GUIDE: Getting To Know Your Titration Sample Prep

1. Choose the Right Sample Size

- Choosing the correct sample size is one of the most important criteria for ensuring that titration results will be accurate, efficient, and cost effective. Using a sample that is too small can yield inaccurate results because it offers very poor resolution in terms of data. When data is limited, it is very difficult to interpolate where the true equivalent point is. This results in poor repeatability and accuracy. Conversely, using too much sample will result in higher chemical costs due to excess titrant use, as well as excess chemical waste produced. The ideal sample size will consume titrant volume in the range 25-75% of the total burette volume.
- If the estimated concentration of our sample is known, there is an easy way of determining the appropriate sample size based on titrant consumption using the titration equation!
- Titration Equation
  - $$CA = \frac{VT*CT*RR*MM*CF}{SA}$$
    - **CA** is the concentration of the analyte (the unknown that is being measured)
    - **VT** is the volume of titrant used to reach the end point
    - **CT** is the concentration of titrant
    - **RR** is the stochiometric reaction ratio of the analyte:titrant, in that order
    - **MM** us the molar mass of our analyte
    - **CF** is a conversion factor to adjust the results to the result units of choice (if necessary)
    - **SA** is the sample size of our analyte, and can be a mass or a volume

- The titration equation can be rearranged to solve for sample size. Solving for the sample size is easy – just plug in the known values into the equation.
- Sample Size Equation
  - $$SA = \frac{VT*CT*RR*MM\ \ CF}{CA}$$

2. Use a Representative Sample

- Sample size is not the only consideration for working with complex sample matrices. It is crucial to ensure that a representative sample be used for accurate determination of an analyte. A representative sample is one that embodies the sample matrix as a whole in that it contains all the parts all of the parent product or sample in the correct ratios. This is especially important for samples that are not homogeneous by default, such as spice blends or soil. If results are not repeatable, even when proper measurement technique is used, the likely source of error is a non-representative sample.
- There be times when it is hard to guarantee a representative sample within the sample size range recommended for the method. If this is a case, a dilution is an excellent way to both assuring a representative sample, while still using a sample size that is suitable for good data resolution. A dilution is also a good idea if the sample size suggested by the previous section is too small to practically measure out. With a dilution, a larger amount of sample is weighed and added to a volumetric flask. Deionized water is added to the flask to bring the contents to the desired volume. The mixture is then allowed to stir for a period of time to become homogenized and or to extract the analyte. A small aliquot of this mixture is then titrated to an endpoint. With the Hanna Instruments automatic titration systems, the user is able to program the dilution into the titrator, so the results will be adjusted for the dilution factor.
- To program a dilution into the titrator you will need:
  - Size of Analyte to Be Diluted (Sample Size): The mass or volume of the material added to the volumetric glassware
  - Final Volume: The volume once the deionized water has been added to the sample
  - Aliquot size: The volume of the sample that is being used for the titration.

3. Using the Proper Measurement Tools and Techniques

- Using the proper measurement tools and techniques are crucial components in the strategy to improve the accuracy of titration results. Recall from our titration equation, that the sample size is directly factored into the results.
- If the sample size that is input into the titrator is inaccurate, the titration result will be equally inaccurate. It is therefore important to ensure that you are able to obtain sample aliquots with the appropriate tools. Typically, liquid samples are measured out by volume and solid samples are measured by mass.
- **Liquid Samples.**
  - Beakers and Erlenmeyer Flasks
    - Beakers and Erlenmeyer flasks, while they may contain graduated markings to indicate volume of sample, are primarily use for the holding, pouring, or mixing of solutions. They are typically not rated with an accuracy statement for measuring specific volumes. Using tools such as these to measure a sample size may cause fluctuation in results, thus hindering the repeatability of your testing.
  - Transfer Pipettes
    - Disposable transfer pipettes (not to be confused with disposable volumetric pipettes) are another tool that may seem accurate due to their markings, but are generally not rated for accuracy. They are not recommended tools for volumetric measurement, but they are however, great tools for reagent addition that does not require precise addition.
  - Graduated Cylinder
    - Graduated cylinders are designed for measuring and pouring liquids. Graduated cylinders typically have an error tolerance of 1%, and are usually considered less accurate then volumetric flasks and pipettes. They are fast and easy to use, and can be a good choice for high throughput environments.
  - Volumetric Flasks
    - Volumetric flasks are accurate for a specific volume of liquid. They do not typically have graduated markings to measure out different volumes of solution, but they are the glassware of choice for making accurate dilutions.
  - Volumetric Pipettes
    - Volumetric pipettes typically offer the greatest amount of accuracy and are ideally suited for transferring liquids from once source to another. This type of pipette includes disposable plastic pipettes, glass pipettes, and auto pipettes. In order to achieve accuracy using these tools, it is crucial that the proper technique be used when sampling. The two most important factors are the aspiration angle and the immersion depth. When collecting a sample with a pipette, the pipette should be held vertically to ensure the proper amount of liquid is aspirated. The pipette should only be submerged in the sample enough to be able to aspirate the desired amount without pulling in air. Furthermore, the sample should be aspirated and dispensed a few times to prime the burette tip prior to transferring a final aliquot of sample to the titration vessel. When dispensing liquid from a pipette, the pipette should be held at an angle between 20-45 degrees directly over the center of the beaker. Care should be taken not to forcibly expel any remaining liquid from the pipette.
- **Liquid Handling Best Practices**
  - Even among the same type of glassware, there is a class system for quantifying accuracy. Class-A glassware is the most accurate, and is usually accurate to two decimal places. This class of glassware will usually come with a certificate that specifies the accuracy of the tool. Class-B glassware has higher tolerance of error than Class-A, and typically have an accuracy statement of one decimal place. As such, Class-A glassware tends to be more expensive than Class-B. For high accuracy needs, Class-A glassware is recommended and worth the investment. It is also helpful to use volumetric glassware that is geared toward the sample size that is being measured. Measuring 10 mL sample in a 10 mL graduated cylinder, will be more accurate then measuring 10 mL with a 100 mL graduated cylinder.

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- In order to achieve accuracy when taking volumetric measurements, it is crucial to ensure that the volume is read correctly. Water tends to curve at the top of the volume, making it difficult to define the measurement. This curvature is called the meniscus. When reading the volume on volumetric glassware, the bottom of the meniscus should be on the marking of the desired volume
- When adding a liquid sample to a beaker, make sure that the sample is added to the center of the beaker and that the sample is not stuck to the sides of the beaker. In most cases, a small amount of deionized water can be used to wash any remnants on the side of the container into the sample.
- Glassware should be rinse with deionized water and dried between samples, or if using an auto pipette, a new tip should be used for each different sample. All glassware should be cleaned with laboratory soap, acid rinsed (if necessary), and rinsed with deionized water before storage.
- Some liquid samples are too viscous to be measure out accurately volumetrically. In these cases, mass can be used in lieu of volume. However, we have to be careful here because if our final units are related to volume, we have to account for the density of the sample in our results calculation for accurate computing.

• **Solid Samples**

- Just like with liquid handling, it is important to use the proper tools and techniques when working with solid samples.
- **Understanding the distinction between scales vs. balances is key**. We often use the terms scale and balances interchangeably, but there are distinct differences between them.
- Scales tend to be able to handle a wide range of mass (both heavy and light). They lend themselves well to measuring ingredients or bulk product quickly. Scales are usually less expensive than balances. However, their open design and poor resolution do not make them suitable or ideal for measuring sample sizes for titration. They will introduce variability and thus affect your titration repeatability.
- Analytical balances are typically more sophisticated than scales. Additionally, they often have features such as shields to protect the sample from air currents that would otherwise cause the results to drift. Analytical balances also vary widely in terms of resolution and pricing so It is important to choose the correct analytical balance for your typical sample sizes. Below are the recommended resolutions based on the desired sample size.
- It is recommended that all balances be calibrated yearly.

Sample Size	Balance Resolution
1 gram	0.1 grams
0.1 grams	0.01 grams
0.01 grams	0.001 grams
0.001 grams	0.0001 grams

• **Solid Samples Best Practices**

- When setting up an analytical balance, choose a spot that is away from doors, fume hoods, and vents to further reduce the possibility of interference. In order to be accurate, balances should be leveled appropriately and calibrated per the manufacturer's instructions. A set of weights can be purchased to ensure that the balance is reading properly.
- Balances should be tared, or zeroed, with the weighing vessel prior to the addition of sample. For best results, take the mass of the sample directly in the titration beaker ensuring no product spills onto the balance. If using a weigh boat, rinse the contents of the weigh boat 3 times with deionized water to ensure all product is accounted for. Since deionized water, in most cases, does not contain the analyte being tested, it can be added without fear of interference.
- You should be familiar with the accuracy of your measuring tools as the final calculated titration result will only be as precise as your least precise variable in the titration equation.

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4. Using the Right Type of Water

- Just like with glassware, all water is not created equal. There are different classifications of water based on the purification process it undergoes. When preparing samples it is important to ensure that you have, and use, the correct water.

- **Tap Water**
  - Tap water is the raw water that comes through the faucet from a private well or municipal source. Tap water contains all types of contaminants including minerals, disinfectants, and those which contribute to pH, acidity, and alkalinity. Due to the presence of potential contaminants, raw tap water is not recommended for lab analysis without further purification. Tap water, typically, has a total dissolved solids (TDS) level of 100-500 parts per million (ppm).

- **Reverse Osmosis**
  - Reverse osmosis, abbreviated as RO water, is water that been purified through being pressure forced through a semipermeable membrane. Contaminants are trapped in the filter, whereas the clean water is allowed to pass through the membrane. RO water removes 98% of total dissolved solids (TDS), but does not remove all pesticides, solids, or VOCs. RO water contains a TDS <100 ppm.

- **Distilled Water**
  - Distilled water, abbreviated as DH_2O, is water that has been purified through the process of distillation. Here, water is boiled, then the vapor is condensed into a sterile storage container, all while leaving solid contaminants behind. However, anything with a boiling point that is lower than water, like volatile organic compounds (VOCs), will be carried over into the distillate. Bottled water is not the same as distilled water, as it is often fortified with minerals. Distilled water has a typical TDS value of <0.5 ppm.

- **Deionized Water**
  - Deionized water, abbreviated DI H_2O, removes nearly all contaminants and is the gold standard of water for lab analysis. First, water is prefiltered through series of filters including physical, carbon, and reverse osmosis. The water then passes through cation and anion DI resins. Here, positive and negative ions are captured and replaced with with H+ and OH- ions, which combine to form pure water. Deionized water is typically measured using resistivity, and should have a value of at least 18 MΩ·cm.

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