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APPLICATION NOTE

# Monitoring Size and Zeta Potential Changes with Temperature at Different pHs for Magnetic Microspheres

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## Introduction

Magnetic microspheres are composite microspheres formed by combining magnetic inorganic particles with organic polymers. Magnetic composite microspheres not only possess numerous properties of ordinary polymeric microspheres but also exhibit magnetic responsiveness. They can be modified with functional groups (such as -OH, -COOH, -CHO, $-NH_2$, etc.) through methods like copolymerization and surface modification. Additionally, they exhibit directional functionality under the influence of an external magnetic field. Since the 1970s, magnetic microspheres have found widespread applications in various fields, including biomedicine, cell biology, and separation engineering. Ideal magnetic microspheres need to have a sufficiently large specific surface area, uniform surface ligand connections, and a stable separation environment to ensure efficient magnetic separation.

In this application note, the BeNano 90 Zeta was used to monitor the changes in size and zeta potential of magnetic microspheres at different pHs with temperature variations.

Zeta potential is one of the key indicators of the particle system stability. A higher absolute value of zeta potential indicates stronger repulsive forces between particles and therefore higher system stability.

## Instrumentation

Employed with the dynamic light scattering (DLS), static light scattering (SLS), and electrophoretic light scattering (ELS) technologies, the BeNano 90 Zeta was used for the size, molecular weight, and zeta potential measurements.

A solid-state laser beam with a wavelength of 671 nm and a power of 50 mW was used to illuminate the sample. An avalanche photodiode (APD) detector coupled with fiber is used to collect scattered light signals from 12° for zeta potential measurement and 90° for size and molecular weight measurements, respectively.

## Theory

### *Dynamic light scattering (DLS)*

DLS is a sizing technology measuring the diffusion behavior of the particles dispersed in liquids. When nanoparticles are suspended in the liquid medium, the continuous random movement of the nanoparticles are defined as the Brownian motions, whose speed related to the sizes of particles. When a laser beam illuminates the nanoparticles in suspensions, the intensity of scattered light fluctuates due to the Brownian motion of particles. The intensity of the scattered light is then detected by APD and converted to a correlation function using the correlator. By analyzing the correlation function, the diffusion coefficient (D) that describes the speed of Brownian motion is thereby calculated. The hydrodynamic diameter ($D_H$) is obtained using the Stokes-Einstein equation:

$$D=\frac{K_B T}{3\pi\eta D_H}$$

where $k_B$ is the Boltzmann's constant, T is the temperature, and $\eta$ is the viscosity of the solvent.

*Electrophoretic Light Scattering (ELS)*

In an ELS experiment, a laser beam irradiates the sample, where the scattered light is detected at a forward angle of 12°. The sample solution or suspension is subjected to an electric field applied to both ends of the sample cell, resulting in the electrophoretic movement of the charged particles. As a consequence, the scattered light experiences a frequency shift compared to the incident light due to the Doppler effect. The scattered light signals with a frequency shift are converted to phase shift via PALS analysis. By the phase plot, the velocity of electrophoretic movement per unit electric field, which is denoted as the electrophoretic mobility μ, is obtained. Through Henry's equation, one can relate the electrophoretic mobility μ and its zeta potential ξ as follow:

$$\mu = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta} f(k\alpha)$$

where $\varepsilon_0$ is the solvent dielectric constant in vacuum, $\varepsilon_r$ is the relative dielectric constant, η is the solvent viscosity, $f(k\alpha)$ is the Henry function, $k$ is the reciprocal Debye length, $\alpha$ is the particle radius, and $k\alpha$ refers to the ratio between the thickness of the double layer and the particle radius.

Zeta potential is one of the key indicators of the particle system stability. A higher absolute value of zeta potential indicates stronger repulsive forces between particles and therefore higher system stability.

## Experiment

The measured magnetic microsphere sample was a commercialized microsphere, and its surface was modified with unknown functional groups through copolymerization or chemical bonding.

The stock solution of magnetic microspheres was diluted with distilled water, and its pH value was measured to be 6. A certain amount of magnetic microspheres was diluted with HCl solution to a pH of 3, and another amount was diluted with NaOH solution to a pH of 9.

Samples with pH=3, 6 and 9 were separately loaded into PS cuvettes. The size measurements were conducted by increasing the temperature from an initial setting of 25°C to a final temperature of 60°C, with a temperature interval of 1°C.

Additionally, size measurements with decreasing temperature were performed by setting an initial temperature at 25°C, a final temperature at 0°C, and using a temperature interval of 1°C.

Zeta potential vs. temperature trend measurements are conducted by introducing samples with pH values of 3, 6, and 9 into folded capillary cells. The temperature settings for the zeta potential measurement align with those used for the size vs. temperature trend measurement.

## Results and Discussion

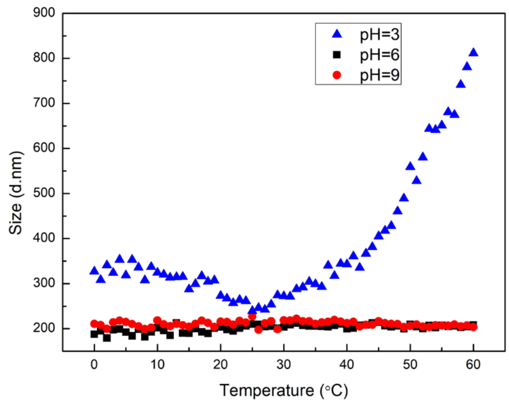


***Figure 1.*** *Size vs. temperature trend results of magnetic microspheres with pH=3, 6 and 9*

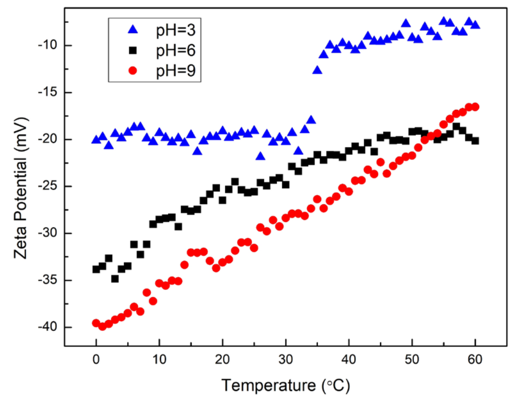


***Figure 2.*** *Zeta potential vs. temperature trend results of magnetic microspheres with pH=3, 6 and 9*

Figures 1 and 2 show the temperature-dependent changes in size and zeta potential of magnetic microspheres at different pHs (3, 6, and 9). It can be observed that at 25°C, the Z-average size of all three samples is around 200 nm, and the zeta potential is negative, indicating negatively charged particles. At 25°C, the higher the pH, the greater the absolute value of the zeta potential.

Within the range of 0-60°C, the size of magnetic microspheres in environments with pH values of 6 and 9 remains relatively stable. However, at pH 3, the sensitivity of particle size to temperature is higher; around 25°C, the particle size is at its minimum. Both cooling and heating stimulate an increase in particle size, indicating the formation of aggregates within the system.

Over the temperature range of 0 to 60°C, the absolute zeta potentials at pH 6 and 9 are higher than that at pH 3 at the same temperature. The higher zeta potential demonstrates stronger interactions between the particles, which improves the stability of the particle system and reduces the likelihood of the formation of large particle aggregates due to external stimuli.

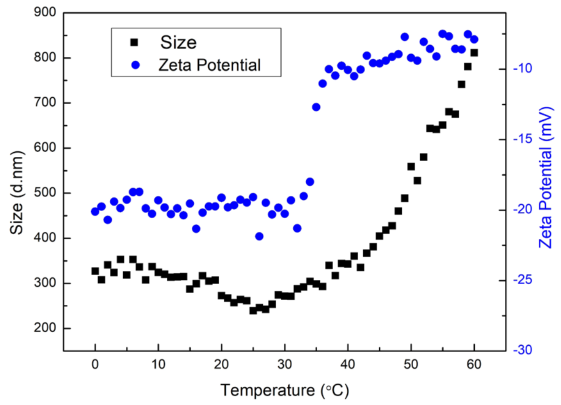


***Figure 3***. *Size and zeta potential results of magnetic microspheres at different temperatures with pH=3*

Figure 3 depicts the temperature-dependent changes in size and zeta potential of magnetic microspheres at pH=3. It can be observed that at 25°C, with increasing or decreasing temperature, the Z-average size tends to increase, especially during the heating process. When the temperature exceeds 34°C, a sudden change in zeta potential occurs, decreasing rapidly from -17.99 mV to around -12.7 mV. Simultaneously, a rapid increase in particle size is observed. It further demonstrates that system stability can be evaluated through zeta potential, with a decrease indicating an unstable state and a higher likelihood of particle aggregation.

## Conclusion

In this application note, the BeNano 90 Zeta was utilized to measure the size and zeta potential of a magnetic microsphere sample. The study investigated various pH levels (3, 6, and 9) and differernt temperature conditions. The findings suggest that the stability of the magnetic microspheres system is notably robust at pH 6 and 9, displaying minimal variations in particle size as temperature changes. However, at pH 3, the system's stability is more susceptible to temperature fluctuations. The observations indicate that in varying pH and temperature settings, particle systems with zeta potential absolute values more than 20 mV demonstrate higher stability.

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