APPLICATION NOTE

How to correctly perform titration measurements using Exaqua photometer with Exatitr system

exatitr

How to correctly perform titration measurements using Exaqua photometer with Exatitr system

INTRODUCTION

This application note is a guide and a set of recommendations, aimed to help properly perform titration tests using the Exaqua photometer with Exatitr system. It is intended for both lab technicians and people who are new to water analysis, and it can be considered as an extension of the manual. This application note discusses the basic principles of titration measurements, gives an overview of the types of titration methods, and shows best practices for sample preparation, calibration and the measurement procedure itself on the Exaqua photometers. By applying advice given in this document, the user will obtain more consistent and accurate results, fully utilizing the advantages provided by the Exatitr system.

exaqua®
photometer reinvented

WHAT IS COLORIMETRIC TITRATION?

Colorimetric titration is an analytical technique that allows for precise determination of the concentration of a substance in a water sample. It involves adding a known amount of titrating agent, called the titrant, to the analysed solution, which then reacts with the analyte until the equilibrium point is reached. The equilibrium point, also known as the end point of titration, is characterized by a sudden and distinct change in the colour of the sample. Based on the known quantity of titrant added, the concentration of the substance in the tested sample can be calculated.

Titration methods have been the gold standard in water parameters analysis, especially for parameters such as calcium, magnesium or carbon dioxide. Using the titration technique, accuracy levels of less than 1 % can be achieved, which is unattainable with even the best colorimetric methods.

Traditional titration is one of the most important techniques used in analytical laboratories and its effective performance requires laboratory experience and the use of appropriate equipment.

EXATITR TITRATION

Photometer-assisted titration is a major improvement over typical colorimetric methods in almost every aspect. Exatitr is a miniaturized, portable titration setup, with photometer-assisted detection of the reaction progress and the end point of the titration. Titrant is added from a syringe mounted on the test vial - the volume used is read from the scale on the syringe. The end of titration is indicated by the photometer both visually and with an acoustic signal.

The Exatitr system guides the user through the titration process, detects the end of the reaction, converts the amount of reagent used into the concentration of the analyte, converts to alternative units and also stores the result for further processing.

Exatitr owes its convenience to its proprietary Rayject technology, which eliminates the need to cover the vial from external light.

PERFORMING EXATITR MEASUREMENT

WHAT IS LIKE TO WORK WITH EXATITR SYSTEM?

Exaqua is the first photometer on the market with the functionality of continuous colour measurement of the solution during the titration. Colorimetric titration can be performed without need to cover the tube from ambient light. The mounted syringe enables you to dispense the reagent with one hand, while the other holds the photometer. The measuring system performs continuous analysis of the sample during titration. The system's interface provides information on both the progress of the reaction and when the titration is completed.

PREPARING TO PERFORM TITRATION TESTS USING THE EXAQUA PHOTOMETER

This section is a step-by-step overview of the actions preceding a titration measurement, supplemented with hints. It is both an extension of **Chapter 15 Titration methods** from the Exaqua manual and a supplement to the titration method procedures.

1. Prepare the necessary reagents and accessories - Exaqua reagent kits contain everything you need to perform a titration test.
   If you are performing measurements in the field and are using reagent cases, make sure you take all the necessary components of the kit.

Each titration test requires:
- Exaqua photometer,
- reagent kit,
- tall vial with a cap with a hole,
- 5 ml syringe,
- 1 ml syringe with a tip,
- spatula (if one of the reagents is in powder form).

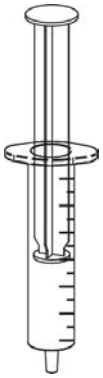
Note:
Using the same spatula or the same syringe for different sets of reagents is not recommended.

2. Read the method instructions and familiarize yourself with the steps of the Guide – doing a dry run beforehand will let you perform the test with more confidence, reducing the chance of mistakes. Video instructions are also available for all methods, including titration methods. They can be found on the specific product page www.exaqua.com/products/reagents or by scanning the QR code found on the reagent kit box. For reagent cases, the QR codes can be found in the included booklet.
3. Rinse the vial (it is especially crucial for vials that have been used before).
   - » It is recommended to use distilled water – add a few millilitres of water to the vial, cap the vial, shake, stir, turn several times - let the water wash the walls and dissolve potential residues from previous measurements and impurities that have adsorbed on the inner surfaces of the glass. Finally, pour out the water and shake off the droplets that remained inside. In case of titration, the vials rinsed with distilled water do not have to be perfectly dry before measurement.
   - » If distilled water is not available - rinse the vial with water sample. When doing so, it is important to thoroughly eliminate the water remaining in the vial after rinsing. Do not try to dry it in the oven, shaking out droplets over a paper towel is sufficient. It is also important that the vial is dry from the outside - this will prevent the formation of streaks that could interfere with absorbance measurements, as well as contamination of the interior surface of the photometer socket.
   - » When measuring calcium and magnesium content in marine water, the vials can be rinsed using tap water, proceeding as if distilled water was used. The calcium and magnesium content

of tap water is low in comparison to the levels recorded in seawater, so even incomplete shaking off of tap water after rinsing will have no noticeable effect on the test result.

4. Rinse the 5 ml syringe three times with the tested water - repeatedly drawing the full syringe and emptying it.

   A small amount of water may remain in the tip of the syringe, such a situation is acceptable.



5 ml syringe

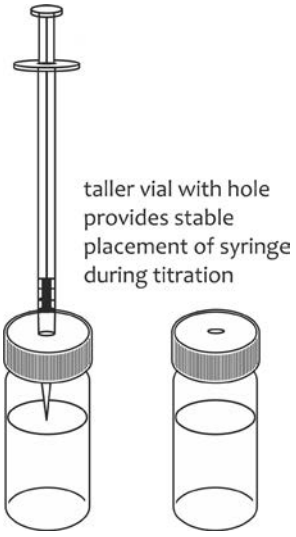
> **Note:**
> Do not attach a tip to the 5 ml syringe.

5. Start up the photometer and, if it has been more than two weeks since you last used the instrument or the ambient temperature has changed by more than 5 °C, perform a calibration. The photometer can request calibration automatically if it detects that one of the above conditions has occurred.

   Calibration can also be performed at any time by entering **MAIN MENU** (the **Home** ⌂ key) **Settings → Diagnostics → calibration**.

USING A TALLER VIAL AND A CAP WITH A HOLE FOR TITRATION METHODS

Special, taller than usual vials and a cap with a hole are provided for Exatitr titration methods. This type of vial prevents the solution from leaking out when the sample is mixed during the addition of the titrant. The hole in the cap provides a place for stable placement of the syringe tip during titration. Using a shorter Exaqua vial will result in the syringe tip ending up too low, causing it to become submerged in the test sample and to interfere with the measuring light beam. Situations of this kind must be avoided.



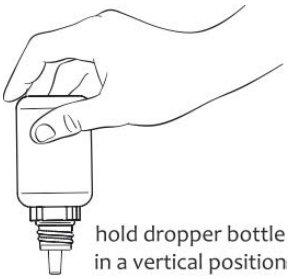
PERFORMING THE EXAQUA TITRATION TEST

With clean or rinsed vials, a calibrated photometer and a set of reagents, the user is ready to perform a titration test.

1. Press the **GUIDE** context button to take advantage of the guide system which gives step-by-step instructions how to perform the test for a selected method.
2. Take the appropriate amount of water sample with a 5 ml syringe (water should be the same one with which the syringe and the vial were rinsed).
   - Push the syringe plunger all the way in and dip the syringe into the sample solution. Draw out the water by pulling out the piston.
   - In most cases, 5 ml of water is needed.

> **Note:**
> Some tests require a different volume, such as titration method Z463 (Magnesium, marine water) uses 3 ml of test water.

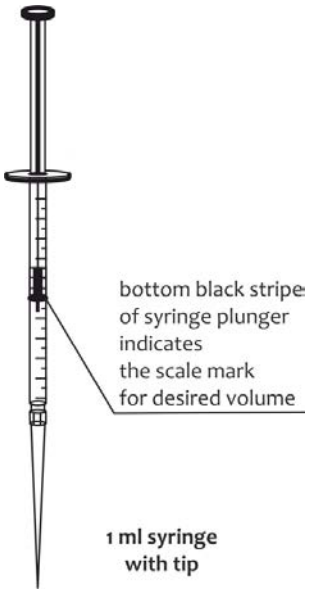
   - Carefully read the GUIDE prompts to avoid confusion.
   - When taking water, avoid leaving air bubbles inside the syringe. Drawing the liquid too quickly increases the chances of their formation, drawing the water at a slower speed should guarantee perfect filling of the syringe.
   - When taking water, it is a good idea to draw a little more than needed and then expel the excess by lowering the plunger to the desired volume.
3. Pour the water into the vial.
4. Add reagents according to the instructions.
   - Remember to hold the dropper bottle vertically over the vial when dispensing reagent, rather than tilting it at an angle. It is important that only fully formed drops are added.



   - When adding powdered reagent - a flat scoop of reagent should be added, the spatula must be filled flat to the brim, with no excess.

5. Put a cap with a hole on the test vial and place it in the photometer socket. Press the **ZERO** key. From this point until the end of the measurement, do not remove or twist the vial. Further mixing of the sample can be done by shaking the photometer.

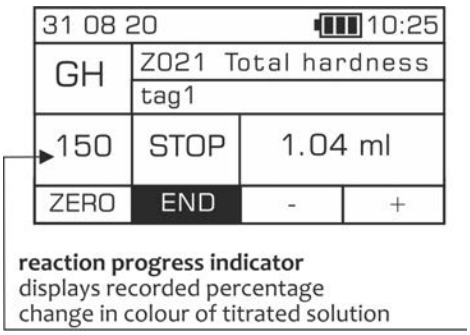
6. Take 1 ml of titrating reagent using 1 ml syringe with a tip.
   - Since a portion of reagent will be in the tip, syringe will appear to not be fully filled with liquid – in this case the volume of reagent is not indicated by the liquid level but by the position of the lower black strip on the piston.
   - When taking reagents, avoid air bubbles inside the syringe. Taking the liquid too quickly increases the chances of their formation, drawing at a slower speed should guarantee perfect filling of the syringe.
   - When drawing reagents, it is a good idea to acquire a little more than needed and then expel the excess by lowering the plunger to the desired volume.



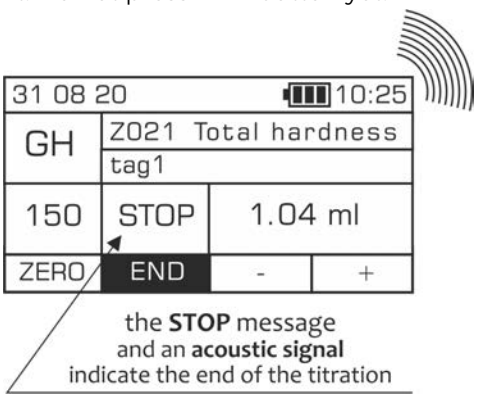
7. Place the syringe with the reagent in the hole in a cap. For the full stability and comfort of dispensing, it is recommended to push the syringe down until it's firmly mounted in place, so that it will not wobble during the mixing.

> **Note:**
> When mounting the syringe, hold it by the barrel and avoid pressing down on a plunger as it will cause accidental dispensing of the reagent.

8. With the setup fully assembled, press **MEAS** key to activate continuous measurement process.
9. Begin the titration by carefully dispensing the reagent from the syringe, mixing after each portion is added.
   - This process requires careful attention, especially when performed for the first time.
   - The portions of the titrating agent are not determined by the drop size – the plunger of the syringe can be pushed down to dispense any amount of reagent, the liquid will detach from the syringe tip during mixing
   - When performing the subsequent titration test on a sample with similar parameters, you can estimate the amount of reagent you will use beforehand. In such case, the titration process can be accelerated by initially adding larger portions of reagent and then decreasing them when approaching the expected titration end point.
   - The indicator on the left side of the display informs about the approaching titration end point. It shows the recorded percentage change in colour, which directly informs about the progress of the titration. At the beginning, the indicator reading remains at low levels. Over the course of the reaction it starts to rise.

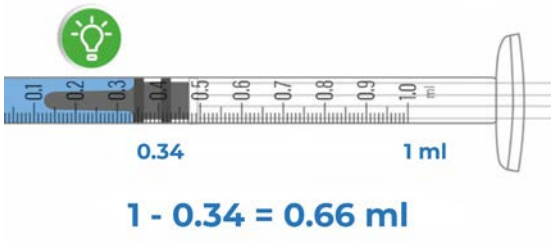


   Sharp but temporary spikes on the indicator can be observed during mixing. If the reading will start stabilizing at higher values then the end point of titration is approaching. You can expect the sudden spikes of the indicator reading after adding further portions of the reagent. For better accuracy you should decrease the size of added portions.
   - A reading reaching 100 indicates the end of titration. An audible acoustic signal will be heard (provided the beeper is enabled) and the message **GO** will be replaced by **STOP**. If the colour change value remains above 100 % for at least 5 seconds, you can stop adding the reagent. Do not press **END** button yet.



   - If despite adding full syringe of reagent the titration end point was not reached, draw another 1 ml portion of the reagent and continue dispensing.
10. From the syringe scale read the volume of the reagent used during titration.
    - Be aware that the scale on the syringe shows the amount of reagent left in the syringe, so to obtain the amount of reagent used perform the following calculation:

Used volume = 1 – volume read from syringe scale [ml]



For example, if after the titration bottom black stripe of the syringe plunger indicates 0.34 ml, then the volume of the used reagent is:

1 – 0.34 = 0.66 ml.

This is the value you should input into the photometer.

- Enter the volume of the used reagent using the **"+"** and **"-"** keys or the numeric keypad. The "+" and "-" keys adjust the value by 0.01 ml, they can also be held down for a faster selection of the desired value. The numeric keypad is a convenient alternative input method - the result is entered digit by digit beginning with the number before the decimal point. For the previously calculated result of 0.66 ml, this is a sequence of 0-6-6. In case of a mistake, the value can be corrected with the "+" and "-" keys or entered from the beginning
- Having entered the volume of reagent used, end the test with the **END** key. The photometer will display the calculated value of the measured parameter.

WHAT CAN DECREASE THE ACCURACY OF THE MEASUREMENT?

» Water remaining in the vial after rinsing

Measurement was performed on the larger volume of the sample than required – a larger volume of reagent will be used to titrate such a sample and obtained result will be inflated. This is not an issue if the vial was rinsed with the distilled water.

» Adding the titrating reagent too fast or in too big portions while being near the titration end point

The end point has been exceeded – the greater the excess of the added reagent, the more inflated the result will be.

» Inefficient mixing

Results in falsely inflated values of the reaction progress indicator. Failing to mix the sample properly can cause the progress value to exceed 100 %, prematurely signalling the end of the titration. Mix the contents after each added portion of reagent by shaking the photometer. Finish the titration only if the indicator maintains the **STOP** message for at least 5 seconds.

» Finishing the titration before absorbance stabilizes

Even after thorough mixing you should be sure that the reaction progress indicator remains above 100 % value for at least 5 seconds.

» Using the same spatula or syringe for several types of methods

Using the same accessories for several types of methods can lead to reagent contamination or unwanted chemical reactions, resulting in reduced reagents performance and thus lower accuracy.

» Using a smaller vial in titration methods

During mixing liquid can spill out if smaller vial is used, generating error by changing the sample volume. What's significantly more important, in a smaller vial a syringe tip will be too low and will interfere with the measuring light beam.

» Incorrect dispensing of reagent from a dropper bottle

Drops dispensed by holding the bottle at an angle instead of holding it vertically may differ in volume, causing an error in amount of reagent added. Such situation can lead to incorrect reaction conditions and thus interfere with end-of-titration detection.

» Incorrectly scooping the powder reagent into the spatula

The incorrect amount of powder reagent, especially if amount added is lower than specified in the instructions, leads to incorrect reaction conditions and thus interferes with the detection of the end of the titration.

» Incorrect filling the syringe with titrant reagent

Presence of air bubbles - leads to discrepancies between the amount read and the actual amount of reagent dispensed.

Reading the volume using the level of the liquid instead of the position of the plunger - leads to an incorrect reading of the amount of reagent consumed and further leads to incorrect results.

Not using a tip for 1 ml syringes - the included tip allows for both stable placement of the syringe and more accurate dispensing of the reagent.

TROUBLESCHOOTING

» Method: Z462 – Calcium Ca Marine water

Problem: Despite the further addition of the titration agent, the reaction progress indicator is "stuck" at a value below 100 %.

Cause: Extremely unfavourable conditions for the test, including low pH, low KH, and high magnesium concentrations make it difficult to create a suitable reaction environment.

Solution: Perform the measurement again with an increased amount of reagent Ca-1 - 15 drops instead of 13.

» Method: Z463 – Magnesium Mg Marine water

Problem: More than 1 ml of titrant reagent was used during the test and the final result is too high.

Cause: 5 ml instead of 3 ml of water sample was used for the test, so more titrant was needed to titrate the sample. The result obtained is inflated.

Solution: Perform the measurement again, ensuring to take only 3 ml of water.

» Method: Z473 – Magnesium Mg Fresh water

Problem: The measurement result shows magnesium content of less than 3 ppm.

Cause: The magnesium test is a differential test where the magnesium level is calculated by subtracting the calcium content from the combined magnesium and calcium content. The measurement result is therefore a difference between two values with measurement uncertainties. If the value of this difference is comparable to the uncertainty, obtained measurement uncertainty of these sub-measurements may cause their difference to be of a random nature.

Solution: If the calcium concentration is significantly higher than the magnesium concentration, conduct a measurement with increased resolution. This involves taking a 10 ml water sample and adding double the amounts of Reagents Mg-1 (i.e. 20 drops). Titrate the sample as usual. To obtain the measured level of magnesium, divide the added volume of Mg-2 reagent by 2.

» Method: Z630 – Carbon dioxide CO_2

Problem: After using the reagent kit for a prolonged period of time, the measurements start showing inflated results.

Cause: Reagent CO_2-2 is capable of binding carbon dioxide from the surrounding air. Leaving the bottle uncapped for too long causes the reagent to react with the CO_2 present in the environment and thus degrades the performance of the reagent.

Solution: Ensure that Reagent CO_2-2 is left open as short as possible during testing.

ul. Siewna 15
94-250 Łódź, Polska
biuro@exaqua.com, www.exaqua.com

© Copyright 2020 – 2023 Exaqua

ver. 01.12.2023