

Titration in Analytical Chemistry

Titration methods are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte.

In **volumetric titrations**, the volume of a standard reagent is the measured quantity.

A **standard solution** is a reagent of known concentration that is used to carry out a volumetric titration.

The **titration** is performed by slowly adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete.

Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution.

The **equivalence point** is the point in a titration when the amount of added standard reagent is equivalent to the amount of analyte.

The **end point** is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

In volumetric methods, the **titration error, E_t** , is given by

$$E_t = V_{ep} - V_{eq}$$

where V_{ep} is the actual volume of reagent required to reach the end point and V_{eq} is the theoretical volume necessary to reach the equivalence point.

A **primary standard** is an ultrapure compound that serves as the reference material for a titration or for another type of quantitative analysis. Important requirements for a primary standard are the following:

1. High purity. Established methods for confirming purity should be available.
2. Atmospheric stability.
3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.

4. Modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

A **secondary standard** is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

The ideal standard solution for a titrimetric method will

1. be sufficiently stable so that it is necessary to determine its concentration only once;
2. react rapidly with the analyte so that the time required between additions of reagent is minimized;
3. react more or less completely with the analyte so that satisfactory end points are realized;
4. undergo a selective reaction with the analyte that can be described by a balanced equation.

Principles of Neutralization Titrations

The standard reagents used in acid/base titrations are always strong acids or strong bases, most commonly HCl, HClO₄, H₂SO₄, NaOH, and KOH. Weak acids and bases are never used as standard reagents because they react incompletely with analytes. *Nitric acid is seldom used because its oxidizing properties offer the potential for undesirable side reactions. Hot concentrated perchloric and sulfuric acids are potent oxidizing agents and are very hazardous.*

An **acid/base indicator** is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form.

Some Important Acid/Base Indicators				
Common Name	Transition Range, pH	pKa*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65	R – Y	1
	8.0–9.6	8.96	Y – B	
Methyl yellow	2.9–4.0		R – Y	2
Methyl orange	3.1–4.4	3.46	R – O	2
Bromocresol green	3.8–5.4	4.66	Y – B	1
Methyl red	4.2–6.3	5.00	R – Y	2
Bromocresol purple	5.2–6.8	6.12	Y – P	1
Bromothymol blue	6.2–7.6	7.10	Y – B	1
Phenol red	6.8–8.4	7.81	Y – R	1
Cresol purple	7.6–9.2		Y – P	1
Phenolphthalein	8.3–10.0		C – R	1
Thymolphthalein	9.3–10.5		C – B	1
Alizarin yellow GG	10–12		C – Y	2

*At ionic strength of 0.1.

†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $\text{HIn} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{In}^-$; (2) Base type: $\text{In} + \text{H}_2\text{O} \leftrightarrow \text{InH}^+ + \text{OH}^-$

Reagents for Neutralization Titrations

Preparation of Standard Acid Solutions

Solutions of HCl, HClO₄, and H₂SO₄ are stable indefinitely. Restandardization is not required unless evaporation occurs. Standard solutions of nitric acid are seldom used because of their oxidizing properties.

To obtain most standard acid solutions, a solution of an approximate concentration is first prepared by diluting the concentrated reagent. The diluted acid solution is then standardized against a primary-standard base.

The Standardization of Acids

Sodium Carbonate

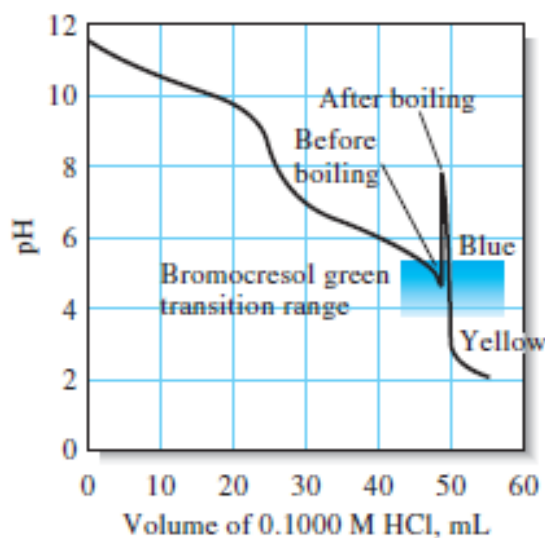


Figure 1 Titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl. After about 49 mL of HCl have been added, the solution is boiled, causing the increase in pH shown. The change in pH when more HCl is added is much larger after boiling.

As shown in Figure 1, there are two end points in the titration of sodium carbonate. The first, corresponding to the conversion of carbonate to hydrogen carbonate, occurs at about pH 8.3; the second, involving the formation of carbonic acid and carbon dioxide, appears at about pH 3.8. The second end point is always used for standardization because the change in pH is greater than that at the first. An even sharper end point can be achieved by boiling the solution briefly to eliminate the reaction product, carbonic acid and carbon dioxide. The sample is titrated to the first appearance of the acid color of the indicator (such as bromocresol green or methyl orange). At this point, the solution contains a large amount of dissolved carbon dioxide and small amounts of carbonic acid and unreacted hydrogen carbonate. Boiling effectively destroys this buffer by eliminating the carbonic acid:



The solution then becomes alkaline again due to the residual hydrogen carbonate ion. The titration is completed after the solution has cooled, resulting in a substantially larger decrease in pH during the final additions of acid. A more abrupt color change is the result.

Other Primary Standards for Acids

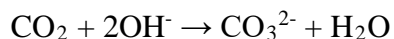
Na₂CO₃ (1:2), TRIS (1:1), Na₂B₄O₇·10 H₂O (Sodium tetraborate decahydrate) (1:2), HgO (1:2), Ti₂CO₃ (1:2)

Preparation of Standard Solutions of Base

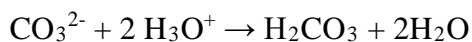
Sodium hydroxide is the most common base for preparing standard solutions, although potassium hydroxide and barium hydroxide are also used. These bases cannot be obtained in primary-standard purity, and so, all must be standardized after they are prepared.

The Effect of Carbon Dioxide on Standard Base Solutions

In solution as well as in the solid state, the hydroxides of sodium, potassium, and barium react rapidly with atmospheric carbon dioxide to produce the corresponding carbonate:

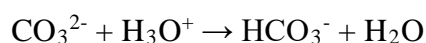


Although production of each carbonate ion consumes two hydroxide ions, the uptake of carbon dioxide by a solution of base does not necessarily alter its combining capacity for hydronium ions. Thus, at the end point of a titration that requires an acid-range indicator (such as bromocresol green), each carbonate ion produced from sodium or potassium hydroxide will have reacted with two hydronium ions of the acid.



Because the amount of hydronium ion consumed by this reaction is identical to the amount of hydroxide lost during formation of the carbonate ion, no error results from the reaction of the hydroxide with CO₂.

Unfortunately, most applications of standard base require an indicator with a basic transition range (phenolphthalein, for example). In this case, carbonate ion has reacted with only one hydronium ion when the color change of the indicator is observed:



The effective concentration of the base is thus diminished by absorption of carbon dioxide, and a systematic error (called the carbonate error) results.

Absorption of carbon dioxide by a standardized solution of sodium or potassium hydroxide leads to a negative systematic error in analyses in which an indicator with a basic range is used; there is no systematic error when an indicator with an acidic range is used.

Carbonate ion in standard base solutions decreases the sharpness of end points and is usually removed before standardization.

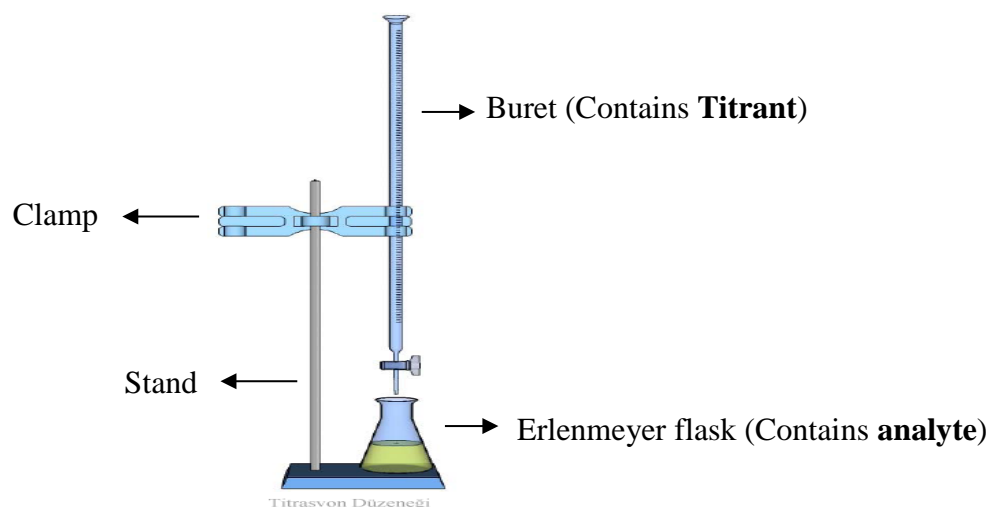
Solutions of bases should be stored in polyethylene bottles rather than glass because of the reaction between bases and glass. Such solutions should never be stored in glass-stoppered bottles; after standing for a period, a stopper is often impossible to remove.

Standard solutions of strong bases cannot be prepared directly by mass and must always be standardized against a primary-standard acid.

The Standardization of Bases

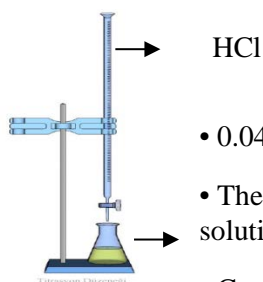
KHP (Potassium hydrogen phthalate), $\text{KH}(\text{IO}_3)_2$ (Potassium hydrogen iodate), benzoic acid, oxalic acid

Titration setup



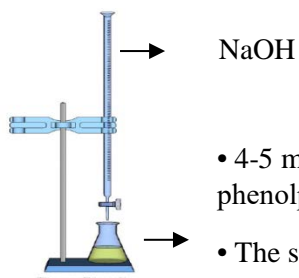
Experimental Procedure:

Standardization of HCl



- 0.04 - 0.05 g Na_2CO_3 + 50 mL of purified water + 3 drops of methyl red → Yellow solution
- The solution is titrated until the color of the onion skin is observed. When this color is seen, the solution is heated until it becomes yellow again.
- Cool the solution and continue titration until a second time onion skin color appears (~ 1 mL HCl).

Standardization of NaOH



- 4-5 mL of standardized HCl solution + 20 mL of purified water + 3 drops of phenolphthalein → Colorless solution
- The solution is titrated to the point where the pink color is first seen.