



How to carry out a pH Titration

Abstract

Describes the main steps in setting up and carrying out a pH titration, with guidelines for selecting the titrant and the sample wt%, and some pitfalls to avoid.

1 Introduction

A great deal of information can be obtained about a colloidal system by examining the way its zeta potential and particle size vary as a function of pH. But such measurements are not easy to perform with standard techniques such as light scattering, for these only work on dilute samples. Thus after each addition of the acid or base one would have to take a sample from the system and dilute it in an appropriate way to make a measurement.

In most cases that involves centrifuging the sample to obtain some clear liquid and then adding some of the concentrate to that liquid so that the solution concentration of all the ions remains the same in the dilute sample as it was in the concentrate. One could then do the measurement of size and zeta (sometimes using two different instruments).

In the AcoustoSizerII and ZetaProbe there is no need for this dilution, since these devices work on concentrated colloids. This makes the titration process much simpler and faster. A pH titration from 4 to 10 can be carried out in under twenty minutes.

Usually one of the main aims of a pH titration is the determination of the **isoelectric point** (iep). This is the pH at which the zeta potential is zero. It is determined by measuring zeta while titrating the suspension with acid and/or base over a range of pH values.

The iep gives a valuable indication of the pH-range over which a suspension will be stable. Many stable colloids can be prepared by simply adjusting the pH of the dispersion to a value *at least* two pH values away from the iep. A colloidal dispersion is at its most unstable near the iep, and thus is most likely to flocculate or cream near this pH. In general, the further from the iep the more stable the dispersion.

Another application of the iep is the determination of the outer coating of titania. Titania particles are a major component of housepaints. To give them desirable properties the particles are usually coated with a thin layer of some other oxide like alumina, silica or zirconia. Clean titania displays an iep around pH 5. The iep occurs at about pH 2 for a silica coating, about pH 9 for an alumina coating and about pH 6 for a zirconia coating. Partial

coatings have iep values somewhere between that of the coating material and the titania. Thus the iep provides a measure of the type and the quality of the coating, and for this reason it is regularly used in Q.C. labs to check on product variability.

2 The titration procedure

First prepare a dispersion of the colloid for titration. The amount required depends on the flow loop or sample cup option used. For example, the standard ZetaProbe cup requires a minimum volume of 200 mLs. A suitable acid or base titrant is then selected to perform the titration. Tables 1 and 2 provide some basic guidelines for choosing a suitable titrant.

In an acid titration, hydrogen ions will bond to particle surface groups, and in a base titration hydrogen ions are released from the surface and react with hydroxyl ions from the base. Thus the total volume of acid or base required to go from one pH to another depends on the surface site density and on the total surface area of the particles. Clearly the acid or base demand increases with particle concentration and surface area. If the titrant concentration is too low a large volume will be required, and the sample vessel may overflow during the titration. If the titrant concentration is too high, there is a danger that the titrant additions required for a pH step may be smaller than the minimum volume allowed by the syringes, and as a result the pH algorithm will overstep the mark.

Background Electrolyte	Acid	Base
potassium salt	-	KOH
sodium salt	-	NaOH
nitrate salt	HNO ₃	-
chloride salt	HCl	-

Table 1: Choosing a suitable titrant

The suggested acid and base concentrations in table 2 are estimates based on a particle diameter of 300 nm. For smaller particles, a higher titrant concentration is needed. For a given type and concentration of particle, the titrant demand is inversely proportional to the square of the particle size.

Although the AcoustoSizerII and ZetaProbe can be used with very concentrated suspensions, there are some practical considerations that might limit the particle concentration used in a pH titration. For one thing the volume of titrant required might be so large that it might cause an overflow during a titration. Although it is possible to pause the titration and remove some colloid, this is often inconvenient. Secondly, a concentrated colloid will become very viscous near the iep and it will be difficult to thoroughly mix in the titrant. For these reasons it is usually advisable to work at particle concentrations of less than 10 volume percent.

% w/w	Concentration of Titrant (M)
2-3	0.1
3-6	0.2
6-10	0.5
10-20	1.0

Table.2: Choosing a suitable titrant concentration

Prior to performing a titration it is necessary to wash the burettes and pipette tips with the titrant at least three times. To do this, choose the **Burette Control** from the main software panel.

Beginning at the pH at which the initial dispersion has been made up, one would normally titrate with base or acid to one of the extremes (either pH 3 or pH 11). It is alright to move outside that range, it should be remembered that most of the interesting behaviour of charged colloidal systems occurs when the total ion concentration is relatively low (less than about 0.01 M). The software allows for multiple titration legs, up and down the pH axis.

As well as specifying the start and end points of the titration it is necessary to specify the pH the pH increment between successive points. In nearly all colloids, the variation of particle size and zeta as a function of pH follows a smooth curve without any sudden steps. For this reason there is usually no need to choose pH increments of less than 0.5. The software allows smaller pH steps than this, but in most cases this usually just adds time to the pH titration without providing any more information.

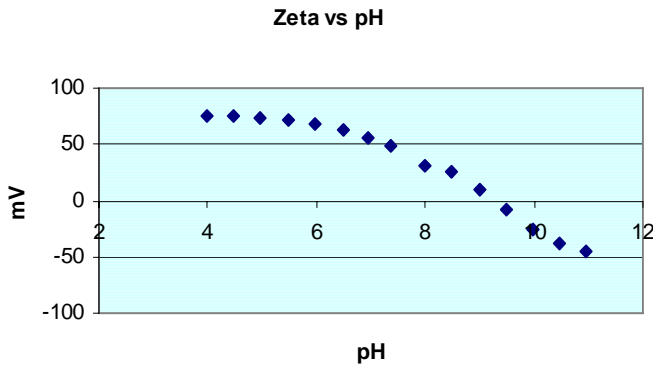
The AcoustoSizerII and ZetaProbe are designed to perform from pH 13 down to pH 1 but at the extreme ends, the solutions are very corrosive and the colloidal particles may start to dissolve. That can cause problems later if the material re-precipitates when the pH is moved closer to the neutral value.

3 Sample titration

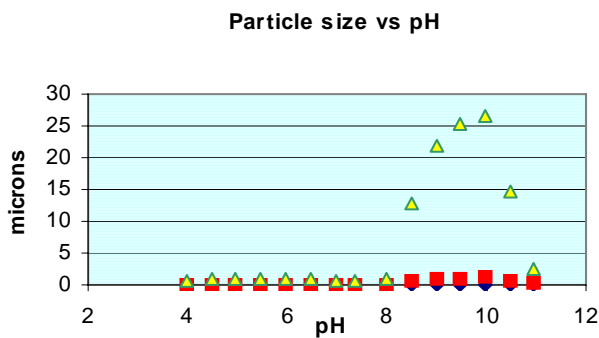
In the figures on the following page we show AcoustoSizer II measurements of zeta potential and particle size as a function of pH for a 10 wt% alpha alumina.

The titration in this case was carried out with 1 M KOH. A volume of 0.73 mls of titrant was used in this titration.

From the first figure it can be seen that the iep for this alumina is a bit above 9. The AcoustoSizer uses an extrapolation formula to give a more accurate estimate the iep, which in this case is 9.3.



The second figure shows the measured particle size distribution as a function of pH. The quantity d50 in this figure is the median particle size and d15 and d85 represent the 15th and 18th percentile sizes. In the neighbourhood of the iep the particles begin to flocculate, and the size distribution becomes much broader.



In this unstable region the measured size depends on factors such as the pump speed or stirring rate, since the shear forces from the flow limit the floc size. The size will also depend on factors such as the particle concentration and the time between measurements.

The size data in this case was obtained from the AcoustoSizer attenuation measurements while the zeta potential was determined from the ESA measurements.



Clearly the pH titration data tells us a lot about the colloid, and for this reason it is probably the most commonly used option in the ZetaProbe and AcoustoSizerII.