

A Report Submitted to the Faculty Research Grant Committee

**Purchase and Installation of a Zeta Potentiometer at
Arkansas Tech University**

**(Grant Research Title: A Zeta Potentiometer for the Electrophoretic
Deposition of Hydroxyapatite)**

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ABSTRACT

A Malvern model Zetasizer Nano Z zeta potentiometer was recently purchased, installed, and tested at Arkansas Tech University (McEver Building, Instrument Lab). The total cost of the "demo" instrument was \$30,230, which included the instrument, installation, training and a one-year warranty (new instrument cost is \$43,000 plus tax). One important function of the zeta potentiometer is to measure the stability of colloids in solution (suspended particles) as a function of temperature and surface charge (a function of solution pH). This information is required for effective electrochemical deposition of these colloids as films onto metal substrates. This process is called electrophoretic deposition (EPD). Our group at ATU is interested in the EPD of hydroxyapatite (synthetic bone, synthesized in our laboratory) onto titanium substrates (mimicking titanium implants). Eventually, with appropriate funding, this instrument will be upgraded (by adding components) to a state-of-the-art model Zetasizer Nano ZS for the simultaneous and automated determination of zeta potential (using an auto titrator), particle size distribution analysis, and molecular weight.

INTRODUCTION AND BACKGROUND

Human bone is an inorganic/organic composite material made up of collagen, a calcium phosphate mineral, and small amounts of sodium, magnesium, fluorine and other trace elements. The crystal structure of the calcium phosphate in natural bone and teeth resembles that of a substance called hydroxyapatite (HAP).^{1,2,3,4,5} This makes HAP an attractive material for biomedical applications such as a surgical implant material in orthopedics and dentistry due to its excellent biocompatibility and osteoconduction properties.^{6,7}

But because HAP is a metal oxide ceramic material, it is brittle and lacks the mechanical properties necessary for total bone replacement. Instead, metallic implants have been used for many years to repair and replace bone. More recently, studies have been directed at improving metallic implant fixation using physical and chemical methods. To improve chemical adhesion and biocompatibility, HAP has been used to promote bone growth and fixation towards implant surfaces and was found to encourage faster recovery times for the recipient.⁸ However, HAP coatings are currently deposited by high-temperature plasma spraying techniques that result in unpredictable films consisting of undefined phases (chemical composition unknown), and undesirable thick films (causing micro-cracking). In contrast, electrophoretic deposition (EPD) has been shown to provide high-quality and reproducible coatings on metallic substrates, in particular, HAP coatings on medical-grade titanium, TiAl6V4.⁹ Although relatively inexpensive, EPD requires **zeta potential measurements** to determine the charge on the colloidal particles and relative

stability of the particles (so as to prevent unwanted clumping or aggregating) prior to deposition onto the metallic substrate.

PURCHASE, ACQUISITION AND INSTALLATION OF THE ZETA POTENTIOMETER

We are pleased to report that full funding for the total cost of the zeta potentiometer was appropriated from several sources and the “demo” model was ordered for a total price of \$30,230 including installation, on-sight training, and a one-year warranty (compare: the cost of a brand new instrument is \$43,000 plus tax). The instrument arrived at Tech over the summer, and was installed on September 18, 2008. In this report we present a very “brief” description of how the zeta potentiometer works, some theory behind the zeta potential, the data that can be acquired, and how we can use this data to form the desired films by the electrophoretic deposition (EPD) process.

WHAT IS THE ZETA POTENTIAL AND WHY IS IT IMPORTANT?

Our research group at ATU is currently investigating electrophoretic deposition (EPD) as an inexpensive, fast and superior method of depositing films onto metallic substrates. In contrast to conventional electrochemical plating methods, where “molecules” are deposited onto electrodes, EPD involves the migration and deposition of “colloids” or suspended “nano-particles” onto electrodes (metallic substrates) as stable films. For EPD to work, however, the suspended particles must be properly characterized in terms of particle size (this

will be measured at UALR until this capability is added to our instrument) and surface charge (related to the zeta potential and electro-mobility). The pH of the solution (initial phase: 98% ethanol; pH adjusted with HCl or NaOH) and/or conductivity will be adjusted to optimize the charge of the suspended nano-particles so that migration to the appropriate electrode will occur most efficiently.

What is meant by the “surface charge” of the suspended nano-particles? The net charge at the particle surface affects the distribution of ions in the surrounding interfacial region resulting in an increased concentration of counter ions – thus an **electrical double layer** exists around each particle as depicted in Figure 1. The liquid layer surrounding the particle consists of a strongly bonded inner layer (Stern layer) and a loosely bonded outer layer (diffuse region). Within the diffuse layer is a hydrodynamic shear plane, and the charge at this shear plane is called the **zeta potential**. We are interested in optimizing the zeta potential because this affects the particle stability (to prevent flocculation) and its electro-mobility. If all the particles have a large negative or positive zeta potential they will tend to repel each other and there is no tendency for the particles to come together. In general, particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable.

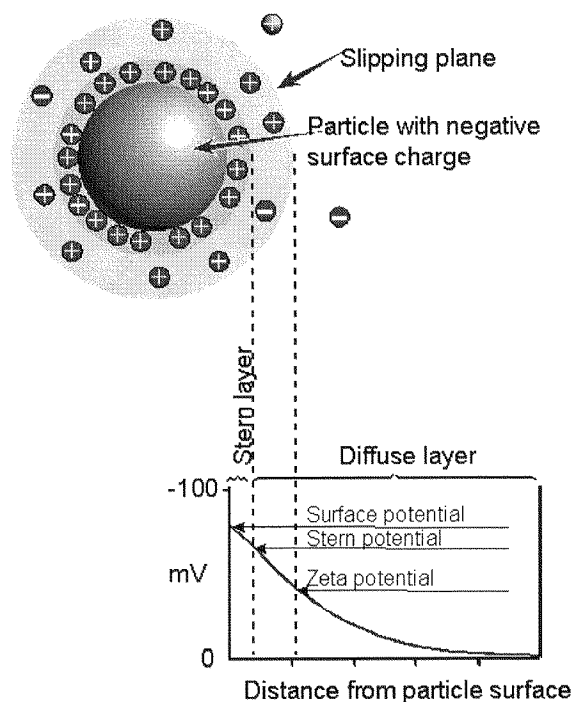


Figure 1 The electrical double layer of a suspended nano-particle.

The most important parameter affecting the zeta potential is the solution pH. In fact, it makes no sense to quote a zeta potential without also quoting a corresponding pH value. The graph shown in Figure 2 shows how pH could affect the zeta potential. In basic solution (high pH) the suspension of particles acquires a negative charge, whereas in acidic solution (low pH) the particles acquire a positive charge. A certain point is reached where the particle has zero charge (neutralized) – this is the **isoelectric point**. From this graph it is likely that most efficient mobility of these particles (in this case) will occur below a pH of 4 or above a pH of 8. Of course, the electro-mobility depends on other factors as well including particle size (measured at UALR), strength of the electric field (voltage gradient), and dielectric constant and viscosity of the solution.

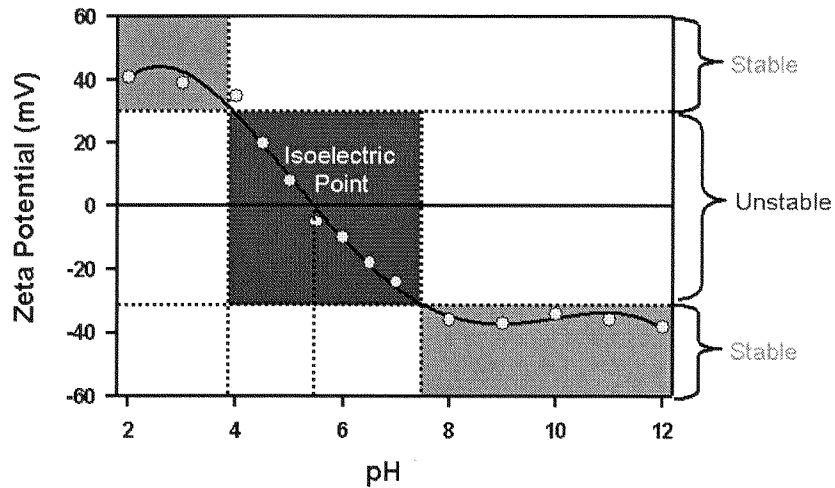


Figure 2 Plot of pH versus zeta potential for a colloidal suspension.

THE OLD WAY OF MEASURING THE ZETA POTENTIAL (RELATED TO THE ELECTROPHORETIC MOBILITY)

Early methods of measuring the electrophoretic mobility involved the process of directly observing individual particles using ultra-microscope techniques and manually tracking their progress over a measured distance as shown in Figure 3.

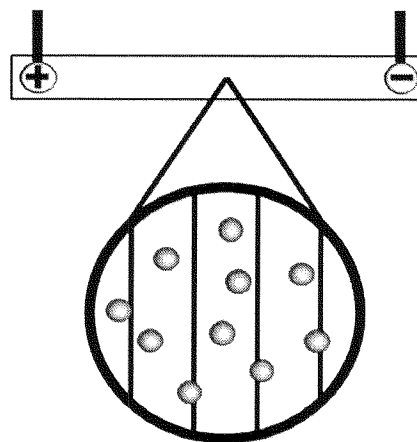


Figure 3 Measuring electrophoretic mobility by timing the movement of particles in a capillary cell using a microscope.