>Figure 1</i> on page 13, item 6	50082-10
Delivery tubing for titrant, stopcock to sample, without anti-diffusion tip, see <i>Figure 1</i> on page 13, item 2	A25B630
Delivery tubing for titrant, stopcock to sample, with anti-diffusion tip, see <i>Figure 1</i> on page 13, item 2	50082-40
Electrode, dual platinum, see <i>Figure 1</i> on page 13, item 5	50086-00
Magnetic stir bar, see <i>Figure 1</i> on page 13, item 8	50085-00
Tubing for titrant, stopcock to burette, see <i>Figure 1</i> on page 13, item 16	A25B600
Temperature Probe, see <i>Figure 1</i> on page 13, item 4	50087-00

Accessories

Kyoline thermal printer with cable, 115 V ac	A70P021
Kyoline thermal printer with cable, 230 V ac	A70P020
Kyoline thermal paper, 10 rolls/pkg	A70P025
RS232 PC interface cable	A95X501

Appendix D Low Level Standards & Testing

The analysis of standard solutions for method verification is an essential part of maintaining a thorough laboratory QA/QC program. Analyzing standards ensures accuracy, maintains consistent performance, and provides documented proof of results. In many cases, verification of a method will be performed by analyzing a standard at a similar concentration to that of a typical sample. However, such a procedure is not always feasible in every situation. One particular situation in which preparing a standard at typical sample concentrations is not feasible is in the case of low range chlorine analysis. Preparing an accurate low-level chlorine standard is difficult, as there are multiple potential sources of error that can affect standard accuracy.

For verification of low range chlorine analysis, Hach recommends the preparation of chlorine standard solutions at concentrations no lower than 0.10 mg/L. Preparation of chlorine standard solutions at lower concentrations is not recommended for method verification.

It is important to understand the practical limitations of preparing a low-level chlorine standard. Some of the potential error sources in the preparation of a low concentration chlorine standard solution include:

- 1. Dilution Water** - The dilution water used to prepare a chlorine standard must be chlorine-demand free. For accurate results, the water used to prepare a chlorine dilution should be 18 megohm, organic free (< 20 g/L of total organic carbon), amine free, and sterile (this can be achieved by filtration through a 0.2 µm filter). Dilution water may also be tested for chlorine demand by following the procedure indicated in Standard Methods for the Examination of Water and Wastewater 2350B.
- 2. Atmospheric Exposure** - To avoid oxidation and loss of chlorine, low-level chlorine standards must be prepared under a high-purity inert gas headspace. Nitrogen and argon are acceptable gasses to use in this application. Contact with atmospheric gasses, ammonia vapors, and exposure to ambient light must be avoided.
- 3. Containers** - The containers in which chlorine standards are prepared and handled will affect accuracy. It is important that all containers be chlorine-demand free. Plastic containers should be avoided, as they can leach organics into water and be a source of chlorine demand. Glass, Teflon, and PET are preferred materials for wetted parts of the system. All parts should be pretreated for chlorine demand by soaking in a dilute bleach solution (5 drops of commercial bleach per liter of water) followed by rinsing with copious amounts of chlorine-demand-free deionized water. Amber glass containers should be avoided.
- 4. pH** - The pH of the solution also affects the stability of a prepared chlorine standard solution. Chlorine is more stable as hypochlorite ion (at pH > 9) than as hypochlorous acid. The pH of chlorine standard solutions prepared in deionized water is typically < 9, meaning that the prepared standard solution is unstable and must be prepared immediately prior to analysis.
- 5. Equivalent Standards** - With the many potential sources of error in the preparation of chlorine standard solutions, it may be tempting to prepare a chlorine equivalent standard from potassium permanganate. However, the use of permanganate standards for chlorine verification is not recommended. Although permanganate is an oxidant, permanganate standards will not necessarily produce equivalent results with DPD or amperometric methods. Dilute permanganate standards are also very unstable and must be prepared immediately before use. Finally, the cleanliness of glassware and dilution water used in the preparation of permanganate standards is critical to accuracy.

In order to assess the accuracy of a chlorine analysis method, such as DPD, Hach recommends the preparation of a chlorine standard solution at a concentration greater than 0.10 mg/L. The actual concentration of the prepared standard must be verified, because the many potential error sources mean that the actual concentration of the standard solution may not match the theoretical calculated concentration of the standard.

Also, because a chlorine standard solution is not prepared from a primary standard, the actual concentration of the prepared chlorine standard used for verification should be determined through a separate reference method, such as amperometric titration. Amperometric titration is a method that is traceable to a primary standard. The PAO titrant is traceable to arsenic trioxide, a primary standard. Standardization of PAO versus arsenic trioxide can be performed using the AutoCAT 9000 amperometric titrator. A certificate of analysis for the PAO titrant is also available for download from www.hach.com.

Additionally, the calibration curves for colorimetric chlorine analyses that are programmed into Hach colorimeters and spectrophotometers are the result of multiple standards (referenced to amperometric titration) analyzed with multiple lots of reagent. Verification of the method with chlorine standards is recommended—however adjustment of the existing calibration curve or recalibration of the instrument is advised against.

Verification can be performed by preparing a chlorine standard solution or through standard additions (sample spike). Procedures for standard additions can be found in the "Accuracy Check, Standard Additions Method" section of any Hach procedure or in the Hach Water Analysis Handbook. Many Hach spectrophotometers will automatically calculate and graph standard additions, as well. It is suggested that chlorinated wastewater or tap water be dechlorinated using UV prior to the addition of a chlorine spike.

For any questions or concerns regarding the preparation of chlorine standard solutions for method verification, please contact Hach Technical Support at 1-800-227-4224 or email techhelp@hach.com.

Appendix E AutoCAT 9000 Validation Study

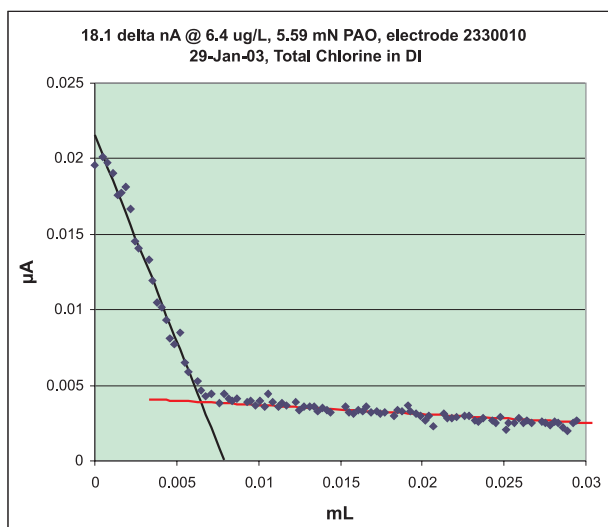
An AutoCAT 9000 chlorine amperometric autotitrator was tested in a validation study to see whether the instrument could in fact routinely measure chlorine concentrations in the low ppb ($\mu\text{g/L}$) range, according to Standard Method 4500 Cl D.

The instrument was a production unit without modification. All glassware used was pretreated for chlorine demand. Reagent grade, organic free, deionized water ($> 18 \text{ Mohm}$) was used in the preparation of standard solutions. Chlorine standards were prepared from stock solutions that were kept under a high-purity nitrogen headspace blanket, under positive pressure, and diluted with reagent grade water using Class A volumetric pipettes for samples. The PAO titrant was standardized prior to the tests. In these low $\mu\text{g/L}$ tests, the smallest volume increment was selected, $0.3\mu\text{L}$, for titrant delivery.

Data from the instrument was output through an RS232 serial port, pairing dispensed titrant volume with current output. Endpoint determination and results calculation were performed on the instrument using the instrument's embedded endpoint determination algorithm and embedded equations. Additionally, these data pairs were then imported into a spreadsheet program for graphing and analysis, to validate the instrument calculated results. A representative titration curve, from data imported into the spreadsheet program and graphed, is shown in *Figure 1*.

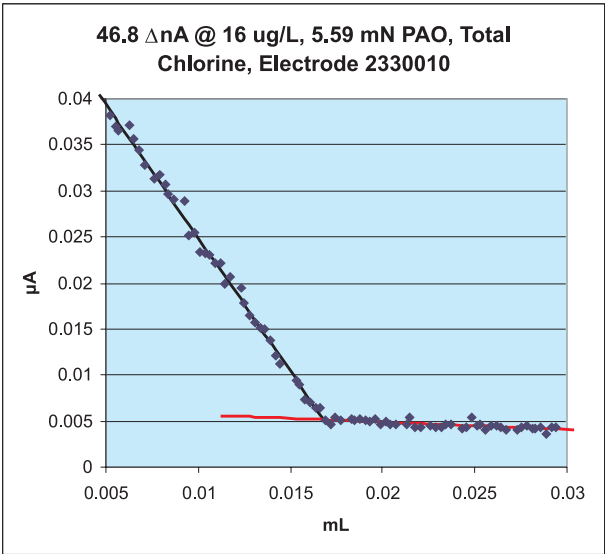
Linear regression analysis was conducted on the data segments prior to, and after the 'dead-stop' endpoint, with the intersection of these line-fits used to calculate the endpoint, in μL of titrant; the sample volume and titrant normality were then used with this endpoint volume to calculate a chlorine concentration of $6.4 \mu\text{g/L}$. The r^2 correlation coefficient was found to be 0.973 prior to the endpoint, and 0.840 after the endpoint, with a signal to noise ratio of approximately 25:1. The instrument itself showed a calculated result of $6.3 \mu\text{g/L}$, using the embedded endpoint determination and results calculation routines.

Figure 1 Titration Curve— $6.4 \mu\text{g/L}$ Chlorine



A comparison graph at a chlorine concentration of 16 µL Cl₂ is shown in *Figure 2*.

Figure 2 Titration Curve—16 µg/L Chlorine



Spreadsheet analysis of the data pairs, utilizing linear regressions of the line segments prior to and after the endpoint, and results calculation, resulted in equivalent results to those displayed on the instrument, again with excellent correlation and signal to noise.

MDL, Accuracy, and Precision Determination

After these trials were concluded, demonstrating the instrument capability to measure low µg/L chlorine concentrations, per Standard Method 4500 Cl D, experiments were conducted to determine the Method Detection Limit (MDL), according to 40 CFR Part 136, Appendix B.

This MDL calculation involves replicate analyses, where the sample concentration must be within the range 1 to 5 times the calculated MDL. The MDL is calculated as the Student's t value (at the 99% confidence interval), times the standard deviation. For seven replicates, the Student's t value (at the 99% confidence interval) is 3.143.

The experimental conditions, and apparatus for this series of experiments was the same as for the screening studies described above. Great care was observed during the required sample manipulations to minimize experimental error.

Seven replicate measurements were initially run, at a sample chlorine concentration of 6.5 µg/L. An analysis of the standard deviation resulting from these trials determined that the sample concentration was too high, outside the range 1 to 5 times the calculated MDL. A second set of seven replicate measurements was then conducted on a chlorine sample concentration of 4.1 µg/L. An analysis of the calculated MDL from this series of trials showed that the sample concentration was within the stipulated range.

The resulting MDL, in accordance with 40 CFR, Part 136, Appendix B, was thus determined to be 1.2 µg/L using this instrument. A summary of these trials can be seen in *Table 1*.

Table 1 Method Detection Limit

Method	Standard	Standard Deviation	Student t	Calculated MDL
4500 Cl D	6.5 µg/L	±0.40 µg/L	3.143	1.3 µg/L
4500 Cl D	4.1 µg/L	±0.37 µg/L	3.143	1.2 µg/L

For low-range determination of total chlorine, the instrument thus appears to be suitable for facilities that are required to meet NPDES discharge limits, in the low µg/L range, as determined by 40 CFR, Part 136, Appendix B.

A proposed revision to this statute was published in March 2003. This Proposed Rule is written with more specific language covering the determination of the Minimum Level of Quantitation (ML), in addition to the method detection limit (MDL). Applying this calculation to the instrument MDL of 1.2 µg/L, the ML for this instrument is determined to be 3.8 µg/L, based on the seven replicates tested.*

Many facilities have budget constraints, and would prefer that instrumentation cover not only very low concentration ranges, but additionally are suited for higher concentration range determinations, at the various points of process that require mg/L concentrations of disinfectant for the control of biological growth. Using the same normality of titrant, the test instrument is capable of measuring chlorine concentrations of up to 5 mg/L. Additionally, the instrument will automatically correct for sample dilutions, enabling determinations above this stated range.

An assessment of the instrument was conducted in drinking water and municipal wastewater discharge waters. The percent recoveries for the various amperometric titration methods, in these sample matrices, are summarized in *Table 2*.

Table 2 Percent Recovery in Drinking Water and Wastewater

Method	Sample Type	Spike Level, mg/L Cl ₂	Average % Recovery	% Recovery Range
Free Chlorine	Drinking Water	Free Cl ₂ at 0.060 mg/L	92.6 (n=4)	87.5—98.0
		at 0.220 mg/L	89.7 (n=6)	89.2—92.7
		at 0.530 mg/L	91.0 (n=4)	85.4—93.5
Total Chlorine Forward	Drinking Water	Free Cl ₂ at 0.196 mg/L	101.2 (n=4)	100.3—101.9
		at 0.391 mg/L	99.8 (n=4)	99.0—100.4
		NH ₂ Cl at 0.196 mg/L	93.4(n=4)	93.0—93.9
		at 0.391 mg/L	93.5 (n=3)	93.0—94.0
	Denitrified WasteWater Effluent (Source #1)	NH ₂ Cl at 0.489 mg/L	87.3 (n=6)	82.2—90.7
		at 0.975 mg/L		
		at 1.459 mg/L		
	Denitrified WasteWater Effluent (Source #2)	NH ₂ Cl at 0.489 mg/L	93.6 (n=6)	88.8—95.8
		at 0.975 mg/L		
		at 1.459 mg/L		

*.US EPA, 40CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Procedures for Detection and Quantitation", RIN 2040-AD53, Federal Register, Vol. 68, No. 48, Proposed Rules, March 12, 2003.

Table 2 Percent Recovery in Drinking Water and Wastewater (continued)

Method	Sample Type	Spike Level, mg/L Cl ₂	Average % Recovery	% Recovery Range
Total Chlorine Back	Drinking Water	Free Cl ₂ at 0.465 mg/L	97.3 (n=4)	95.8—99.1
	Denitrified WasteWater Effluent (Source #1)	NH ₂ Cl at 0.423 mg/L	87.23 (n=4)	73.5—94.8
		at 0.844 mg/L	93.09 (n=3)	91.8—93.8
		at 1.262 mg/L	88.56 (n=3)	85.3—91.9
	Denitrified WasteWater Effluent (Source #2)	NH ₂ Cl at 0.423 mg/L	92.59 (n=3)	88.9—97.2
		at 0.844 mg/L	98.06 (n=3)	96.8—98.8
		at 1.262 mg/L	95.01 (n=3)	89.9—98.0

Testing was also conducted to determine the precision of these methods at a variety of concentrations. The results of these studies are shown in *Table 3*, and represent the variability of results from seven replicate analyses, covering the 0–5 mg/L measurement range, at the 95% confidence interval.

Table 3 Precision

Method	Concentration (mg/L Cl ₂)	95% Confidence Limits (mg/L Cl ₂)
Free Chlorine	0.277	0.251–0.303
	1.924	1.778–2.070
	4.942	4.650–5.234
Total Chlorine Forward Titration	0.0090	0.0084–0.0096
	0.423	0.413–0.433
	4.241	4.165–4.317
Total Chlorine Back Titration	0.023	0.020–0.026
	0.398	0.370–0.426
	1.313	1.287–1.339
	4.751	4.689–4.813

Analysis Guidelines

When using an autotitrator for amperometric determinations of chlorine at the various concentrations typically found in power plants, including low µg/L concentrations in the final discharge waters and post dechlorination upstream of RO systems, in addition to the higher mg/L concentrations required for cooling water biofouling control, it is important that the operator have dedicated glassware for each sampling point in order to prevent sample carryover, which could otherwise result in falsely high readings where low concentration determinations are required.

Accuracy in measuring the sample volume will be facilitated by the use of 200-mL Kohlrausch Class A volumetric flasks. Originally developed for the determination of sugar content in sugar beets, these volumetric flasks differ from standard volumetric flasks in that they have a wide mouth, which makes it easier to transfer samples quickly to the titration beaker, without excessive chlorine loss. The sample volume accuracy achieved by using the Kohlrausch flask is much better than that achieved by using a graduated cylinder.

Electrode fouling can occur, especially when amperometric titration is conducted in wastewater effluent. In amperometric titrators that employ a single platinum electrode in conjunction with a reference electrode, it is important not only that the platinum

electrode is clean, but also that the reference electrode has sufficient electrolyte, and that the reference junction is not fouled. In titrators that employ dual platinum pins, without a reference electrode (a biamperometric system), there is no reference electrode to maintain. The instrument tested utilizes the biamperometric system, and the polarity of the potential is reversed with each subsequent titration, to automatically strip any anodic or cathodic electrochemical depositions. Additionally, the instrument has a built-in electrode cleaning method, which should be performed periodically, to assure optimum performance.

Proper storage and standardization of titrants is an important consideration. Phenylarsine oxide (PAO) is very stable, with a shelf life of over 1 year. This titrant can be standardized when used, or the certificate of analysis can be obtained for the titrant lot in use. When performing back titration, per Standard Method 4500 Cl C, 28.2 mN iodine titrant is used. This titrant is much less stable than PAO, and thus titrant standardizations with sodium arsenite or PAO should be conducted more frequently.

Manually added sample conditioning reagents, potassium iodide (KI), acetate pH 4 buffer, and phosphate pH 7 buffer, should also be of known purity. The pH 7 phosphate buffer, used for free chlorine determinations, is a growth medium for micro-organisms: these microbes have chlorine demand, and thus can result in false negative values, errors that can be significant during low $\mu\text{g/L}$ chlorine determinations. A formulated powder of the pH 7 buffer, available in single unit-doses for the 200 mL sample, is a preferred alternative for low-level measurements. When KI solutions are used instead of the direct addition of KI powder, care must be taken to prevent conversion of the KI in solution to iodine, otherwise false positive results can be obtained, which again can be significant sources of error in low $\mu\text{g/L}$ determinations. Factors that catalyze conversion of KI to iodine include sunlight, iron present as a colorant in amber glass bottles, and the possible uptake of chlorine from the atmosphere in areas where high concentrations of chlorine are found. The pH 4 acetate buffer does not promote microbial contamination, and is very stable.

Familiarization of operators with the instrument is essential for accurate and reproducible chlorine measurements. Even though guided through the proper method sequence, there are instrument settings that are appropriate for optimization of the instrument for chlorine measurement at specific points of process. Whenever possible, senior operators, or laboratory analytical staff with experience in instrumental quantitative analysis, should work to reduce instrument operation to easily followed Standard Operating Procedures (SOPs), which can then be located at the measurement station. Consultations with the manufacturer's technical support staff may be required to fully integrate the autotitrator into the daily operator routine.

Conducting MDL and Proficiency Trials

When conducting internal MDL and operator proficiency trials, it is extremely important that proper sample preparation procedures and analytical controls are in place: without proper analytical procedures, there is a high probability that the variability of sample standard preparation will be determined, instead of a determination of the method detection limit, or staff proficiency in running the instrument.

Preparation of standards in the low end of the part per billion range is non-trivial: one part per billion is equivalent to one penny in ten million dollars; one foot in a journey to the moon; one second, in thirty two years. The preparation of these standards is even more difficult for chlorine, which is highly reactive, and quite volatile. Through proper training however, scrupulous attention to detail, appropriate volumetric ware and

laboratory technique, preparation of chlorine standards in the low parts per billion range can be achieved.

A distinction must be made regarding skill levels required to run the autotitrator to obtain accurate and reproducible trace chlorine measurements, versus the skill level required to accurately conduct MDL studies. For routine measurements, the operator must be able to properly measure a 200-mL sample, observing correct sample handling techniques, follow SOPs, and the menu-driven steps of instrument operation. Conducting valid MDL studies however requires great care in conducting serial dilutions, scrupulous attention to detail and accuracy during the multi-step standard preparation process. These analyses require proper equipment, an environment free of airborne chlorine, and very careful sample manipulation to assure reproducible replicate sample concentrations and sample volumes.

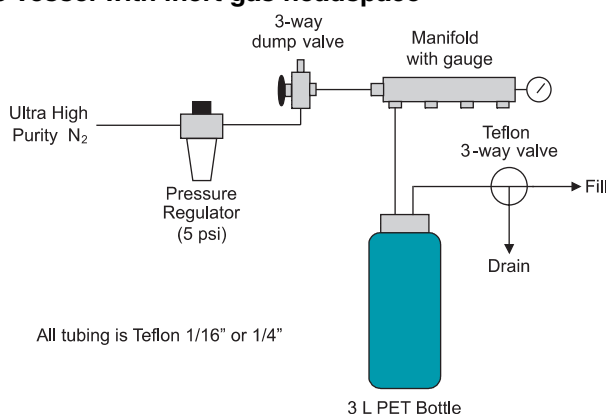
General considerations:

1. Use organic-free 18.2 Mohm water.
2. All apparatus must be PET, Teflon, or glass.
3. Do not use amber glass.
4. Pre-treat all apparatus for chlorine demand.
5. Thoroughly rinse all apparatus after pre-treatment.
6. Use ultra-high purity nitrogen to pressurize bulk standard container to 5 psi.
7. Carefully fill volumetric ware and transfer without agitation.
8. Immediately analyze each 200-mL aliquot.

The schematic in *Table 3* shows a setup for maintaining a 3-Liter reservoir of chlorine standard solution under positive pressure inert gas headships. The constant 5-psi nitrogen pressure in the reservoir headspace helps to maintain the chlorine standard at a constant concentration.

Chlorine standard solutions, in sealed ampoules, with certificates of analysis, in the range 25-75 mg/L are available. Dilution of aliquots of these standards in 1 to 3 liters of reagent grade water will result in a stock solution at concentrations in the 1 to 2 mg/L range, which will be stable for a period of days, if kept in a pre-treated sealed vessel, under positive pressure inert gas. Spiking reagent grade water with this stock solution will result in replicate 200-mL sample aliquots that will be consistent during the MDL studies.

Figure 3 Setup for chlorine vessel with inert gas headspace





Be Right

General Information

At Hach Company, customer service is an important part of every product we make. With that in mind, we have compiled the following information for your convenience.

Hach Company certifies this instrument was tested thoroughly, inspected and found to meet its published specifications when it was shipped from the factory. The AutoCAT 9000 titration workstation has been tested and is certified as indicated to the following instrumentation standards:

Product Safety

UL 61010A-1 (ETLus listing mark)

CSA C22.2 No. 1010.1 (ETLc certification mark)

Certified by Hach to EN 61010-1 Amd.'s 1 & 2 per 73/23/EEC, supporting test records with APAVE, report No. 20111436.

Immunity

EN 61326:98 (EMC Requirements for equipment for measurement, control and laboratory use) per 89/336/EEC EMC: Supporting test records by Hach Company, certified compliance by Hach Company.

Standards include:

EN 61000-4-2 (IEC 1000-4-2) Electro-Static Discharge

EN 61000-4-3 (IEC 1000-4-3) Radiated RF Electro-Magnetic Fields

EN 61000-4-4 (IEC 1000-4-4) Electrical Fast Transients/Burst

EN 61000-4-5 (IEC 1000-4-5) Surge

EN 61000-4-6 (IEC 1000-4-6) Conducted Disturbances Induced by RF Fields

EN 61000-4-11 (IEC 1000-4-11) Voltage Dips, Interruptions and Variations

Emissions

Per 89/336/EEC EMC: EN 61326:1998 (Electrical Equipment for measurement, control and laboratory use-EMC requirements) Class "B" emission limits. Supporting test records by Intellistor O.A.T.S. (NVLAP # 0369) and certified compliance by Hach Company.

Standards include:

EN 61000-3-2 Harmonic Disturbances Caused by Electrical Equipment

EN 61000-3-3 Voltage Fluctuation (Flicker) Disturbances Caused by Electrical Equipment

Additional Emissions Standard/s include:

EN 55011 (CISPR 11), Class "A" emission limits. Supporting test records with AEMC Measures (CB # 1-0543) report No. L01033.

CANADIAN INTERFERENCE-CAUSING EQUIPMENT REGULATION, IECS-003, Class A: Supporting test records with AEMC Measures (CB # 1-0543) report No. L01033, certified compliance by Hach Company.

This Class A digital apparatus meets all requirements of the Canadian Interference- Causing Equipment Regulations.

Cet appareil numérique de la classe A respecte toutes les exigences du Règlement sur le matériel brouilleur du Canada.

FCC PART 15, Class “A” Limits: Supporting test records with AEMC Mesures (CB # 1-0543) report No. L01033, certified compliance by Hach Company.

This device complies with Part 15 of the FCC Rules. Operation is subject to the following two conditions:

(1) this device may not cause harmful interference, and (2) this device must accept any interference received, including interference that may cause undesired operation.

Changes or modifications to this unit not expressly approved by the party responsible for compliance could void the user's authority to operate the equipment.

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to Part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference, in which case the user will be required to correct the interference at his own expense. The following techniques of reducing the interference problems are applied easily.

1. Disconnect the Model AutoCAT 9000 Titration Work Station from it's power source to verify that it is or is not the source of the interference.
2. If the Model AutoCAT 9000 Titration Work Station is connected into the same outlet as the device with which it is interfering, try another outlet.
3. Move the Model AutoCAT 9000 Titration Work Station away from the device receiving the interference.
4. Reposition the receiving antenna for the device receiving the interference.
5. Try combinations of the above.

How To Order

By Telephone:

6:30 a.m. to 5:00 p.m. MST
Monday through Friday
(800) 227-HACH
(800-227-4224)

By FAX: (970) 669-2932

By Mail:

Hach Company
P.O. Box 389
Loveland, CO 80539-0389
U.S.A.

Ordering information by E-mail: orders@hach.com

Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

Technical and Customer Service (U.S.A. only)

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use. Specialists in analytical methods, they are happy to put their talents to work for you.

Call **1-800-227-4224** or E-mail techhelp@hach.com.

International Customers

Hach maintains a worldwide network of dealers and distributors. To locate the representative nearest you, send E-mail to intl@hach.com or contact:

In Canada, Latin America, Africa, Asia, Pacific Rim:

Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:

HACH Company, c/o
Dr. Bruno Lange GmbH
Willstätterstr. 11
D-40549 Düsseldorf
Germany
Telephone: +49/[0]211.52.88.0
Fax: +49/[0]211.52.88.231

Repair Service

Authorization must be obtained from Hach Company before sending any items for repair.
Please contact the HACH Service Center serving your location.

In the United States:

Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:

Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134
E-mail: canada@hach.com

**In Latin America, the Caribbean, the Far East, the
Indian Subcontinent, Africa, Europe, or the Middle East:**

Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

Hach Company warrants this product to the original purchaser against any defects that are due to faulty material or workmanship for a period of **one year from date of shipment**.

In the event that a defect is discovered during the warranty period, Hach Company agrees that, at its option, it will repair or replace the defective product or refund the purchase price, excluding original shipping and handling charges. Any product repaired or replaced under this warranty will be warranted only for the remainder of the original product warranty period.

This warranty does not apply to consumable products such as chemical reagents; or consumable components of a product, such as, but not limited to, lamps and tubing.

Contact Hach Company or your distributor to initiate warranty support. Products may not be returned without authorization from Hach Company.

Limitations

This warranty does not cover:

- damage caused by acts of God, natural disaster, labor unrest, acts of war (declared or undeclared), terrorism, civil strife or acts of any governmental jurisdiction
- damage caused by misuse, neglect, accident or improper application or installation
- damage caused by any repair or attempted repair not authorized by Hach Company
- any product not used in accordance with the instructions furnished by Hach Company
- freight charges to return merchandise to Hach Company
- freight charges on expedited or express shipment of warranted parts or product
- travel fees associated with on-site warranty repair

This warranty contains the sole express warranty made by Hach Company in connection with its products. All implied warranties, including without limitation, the warranties of merchantability and fitness for a particular purpose, are expressly disclaimed.

Some states within the United States do not allow the disclaimer of implied warranties and if this is true in your state the above limitation may not apply to you. This warranty gives you specific rights, and you may also have other rights that vary from state to state.

This warranty constitutes the final, complete, and exclusive statement of warranty terms and no person is authorized to make any other warranties or representations on behalf of Hach Company.

Limitation of Remedies

The remedies of repair, replacement or refund of purchase price as stated above are the exclusive remedies for the breach of this warranty. On the basis of strict liability or under any other legal theory, in no event shall Hach Company be liable for any incidental or consequential damages of any kind for breach of warranty or negligence.



HACH COMPANY
WORLD HEADQUARTERS
P.O. Box 389
Loveland, Colorado 80539-0389
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FAX: (970) 669-2932

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

In the U.S.A. - **Call toll-free 800-227-4224**

Outside the U.S.A. - **Contact the HACH office or distributor serving you.**

On the Worldwide Web - **www.hach.com**; E-mail - **techhelp@hach.com**
