A New Approach – Concentration Measurement of Bases and Acids using a Refractometer

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Routine concentration measurements of e.g. bases and acids are one of the main tasks in a chemical laboratory. The conventional method to determine the content of a base or acid is titration – either manual or automatic.

Here a new approach is presented, in which refractometers are used for concentration measurements of binary solutions such as acid or base solutions. It is shown that refractometry can be a very interesting and powerful alternative to titration.

Titration

Titration is a quantitative analytical method in which the composition of a solution (analyte) is determined by addition of a reagent solution (titrant). The addition of the titrant must take place until end of the so-called neutralisation reaction. From the amount of titrant spent the concentration of the analyte can be calculated.

The amount of titrant added to the analyte must be recorded continuously during the titration process against a suitable indicator (this results in a titration curve; see below). This could be a colour change of an added chemical indicator, e.g. phenolphthalein or the monitoring of the change in pH or electric conductivity. For each titration process an indicator needs to be established, which is suitable for monitoring the neutralisation reaction. Additionally the indicator must be fast enough to follow the changes caused by the added titrant.

A titration curve is a graphical representation of the titration progress, where on the x-axis the consumption of titrant is plotted, whereas the y-axis shows e.g. the pH of the solution *(ref. figure 1)*.

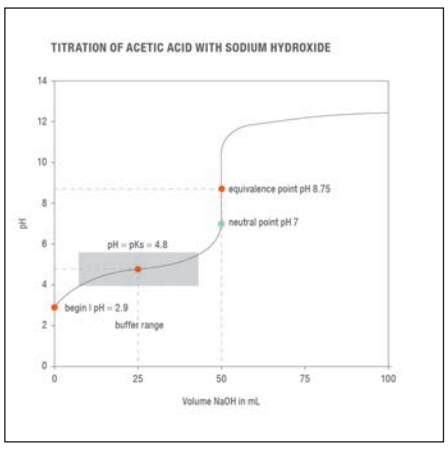

Figure 1. Titration of acetic acid against a strong base (NaOH). In the beginning of the titration the solution is acid. While adding more and more NaOH the pH slightly increases, then makes a steep rise, passes the equivalence point (turning point), and finally increases slightly again when the solution is alkaline (surplus of NaOH).

The endpoint of the titration (equivalence point) is the point at which the amount of added titrant is equivalent to the amount of analyte consumed.

The equivalence point does not have to be at pH 7, but depends on the acid; its acid constant, puffer capacity, and on how many H-atoms can be donated by the acid. For instance, phosphorus acid can donate 3 H-atoms resulting in 3 turning points of the titration curve. This could result in limitations of the processing of such a titration curve.

Before a titration can be started, the operator needs to determine, which titrant should be used, which indicator should be taken (e.g. pH electrode), and what would be the optimum dosing speed of the titrant.

The accuracy of the titration depends on the accuracy of the concentration of the titrant, which needs to be exactly known, the accuracy of the dosing system (e.g. burette), and finally on the accuracy and response time of the equivalence point detection, e.g. pH sensor.

As the volumes are temperature-dependent the titration has to be done at a fixed temperature or a corresponding temperature correction needs to be performed, which is a source of further inaccuracies. In practice the titration usually is carried out at room temperature, so that temperature errors are expected.

For performing a titration, additional equipment is necessary, e.g. glass ware, a balance, a magnetic stirrer, volumetric bottles, standard solutions, etc.

A titration system requires further inspection and maintenance efforts, e.g.

- checking the dosage system for leakage
- checking the tightness of piston and valves
- checking the titration syringe/burette for any damages or obstructions

Further tasks for the operator to avoid wrong measuring results are

- cleaning all parts of the dosage system
- checking the dosage system for air bubbles
- performing basic cleaning and checking the volume according to the international standard ISO 8655
- checking the proper functioning of the electrodes; especially electrodes made of glass as they can easily break
- taking care that the electrodes are stored properly in a buffer solution
- checking the concentration of the titrant and the validity of standards used
- optimising the dosing rate

After all these measures were taken the titrator can be operated and the concentration of the acid or base in question can be determined.

Take the fast lane: Concentration measurement with a refractometer

Many processes define titration as the method of choice if e.g. concentration measurement of bases or acids is necessary, even if this is a time-consuming, expensive, and labour-intense procedure.

It is time for thinking about alternatives: The refractive index of a binary solution depends on the content of the dissolved substance in this solution. This opens the way to benefitting from the advantages of refractometry for fast and easy concentration measurements of acids and bases.

For a concentration measurement with an Abbemat refractometer from Anton Paar just one drop of sample is required and the result is obtained within seconds without the consumption of any further chemicals. The accuracy of the result depends on the accuracy of the refractometer model only and not on the accuracy of titrant, indicator, burette, temperature, or further calculations.

The refractometer needs to offer the right method for the intended application, e.g. concentration measurement of hydrochloric acid. Abbemat refractometers from Anton Paar offer more than 200 methods covering applications in the pharmaceutical, chemical, food, or beverage industries.

Among these are hydrochloric acid, sodium hydroxide, or sulphuric acid. If the required method is not available, it can be easily defined on the instrument.

Figure 2. Abbemat refractometers from Anton Paar are capable of measuring the concentration of acids and bases within seconds from just a drop of sample. They are a very economical alternative to conventionally used titrators.

Abbemat refractometers measure the concentration of acids and bases independently of the operator within seconds with no need of user interaction: The operator just needs to apply a drop of sample on the measuring prism of the refractometer and press 'Start'.

Abbemat refractometers have no moving parts and thus virtually no wear, so that they pay off within a short period of time compared to titrators, which require consumables, additional glassware, chemicals, and detectors, which need regular maintenance and replacement, e.g. if broken.

Table 1. Comparison of Abbemat refractometer with titration

	Abbemat	**Titration**
Measuring time	4 s to 10 s	30 s to 120 s
Sample preparation	No	Yes
Consumables	None	Yes
Costs by device and consumables	€4000 to €12000	€2000 to €12000
Average lifetime	>10 years	~5 years for pump ~10 years for pH electrode (less for conductivity electrodes)

Compared to a titration system the Abbemat sample well or optionally used micro flow cell can be cleaned easily with deionised water and can be used immediately for the next measurement.

Operator safety and chemical resistance

There is a wide range of basic chemicals that is required in production processes in almost every industrial area. Often these chemicals are strong acids or bases being corrosive and toxic, e.g. hydrochloric acid, sodium hydroxide, or sulphuric acid.

For these applications the Abbemat refractometer can be equipped with a micro flow cell made of PFA, which is resistant against strong acids or bases. The flow cell is conveniently filled by using a syringe and makes the handling safe for the operators because they do not get in contact with the acid during the measurement.

Figure 3. A micro flow cell attached to the measuring prism of an Abbemat refractometer allows convenient concentration measurements of aggressive or toxic chemicals and avoids human contact with the chemical.

Chances and limitations

Refractometers offer very fast and precise concentration measurements on binary solutions and could replace titration in many routine applications.

Limitations are given by the fact that refractometers can measure the concentration of binary solutions only. If the concentration of an acid or base in a multicomponent mixture should selectively be measured, a refractometer cannot be used.

However, refractometers can still be used for a very fast quality control of such multi-component mixtures to check, if the composition of the whole mixture is as desired.

Additionally, refractometers can be used for checking the concentration of the titrants used later on for the titration procedure.

Summary

Refractometers are fast and economical instruments if the concentration of binary solutions, e.g. acids or bases, has to be determined.

Abbemat refractometers offer several advantages compared to titration and should be considered as the method of choice, when the concentration of binary chemical solutions, e.g. acids or bases, needs to be measured.

Abbemat refractometers from Anton Paar already offer methods for applications in all industries. If required, further methods can easily be programmed on site or developed by the Anton Paar application development team.