Manual vs. Automated Titration: Benefits and Advantages to Switching

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Titration is one of the most commonly used analytical methods. Manual, semi-automated, and fully automated titrations are well-known options and are examined in detail in several academic studies. This white paper summarizes the advantages and benefits of automated titration in comparison to manual titration. The increase in accuracy and precision of measurements as well as significant time and cost savings are discussed.

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Beginnings of titration

Titration is a primary analytical method that is very easy to perform—a buret, a titrant, and a suitable endpoint indicator are the only required items. Therefore, it is not surprising that this is also one of the oldest quantitative analytical methods.

The first buret was invented in the 18th century by Francois Antoine Henri Descroizilles[1], and was further developed by Karl Friedrich Mohr who wrote the first book about titration titled «Instructional Book of Titration Methods in Analytical Chemistry» back in 1855.

Principles of titration

Amedeo Avogadro first proposed in 1811[2] that the amount of molecules in a particular volume of gas always remains the same at standard conditions, no matter what type of molecules it contains.

A century later in 1909, Jean Perrin defined the term «**Avogadro constant**» as exactly 32 grams of oxygen molecules (a «mole» of O_2)[3]. This constant meant that a defined amount of mass of a particular substance contains a specific amount of molecules; therefore, the amount of molecules in a volume of solution is also defined. Titration was born—it is just as simple as counting the molecules of a substance (the analyte) in a sample matrix.

The volume of titrant, which is used to facilitate a chemical reaction with the analyte, is determined via titration. All chemical reactions take place in defined stoichiometric ratios. Therefore, the concentration of the analyte can be determined by knowing the exact concentration of the titrant and calculating its consumption (volume) with a measurable endpoint.

A typical benchtop setup for a manual titration is shown in **Figure 1**.

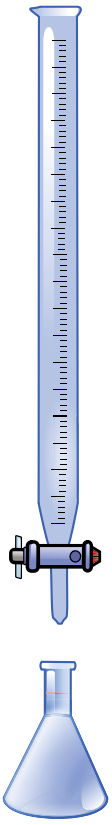

Figure 1. Typical setup for a manual titration. The buret is filled with titrant, and the Erlenmeyer flask contains the sample solution which includes the analyte to be measured.

Determination of pH with titration indicators

There are several variations of titration, with pH titrations being the most common. The pH value at the endpoint may vary, as the acid dissociation constant (pK_a) differs depending on each individual acid. **Figure 2** shows a selection of pH indicators that cover the majority of the pH range from 0–14.

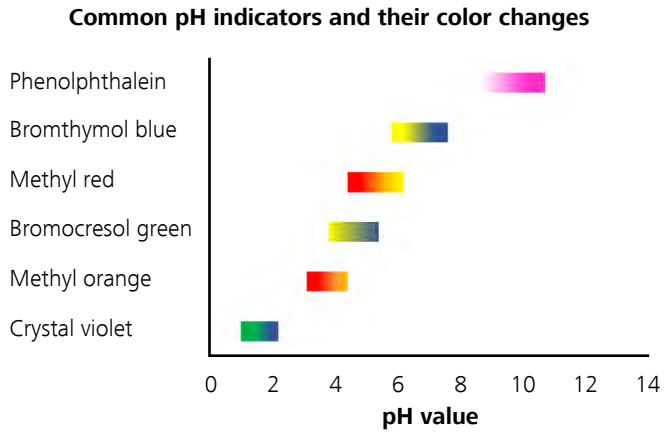

Figure 2. Color changes of different pH indicators depending on the pH value.

The endpoint of other titration types, like redox, complexometric, or argentometric titrations, can also be determined by the color change of a suitable indicator. Some examples of the indicators used for these different reaction types are listed in **Table 1**.

Type of Titration	Indicator
Complexometric	Eriochrome black T Murexide
Argentometric	Potassium dichromate Ammonium iron(III) sulfate
Redox	Change of color from titrant (e.g., potassium permanganate) Starch solution

Table 1. Common endpoint indicators used for different reaction types.

The color change for each of these indicators, especially for the complexometric reactions, is difficult to accurately predict as it depends on both the pH value and the complexed metal.

Difficulties of manual titration

Although manual titration is nearly 200 years old, it is still frequently used and mentioned in several standards and norms. However, manual titrations face some difficulties.

Visual perception of the endpoint

Each person experiences colors and color intensity differently. This leads to some deviations or bias depending on the individual analyst performing a manual titration. **Figure 3** illustrates this point and the difficulty in determining an endpoint visually.

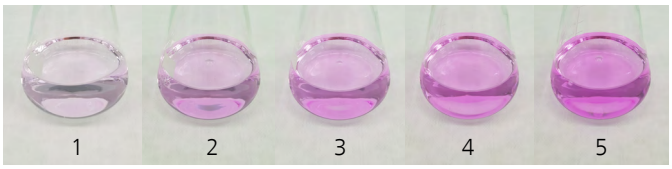

Figure 3. Titration of c(HCl) = 1 mol/L with c(NaOH) = 1 mol/L and phenolphthalein as the indicator. Each of these images differs only in the addition of a single drop of the NaOH titrant.

The intensity of the colors obtained in **Figure 3**, 1–5 differ only by approximately 50 µL NaOH titrant in each case. The question arises regarding where the "correct" endpoint should be chosen. If this is not handled in exactly the same manner by different analysts, then the precision of the measurement will suffer.

Drop size

With manual titration, results can only be as accurate as the smallest drop size from the buret. In the pharmaceutical industry, one drop is defined to be 50 µL. This means that a maximum accuracy regarding a drop size of 50 µL can be achieved. Assuming a consumption of about 5 mL titrant, this may lead to an error of up to 1%.

Error of buret

As with all glassware, the buret itself has a specific tolerance. In case of a 50 mL buret, the allowed tolerance is 50 µL. However, this is not the only error source resulting from handling a buret, such as the Parallax error. This error occurs if the analyst does not view the meniscus horizontally, but from an angle. Meniscus readings are different depending on the viewing angle, as shown in **Figure 4**.

All of the previously discussed points show that manual titration is easy to perform but is influenced by the user. Also, manual titration is not very advantageous cost-wise due to the high amount of time needed for cleaning, refilling the buret, as well as manually calculating the results. Safety of

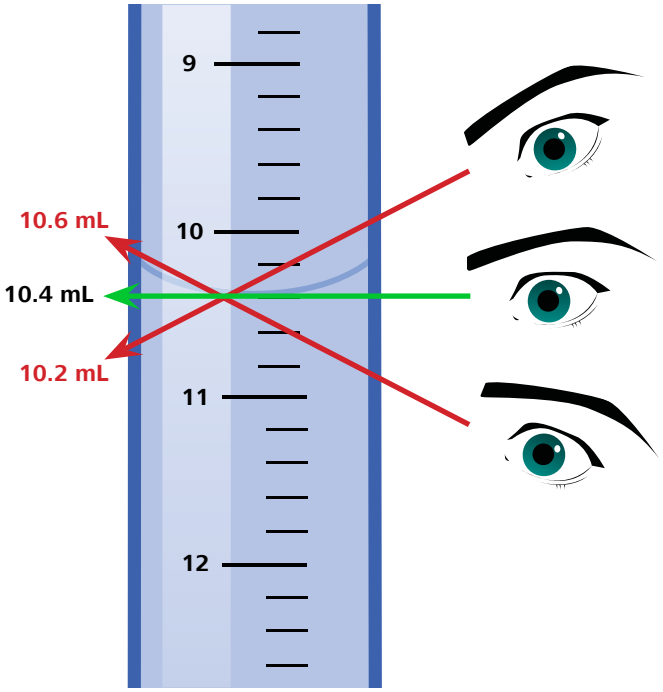

Figure 4. Parallax error occurs if the user reads the meniscus values from different visual angles.

the lab personnel is not guaranteed, as chemicals can be spilled easily while refilling the buret. Data integrity is another point to consider for manual titrations, since all data must be transferred manually into a notebook or computer. The calculations are not carried out automatically, increasing the risk of errors. Human error is a likely possibility in this situation.

Development of semi-automated titration

To overcome the limited accuracy and precision of manual titrations, an electronic buret can be used. It consists of a motor-driven spindle and a glass cylinder, which is filled with titrant. Furthermore, recent generations are equipped with a built-in stirrer and allow the user to carry out calculations automatically and save results on a storage device (e.g., USB stick or PC), or print the results directly after analysis.

Semi-automated titration: even more accurate

When switching from manual methods to semi-automated titration, the main improvements relate to the accuracy and precision. Electronic burets can dose as precisely as 2.5 µL for a 50 mL cylinder unit, which enhances the accuracy by a factor of 20 compared to a manual titration. However, the biggest disadvantage still persists: the subjectivity of visual perception. Therefore, the next step in the evolution of titration is automated potentiometric titration.

Automated potentiometric titration overcomes the remaining disadvantages

Automated potentiometric titration was developed in the mid-1960s. The collection of data, equivalence point determination, and evaluation can be done automatically. The benefits are tremendous:

- improvements in both accuracy and precision
- reduced time for tedious manual processes
- minimized potential for human error

Improved accuracy and precision

A resolution of 10,000–100,000 steps can be achieved with modern auto-titrators. This corresponds to a precision of 5 µL down to 0.5 µL for a 50 mL motor-driven buret. The precision can be further enhanced by using a motor-driven buret with a smaller volume.

Visual perception no longer matters

Automated titration could not have been established without the development of sensors. In 1909, the first glass electrode for potentiometric titration was built. Potentiometric sensors allow an endpoint or equivalence point determination independent from a color change or bias from an analyst.

As various samples require different electrode properties, there are currently a large number of sensors available. **Table 2** lists some examples for the different types of titration.

One sensor in particular must be mentioned when discussing automating titrations: the Optrode. As titrations with color indications are still common, the Optrode was developed – a sensor which is able to detect minute color differences by determining the change in absorbance at a specific wavelength, then converting the absorption into a measureable potential. In such a way, also colorimetric titrations become more accurate and precise, as they no longer depend on the visual perception of laboratory analysts.

Traceable results for data integrity

During manual titration procedures, all results are read from the buret and written into the lab journal or typed manually into software. This is an error-prone process, with a high likelihood of the values transferred incorrectly. To solve this issue, automated titrations record the measured values into a measuring point list and the result calculation is performed automatically on the device. These results can be exported as a PDF file or printed with date and time stamp.

Less sample necessary

To achieve acceptable accuracy and precision values with manual titration, a large volume of sample is used to obtain a titrant consumption within a certain range, to overcome the error of the volume addition which might be up to 0.05 mL.

Table 2. Specific electrodes for different applications.

Sensor	Application
Unitrode 	Universal laboratory use, pH 0–14
Aquatrode plus 	Water, general, pH 0–13
Pt Titrode 	For redox titrations without any change in pH value
Ag Titrode 	For argentometric titrations without any change in pH value
Optrode 	For titrations with indicators and a color change

On the contrary, the volume addition by a motor-driven buret might go down to 0.5 µL. This enables the operator to reduce the sample size and to use less chemical reagents. It is recommended to utilize between 10–90% of the cylinder volume of the buret and to adjust the sample size accordingly.

Titrations become more cost-effective

The most expensive part in any manual titration is the cost of labor. Lab personnel must be properly trained and are also fully occupied during titration work. This changes completely with automated titrations. The method on the autotitrator is programmed once and can be recalled at any time by any user simply by pressing a button.

A comparison was made to determine the analysis time needed for a series of five titrations performed both manually and automatically. The results are summarized in **Table 3**.

	Automated titration	Manual titration*
Mean value	10.0023 mL	9.92 mL
Standard dev. abs.	0.009 mL	0.04 mL
Standard dev. rel.	0.09%	0.4%
Total duration	32 min 33 s	14 min 53 s
Duration with needed presence of analyst	**1 min 33 s**	**14 min 53 s**

* For manual titrations, phenolphthalein was used as the indicator.

Table 3. Summary of five determinations of 10 mL c(NaOH) = 0.1 mol/L with c(HCl) = 0.1 mol/L. All titrations were performed with the same solutions and pipets.

In this case, manual titration is faster than the automated method, but with much less accurate results. The mean analysis time per automated titration was measured at 6 min 12 s, meaning that over the series of five determinations, the presence of the lab analyst only accounted for about 1 min 33 s per analysis. Compared to the manual titration where the lab analyst is needed during the entire titration, this accounts for a significant amount of time saved.

The time during each analysis can then be used to either prepare the next sample or work on another system in parallel. In this way the throughput is increased and the cost per analysis is decreased.

Summary

This white paper explains the advantages of automated titration over manual methods. Besides significant improvements in productivity, accuracy, and precision, the human influence on the analysis is reduced to a minimum. All these points make automated titration easier to use than manual titration, as well as results being more comparable and reproducible.

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