

Validation of the Analysis of Respirable Crystalline Silica (Quartz) in Foams Used with CIP 10-R Samplers

CÉLINE EYPERT-BLAISSON*, JEAN-CLAUDE MOULUT,
THIERRY LECAQUE, FLORIAN MARC and EDMOND KAUFFER

Institut National de Recherche et de Sécurité (INRS), Centre de Lorraine, Département Métrologie des Polluants, Laboratoire d'Analyses Inorganiques et de Caractérisation des Aérosols, Rue du Morvan, CS 60027, 54519 Vandoeuvre Les Nancy Cedex, France

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Sampling the respirable fraction to measure exposure to crystalline silica is most often carried out using cyclones. However, low flow rates ($<4 \text{ l min}^{-1}$) and continuing improvement in workplace hygiene means less and less material is sampled for analysis, resulting in increased analytical uncertainty. Use of the CIP 10-R sampler, working at a flow rate of 10 l min^{-1} , is one attempt to solve current analytical difficulties. To check the ability of the analysis of quartz sampled on foams, known amounts of quartz associated with a matrix have been injected into foams. The results obtained show that the proposed protocol, with prior acid attack and ashing of the foams, satisfies the recommendations of EN 482 Standard [CEN. (2006) Workplace atmospheres—general requirements for the performance of procedures for the measurements of chemical agents. Brussels, Belgium: EN 482 Comité Européen de normalization (CEN).], namely an expanded uncertainty of $<50\%$ for quartz weights between 0.1 and 0.5 times the 8-h exposure limit value and $<30\%$ for quartz weights between 0.5 and 2 times the 8-h exposure limit value, assuming an exposure limit value equal to 0.1 mg m^{-3} . Results obtained show that the 101 reflection line allows a quartz quantity of the order of $25 \mu\text{g}$ to be satisfactorily measured, which corresponds to a 10th of the exposure limit value, assuming an exposure limit value of 0.05 mg m^{-3} . In this case, the 100 and 112 reflection lines with expanded uncertainties of $\sim 50\%$ would also probably lead to satisfactory quantification. Particular recommendations are also proposed for the preparation of calibration curves to improve the method.

Keywords: CIP 10-R; foam; quartz; X-ray diffraction

INTRODUCTION

Methods of analyzing respirable crystalline silica are based on X-ray diffraction (XRD) (AFNOR, 1995a, b; OSHA, 1996; NIOSH, 2003b; HSE, 2005) or infrared spectroscopy (NIOSH, 2003a; AFNOR, 2005; HSE, 2005). The sensitivity of these methods depends on the quantity of material analyzed and this frequently depends on the sampling time and volume of air sampled. Moreover, use of cyclone samplers with flow rates such as the Dorr Oliver (1.7 l min^{-1}) sampler

and improvements in workplace hygiene has lead to less material being available for analysis. The French average exposure limit value (0.1 mg m^{-3}) may be reduced as a result of the most recent study led by National Institute for Occupational Safety and Health (NIOSH, 2002), which recommends a limit value of 0.05 mg m^{-3} and that of the American Conference of Governmental Industrial Hygienists (ACGIH, 2006), which recommends an even lower limit value (0.025 mg m^{-3}). The analytical uncertainty of the results is high because the quartz content in many samples is currently close to, or below, the quantification limit. The CIP 10 R sampler (Courbon *et al.*, 1988) enables air to be sampled at a flow rate of 10 l min^{-1} because a lower backpressure is

*Author to whom correspondence should be addressed.
e-mail: celine.eypert-blaison@inrs.fr

obtained with a foam and spinning cup than with a cyclone and filter.

Use of a cyclone (with a 25-mm diameter filter) allows the quantity of quartz sampled to be directly analyzed (HSE, 2005), whereas the CIP 10-R requires indirect analysis with ashing of the sampling foam (AFNOR, 1995a). Concerning the preparation methods used (direct or indirect), the following comments can be made:

1. Comparison of direct and indirect methods carried out during earlier studies showed that the indirect method associated with ashing at 600°C of the foam resulted in an underestimation in quartz content in the order of 13%, probably due to losses during preparation or to transformation of the mineral compounds (Kauffer *et al.*, 2005). If the sample contains some calcite, there is a risk that some of the silica would be transformed into calcium silicate (NIOSH, 2003b). It had also been noted that the underestimation was more pronounced with filters containing calcite (23%) than for those in which none had been detected during qualitative analysis of XRD pattern (8%).
2. With large quantities of material and in order to correct matrix effects, one possible option is to filter the calcined material onto a polycarbonate filter of low absorbency. This filter has the characteristic of being very smooth and it was noted that calibration curves are not linear at low quartz weights, probably due to preferential orientation of the quartz particles (AFNOR, 1995a; Kauffer and Moulut, 1986; Edmonds *et al.*, 1977; Smith, 1997). This phenomenon decreases when the weight of deposited quartz increases. In this case, the surface becomes more uneven and the calibration curves become linear after corrections for absorption (in the case of high quartz loading).

On the other hand, with an indirect analysis method, calibration can be carried out by liquid filtration of suspensions containing known quantities of standard quartz using the usual methods available in any laboratory. Unlike the indirect method, the direct method is sampler specific and is more complicated insofar as the standard filters must be prepared by sampling airborne reference quartz, in order to guarantee that the distribution of the particles will be the same on both standard filters and analytical filters.

Research to resolve difficulties linked to the sensitivity of quartz analysis methods is currently being carried out in several countries. The research relates primarily to increasing the flow rate of the different cyclones used to collect the respirable fraction sam-

ple. However, this is a solution of limited potential due to the use of personal pumps, which seem, at present, for most of them, to be incapable of operating at flow rates $>4 \text{ l min}^{-1}$. Use of the CIP 10-R sampler at a flow rate of 10 l min^{-1} is investigated as a solution to current analytical difficulties.

The aim of this study was to validate the use of the CIP 10-R for determining crystalline silica by XRD. This method, though described in several standards, still needs to be validated. In particular, the characteristics of the method must be compared to the general performance requirements recommended in the EN 482 Standard (CEN, 2006) when a measured concentration has to be compared to an exposure limit value. In addition, some modifications are made to the method in order to resolve analytical difficulties linked to possible transformation of certain minerals during ashing or to non-linearity of the calibration curves at low quartz loading when particles are deposited on a flat surface.

MATERIALS AND METHODS

Protocol

Respirable fractions of quartz, calcite, and iron oxide (hematite) dust obtained by liquid sedimentation were used to make binary mixtures (quartz + calcite and quartz + iron oxide). These mixtures are composed of quartz (10 and 50%) and calcite or iron oxide (hematite). In the case of large quantities of dust sampling, elements in the sample may absorb the X-ray radiation. Mass absorption coefficients (for the copper $K\alpha$ radiation) for the substances involved are equal to $35 \text{ cm}^2 \text{ g}^{-1}$ (quartz), $75.6 \text{ cm}^2 \text{ g}^{-1}$ (calcite), and $230.4 \text{ cm}^2 \text{ g}^{-1}$ (iron oxide), respectively. CIP 10-R foams were spiked with various quantities of these mixtures (from 0.24 to 7 mg for quartz + calcite mixtures and from 0.24 to 6 mg for quartz + iron oxide mixtures). The quantity of quartz measured by XRD was determined according to the following protocol:

1. Acid attack of the foam and the minerals with dilute hydrochloric acid (3N)
2. Filtration of the solution on a polyvinylchloride (PVC) filter (25-mm diameter, 0.4- μm pore size)
3. Ashing of the foam and PVC filter at 600°C in a platinum crucible
4. Addition of $\sim 1.5 \text{ mg}$ of calcium fluoride (average = 1.56 mg, SD = 0.18)
5. Filtration of the dust (ashed residue and calcium fluoride) on a preweighted polycarbonate filter (25-mm diameter, 0.4- μm pore size).

The reason for the acid attack is to eliminate calcite to prevent the formation of calcium silicate during foam ashing. The purpose of systematically adding 1.5 mg of calcium fluoride, whose mass absorption coefficient is $96.8 \text{ cm}^2 \text{ g}^{-1}$, is to correct the non-linearity of the calibration curves, when only a small mass of material is deposited on the filter (preferential orientation effect). The different combinations between the weight of spiked dust, the nature of the substance, and the addition of calcium fluoride allowed deposits on the polycarbonate filter with different mass absorption coefficient. For this study, the average measured absorption coefficients varied from 52 to $173 \text{ cm}^2 \text{ g}^{-1}$.

Two calibration lines were produced:

- For one, Cal1, the quantities of quartz were deposited directly on the polycarbonate filter, without adding calcium fluoride to illustrate the preferential orientation effect at low quartz quantity.
- For the other, Cal2, ~ 1.5 mg of calcium fluoride was added to the quartz before being deposited on the polycarbonate filter.

To check the consistency of the analytical method, binary mixtures were also analyzed. In this case, a simplified protocol involving neither acid attack nor ashing was employed.

Materials

- Quartz QUIN1 (fraction $< 5 \mu\text{m}$, obtained by liquid sedimentation). The same quartz was used to produce calibration lines and to prepare the mixtures;
- Calcite (Prolabo® ref 22-296-294, fraction $< 5 \mu\text{m}$, obtained by liquid sedimentation);
- Iron oxide (Sigma-Aldrich®, ref. 310050, particle size $< 5 \mu\text{m}$);
- Calcium fluoride (AlfaAesar®, ref 232-188-7, average diameter in volume = $2.34 \mu\text{m}$).

Instruments

The tests were carried using an X'Pert diffractometer (PANalytical) equipped with an automatic 42-station sample changer. The diffractometer operating conditions were as follows:

- fine-focus Cu anode tube with a power of 2.2 kW used at 40 kV and 50 mA,
- proportional detector,
- focal distance of 240 mm,
- secondary graphite monochromator,

- programmable divergence and anti-scattered slits,
- programmable analytical slit: 0.3 mm, and
- sample spinner.

Data collection

Dust to be analyzed is deposited onto a polycarbonate filter disposed on an aluminum support. The qualitative analysis is carried out on a diffraction pattern recorded over a broad range ($5\text{--}75^\circ 2\theta$, scan speed $0.03^\circ 2\theta \text{ s}^{-1}$). The quantitative analysis is carried out on 101, 100, 112, and 211 reflections for quartz (angular width of $1.4^\circ 2\theta$, scan speed of $0.002^\circ 2\theta \text{ s}^{-1}$). Measurements were also taken on diffraction peaks 111 and 200 for aluminum to correct for matrix effects (angular width of $1.5^\circ 2\theta$, scan speed of $0.02^\circ 2\theta \text{ s}^{-1}$). Finally, measurement of 100 diffraction line for a sample of polycrystalline silicon was recorded at regular intervals to correct for any instrumental drift.

As detailed in Appendix 1, the analysis of quartz by XRD, using the conditions described in this part, allowed the bias, relative standard deviation (RSD) and expanded uncertainty of the method to be determined.

Correction of matrix effects

When the weight of material to be analyzed is high (> 1.5 mg, approximately), it cannot be assumed that mass is a linear function of the intensity. Therefore, the matrix absorption effects have to be corrected by using the technique described by Altree-Williams *et al.* (1977). The principle is as follows:

The dust to be analyzed is deposited on a polycarbonate filter. During the measurement, the filter is placed on an aluminum support. The ratio between the intensity of the reflection of the aluminum support carrying either a clean polycarbonate filter or a polycarbonate filter with the mineral dust allows the average absorption of the matrix to be measured and thus to correct the matrix effect (obtaining, thereby, a linear relationship between the measured intensity and the mass of quartz). The correction to be applied depends on the weight of mineral dust to be analyzed, on its absorption coefficient and on the reflection line used.

RESULTS

Calibrations

Table 1 gives the coefficients for the regression lines linking intensity and quartz weight for the two calibrations made (Cal1, without addition of CaF_2 and Cal2, with addition of CaF_2) and the four

Table 1. Coefficients for the regression lines (slope = b Y-intercept = a) linking intensity (counts per second degree) to quartz weight (microgram) for the four reflections used (ns, not significant for a level of statistical significance of 0.05)

	100 Reflection		101 Reflection		112 Reflection		211 Reflection	
	b	a	b	a	b	a	b	a
Cal1 without addition of CaF ₂	0.23	-23.7	1.20	87.9	0.16	ns	0.12	ns
Cal2 with addition of CaF ₂	0.25	-19.4	1.26	ns	0.17	ns	0.12	ns

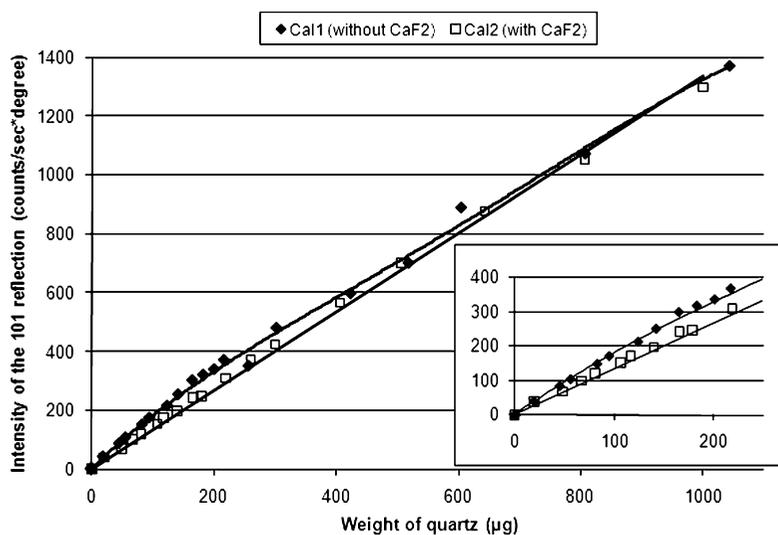


Fig. 1. Intensity measured as a function of deposited quartz weight for two calibrations Cal1 and Cal2 (101 reflection, deposited weight <1000 μg).

reflections used. The quartz weights vary from 0 to 7 mg, approximately, for Cal1 and from 0 to 5 mg, approximately, for Cal2).

It is noted that the calibration without added calcium fluoride leads to a strongly positive Y-intercept ($87.9 \text{ counts s}^{-1} \text{ deg}^{-1}$) for 101 reflection. In this case, the addition of calcium fluoride produces a calibration curve passing through the origin (Y-intercept not significantly different from zero). For a better illustration of the phenomena observed, additional tests on quartz weights <1 mg were also carried out. The calibration curves corresponding to 101 reflection are shown in Fig. 1, which illustrates the fact that the intensity is not proportional to the quantity of quartz, when no CaF₂ is added.

Bias, RSD, and expanded uncertainty

Tables 2 and 3 give, for spiked foams, values for bias $\overline{B}_{j,k}$ and RSD $S_{j,k}$ for the different weights of quartz studied. Table 2 refers to quartz + calcite mixtures, whereas Table 3 concerns quartz + iron oxide mixtures. In both cases, the values obtained for calibrations Cal1 and Cal2 are presented for the

different diffraction lines studied. Tables 4 and 5 present the same results obtained from the direct analysis of the binary mixtures used to spike the foams. In this case, the dusts were analyzed without prior ashing or acid attack. Iron oxide interferes with the 112 reflection for quartz, which explains why the results for this reflection are absent from Tables 3 and 5. Moreover, calcite interferes with the 211 reflection for quartz, which explains why the results for this reflection are lacking in Table 4.

Figures 2 and 3 illustrate the data from Tables 1 and 2 for the analysis of spiked foams (101 reflection). For reason of clarity, these figures are restricted to quartz weights <1 mg. Additionally, Figs. 4 and 5 illustrate the data from Tables 4 and 5 for the analysis of the binary mixtures (101 reflection).

Table 6 gives the expanded uncertainty for the four reflections studied as a function of quartz weight. The expanded uncertainty for the method was calculated from the results obtained for spiked foams, bias, and RSD being calculated from all results obtained on both mixtures studied. The relative error due to sampling was taken to be 5%, the relative

Table 2. Bias and RSD according to quartz weight. Analysis of spiked foams, quartz + calcite mixture. Figures in normal type were obtained with the Cal1 calibration (without added calcium fluoride) and those in bold type were obtained with the Cal2 calibration (with added calcium fluoride)

Quartz weight (μg)	100 Reflection		101 Reflection		112 Reflection		211 Reflection	
	Bias (%)	RSD (%)						
25	62.1	20.5	-261.0	5.5	-22.3	17.2	113.4	71.2
	-5.7	18.9	21.2	5.4	-24.2	16.8	109.9	70.1
51	41.4	11.3	-119.2	14.5	-13.5	12.2	72.7	60.2
	3.6	10.3	15	14.6	-15.7	11.9	69.9	59.2
104	23.7	3.5	-60.8	6.0	-11.3	4.6	6.4	2.9
	1.2	3.0	1.9	3.5	-13.6	4.4	4.7	2.8
312	9.3	1.2	-15.5	0.4	-2.6	1.0	-0.5	2.0
	-3.2	1.0	1.3	0.6	-5.1	1.0	-2.1	2.0
508	13.2	1.7	-6.8	3.4	-2.4	3.2	-1.4	2.8
	2.1	1.6	1.1	3.0	-4.9	3.1	-3.0	2.8
708	5.6	0.6	-6.8	0.7	-4.2	1.4	-1.7	0.7
	-4.2	0.5	-2.6	0.7	-6.7	1.4	-3.3	0.7
1004	2.6	2.3	-5.5	1.7	-5.3	1.6	0.2	1.2
	-6.4	2.2	-4.2	1.6	-7.7	1.6	-1.4	1.2
1502	4.5	2.4	-3.7	1.2	-3.5	1.0	-2.8	1.4
	-4.2	2.2	-4.8	1.1	-5.9	1.0	-4.4	1.3
3493	-1.5	2.1	-5.2	1.6	-5.5	1.2	-5.1	1.0
	-9.2	1.9	-8.8	1.5	-7.9	1.1	-6.7	1.0

Table 3. Bias and RSD according to quartz weight. Analysis of spiked foams, quartz + iron oxide mixture. Figures in normal type were obtained with the Cal1 calibration (without added calcium fluoride) and those in bold type were obtained with the Cal2 calibration (with added calcium fluoride)

Quartz weight (μg)	100 Reflection		101 Reflection		112 Reflection		211 Reflection	
	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)
24	97.9	21.4	-278.3	3.9			-31.9	39.6
	26.4	19.3	9.9	1.7			-33.0	39.0
51	52.3	5.1	-137.3	0.7			-4.4	60.8
	14.0	5.0	-3.6	0.7			-5.9	59.8
99	40.4	8.5	-70.3	4.2			-12.8	26.4
	16.1	8.1	-4.2	3.0			-14.2	26.0
301	23.4	6.4	-25.8	6.0			-15.3	3.9
	9.6	5.9	-7.6	5.6			-16.7	3.9
510	8.7	1.8	-11.6	1.2			-3.5	6.4
	-2.1	1.7	-3.4	1.1			-5.0	6.3
601	5.8	4.9	-20.5	4.1			-12.7	6.9
	-4.4	4.6	-13.9	3.9			-14.1	6.8
1024	4.3	2.5	-9.1	1.9			-8.3	1.7
	-4.8	2.3	-7.7	1.8			-9.8	1.7
1499	0.7	2.5	-7.2	1.6			-9.5	1.7
	-7.7	2.3	-8.1	1.5			-10.9	1.7
2990	-1.0	3.9	-5.2	2.9			-3.6	2.9
	-8.9	3.6	-8.4	2.8			-5.1	2.9

Table 4. Bias and RSD according to quartz weight. Analysis of mixtures of quartz and calcite. Figures in normal type were obtained with the Cal1 calibration (without added calcium fluoride) and those in bold type were obtained with the Cal2 calibration (with added calcium fluoride)

Quartz weight (μg)	100 Reflection		101 Reflection		112 Reflection		211 Reflection	
	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)
550	17.5	2.0	-6.6	2.0	-1.9	2.5		
	6.2	1.7	0.4	1.5	-4.4	2.5		
2700	3.6	2.5	-0.6	2.6	0.4	2.7		
	-4.6	2.4	-3.8	2.4	-2.2	2.6		

Table 5. Bias and RSD as a function of quartz weight. Analysis of mixtures of quartz + iron oxide. Figures in normal type were obtained with the Cal1 calibration (without added calcium fluoride) and those in bold type were obtained with the Cal2 calibration (with added calcium fluoride)

Quartz weight (μg)	100 Reflection		101 Reflection		112 Reflection		211 Reflection	
	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)	Bias (%)	RSD (%)
600	52.4	5.1	25.6	3.0			18.8	3.4
	38.6	4.6	30.2	2.0			16.9	3.3
2900	24.9	2.9	16.3	2.5			11.3	1.8
	15.1	2.7	12.0	2.4			9.5	1.8

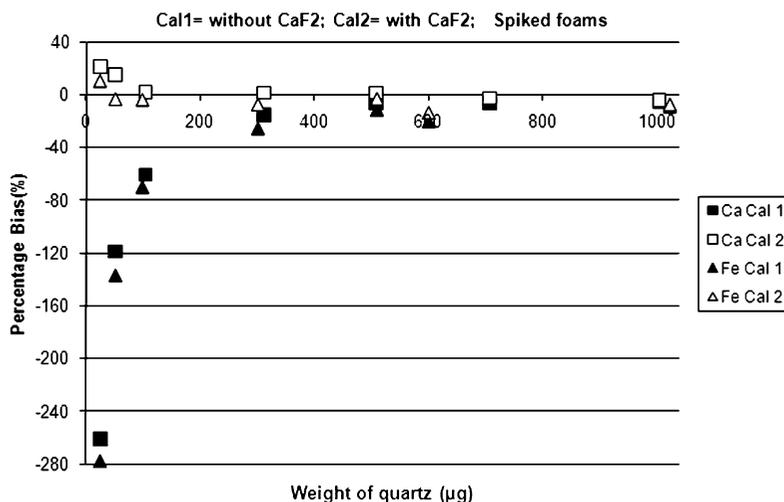


Fig. 2. Percentage bias as a function of quartz weight. Analysis of spiked foams (101 reflection). Results are provided for the two matrices studied (quartz + calcite and quartz + iron oxide) and for both calibrations made (Cal1 without added CaF_2 and Cal2 with added CaF_2).

error due to the sampling convention 11% (CEN, 2009), and the relative error due to comparison of a secondary standard to a primary standard 3% [exact data for different secondary standards are given by Stacey *et al.* (2009)].

Detection limits

Detection and quantification limits were calculated from the standard deviation of the intensity measured for 10 polycarbonate filters onto which ~ 1.5 mg of CaF_2 had been deposited. Detection and quantifica-

tion limits correspond to the quartz weight (Cal2 calibration) calculated from the average measured intensity plus 3 SD (detection limit) or plus 10 SD (quantification limit). The corresponding values are given in Table 7 for the four reflections studied.

DISCUSSION

Assuming a linear fit, Table 1 shows that the Y-intercept is significantly different from zero for the 100 reflection whatever calibration is applied (with

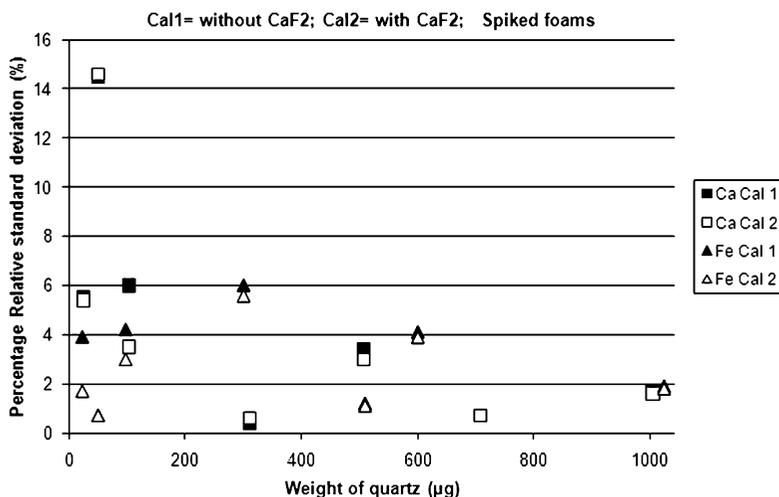


Fig. 3. Percentage RSD as a function of quartz weight. Analysis of spiked foams (101 reflection). Results are provided for the two matrices studied (quartz + calcite and quartz + iron oxide) and for both calibrations made (Cal1 without added CaF₂ and Cal2 with added CaF₂).

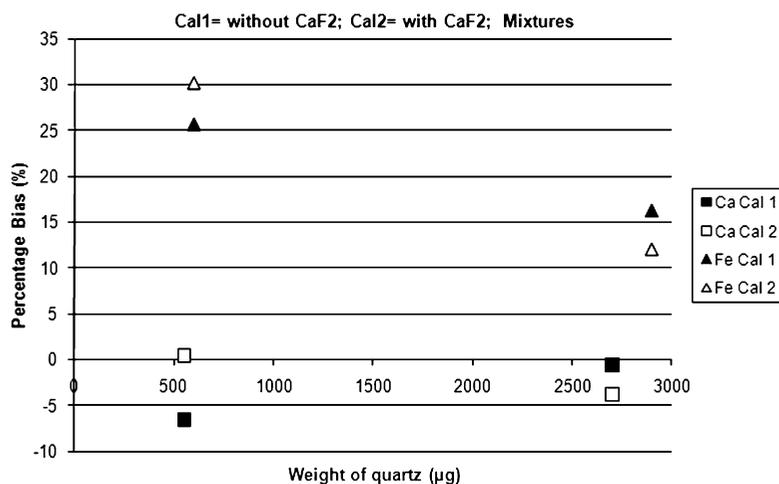


Fig. 4. Percentage bias as a function of quartz weight. Analysis of the mixtures (101 reflection). Results are provided for the two matrices studied (quartz + calcite and quartz + iron oxide) and for both calibrations made (Cal1 without added CaF₂ and Cal2 with added CaF₂).

or without addition of CaF₂). This negative Y-intercept is due to the wide variation in the polycarbonate filter XRD pattern in the angular range concerned (Davis and Johnson, 1982). Adding calcium fluoride reduces the effect but does not eliminate it. For the 101 reflection, the Y-intercept is strongly negative when calibration is applied without the addition of calcium fluoride, whereas the addition of calcium fluoride leads, in this case, to a calibration curve passing through zero (Y-intercept value is not significant). The phenomenon observed here is known: the

presence of flat surface on crushed grains of quartz would tend to orient the particles where the substrate is very smooth (Edmonds *et al.*, 1977; Smith, 1997). This phenomenon disappears progressively with increasing weights deposited on the filter, the surface becoming more and more uneven. It is particularly pronounced when the mass deposited is low (<300 µg), as shown in Fig. 1, which presents the relationship between the measured intensity for the 101 reflection and the mass of quartz deposits for weights <1 mg. It is noted that the intensities corresponding to deposits

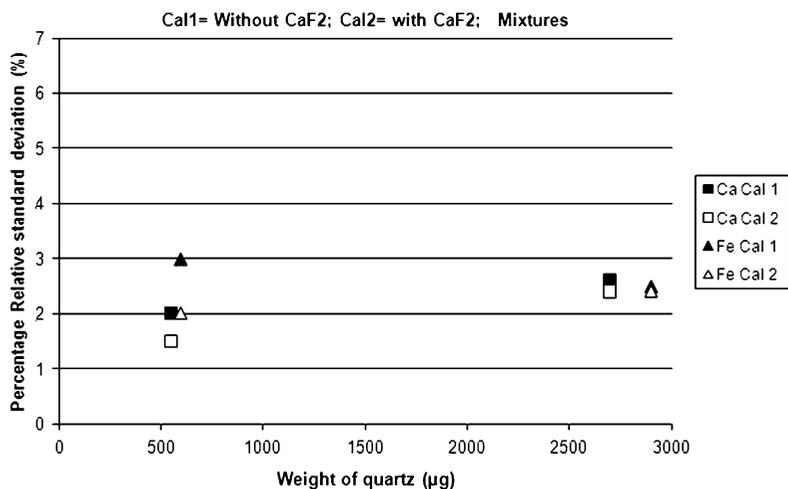


Fig. 5. Percentage RSD as a function of quartz weight. Analysis of the mixtures (101 reflection). Results are provided for the two matrices studied (quartz + calcite and quartz + iron oxide) and for both calibrations made (Cal1 without added CaF₂ and Cal2 with added CaF₂).

Table 6. Expanded uncertainty expressed as a percentage for the four reflections studied and for different quartz weights. These quartz weights are also expressed as a fraction of the exposure limit value, assuming an 8-h sampling period using the CIP 10-R sampler (flow rate of 10 l min⁻¹) and for an exposure limit value equal to 0.1 mg m⁻³

Quartz weight (µg)	Exposure limit fraction	100 Reflection Expanded uncertainty	101 Reflection Expanded uncertainty	112 Reflection Expanded uncertainty	211 Reflection Expanded uncertainty
25	0.05	59	41	63	199
51	0.11	35	40	46	161
102	0.21	35	25	37	49
307	0.64	29	27	26	34
509	1.06	24	24	26	27
643	1.34	26	33	27	34
1014	2.11	26	27	28	28
1500	3.13	27	27	26	30
3242	6.75	30	29	28	27

Table 7. Detection and quantification limits calculated for 100, 101, 112, and 211 reflections

	100 Reflection	101 Reflection	112 Reflection	211 Reflection
Detection limit (µg)	17	2	18	37
Quantification limit (µg)	50	6	61	124

without added calcium fluoride are significantly higher than the intensities corresponding to the deposits with added calcium fluoride. This non-linearity in the calibration curve, near the origin, was previously mentioned but not completely explained for quartz deposited on PVC filters (HSE, 2005) or on silver filters (Aintree-Williams, 1977). For 112 and 211 reflections, the addition of calcium fluoride does not change the parameters of their calibration curve significantly.

Thus, the addition of calcium fluoride to the quartz when preparing the calibration curve is essential since this permits reliable results to be produced when low weights of quartz are sampled by the foam, when using the most intense reflection (101). To remove these preferential orientation effects, the solution retained for this work was to add a constant quantity of calcium fluoride when producing the calibration curve and when treating the foams. Adding CaF₂ at the time of calibration allows a linear

relationship to be obtained between intensity and mass of quartz deposited.

However, two alternative solutions could be envisaged to avoid the addition of calcium fluorite:

1. The first consists in producing a calibration curve with forced zero intercept, as described in the OSHA method (OSHA, 1996), which can result in a curve close to that obtained by adding CaF_2 (Cal2) as far as standard filters with important masses of quartz (>1 mg) are taken into account. This solution however has the drawback of overestimating the mass of quartz for samples with low quartz and dust loadings. In this case, preferential orientation effects will not be corrected during the analysis, which can lead to an overestimation of the mass of quartz that can reach $\geq 30\%$. In addition, choosing not to add calcium fluorite and forcing the zero intercept is a device which can improve the results for the 101 reflection but which cannot be applied for the 100 reflection regarding the origins of its Y-intercept.
2. The second solution consists in fitting the calibration curve to a polynomial of an appropriate degree in order to reproduce the non-linearity of this curve. This solution is also unsatisfactory in that low quantities of quartz associated with high quantities of dust would lead to an underestimation of quartz quantities. In this special case of high dust quantity, no preferential effect is expected on the analytical filter. Thus, choosing the calibration curve that takes this effect into account is inadequate.

The bias and to a lesser extent the RSD of the results determined from foams spiked with known quantities of quartz associated with a matrix (calcite or iron oxide) depends, as expected, strongly on the calibration curve used. This is mainly true for low quartz quantities (Tables 2 and 3 for all reflections and Figs. 2 and 3 for the 101 reflection). This effect is particularly pronounced for the most intense reflection of quartz (101). It is also noted that the bias and RSD are strongly deteriorated for the 211 reflection when the quantities of quartz analyzed are ≤ 50 μg . This is consistent with the limit of detection measured for this reflection (37 μg , Table 7). Considering only the tests for which the quantity of quartz spiked into the foams is >500 μg , the average bias for all reflections is negative, $\sim 6\%$ (-4.7% for quartz + calcite mixtures and -7.6% for quartz + iron oxide mixtures). This bias is probably due to losses occurring during the different steps of sample preparation

(see Protocol section). Similar losses were also observed in a previous study after recovery of calcined residue from PVC filters (Kauffer *et al.*, 2005). The larger bias observed for lower quantities of quartz is probably explained by an imperfect calibration curve even when care is taken to add calcium fluoride during its preparation.

The results presented in Table 6 (expanded uncertainty expressed as a percentage) show that the general performance requirements of the EN 482 Standard (CEN, 2006) are respected, namely an expanded uncertainty of $<50\%$ for quartz weights between 0.1 and 0.5 times the 8-h exposure limit value (assuming an exposure value limit equal to 0.1 mg m^{-3}) and $<30\%$ for quartz weights between 0.5 and 2 times the 8-h limit value. The Table 6 data also indicate that the 101 reflection allows quartz quantities of ~ 25 μg to be satisfactorily measured, which corresponds to a 10th of the exposure limit value, assuming a limit value equal to 0.05 mg m^{-3} . The 100 and 112 reflections having expanded uncertainties of $\sim 50\%$ would probably also lead to satisfactory quantification of low quartz weights. These results were obtained for two different matrices (quartz and calcite and quartz and iron oxide). The first mixture tested the effectiveness of the acid treatment used to eliminate the calcite and to prevent thereby the formation of calcium silicate. The second tested the effectiveness of the method used to correct matrix effects in the case of particularly absorbent matrices. Table 7, which gives the detection and quantification limits of the method, shows that the three reflections (100, 101, and 112) allow quantification to the 10th of the value of the current exposure limit. These results confirm the data previously obtained on spiked foams.

It is to be noted that the differences between performance of the proposed method and the requirements of EN 482 being small, any modification of the protocol is likely to compromise the satisfaction of EN 482 requirements, especially for low quartz content.

In a study using WASP proficiency testing results for quartz measurement, Stacey (2005) calculated RSD for a direct analysis method dealing with XRD. It can be noted that respecting the requirement of EN 482 (CEN, 2006) when using the direct on-filter analysis approach (HSE, 2005) is not possible. A quartz loading of 15 μg represents one-fifteenth of a limit value of 0.1 mg m^{-3} when sampled with a cyclone operating at 2.2 l min^{-1} . When using the direct on-filter analysis approach, a level of 15 μg would have an estimated confidence level of $\pm 65\%$ [Table 4 from the report of Stacey (2005)]. The requirements

of EN 482 (CEN, 2006) are that the expanded uncertainty at one-tenth of the limit value should be within 50%. It can also be noted that for these sampling conditions, it is not possible to respect the requirements of the EN 482 Standard, especially since the confidence interval does not take into account all the uncertainties component involved in sampling.

Lastly, the binary mixtures prepared for this study (quartz + calcite and quartz + iron oxide at 10 and 50% quartz) were also analyzed. For this, ~5 mg of different mixtures were directly filtered onto a polycarbonate filter and analyzed according to the method described in this paper. For this analysis, the dust was not calcined at 600°C since the purpose of ashing is only to eliminate the foam. Similarly, no acid attack was carried out since, without ashing, there is no risk that the calcite would react with the quartz to form calcium silicate. The results obtained show that if the RSD is comparable with that measured in the case of spiked foams for the same quartz content (Figs. 5 and 3, and Tables 2–5), then this is not true for bias (Figs. 4 and 2), mainly in the case of quartz + iron oxide mixtures at 10%. It is noted that in this case, the bias is strongly positive (Fig. 4), whereas in the case of spiked foams, it was fairly negative and of weaker amplitude (Fig. 2). Figs. 6–8 (magnified $\times 1500$) display the images obtained by scanning electron microscopy for non-calcinated particles from a quartz + iron oxide mixture at 10%. X-ray picture of the element silicon shows that the largest particles are silica (Fig. 8), whereas the X-ray picture of the element iron shows that the smallest particles are iron oxide (Fig. 7). Using the electron back-scattered technique, where contrast is a function of the atomic number of the minerals, the particles of iron are brighter than those of silica (Fig. 6). It is also seen that the silica particles are dissociated from the iron oxide particles and are larger. It is likely, therefore, that the strongly positive bias measured during analysis of the mixtures is due to a micro-absorption effect (Jenkins and Synder, 1996). The incident electron beam used in XRD is absorbed less by the silica particles than if it had passed through a medium having the same average absorption coefficient as the mixture. The matrix effects are, therefore, probably over-corrected, resulting in a strongly positive bias. The situation is different when the material is calcined, as can be seen in Figs. 9–11 (magnification $\times 1500$). In this case, the particles of iron oxide are closely associated with silica particles, as seen in the X-ray picture for the elements silicon (Fig. 11) and iron (Fig. 10). The XRD diagrams for calcined material show no evidence of new phases, which demonstrates that the iron oxide particles are proba-

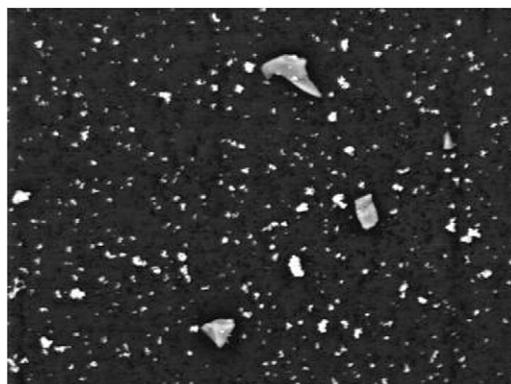


Fig. 6. Non-calcined dust. BEI image.

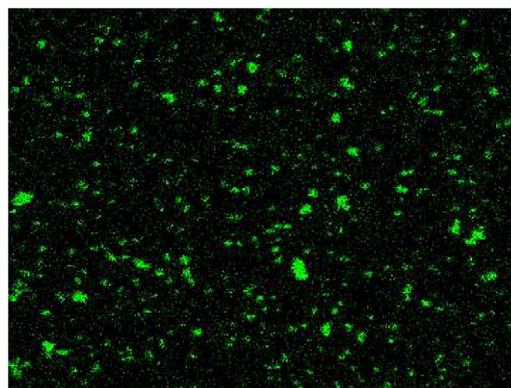


Fig. 7. Non-calcined dust. Fe diagram.

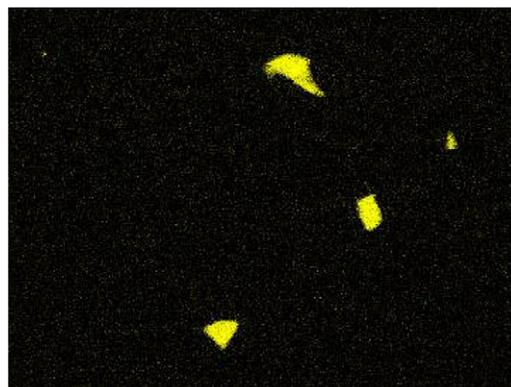


Fig. 8. Non-calcined dust. Si diagram.

bly joined together with the quartz particles. The absorption coefficient of these new entities is different from that of the quartz particles and closer to the mean absorption coefficient of the mixture, resulting in a different matrix effect correction and a lower bias value.

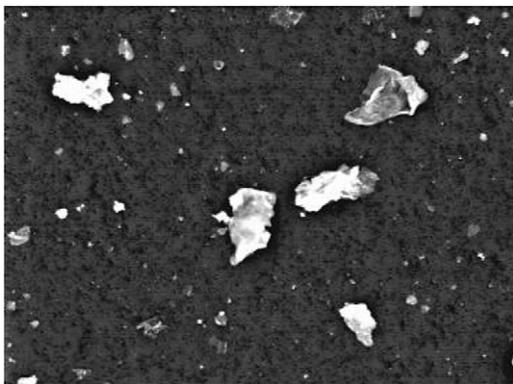


Fig. 9. Calcined dust. BEI image.

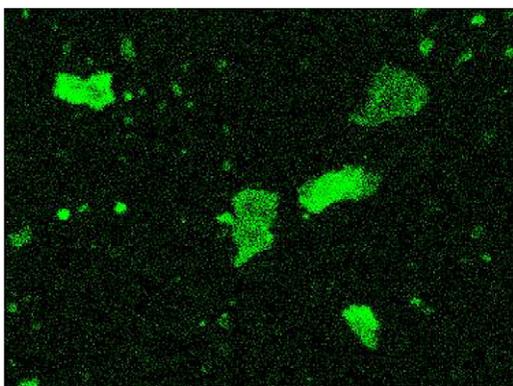


Fig. 10. Calcined dust. Fe diagram.

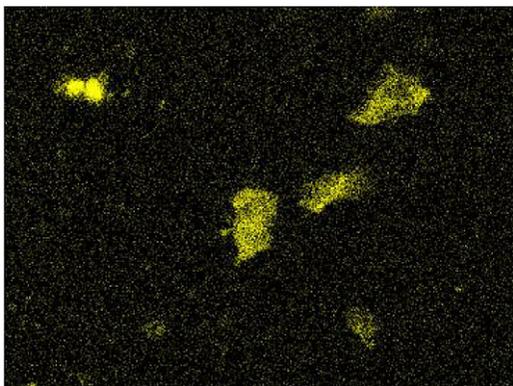


Fig. 11. Calcined dust. Si diagram.

CONCLUSIONS

Due to its high flow rate (10 l min^{-1}), the use of the CIP 10-R sampler to measure silica concentration in air allows larger quantities of dust to be sampled than most cyclones would allow. Whereas its

use implies an indirect analysis to recover the dust sampled by foam, the interpretation of the XRD pattern is simplified and permits more reliable analysis of the phases present.

The proposed analysis protocol, incorporating prior acid attack and ashing of the foams, satisfies the requirements of the EN 482 Standard in terms of expanded uncertainty in a range from 0.1 to 2 times the 8-h exposure limit value, for a limit value equal to 0.1 mg m^{-3} . The results can still be regarded as satisfactory for limit values twice as low. The study made it possible to show the importance of having a sufficient amount of matter on the analytical filter, both at the time of calibration and during the analysis, in order to prevent deposits exhibiting preferential orientation of the quartz particles.

Whereas this observation was made for a mixture prepared from very different constituents in terms of their size and their absorption coefficient, this study finally demonstrated that, in an extreme case, preparation of the sample substantially modified the analytical bias.

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APPENDIX 1

The bias B_{ij} is given by:

$$B_{ij} = \frac{(Qm_{ij} - Qt_{ij})}{Qt_{ij}},$$

where Qm_{ij} is the measured quantity of quartz for sample i of matrix j , Qt_{ij} is the true quantity of quartz determined from the mixture constituents for sample i of matrix j .

For a given matrix j , n samples (usually 3) were prepared for different quantities k of quartz. In this way, the average bias $\bar{B}_{j,k}$ and RSD $S_{j,k}$ associated with these different quartz quantities can also be determined.

$$\bar{B}_{j,k} = \frac{1}{n} \sum_{i=1}^n B_{ij},$$

$$S_{j,k} = \left(\frac{1}{n} \sum_{i=1}^n (B_{ij} - \bar{B}_{j,k})^2 \right)^{0.5}.$$

By grouping the results obtained for the two matrices studied, one can also determine the average bias \bar{B}_k and the RSD S_k for all matrices and for the different quartz quantities studied.

The expanded uncertainty, integrating the sampling uncertainty (S_{samp}) due to flow rate variations,

uncertainty with regard to sampling convention (S_{conv}) and the uncertainty introduced when linking a secondary calibration material to a primary calibration material (S_{cal}) for different quartz quantities k studied is given by:

$$U_k = 2 \times \sqrt{B_k^2 + S_k^2 + S_{\text{samp}}^2 + S_{\text{conv}}^2 + S_{\text{cal}}^2}$$

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