Chapter 2

Experimental Instruments and Testing Procedures

2.1 Test Apparatus and Instruments

The descriptions for the major test apparatus and analytical instruments used for the investigation, including the measured parameters, range, model number, and manufacturer, are listed in Table 2-1 and briefly described as follows:

- Particle size analyzer I, designated as PSA-I, is a large scale particle size analyzer with a measurement range from 0.1 to 2000 μm. Figure 2-1 is a photograph of the PSA-I instrument.

- Particle size analyzer II, designated as PSA-II, is a small scale particle size analyzer with a measurement range from 0.002 to 5 μm. PSA-II is equipped with disposable sample cells that eliminates the cross sample residue influence. Figure 2-2 is a photograph of PSA-II instrument.

- Zeta potential meter. The zeta potential meter and PSA-II are integrated in one unit. The measurement range of the zeta potential meter is from 0.1 to 200 mV with the particle size range from 0.002 to 30 μm. The resolution is sample dependent and in the range of 0.1% to 5%.

- Jar test apparatus: A Phipps and Bird (Model PB-700™ as shown in Figures 2-3 and 2-4) was used. Dimensions of each jar are 11.5 X 11.5 X 21 cm depth which is capable for testing a volume of 2,000 ml water sample. Each jar is equipted with a flat stirring paddle (7.6 X 2.5 cm or 19.3 cm^2). For MC jar test, the area of the paddle was increased to 38.7 cm^2 for MC jar test in order to generate more rigorous turbulence for keeping micro-sand in suspension.

- Turbidity meter.

- pH meter.

- Balance.

Table 2-1. Specifications of Major Instruments

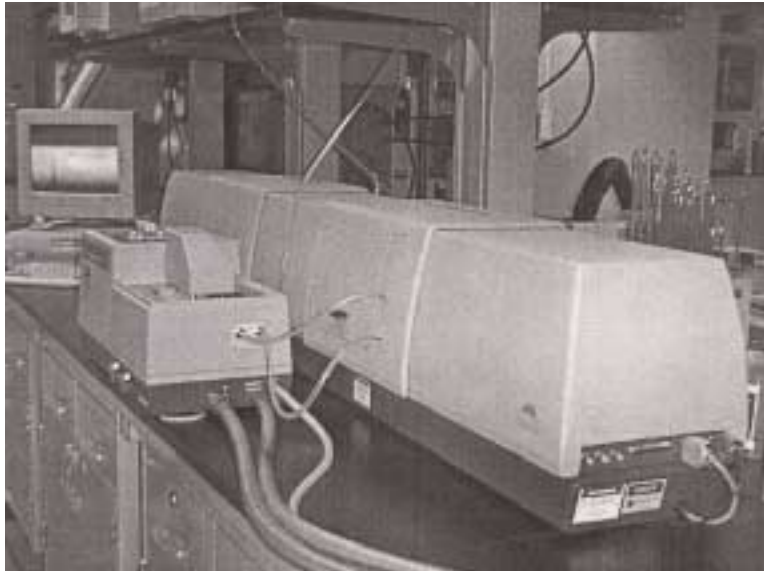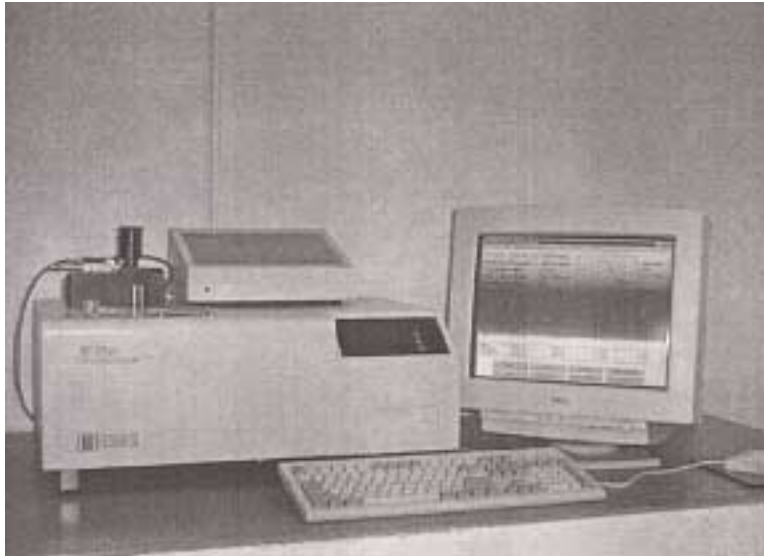| Apparatus/ Instrument	Measurement Parameter	Measurement Range	Model No.	Manufacturer
″ PSA-I	Particle size	0.1—2000 μm	Master-Sizer X	Malvern Instruments Inc. Southborough, MA
PSA-II	Particle size	0.002—5 μm	90 Plus combined ″ with ″ ZetaPlus	Brookhaven Instruments ″ Corporation ″ Holtsville, NY
Zeta potential meter	Zeta potential	0.1—200 mV		
pH meter	pH	1—14		
TOC Analyzer	TOC	4—10000 ppb	700 TOC	O.I. Analytical College Station, TX
Stirrer	Jar Test	0—300 rpm	PB-700™ Jar tester	Phipps & Bird Richmond, VA
Turbidity meter	Turbidity	0—1000 NTU	DRT-15CE	HF Scientific Inc. Fort Myers FL
Balance	Weight	0—210 grams	XS-210	Denver Instrument Co. Arvada, CO

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Figure 2-1. Particle size analyzer

Figure 2-2. Particle size analyzer II with zeta potential meter
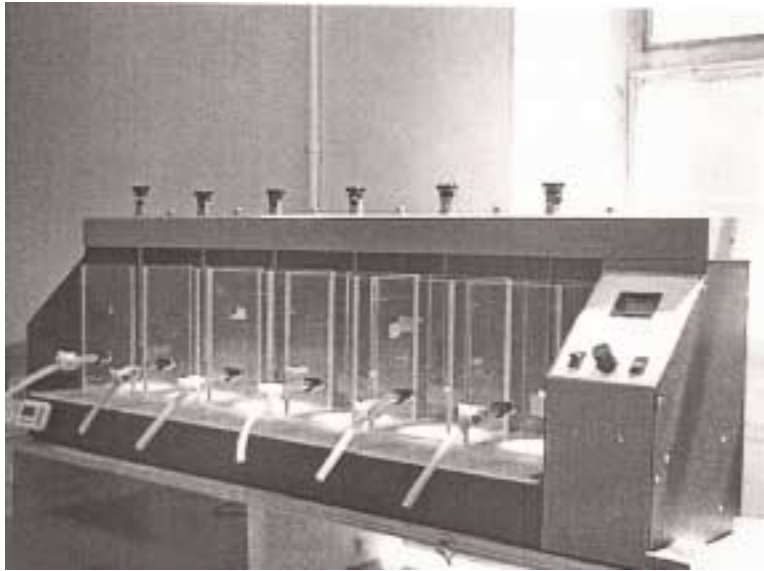
Figure 2-3. Six stirrer jar apparatus

2.2 Testing Procedures

With the exception of zeta potential measurement, all parameter
measurement procedures were based on USEPA procedures or Standard
Methods. The measurement procedures are summarized in Table 2-2.

Table 2-2. Parameter Measurement Procedures

Parameter	Sample Type	Method No.	Method Title	Reference
Particle Size	Stormwater Microcarrier	2560	Particle count and size distribution	Standard Methods[1]
Zeta Potential	Stormwater	Appendix B	Zeta potential measurement	Manufacturer
MC Weighted Jar Test	Stormwater Microcarrier	I-1	Coagulation and flocculation	AEEP[2] (modified)
pH	Stormwater	150.1	pH (electrometric)	EPA[3]
Volatile Solids	Stormwater	160.4	Residue, Volatile	EPA[3]
Turbidity	Stormwater	180.1	Turbidity (Nephelometric)	EPA[3]
Suspended Solids	Stormwater	160.2	Residue, Non-filterable	EPA[3]
Total Solids	Stormwater	160.3	Residue, Total	EPA[3]

[1]Standard Methods, 18th edition supplement (1995). [2]Environmental
Engineering Unit Operations and Unit Processes Laboratory Manual, Association
of Environmental Engineering Professors (1971). [3]Methods for Chemical
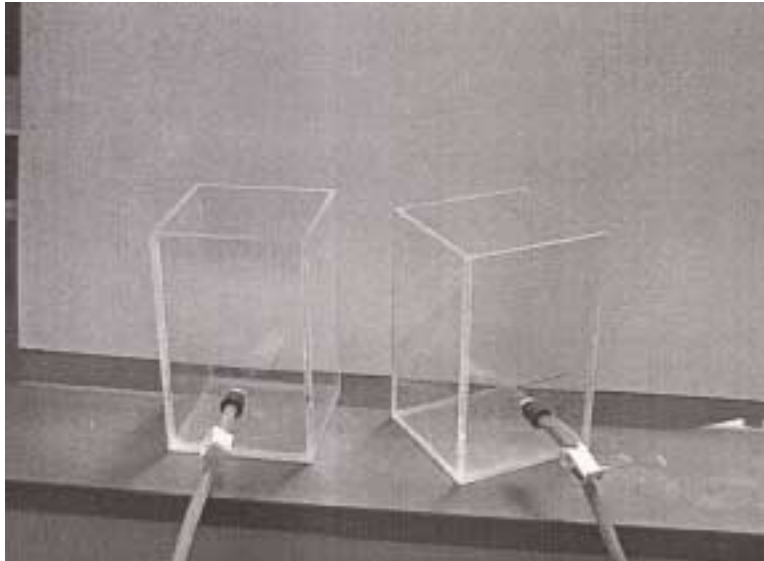Analysis of Water and Wastes, EPA-600/4-79-020 (1983).

Figure 2-4.   Square jars

MC Weighted Jar Test

The jar test has been used as a method for evaluation of the effectiveness of coagulants and coagulant aids for removal of solids in water treatment for many decades. Detailed jar test procedure can be found in numerous publications (Cohen, 1957; Black et al., 1957, 1969; Camp, 1968; AEEP, 1971; ASTM, 1996). However, the MC weighted jar test is a new application due to the different physical characteristics of the mixture.

In the MC weighted jar tests, water samples of equal volume (1,000 ml) were poured into a series of six 2-litter square beakers on a multiple stirring machine equipped with a variable speed drive. After precalculated dosages of the microcarrier, coagulant, and coagulant aid (i.e., flocculant, polymer, or polyelectrolyte) had been added to the beakers, the contents were rapidly stirred to simulate flash mixing and then reducing stirred to simulate flocculation. After a given period of time, the stirring was stopped and the floc formed was allowed to settle.

During the process, illumination aids were used in watching floc formation; however, heating effects from the light were avoided. The controlling parameters are enumerated as follows:

1. The volume of the sample.

2. The size and shape of the container.

3. Peripheral speed and time of rapid mixing.

4. Peripheral speed and time of slow mixing.

5. Type and dosage of microcarrier, coagulant and coagulant aid (i.e., flocculent, polymer, or polyelectrolyte).

The principal procedures include the following steps:

1. Collect storm surface runoff sample, prepare synthetic sample (see Section 3.1), or CSO sample. Measure the sample for pH value and turbidity reading.

2. Pour 1,000 ml of the water sample into each two-liter jar on the jar-test apparatus and check stirrer operation. A light table facilitates viewing of the contents of the beakers.

3. Add controlled amounts of MC, coagulant, and flocculant dosage to the designated jars.

4. Flash mixing for 20—60 seconds at 100—200 rpm.

5. Slow mixing for 10—120 seconds at 30—60 rpm. Record the elapsed time before a visible floc is formed. If large flocs are formed, it may be desirable to reduce the paddle speed. Record the appearance of the floc formed.

6. After flocculation, remove the paddles and settle for 2—30 minutes.

7. Collect the supernatant from the sampling port on each jar and measure the turbidity; the settled solids should not be disturbed during sampling. Select and recored the dosage of coagulant and flocculant based on the supernatant clarity and settleability of floc.

Particle Size Determination

Principle

Both particle size analyzers (PSA-I and PSA-II) used in this study are based on light-scattering techniques using a Helium-Neon laser as the light source. However, the signal collection and conversion for the two instruments are different.

In the PSA-I system, the direct path of the light beam through the flow cell is scattered by a particle as it flows through the measurement zone with the fluid (see Figure 2-5). Scattered light over a fixed range of angles is collected by a photo-voltaic cell. Based on the principles of Fraunhofer diffraction, particle size can be determined from the angle (θ) and intensity (I) of scattering as follows:

$$I \propto \frac{\alpha^2 J_1^2(\alpha \sin\theta)}{\sin^2\theta} \qquad ; \qquad \alpha = \frac{2\pi a}{\lambda}$$

where a is the particle radius; J_1 is the first order Bessel function; and λ is the wavelength. For multi-particles, the resulting responses from all particles are collected and mathematically deconvoluted to generate the size distribution.

In the PSA-II system, the scattered light is collected at a 90 degree angle to the light source (see Figure 2-6). The photon correlation spectroscopy of quasi-elastically scattered light technique, based on correlating the fluctuations about the average scattered light intensity, is the measurement mechanism. The total measurement time is divided into small intervals called delay times. These intervals are selected to be small compared
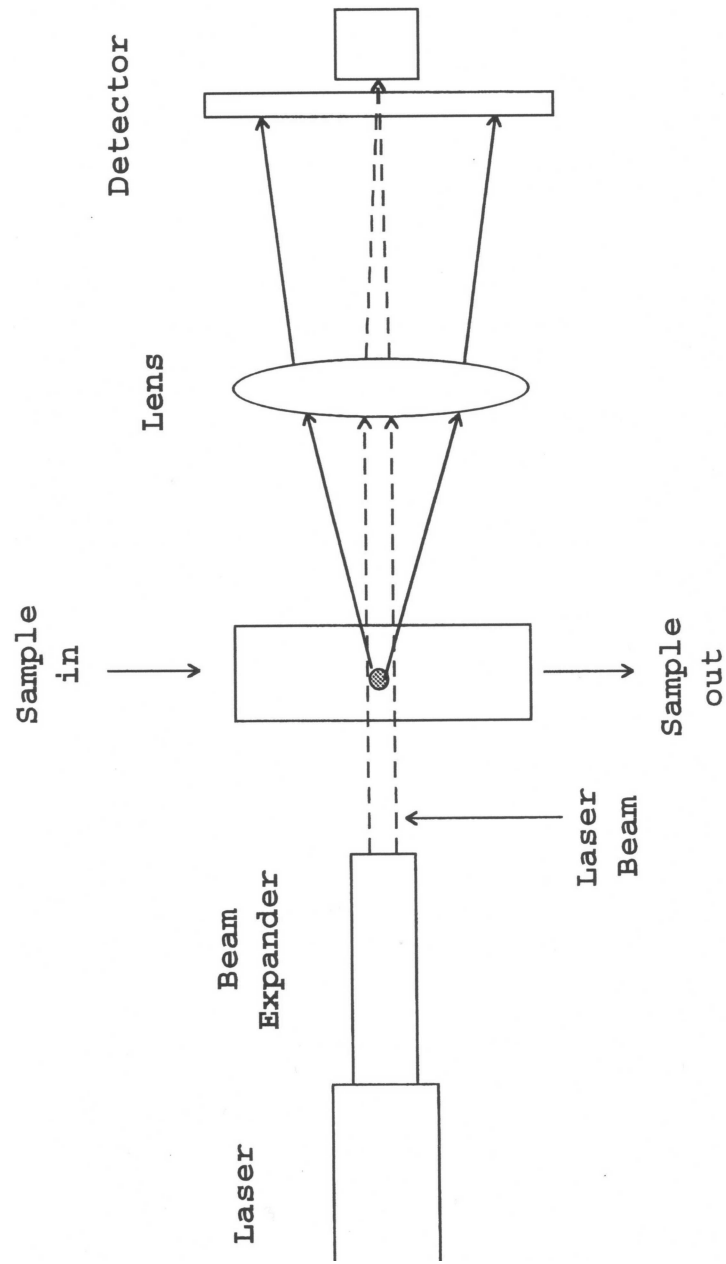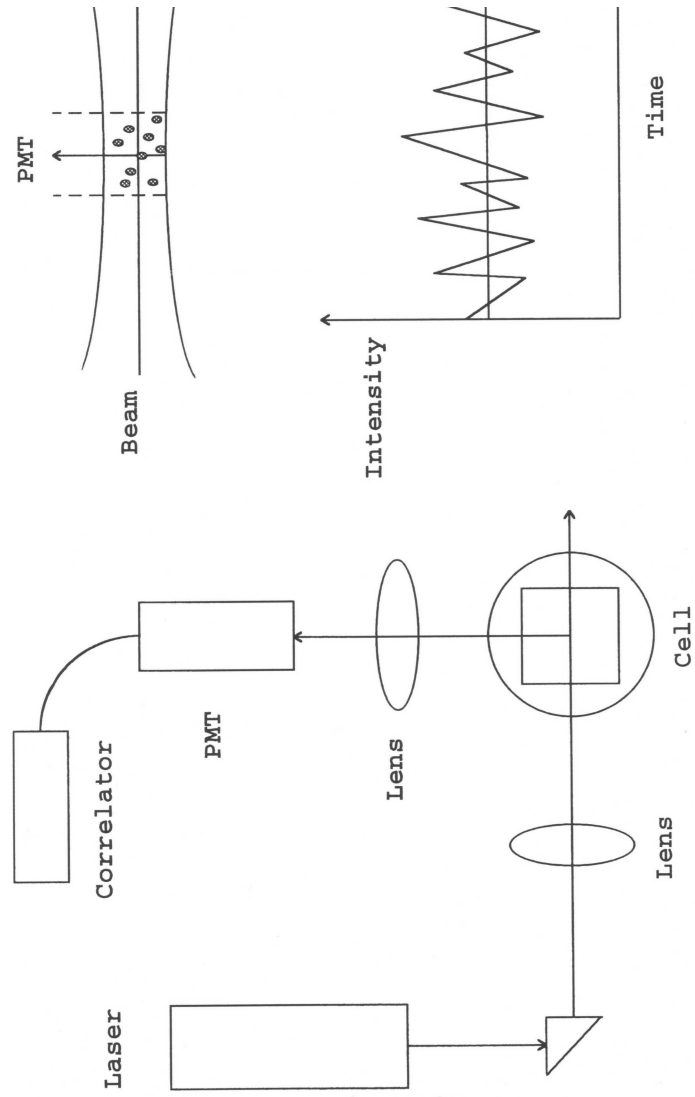
Figure 2.5   Principles of Particle Size Analyzer I

Detector

Lens

Sample
in

Sample
out

Laser
Beam

Beam
Expander

Laser

PMT: Photo Multiplier Tube

Figure 2.6 Principles of Particle Size Analyzer II

with the time it takes for a typical fluctuation to relax back to the average. The scattered light intensity in each of these intervals, as represented by the number of electrical pulses registered during each delay time, fluctuates about a mean value. The intensity auto-correlation function is formed by averaging the products of the intensities in these small time intervals as a function of the time between the intervals (delay times). As the delay time increases (t), the correlation (c) decreases and the function approaches the constant background term B. In between these two limits the function decays exponentially for a monodisperse suspension of rigid, globular particles and is given by

$$c(t) = Ae^{-2\Gamma t} + B$$

where A is an optical constant determined by the instrument design, and Γ is related to the relaxation of the fluctuations by

$$\Gamma = D q^2$$

where D is the transitional diffusion coefficient. The value of q is calculated from the scattering angle (θ = 90 degrees), the wavelength of the laser light ($\lambda = 0.635$ μm), and the index of refraction (n) of the suspending liquid. The equation relating these parameters can be expressed as

$$q = \frac{2\pi n}{\lambda} 2\sin\left(\frac{\theta}{2}\right)$$

For a sphere, there is

$$d = \frac{kT}{3\pi\eta D}$$

where d is the particle diameter; k is Boltzmann's constant; T is the temperature; and η is the viscosity of the liquid in which the particle is moving. The above equation is based on the assumption that the particles are moving independently of one another. In case a particle is not spherical, the d calculated from the above equation is considered as a particle size indicator.

Measurement Procedure

The principal steps for particle size distribution measurement, in accordance with the Standard Methods For Examination of Water and Wastewater (Standard Methods, 1995), are enumerated as follows:

1. Preparation. The instrument and any sample handling unit should be switched on and any connections between the optical unit, sample handling unit and computer should be in place. The correct range lens should be fitted to the

instrument and the lens caps removed. Any sample cell
should be correctly fitted and the windows should be
clean. In particular, the correct instrument range should
be selected.

2. Background measurement. A background measurement is
    necessary before any sample measurement.

3. Blank sample measurement. Measure at least one blank
    sample of particle-free water.

4. Calibration. Calibrate by determining the channel number
    into which particles of known size are sorted by the
    instrument. Use spherical particles manufactured for this
    purpose. Use three sizes of calibration particles in
    similar concentrations to calibrate a sensor. Calibrate
    under conditions identical with those of the sample
    measurement, e.g., settings on the instrument, flow rate,
    and type of sample cell.

5. Measurement of samples. The light scattered by the
    particles must be measured for a suitable period to ensure
    that all particles are represented in the measurement and
    to average out fluctuations caused by the dispersing
    medium. A suitable measurement period is 10 to 30 seconds
    depending on the size range of the distribution.

6. Data reporting. Particle concentrations should be shown
    in both tabular and graphical formats.

In the course of experiments, it was found that the large
particles (> 5 μm) produced interferences during the measurement
of small particles (< 5 μm). Furthermore, the measurement of
small particles was found to be inconsistent in the presence of
large particles, even if a low concentration of large particles
existed. In order to eliminate the interferences from large
particles, a special filtration process was necessary before
measuring the small particle size. An attempt was made with
different types as well as different pore size filters. It was
concluded that filter paper (regardless of type) was not suitable
for this experiment. Having experimented with other filtering
processes, a disposable nylon syringe filter with 5 μm pore size
was found to be suitable for the study.

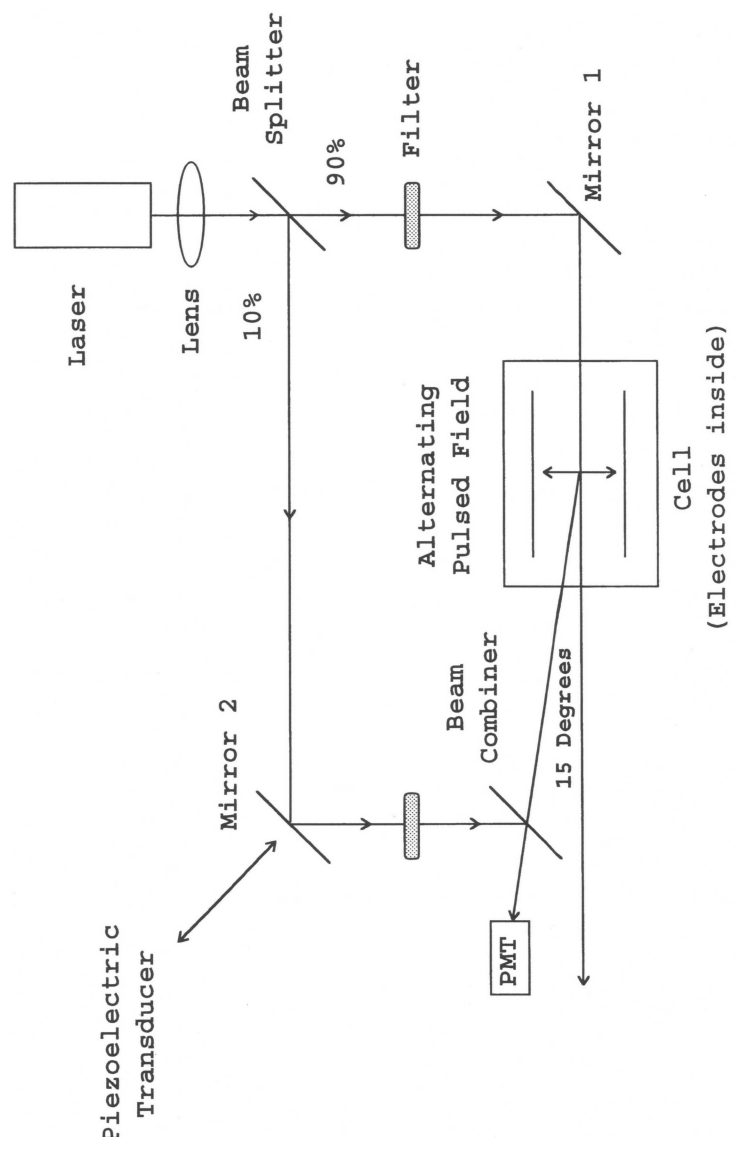### *Zeta Potential Measurements*

Principle

The basic principles of zeta potential measurements include three
different aspects. First, the velocity (V) of charged colloidal
particles in liquids between the electrodes is measured by a
laser Doppler shift. Second, the electrophoretic mobility (μ)
is determined based on the measured velocity and the electric
field strength (E) by the equation $V = \mu E$. The zeta potential (ζ)
can be calculated from the solution conditions and the mobility

by the equation $\zeta = \mu\eta/\varepsilon$ where η is the viscosity of the liquid and ε is the dielectric permittivity. However, the equation is only correct for certain combination of particle size and ionic strength. Either mobility or zeta potential may be used as measures of dispersion stability although zeta potential is used more widely. The principles of zeta potential measurement are illustrated in Figure 2-7.

Measurement Procedure

A detailed testing procedure that is recommended by the manufacturer is given in Appendix B. Major steps are outlined as follows:

1. Instrument preparation.

2. Background measurement.

3. Blank sample measurement.

4. Calibration.

5. Sample preparation.

6. Clean the electrodes and insert the electrode assembly into the cell.

7. Insert the cell into the cell compartment.

8. Make a measurement.

Laser

Lens

Beam
Splitter

90%

Filter

Mirror 1

10%

Alternating
Pulsed Field

Cell
(Electrodes inside)

Mirror 2

Beam
Combiner

15 Degrees

PMT

Piezoelectric
Transducer

PMT: Photo Multiplier Tube

Figure 2.7   Principles of Zeta Potential Measurement