

WHITEHOUSE SCIENTIFIC BCR 'MIRROR' STANDARDS
(Project MATI-CT92-0023)

Methodology Details for Electrical Sensing Zone Method - Dr J Lloyd

Introduction

This procedure follows a draft ISO standard and is designed to produce comparable, traceable results. It is essential that the procedure is followed exactly by all participants **DO NOT USE YOUR OWN PROCEDURES**. Primary Calibration Material will be supplied (Either NIST or BCR). Secondary calibration material will also be supplied for linearity checks.

It may be necessary to change the electrolyte for the final accreditation.

Procedure

1. Electrolyte

1.1. Preparation

Prepare electrolyte for 1-10 μ m and 1-30 μ m samples as follows:-

Prepare 5% solution of Na(PO₃)₆ in distilled water. Filter through 0.8 μ m using vacuum filtration if possible.

For 1-100 μ m material prepare electrolyte as above but use 40% glycerol/60% distilled water.

1.2. Instrument/Electrolyte Noise Check

With fresh electrolyte, including any glycerol and dispersing agent to the correct concentration. Obtain a size distribution and calculate the equivalent volume. This should be less than 1% of the volume measured with the test material in the instrument. If it is not refilter the electrolyte through a 0.8 μ m or smaller membrane filter, preferably using vacuum filtration, and recheck. If the noise level is still too high, the instrument should be checked by the Manufacturer for correct balancing of the electronics.

2. Preliminary Instrument Check

2.1. Latex Calibration

Before each certification run, calibrate the instrument with the primary calibration latex. Count a large number of particles (about 100,000). Select the modal value from the histogram. If the histogram has a clear double peak then the use of a pulse edit facility will remove the false peak due to the artefact observed when very monosized particles are sized. If your instrument does not have this facility, choose the peak corresponding to the smaller channel number. The second peak will only be apparent for the 100 μ m orifice tube. Switch off the edit facility after the calibration.

Orifice Diameter ¹ μ m	Primary Calibration Size ² μ m	Secondary Calibration Size μ m	Secondary Calibration Size μ m
50 (48)	10	2.8	5
100 (95)	10	5	30?
2003 (190)	10	20	30?

Table 1: Latex sizes for calibration and linearity check

¹ If using the Electrozone or other Electrical Sensing Zone method use nearest available orifice sizes.

² This calibration latex will be supplied for the accreditation but for the mirror samples use standard calibration latex of similar size and will be either NIST or BCR.

³ This orifice size may be changed if there is too many particles greater than 100 μ m are present in the reference material.

2.2. Linearity Check

After the calibration with the primary latex, measure the sizes of the latexes according to Table 1, for each orifice tube.

Record the measure size for each secondary calibration material. Calculate the % difference between instrument and standard size and record the %.

2.3. Instrument/Electrolyte noise Check

With fresh electrolyte, including any glycerol and dispersing agent to the correct concentration. Obtain a size distribution and calculate the equivalent volume. This should be less than 1% of the volume measured with the test material in the instrument. Record the noise instrument volume per ml of suspension. If the value is greater than 1%, filter the electrolyte through a 0.8 μ m membrane filter, preferably using vacuum filtration, and recheck. If the noise level is still too high, the instrument should be checked for correct balancing of the electronics.

2.4. Siphon volume

Using a suspension of latex, measure three times the total particle count with the 0.5ml siphon volume. Switch to 2ml volume and measure the total particle counts at least three times. Since the siphon volume at 0.5ml is guaranteed to 0.2% this will standardise the volume at the 2ml setting to a measurable degree of accuracy. Record all counts.

Check balance with a standard weight traceable to standard kilogram. Record all weighings.

3. Sample Preparation

Obtaining mass traceable samples has not been easy, the following method has proved in our laboratory to be the best. A stock suspension is prepared using all of the sample. This is suspended in the electrolyte which is 5% Na(PO₃)₆ (for the 1-100 μ m sample the electrolyte which is 40% glycerol/60% Na (PO₃)₆). The beaker containing the suspension is then placed in a ultrasonic bath for 45s. 5ml (10ml for 1-100 μ m samples) of this suspension is withdrawn using a micro pipette from the well stirred stock solution and is then added to approximately 400ml electrolyte and placed from the well stirred stock solution and is then added to approximately 400ml electrolyte and placed in the ultrasonic bath for approximately 15s. *The best beaker is round bottomed with a baffle of about 400ml capacity.*

3.1 Preparation of Stock Solution (suspension)

Remove label etc. from the sample vial, and weigh	$M_{\text{sample+vial}}$
Weigh dry beaker	M_{beak}
Wash sample into beaker with electrolyte and make up volume to approx. 400ml. Weigh	$M_{\text{beak+sample+elec}}$
Dry vial and weigh	M_{vial}
Mass of sample	$M_{\text{sample}} = M_{\text{sample+vial}} - M_{\text{vial}}$
Mass of electrolyte	$M_{\text{elect}} = M_{\text{beak+sample+elec}} - M_{\text{beak}} - M_{\text{sample}}$
Density of electrolyte	ρ_e
Density of sample	ρ_s
Weight of suspension	$W_{\text{susp}} = M_{\text{samples}} + M_{\text{elects}}$
Concentration of Stock Solution g/g	$C_{\text{stock}} = M_{\text{sample}} / W_{\text{susp}}$

3.2 Preparation of suspension for analysis

Mass of dry beaker	M_{beak2}
Mass of beaker + approx. 400ml electrolyte	$M_{\text{beak2+elect}}$
Extract approx. 5ml (or 10ml) from stock solution and add to beaker	$M_{\text{beak2+elect+extr}}$
Mass of extract	$M_{\text{extr}} = M_{\text{beak2+elect+extr}} - M_{\text{beak2+elect}}$
Weight of solids added	$M_{\text{solids}} = M_{\text{extr}} * C_{\text{stock}}$
Weight of electrolyte	$M_{\text{elect2}} = M_{\text{beak2+elect+extr}} - M_{\text{beak2}} - M_{\text{solids}}$
Volume of electrolyte	$V_{\text{elect2}} = M_{\text{elect2}} / \rho_e$
Volume of solids	$V_{\text{solids}} = M_{\text{solids}} / \rho_s$
Volume of solids/ml suspension	$= V_{\text{solids}} / (V_{\text{solids}} + V_{\text{elect2}})$

See appendix 1 for method of measuring the densities ρ_e and ρ_s .

4. Analysis

4.1 Select orifice tube according to following table:-

erm size range μm	Orifice Tube μm	Siphon Volume ml	Max count for 5% coincidence
1-10	50	0.5	160,000
3-30	100	0.5	20,000
10-100	200	2.0	10,000

Table 2

4.2

Select **maximum** number of channels for the instrument and set the lowest channel to that equivalent to the size of the minimum particle size.

4.3

Select the siphon volume, make an analysis and ensure that the total count is less than that specified for 5% coincidence in Table 1 or the coincidence level indicated by the instrument (whichever is the smaller). If the coincidence count is exceeded, add more filtered electrolyte and record the new weight total weight $M_{\text{beak2+elect+extr}}$ when the count is not above 5% coincidence count level. Recalculate the new volume concentration. Accumulate the results for a number of runs until the total count is above 1000,000. Record this result and repeat 5 times.

4.4 Calculate the instrument volume concentration as follows:-

Obtain an analysis of the material under test as specified above at the maximum resolution of the instrument. Either using the software of the instrument or from the data obtain the total volume of the particles per ml of suspension. Calculate the volume using the following equation:-

$$\text{Volume} = \sum_i \frac{(\pi \times d_i^3)}{6}$$

$$\text{where } d_i = \text{mean size of channel limits} = \frac{d_i + d_{i+1}}{2}$$

The instrument particle volume concentration is this volume divided by the siphon volume. This concentration is now compared to the actual volume concentration obtained above. These values should agree to within 5%. If they do not, attention should be given to the stirring in the beaker, as there may be segregation in the vessel. Repeat the check.

If this value is not within the value calculated above to less than a 5% difference, check the stirring. If it is not possible to match the concentrations, adjust the volume concentration and repeat the analysis.

4.5. Obtain 5 replicates for each dispersion.

4.6. Repeat for at least 4 more dispersions each produced as above.

5. Reporting

5.1.

Send all data on a 3½" computer disk. If you are using a Multisizer with Acucomp the computer files on the hard disk should be copied. If not please save the data as an ASCII file and if possible send a key.

5.2.

In addition to the above please complete the data sheet and send to the Working Group Leader, John Lloyd, Department of Chemical Engineering, University of Technology, Loughborough. LE11 3TU. UK.

6. Data Sheet for Electrical Sensing Zone Method

Sample Number	<input style="width: 50px;" type="text"/>	1-10 μ m	Laboratory	<input style="width: 100px;" type="text"/>
	Instrument/Electrolyte noise check		1-10 μ m (10179)	<input style="width: 100px;" type="text"/>
Instrument volume/ml	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Latex Calibration				
Latex Size	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Instrument Size	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
% Difference	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Siphon Volume				
Count at 0.5ml	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Count at 2.0ml	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Average Count at 2.0ml /Average Count at 0.5ml =				<input style="width: 30px;" type="text"/>
Standard Weights				
Standard Weight	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Balance Reading	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>		<input style="width: 30px;" type="text"/>
Stock Solution				
Density of solids	<input style="width: 30px;" type="text"/>	g/ml		<input style="width: 30px;" type="text"/>
Density of electrolyte	<input style="width: 30px;" type="text"/>	g/ml		<input style="width: 30px;" type="text"/>
Mass of vial + sample	<input style="width: 30px;" type="text"/>			g
Mass of Dry Beaker	<input style="width: 30px;" type="text"/>			g
Mass of beaker + sample + elect	<input style="width: 30px;" type="text"/>			g
Mass of vial	<input style="width: 30px;" type="text"/>			g
Mass of sample	<input style="width: 30px;" type="text"/>			g
Mass of electrolyte	<input style="width: 30px;" type="text"/>			g
Weight concentration	<input style="width: 30px;" type="text"/>			g/g
Volume of electrolyte	<input style="width: 30px;" type="text"/>			ml
Volume of solids	<input style="width: 30px;" type="text"/>			ml

Calculation of weight concentration after dilution

	Run 1	Run 2	Run 3	Run 4	Run 5	
Mass of Beaker	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Mass of Beaker sample	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Mass of Beaker + electrolyte + extract	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Mass of Extract	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Mass of solids added	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Mass of electrolyte	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	g
Volume of electrolyte	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	ml
Volume of solids	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	ml
Vol solids/ml suspension x 10 ⁶	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	μ m ³

Calculation of machine volumes

Sample Volume	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	ml
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
Average Machine Volume/ml	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	μ m ³
% error	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
Particle Counts	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	
Average particle counts	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	<input style="width: 30px;" type="text"/>	

Weight undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

Number undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

ORDER 1. SAMPLE 1-10µm. LOT 10179 A. INDIVIDUAL RESULTS - A-C

Weight undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

Weight undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

Weight undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

Number undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

ORDER 2. SAMPLE 1-10µm. LOT 10179 B

Weight undersize distribution results

						Average	Std Dev
10%							
25%							
50%							
75%							
90%							

Number undersize distribution results

					Average	Std Dev
10%						
25%						
50%						
75%						
90%						

Appendix Measurement of Density

A.1 Principle

The immersed density of a representative sample of the powder is determined by liquid displacement in a density bottle.

A.2 Immersion liquid

This will be the electrolyte solution and dispersant to be used for the particle size analysis.

A.3 Procedure

A.3.1 General. Maintain the water bath at the same operating temperature throughout the following procedure.

A.3.2 Determination of density of electrolyte/dispersant solution.

- a) Clean and dry the density bottle and stopper and weigh to an accuracy of $\pm 0.0005\text{g}$.
- b) Fill the bottle with de-aerated distilled or deionized water at room temperature and, without using undue force, insert the stopper with slight twist, taking care to avoid trapping air bubbles.
- c) Immerse the bottle nearly to the top of its neck in the water bath and leave for at least 30 minutes.
- d) After ensuring that air bubbles are absent and that the bottle is filled to the top of the capillary bore, remove with dry filter paper any water on the top of the neck of the bottle where stopper and neck meet, and dry sides and the top of the stopper, taking care not to withdraw any from the capillary.
- e) Remove the bottle from the water bath, wipe it free of water with the minimum of handling and weigh to an accuracy of $\pm 0.0005\text{g}$.
- f) By topping up the bottle with more distilled or deionized water, repeat operations c) to e) twice, thereby making two additional weighings of the bottle filled with water.
- g) Calculate the mean of these three weighings, and from the difference between this mean weighing and the first weighing of the bottle and stopper alone, calculate the mass (W_1) of water to fill the bottle at the selected operating temperature.
- h) Repeat operations a) to g), but filling the bottle with the electrolyte/dispersant solution instead of water, and determine the mass (W_2) (average of three weighings) of the liquid to fill the same bottle at the selected operating temperature.

Calculate the density of the electrolyte/dispersant solution, to the nearest 0.5kg/m^3 , from the equation.

$$\rho_L = \frac{W_2}{W_1}$$

NOTE: Table 3 gives the variation in the density of pure water with temperature.

Temperature °C	ρ_w
18	998.6
19	998.4
20	998.2
21	998.0
22	997.8
23	997.6
24	997.3
25	997.1
26	996.8
27	996.5
28	996.3

Table 3. Density of pure water, ρ_w

A.3.3 Determination of immersed density of powder. Using the procedure described in D.3.2., calibrate the density bottle and stopper by determining the mass (W_3) (average of three weighings) of the bottle, stopper and electrolyte/ dispersant solution to fill the bottle at the selected operating temperature.

- a) Clean and dry the calibrated density bottle and stopper and weigh to an accuracy of $\pm 0.0005\text{g}$.
- b) Weigh out to an accuracy of $\pm 0.0005\text{g}$ to 10g to powder taken representatively (W_4). Disperse by spatulation with dispersant, or by the method chosen for the particle size analysis, transfer to the weighing bottle using a small funnel, and washing the electrolyte. Half of three-quarters fill the bottle with electrolyte, ensuring that the powder is thoroughly dispersed by treating the ultrasonics where possible, care being taken to keep the particles clear of the neck of the bottle.
- c) Fill the electrolyte/dispersant solution and insert the stopper.
- d) Using the same procedure as described in D.3.2. Determine the mass (W_5) (average of three weighings) of the bottle stopper, powder sample and electrolyte/ dispersant solution to fill the bottle at the selected operating temperature.

A.4 Calculation

Calculate the immersed = density ρ of the sample of powder to the nearest 1kg/m^3 from the equation

$$\rho = \frac{W_4 \rho_L}{W_3 + W_4 - W_5}$$

Appendix - Whitehouse Scientific Procedures

Elzone Electrical Sensing Zone Method

The methodology was according to the specified guidelines (see appendix) with the following modifications for the Elzone 280 PC.

A 400ml beaker was not available for the ESZ, so on having a capacity of 210ml was used. This had the advantage that it only weighed 104gm so it could be weighed to 0.1mg on a microbalance. A calibration weight of 100.0000gm was used and the balance calibrated immediately before a weighing.

The balance itself was mounted on a vibration free platform so that a true reproducibility of 0.1mg was achievable. This was very important as will be seen later.

Considerable difficulty was experienced in withdrawing reproducible 5ml aliquots from the stock suspensions, especially in the case of 10-100 μm sample. Because of the accuracy of weighing system it was therefore decided to add the dry powder directly to the measuring beaker. The 3-30 μm and 10-100 μm samples were first subdivided on a 16 stage spinning riffler to ensure good reproducibility. The 1-10 μm sample was sampled by spatula because there was less of a chance of size segregation and the quantities involved were only 3-5 milligrams.

The volume of the electrolyte was metered in directly using a 10ml Eppendorf Pipetter. Separate tests were carried out to show that the reproducibility was to within 0.1%.

The electrolyte was filtered through a 0.05 μm filter and the particle count was never above about 60 for any siphon volume. A 30% glycerol solution (rather than the recommended 40%) was used to speed up the filtration process. This was found to be quite adequate for the keeping the 10-100 μm samples in suspension.

In the case of the 10-100 μm sample, the reduced volume of the measuring beaker limited the number of tests to 4 rather than 5 but the reproducibility was excellent so 5 were not necessary.

There was considerable difficulty in obtaining good volume balances from the 3-30 μm sample. Losses of over 20% being quite typical. Given the high stirring speed, it was unlikely that particles were settling out, but there was some evidence that prolonged stirring could, in some cases, produce a scum on the top of the beaker, which could account for the particle loss. After running most of the 16 samples, it was decided to only use the data where volume balances were below 20%.

Where possible the data generated was compared to other methods of sizing. Excellent agreement was obtained with the Andreasen Pipette for the 1-10 μm and 3-30 μm samples and with the Microscope volume and Electroformed sieve analysis for the 10-100 μm sample.