

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

Methodology Details for Gravitational Sedimentation - Prof. K Leschonski

1. Experimental

1.1 Equipment

Apart from the pipette and the sedimentation vessel, additional equipment is necessary for sedimentation analysis:

- o ultrasonic bath to disperse the samples
- o thermostated water bath, constant to 0.1°C to keep the pipette in thermal equilibrium during the analysis
- o 20 numbered and weighed aluminium dishes
- o analytical balance (0.1mg accuracy)
- o thermometer (0.1°C accuracy)
- o water jet air pump
- o heating plate for evaporating the sedimentation liquid
- o oven for drying the samples
- o dessicator
- o stop watch
- o wash bottle filled with distilled water
- o wash bottle filled with sedimentation liquid
- o crucible tongs

1.2 Calibrations

Fill the vessel, with the pipette in situ, with distilled water to the inscribed calibration marks (100mm for the 1-10µm samples, 200mm for the 3-30 and 10-100µm samples) and weigh.

Repeat this process several times. On each occasion the water temperature is measured. Calculate the appropriate water density. Calculate the volume from the measured mass of water. The height of sedimentation, h , changes with each sample extraction. The decrease in sedimentation heights from both the 200mm and the 100mm calibration marks are measured to 0.1mm. Therefore extract at least 10 x 10 cm³ samples of distilled water via the pipette. Measure the drop in sedimentation height. The mean decrease in sedimentation height per sample extraction is then calculated.

1.3 Time-Table Set Up

Samples should be taken at fixed size intervals, given in the form fixed in this guideline.

To calculate the extraction time you have to fill in the missing values of:

- solid density, ρ_s ,
- measurement temperature,
- volume of the sedimentation vessel,
- mean drop in sedimentation height, Δh ,
- tabulated values for liquid density and
- viscosity of dispersant

(see examples in tables 1 - 3)

1.4 Preparation of the Aluminium Dishes

Place the dishes in an oven at 100°C and let them dry for about 2 hours. Allow the dishes to attain room temperature in a dessicator for about 1-2 hours. The dessicator should contain only one layer of dishes. Weigh the dishes to 0.1mg.

1.5 Determine the Concentration of the Dispersant

Fill the instrument partly with dispersant solution - a 0.1 mass % aqueous solution of sodium hexametaphosphate is used for the 1-10µm and 3-30µm samples. For these samples distilled water is used as sedimentation liquid.

Withdraw 4 x 10 cm³ samples and transfer each to separate dried aluminium dishes. Evaporate the samples to dryness in an oven at 80-90°C, allow to cool to room temperature in a desiccator (not longer than 3-4 hours). Weigh to 0.1mg and calculate the dispersant concentration.

For the coarse size range 10-100µm a 40% ethylene glycol/ 60% distilled water mixture is used without the sodium hexametaphosphate so determining the concentration of the dispersant is not required.

1.6 Sample Preparation

The sample masses provided for the round-robin tests are of the size of 1g. Weigh to 0.1mg and make sure that the volume concentration c_v does not exceed $2 \cdot 10^{-3}$:

$$c_v = \frac{V_s}{V_{fl}} = \frac{m_s}{\rho_s V_{fl}} \quad (1)$$

where m_s = sample mass, ρ_s = particle density and v_{fl} = volume of suspension in the sedimentation vessel at the beginning of the experiment.

The sample mass can be calculated from the following equation:

$$m_s = c_v \rho_s V_{fl} \quad (2)$$

Add approximately 150cm³ of the dispersant solution to the solid sample. Place the suspension in an ultrasonic bath for 5 minutes for efficient dispersion. Transfer it to the sedimentation vessel. Add dispersant solution until the 200mm mark is reached, with the pipette in position within the instrument. The instrument is then transferred to a thermostat set at 20°C. Allow to reach thermal equilibrium.

2. Size Analysis

2.1 Homogenisation of the Suspension

Remove the instrument from the thermostat and wipe it dry. To homogenise the suspension in the vessel a special mixing procedure is suggested:

Take the pipette plunger into your right/left hand so that the capillary stands out between your index and your middle finger. Press the palm of your hand against the vessel, the thumb put on the ground-in stopper.

With the left/right hand take the bottom of the sedimentation vessel. Move the apparatus in an angle of 180° to the left and right side and to the front so that the bottom of the vessel points to the top and to the ground. Repeat this process for about one minute once in a second.

2.2 The Initial Mass Concentration $c_{m/0}$

The initial mass concentration may also be determined experimentally. The following procedure should then be applied:

Thoroughly mix the suspension as described above. Put the apparatus down beside the water bath and connect it to the pump. The pressure should be adjusted to allow a suction time of 20 seconds. Fill the pipette until the 10 cm³ mark is reached. Close the two way tap and turn the pump off. The withdrawal of the sample should be completed before the largest particles have settled past the measuring zone (tip of the pipette). Turn the tap and let the suspension run out into one of the alumina dishes. Clean the pipette by sucking in a small amount of distilled water through the outlet of the pipette. Let the water flow back into the dish. Repeat this process one more time. Put the aluminium dish onto the heating plate and let the liquid evaporate gently. Take two more samples in the same manner after re-dispersion of the sample. After the third extraction repeat the process of manual dispersion.

2.3 Sampling

Put the instrument back in the water bath. Make sure that it attains a vertical position to avoid errors due to wall effects or convection. Start the stopwatch. Samples are extracted according to the pre-determined timetable, see example.

As the settling velocity of the larger particles in the 10-100µm size range is high, there is normally only very short time between each extraction. To avoid problems, it is suggested that the sampling is done in three steps as shown in the example time-table. Between each of these three steps the suspension is re-dispersed. Because of an extraction time of about 20 seconds, the sampling should be started 10 seconds before the pre-determined time.

2.4 Drying the samples

After evaporation of the liquid allow the aluminium dishes to dry in an oven at 90°C for one hour. Put the dishes into a dessicator. Each dessicator should contain only one layer of dishes. Allow the samples to obtain room temperature. This lasts approximately one hour. Place the dessicator near the balance. The samples are then weighed to 0.1mg. Use a pair of crucible tongs for the handling of the dishes. The mass of dispersant has to be subtracted from the measured masses.

2.5 Calculation of Q_3

Calculate the particle size distribution, Q_3 versus x_w . If the withdrawn sample volumes are the same (-10 cm^3), Q_3 is equal to the ratio of the mass, m , of particles in the sample withdrawn at time to the mass, m_0 , in samples withdrawn from the initially homogeneous suspension:

$$Q_3 = \frac{m}{m_0} \quad (3)$$

Otherwise the formula has to be corrected with the actual withdrawn volumes:

$$Q_3 = \frac{mV_0}{m_0V} \quad (4)$$

3. Report

The report should contain the following information:

- o name of institution
- o name of sample and density
- o description of apparatus, (pipette type, vessel volume)
- o type of sedimentation fluid (density, viscosity, temperature)
- o type and duration of dispersion
- o table containing the measured data, graphical representation of $Q_3(x)$

Results should be reported in written form and on a floppy disk either in Excel or Lotus 1-2-3 format.

Table 1: Gravitational Sedimentation (Andreasen Pipette), Size and time-table for 10-100 μm standard

size range: 10-100(μm)	solid density, ρ_s : <i>2,7</i> – <i>by way of example</i>	(g/cm^3)
sedimentation liquid:	liquid density, ρ_f : <i>1,0514</i>	(g/cm^3)
40 mass % ethylene glycol	viscosity, η : <i>2,826 10²</i>	($\text{g}/\text{cm s}$)
	vessel volume, V : <i>560</i>	(cm^3)
temperature, T : 20 ($^\circ\text{C}$)	sedimentation height, h : 20	(cm)
	mean drop in sedimentation height, Δh : <i>0,63</i>	(cm)
	weight of sample, m : <i>2,2786</i>	(g)
	concentration, $c_{v,0}$: <i>1,507 10³</i>	

numbers in italic = assumed values, must be verified by each participant!

$$t = \frac{18\eta h}{(\rho_s - \rho_f) g x_w^2} ; t[\text{min}] = 524,21 \frac{h[\text{cm}]}{x_w^2[\mu\text{m}]}$$

3 determinations of concentration of homogenous suspension: $20\text{cm} - (3 \times 0.63\text{cm}) = 18.11\text{cm}$

	No.	$x(\mu\text{m})$	$h(\text{cm})$	$t(\text{h:mins})$	
I	1	98,6	18,11	0:00:59	
	2	49,3	17,4	0:03:45	re-disperse
II	3	82,8	16,77	0:01:17	
	4	41,5	16,14	0:04:55	re-disperse
III	5	69,7	15,51	0:01:40	
	6	34,9	14,88	0:06:24	re-disperse
	7	58,6	14,25	0:02:11	
	8	29,4	13,62	0:08:16	
	9	24,8	12,99	0:11:04	
	10	20,9	12,36	0:14:50	
	11	17,6	11,73	0:19:51	
	12	14,8	11,08	0:26:31	
	13	12,5	10,45	0:35:04	
	14	10,5	9,82	0:46:47	

Table 2: Gravitational Sedimentation (Andraeen Pipette) Size and time-table for 1-10 μ m standard

size range: 1-10 (μ m)	solid density, ρ_s : <i>2,7</i> – <i>by way of example</i>	(g/cm ³)
sedimentation liquid:	liquid density, ρ_f : <i>1,0</i>	(g/cm ³)
0.1 mass % sodium hexametaphosphate	viscosity, η : <i>1 \cdot 10^2</i>	(g/cm s)
	vessel volume, V : <i>280</i>	(cm ³)
temperature, T: 20 (°C)	sedimentation height, h : 10	(cm)
	mean drop in sedimentation height, Δh : <i>0,63</i>	(cm)
	weight of sample, m : <i>1,1393</i>	(g)
	concentration, $c_{v,0}$: <i>1,507 \cdot 10^3</i>	

numbers in italic = assumed values, must be verified by each participant!

$$t = \frac{18\eta h}{(\rho_s - \rho_f) g x_w^2} ; t[\text{min}] = 179,89 \frac{h[\text{cm}]}{x_w^2[\mu\text{m}]}$$

3 determinations of concentration of homogenous suspension: 10cm - (3 x 0.63cm) = 8.11cm

No.	x (μ m)	h(cm)	t(h:mins)
1	10,1	8,11	0:14:18
2	8,5	7,48	0:18:37
3	6	6,85	0:34:41
4	4,3	6,22	1:00:31
5	3	5,59	1:51:44
6	2,1	4,96	3:22:20
7	1,5	4,33	5:46:11
8			
9			
10			
11			
12			
13			
14			

Table 3: Gravitational Sedimentation (Andreasen Pipette) Size and time-table for 3-30 μ m standard

size range: 3-30 (μ m)	solid density, ρ_s : <i>2,7</i> – <i>by way of example</i>	(g/cm ³)
sedimentation liquid:	liquid density, ρ_f : <i>1,0</i>	(g/cm ³)
0.1 mass % sodium hexametaphosphate	viscosity, η : <i>1 \cdot 10^2</i>	(g/cm s)
	vessel volume, V : <i>560</i>	(cm ³)
temperature, T: 20 (°C)	sedimentation height, h : 20	(cm)
	mean drop in sedimentation height, Δh : <i>0,63</i>	(cm)
	weight of sample, m : <i>2,2786</i>	(g)
	concentration, $c_{v,0}$: <i>1,507 \cdot 10^3</i>	

numbers in italic = assumed values, must be verified by each participant!

$$t = \frac{18\eta h}{(\rho_s - \rho_f) g x_w^2} ; t[\text{min}] = 179,89 \frac{h[\text{cm}]}{x_w^2[\mu\text{m}]}$$

3 determinations of concentration of homogenous suspension: 20cm - (3 x 0.63cm) = 18.11cm

No.	x (μ m)	h(cm)	t(h:mins)
1	29,3	18,11	0:03:48
2	24,7	17,4	0:05:09
3	20,8	16,77	0:06:58
4	17,5	16,14	0:09:29
5	14,8	15,51	0:12:44
6	12,4	14,88	0:17:25
7	10,5	14,25	0:23:15
8	8,8	13,62	0:31:38
9	7,4	12,99	0:42:40
10	6,3	12,36	0:56:12
11	5,3	11,73	1:15:07
12	4,4	11,08	1:42:57
13	3,7	10,45	2:17:19

Table 4: Gravitational Sedimentation (Andreason Pipette) – Participant Report Layout

size range: 3-30 (μm)	solid density,	ρ_s :	(g/cm^3)
sedimentation liquid:	liquid density,	ρ_f :	(g/cm^3)
0.1 mass % sodium hexametaphosphate	viscosity,	η :	($\text{g}/\text{cm s}$)
	vessel volume,	V:	(cm^3)
temperature, T: 20 ($^{\circ}\text{C}$)	sedimentation height,	h: 20	(cm)
	mean drop in sedimentation height,	Δh :	(cm)
	weight of sample,	m:	(g)
	concentration,	$C_{v,0}$:	

$$t = \frac{18\eta h}{(m_s - m_f) g x_w^2}; t[\text{min}] = \dots \frac{h[\text{cm}]}{x_w^2[\mu\text{m}]}$$

3 determinations of concentration of homogenous suspension: 20cm - 3 x Δh cm = cm

No.	x (μm)	h(cm)	t(h:mins)
1	29,3		
2	24,7		
3	20,8		
4	17,5		
5	14,8		
6	12,4		
7	10,5		
8	8,8		
9	7,4		
10	6,3		
11	5,3		
12	4,4		
13	3,7		

Appendix – Whitehouse Scientific Procedures

Gravitational Sedimentation - The Andersen Pipette

For maximum accuracy, particular attention was paid to the temperature control of the water bath, the stability of the Andreason Pipette and the precision of the analytical balance.

(i) The Water Bath

High capacity (60 litres) controlled to 0.01 $^{\circ}\text{C}$ (rather than the specified 0.1 $^{\circ}\text{C}$) using an ultrathermostat (manufactured by Heto), specially constructed in plate glass for good visibility and more importantly, a perfectly flat base. Water depth 33cm for complete submersion for the Andreason Pipette up to the tap. Totally level, checked by spirit level.

(ii) The Andreason Pipette

British type, horizontal extraction holes but no 1ml flush bulb. Mounted onto a 10mm thick 100 x 100mm glass base sub-assembly. Verticals checked with respect to base. Lead weights added to reduce buoyancy when the instrument is only half filled. These modifications ensured perfect orientation and stability in the water bath.

(iii) The Electronic Balance

Mettler AJ100 accurate to 0.1mg mounted on special anti-vibration table. Maximum weight 110gm. Accuracy checked with calibration weight.

Stability detector set to slowest measuring time for highest reproducibility. Intergration time set to shorten measuring cycle.

The above attention to detail enabled the samples to be weighed to a reproducibility of 0.2mg whether the sample was weighed after 1 hour or 24 hours in the dessicator. This was especially important for the final sample in the 3-30 μm series which only weighed 12mg in total.

(iv) Sample Dispersion

The 3-30 μ m samples were dispersed in about 30ml of the 0.1% solution of sodium hexametaphosphate and placed in a 40 watt ultrasonic bath for 5 minutes with occasional mechanical stirring. The suspension was then washed into the Andreasen Pipette ready for measurement.

In the case of the 1-10 μ m samples, considerable difficulty was experience in obtaining a good dispersion, large agglomerates were seen even after 10 minutes. Without the facility of a high intensity probe, it was evident that good dispersions were almost impossible to achieve. For this reason, all the samples were combined and placed in a miniature Waring blender and mixed at 12,000rpm for 2 minutes. To ensure that dispersion was complete, the combined sample was passed through a 20 μ m sieve and returned to the blender while running using a hypodermic needle attached to the Eppendorf pipette. These were placed in the ultrasonic bath for 2 minutes before being washed in the Andreasen Pipette.

N.B. See excellent comparisons with the Electrical Sensing Zone method.