Chloride by Autotitrator: Quick Start Guide

V1.1 (C. Bennight 10/2/2011; Approved by DJH 10/23/2013)

Introduction

This manual describes the operational methods, standard maintenance, and systems integration of the Metrohm 785 DMP Chloride Autotitration System (***Figure 1***). Methods describes in this manual are based on the Metrohm manual, Metrohm Application Bulletin 130/2 e (*Chloride titrations with potentiometric indication)*, and email correspondence with Gretchen A. Robertson at the Scripps Institution of Oceanography.

This manual covers the USIO standard method for the determination of chloride via potentiometric titration, Variation A – with Nitric Acid.

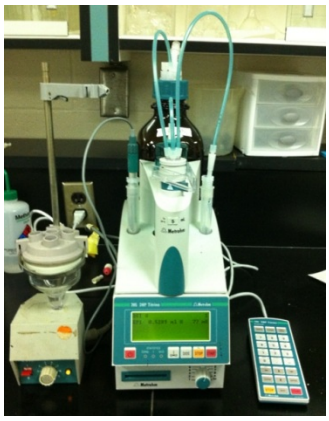

Figure 1. Chloride Autotitration System.

Theory of Operation

The Cl autotitrator uses a potentiometric endpoint to determine the amount of free (unbound) chloride in a solution. A silver nitrate reagent is aliquotted into an unknown solution with some amount of dissolved chloride in solution. As the silver nitrate is added the following reaction occurs.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

The product, AgCl, is insoluble in water and precipitates. A silver-specific electrode in the solution measures a value proportional to the amount of free silver in solution.

As the silver chloride reagent is added, a measurement (in mV) is taken from the silver-specific electrode. If we consider the function of volume added versus the electrode reading and find the volume where the second derivative of the function is 0 (or the inflection point), we have found our equivalence point (***Figure 2***).

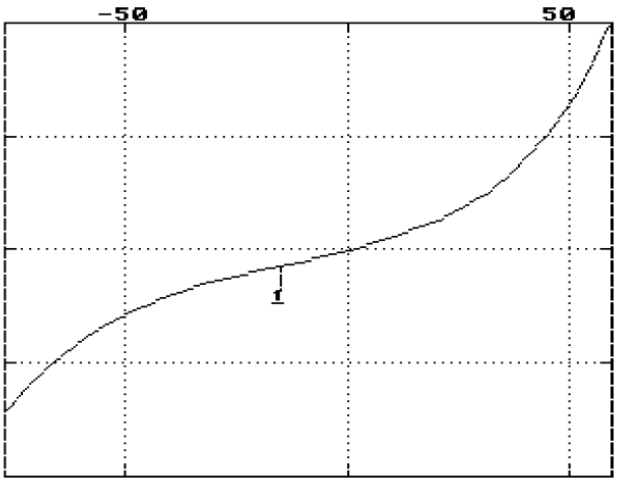

Figure 2. Potentiometric Equivalence Point.

For most purposes, this first equivalence point corresponds to the volume where all free chloride has been converted to AgCl. Knowing the volume of reagent added, the concentration of reagent, and the stoichiometric ratio between reagent and chloride (1:1), we can determine the amount of chloride contained in the solution:

$$[Cl^-] = ([AgCl] \times Volume_{(AgNO3)})/Volume_{(Sample)}$$

(Note: A value in brackets ([]) indicates the concentration of the item enclosed in brackets.)

$Volume_{(AgNO3)}$ is simply the volume of reagent added when the first equivalence point is reached.

Assumptions

It is assumed that the first equivalence point corresponds to that of the AgCl reaction. Silver forms sparingly soluble precipitates with other anions as well as chloride. Solutions with high concentrations of bromide or iodide may cause an erroneous first equivalence point (as they titrate before chloride). In these cases, the method on the instrument will need to be adjusted to run past the first endpoint and to determine the $Volume_{(AgNO3)}$ value. The reagent volumes for the non-chloride endpoints must be subtracted from the reagent volume for the chloride endpoint. It should be fairly obvious which the chloride endpoint is, and chloride will typically be many times more concentrated in situ than other anions.

Apparatus, Reagents, and Materials

Hardware

785 DMP Titrino

The 785 DMP is the primary piece of the instrument. All other components connect to it and it provides the logic and outputs to run the titration (***Figure 3***).

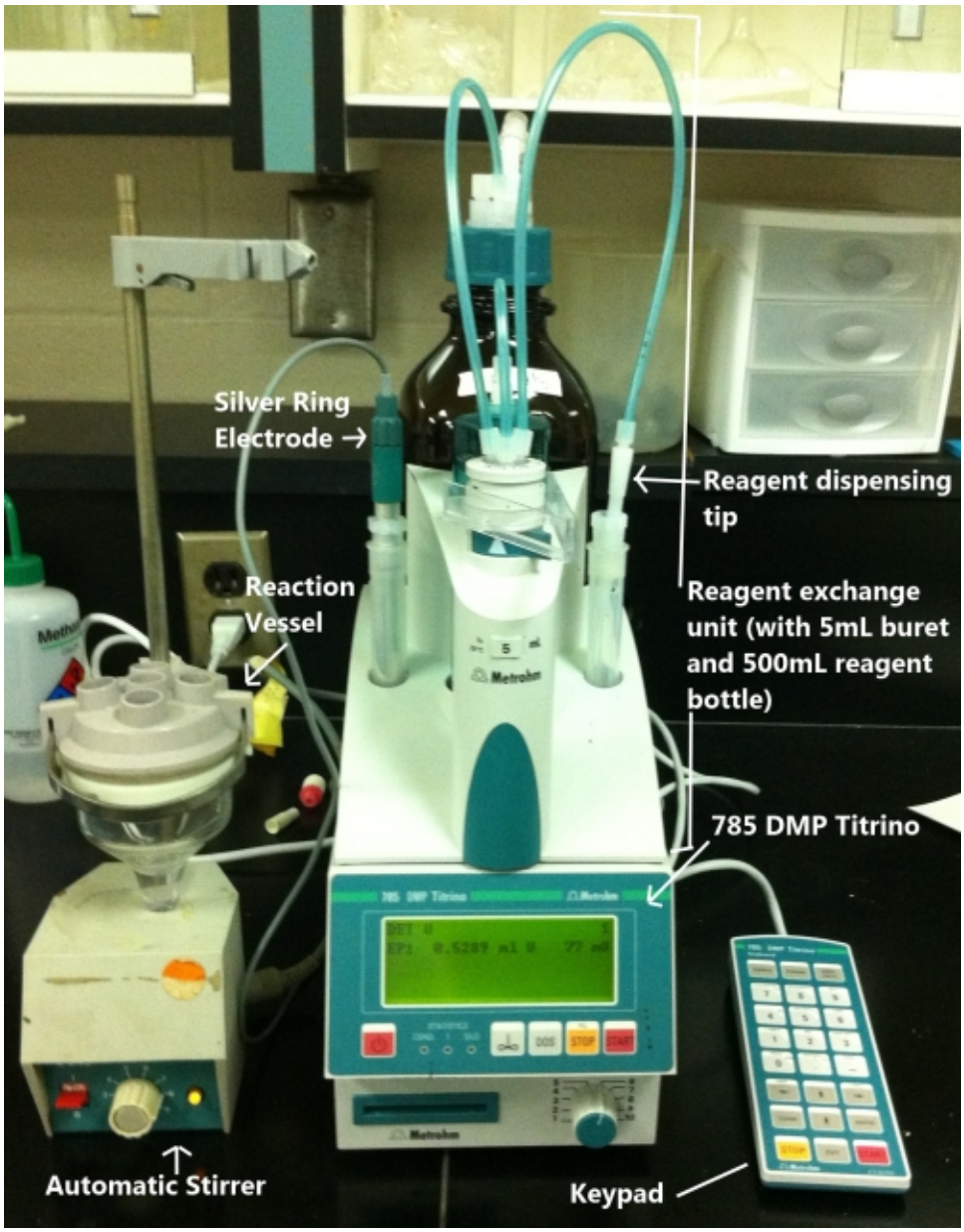

Figure 3. Titrino Autotitrator.

Reagent Exchange Unit

This interchangeable unit contains the following:

–500 mL reagent bottle
–Exchange burette (5 mL)
–Reagent tubing
–Reagent dispensing tip

Titrino Keypad

This auxiliary data entry device can be used to control the Titrino manually. It is not needed for any of the methods described in this manual.

Silver Electrode

Specifically, a Metrohm 6.0430.100, their "Ag Titrode," this electrode combines a standard silver ring electrode with a pH membrane to serve as the reference. It is the only electrode required for this method. It measures the concentration of silver ions in solution.

Automatic Stirrer

This electronic stirrer is controlled by the 785 DMP Titrino. Note that the stir bar will not activate until the titration has started.

Reaction Vessel

This is a non-water-cooled narrow bottom reaction vessel. The electrode and reagent dispensing tip are inserted down into the narrow portion of the vessel to reduce the volume required for the overall reaction.

Reagents

2 M nitric acid solution

Dilute 152 mL of trace-metal grade nitric acid in 1 L of 18 MΩ deionized (DI) water (reagent water). **Note**: Always add acid to water. This reaction can generate heat. Wear gloves and eye protection.

0.10 N silver nitrate solution

Dissolve 1.699 g silver nitrate in 1 L reagent water.

Dilution Solution

To make 500 mL of acid-based dilution solution, add the following to a 500 mL volumetric flask:

Solution	Volume (mL)
18 mΩ DI water (reagent water)	370
0.2 N trace metal grade nitric acid in reagent water	80
0.2% polyvinyl acid (PVA) in reagent water	50

Note: Make this solution fresh for each run (typically keep no longer than 1 day). Adjust proportions of solution to make the desired final volume.

General Equipment Setup and Operation

Setting Up The Instrument

To install the instrument for the first time:

1. Remove the 785 DMP unit from the container, locate the following cords, and plug them into the indicated slot (***Figure 4***):
   –Connection 11: Power cord
   –Connection 9: Silver Titrode cord (connected to titrode)
   –Connection 12: Electronic Stirrer cord (connected to electronic stirrer assembly)
   –Connection 7 (bottom): Serial Cord (straight-through, Female/Female) (A2 on back of device)
   –Connection 10: Keyboard cord (connected to the keyboard device)
2. Connect the other end of the serial cable to the back of the computer host that will control this device.
3. Power on the instrument by pressing the power button on the front panel of the 785 DMP unit.
4. Flip the power switch up on the front of the electronic stirrer (stirring will not start until the run actually begins – controlled by the 785DMP unit).

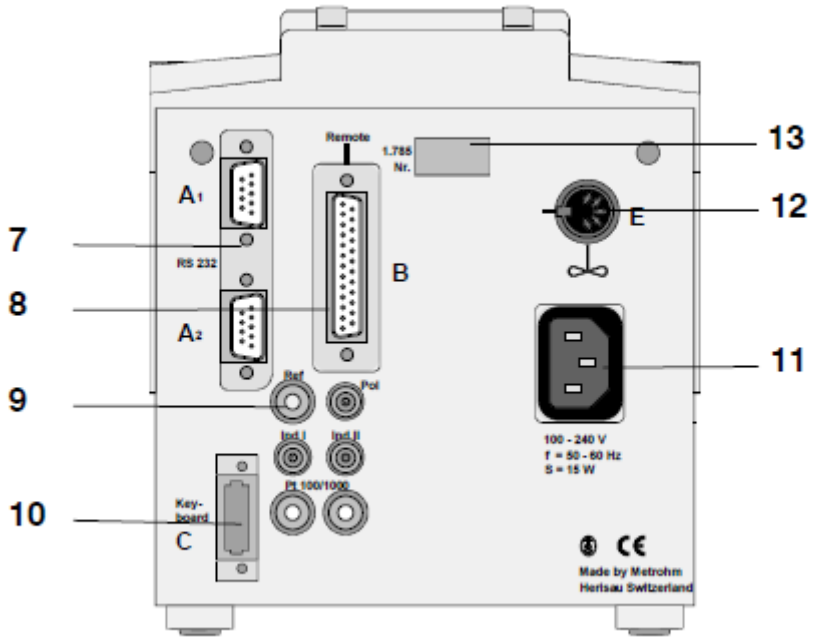

Figure 4. 785DMP Connector Slots.

Operation

Purging the lines

The lines connecting the reagent bottle to the reagent dispensing tip must be purged before analysis can begin. Wear gloves and safety glasses for this operation.

1. Place the acid dispensing tip in a Ziploc bag—but make sure it's not completely air tight.
2. Tap, clamp, or have an individual hold the bag and tip up so it is the highest portion of the system.
3. Turn the dispensing speed knob in the bottom right of the device fully clockwise to its maximum setting (if it isn't there already).
4. Press and hold the **DOS** button on the front of the 785 Titrino. While the unit is dispensing flick the reagent lines with your fingers to dislodge any stuck air bubbles.

   Note that in **DOS** mode you will only be moving fluid (and thus purging) lines between the exchange burette and the reagent dispensing tip.
5. When the burette has exhausted its capacity (5 mL), press the **FIL** button on the front of the 785 Titrino. This will cause the burette to aspirate reagent from the bottle. While this is occurring, flick the exchange lines between the burette and the reagent bottle to dislodge air bubbles.
6. Repeat steps 4 and 5 until no air bubbles are visible in any of the exchange lines.

Shutting down the instrument

1. Rinse the dispensing tip in DI water and store in DI water (add a small amount to the housing in the exchange unit where the tip sits).
2. Rinse the electrode in a 3 M sodium nitrate solution or 2 M nitric acid solution followed by DI water.
3. Store the electrode in 3 M KCl solution (add to the housing in the exchange unit where the electrode sits).

Analyzing Samples

1. Place stir bar in bottom of reaction vessel.
2. Pipette 100 µL of sample into the bottom of the reaction vessel.
3. Pipette 4 mL of dilution solution into the bottom of the reaction vessel.
4. Insert the electrode and reagent dispensing tip into the reaction vessel.
   Note: The bottom of the electrode and reagent tip should be slightly above the stir bar—they should not come into contact with it.
5. Start the software – **ClAutotitrator**.
6. Log in using LIMS username/password.
7. Select the sample to be measured by filling in Expedition, Site-Hole, Sample Name, and Sample (***Figure 5***).
8. Click the **measure** button (***Figure 6***).
9. While the instrument is running, the plot displays the current data set as well as instantaneous values for volume of reagent added, current value, run time, and current titrator status. No interaction is required.
10. When the run is complete a sound will play and a window will pop up telling you that the run is finished (***Figure 7***). Click **Save** to upload the data to LIMS.

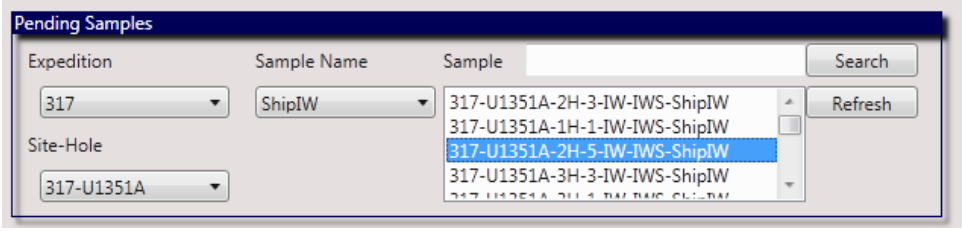

Figure 5. Enter Sample Information.

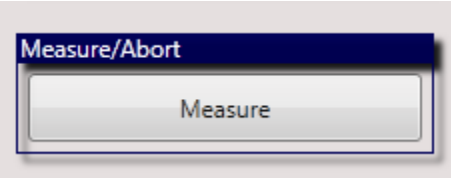

Figure 6. Measure Sample.

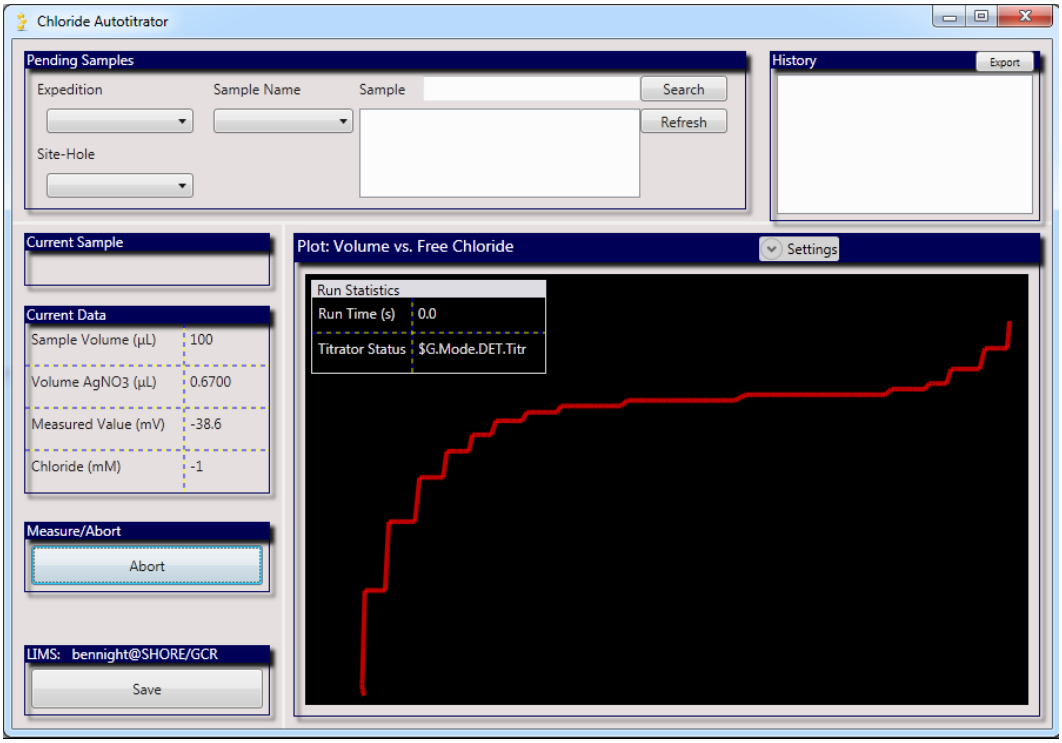

Figure 7. Run Complete.

QAQC

IAPSO is used a standard for this analysis. The certified value, typically ~559 mM, is printed on the outside of each bottle. For quality control purposes, IAPSO shall be run as a sample as follows:

–Before every run

–As the last sample of any run

–Every 5 samples or 2 hours, whichever comes first.

LIMS Integration

–Data for this analysis is stored under analysis **TITRA_MAN**.

–Data are logged against the instrument **TITRINO_785**.

–LIMS component definitions:

Component	Alias	Unit	Description
chloride	Chloride	mM	Concentration of chloride
titrant_amount	Titrant Amount	mL	Amount of titrant added to solution to achieve end point

Health, Safety, and Environment

The primary safety concerns for this instrument and method relate to chemical handling and disposal.

Nitric Acid

2 M nitric acid is required by this method; if it is made in house then, handling of concentrated nitric acid is required. Nitric acid is an oxidizer and should not be brought into contact with any organic materials.

Nitric Acid, Concentrated

–Open and handle concentrated nitric acid in a working fume hood.

–When diluting, always add acid to water.

–Wear gloves and safety glasses at all times when handling concentrated nitric acid.

–Body contact: rinse immediately with copious amounts of water.

–Clothing contact: remove the clothing and rinse with water and/or acid neutralization solution.

–If a spill occurs apply an acid neutralization solution to the spill area.

Nitric Acid, Dilute (2 N)

–Store this solution in the non-organic acid section of a ventilated fume hood storage cabinet.

–This acid can be aliquotted outside of a fume hood.

–Always wear gloves worn when using this solution.

–Neutralize or flush with copious amounts of water for disposal of this solution or waste products.

–Follow the recommendations for the concentrated solution above if contact with skin or clothing.

Silver Nitrate Solution (0.10 N)

The primary hazard from silver nitrate solution is contact with body parts. It forms a silver compound and turns black, staining the skin and other membranes until they are naturally replaced by the body (typically 1–3 weeks). Certain individuals may also exhibit redness, swelling, and rash-like symptoms in the afflicted area. Of particular concern is getting the solution in the eye. Care should be taken to avoid this.

–Use gloves and eye protection when transferring the stock solution to the reagent bottle.

–Use gloves when handling the waste solution—it contains a small amount of unreacted silver.