

IVHHN GUIDELINES FOR GRAIN-SIZE DISTRIBUTION ANALYSIS

Introduction

Grain-size distribution (GSD) analysis is a vital step in the assessment of the health hazard of volcanic ash, giving the quantity of respirable ($< 4\mu\text{m}$) and sub- $10\mu\text{m}$ particles in a bulk sample. Analyses should be carried out on several individual ash samples from any one eruption. Grain-size analysis can be carried out for specific locations (to assess hazard to a town, for example) or for multiple locations in order to determine the total amount and distribution of fine ash produced by a given eruption. In this case, ash samples should be collected from multiple sites, with priority for sites along the dispersal axis as distal areas are commonly richer in fines than proximal areas. The resulting grain-size distributions should be averaged to obtain a total grain-size distribution using a 'weighted average' (see Appendix 1 for method). This final distribution can be considered representative for a specific eruption. Techniques for grain-size analysis vary greatly in their applicability, technology and affordability. The most-commonly-used techniques are summarised below.

Pre-analysis sample preparation

Achieving a representative sample is vital for powders which are of heterogeneous composition and grain size, especially when a sub-sample may consist of only a few mg of material. Before size analysis takes place, it is important to make sure the sample used is representative of the whole sample. Horwell (pers. comm.) found that inverting a sealed container of volcanic ash several times was sufficient to mix the sample, which should then be left for several minutes to allow the fines to settle before removing the sample. Other techniques include: 1) Cone and quartering technique where a sample is cut into four piles using a knife. Two opposing piles are removed and re-bagged and the other two again formed into a cone, and the procedure repeated until a sample of the correct size is obtained. This method can leave fines on the cutting surface from the discarded piles and risks high levels of fine ash exposure for the worker. 2) Spinning riffler technique where the ash is slowly vibrated down a shaft at the end of which are twenty trays which rotate at a slow speed. The ash drops into the trays and each tray passes under the shaft at least twenty times (depending on the amount of sample being separated). One tray is then removed from the rotator, the contents emptied onto paper and mixed and then samples removed for grain-size analysis. 3) Riffle box technique where a dry powder is poured into a box containing dividers. Both techniques 2 & 3 work well but obtaining the equipment may be difficult.

Grain-size Analysis Techniques

- **Laser-diffraction analysis (Low Angle Laser Light Scattering).** The most time-efficient and robust way to obtain GSD analyses is by using a laser-diffraction analyzer. There are many laser-diffraction analysers on the market, such as the Malvern Mastersizer, the Coulter LS Particle Size Analyzer, or the Microtrac S3500 Analyzer. Laser diffraction is used to detect particle sizes in the range of ~ 0.1 to $2000\mu\text{m}$ equivalent spherical diameter (depending on the instrument) using light scattering theory. The refractive and absorption indices for the material must be known for accurate measurements to be made. Horwell (pers.comm.) found that a refractive index of 1.56 and absorption of 0.1 was suitable for andesitic ash samples, but it is preferable to make independent measurements of these parameters for the specific ash being studied (see Appendix 2 for methods for calculation and measurement of refractive index). Powders can be measured by laser diffraction either in water or air, with aggregation being reduced using water and treatment with ultrasound. One sample takes approximately five minutes to run. Samples should be dried and sieved to exclude particles $> 2000\mu\text{m}$ (2mm) diameter. Laser-diffraction analysis can be expensive (purchasing equipment costs \sim US\$60,000). Companies such as Malvern Instruments and Coulter will analyse samples at \sim US\$150/sample (with discounts for multiple samples). Alternatively, laser-diffraction analysers are common in geography/environmental science departments at universities in Europe and the US.
- **Sieving.** Sieving is a simple, portable, inexpensive and widely-used method of classifying powders according to their physical size alone, independent of other physical or chemical properties, by using a series of woven wire or punch plate sieves arranged in decreasing order of aperture size. Sieving can be performed manually or by machine agitation. Key variables that influence sieving results include particle

shape, presence of very fine particles, initial sieve loading, time and method of agitation, and aggregation of the powder. Reproducibility is often poor due to these variables. Ash samples should be dried in an oven first (at no more than 40°C for 24 hours), then sieved at least at 1 ϕ intervals down to 63 μm (4 ϕ) (see Appendix 3 for Phi scale). If used in conjunction with laser diffraction analysis, samples need only be sieved to 2 mm. The disadvantages of the technique are that it is difficult to sieve < 63 μm and it is easy to lose much of the fine fraction through air turbulence during the sieving. An alternative to dry sieving is wet sieving, which alleviates some of the size difficulties but has poor reproducibility. Unusual particle shapes can cause problems. For example a long-thin particle may pass through a sieve aperture in one direction and not in the other direction and flat particles may be retained in a sieve that easily passes equi-dimensional particles of the same volume. In both dry and wet sieving orientation of particles through the sieve apertures is affected by duration of sieving and operating method (e.g. tapping). Sieving is often carried out prior to other size-selective techniques such as the SediGraph method. Sieving is not suitable for the assessment of the quantity of respirable material (< 4 μm) in a sample, but gives a good first approximation of the amount of fine material, particularly where an inexpensive technique is a priority. Where sieving is the only technique to be used, care must be taken to clean sieves thoroughly and to regularly check for breaks.

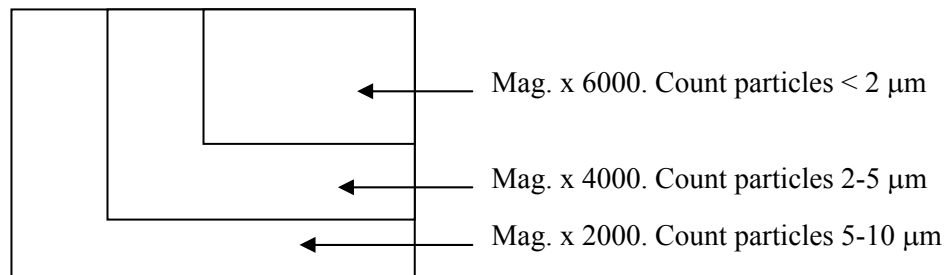
- **Sedimentation.** Sedimentation methods are based on the application of Stokes' Law, which describes the terminal velocity for an isolated sphere settling in a viscous liquid under the influence of an accelerating force such as gravity. Sedimentation techniques can be cumulative or incremental. In the cumulative method, the rate at which the particles settle is determined, typically, by weighing the mass of settled particles at a certain depth over time. In the incremental method, the change in concentration or density of the material with time is measured at known depths, typically using optical or X-ray sensing. Sedimentation methods are best suited to particles in the range 2-50 μm and, therefore, may not be appropriate for bulk volcanic ash samples. One needs to know the density of the material but volcanic ash is composed of minerals of varying density, with use of an average density often giving spurious results. Temperature must be accurately controlled in order to keep viscosity constant.

Measurement of a sample by the cumulative method can be carried out at little cost in a standard laboratory. Gravitational sedimentation has limited practical value for particles under a few micrometers in diameter due to the prohibitively long settling times (several hours). The experiment can be hastened by increasing accelerating forces through use of a centrifuge. Stokes' Law is only valid for spheres which are the most-compact shape for the volume or surface area they possess. Most volcanic particles will possess more surface area than a sphere and, therefore, will settle more slowly. Stokes' Law only applies to gravitational settling and not to particles affected by Brownian motion. For example, particles < 0.5 μm diameter give errors in excess of 100 % unless correction terms are applied. Particles > ~ 50 μm will also settle more slowly than the velocity predicted by Stokes' Law. The upper size limit can be increased by using a suspending fluid with a higher viscosity. The underlying principles for centrifugal sedimentation are largely the same as in the gravitational case, but the calculations and measurement geometry are more complex because the particle velocity increases with distance from the centre of rotation.

Incremental sedimentation techniques can be carried out using instruments such as the X-ray SediGraph, manufactured by Micromeritics. This method measures the size distribution of particles using Stokes' Law. The sample is suspended in a fluid, and the mass settled over time is detected, usually by soft X-rays. The method is useful for wide size distributions, but is sensitive to shape and density variations within single samples. The SediGraph uses a narrow, horizontally-collimated beam of X-rays to directly measure the relative mass concentration of particles in a liquid medium. Each mass measurement represents the cumulative mass fraction of the remaining fine particles. The SediGraph also determines particle size from velocity measurements by applying Stokes law under the known conditions of liquid density and viscosity and particle density. Settling velocity is determined at each relative mass measurement from knowledge of the distance the X-ray beam is from the top of the sample cell and the time at which the mass measurement was taken.

- **Microscopy.**
 - 1) Scanning electron microscopy (SEM) can be used to count the number of particles in different size fractions. This technique is especially valuable for assessing the GSD of airborne filter-collected samples,

as opposed to bulk ash fall. This can be done through automated image analysis, but this introduces great errors from aggregated particles. Manually, this time-consuming technique can be hastened using the following method: Choose a field of view with magnification at, for example, 2000. Using 1 μm bins, count all the particles 5-10 μm diameter. At x 4000 magnification, count all the particles between 2-5 μm . Zoom in to 6000 mag. and count the number of particles < 2 μm diameter. NB. Diameter = length of longest axis (maximum axis diameter = MAD).



Repeat this process for at least 10 fields of view. Multiply particle numbers in x 6000 view by 3, and x 4000 view by 2 so that it is as if every particle in the x 2000 field were counted. These data will give you a percentage by count. In order to compare with laser diffraction data, these data must be converted to volume % and the laser diffraction data should be converted from equivalent spherical diameter to maximum axis diameter (MAD). In order to do this, an average aspect ratio for the particles is needed, which is easily obtained through image analysis. Horwell (pers.comm.) found this technique to be as accurate as laser diffraction techniques but is much more labour intensive and possibly as costly, if instrument time is charged.

2) Automated microscopy and image analysis techniques (e.g. Pharmavision 830). The PharmaVision 830 enables reliable, repeatable and routine characterization of particle size and particle shape using automated microscopy and image analysis techniques. Particle shape information is generated from the analysis of thousands of particles and displays of particle size and particle shape data are supported by images of all the particles to provide further visual understanding of the measurement data. A number of shape parameters are calculated for each particle in order to increase the sensitivity of the analysis to subtle variations in particle morphology.

- **Electrozone sensing** The electrical zone sensing (EVS) technique is based on the Coulter principle. In this method, the powder is dispersed at a very low concentration in an electrolytic (i.e., conducting) solution, which is then drawn through a small aperture in an insulating wall on either side of which electrodes are placed. As each particle enters the aperture, or sensing zone, a voltage is applied and the volume of solution displaced by the particle causes a transient change in the measured electrical impedance across the opening. The amplitude of this impedance pulse is proportional to the particle's volume. By accumulating pulses over time, a GSD is constructed. Different size apertures can be used depending on the size range of interest. Problems of particle orientation are solved by measuring the area under the pulse peak. For materials of a relatively wide particle-size distribution, the method is slow as aperture size must be altered and there is a danger of blocking small apertures. Porous particles give significant errors as can the coincident passage of two or more particles through the sensing zone.

In general these different methods measure subtly different properties and, consequently, are not necessarily comparable. If two different techniques are being used on the same sample for different grain size ranges there should be sufficient overlap to allow calibration and integration of the methods with one another.

Appendices

Appendix 1 – Calculation of total grain size distribution of a tephra fall deposit.

1) Weighted average. The weighted average is an average calculated by taking into account not only the frequencies of the values of a variable but also a "weighting factor", in this case either the thickness or the mass/area of the deposit for a given site. Each observed thickness or mass/area value for each size fraction is added and then divided by the total thickness or mass/area for that given fraction, then the total is multiplied by 100.

2) Voronoi tessellation. This method of spatial analysis that can be defined as the partitioning of the plane such that, for any set of distinct data points, the cell associated with a particular data point contains all spatial locations closer to that point than to any other. The Voronoi Tessellation technique provides a statistical method for the calculation of total GSDs that deals with non-uniform data sets without introducing arbitrary sectors. The use of such a technique makes comparisons amongst different tephra-fall deposits analysed by different authors more consistent (Bonadonna and Houghton 2004). There are hundreds of different algorithms for constructing various types of Voronoi diagrams. You can download a MatLab function for the calculation of the total GSD of tephra-fall deposits based on the Delaunay Triangulation from the web page of the IAVCEI Working Group on Modelling Volcanic Tephra-Fall Hazards:

<http://www.soest.hawaii.edu/IAVCEI-tephra-group/grainsize.htm>

Appendix 2 – Measurement and calculation of refractive index

Light scattering theory uses the optical properties of particles to calculate their grain sizes. It is important, therefore, to have accurate data on the properties of the powder being tested. Volcanic ash is heterogeneous, being composed of minerals such as plagioclase feldspar, crystalline silica, glass, amphibole, pyroxene and iron oxide which all have different refractive indices (RI) and absorptions (how opaque or transparent the mineral is) and are present in different proportions in different ash samples. It is difficult, therefore, to give an accurate estimation of the mean optical properties of an ash sample.

Refractive index is calculated by:

$$m = n - ik \quad \text{where } i = \sqrt{-1}$$

and k , the imaginary component of the refractive index, is related to the absorption coefficient of the material. For non-absorbing (i.e., transparent) particles, $k = 0$. Both the real part of the refractive index, n , and the imaginary part, k , are wavelength-dependent. Scattering arises due to differences in the refractive index of the particle and the surrounding medium (or internal variations in heterogeneous particles). Therefore, in order to use a scattering model to calculate the GSD that produced a specific scattering pattern, one must first know the complex refractive index of both the particles and the medium (typically, the latter is selected such that $k = 0$).

In the past, an RI of 1.63 has been used on ash, representing an andesitic rock (C. Bonadonna and W.I. Rose, personal communication). This RI was drawn from indices used for remote sensing where values appropriate for infrared radiation were used which are higher than the RI needed for laser diffraction (RI varies with light wavelength used). It may be more accurate to use the optical properties of the most common mineral (often plagioclase). Values obtained from RI tables for individual minerals in ash are as follows (Kerr 1977):

Volcanic glass	=	1.48-1.61
Cristobalite	=	1.484 (α), 1.487 (γ)
Plagioclase (labradorite)	=	1.555-1.563 (α), 1.562-1.571 (γ)
Hornblende	=	1.614-1.675 (α), 1.633-1.701 (γ)
Clinopyroxene (augite)	=	1.688-1.712 (α), 1.713-1.737 (γ)
Orthopyroxene (enstatite)	=	1.650-1.665 (α), 1.658-1.674 (γ)
Spinel	=	1.72-1.78

From the information above, an average plagioclase value of 1.56 can be estimated.

The composition of volcanic glasses varies to such an extent that the RI given above covers a wide range of refractive indices compared with other minerals. The RI of glass can be measured using the traditional **Becke Line method**. The particles are set on a glass slide and immersed in a few drops of liquid with a known refractive index. A bright line, the 'Becke Line', is observed with a petrological microscope on the edge of the grain if the refractive index of the mineral and liquid are different. The apparent movement of this line into the mineral or into the liquid during lowering or lifting of the objective determines whether the mineral or liquid has the higher refractive index. Grains are immersed in several liquids until one is found where the Becke Line cannot be seen because the grain and liquid have almost identical refractive indices. The Becke Line moves into the medium with the higher refractive index when the objective is lifted or the stage is lowered.

The average RI for a sample can also be estimated by summing the RIs for the component minerals, adjusted to reflect the proportion of the minerals in the ash sample being analysed. An example calculation is given below.

Table 1. Calculation of an average Refractive Index for the Soufrière Hills ash, taking into account proportions of minerals and RIs calculated for individual minerals (either from Kerr 1977, see above, or by the Becke Line method for glass).

Mineral	Wt. %	Average RI	Proportional RI
Crystalline silica	14.7	1.49	0.22
Glass	21.4	1.53	0.33
Plagioclase	48.6	1.56	0.76
Pyroxene	8.9	1.69	0.15
Amphibole	3.9	1.66	0.06
Oxides	2.5	1.75	0.04
Total	100.0		1.56

Therefore the two best estimates of RI to use for the Soufrière Hills ash are both 1.56. Comparison of GSDs from laser diffraction using either RI = 1.56 or 1.63 do not show a significant difference in results but 1.56 is likely to be more accurate for andesitic ash samples. We recommend that a procedure, such as that recommended here, is carried out to determine the RI for every tephra sample measured.

The standard absorption used on ash has been 0.1 (close to transparent). The influence of absorption becomes more important as the particle size decreases. As a general rule of thumb, the darker or more coloured a specimen appears, the higher the imaginary component. For white powders, such as high-purity alumina, $k = 0$. Andesitic ash, for example, is generally grey in colour, and therefore one can anticipate a relatively low value for the imaginary component ($k = 0.1$).

Appendix 3 – The Phi (ϕ) Scale

$\phi = \log_2 \text{mm}$	
μm	ϕ
< 63	> 4
63	4
125	3
250	2
500	1
1000	0
2000	-1

References

Laser diffraction analysers:

Malvern Instruments:

http://www.malvern.co.uk/malvern/rw_malvern.nsf/vwa_docref/IWTM%20particle%20size

Beckman Coulter: http://www.beckman.com/products/instrument/partChar/pc_ls230.asp

Microtrac: <http://www.microtrac.com/products1.htm#The%20New%20S3000%20Analyzer>

Further information: <http://ciks.cbt.nist.gov/~garbocz/nist6883/node3.htm>

“The basic principles of particle size analysis”. An internal document written by Dr Alan Rawle, Malvern Instruments Ltd, downloadable from the Malvern website given above.

Sieving:

Further information on dry and wet sieving techniques:

http://www.retsch.de/downloads/tr_sieving_chemical_engineering_0301_en.pdf

<http://ciks.cbt.nist.gov/~garbocz/nist6883/node7.htm>

Sedimentation:

Micromeritics: http://www.micromeritics.com/products/sedigraph_overview.aspx

Further information on sedimentation: <http://ciks.cbt.nist.gov/~garbocz/nist6883/node6.htm>

Microscopy:

Pharmavision: http://www.malvern.co.uk/LabEng/products/pharmavision/pvs_830.htm

Electrozone sensing:

Beckman Coulter: http://www.beckmancoulter.com/products/instrument/partChar/pc_multisizer3.asp

Further information: <http://ciks.cbt.nist.gov/~garbocz/nist6883/node4.htm>

Refractive Index:

Further information: <http://ciks.cbt.nist.gov/~garbocz/nist6883/node3.htm>

Kerr, P.F., 1977. Optical Mineralogy. McGraw-Hill Book Company, New York, London, pp 492

Overview of interpretation of ‘diameter’:

http://www.micromeritics.com/products/article_interpretation.aspx

Voronoi tessellation

Bonadonna, C. and Houghton, B.F., 2005. Total grainsize distribution and volume of tephra-fall deposits, Bulletin of Volcanology, in press. DOI: 10.1007/s00445-004-0386-2.

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