



Particle Size Studies in the Preparation of AQCS Reference Materials

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Particle size determination is one of the important steps in the characterization of physical properties of each particulate material. However, particle size distribution effects also a chemical composition of the material in terms of homogeneity and representativeness of the sample, as well as allows or not a possible sub-sampling of the material. All this is of great importance in the preparation of reference materials for which the chemical composition and physical properties have to be extremely well characterized. In the present paper we intend to present same efforts which have been done by Analytical Quality Control Services (AQCS) of the International Atomic Energy Agency (IAEA) in the field of particle size determination in the production of reference materials. The Malvern product MasterSizer X, based on laser light scattering is used for this purpose and the technique is also shortly discussed.

INTRODUCTION

Reference material is by definition a material or substance one or more properties of which are sufficiently well established to be used for calibration of an apparatus, the assessment of the measurement method, or to assigning values to materials. Composition standards - reference materials (RMs), which are in the case of solid samples normally particulate materials have also to fulfill these requirements, with only exception that they are not predicted for calibration purposes. RMs are widely used for assessment of analytical methods and for analytical quality control. In this case the matrix of RM and the content of elements have to be as much as possible similar to the analyzed samples. For this reason a large number of new RMs is produced worldwide, while at the same time the formal requisitions for the production, quality and characterization of RMs are becoming more strict and uniform as ever before.

One of the parameters in characterization of the particulate material is its particle size distribution. In the case of RMs particle size distribution is important for different reasons, and some of them can be pointed out as follows: a) RMs are normally prepared from a bulk natural samples and are then divided into smaller units (bottles of 5 up to 1000 g sub-samples). The main objective of sub sampling is to reduce the amount of material in such a way, that the distribution heterogeneity is minimized. The decrease of distribution heterogeneity is favored by a large number of particles. A draw back of increasing the number of particles is that in general the constitution heterogeneity will increase. So the individual particles become more different, but the samples become more alike if all other conditions remain constant.¹ b.) The amount of RM used for separate analysis is often based on calculation of sampling constants. It was shown in many theoretical and practical works that the average particle mass (it is in direct

relation to the particle volume if the density is constant) is a parameter to be known for exact calculation of sampling constants. In the case of known particles' mass (volume and density) a proper sample mass for analysis can be determined and the oversampling can be avoided.² c.) In the case that there is any suitable RM available for certain purpose, e.g. the lack of certified particulate reference materials relevant to air pollution studies, it is possible to use other RM with similar chemical composition with a prerequisite that physical properties (also a particle size distribution) are as similar as possible to the test samples. d.) The uncertainty of sampling, which is assigned to the sampling of RM will be according to the facts above minimized if the particle size will be smaller. Generally, the smaller particles will normally improve the representativeness and homogeneity of the sample, and will in the same time decrease the sampling constant and sampling uncertainty for RM. There are also some other facts and limitations in connection to particle size distribution. In the work of Fujimori and Ishikawa was shown that in coal analysis the particle size has an important effect on the analytical results.³ The authors reported that for the most accurate results of coal microanalysis the samples have to contain the major particle size fraction around 70 μm . Above this number, as well as when the major particle size fraction is lower than 40 μm the uncertainty of analytical results increases or at least special precautions have to be taken into account while handling the samples.

During 1993/94 a Malvern product MasterSizer X has been put in a routine use for particle size determination in IAEA AQCS program of production and characterization of reference materials. This instrument, based on laser light scattering, allows measurements of the size structure of practically any one material phase in another if the refractive index of the supporting medium is different to that of the analyzed material. The technique is absolute, simple, fast, non intrusive, precise and wide ranged. Although there are many techniques available for particle size determination (different optical methods, mechanical methods, gravitation methods, osmotic methods, etc.)⁴, this is at the moment the technique predominant in precision and in the range of particle size bands which can be determined by a single measurement. Up to 100 size bands can be displayed covering a range of up to 600 : 1 in size capability of any single range. By changing the four lenses (45 mm: 0.1 - 80 μm , 100 mm: 0.5 - 180 μm , 300 mm: 1.2 - 600 μm , and 1000 mm: 4.0 - 2000 μm) a high distribution of particle sizes can be measured. The results of measurements using laser diffraction are expressed in terms of volume of equivalent spheres. It is also possible to correlate these results with values from some other techniques by applying a shape correction using the result modification procedure built into the software program of MasterSizer X. The instrument is equipped with two different sample dispersion units. The first one is powder suspension unit and the second one is a dry powder feeder. With a powder suspension unit it is possible to use different supporting media (water or various organic solvents), so that the most appropriate liquid type for a specific material can be chosen. Although the use of MasterSizer X is relatively simple, the results can be influenced by the operating conditions, e.g. feed rate, sample pump power, the use or not of ultra sound stirrers, unsuitable dispersant and/or surfactant, etc. For this reason the use of reference material certified for particle size distribution for testing the operating performances is an essential part of measurements. At the same time some experience of the operator in testing different samples is obvious.

In the recent time some programs have been initiated by the IAEA for preparation of new advanced reference or intercomparison materials. The latest materials, IAEA-085 human hair spiked with methylmercury and IAEA-086 human with low methylmercury level, IAEA-335A lichen for trace elements, IAEA-326/327 soil samples to be certified on radionuclides, and IAEA-396 urban dust, which should be used in the intercomparison study on the determination

of trace elements in materials relevant to air pollution studies, have also been, among the others already certified reference materials, characterized on particle size distribution in our laboratory. The aim of this work was to characterize these samples with one more independent technique, as well as to prove if the samples are suitable for the intended purpose from the point of particle size distribution.

EXPERIMENTAL

Preparation of the materials:

IAEA-085/086 human hair have been prepared from the same 10 kg bulk sample. The material was cut to uniform 1 cm lengths, and cleaned with acetone and deionized water. The material was then split into two approximately same portions and was radiation sterilized. One portion was labeled with methylmercury (IAEA-085). Both the labeled and unlabeled portions of the hair were cryogenically homogenized using the stainless steel "CryoPalla" mill and subjected to consecutive millings, until approximately 70 % of each material was below 71 μm grain size. Samples were distributed to plastic bottles in aliquots of 5 g.⁵

IAEA-335A lichen sample (*Pseudevernia fufurnacea*) was collected in 1994. Parts of the material which were not lichen were eliminated from the sample, which was then grounded bellow 300 μm and milled in the air jet-mill at the IAEA Seibersdorf Laboratories.⁶

IAEA-326 black soil and IAEA-327 podsolic soil were collected in 1990. The bulk samples of approximately 320 kg of each material were air-dried, milled using a vibration mill MVO-200 and homogenized. Samples were distributed to plastic bottles in aliquots of 250 g and radiation sterilized.⁷

IAEA-396 urban dust material was collected in Vienna in 1994. Both bulk sample of around 5 kg was sieved trough 100 μm sieve and then homogenized for two hours using a V shaped homogenizer. Sample was then distributed to plastic bottles in aliquots of 20 g and radiation sterilized.⁸

Particle size determination:

Malvern instrument Mastersizer X was used for the determination of particle size distribution in all cases. As a feeding source for the material a MSX 14 sample suspension unit was applied, and tap water used as a supporting medium. Possible addition of surfactant (detergent) and exact measuring conditions including the lens applied are given in the section Results and Discussion for each material respectively. Approximately 100 mg of each material were used for single measurement. Sub-samples for these measurements were taken randomly from the randomly selected bottles after preparation described above. No additional pretreatment of the samples was performed if not stated otherwise.

RESULTS AND DISCUSSION

The results are presented in a graph forms, while this is the most practical way. In this case the particle size distribution and the difference between samples is easily evident. It has to be pointed out that the samples were treated as a polydisperse system of solid particles in water and that the results are expressed as a percent volume fraction. For each sample at least four measurements were performed. Standard deviations of repetitive measurements of the same material did not exceed 2 % in each particle size range. However, only one curve is presented for a single material to avoid confusion. All additional data including numerical and statistical data are available directly from the authors. A comparison of our measurements of BCR No. 70 reference material with a certified values is presented in a table form later in this chapter.

IAEA-085/086 (Human Hair):

Lens: 300 mm (range 1.2 - 600 μm)

Suspension: in water, no surfactant added

Ultrasonic stirrer: yes (level 7)

Pump power: 7

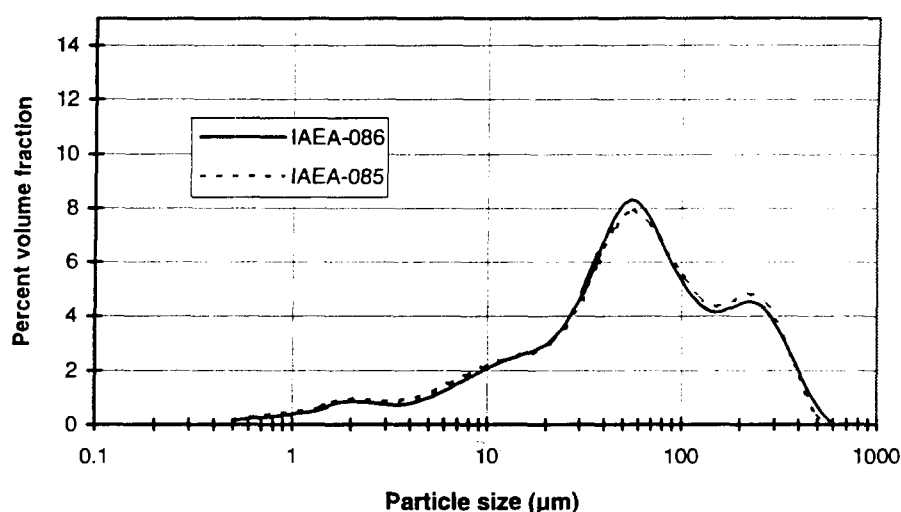


Figure 1: Particle size determination in two human hair materials, IAEA-085 spiked with methylmercury and IAEA-086 normal methylmercury level.

As stated in the paragraph of preparation of these two materials, which were consecutive milled, the expected particle size distribution is such that approximately 70 % of each material contains particles smaller than 71 μm . This was clearly proved by our measurements and there is practically no difference between samples IAEA-085 and IAEA-086 concerning particle size distribution.

IAEA-335A (Lichen):

Lens: 300 mm (range 1.2 - 600 μm)

Suspension: in water, surfactant added (few drops of detergent)

Ultrasonic stirrer: yes (level 3)

Pump power: 3

In the case of IAEA-335A Lichen sample a particle size measurements were used in order to control the operating conditions and effectiveness of the air jet-mill in IAEA Seibersdorf Laboratories. The original sample after preparation described above was three times milled in our air jet-mill. The results of particle size distribution are graphically presented in Fig. 2.

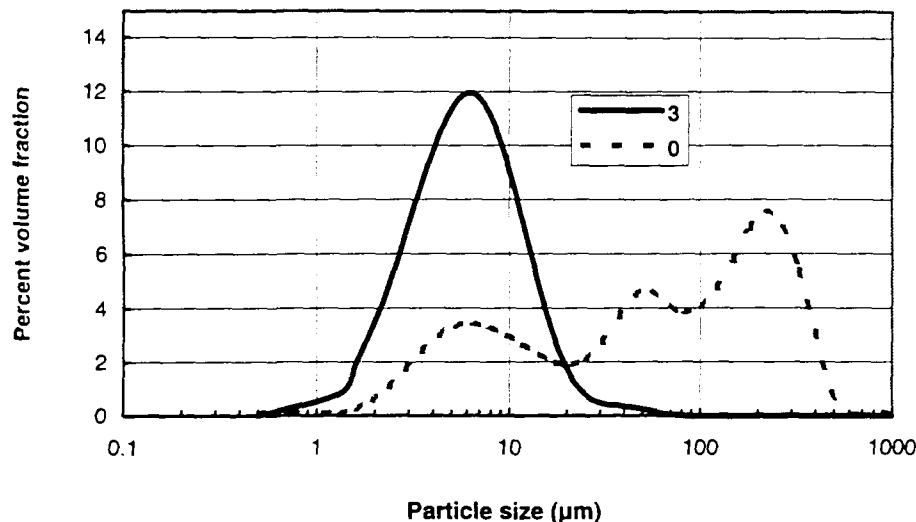


Figure 2: This graph gives an example of air jet-mill control in preparation of IAEA-335 Lichen sample, where line 3 shows the particle size distribution after the third air jet milling of the original material (0).

With these measurements it was clearly found out that the air jet milling largely improves the uniformity of the sample. 90 % of the material contain the particles smaller than 14 μm, while the peak of the distribution curve can be found at 6.26 μm after the third milling operation. Theoretically is expected that the homogeneity of the material was improved, but this is still to be proved by chemical analysis of all three fractions.

IAEA-326/327 (Soil):

Lens: 300 mm (range 1.2 - 600 μm)
 Suspension: in water, no surfactant added
 Ultrasonic stirrer: yes (level 7)
 Pump power: 7

Particle size measurements in IAEA-326 and IAEA-327 soil materials showed a major particle size of 15.87 and 11.72 μm respectively, while larger particles with a diameter of 330 μm or 180 μm are also present. From the Fig. 3 it is evident that the shape of the curves is not ideal, but it can be pointed out that these two materials are intended for use in intercomparison on determination of radionuclides in soil samples. In this case a normal sample amount for a separate analysis is at least few grams up to 100 g. In homogeneity tests, by measuring Sr-90 was found that the materials are homogeneous for a sample size greater or equal to 10 g.⁷ In this case the particle size described does not have any effect on the results and the samples can be considered as appropriate from this point of view.

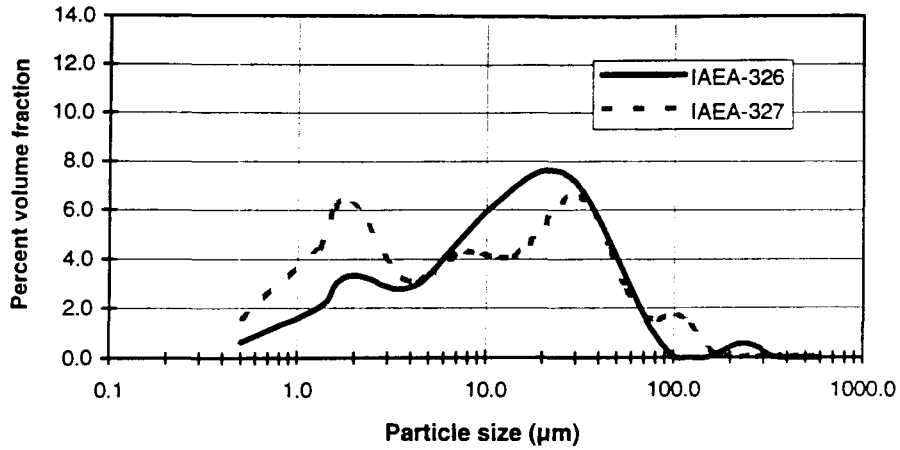


Figure 3: Particle size distribution in two soil materials, IAEA-326 (black soil) and IAEA-327 (podsollic soil).

IAEA-396 (Urban Dust):

Lens: 100 mm (range 0.5 - 180 µm)

Suspension: in water, surfactant added (few drops of detergent)

Ultrasonic stirrer: yes (level 7)

Pump power: 7

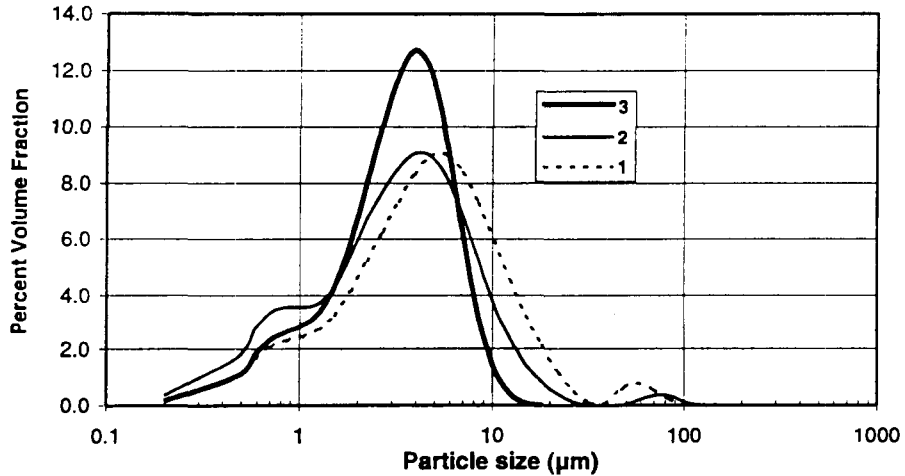


Figure 4: Particle size distribution in IAEA-396 (urban dust) material, where lines 1, 2 and 3 show the particle size distribution after the first, second and the third air jet mill operation.

The challenge of this material is to be used as a reference material relevant to air pollution studies. In this case a particle size distribution is of special importance and it is expected that such material would have a particle size distribution peak at 10 µm diameter and similar distribution on both sides of the curve. Our results of the particle size distribution show the IAEA-396 urban dust material as very promising for this purpose. After some additional treatment, e.g. sieving or air jet milling, this material could probably cover these requirements.

Control sample - BCR No. 70:

For testing the operating conditions of MasterSizer X a certified reference material BCR No. 70 Quartz, with certified cumulative particle size distribution was measured. Measurements were performed by two different lenses (45 mm and 100 mm) and are compared with reference values in Table 1.

Particle size (μm)	Reference value ⁹	Our measurements	
	% mass fraction (uncertainty)	Lens 45 mm	Lens 100 mm
		\bar{x} (\pm S. D.)	\bar{x} (\pm S. D.)
1.20	10.0 (2.8)	13.1 (0.04)	14.2 (0.34)
1.40	13.4 (2.9)	16.1 (0.05)	17.1 (0.44)
1.70	22.0 (3.9)	21.4 (0.09)	22.2 (0.64)
2.00	27.4 (2.6)	28.1 (0.13)	28.7 (0.88)
2.40	37.4 (3.2)	33.3 (0.16)	34.3 (1.04)
2.90	49.5 (3.8)	42.5 (0.24)	43.9 (1.23)
3.50	60.2 (2.9)	52.6 (0.35)	54.9 (1.20)
4.80	76.8 (2.6)	66.6 (0.54)	70.6 (1.69)
5.70	83.2 (2.7)	76.5 (0.71)	81.1 (1.72)
6.70	88.1 (1.6)	82.3 (0.80)	86.6 (1.72)
8.00	92.4 (1.4)	89.4 (0.91)	92.7 (1.53)
9.50	95.4 (1.4)	93.0 (0.94)	95.5 (1.29)
11.30	97.6 (1.1)	96.6 (0.92)	98.0 (0.86)
20.00	99.8 (0.8)	99.3 (0.70)	99.9 (0.15)

Table 1: Results of measurements of BCR No. 70 reference material. Particle size distribution is in all cases expressed as a % mass fraction undersize. A density of the material is 2642 kg.m^{-3} . The number of our measurements was in all cases four.

It has to be immediately clarified that the material BCR No. 70, currently used in our laboratory, was certified with respect to the cumulative distribution by mass of the Stokes diameters of the particles as measured by sedimentation analysis in the gravity field (Pipette Method) and some deviations of results from certified values should be expected by using an other method.⁹ Results of laser light scattering are expressed in terms of the volumes of equivalent spheres. This will in a theoretical case when sample consists only of ideal cylindrical particles result in around 12 % lower results of particles diameter in comparison to the sedimentation technique. However, the particles shape in the material, as proved by light microscopy, is not ideal neither uniform what consequently results in the fact that shape correction in our measurements could not be applied. Thus difference between our results and the certified values lays in an acceptable range between 0 and maximally 9.8 %, but these results are still not the best prove of quality of our measurements. In this case the most reliable comparison with reference values is the mass fraction covered in the whole particle size range. The particle mass fraction in the range between 1.20 and 20.00 μm is extremely well covered with both lenses applied. The results obtained are largely repetitive giving a standard deviations smaller than 1 and 2 % respectively. It is also important that comparison between our results

obtained by 45 mm and 100 mm lenses gives much smaller difference which does not exceed 6 % in any case, what supports the statements written above and additionally proves the validity of our measurements.

CONCLUSION

The fact that particle size (mass) distribution has an important influence on homogeneity and consequently on sub-sampling of particulate materials is well known for a long time. Looking from the point of number of units (particles) in a sample, Benedetti-Pichler has calculated the minimum mass of sub-sample required to be representative for analysis.¹⁰ His calculation, based on the assumption that an average density of particles in sample is 3 g.cm^{-3} and that the particles are of cube shape, showed that the edge of the cube (particle or unit) should be 0.1 mm, 45 μm , 22 μm , and 4.5 μm if sub-samples of weight 10 g, 1 g, 0.1 g, and 1 mg, respectively, are taken. Transferring this into the diameters of the equivalent spheres, as the results of laser light scattering are presented, this will give a main particle diameters of 0.12 mm, 55.6 μm , 27.3 μm , and 5.57 μm , respectively. A short look to these numbers can result in an impression that many samples which are daily analyzed in laboratories do not correspond to this requirement. However, this is only one respect of homogeneity and must not be considered separately from the homogeneity assessed on the basis of results obtained by chemical or other methods of analysis. In usual laboratory procedures homogeneity of the sample is evaluated in respect to the occurrence of element(s) of interest in randomly selected sub-samples as analytically determined. It should be noted that homogeneity established in this way is only valid for the components investigated, and may not apply to uncertified analytes.¹¹ Concerning Rms, appropriate homogeneity of the material is assessed by statistical comparison of the analytical results obtained for components investigated with a target value assigned to homogeneity of the specific RM. The importance of known particle size distribution is in any case not diminished. It can not be avoided as a background for calculation of sampling constants for the analyses, as well as an additional independent information on the uniformity of RM.

The importance of known particle size distribution in production of RMs is nowadays merely rised with the formal requirements concerning the preparation of RMs, e.g. the uniformity of RM, uncertainty assigned to the sub-sampling of RM, the fit of the RM composition and structure for intended purpose, etc. The uncertainty in sub-sampling of RM is, however, connected to the amount of the sample taken for analysis. A large number of analytical methods (specially the newly developed techniques) require only a small amount of the sample for separate analysis so that micro-heterogeneity of the material becomes important.¹² Another fact concerning RMs is that RMs are relatively expensive and in normal laboratory procedures they are used in the smallest amounts possible. The method has been developed by Pauwels and Vandecasteele for determination of the minimum sample mass of a solid certified RM (CRM) to be used in chemical analysis, where authors have also stated that for more general use of CRM it is the responsibility of certifying bodies to perform microhomogeneity studies as an integral part of the certification procedure.¹³ From this point of view, a known, controlled and uniform particle size distribution could serve as an additional indicator of the quality of RM. From the other hand, some techniques, e.g. laser plasma spectroscopy, requires samples with particle size between 0.2 and 1.2 mm to obtain the most accurate results and to minimize the grain size effect.¹⁴ It is also known that there is still a lack in availability of RM for XRF analysis on the field of air borne inorganic pollutants (see Wätjen et al. for review¹⁵). All these examples support the need for controlled and exactly determined particle size distribution of RMs.

The measurements of particle size distribution in some certified RM and new intercomparison materials produced by IAEA AQCS presented in this paper, show that the use of laser light scattering technique allows fast and reliable determinations of particle sizes in the small amounts of the sample (sub-sample), and give very useful information on uniformity of the sample from this point of view. It allows direct control of grinding, sieving and air jet-milling processes in preparation of RM. The materials IAEA-085/086, IAEA-326/327, and IAEA-396 have been measured in the form in which they are already distributed as intercomparison materials and for which a homogeneity was determined by chemical analysis. In these cases a particle size distribution described is only an additional independent information on physical properties of the material. It is also planned that particle size determinations will be accompanied by chemical analysis of each separate fraction in the preparation step, e.g. air jet-milling of IAEA-335 and IAEA-396 materials, to study the relation of particle size distribution to chemical composition and homogeneity of the material on the micro scale. Nevertheless, routine application of MasterSizer X for particle size determinations in the production of new solid particulate intercomparison and RMs now allows the control of some preparation steps in production of RMs and allows better internal quality control, what consequently rises the performances of IAEA Analytical Quality Control Services.

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