



ZetaProbe Applications

Determining the isoelectric point (i.e.p)

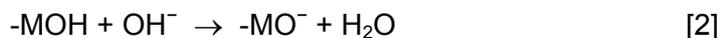
The insoluble metal oxides like titania, zirconia, alumina, and silica have a wide variety of uses in ceramics, catalysis, agriculture and many other areas of industry and technology. One of the most significant properties of an insoluble oxide (and of many other materials like the paint pigments) is the isoelectric point. The ZetaProbe is the ideal instrument for determining the i.e.p. of such materials.

1 What is the i.e.p. ?

At the isoelectric point of the solid, its zeta potential is zero. This is found by adjusting the pH to the appropriate value. The oxide surface responds by becoming more positive as the pH is lowered by undergoing the following reaction:



If the pH is raised it becomes more negative:



The surface therefore tends to be more negative the higher the pH and more positive the lower the pH. At some intermediate pH, zeta will be zero and that is the i.e.p. These ions which are responsible for generating the surface charge are called the ***potential determining ions*** for the system. The H^+ and OH^- ions are potential determining ions for oxides and clay minerals and also for proteins and for some other systems as well.

2 Why is the i.e.p. important?

Pure oxides have well defined iso-electric points which can be used to verify the cleanliness of their surfaces. The Table below shows the approximate values for some common oxides. The value quoted for silica is approximate because there is some doubt about whether it indeed has an i.e.p. in the accepted sense. The negative surface charge certainly decreases to near zero below pH 3 but it is very difficult, perhaps impossible, to observe a genuine positive zeta value for this substance in dilute simple salt solutions.

pH of the isoelectric point of various oxides

Oxide	pH of i.e.p.
Silica (SiO ₂)	2 - 3
Titania (TiO ₂)	5.8
Haematite (Fe ₂ O ₃)	6.5
Alumina (Al ₂ O ₃)	9.1

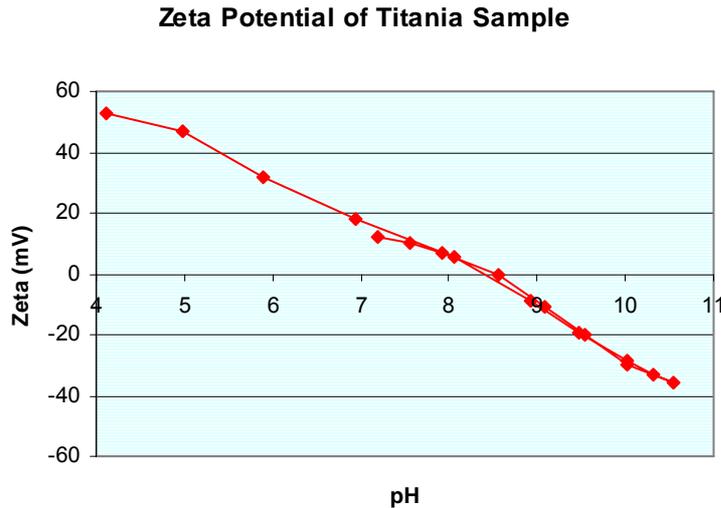
By measuring the i.e.p of an oxide suspension, which can be very easily done with the ZetaProbe, one can readily verify the cleanliness of its surface. If the particles in a suspension carry an unexpected contaminant it can completely alter the chemical processing behaviour of the suspension.

Although the i.e.p. value for titania is usually quoted as pH 5.8 that value is rarely observed because commercial titania is normally covered with one or more layers of either silica, alumina or zirconia or a combination of those oxides, in order to improve its performance in various situations. The i.e.p remains an important characteristic of the surface in this case because it helps to identify the coating layer and allows one to easily determine whether a supplier is properly controlling a particular product.

3 Determining the i.e.p. by titration

One must first prepare a suspension which is sufficiently well dispersed to provide a stable zeta potential. One then varies the pH and records the zeta potential over a suitable range. The traditional method of doing this, using microelectrophoresis or light scattering, is extremely tedious. After each pH adjustment one must remove a small sample and dilute it with a suitable solution before measurement. Ideally that diluting solution would have the same pH and salt composition as the suspension and of course that is changing at each step in the titration. If one diluted with a solution of the wrong composition the zeta potential could be quite significantly affected. Not surprisingly this method often gave rise to unreliable results. Even when the dilution process itself is conducted with great care, the possibility of contamination is always present. Greenwood and Bergstroem [1] give an example of an oxide (Ce-ZrO₂) for which microelectrophoresis gave variable results in this sort of experiment because a component of the oxide itself could dissolve out in the dilution process and alter the result. Their electroacoustic results were much more reliable.

Fortunately that dilution procedure is now a thing of the past. The electroacoustic method allows the measurement to be done on the undiluted suspension with zeta being measured after every addition of acid or base. The figure below shows a typical plot of zeta as a function of pH for a titania suspension obtained using electroacoustics. Note the high degree of reproducibility of the results as the i.e.p. is traversed first from below and then from above. The i.e.p. is close to pH 9 suggesting that this titania has an alumina coating. This entire titration can be done in less time than it takes to obtain one or two points by the light scattering or microelectrophoresis method.



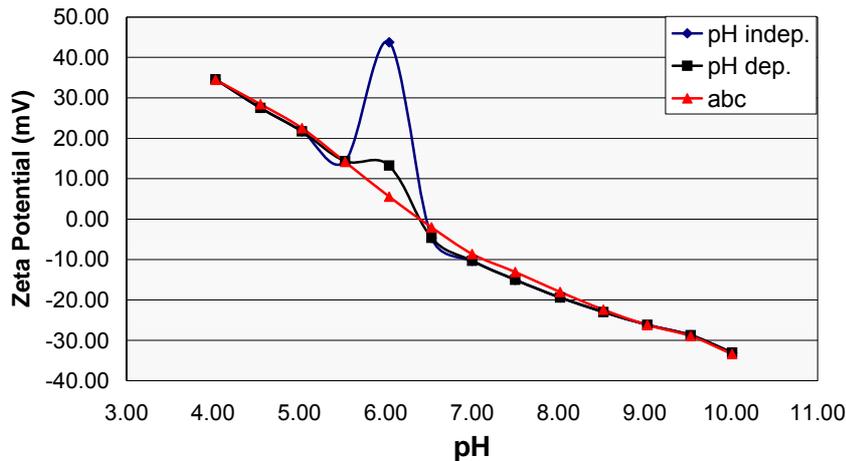
4 Background corrections

The determination of the i.e.p is straightforward when the salt concentration is relatively low (say equal to or less than 10 mM). There are some cases, however, when one wishes to determine the i.e.p as a function of salt concentration and then more care is needed. The problem lies in the fact that the electroacoustic method, which is used in the ZetaProbe, picks up a signal from the background salt as well as the signal from the particles. Normally the salt signal is too weak to affect the results but in the neighbourhood of the i.e.p when zeta is approaching zero that may no longer be the case. If the salt concentration is high enough that signal may be sufficient to disturb the measurement of the i.e.p.

Fortunately we are able to compensate for that effect. The signal from the salt has a different form from that of the particles. (It is independent of frequency whereas the particle effect depends on the frequency.) The ZetaProbe is provided with software which enables that background salt signal to be automatically deducted so that a true i.e.p is obtained. No other electroacoustic instrument is able to do this correction in because the correction it requires electroacoustic measurements over a range of frequencies, and we hold the patents on that

The figure below shows a comparison of the result obtained on a zirconia dispersion with the ZetaProbe using three different methods to correct for the background salt effect. The curve marked pH indep. is obtained by using a measurement of the salt effect at its natural pH and subtracting that from the signal at all pHs. It gives rise to rather dramatic fluctuations in zeta near the i.e.p. The curve marked pH dep. is obtained by plotting the signal for the background salt over the whole pH range and subtracting that from the suspension signal to estimate zeta. It is obviously an improvement but that still means making two titrations instead of only one. The third and smoothest curve, marked abc, shows the application of the automatic background correction (abc) method described above. Clearly the manual methods produce fluctuations near the i.e.p which in some cases can lead to significant error especially at higher salt concentrations. Some literature results are in error for that reason.

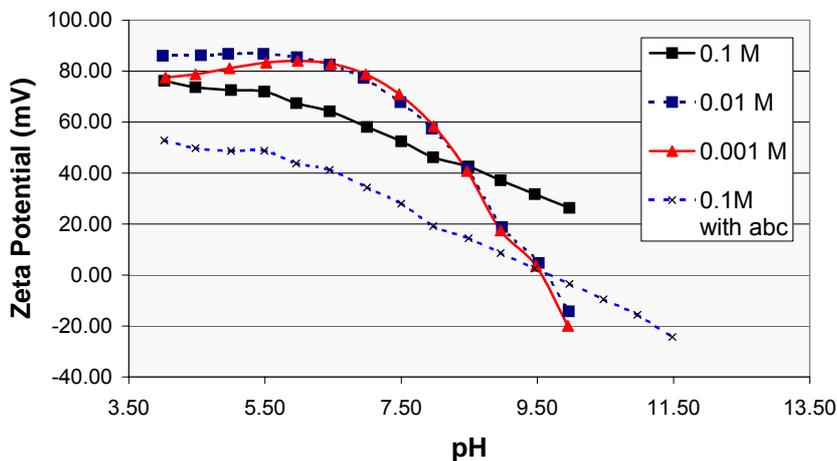
Comparative Background Correction for a 0.1M Zr Dispersion



A rather more striking result is shown by the comparison below

In this figure we show the result for the titration of an alumina sample at low salt (0.001 and 0.01M) without correction and the result at 0.1M with and without correction. The background corrections at low salt were negligible but at the highest salt concentration there is no accessible i.e.p. until one applies the correction and then the agreement with the values at low salt is essentially exact. Accurately determining that i.e.p. by light scattering or microelectrophoresis at 0.1 M salt concentration would be near enough to impossible.

Alumina Dispersions with and without Auto Background Correction



Reference

1. Greenwood, R., and Bergstroem, L. (1997) *J. European Ceram. Soc.* **17**, 537-548.