RESPIRABLE CRYSTALLINE SILICA: ANALYSIS METHODOLOGIES

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ABSTRACT

This paper describes different analysis methodologies in occupational environments and raw materials. A review is presented of the existing methodologies, the approximations made, some of the constraints involved, as well as the best measurement options for the different raw materials. In addition, the different factors that might affect the precision and accuracy of the results are examined.

With regard to the methodologies used for the quantitative analysis of any of the polymorphs, particularly of quartz, the study centres particularly on the analytical X-ray diffraction method. Simplified methods of calculation and experimental separation are evaluated for the estimation of this fraction in the raw materials, such as separation methods by centrifugation, sedimentation, and dust generation in controlled environments.

In addition, a review is presented of the methodologies used for the collection of respirable crystalline silica in environmental dust.

1. INTRODUCTION

In 1997, the International Agency for Research on Cancer (IARC) classified crystalline silica as a human carcinogen (group 1), though later studies determined that the carcinogenicity of crystalline silica had not been detected in every studied industrial circumstances but that it depended on the inherent characteristics of the crystallinity of the silica polymorphs, such as the amorphous surface content, degree of crystallinity, particle diameter, specific surface area, shape, density, and electrostatic properties [1].

Quartz is the most abundant polymorphic form of silica and it is used, for example, in glass, brick, abrasives, mortar, and ceramics manufacturing. Cristobalite and tridymite polymorphs are present in industries in which quartz or amorphous silica is thermally treated at high temperatures (above 900ºC), and they are used in siliceous refractory materials. As a result, exposure to crystalline silica can occur in a great variety of industrial environments, such as grinding, construction, mining, agriculture, and smelting.

Moreover, the entry into force of the REACH regulation (Regulation no. 1907/2006 of the European Parliament and Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals) totally modified the previous legislative framework (prior to 1 June 2007) on chemicals in the European Union with the main aim of assuring a high level of protection for human health and the environment. In this sense, it makes each industry responsible for managing the risks associated with the substances that the industry involved makes, imports, sells, and uses in its processes.

It thus becomes necessary to measure respirable crystalline silica in occupational environments, which are increasingly cleaner, as well as the presence of the respirable crystalline silica content in the raw materials handled in the ceramic industry.

1.1. What is the respirable fraction?

The air that we breathe contains suspended particles. Whenever we breathe, these particles enter our respiratory apparatus. Most are retained in the nose and mouth or are deposited in the trachea or the bronchi, where they are removed by expectoration. However, the finest particles reach the lung alveoli, and it is those particles that are termed the respirable fraction. When particles such as silica or coal accumulate in lung tissue, they can lead to the formation of a fibrous tissue, reducing the gas exchange capacity and causing so-called pneumoconiosis.

In order to determine which particles make up the respirable mass fraction, a probability function is applied, which is defined in standard EN 481 on the basis of the particle aerodynamic diameter (Figure 1), the aerodynamic diameter of a particle being defined as the diameter of a spherical particle, of 1 g/cm^3 density, which has the same terminal or settling velocity in air as the particle of interest.

The respirable fraction (E_R) corresponds to a cumulative log-normal distribution with a median of 4.25 µm and a geometric typical deviation of 1.5.

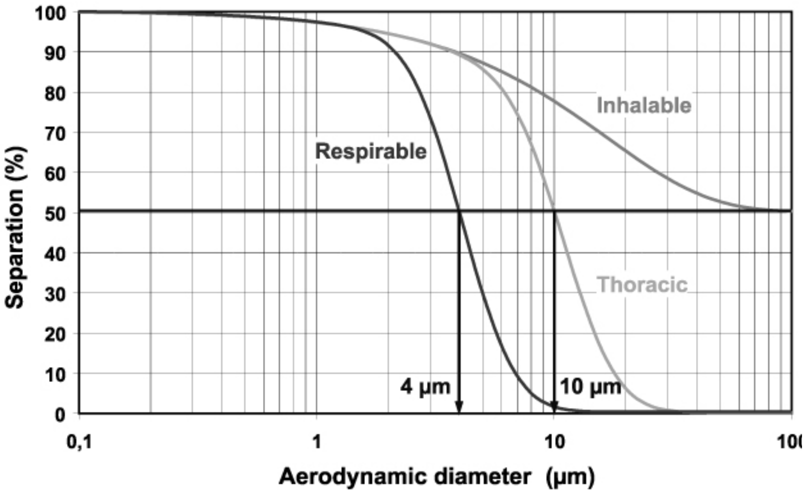


Figure 1 Representation of the inhalable, thoracic, and respirable fraction as a percentage of the total aerosol.

Crystalline silica appears in the following forms: Quartz, Cristobalite, and Tridymite. However, the presence of the last two is very minor, so that the presence of crystalline silica is assumed to be that of crystalline quartz.

1.2. Measurement methods of crystalline silica

There are different methodologies for the determination of silica, which include chemical methods [2] and instrumental methodologies, such as infrared spectrometry and X-ray diffraction [3].

Of these methods, the **chemical method** displays low accuracy. It is also tedious, affected by the presence of silicates or amorphous silica, and is unable to differentiate between silica polymorphs. For these reasons, this method is no longer used.

Infrared spectrometry is based on the fact that the chemical bonds of the substances have specific vibration frequencies that correspond to the energy levels of the molecules. These frequencies depend on the shape, surface area, and potential energy of the molecule, as well as on molecular geometry, atomic masses and, possibly, the vibrational coupling. Despite being a rapid technique with appropriate resolution, it does not distinguish between silica polymorphs and accuracy depends on the matrix. In addition, the presence of silicates can, once again, interfere in the results.

The **X-ray diffraction** (XRD) technique is based on the optical interferences that take place when a monochrome radiation crosses a slit of comparable thickness to the radiation wavelength. The X-rays are diffracted at angles that depend on the atomic distances. The surface analysis or random powder method consists of beaming X-rays on a sample, made up of a multitude of crystals, in all possible directions. For that reason, Bragg's law: $n\lambda = 2d \sin\theta$ can be applied, where 'd' is the distance between the interatomic planes that produce diffraction.

X-ray diffraction is a non-destructive method that is used in analysing a wide range of materials for the qualitative identification of the mineralogical composition of a crystalline sample. The methodology is not affected by the silicates that are present and is able to distinguish silica polymorphs.

Figure 2 Model D8 Advance diffractometer

2. RESPIRABLE CRYSTALLINE SILICA ANALYSIS IN RAW MATERIALS

2.1. Methods

The methods that exist for the determination of respirable crystalline silica in dusty materials can be divided into two types, based on whether or not any type of experimentation is performed to separate the respirable fraction:

- Methods by calculation
- Experimental methods

2.1.1. Methods by calculation

The method consists of determining the mass percentage of respirable crystalline silica (E_RSC) from the particle size distribution, after previously determining the percentage of quartz in the original sample.

In order to be able to calculate the crystalline silica percentage from the particle size distribution, the probability function described in standard EN 481 needs to be applied.

$$E_R = \int_{x=0}^{X=\infty} pdf(x) \bullet P(x)dx$$

Equation 1.

where *pdf (x)* is the probability density function for an aerodynamic size x (particle size distribution); *P(x)* is the probability that the particle of aerodynamic size x will reach the lung alveoli according to standard EN 481 and x is the aerodynamic size corresponding to $x = D\sqrt{\rho_R}$ where D is particle physical size and ρ_R is particle density relative to that of water.

Respirable crystalline silica is expressed according to equation 2:

$$E_R SC = E_R \ \varphi_{SC}$$

Equation 2.

where φ_{SC} is the mass fraction of crystalline silica in the sample.

This method assumes that the quartz particle size distribution is identical to that of the sample as a whole.

2.1.2. Experimental methods

2.1.2.1. Sedimentation method

This method is based on Stokes' law, according to which particle settling velocity depends on particle density and size, as well as on fluid density.

Using Stokes' law and standard EN 481, settling time can be calculated from equation 3:

$$t = h \ \frac{18 \quad \eta}{(\rho_s - \rho_l)\ g} \ \frac{4}{9} \ \frac{\rho_R}{\langle x \rangle^2}$$

Ecquation 3.

where t is settling time (s), h is the height (m) of the column of supernatant liquid after a time t; η is the dynamic viscosity of the liquid (kg/ms); g is the gravitational acceleration (m/s^2), ρ_S is particle density (kg/m^3), ρ_l is the density of the liquid medium (kg/m^3), ρ_R is the density of the solid particles relative to that of water; <x> corresponds to a value of 4.25 µm.

Based on the separated fraction, the amount of crystalline silica present in the sample is quantified by X-ray diffraction.

2.1.2.2. Method of separation by centrifugation

This method is based on the separation of fractions of certain particle sizes in a suspension by centrifugation.

A test bench of hydrocyclones is used (Figure 3), consisting of a tank (1) in which the feed suspension is prepared, and a pump (2) that impels the suspension to the installed hydrocyclone (3). The feed flow rate is regulated by a bypass valve (4) and a feed valve (5), and the pressure in the pipe is displayed by a pressure gauge (6).

The choice of the input and output nozzle diameters enables the cut-off size of the coarse and fine fraction in the stream to be selected.

After the separation of the fine fraction, the respirable crystalline silica is quantified by X-ray diffraction, as in the foregoing cases.

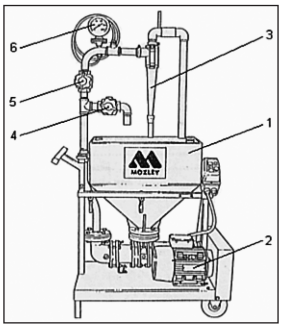


Figure 3 Hydrocyclone test bench

2.1.2.3.Dust chamber method

This method differs from the methods set out in sections 2.1.2.1 and 2.1.2.2, as it does not completely separate the fine fraction of the sample.

The test for the determination of the dustiness of the stored bulk materials is described in standard UNE EN 15051:2007. On the basis of this standard, an assembly was developed, using Method B (continuous fall).

The operating principle of the continuous fall test consists of letting the test material fall from a certain height on a rising air stream. The larger the quantity of material that is incorporated into the air stream, the more airborne dust will the material be able to emit.

The sampling unit basically consists of a cylindrical duct through which a rising air stream circulates at a flow rate of 53 l/min (Figure 4). The test material is proportioned at a rate of 6 to 10 g/min from the top of this duct. The powder is dropped through an inner tube concentric to the duct through which the air rises. This tube is shorter than the outer duct, so that the powder is released countercurrent to the airflow. A pair of sampling heads are positioned slightly above the discharge position of the material, in order to sample the relevant health-related particle size fractions. The studied fractions are the inhalable and the respirable fractions (UNE EN 481:1995).

The test enables the mass fraction of inhalable dust (w_I) and respirable dust (w_R), in the dusty material to be evaluated. The determination is direct. The mass fraction of inhalable dust is thus the mass captured in the sampler of this fraction, corrected by the relation between the sampled flow rate and the total flow rate, and divided by the settled mass in the collector container located at the bottom of the assembly:

$$w_I = \frac{\Delta m_I}{m_c} \frac{Q_{tot}}{Q_I}$$

where:

Δm_I is the powder mass captured by the inhalable dust sampler; m_c is the settled mass in the collector container, Q_{tot} is the total flow rate, and Q_I is the intake flow rate of the inhalable dust sampler.

The mass fraction of respirable dust w_R is defined in an equivalent way.

Figure 4 Assembly for the measurement of the dustiness of bulk materials by the continuous fall method. Schematic illustration of the test assembly parts.

The results obtained can be used to classify bulk materials according to their proneness to emit dust. Standard UNE EN 15051:2007 indicates that this classification shall be made in accordance with the criteria set out in Table 1.

Category of dust emittability	**Mass fraction of inhalable dust,wI (mg/kg)**	**Mass fraction of respirable dust, wR (mg/kg)**
Very low	<250	<25
Low	250 to 2500	25 a 125
Moderate	>2500 to 12500	>125 to 1250
High	>12500	>1250

Table 1. Classification of dusty materials as a function of the test result.

2.2. Materials, methodologies, and experimentation

Different materials were analysed using the calculation, sedimentation, and centrifugation methods, in order to determine the equivalences between the methods.

2.2.1. Materials

The materials analysed during the experimentation are detailed in Table 2. Different raw materials of varying nature, typically used in the ceramic industry, were selected. The following materials were studied: four clays and two kaolins (clayey nature), two feldspars (aluminosilicates), and a quartz (oxide).

2.2.2. Experimental procedures

2.2.2.1. Quantification of crystalline silica

Crystalline silica was quantified by means of the X-ray diffraction technique, using a BRUKER theta-theta model D8 Advance diffractometer with copper radiation ($K\alpha$ λ = 1.54183Å) and VANTEC solid-state detector. Data were recorded from 2θ of 5º to 90º, with a step size of 0.015º and acquisition time of 1.2s. Quantification was performed by the Rietveld method using fluorite as internal standard.

2.2.2.2. Particle size distribution

Particle size distribution was determined by the sedimentation method (X-ray absorption measurement) and the wet laser diffraction method.

A MICROMERITICS SEDIGRAPH 5100 instrument was used for particle size analysis in the first method. The test was conducted after previously sieving the sample with a 63-micron mesh. A MALVERN MASTERSIZER 2000 laser diffraction instrument was used in the second method

2.2.3. Results

The results of the crystalline silica quantification in the analysed samples are detailed in Table 2. Table 3 presents the results for respirable crystalline silica. Table 4 lists the results of one of the clay samples with the dust chamber method.

The first column in Table 3 shows the value obtained by the calculation method, using a particle size distribution determined by X-ray absorption. The second column lists the results of the theoretical calculation; however, in this case, the particle size distribution was determined by laser diffraction. The third and fourth columns detail the results corresponding to the experimental methodologies.

	Quartz	Clays				Kaolins		Feldspars	
	Quartz	Clay 1	Clay 2	Clay 3	Clay 4	Kaolin 1	Kaolin 2	Feldspar 1	Feldspar 2
Quartz	96±2	22±1	30±2	13±1	33±2	6±0.5	2±0.5	5±0.5	16±2
Cristobalite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tridymite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 2 Percentage by weight of crystalline silica (Quartz, Cristobalite, and Tridymite) of the tested materials

	Calculation method (Sedimentation)	Calculation method (Laser diffraction)	Sedimentation method	Hydrocyclone method
Quartzes				
Quartz 1	16±1	19±2	11±1	15±1
Clays				
Clay 1	18±2	5±0.8	14±1	15±1
Clay 2	22±2	21±2	13±1	14±1
Clay 3	11±1	9±1	5±0.7	7±1
Clay 4	25±2	12±1	21±1	24±1
Kaolins				
Kaolin 1	3.5±0.6	1.4±0.5	1.5±0.5	1.5±0.5
Kaolin 2	0.7±0.2	0.4±0.1	0.5±0.1	0.4±0.1
Feldspars				
Feldspar 1	0.5±0.1	0.1±0.1	0.5±0.2	0.4±.02
Feldspar 2	1.4±0.5	0.9±0.3	1.5±0.4	1.7±0.5

Table 3 Mass percentage of respirable crystalline silica of the tested samples determined by the different methodologies.

The measurement technique for dust generation is innovative in Spain and is currently being fine-tuned. Some preliminary results are presented.

Sample	w_I (mg/kg)	w_R (mg/kg)	Category of dust emittability
Clay 4	14 100 ± 400	240 ± 60	Moderate to high

NOTE: Mean ± standard deviation of five repetitions.

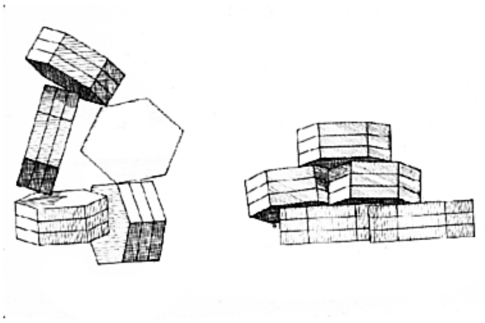
Table 4. Results obtained with Clay 4.

2.2.4. Discussion of results

The discussion of the results obtained by the different methodologies is based on the nature of the analysed materials. Two large groups may be distinguished: materials predominantly made up of clay minerals (clays and kaolins) and materials consisting of silicates and aluminosilicates.

In the **quartz** sample, the experimental methods provided lower values than those obtained in the calculation methods. This was due to the low tendency to remain suspended. As the approximation of assuming that quartz particles have a roughly spherical shape is acceptable, there were no significant differences in the values obtained by the different particle size distribution methods.

In the **clay** samples, a diversity of results was observed. First, the source and genesis of the samples was observed to influence the resulting percentage of respirable crystalline silica. Two samples, namely clays 2 and 4, which had a similar percentage of crystalline silica, displayed very different respirable crystalline silica contents, which may be explained in terms of their particle size distributions. The percentage of fine particles was much greater in clay 4.



In the case of the clays, significant differences were noted in the calculation results, depending on the technique used to determine the particle size distribution. The values obtained for silica using the laser diffraction technique were smaller, because the distribution obtained by this method gave rise to coarser particle sizes than by the sedimentation method. One of the reasons is that clays contain minerals with plate-like particles. Although these particles have a low settling velocity, they have a high equivalent volume, so that the particle sizes obtained by laser diffraction are larger. In contrast, in the analysed clays, the experimental methods exhibited similar values.

In addition, for these types of samples, different results were observed between the calculation and the experimental methods, the latter being lower. This is because in the calculation method, it is assumed that the quartz distribution in the material is similar to that of the other constituents. This is not true in clays, because quartz exhibits a coarser particle size than the other clay minerals.

If the results obtained are compared with the preliminary data from the dust generation chamber, the quantity of respirable or inhalable dust was observed to be lower than what was to be expected by the described analytical methods. This is because in the analytical determinations, the samples are prepared in solutions, and agents are added that inhibit flocculation in order to avoid particle agglomeration and thus obtain homogeneous suspensions. In dust generation, though the agglomerates are made up of small-sized silica particles, their ability to remain suspended in air is low. In addition, the moisture content of the material can influence its ability to agglomerate and can reduce particle suspendability.

The case of the studied **kaolins** was similar to that of the clays; however, since they had a smaller quartz content, the differences were smaller.

In the **feldspars**, since the quartz and the other minerals contained have a similar shape and behaviour in a fluid, the results provided by the different methodologies were comparable.

2.2.5. Conclusions

The calculation and experimental methods yielded similar results in samples in which all the components had minerals with a similar morphology and density, such as the quartzes and feldspars, but they overestimated the presence of respirable crystalline silica in the case of samples with a heterogeneous mineralogy, such as the clays and kaolins. This difference became more evident in the clays because, in general, they had a larger percentage of quartz.

The dust generation methodology is expected to provide values of respirable crystalline silica closer to those found during the actual processing of the material, taking into account variables such as moisture content, agglomerate size, etc.

3. ANALYSIS OF RESPIRABLE CRYSTALLINE SILICA IN OCCUPATIONAL ENVIRONMENTS

Particle sampling in occupational environments is performed by active collection with filters. Active collection refers to the need to use an active system, usually involving a pump to make the air flow through the sampler or to fill an inert container by means of different devices with collection pumps.

Since the usual objective in industrial hygiene is the obtainment of personal samples (in a worker's breathing area), the apparatus used is a lightweight (maximum 1.2 kg) diaphragm or piston pump, with a low flow rate and operational autonomy (minimum 2h, recommendable, 8 h), and a relatively limited flow rate margin regulated by a control mechanism [4]. These units must be fitted with an automatic control that keeps the volume flow rate constant in the case of filter saturation.

The pollutant present in the air, in the form of an aerosol, is retained on a filter, usually 37 mm in diameter with a pore size between 0.45 and 5 µm, which may be made up of different materials: mainly cellulose esters, glass fibre, PVDF or PTFE, though PVC copolymer is also used for collecting crystalline silica.

The different types of personal samplers and their characteristics are detailed in Table 5.

Apparatus	Flow rate (l/min)	Sampler
Nylon cyclone 10mm	1.7	Filter
IOM multidust	2.2	Filter and foam
Plastic or aluminium cyclone	2.2 / 2.5	Filter
GK 2.69	4.2	Fibreglass or teflon
CIP 10-R	10	Polyurethane foam
PGP-FSP 2 PGP-FSP 10	2 10	Membrane filter

Table 5 Personal samplers and their characteristics.

At present, the occupational exposure limit in Spain (VLA) for respirable quartz is 0.1 mg/m^3. To assure clean environments, with concentrations five times below the limit, this generates an analytical problem owing to the low concentration to be detected.

The sampling methodology used at present by means of cyclones entails the constraint of a low air sampling flow, between 1.7 and 2.2 L/min, which makes it difficult to detect very low concentrations.

An alternative to sampling with cyclones and membrane filters is the use of samplers that allow much greater flows, known as foam pad samplers, which could improve the detection and quantification limits of crystalline quartz because they collect larger quantities of dust [5,6].

Figura 5. Sampler CIP 10R

The fine-tuning of the method [7] using polyurethane foams with the CIP 10-R personal sampler allows a sufficient quantity of silica to be collected for analytical determination and, thus, the detection and quantification limits to be lowered, since the personal sampling pump allows respirable dust with a flow of 10 L/min to be collected. It has a high-speed rotating cup that contains polyurethane foam on which the particles are collected. It is a lightweight, compact apparatus, weighing about 300 g, which can be used for both personal and environmental sampling.

To prepare the calibration curves of quartz and cristobalite, certified reference materials are available: SRM 2951-2957 and SRM 2960-2967.

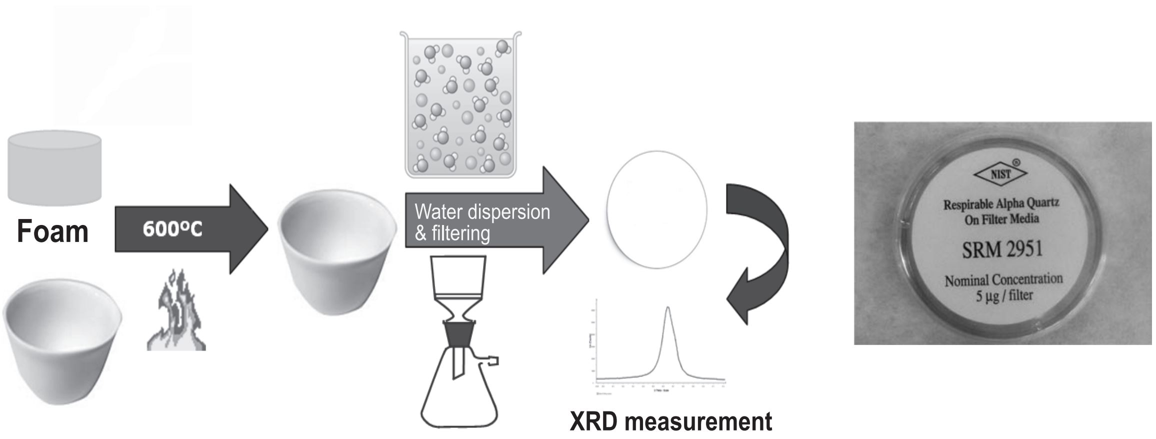


Figure 6 Work scheme for measurements with CIP-10R foams

The results obtained for different workplaces, using samplers based on cyclones or foams (CIP) after 6 hours' sampling, are detailed in Table 6. The processed air volume in the case of the cyclone was about 0.8 m^3, while in the case of the CIP it was about 3.6 m^3. The presence of cristobalite or tridymite was not detected in the samples.

	Area 1		**Area 2**		**Area 3**	
	Cyclone	**CIP**	**Cyclone**	**CIP**	**Cyclone**	**CIP**
Quartz	<0.025	<0.006	<0.025	0.010 ±0.003	0.04 ± 0.01	0.027 ± 0.006

Table 6 Respirable crystalline silica concentrations (mg/m^3) for three work areas using cyclone and foam (CIP) samplers.

Two samplers with the same sampling volume were compared. In the case of the cyclone, sampling was performed for a total of 10 hours, compared to sampling for 2.5 hours with the CIP sampler.

	Area 4		**Area 5**	
	Cyclone	**CIP**	**Cyclone**	**CIP**
Quartz	0.012 ± 0.006	0.014 ± 0.005	<0.01 ± 0.005	0.009 ±0.004

Table 7 Respirable crystalline silica concentrations (mg/m^3) of two work areas using cyclone and foam (CIP) samplers processing the same air volume.

As may be inferred from the data in Tables 6 and 7, the results of the two samplers were comparable for low values of silica, the CIP sampler providing a better detection limit at the same sampling times.

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