

More Reliable, Faster Determination of Isoelectric Point with the Agilent 7020 ZetaProbe

Application Note



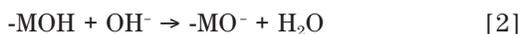
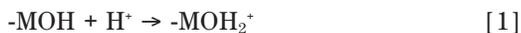
Abstract

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 key properties of an insoluble oxide (and of many other materials like paint pigments) is the isoelectric point (IEP). The Agilent 7020 ZetaProbe is the ideal instrument for determining the IEP of such materials. The ZetaProbe uses electroacoustic measurements to produce reliable, repeatable results in less time than it takes with either light scattering or microelectrophoresis, and there is no need to work with dilute samples.



What is the isoelectric point?

The isoelectric point of a solid is the pH value at which its zeta potential is zero. The reason that there is an IEP for the oxide surfaces is that the particle charge is determined by a competition between two reactions – one that makes the surface positive and one that makes it negative:



At low pH values the first reaction dominates and the surface is positive, while at high pH the second reaction prevails and the surface becomes negative. Thus, at some intermediate pH, the two reactions will be in balance and zeta will be zero. This is the IEP. The ions that 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, as well as for proteins and for some other systems.

Why is the isoelectric point important?

Pure oxides have well-defined isoelectric points that can be used to verify the cleanliness of their surfaces. Table 1 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 IEP 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.

Table 1. pH of the isoelectric point of various oxides

Oxide	pH of isoelectric point
Silica (SiO_2)	2 - 3
Titania (TiO_2)	5.8
Haematite (Fe_2O_3)	6.5
Alumina (Al_2O_3)	9.1

The IEP values in this table only apply to pure surfaces. In practice, the IEPs can be shifted by a small amount of surface-active contaminant, and for this reason IEP measurements are regularly used to verify sample cleanliness. If the particles in a suspension carry an unexpected contaminant, the contaminant can completely alter the chemical processing behavior of the suspension, and for this reason a clean surface is vital. The ZetaProbe is the ideal instrument for measuring the IEP.

Although the IEP 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, to improve its performance in various situations. The IEP 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.

Faster, more reliable determination of isoelectric point by titration

To determine the isoelectric point by titration, one must first prepare a suspension that 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 has the same pH and salt composition as the suspension; of course, these values are changing at each step in the titration. If one dilutes with a solution of the wrong composition, the zeta potential could be quite significantly affected. Not surprisingly, this method often gives 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-ZrO_2) 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 no longer necessary. The electroacoustic method used by the Agilent 7020 ZetaProbe allows the measurement to be done on the undiluted suspension, with zeta being measured after every addition of acid or base. Figure 1 shows a typical ZetaProbe plot of zeta as a function of pH for a titania suspension. Note the high degree of reproducibility of the results as the IEP is traversed first from below and then from above. The IEP is close to pH 9, suggesting that this titania has an alumina coating. This entire titration can be done in under half an hour – less time than it takes to obtain one or two points by the light scattering or microelectrophoresis method.

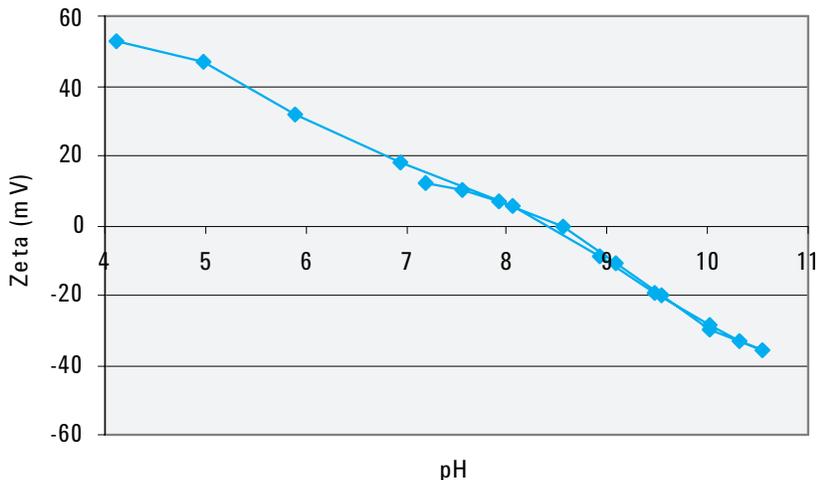


Figure 1. The ZetaProbe delivers very reproducible results for the zeta potential of this titania sample – and is much faster than techniques that require sample dilution.

Accurate determination of IEP in difficult high-salt samples

The determination of IEP is straightforward when the salt concentration is relatively low (equal to or less than 10 mM). There are some cases, however, when one wishes to determine the IEP 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 near the IEP, when zeta is approaching zero, that may no longer be the case. If the salt concentration is high enough, the salt signal may be sufficient to disturb the measurement of the IEP.

Fortunately, the ZetaProbe is 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 that can automatically subtract the background salt signal so that a

true IEP is obtained. No other electroacoustic instrument is able to do this correction because the correction requires electroacoustic measurements over a range of frequencies, and we hold the patents on that.

Figure 2 shows a comparison of the result obtained on a zirconia dispersion with the ZetaProbe using three different methods

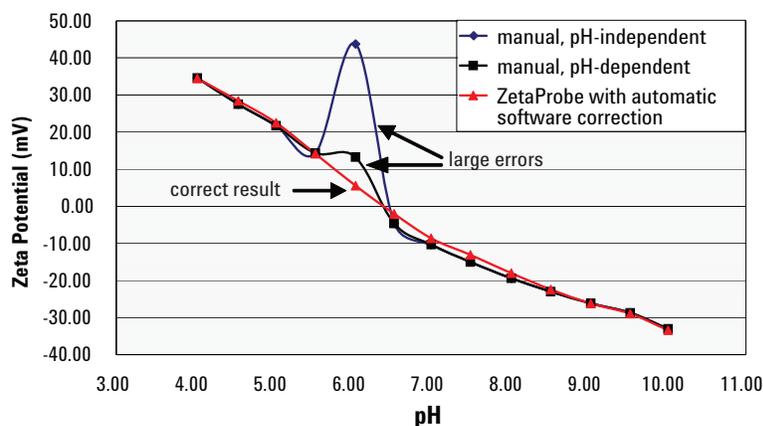


Figure 2. The ZetaProbe software automatically subtracts the salt background, to provide an accurate IEP for this 0.1M zirconia dispersion. The two manual background subtraction methods take more time and show errors at the IEP.

to correct for the background salt effect. The curve marked “manual, pH-independent” 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 IEP. The curve marked “manual, pH-dependent” 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 “ZetaProbe with automatic software correction,” shows the application of the automatic background correction method described above. Clearly, the manual methods produce fluctuations near the IEP, which in some cases can lead to significant error, especially at higher salt concentrations. Some literature results are in error for that reason.

A rather more striking result is shown by the comparison in Figure 3. 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 IEP until one applies the correction. Then the agreement with the values at low salt is essentially exact. Accurate determination of that IEP by light scattering or microelectrophoresis at 0.1M salt concentration would be nearly impossible.

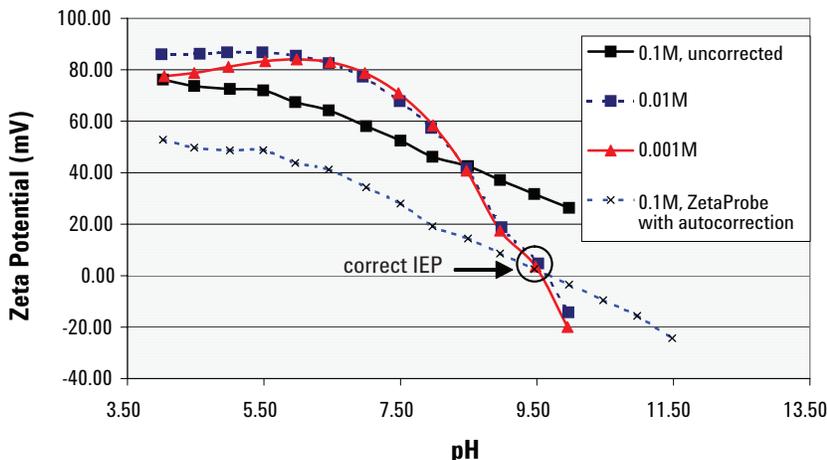


Figure 3. With software autocorrection for high (0.1M) salt background, the ZetaProbe delivers an accurate IEP for these alumina dispersions. This difficult determination is nearly impossible with other techniques.

Conclusion: reliable results with less effort

The isoelectric point is a valuable diagnostic for cleanliness and surface coating of metal oxides. The Agilent 7020 ZetaProbe is the ideal instrument for measurement of zeta potential, which is used to pinpoint the IEP. While techniques based on light scattering and microelectrophoresis are often used for measurement of zeta potential, these methods are plagued with unreliable results because of artifacts introduced in the mandatory sample dilution process. The ZetaProbe uses an electroacoustic technique that enables measurement of the zeta potential in undiluted suspensions, producing reliable, repeatable results in less time.

The ZetaProbe also enables the accurate measurement of zeta potential in samples that contain high levels of salt, a determination that is virtually impossible by light scattering or microelectrophoresis. Unlike other electroacoustic instruments, the ZetaProbe uses patented multifrequency measurements, which enables proprietary software to subtract a salt background, delivering accurate results even with difficult samples.

Reference

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

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Printed in the U.S.A. March 3, 2008
5989-8051EN