Assessment of homogeneity of candidate reference material at the nanogram level and investigation on representativeness of single particle analysis using electron probe X ray microanalysis

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Abstract. Particulate samples of a candidate reference material are evaluated on their homogeneity from bottle to bottle using electron probe X ray microanalysis technique. The evaluation on the homogeneity is done by the utilization of the Kolmogorov — Smirnov statistics to the processing of the quantitative electron probe X ray microanalysis data. Due to a limitation, existing even in computer controlled electron probe X ray microanalysis, in terms of analysis time and expenses, the number of particles analyzed is much smaller compared to that in the sample. Therefore, it is investigated whether this technique provides representative analysis results for the characteristics of the sample, even though a very small portion of the sample is really analyzed. Furthermore, the required number of particles for the analysis, to insure a certain level of reproducibility, e.g. 5% relative standard deviation, is determined by the application of the Ingamells sampling theory.

Keywords

reference materials, electron probe X ray microanalysis, homogeneity, Kolmogorov — Smirnov statistics, Ingamells sampling theory

Introduction

Homogeneity is one of the essential attributes of reference materials. Normally its estimation is a two-step process. In the first step, one or a number of bulk analytical techniques (most often neutron activation analysis (NAA), atomic absorption and emission, X ray fluorescent (XRF) and/or mass spectrometry [1]) are used. The statistical evaluation of the obtained data is done in the second step (for details see e.g. reference [2]). Still, such approach allows to evaluate the homogeneity of the reference materials (RMs) only down to the microgram level and cannot be applied to lower amounts [3].

In order to reach the nanogram level, one should use microanalytical rather than bulk techniques. However, the assessment of homogeneity of the samples of candidate RMs with the help of microanalytical techniques cannot be considered as a routine procedure due e.g. to the fact that the majority of microanalytical techniques are not standardized themselves. Electron probe X ray microanalysis (EPXMA), which is widely used for qualitative and quantitative analysis of individual particles, is not an exception. On the other hand, computer controlled EPXMA (CC EPXMA) is capable to determine the compositions of large number of individual particles in an automatic and rather non-destructive manner. Therefore, its application to homogeneity studies of powder samples looks very attractive.

The present paper describes an approach, which allows to apply EPXMA to the estimation of the homogeneity of the powder samples of candidate RMs. It is based on the utilization of the Kolmogorov — Smirnov statistics to the processing of EPXMA data.

Single particle analysis using CC EPXMA is an ultimate microanalysis technique available currently; it analyzes individual particles of micrometer size. Morphological and chemical information on individual particles can be obtained. Since EPXMA analysis time, and thus analysis expenses, increase by the increase of the number of analyzed particles, the number of particles analyzed are strictly limited, even with CC EPXMA. And thus, it is important to know whether the information obtained from a very small portion of sample represents the characteristics of sample. One of objectives of this work is to investigate how a small portion of the sample can be analyzed to insure representative analysis on the sample.

Experimental

Samples and sample preparation.

A candidate RM, namely IAEA-413, which is single cell algae grown with added toxic elements, is studied in the current research. This candidate RM is produced by re-mixing a candidate RM which was previously characterized using various analytical techniques, such as NAA, XRF, particle induced X ray emission (PIXE) and EPXMA [3,4] Six different bottles out of an RM batch were sampled. Since the samples were dry powders, they could not be analyzed directly by EPXMA but had to be transferred and spread onto Nuclepore polycarbonate filter. The Nuclepore filter is an ideal substrate for the CC EPXMA because of its microscopic flatness. Well separated particles were produced by the liquid suspension technique as follows [5]. A small portion of the powder is dispersed in an inert liquid, *n*-hexane. From this suspension the appropriate amount, to get an optimal loading, is pipetted into a filtering funnel with vertical sides, filled with *n*-hexane. This suspension is then sucked through a 25 mm Nuclepore filter, 0.4 μm pore-size, supported by a glass filter. Six samples from the different bottles of the candidate RM were analyzed. A sample from a bottle was repeatedly analyzed to investigate the reproducibility of the obtained data using CC EPXMA.

CC EPXMA

Analysis of the samples was done on these filters, after carbon coating to avoid charging, using a JEOL 733 scanning electron microscope (SEM) with energy-dispersive X ray (EDX) detection attachment. Automated single particle analysis was performed and 2,000 particles were analyzed for each sample. For the analysis an accelerating voltage of 20 kV and a beam current of ca. 1 nA were used. X ray spectra, collected for 20 seconds, provided information about the chemical composition of the individual particles, and also morphological information, such as diameters, was determined. The magnification of 300, used in the measurements, determined the minimum detectable diameter, which is about 1 μm.

Results and discussion

Summary on procedures for data analysis

- **Evaluation of the total mass of the analyzed microparticles per sample.**

A very rough evaluation of the total mass M of the N analyzed microparticles per sample was done as follows. Let an average microparticle have an average volume V and average density p. Then

$$M = N * p * v \qquad (1)$$

The average density is roughly estimated as 0.7 g/cm^3 which is the density of *n*-hexane (some of the particles in suspension with *n*-hexane had a density lower than that of *n*-hexane, some higher). The average volume can roughly be estimated from the size distributions of the particles assuming that they are spherically shaped (according to SEM observations). Based on these data we estimate the average volume as 220 μm^3. Hence, the total mass, M, is estimated as 300 ng when 2,000 particles are analyzed.

- **Assessment of the reproducibility of sampling**

To estimate the reproducibility of sampling, the size distribution (distribution of the diameters) of the particles for the six samples was determined. The size distribution of each sample was compared with one of the samples (the target sample), arbitrarily chosen, with the help of the two-sided Smirnov statistical test.

The Smirnov statistical test is to determine whether two distributions of data are identical or not. This test belongs to the variety of nonparametric statistical tests. Other tests, e.g. the *t* test, can be used too, but the advantage of this Smirnov test is its consistency against all types of differences that may exist between two distributions. To the contrary, the *t* test assumes that the distributions to be tested are normal distributions. For more detail on this test, one can refer to the book by Conover [6] and also to a work [4] where a similar candidate RM was investigated using the Smirnov test.

This test is applied in the following way:

(a) Each distribution is normalized on a maximum value. Therefore, after normalization, the maximum value in each distribution equals 1.

(b) The difference between the target distribution and that for a sample (Δ) is calculated for each bin, where the number of bins is 50.

(c) The maximum value of Δ's is compared with a certain critical value T for a certain significance level taken from the two-sided Smirnov test tables [6]. If the maximum value of Δ's > T, the difference between the distributions is considered significant; otherwise it can be neglected.

- **Evaluation of the composition differences between the samples from different bottles**

To evaluate composition differences between the samples, the distributions of concentrations of the six most often detected elements were investigated for each sample. These concentration distributions for each sample were compared then with the target one with the help of the two-sided Smirnov statistical test as described previously. Also, for each measured data with total 2,000 particles, data with a smaller number of particles, such as 1800, 1500, 1200, 900, 600, 300, 100 and 50, were generated by selecting particles randomly from the original data, using a random number generating function in the Microsoft Excel program. The data with the smaller number of particles were compared again to check whether their compositional distributions are identical also in the smaller mass range, using the Smirnov test.

- **Assessment on representativeness of the data measured using CC EPXMA**

One sample from a bottle was repeatedly analyzed seven times during a two months period and at different areas of the loaded filter, to investigate whether each data is reproducible. The reproducibility was checked using the Smirnov test. Also, it was evaluated how many particles need to be analyzed to achieve a certain relative standard deviation (RSD) for the measurement, e.o. a certain level of reproducibility. For this purpose, Ingamells sampling theory [7] was applied to determine what mass of the sample is needed to achieve a certain level of reproducibility. In the Ingamells theory, therequired sample weight, w, if the sample is homogeneous, to achieve 1% RSD at 68% confidence, is given in Eq. 2.

$$K_s = R^2 * \omega, \qquad (2)$$

where K_s is sampling constant which is the sample weight to achieve 1% RSD at the 68% confidence level and R is RSD in%. When K_s is obtained from measurements, required sample mass to achieve a certain level of reproducibility is easily calculated from Eq. 2.

Using the theory, it was determined how many particles need to be analyzed in CC EPXMA analysis, to ensure 5% RSD for each chemical element.

Results

- **Homogeneity test from bottle to bottle for the IAEA candidate RM**

In the previous study, the candidate RM was characterized using various analytical techniques [3,4]. Since the candidate RM was observed to have variations in its composition from bottle to bottle, the EPXMA technique was used to investigate which bottles are different from others, if there are, at the nanogram level, which is not possible to check with other analytical methods.

The size distributions of samples from different bottles were tested, whether they are same or not, on the basis of the two-sided Smirnov statistics. They were compared with a target sample from a bottle, namely "bottle 8", which is arbitrarily chosen out of six available bottles. As an example, the size distributions are shown in Fig. 1. The distributions are not normal distributions, so that the Smirnov test, which does not assume that the distributions of interest are normal distribution, is used in this work. The results of the statistics, namely the maximum difference between the target distribution and those of different samples along with corresponding critical values T, are given in Table I (the results of the first row in Table I is for the size distributions; the others for elemental concentrations.). It was found that, with a probability $p = 0.90$. the size distributions are identical for all the bottles except bottle 40. As shown in Fig. 1, the size distribution of bottle 40 is significantly different from others. Also, the average values of the particle diameters from different bottles are shown in Fig. 2 to demonstrate visually that the average diameter of bottle 40 is not same as for the others. Even if all the samples, except one of bottle 40, are same in their sizes at the 300 ng (equivalently, 2,000 particles) level, their homogeneity is not guaranteed at the lower mass range. The number of particles in each data was reduced systematically, using a random number generator of the Microsoft Excel software, from 2,000 and down to 50. In terms of the mass of the analyzed samples, the minimum mass investigated is about 8 ng (50 particles). As shown in Table II, they are the same down to about 15 ng (100 particles). At the 8 ng level, the sample from bottle 32 is different from the others. In other words, the sizes of samples from different bottles, except bottle 40, are the same down to 15 ng level.

TABLE I. RESULTS OF THE SMIRNOV TEST OF SAMPLES FROM DIFFERENT BOTTLES TO THE TARGET SAMPLE (SIGNIFICANT LEVEL $P = 0.90$ AND CRITICAL VALUE $T = 0.24$). THE NUMBER OF PARTICLES IN EACH DATA IS 2,000 (ABOUT 300 NG). DIFFERENT DISTRIBUTIONS FROM THE TARGET DISTRIBUTION ARE SET IN BOLDS.

Variable	Bottle 16	Bottle 24	Bottle 32	Bottle 40	Bottle 48
	Maximum difference between distributions				
Diameter	0.06	0.12	0.16	**0.39**	0.01
Mg	0.02	0.02	0.02	0.06	0.01
P	0.02	0.03	0.19	**0.62**	0.10
S	0.02	0.04	0.13	**0.54**	0.08
K	0.03	0.03	0.19	**0.59**	0.08
Ca	0.02	0.03	0.05	**0.35**	0.05
Fe	0.01	0.01	0.01	0.07	0.03

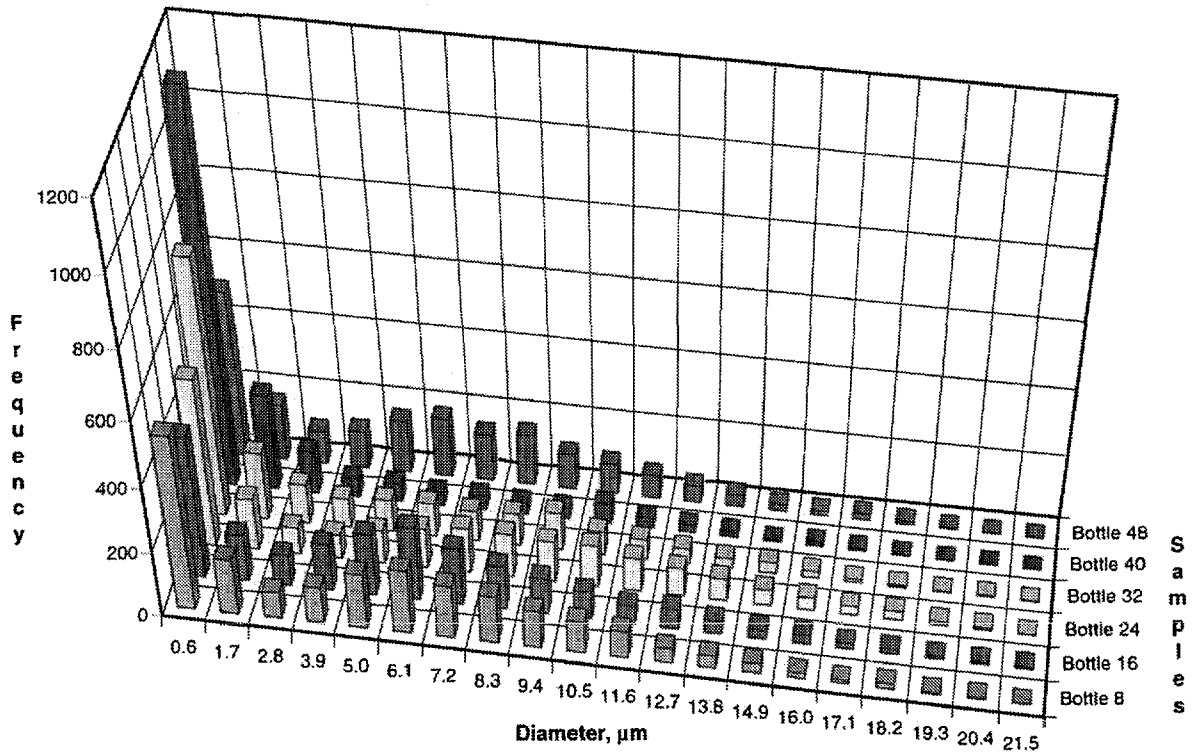

FIG. 1. *Size distributions for six samples from different bottles.*

TABLE II. RESULTS OF THE SMIRNOV TEST FOR SIZE DISTRIBUTIONS OF SAMPLES TO THE TARGET SAMPLE (SIGNIFICANT LEVEL $P = 0.90$ AND CRITICAL VALUE $T = 0.24$). THE NUMBER OF PARTICLES IN EACH DATA IS VARIED DOWN TO 50. DIFFERENT DISTRIBUTIONS FROM THE TARGET DISTRIBUTION ARE SET IN BOLDS.

No. of particles	Bottle 16	Bottle 24	Bottle 32	Bottle 40	Bottle 48
	Maximum difference between distributions				
2,000	0.06	0.12	0.16	**0.39**	0.01
1,800	0.06	0.12	0.16	**0.39**	0.02
1,500	0.06	0.12	0.17	**0.40**	0.02
1,200	0.07	0.12	0.18	**0.40**	0.02
900	0.07	0.14	0.15	**0.36**	0.03
600	0.10	0.14	0.15	**0.36**	0.07
300	0.04	0.17	0.15	**0.33**	0.05
100	0.10	0.10	0.17	**0.44**	0.16
50	0.12	0.14	**0.26**	**0.34**	0.20

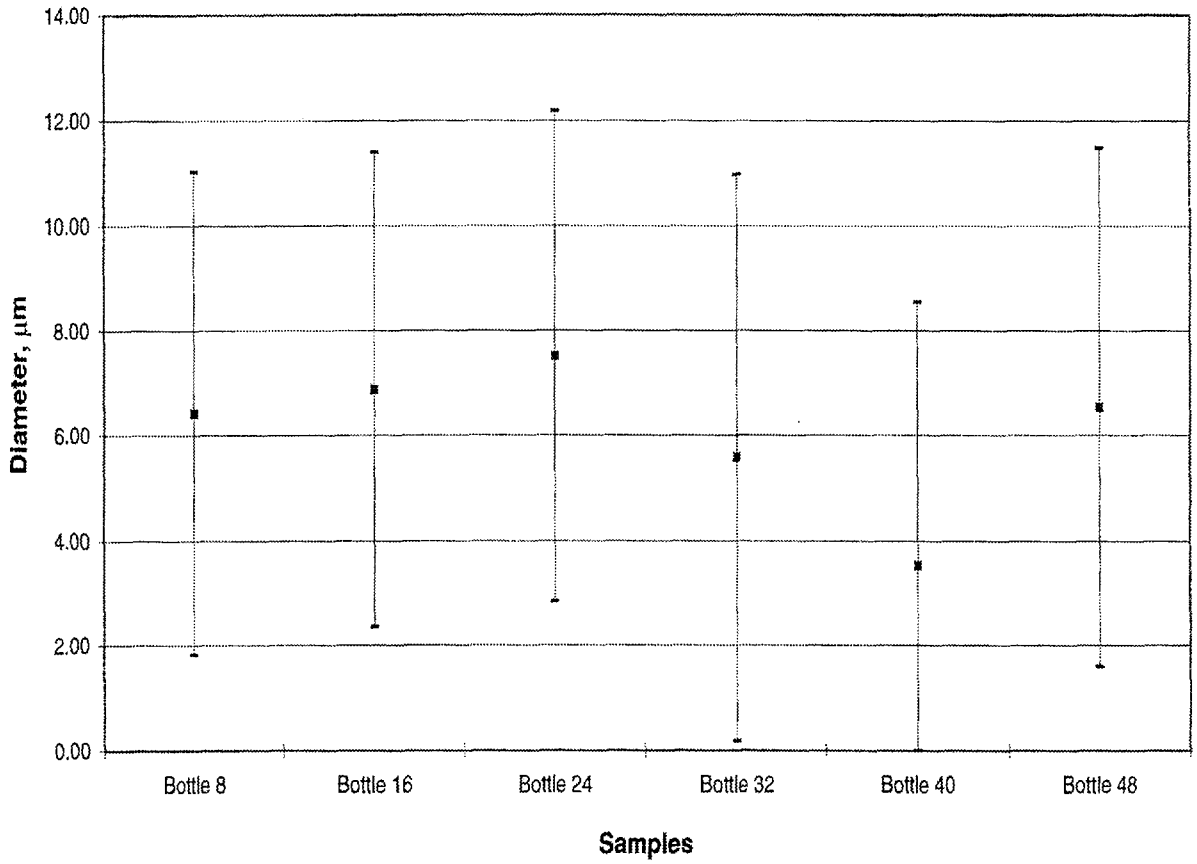

FIG. 2. *Averages of diameters, with their standard deviations, for six samples.*

For the candidate RM, Mg, P, 5, K, Ca, and Fe were the most often met elements. Among those elements, P, 5, and K are major elements. Their average concentrations, which were obtained from the intensities measured by Si(Li) EDX detector, range from 20% to 40% for all the analyzed samples. Mg, Ca, and Fe are minor elements, of which the concentrations are in the range from a percent to several percents. The similarity of the concentration distributions of these elements for each sample was tested, in the same way as it was done for the size distributions. The result of the two-sided Smirnov statistical test for the data of 2,000 particles is given in Table 1. They are all same, except bottle 40, with a probability as high as $p = 0.90$. In other words, all the samples, except bottle 40, are the same in their compositions at the 300 ng level. Bottle 40 is different for the major components such as P, S, and K, and also the minor components, such as Ca. The distributions of the Mg and Fe concentrations are all same including bottle 40; the reason for this is not clear, though. In Fig. 3, as an example, the distributions of the S concentrations are shown to demonstrate visually that bottle 40 is different from the others. Also, the number of particles in each data was reduced in the same way as it was done for the size distributions. One of the samples starts to be different from others at about 8 ng level. As shown in Table III, the sample from bottle 32 is different from the others for one of the major components, namely K. However, the difference also might be due to the instrumental instability; from the repeated measurements for a sample, it was found that the measurements do not provide reproducible results at this very low level, as described in the next section.

- **Reproducibility of repeated measurements for a sample prepared from a bottle**

A sample from bottle 8 was analyzed seven times repeatedly at different times and at different areas of the loaded filter; there are a huge number of particles on the loaded filter and only a very small part of the sample (2,000 particles each time) is analyzed using CC EPXMA.

TABLE III. RESULTS OF THE SMIRNOV TEST FOR COMPOSITIONAL DISTRIBUTIONS OF SAMPLES TO THE TARGET SAMPLE (SIGNIFICANT LEVEL p = 0.90 AND CRITICAL VALUE T = 0.24). THE NUMBER OF PARTICLES IN EACH DATA IS 50 (ABOUT 8 ng). DIFFERENT DISTRIBUTIONS FROM THE TARGET DISTRIBUTION ARE SET IN BOLDS.

Variable	Bottle 16	Bottle 24	Bottle 32	Bottle 40	Bottle 48
	Maximum difference between distributions				
Mg	0.14	0.08	0.06	0.02	0.04
P	0.10	0.20	0.16	**0.52**	0.12
S	0.12	0.08	0.16	**0.42**	0.16
K	0.14	0.10	**0.28**	**0.58**	0.12
Ca	0.06	0.02	0.06	**0.44**	0.10
Fe	0.02	0.04	0.06	0.04	0.04

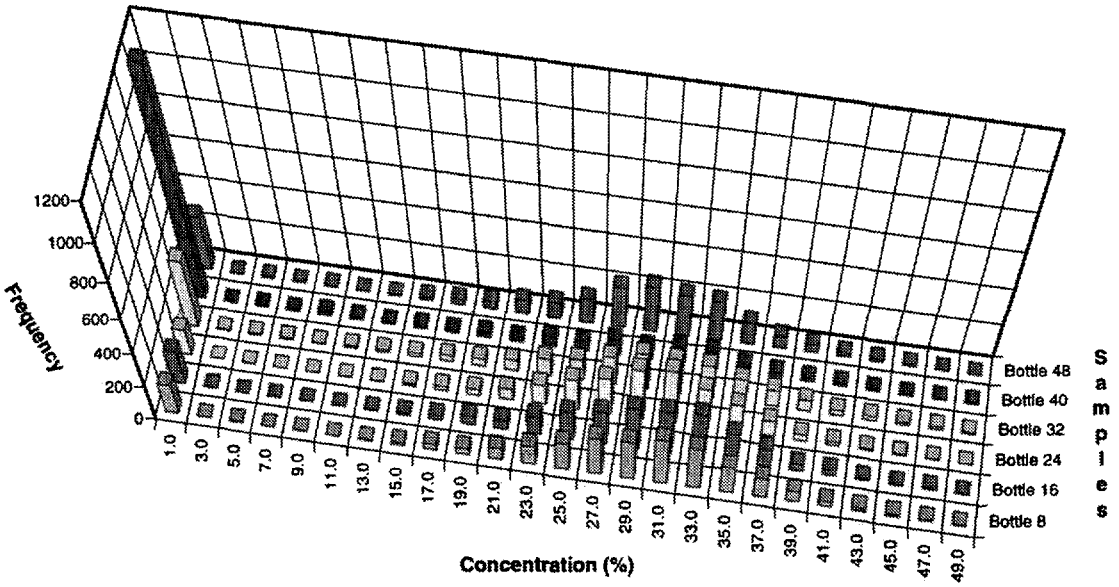

FIG. 3. *Distributions of S concentration for six samples.*

The similarities of the size distributions of those data were tested, on the basis of the two-sided Smirnov statistics. As an example, the size distributions and the results of the statistics along with corresponding critical values T, for the data of 2,000 particles each, are given in Fig. 4 and Table IV. It was found that, with a probability p = 0.90, the size distributions are identical for all the data. Even if all the data are the same in their sizes at the 300 ng level, their homogeneity was checked at the lower mass ranges. Also, the number of particles in each data was reduced in the same way as it was done previously. As shown in Table V, they start to be different at the 8 ng (50 particles) level. At the 8 ng level, two among seven data are different from the others. In other words, the sizes of the particles of a sample are the same for the different measurements at the 15 ng level.

Again, the similarity of the concentration distributions of the elements for each data was tested, in the same way as it was done for the size distributions. The result of the two-sided Smirnov statistical test for the data of 2,000 particles is given in Table IV. They are all the same with a probability as high as p = 0.90. In other words, all the different areas in the loaded filter, measured at

the different times, are the same for their compositions at the 300 ng level. Also, the data with a reduced number of particles were examined. As shown in Table 6, they start to be different at the 15 ng level. At the 15 ng level, two among seven data are different from the others for one of the major components, namely K. At the 8 ng level, four among seven data are different from the others in the major components, namely K and S. In other words, the data obtained from the same sample are reproducible for its compositions down to 45 ng (300 particles) for this candidate RM, regardless of what part of the sample, and also when it is measured. This result means that the single particle analysis using CC EPXMA provides representative information both for morphology and compositions on particulate sample, even though a very small portion of the sample is analyzed.

TABLE IV. RESULTS OF THE SMIRNOV TEST OF DATA FROM THE BOTTLE 8 TO THE FIRST DATA (SIGNIFICANT LEVEL P = 0.90 AND CRITICAL VALUE T= 0.24). THE NUMBER OF PARTICLES IN EACH DATA IS 2,000 (ABOUT 300 ng). ALL THE DISTRIBUTIONS ARE SAME, WITH NO MAXIMUM DIFFERENCE EXCEEDING THE CRITICAL VALUE.

Variable	Data 2	Data 3	Data 4	Data 5	Data 6	Data 7
	Maximum difference between distributions					
Diameter	0.08	0.16	0.19	0.19	0.16	0.09
Mg	0.02	0.01	0.01	0.02	0.01	0.01
P	0.05	0.05	0.04	0.08	0.05	0.05
S	0.09	0.15	0.12	0.14	0.15	0.06
K	0.14	0.18	0.15	0.13	0.18	0.08
Ca	0.01	0.02	0.01	0.03	0.02	0.01
Fe	0.01	0.01	0.01	0.01	0.01	0.00

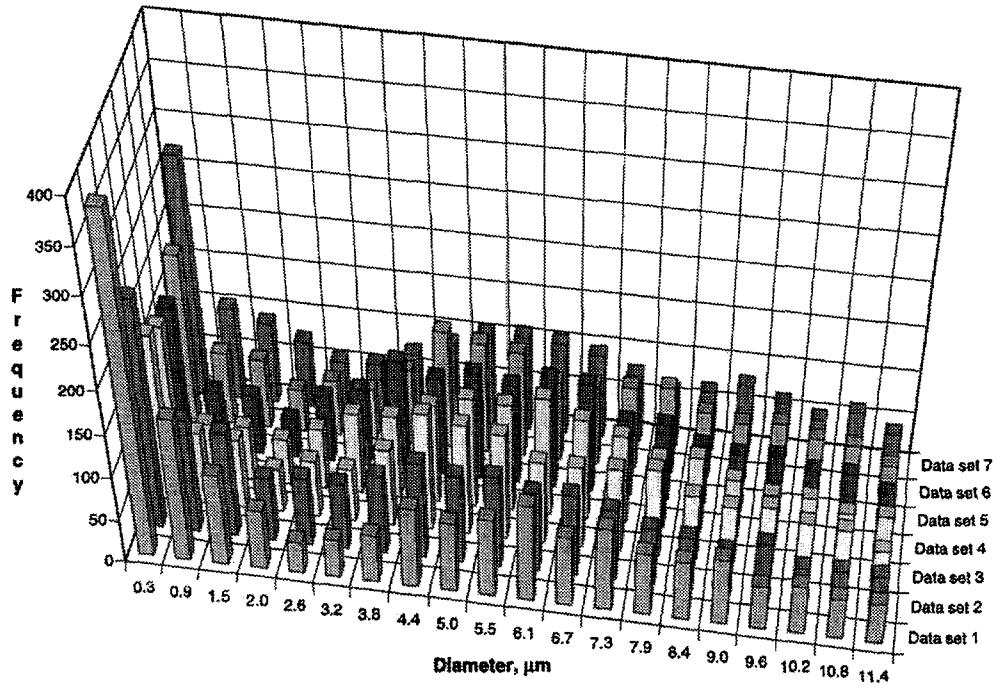

FIG. 4. *Size distributions of seven data for a sample, measured at different areas and times.*

What is the minimum number of particles to be analyzed to guarantee 5% reproducibility in CC EPXMA measurements?

The data measured for the sample prepared from bottle 8 were investigated to determine how many particles need to be analyzed to ensure the reproducibility at a certain level, for example, 5% RSD. Since particles in this sample are homogeneous in their sizes down to 15 ng (100 particles), each RSD for each chemical element was calculated for each data with a smaller number of particles down to 100, to apply the Ingamells sampling theory. If the morphology of the particles is homogeneous, which, for sure, is true for this sample down to 15 ng, the sample weight, w, in Eq. 2 can be converted into the number of particles analyzed. By fitting the data using Eq. 2 (an example of the results of fitting data is shown in Fig. 5.), the sampling constants, K_s for chemical elements are determined. Table VII shows those K_s values for the elements, and also the minimum number of particles needed to achieve 5% RSD in the measurements. The major elements in the sample, e.g. P, S, and K, show the smaller K_s values than those of the Mg, Ca, and Fe elements. For the minor chemical components, it is necessary to analyze more particles to get representative information on the sample. In Fig. 6, is shown the relationship between the number of particles needed to assure 5% RSD in the measurements and the average concentration of each element. Clearly, they are correlated; the less concentrated the element is, the more particles need to be analyzed for the analysis of the element. The number of particles required to be analyzed increases exponentially as the concentration of elements decreases.

TABLE V. RESULTS OF THE SMIRNOV TEST FOR SIZE DISTRIBUTIONS OF DATA FROM THE BOTTLE 8 TO THE FIRST DATA (SIGNIFICANT LEVEL P = 0.90 AND CRITICAL VALUE T= 0.24). THE NUMBER OF PARTICLES IN EACH DATA IS VARIED DOWN TO 50. DIFFERENT DISTRIBUTIONS FROM THE TARGET DISTRIBUTION OF THE FIRST DATA ARE SET IN BOLDS.

No. of particles	Data 2	Data 3	Data 4	Data 5	Data 6	Data 7
	Maximum difference between distributions					
2,000	0.08	0.16	0.19	0.19	0.16	0.09
1,800	0.08	0.16	0.19	0.20	0.09	0.09
1,500	0.07	0.15	0.17	0.17	0.09	0.08
1,200	0.09	0.16	0.19	0.19	0.11	0.11
900	0.08	0.17	0.20	0.20	0.10	0.11
600	0.15	0.18	0.23	0.21	0.12	0.12
300	0.08	0.22	0.19	0.20	0.10	0.14
100	0.13	0.14	0.13	0.14	0.16	0.10
50	0.14	**0.28**	0.18	**0.24**	0.12	0.12

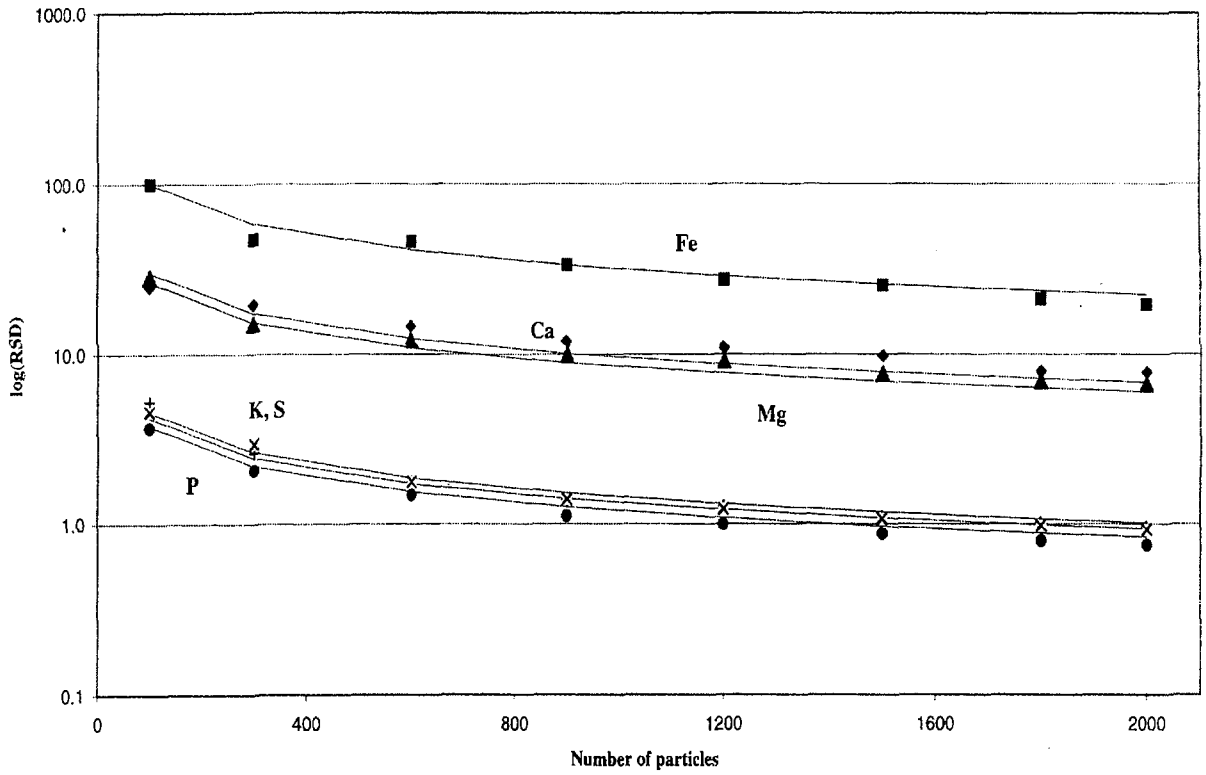

FIG. 5. *RSD vs. number of particles for each data. Ingamells sampling constant for each element is obtained by fitting data using Eq. 2. Resultant fitting curves are shown in solid lines. For the clearer display, RSD axis is in logarithmic scale.*

TABLE VI. RESULTS OF THE SMIRNOV TEST FOR COMPOSITIONAL DISTRIBUTIONS OF DATA FROM THE BOTTLE 8 TO THE FIRST DATA (SIGNIFICANT LEVEL P = 0.90 AND CRITICAL VALUE T = 0.24). THE NUMBERS OF PARTICLES IN EACH DATA ARE 100 (ABOUT 5 ng) AND 50 (ABOUT 8 ng). DIFFERENT DISTRIBUTIONS FROM THE TARGET DISTRIBUTION ARE SET IN BOLDS

Variable	Data 2	Data 3	Data 4	Data 5	Data 6	Data 7
	Maximum difference between distributions					
No of particles = 100						
Mg	0.07	0.03	0.05	0.05	0.04	0.02
P	0.07	0.07	0.18	0.09	0.11	0.07
S	0.09	0.10	0.15	0.12	0.07	0.10
K	0.15	**0.27**	**0.25**	0.21	0.19	0.15
Ca	0.03	0.08	0.06	0.04	0.02	0.04
Fe	0.05	0.05	0.03	0.05	0.03	0.01
No of particles = 50						
Mg	0.04	0.04	0.16	0.04	0.06	0.08
P	0.12	0.12	0.14	0.20	0.14	0.14
S	0.10	0.18	**0.30**	**0.22**	0.10	0.16
K	**0.40**	**0.40**	**0.44**	**0.34**	0.16	0.12
Ca	0.10	0.02	0.10	0.06	0.08	0.08
Fe	0.06	0.04	0.02	0.04	0.04	0.04

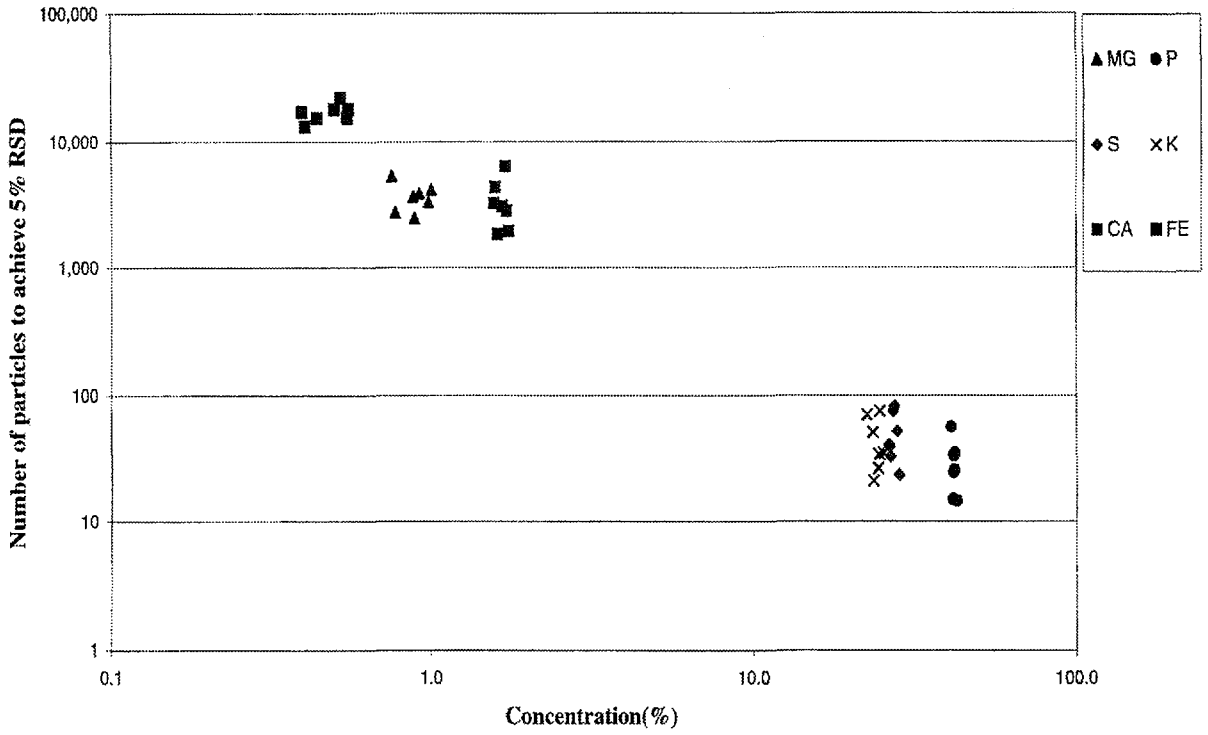

FIG. 6. *The relationship between the number of particles needed to assure 5% RSD and the average concentration of each element. The seven data for the same sample are used for the plot.*

TABLE VII. AVERAGE INGAMELLS SAMPLING CONSTANTS FOR ELEMENTS OBTAINED FROM ALL THE DATA AND AVERAGE NUMBER OF PARTICLES NEEDS TO BE ANALYZED TO ACHIEVE 5% RSD.

	Mg	P	S	K	Ca	Fe
Ks	101,949	3,409	3,308	3,954	76,839	392,073
5% RSD	4,078	136	132	158	3,074	15,683

Conclusions

At the level of ca. 300 ng, particle size distribution and distribution of concentrations of Mg, P, S, K, Ca, and Fe are the same for the samples from the different bottles of a IAEA candidate RM, except for bottle 40. One out of the remaining five samples, which are same at the 300 ng level, becomes different from the other four samples, when the sample mass is as much small as 8 ng.

The seven data measured at different areas and times for the same sample, are the same at the level of 300 ng, both in their sizes and compositions. At the level of 8 ng, two among seven data are different from the others, in terms of their size distributions. For the concentration distributions of the elements, four among the seven data are different at the level of 8 ng.

Even though the number of particles analyzed using CC EPXMA is very small compared to that collected, the major elements for this candidate RM need to be analyzed just for less than 200 particles, to assure 5% RSD in CC EPXMA measurements. For the minor elements, the required number of particles to be analyzed, for assuring 5% RSD, ranges from several thousands to tens of

thousands. The less concentrated an element is, the more particles are required to be analyzed for the element, to achieve meaningful reproducibility. The number of particles required to be analyzed, to insure a certain level of reproducibility, increases exponentially as the concentration of elements decreases.

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