

Producing Samples for the Organization of Proficiency Tests. Study of the Homogeneity of Replicas Produced From Two Atmosphere Generation Systems

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This article describes two atmosphere generation systems used for the production of replicas. The first, the Sputnik system, is based on the Sputnik air sampler developed by the National Institute of Occupational Health in Oslo (Norway). It is used to generate asbestos fibres or silica particles and allows the simultaneous production, by means of sampling on filters, of up to 114 replicas. The second is a multipurpose system that allows dust sampling on foams used with the CIP 10-R device. Twenty samples can be taken simultaneously. In total, 120 series of samples allowed characterization of the variability of the two generation systems used for the production of replicas loaded with asbestos fibres or silica dust. The coefficients of variation characterizing the dispersion of the filter loading in the Sputnik system are <10% for high densities asbestos fibre or silica dust samples. The coefficient of dispersion is on average higher when the asbestos fibre density is lower. The differences observed between the measurements taken on the different crowns of the Sputnik system are low and <2%. The results obtained with the multipurpose system show that replica dispersion is on average equal to 4%, which will allow proposal in the near future of a proficiency test dedicated to the quantitative analysis of crystalline silica on foams sampled with the CIP 10-R device.

Keywords: asbestos; atmosphere generation; replicas; silica; variability

INTRODUCTION

In the field of industrial hygiene, laboratories have procedures to monitor the quality of their analyses. When non-standardized methods are used, these must be validated in conformity with standard ISO/IEC 17025 (2005); comparing the results between laboratories is one of the methods proposed. Participation in inter-laboratory comparison programmes is also a way recommended by this standard to monitor the quality of the services provided. The aim of inter-laboratory proficiency tests is then 2-fold:

analytical method validation and laboratory performance assessment. These requirements have led many bodies to propose proficiency tests. In this respect, the European Proficiency Testing Information System (www.eptis.bam.de) database contains >800 tests in the America, Europe, and Australia. The need to accredit test organizers has been imposed little by little with the development of the standard ISO/IEC 17043 (2010) which describes the criteria concerning the quality to be respected when developing proficiency tests and the use that can be made of these tests by the accreditation bodies. Other documents can also be useful to organizers: ILAC-G13 (2007) on test organizer competence and ISO 13528 (2005) on statistical data processing.

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Among the tests developed within the context of method validation, that employed by Butler and Howe (1999) can be cited for testing sample dissolving procedures. Numerous tests are organized on a regular basis to assess the performance of laboratories, for example, the Proficiency Analytical Testing in the USA (Esche and Groff, 1997) and the Workplace Analysis Scheme for Proficiency tests in the UK (Jackson and West, 1992). In France, the ALASCA [French acronym of Proficiency of Laboratories to Analyse Airborne Chemical Products, (Langlois *et al.*, 2008)] tests are organized by the Institut national de recherche et de sécurité (INRS). When occupational exposure limit values were set for hazardous chemicals and for carcinogenic, mutagenic, or reprotoxic substances, these tests were introduced to lend support to the regulations requiring that technical verifications can be carried out by accredited laboratories. In certain cases (silica, asbestos fibres in workplaces or in the environment for example), participation in proficiency tests is compulsory for bodies wishing to obtain accreditation.

Most of these tests are based on the distribution of replicas, assumed to be equivalent, to participating laboratories. In most cases, these replicas are produced by splitting up a reference sample, as in the case of powders, or by producing aliquots from a mother suspension. Rarer are articles describing the production of replicas by atmospheric sampling, the cost of these devices probably slowing down their entry into general use. In this respect, Baron and Deye (1987) have described an atmosphere generation system capable of producing 320 asbestos fibre-loaded filters at a time. Again in the area of asbestos, a system with a lower capacity allowing the production of 10 replicas has been described by Skogstad *et al.* (1996). A Sputnik air sampler has been developed by National Institute of Occupational Health (NIOH) in Norway. This device produces ~100 replicas. It has been used for instance to produce welding gas-loaded filters (Anglov *et al.*, 1993; Dyg *et al.*, 1994). Stacey *et al.* (2003) also used this device to produce silica particle-loaded filters.

The aim of this article was to describe the validation of two atmosphere generation systems intended for replica production.

The first uses the Sputnik sampler to produce asbestos fibre- or silica particle-loaded filters. This installation allows the production of replicas for the organization of proficiency tests to assess the performance of laboratories in counting asbestos fibres either by phase contrast microscopy (ALASCA MOCP tests, MOCP is the French acronym of Phase Contrast Optical Microscopy) or by transmission

electron microscopy (ALASCA MET tests, MET is the French acronym of Transmission Electron Microscopy) or in analysing crystalline silica (ALASCA SIL tests, SIL is the abbreviation of silica) when the particles have been sampled on a filter by means of a particle selector (Dorr-Oliver Cyclone).

The second is a system termed multipurpose, as various sampling supports can be used. In one configuration, it allows dust sampling on filters and the sequential stoppage of different samplings to produce standard filters. In the second configuration, the conventional alveolar fraction of dust is collected on foams by means of CIP 10-R device (Courbon *et al.*, 1988). Only this second configuration of the system is described in this article. Some 20 replicas can be produced simultaneously in controlled conditions to provide the material for a proficiency test on the quantitative analysis of silica on foams. The CIP 10-R device and the Dorr-Oliver cyclone are two samplers used in France to verify respect of the limit values of occupational exposure to crystalline silica.

DESCRIPTION OF THE SYSTEMS

Sputnic system

The Sputnik sampling system was designed by INRS from an aerosol sampler developed by NIOH with the intention of carrying out inter-laboratory analytical comparisons. It comprises a stainless steel cylinder with a conical base and includes a sampling grid with 114 critical orifices with diameters of ~0.4 mm allowing samples to be taken with a constant flow rate. One hundred and eleven orifices with a flow rate of ~1.8 l min⁻¹ (±1.2%) were used in the experiments described in this article. The orifices are spread over six concentric crowns, the number of critical orifices per crown being:

- 34 on Crown 1,
- 28 on Crown 2,
- 22 on Crown 3,
- 16 on Crown 4,
- 10 on Crown 5,
- 4 on Crown 6.

The diagram of principle is described in Fig. 1a. Figure 1b shows its integration under a laboratory fume hood.

A vacuum pump at the outlet of the system creates a constant vacuum of ~0.3 bar absolute after critical orifices, to ensure a constant flow rate during sampling. A pneumatic control valve maintains inside the sampler a pressure level lower than the atmospheric pressure (-20 Pa) as a safety measure.

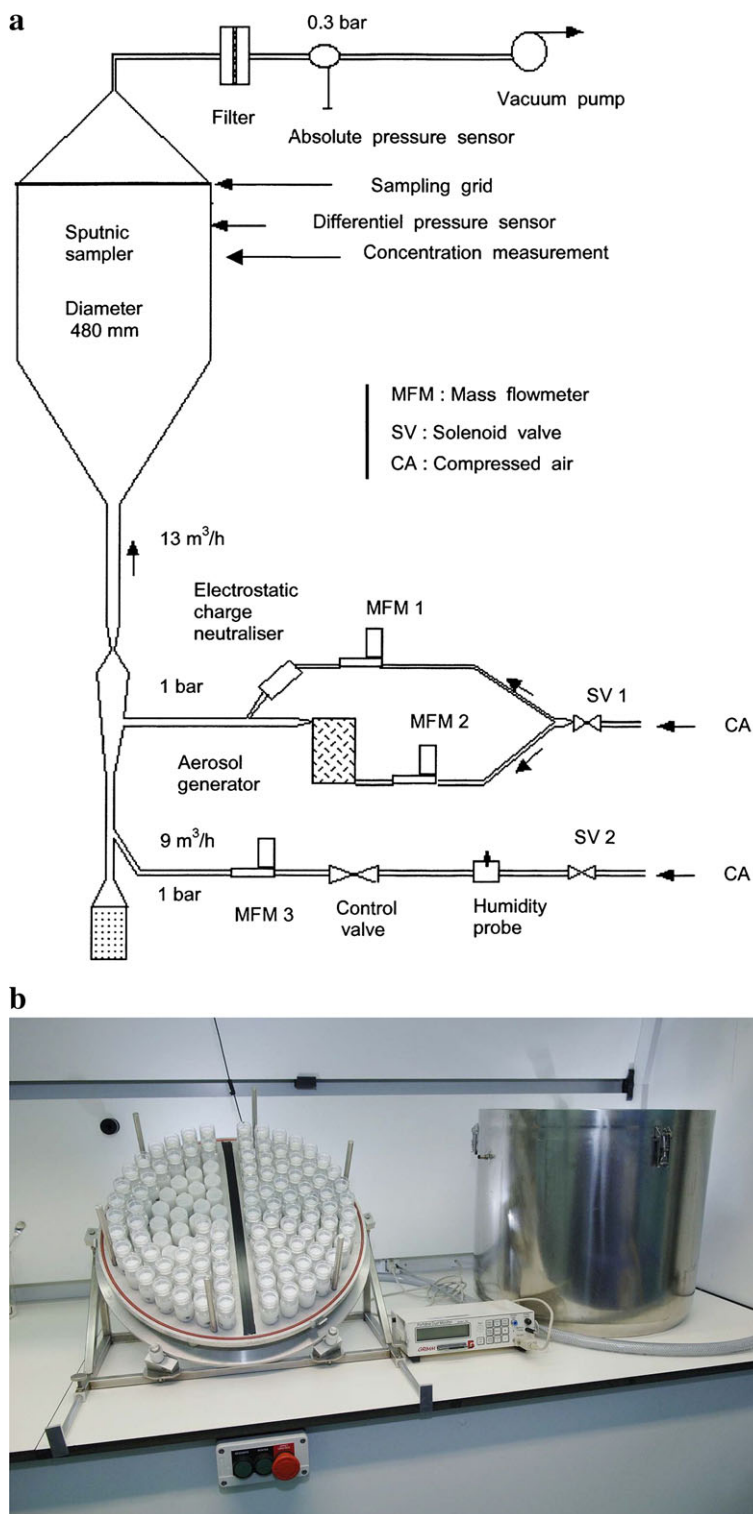


Fig. 1. (a) Diagram of principle of the Sputnic system and (b) Sputnic system located under a laboratory fume hood.

Two aerosol generators are used:

- The first, to generate silica particles, is a rotating-brush PALAS[®] model, type RBG 1000. The stainless steel brush is located at the end of a dust-filled cylinder. The concentration is held constant by setting the piston rise speed in the cylinder. This very conventional type of generator continuously disperses a high quantity of dust. It is well suited to generate silica dust.
- The second, to generate asbestos fibres, is a fluidized bed generator developed by TSI Incorporated. The fibres are introduced into a bed of glass beads by means of a chain. An airflow rate of between 6 and 13 l min⁻¹ fluidizes the fibres. The advantage of this generator is its ability to disperse low quantities of dust, which is particularly suited to generating asbestos fibres (Skogstad *et al.*, 1996).

In both cases, a GRIMM particle counter monitors the change in aerosol concentration in the sampler. The aerosol injection system was designed to create strong turbulence in order to homogenize the aerosols; a straight section then stabilizes the airflow. An air ionization system (corona effect) neutralizes the electrostatic charges of the particles to limit the deposit of particles on the walls of the system and on the sampling heads.

A computer control station is installed remotely to start or stop an experiment and to manage it in the case of an emergency stoppage. A system control and command application were developed with the LABWindows CVI (National Instrument) instrumentation software to monitor the generation process in real time. Flow rate, pressure, humidity, and concentration data are stored on the computer and displayed on a control panel close to the system. A report of the results of the generation parameters can be printed after each experiment to verify the stability of these parameters and to reproduce similar generation conditions from one experiment to another.

Operator safety was taken into account when designing the system and the layout of the installation site. This is maintained at a low pressure compared to the adjacent areas, and a decontamination chamber with a shower is installed in case of accidental asbestos pollution. In addition, a wash hand basin is located under the fume hood for washing the different stainless steel elements. The water used for washing is filtered before being discharged into the drain.

Multipurpose system

This generation system was developed and produced by the company IMF (54320 Maxéville,

France). In this article, only the configuration of the system, which makes it possible to sample simultaneously 20 foams with the CIP 10-R devices is described. Its diagram of principle is given in Fig. 2a. Figure 2b shows its integration under a laboratory fume hood.

The system comprises a cylindrical stainless steel cell fitted to a monoblock chassis. The principle of operation is based, as for the Sputnik system, on maintaining a constant pressure inside the cell by supplying compressed air and suction by means of a vacuum pump. An automation system ensures flow rate regulation, from the sensor data, taking into account the operation of the CIP 10-R devices. In the cell, a rotating plate can accept up to 20 samplers, the rotation of the plate being in alternate directions at a speed of 1 r.p.m.

The aerosol generator is a rotating brush PALAS[®] model, type RBG 1000. It generates under compressed air particles for which static electricity has been eliminated by an air ionization system (corona effect). An air intake then dilutes the aerosol, which arrives *via* the upper section of a cone and then passes through a venturi tube; this creates a turbulent flow to promote homogenization. A honeycomb grid located between the cone and the sampling zone enables laminar flow. The excess aerosol is stopped by an absolute filter so as not to damage the suction system. A nephelometer measures the mass concentration of the suspended dust in real time. The captured dust enters a measurement cell under an infrared beam. The diffused light is measured by a photodetector located at 180°. This measurement indicates the concentration in the system and regulates the concentration by acting on the speed of the piston of the PALAS[®] generator.

The different airflow rates are checked at four points of the installation by three regulation mass flowmeters and a simple mass flowmeter: the first located before the generator, the second before the electrostatic charge neutralization system, the third before the humidity probe, and the last, a non-regulator, before the vacuum pump. A pressure level lower than the atmospheric pressure (−30 Pascal) is maintained inside the cell as a safety measure.

A computer with a synoptic screen controls the system. The flow rate, pressure, relative humidity, and aerosol concentration data are displayed in real time and stored for subsequent consultation. An emergency stop control is foreseen to manage any malfunction in overall safety.

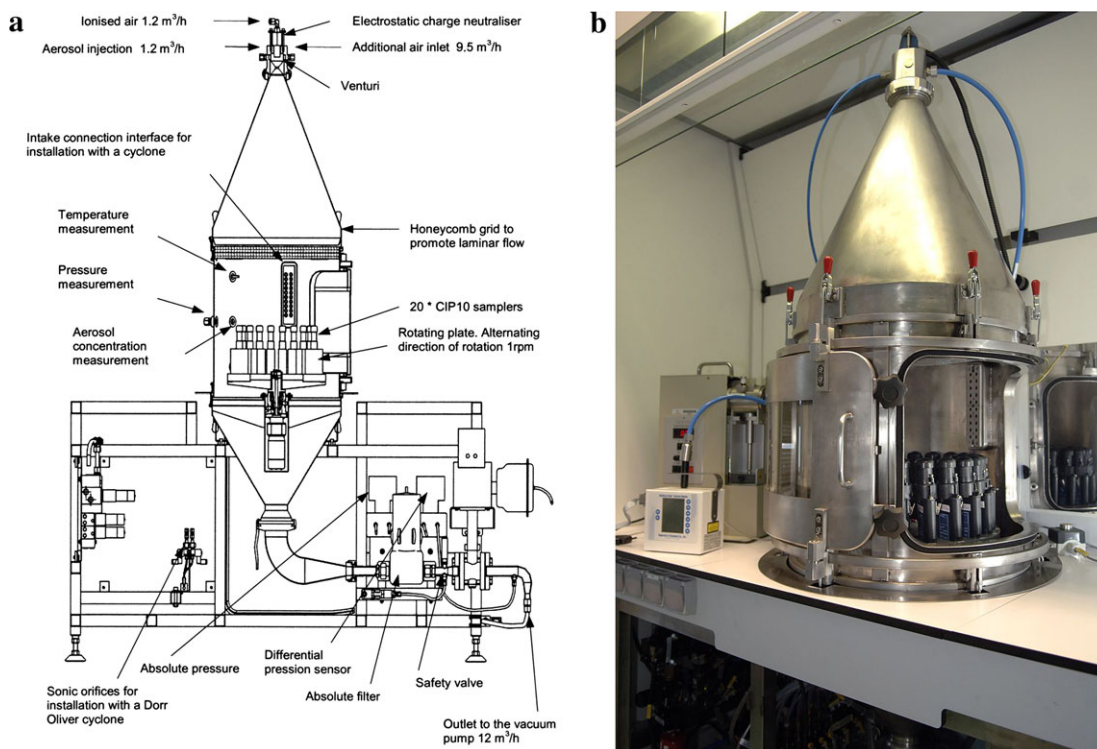


Fig. 2. (a) Diagram of principle of the multipurpose system and (b) Multipurpose system located under a laboratory fume hood.

REPLICA SAMPLING AND ANALYSIS

Sputnic system

The silica samples (α -quartz) were taken on Pall Gelman[®] vinyl polychloride filters, pore diameter 5 μm , housed in 25 mm Millipore[®] cassettes on cellulose pre-filters. The tightly assembled cassettes are preceded by 10 mm Dorr-Oliver cyclones, as described in standard NF X 43-259 (AFNOR, 1990), which allow selection of the respirable fraction of the dust. Forty series of samples were taken. For each, about 50 filters distributed randomly on the Sputnic grid were sampled.

The quartz analyses were carried out on all the sampled filters by X-ray diffraction using a direct method (AFNOR, 1995a). Each analysis was repeated twice (i.e. three analyses per filter). All the replicas distributed during the ALASCA SIL tests are checked by this method. The filter loading levels varied between 50 and 500 μg .

The asbestos fibre samples (chrysotile) were taken on filters made of a cellulose ester mixture located in open-faced Millipore[®] cassettes on cellulose pre-filters. The filters distributed during the ALASCA MET and ALASCA MOCP tests cannot be

checked systematically before distribution to the participants, hence complementary checks are required: before each sampling series, the electrostatic charges on the cassettes are eliminated by means of an ionization capacitive system. Before and after each sampling series, the critical orifice flow rates are measured to ensure that the sampling flow rate remains constant before and after sampling. The aim was to verify that the critical orifices are not obstructed by dust, which would imply cancelling the sample. Thirty-eight series of samples were taken on 25 mm diameter filters and 31 on 37 mm diameter filters. For each, 10 filters, distributed randomly on the Sputnic grid, were analysed to check for homogeneity. On certain occasions, it was possible to analyse a higher number of filters (in the order of 40).

Fibre counting was done in accordance with standard XP X 43-269 (AFNOR, 2002). Each counting was repeated once (i.e. two counts per filter). Repeating the counting allows the calculation of a variance characterizing only fibre dispersion as a function of sampling points on the Sputnic grid, eliminating the variance due to fibre counting.

The counting rules used (observing 200 fields or counting 100 fibres) determine two density ranges:

- Low densities when the stoppage criteria is the number of fields observed.
- High densities when the stoppage criteria is the number of fibres counted.

Account taken of the surface area of an observation field (0.007854 mm^2), the limit density D_l separating the two ranges is equal to $63.7 \text{ fibres mm}^{-2}$.

The density levels of the filters distributed during the ALASCA tests vary between 30 and $650 \text{ fibres mm}^{-2}$.

Multipurpose system

The silica samples were taken from mixtures of crystalline silica (α -quartz) and talc on foams placed in the cups of the CIP 10-R. Eleven series of samples were taken. Twenty CIP 10-R were used for each. The flow rate of the CIP 10-R was measured before and after each sampling series. Thus certain measurements were eliminated when an incident during sampling was observed (incorrect operation of a CIP 10-R for example). The quartz and talc proportions of the mixture were chosen so as to allow three levels of quartz loading:

- The first level corresponds to $\sim 960 \mu\text{g}$ of quartz deposited in the cup. This is the expected amount of quartz for an 8-h sampling in a workplace where the quartz concentration is equal to twice the limit value (0.1 mg m^{-3}).
- Levels two ($480 \mu\text{g}$) and three ($48 \mu\text{g}$) correspond approximately to the amount of quartz expected for samples taken in a workplace where the concentrations are equal to the limit value and one-tenth of the limit value respectively.

Whatever the case, account taken of the sampling duration foreseen, the dust concentration in the cell is adjusted so that the total amount of material sampled is $\sim 5 \text{ mg}$.

The analyses were carried out in conformity with standard NF X 43-295 (AFNOR, 1995b). This involves an indirect analytical method; the different steps leading to the results are:

1. Weighing the cups with foams;
2. Calcinating the foams in crucibles, recovering the ashes by filtration on polycarbonate filters, and weighing the filters; and
3. Analysing the quartz on filters by X-ray diffraction.

Checking the different steps of the preparation ultimately allows calculation of the variance characterizing only the dispersion of the quantity of quartz sampled by subtracting the variance linked to preparation.

DATA ANALYSIS

Data transformation

Fibre sampling. For each experiment performed on the Sputnic system, 10 filters are chosen randomly to assess sampling homogeneity. The y -axes of Figs. 3 and 4 represent the fibre densities obtained during the double counting of 10 filters. The x -axes represent the mean density obtained for each experiment. Figure 3 concerns samples for which density is $>63.7 \text{ fibres mm}^{-2}$: in this case, a logarithmic transformation of the data was carried out (logarithmic scale). Figure 4 concerns samples for which density is $<63.7 \text{ fibres mm}^{-2}$; here a square root transformation of the data was carried out (square root scale).

These figures thus show that:

- The dispersion of the results is approximately constant on a logarithmic scale for the fibre samples when the fibre density is $>63.7 \text{ fibres mm}^{-2}$ (59 experiments).
- The dispersion of the results is approximately constant on a square root scale for the fibre samples when the fibre density is $<63.7 \text{ fibres mm}^{-2}$ (10 experiments).

These observations were already made by several authors (Miller, 1984; Brown *et al.*, 1994, 2002).

It can thus be accepted that

$$\text{Var}(\text{Log}(X)) = a = \text{constant},$$

where X representing the density of fibres per mm^2 for high densities.

$$\text{Var}(\sqrt{X}) = b = \text{constant},$$

where X representing the density of fibres per mm^2 for low densities.

A first-order limited development, such as that described in the article by Grzebyk *et al.* (2005), allows calculation of the variance of the functions $\text{Log}(X)$ and \sqrt{X} and the following relationships to be obtained:

$$\begin{aligned} \text{Var}(\text{Log}(X)) &\approx \text{Var}(X)/\theta^2 = a \\ \text{i.e. Var}(X) &= a \times \theta^2, \end{aligned}$$

$$\text{Var}(\sqrt{X}) \approx (0.5/\sqrt{\theta})^2 \times \text{Var}(X) = b,$$

$$\text{i.e. Var}(X) = 4 \times b \times \theta$$

where θ is the mean value of the measured densities for a given experiment.

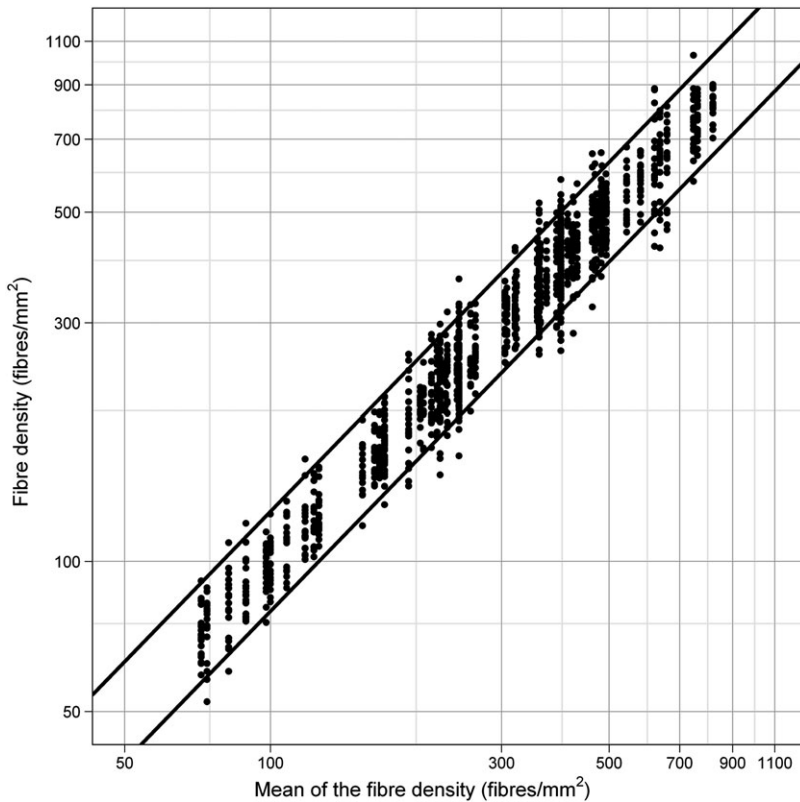


Fig. 3. Logarithmic scale; fibre density as a function of the mean of the fibre density for each experiment. Case of high densities.

If DI is the limit density separating the high densities from the low densities, there must be equality of variance for this density:

$$a \times DI^2 = 4 \times b \times DI \quad \text{i.e. } a = 4 \times b/DI.$$

This latter relationship allows, for samples corresponding to low densities, calculation of the relative variance of heterogeneity, which would be obtained if the stoppage criterion for counting was the number of fibres counted.

Silica sampling. For the silica samples on the Sputnik system or the multipurpose system, the data analysis shows that the dispersion of the results is approximately constant on a logarithmic scale; a logarithmic transformation of the data was therefore carried out.

Calculating the relative variance of heterogeneity

The relative variance of heterogeneity observed is broken down into a variance due to different positions in the system and a variance due to the analytical process. To estimate these two sources of

variability, an analysis of variance with nested random effects was performed on the magnitude measured after appropriate transformation of the data (logarithmic or square root). The random effects in order of nesting are:

- Sampling position (111 positions for the Sputnik system and 20 positions for the multipurpose system).
- Repetition number of the analysis (Two repetitions for counting, three for quantitative analysis of silica, and four for weighing).

For each experiment performed, the analysis of variance with nested effects determines the variance component due to position, eliminating the variance components due to fibre counting, analysis, and sample preparation.

For the silica and asbestos fibre samples taken with the Sputnik system, this analysis directly estimates the variance due to different positions in the system; this is termed the relative variance of heterogeneity of the system.

On the other hand, for the samples taken on the multipurpose system, the different steps of the analytical method used must be taken into account as follows:

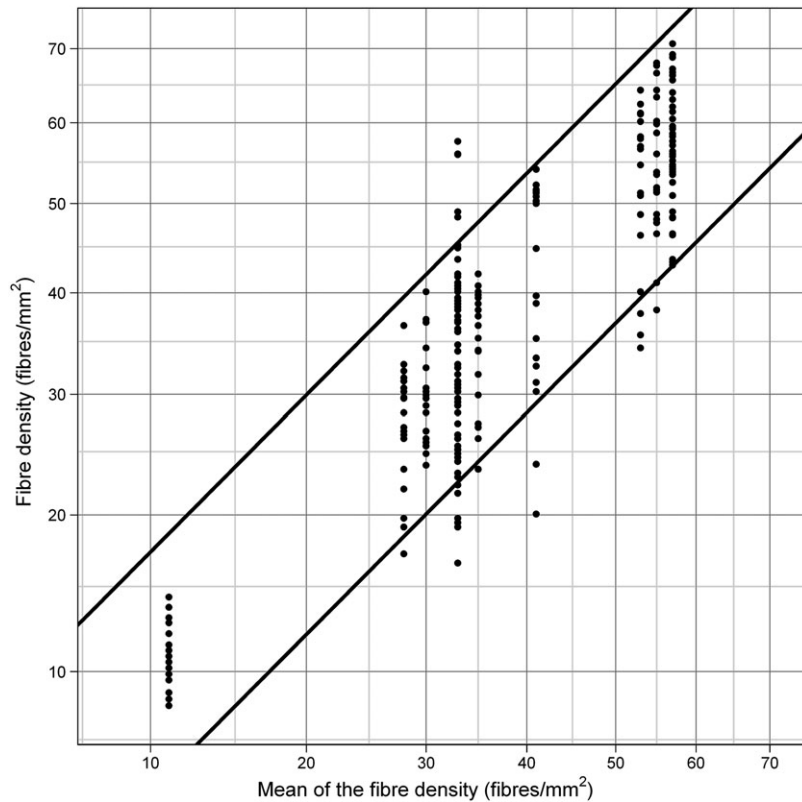


Fig. 4. Square root scale; fibre density as a function of the mean of fibre density for each experiment. Case of low densities.

1. Weighing the cups with foams;
2. Calcinating the foams in crucibles, recovering the ashes by filtration on polycarbonate filters and weighing the filters; and
3. Analysing the quartz on filters by X-ray diffraction.

An analysis of variance is computed using the weight of the foams (V1), the weight of the filters (V2), and the weight of quartz determined by the analysis (V3).

Using the X-ray diffraction analysis, the calculated variance V3 combines the component due to position with the variance components due to the different preparation steps. The latter can be estimated by $V2 - V1$, so that the variance characterizing the dispersion of the amount of quartz sampled alone is equal to $V3 - (V2 - V1)$.

RESULTS AND DISCUSSION

Figures 5 and 6 represent the relative variances of heterogeneity of the systems obtained for each of the experiments carried out.

Figure 5, concerning asbestos sampling using the Sputnic system, shows the relationship between the

relative variance of heterogeneity and the mean of the fibre density for asbestos fibres sampled on 25 mm cassettes [(A-25), 38 experiments] and on 37 mm cassettes [(A-37), 31 experiments)].

Figure 6, concerning quartz sampling using both systems, shows the relationship between the relative variance of heterogeneity and the mean of the mass of quartz sampled on the filters [Sputnic system (S-Sputnic), 40 experiments] or on the foams [multi-purpose system (S-Multipurpose system), 11 experiments].

The means of the relative variances of heterogeneity and the coefficients of variation characterizing the different sampling series are presented in Table 1. Knowing the relative variance of heterogeneity is useful when the assigned value in proficiency tests (best estimation of the true value of the quantity of matter on each support sampling) is determined by the participants. This is generally the case for the fibre counting tests. For this reason, the relative variance of heterogeneity must be added to the relative analytical variance (square of the coefficient of variation of the analytical method) to determine the reference variance to which the variance characterizing the dispersion of

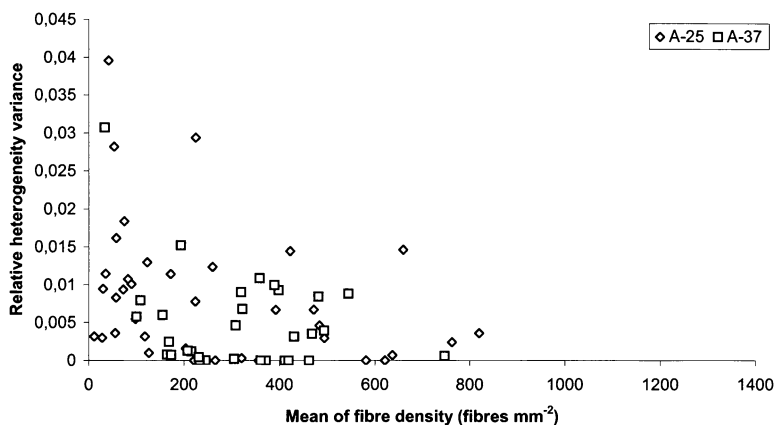


Fig. 5. Relative variance of heterogeneity as a function of mean fibre density for asbestos fibres sampled on 25 mm cassettes (A-25) and on 37 mm cassettes (A-37).

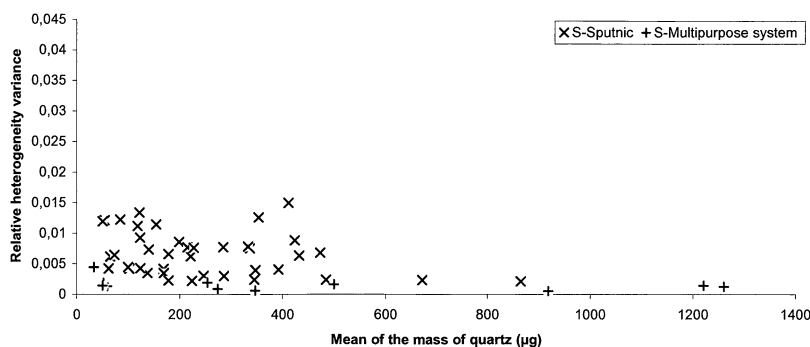


Fig. 6. Relative variance of heterogeneity as a function of the mean of the mass of quartz sampled on filters (S-Sputnic) or on foams (S-Multipurpose system).

Table 1. Mean relative variance of heterogeneity and coefficient of variation for the different sampling series

	Number of measurements	Mean relative variance of heterogeneity	Mean coefficient of variation (%)
Asbestos-25 low densities	9	0.0137	11.7
Asbestos-25 high densities	29	0.0066	8.1
Asbestos-37 low densities	1	0.0307	17.5
Asbestos-37 high densities	30	0.0040	6.3
Silica-Sputnic system	40	0.0067	8.2
Silica-multipurpose system	11	0.0016	4.0

the results of a laboratory is compared. The classification of the laboratories participating in the tests is thus independent of the quality of the replicas.

The results presented in Table 1 show that the coefficients of variation characterizing the dispersion of samples during the different experiments on the Sputnic system vary from 6.3 to 17.5%. The results concerning the silica and fibre samples when the density is >63.7 fibres mm^{-2} are very close (coeffi-

cient of variation of between 6.3 and 8.2%). It shows that the coefficient of variation depends little on the diameter of the cassette used for the asbestos samples (25 or 37 mm) or on the nature of the aerosol generated (asbestos fibres or silica). It also shows that the analysis of variance with nested random effects used to process the data eliminates the analytical error and yields close results for two pollutants (silica and asbestos fibres) for which analytical

uncertainties are very different (a few percent for one and a few tens of percent for the other). The highest dispersion coefficients were obtained for asbestos fibres when the fibre density on the filters was <63.7 fibres mm^{-2} (11.7% on average for the samples on 25 mm cassettes, 17.5% for the samples on 37 mm cassettes but only one determination). A difference in the statistical data processing could be mentioned to explain this, a square root transformation having been carried out in this case compared to a logarithmic transformation for the high densities. This explanation does not however seem plausible as carrying out a logarithmic transformation on the data corresponding to low densities results in further increasing the relative variance of heterogeneity.

The mean coefficient of variation obtained for the silica samples with the multipurpose system is the lowest of all the experiments described in this article (4%). This is probably due to the design of the system itself, all the samplers being located on the same crown of a rotating plate. This certainly guarantees better sampling homogeneity but at the price of producing replicas in a more limited number (20 compared to 111 with the Sputnic system). This coefficient of variation characterizes the variation in the quantity of quartz on the foams and it is this value, which is useful to know to organize a proficiency test intended to quantitative quartz analysis. However, these are mixtures that were generated (quartz + talc) and the coefficient of variation characterizing the variation in the quantity of mixture present in the foams is much lower [(1.8%), data obtained from variance V1, Calculating the Relative Variance of Heterogeneity section].

For the samples taken with the Sputnic system, we sought to ascertain whether differences might exist between the different crowns of the Sputnic grid. To do this, the magnitude measured (fibre density on the filter or amount of quartz on the filter) was divided by the mean measured magnitude for a given experiment to compare the results of one experiment with another. Normalized results close to unity were thus obtained, whatever the experiment considered. Table 2 presents the results obtained for all the experiments. For the samples taken on open-faced cassettes, the means are no different from one crown to another ($P = 0.12$ for the 25 mm diameter cassettes, $P = 0.26$ for the 37 mm diameter cassettes). For the silica samples, the means from one crown to another are statistically different ($P = 0.00$). Whatever the case, the mean variations from one crown to another are low. If Crown 6 for which only limited results are available is excluded, the divergences compared to unity are at most 2% and no gradient is observed.

Table 2. Mean of the normalized results, crown by crown, for the fibre samples and the silica samples taken on the Sputnic system

Crown number	Fibre samples on 25 mm cassettes	Fibre samples on 37 mm cassettes	Silica samples
1	0.98 (213)	1.00 (290)	1.00 (1949)
2	1.00 (209)	1.00 (272)	0.99 (1545)
3	1.02 (132)	1.02 (150)	1.00 (1068)
4	1.01 (99)	0.98 (130)	1.01 (879)
5	1.01 (75)		1.01 (564)
6	1.05 (8)	1.03 (38)	0.98 (153)

The figures in brackets correspond to the number of measurements. Remark: On account of the larger size of 37 mm cassettes, no sample could be taken on Crown 5.

Several publications describe the use of the Sputnic air sampler for producing replicas. The article of Stacey *et al.* (2003) mentions a coefficient of variation of 5.6% for producing silica-loaded replicas with the Sputnic air sampler. This value, which includes an analytical uncertainty of $\pm 5\%$, the analyses having been carried out by infrared spectrophotometry, is lower than that the one determined in this article. In another article, Stacey (2005) published close results for three quartz generations (coefficients of variation of 5.6, 5.0, and 4.9%). This time, it is stated that the number of samples was equal to 49 for each generation; it should however be borne in mind that it is not known if the choice of the critical orifices used resulted from random selection. In our experiments, 50 samples were taken for each generation; the critical orifices used were chosen randomly from the 111 positions, meaning that all the sampling positions were used during all the experiments. This may explain the higher replicate variability. Moreover, the mean coefficient of variation determined in this article (8.2%) for the production of quartz-loaded filters with the Sputnic system is the mean of a large number of determinations (40). Figure 6 indicates a dispersion of the values of the relative variances of heterogeneity observed as a function of the experiments. For some, the corresponding coefficient of variation can be very low. Thus, the difference between the results published by Stacey *et al.* (2003) and Stacey (2005) and those presented in this article can also be explained by the number of experiments performed by the authors to determine the coefficient of variation. Finally, in the experiments of Stacey (2005), a modified fluidized bed generator coupled to a dust box was used, whereas in this study, it was a rotating brush generator coupled directly to the Sputnic system. This may also contribute to explain the differences observed.

Welding gas fume aerosols have also been generated using the Sputnic sampler (Anglov *et al.*, 1993).

Coefficients of variation characterizing dust dispersion in the generation system of 13.9, 6.1, and 6.3% were measured for iron, manganese, and titanium, respectively. In this case, the values considered as outliers were removed from the calculation, whereas for the results presented in this article, the only data excluded were those based on the observations made at the time of sampling (incidents at generation level or poor flow rate stability measured before and after sampling).

The homogeneity of the Sputnic air sampler was also determined during experiments aimed of producing hexavalent chromium-loaded replicas, again by generating welding gas fumes (Dyg *et al.*, 1994). In this case, a coefficient of dispersion of 3.4% was measured on a series of 98 filters for all the dust (total dust) deposited on the filters (mean = 2.565 mg). On a series of 16 filters, the authors obtained coefficients of variation of 1.7, 1.9, and 4.4%, respectively for total dust, hexavalent chromium, and total chromium. Besides, for welding gas fumes, Stacey and Butler (2008) consider, on the basis of data accumulated by Health and Safety Laboratory, that the 95% percentile of the variability is typically better than 3%.

Other systems have already been employed to generate replicas usable in proficiency tests. In this respect, Baron and Deye (1987) describe a system used to generate asbestos fibres with a fluidized bed aerosol generator to produce 320 replicas at a time. The homogeneity tests carried out show that the coefficient of variation characterizing the dispersion of fibre density measured on the different sampling filters is equal to 14% for fibre densities in the order of a few hundred fibres mm^{-2} . By making the assumption that the coefficient of variation related to counting is $\sim 10\%$ (for 100 fibres counted), it can be estimated that the coefficient of variation characterizing the concentration dispersion in the sampling chamber is equal to 9.8%.

Another system, smaller in size, was described by Skogstad *et al.* (1996). Here again, a fluidized bed generator was used and 10 replicas can be produced at a time. The coefficient of variation determined for amosite fibre density levels ranging from 15 to 250 fibres mm^{-2} was better than 2.6%.

It is difficult to compare the results obtained by different authors as the sampling systems, the number of replicas produced, the number of experiments, and the nature of the dust generated may be different. Even for identical air sampler (Sputnic for example), the data processing or the experimental design can influence the presentation of the results. Regardless, for an organizer of proficiency tests, the important issue is to

know the variability of the replicas that they produce so that this can be taken into account in the interpretation of the results.

CONCLUSION

The exploitation of 120 sampling series enabled characterization of the variability of two generation systems used for the production of replicas loaded with asbestos fibres or silica dust.

The coefficients of variation characterizing the dispersion of filter loading in the Sputnic system are $< 10\%$ for high densities asbestos fibre and silica dust samples. The coefficient of dispersion is on average higher when the asbestos fibre density is lower. The differences observed between the measurements made on the different crowns of the Sputnic system are low and $< 2\%$.

The results obtained with the multipurpose system show that replica dispersion is on average equal to 4%. This will allow to propose in the near future a proficiency test dedicated to the quantitative analysis of crystalline silica on foam sampled with the CIP 10-R device.

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