

Quartz and cristobalite – Determination of quartz and cristobalite in workplace air using X-ray diffraction (XRD)

Air Monitoring Method

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Keywords

quartz; cristobalite; air analyses; analytical method; workplace measurement; hazardous substance; X-ray diffraction; XRD; membrane filter

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Abstract

This analytical method is a validated measurement procedure for the determination of quartz [14808-60-7] and cristobalite [14464-46-1] in workplace air after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a particle filter using a suitable flow-regulated pump. After gravimetric determination, the respirable fraction of quartz or cristobalite retained on the filter is analysed by an X-ray diffractometer. The relative limits of quantification (LOQ) are for a sampling period of two hours with air sampling volumes of 0.24 to 45 m³ for quartz 0.0040 to 0.38 mg/m³ and for cristobalite 0.0020 to 0.19 mg/m³. For a sampling period of eight hours the LOQ are between 0.0010 and 0.094 mg/m³ and between 0.0005 and 0.047 mg/m³, respectively. The expanded uncertainty is 28% for 0.075 mg/m³ of quartz and is estimated to be lower for cristobalite. This analytical method has been accredited by the accident

insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction. This method has been tested and recommended for the determination of quartz and cristobalite in work areas by the German Social Accident Insurance (DGUV). Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

Name	CAS-No.	Molar mass [g/mol]	Formula	Substance-specific concentration values [mg/m ³]
Quartz	14808-60-7	60.08	SiO ₂	OELV 0.05 (R) EF 8 (AGS 2020)
Cristobalite	14464-46-1	60.08	SiO ₂	OELV 0.05 (R) EF 8 (AGS 2020)

EF: excursion factor; OELV: occupational exposure limit value; R: respirable fraction

1 Summary

The mean concentration of quartz and cristobalite in the workplace air can be determined over the sampling period with this method using personal or stationary sampling. During the validation of the method, there was no valid occupational exposure limit value (OELV) in Germany. A plausible substance-specific concentration value was assumed to be 0.15 mg/m³ for the respirable dust fraction. The validation was performed from one tenth to twice this value.

Measurement principle:	A flow-regulated pump is used to draw a defined volume of air through a particle filter. Initially the respirable fraction is determined gravimetrically and then the quartz or cristobalite concentration in the respirable fraction is determined by means of X-ray diffraction.
Limits of quantification:	<p>Absolute: For real dust samples: approx. 0.090 mg of quartz (reflection 0.182 nm) approx. 0.045 mg of cristobalite (reflection 0.404 nm)</p> <p>Relative: Depending on the sampling system used: 0.0040 to 0.38 mg/m³ for quartz 0.0020 to 0.19 mg/m³ for cristobalite for a sampling period of two hours and air sample volumes of 0.24 to 45 m³ 0.0010 to 0.094 mg/m³ for quartz 0.0005 to 0.047 mg/m³ for cristobalite for a sampling period of 8 hours and air sample volumes of 0.96 to 180 m³</p>
Selectivity:	The determination is selective for quartz and cristobalite. However, other dust components can cause interference. Therefore, a conclusive identification of cristobalite can be negatively affected in the case of low proportions of cristobalite.
Advantages:	In comparison to infrared spectroscopy, analysis is generally not greatly affected by interference due to other dust components. Personal measurements are possible.
Disadvantages:	The method requires complex and costly equipment. In contrast to infrared spectroscopy, the detection limit is higher by a factor of approximately two.
Apparatus:	Flow-regulated pump with sampling head and particle filter X-ray diffractometer

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Flow-regulated pump for personal or stationary sampling (in the case of PM 4F, in combination with the sampling device) with a suitable range for the nominal flow rate (e.g. SG10 (10 l/min), from GSA Messgerätebau GmbH, 41469 Neuss, Germany)
- Dust collection devices for personal or stationary sampling of the respirable dust fraction (e.g. FSP-BIA, FSP-10, VC 25F, or PM 4F) with filter cassettes for sampling filters (e.g. from GSA Messgerätebau GmbH, 41469 Neuss, Germany or MPG III / II, from DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Membrane filter (nitrocellulose), pore size 8.0 µm (e.g. type SM11301, from Sartorius AG, 37075 Göttingen, Germany, or AE99, from Whatman GmbH, 37586 Dassel, Germany)

For sample preparation and analytical determination:

- X-ray diffractometer (e.g. 3000 T/T XRD from GE Sensing & Inspection Technologies GmbH (formerly from Richard Seifert & Co), 22926 Ahrensburg, Germany or Stoe Stadi P Bragg-Brentano diffractometer system, from Stoe & Cie. GmbH, 64295 Darmstadt, Germany)
- Long fine focus cobalt X-ray tubes (e.g. C-Tech Co A LFF type, from Malvern Panalytical GmbH (formerly from PANalytical), 34123 Kassel, Germany, or CX-Co 12x04-S 1800 W short anode, from GE Sensing & Inspection Technologies GmbH, 22926 Ahrensburg, Germany)
- Cutting plate for dividing sample filters loaded with dust with a scalpel (self-constructed, see [Figure 1](#)) or punching machine to punch out defined filter pieces from larger loaded sample filters
- Porcelain crucible, high or shallow form (e.g. No. 79C-1 or 33c-4b, from Morgan Thermal Ceramics Haldenwanger GmbH, 84478 Waldkraiburg, Germany)
- Porcelain dishes, Ø 5 cm for covering the crucibles in the furnace (e.g. No. 33D-4, from Morgan Thermal Ceramics Haldenwanger GmbH, 84478 Waldkraiburg, Germany)
- 2H pencil for labelling of the crucibles
- Rack for the crucibles made of metal (for large numbers of samples) for insertion into the muffle furnace for the annealing process (self-constructed, see [Figure 2](#))
- Muffle furnace, preferably programmable (e.g. M110 muffle furnace, from Heraeus GmbH, 63450 Hanau, Germany)
- Heating plate
- Thermal sensor
- Filtration devices with fittings for 25 mm filters and suction pump (e.g. SM 16306, from Sartorius AG, 37075 Göttingen, Germany)
- Analytical balance weighing range: approx. 210 g, readability: 0.01 mg (e.g. RC 210 D, from Sartorius AG, 37075 Göttingen, Germany or ME 235 type from Mettler-Toledo GmbH, 35396 Gießen, Germany)
- Sedimentation vessels, cascade impactors or sampling system for the separation of the respirable fraction of quartz or cristobalite from dusts or materials in powder form (e.g. MPG II or III, from DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Round paint brush, size approx. 4 or 5 made of badger or marten hair, to avoid static charges (e.g. Habico 122-05850, size 4, from Habico Künstlerpinselwerk Bieringer GmbH, 91572 Bechhofen, Germany)
- Nitrocellulose membrane filters, pore size 0.45 µm for the preparation of calibration standards (e.g. No. 11306-30-N, from Sartorius AG, 37075 Göttingen, Germany)

- Silver membrane filters Ø 25 mm, pore size 0.2 µm (e.g. No. 45336, from LABC-Labortechnik GmbH, 53761 Hennef, Germany, or SVX20255 type, from Pieper Filter GmbH, 26160 Bad Zwischenahn, Germany)
- Microlitre pipettes, variable volumes, range between 50 and 1000 µl for the preparation of standards for the calibration from a suspension (e.g. from Eppendorf SE, 22339 Hamburg, Germany)
- Heating circulator, with integrated cooling coil, working temperature range must include 20 °C for the preparation of standards for the calibration from a suspension (e.g. ED-13, from JULABO GmbH, 77960 Seelbach, Germany)
- Desiccator with orange silica gel as a desiccant
- Volumetric flasks 100 ml, 250 ml
- Drying cabinet
- Ultrapure water unit (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)

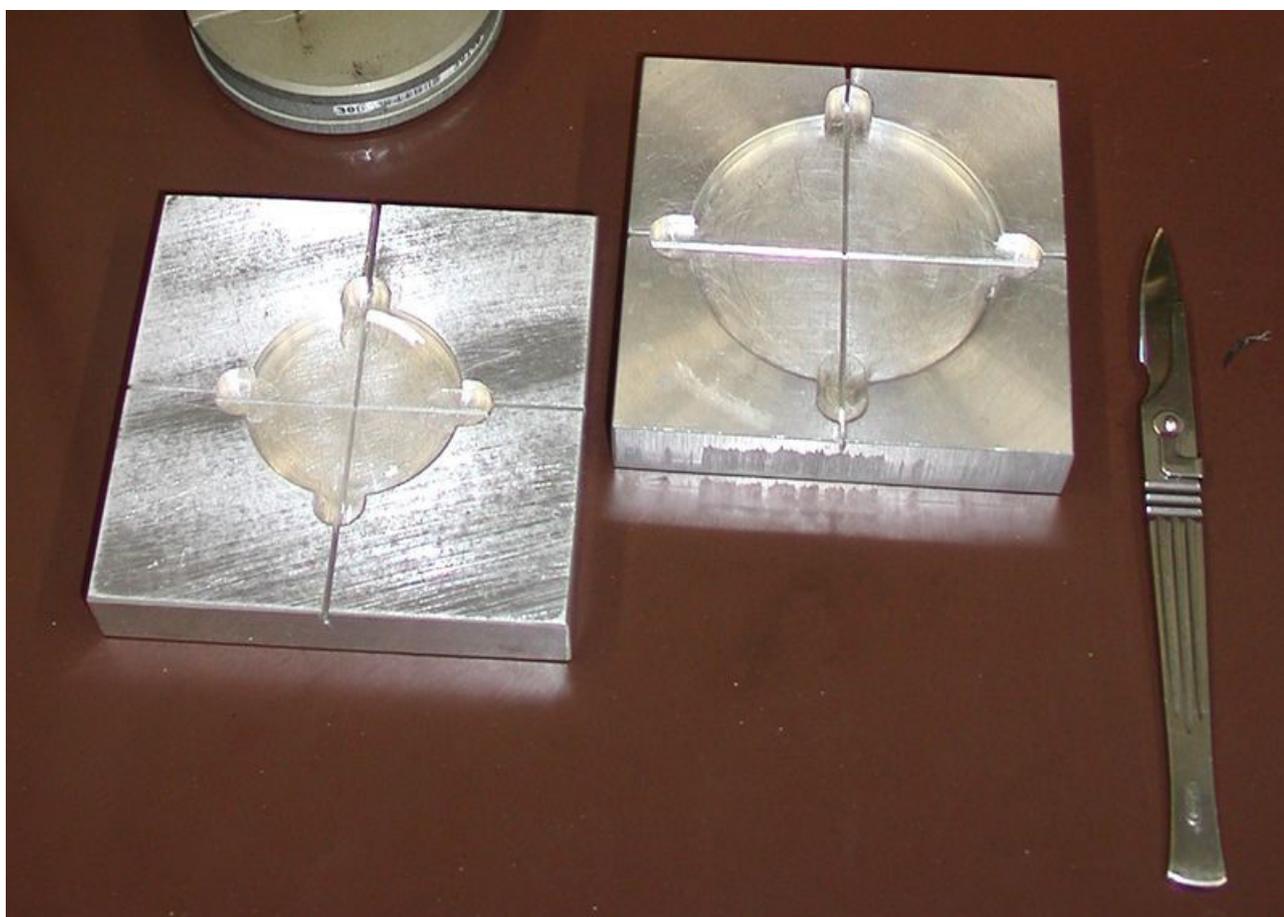


Fig. 1 Cutting plates for dividing membrane filters



Fig. 2 Metal rack for insertion of the crucibles into the muffle furnace

2.2 Chemicals

- 1,3-Butanediol, for synthesis (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)
- Ethanol, denatured, dehydrated (e.g. No. 642, from Werner Hofmann Abt. der Edel-Brennerei Schmittmann GmbH, 40547 Düsseldorf, Germany); alternatively 2-propanol, p. a. (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)
- Acetone, p. a. (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)
- Hydrochloric acid fuming, 37% p. a. (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)
- Quartz dust samples (e.g. Sikron F600 or Millisil W3, from Quarzwerke GmbH, 50226 Frechen, Germany)
- Cristobalite dust samples (e.g. Sikron F6000, from Quarzwerke GmbH, 50226 Frechen, Germany)
- Ethyl cellulose (e.g. Ethocel, from Merck KGaA 64293 Darmstadt, Germany (formerly from Fluka))
- Ultrapure water
- Desiccant, orange silica gel (e.g. Roth P077.2, from Carl Roth GmbH + Co. KG, 76231 Karlsruhe, Germany)
- Eugenol for microscopic analysis for the estimation of the quartz content; refractive index $n_D = 1.542$ (e.g. Merck Millipore, from Merck KGaA, 64293 Darmstadt, Germany)

3 Sampling

A pump draws a defined volume of air through a nitrocellulose membrane filter, which is located in the sampling head of the sampling device. Information on the selection of the sampling device can be found in [Table 4](#) (see [Section 6.2](#)). It is important to ensure that the filters are sealed in dust-proof holders during transport. The containers should be made of a material that avoids static charging.

Specific aspects of dust sampling and possible sources of error are described in DIN EN 481 (DIN 1993) and Hebisch et al. (2005).

4 Analytical determination

In case of dust samples from air sampling where the concentration of silica components is to be determined, the total mass of the respirable dust is also determined as a rule (Hebisch et al. 2005). It is important to know how much material is deposited on the sampling filter, as only a limited mass of annealed dust that has been treated with hydrochloric acid can be used for analysis by means of X-ray diffraction.

In the case of larger amounts of deposited dust, the filter is divided or pieces are die-cut from the filter prior to sample preparation to achieve a deposition on the analysis filter (silver membrane filter) that is as optimal as possible. Alternatively, an aliquot of the residue on ignition is weighed in and used for further analysis.

4.1 Sample preparation

The sample vessels used for preparation are first rinsed with ultrapure water (including prior to their first use) and then with ethanol or 2-propanol, dried and stored at 40 to 50 °C until their next use.

Whether certain partial sections or the whole filters are used for analysis, depends on the mass of deposited respirable dust. It must be ensured that there is at most 2 mg of quartz and cristobalite dust on the filter to be analysed. Experience has shown that the dust mass is reduced by preparation (annealing and treatment with acid), therefore, as a general rule, up to 3 mg of dust from the sampling filter can be used. The loaded membrane filter is first immersed in 1,3-butanediol in a porcelain crucible, then heated on a heating plate in the fume hood to an internal temperature of the crucible of approx. 200 °C for one hour. 1,3-Butanediol has an ignition temperature of 400 °C. An explosive atmosphere may be created when the crucible is heated. Therefore, the annealing at 200 °C must not be carried out in the muffle furnace. To prevent deflagration or sudden burning of the filter, checks should be performed to ensure that the heating plate does not exhibit excessive temperature fluctuations and a maximum temperature of 220 °C in the crucible is not exceeded even for short periods of time. Subsequently, the sample is heated further in the muffle furnace and annealed for at least 2 hours at 550 to 600 °C. After the sample has cooled down, it is treated with hydrochloric acid according to one of the two following options.

Option 1: The crucible with the residue after ignition is filled with hydrochloric acid and treated in the fume hood for at least 30 minutes in a heated ultrasound bath at 70 °C. The liquid in the ultrasound bath must be regularly replaced, in order to minimise corrosion caused by the hydrochloric acid.

Option 2: A weighed aliquot or the entire sample of the residue on ignition with a maximum weight of 3 mg is transferred with 40 ml of hydrochloric acid into a glass beaker and heated on a heating plate in the fume hood for approx. 35 minutes to the boiling point. After cooling down, the glass beaker is filled with ultrapure water to a total volume of approx. 80 ml and homogenised in the ultrasonic bath for at least 30 minutes. The liquid in the ultrasound bath must be regularly replaced, in order to minimise corrosion caused by the hydrochloric acid.

These treatments ensure that components which are soluble in hydrochloric acid, such as carbonates or iron oxides, are dissolved. The remaining suspension is transferred onto a silver membrane filter by means of vacuum filtration. Residual traces of silver chloride from the manufacturing are also removed during this process (see also [Figure 4](#), [Section 4.2.4](#) and additional clarification in the text). It is important to ensure that the filtration holder used has a

uniform diameter of e.g. 20 mm. The suspension of the sample in the crucible or glass beaker is transferred with ultrapure water into the filtration funnel using a wash bottle for rinsing. During filtration, the internal surface of the funnel is first carefully rinsed with ultrapure water using the wash bottle while avoiding disturbance of the precipitation. Towards the end of the filtration process, 2-propanol is used for rinsing. A thin, homogeneous layer of the dust is formed on the analysis filter. The filter is sucked dry and the funnel is carefully removed while the vacuum pump is still operating. The vacuum pump is switched off after the margin area of the filter has completely dried. The filter is lifted from the porcelain frit using tweezers and stored in a closed petri dish, protected from dust, until measurement. The dust deposit on the filter must be as homogeneous as possible. This is checked by visual inspection. If this is not the case, the sample has to be resuspended and the filtration process is repeated.

For the purpose of subsequent identification, the silver membrane filters are marked by thin cuts or are labelled with a 2H pencil at its edges.

Treatment of potassium bromide disks from IR measurements

Potassium bromide disks initially prepared for analysis using FTIR spectroscopy (see Fricke et al. 2016) which are not used for analysis are treated as follows:

The KBr disk is heated in approx. 40 ml of hydrochloric acid in a 100-ml glass beaker on a heating plate in the fume hood for 35 minutes to the boiling point. After cooling, the glass beaker is filled to a total volume of approx. 80 ml with ultrapure water and the suspension is homogenised in the ultrasonic bath for 30 minutes. The suspension is deposited onto a silver membrane filter as described above.

4.1.1 Preparation of calibration standards

Quartz dust with respirable particle sizes similar to those utilised or occurring at the workplace should be used as calibration material. Specific reference materials (e.g. dust derived from grown monocrystals) are not suitable for use, as this may lead to an underestimation of the workplace exposure. A purity of e.g. 95% quartz, i.e. the crystalline proportion, is sufficient. The proportion of other phases in the chosen standard should be below 5% and can be estimated by means of phase contrast microscopy e.g. by application of the analysis procedure according to VDI 3866 Sheet 4 (VDI 2002). For this, the dust is embedded in eugenol on a microscopic slide. In the positive phase contrast, quartz and cristobalite particles appear in hues of blue or grey blue and can therefore be differentiated from other particle types in the dust. As a general rule, synthetic cristobalite typically contains approx. 70% cristobalite, in addition to portions of quartz and amorphous silica. The quartz or cristobalite proportion estimated with phase-contrast microscopy is used in the calibration. Alternatively, cristobalite dusts treated with sodium hydroxide whose quartz content has been determined by X-ray diffractometry can be used. Fractions of amorphous silica as well as amorphous surfaces of quartz and cristobalite particles can be removed by treatment in sodium hydroxide; see e.g. Baumann (1965).

Samples for calibration series are processed in the same way as the samples, to be able to realistically assess the limit of detection of the method based on these calibration standards.

Quartz or cristobalite respirable dust standards can be obtained by means of sedimentation (Schmidt 1962) or cascade impactors. For the method for sedimentation analysis according to Andreasen see Mecchia et al. (2014). Alternatively, quartz or cristobalite dust can also be whirled up with air in a small dust chamber with subsequent sampling of the respirable dust (see Figure 3). The respirable dust is transferred from the filter into a storage vessel using a spatula.

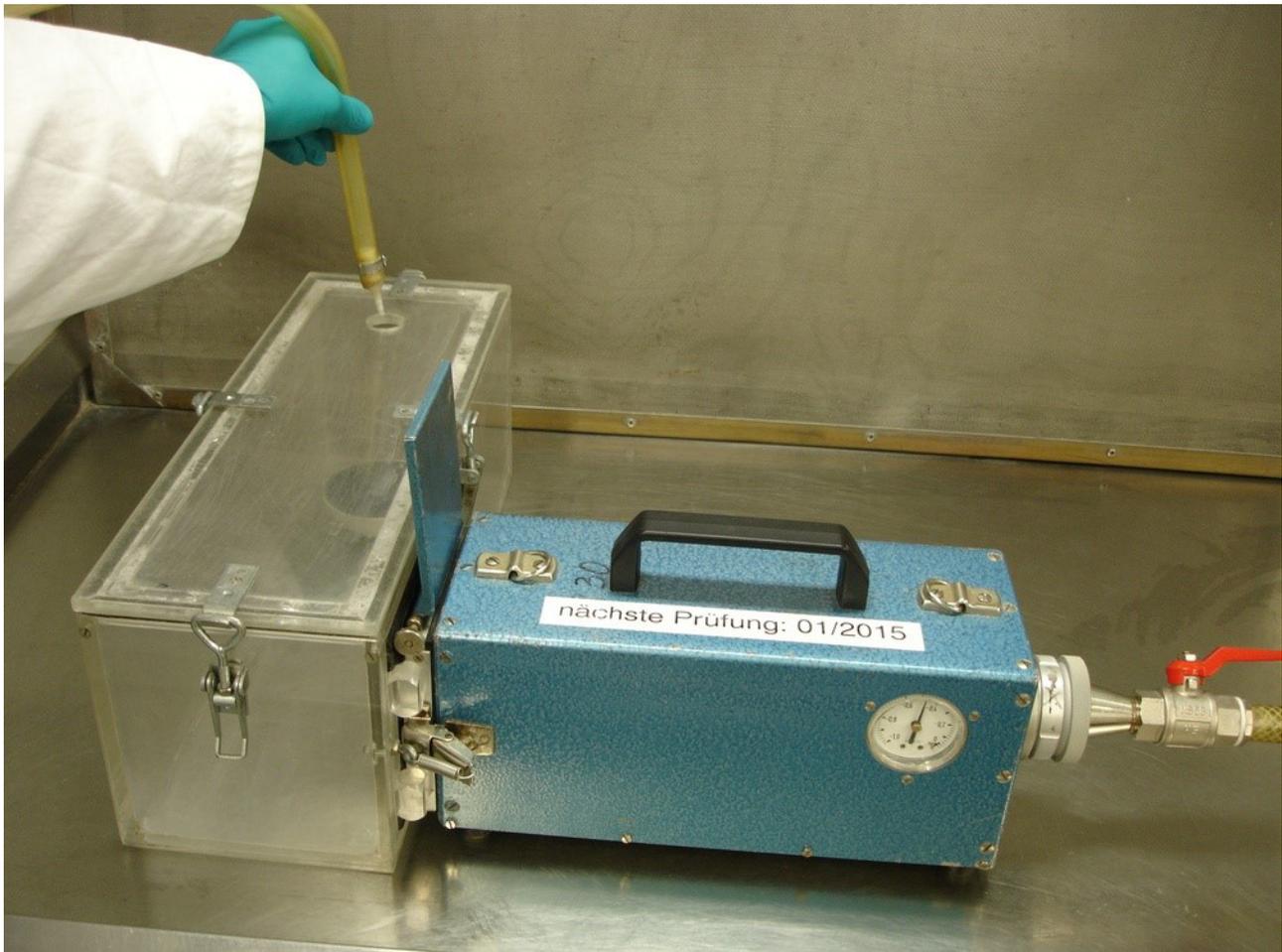


Fig. 3 Example of a custom-made dust chamber for the extraction of respirable dust from quartz or cristobalite powder. The dust contained in a crucible is whirled up in the stream of air. After the dust has been whirled up, the attached sampling device (e.g. MPG III / II) is switched on and the respirable dust is collected.

Two methods proved to be suitable for the preparation of a calibration standard with defined masses of quartz or cristobalite:

Direct weighing: The mass of the standard is weighed, suspended in ultrapure water and filtered through a nitrocellulose filter. It should be noted that in the case of small masses (less than 0.1 mg) weighing errors increase significantly.

Suspension method: A defined amount of the standard is suspended in ultrapure water, ethanol or 2-propanol in a 100- or 250-ml volumetric flask and dispersed in an ultrasonic bath. The flask is filled with the respective solvent to the mark and shaken. After decanting into an Erlenmeyer flask and while stirring with a magnetic stirring bar at 20 °C in a bath thermostat, the necessary amount of suspension for the preparation of the respective calibration standard is taken from this suspension using a microliter pipette and filtered through a membrane filter.

The stirring velocity of the magnetic stirring bar is to be adjusted such that no bubbles are formed in the suspension. These conditions ensure that the dust in the suspension is completely suspended. Repeated withdrawal of a defined volume and subsequent analysis is recommended to check the homogeneity of the suspension. A weighed amount of 10 mg in 100 ml of liquid is suitable for the preparation of calibration samples in a range between 10 and 100 µg. With 100 mg of sample, calibration samples in the range of 100 µg and 1 mg can be prepared.

It is advisable to prepare two calibration series. One calibration should cover the entire application range of the method which is the linear range of the calibration function. For this, the upper limit must be determined by in-house experiments. However, an upper limit of 1 mg is recommended. It should consist of at least 6, but preferably 10 equidistant concentration steps between 0.1 and 1 mg with duplicate determinations in each case. Thus, the linearity of the calibration can be checked and verified for the entire evaluation range. In order to estimate the detection limit and to optimise the evaluation procedure (see [Section 5](#)), a second calibration in the range between 0.01 and 0.1 mg of quartz or cristobalite should be carried out. Again at least 6, but preferably 10 equidistant concentration steps are prepared in duplicate.

If the deposit on the analysis filter is above approx. 1.5 to 2 mg, a deviation from the linearity of the calibration function is likely due to the specific mass attenuation of the radiation (see „[Appendix](#)“). In order to determine the maximum range of the linear progression of the calibration and by this also the application range of this method, further standards should be prepared with masses between 1 and 2.5 mg.

The type of concomitant substances also influences the maximum permissible deposit on the sample filter. Depending on the element-specific mass attenuation coefficients of the sampled dust, lower amounts than with pure quartz dust may be permissible. In this context, the choice of X-ray tube is also relevant (see „[Appendix](#)“).

4.1.2 Preparation of control standards

Standards with a deposit of 1 mg quartz each must be prepared for checking the measurement conditions every working day. Such a standard is analysed after each third to tenth sample of a measurement series. Depending on the number of samples being processed, up to ten of these standards should be used. These standards can also be used for correcting or checking the continuous decrease of intensity of the X-ray tube. The X-ray tube should be replaced when it has reached 60% of its original radiation power. A sufficient number of standards should be prepared for the checks performed every working day. At least two control standards should only be measured at an interval of 6 to 12 months together with the other standards. Thereby, possible changes in the frequently used standards can be detected.

As the standards are regularly used, this can lead to a loss of quartz dust on the filter over time. This can be prevented by impregnating the loaded filter with a thin layer of ethyl cellulose to enhance adherence. For this purpose, a solution with 2 g ethyl cellulose in 90 ml of ethanol is sprayed with a spray bottle from a distance of approx. 10 cm onto the filter. In this case, it must be ensured that there are no sources of ignition close by. The impregnation with ethyl cellulose leads to a decreased intensity of the X-ray reflections of quartz by approx. 3%. Alternatively, approx. 1 ml of 1 g of ethyl cellulose in 100 ml of acetone can be drawn through the silver membrane filter as a final preparation step. After the filter has been sucked dry, the dust adheres to the filter. No reduction in intensity could be detected for this type of preparation. Tests using blank filters are carried out to ensure that the used ethyl cellulose in the solution is X-ray amorphous. The actual reduction in intensity must be determined experimentally and taken into consideration.

Ethyl cellulose solution in ethanol:

2 g of ethyl cellulose are weighed into a 100-ml volumetric flask into which 50 ml of ethanol have been previously placed. The volumetric flask is treated in an ultrasonic bath for one hour and shaken occasionally. Then, further 40 ml of ethanol are added and the solution is shaken.

Ethyl cellulose solution in acetone:

1 g of ethyl cellulose is weighed into a 100-ml volumetric flask into which 50 ml of acetone have been previously placed. The volumetric flask is treated in an ultrasonic bath for one hour and shaken occasionally. Then, the volumetric flask is filled to mark with acetone and shaken.

4.2 Operating conditions and analysis

Radiation: Cobalt K_{α}

Tube voltage: 35 kV

Tube current:	35 or 40 mA
Primary aperture:	As wide as possible or variable Illumination of the sample as large as possible or when a variable aperture is used constant illumination of the sample with approx. 15 × 20 mm
Rotation of the sample holder:	e.g. approx. 60 rpm
Scattering aperture:	2 degrees
K_β filter:	Fe
Receiving slit:	0.5 mm (variable primary aperture) no more than 1 mm
Detector:	Scintillation counter with K _β filter, e.g. 0.025 mm of steel, if working without a primary beam monochromator

The X-ray diffractometer should be configured to yield the highest possible intensity from the X-ray tube and, therefore, to enable a low limit of detection. In this case, the selected goniometer radius (distance from X-ray tube to sample and from sample to detector) should be as small as possible. For achieving a higher intensity, monochromators can be left out. The distance between the lamellae in the Soller aperture can be increased if necessary. To reduce the influence of the mass attenuation of the concomitant dust components and to avoid fluorescence during quartz determination, a cobalt tube has to be used (see „Appendix“).

It must be ensured that the discrimination setting of the scintillation counter is checked with respect to a silver reflection after the installation of a new X-ray tube. Monthly checks are also recommended. If necessary, the reflection of the X-ray diffractometer must be readjusted, if there is divergence in the angular positions of the reflections after a new tube has been fitted.

At least three characteristic X-ray reflections must be evaluated for the determination of quartz. Due to the unfavourable intensity ratios of the characteristic reflections of cristobalite, only the strongest reflection at 0.404 nm is suitable for determining cristobalite. The relevant X-ray reflections with recommended analysis parameters are presented in Table 1. The measurement range of the 22% quartz peak has been extended on the right flank in order to be able to detect possible cristobalite fractions in the sample.

Tab. 1 The strongest X-ray reflections of quartz and cristobalite and recommended analysis parameters

	Quartz		Cristobalite	
Reflection position (relative intensity) ^{a)}	22%	100%	14%	100%
D-spacing [nm] ^{a)}	0.4257	0.3342	0.1818	0.4040
Peak position [degrees, 2-θ]	24.27	31.07	58.99	25.50
Scanning ranges [degrees, 2-θ]	22.6 to 28.0 ^{b)}	29.4 to 32.6	57.0 to 61.0	23.0 to 27.0
Step size [degrees, 2-θ]	0.04	0.04	0.04	0.04
Counts/step [s]	5	4	8	5

^{a)} Data from Powder Diffraction Files 33-1161 and 39-1425 (Gates-Rector and Blanton 2019)

^{b)} The upper limit of this range is extended, in order to obtain information on cristobalite in the sample, if it is present.

The angular ranges should be regarded as the lowest measurement ranges. An extension is advisable, if it enables a better peak deconvolution (‘fit’). The counts should be increased, if necessary, in order to achieve better signal-to-noise ratios.

4.2.1 Determination of the integral intensity of the X-ray reflections of quartz and cristobalite

Generally, the determination of the integral intensity of the X-ray reflections is carried out with the assistance of software. In the case of overlapping peaks, this ensures simultaneous peak deconvolution. In order to optimise the quantification of the investigated reflections intensity, it is advisable to measure the profile of the reflection with reference standards. The characteristic data such as position, full width at half maximum and asymmetry are taken into consideration for peak deconvolution. Particularly in the range of very low quartz contents, determination of the integral intensity based on standards should be applied.

If cross-sensitivities from concomitant minerals in the investigated dust occur, these usually lead to a false positive result. Therefore, for quartz, the concentration is calculated from three different reflections and the lowest concentration is chosen as the result. In the case of implausible results regarding the characteristics of the reflection after peak deconvolution, another reflection must be used for quantification.

4.2.2 Correction for the loss of intensity of the X-ray tube

The continuous decrease in intensity of the X-ray tube can be taken into account by means of a correction factor. The factor is based on the standards used to perform checks every working day. For this purpose, the average relative decrease in intensity of all standards used to perform checks every working day is calculated with respect to the initial conditions (intensity during first use of the X-ray tube).

Additionally, a pronounced continuous decrease in the measured intensity can be caused by ageing of the crystal of the scintillation counter. This effect cannot be separated from the reduction in intensity caused by ageing of the X-ray tube and is taken into account in the method described above.

The intensities determined for the standards should be recorded in a control chart. Based on the progression of the loss of intensity represented in graphic form, emerging problems with the tube (instability or sudden rapid loss of the intensity, replacement due at 60% of its original radiation power, defect of the detector) can be detected at an early stage.

4.2.3 Checking the condition of the detector

Ageing of the crystal must be taken into account when scintillation counters are used. Firstly, this leads to a decrease in the measured intensity and secondly to an increase in background noise. This results in a loss of sensitivity and intensity of the signal. It is advisable to check the absolute level of noise, the signal intensity and the signal-to-noise ratio at intervals of approx. 12 months and to replace the detector if necessary. Replacement is also required, if the detection limit is no longer reached due to the decrease in intensity (see also [Section 6.2](#)).

4.2.4 Other interference

The output and therefore the intensity of an X-ray tube decreases with increasing operating time. Furthermore, ageing of the tube can lead to other interferences in the range of the quartz reflection at 0.334 nm that is particularly relevant for low concentrations. [Figure 4](#) shows these interferences as additional reflections in the diffractograms displayed in blue and green. These can lead to overestimations of concentrations close to the detection limit. In cases like this, the tube must be replaced or as a temporary measure, the diffractogram of the empty silver filter must be subtracted from the diffractogram of the filter with sample. For checking, empty silver membrane filters should be measured at certain intervals, e.g. every two months, to observe changes in the background and to prompt the replacement of the X-ray tube if necessary. It is not necessary to use a filter treated with hydrochloric acid in this case as the relevant interfering peaks appear between 26° and 27° , 30° and 32° as well as 36° and 37° 2θ .

The filter material causes another interference. A filter which has not been treated with hydrochloric acid shows additional peaks at approx. 32.5° and 37.5° 2θ , that appear due to the formation of silver chloride. This is illustrated by the blue and black diffractograms in [Figure 4](#). After the filter has been treated with dilute hydrochloric acid, these peaks no longer occur as can be seen in diffractograms displayed in red and green in [Figure 4](#).

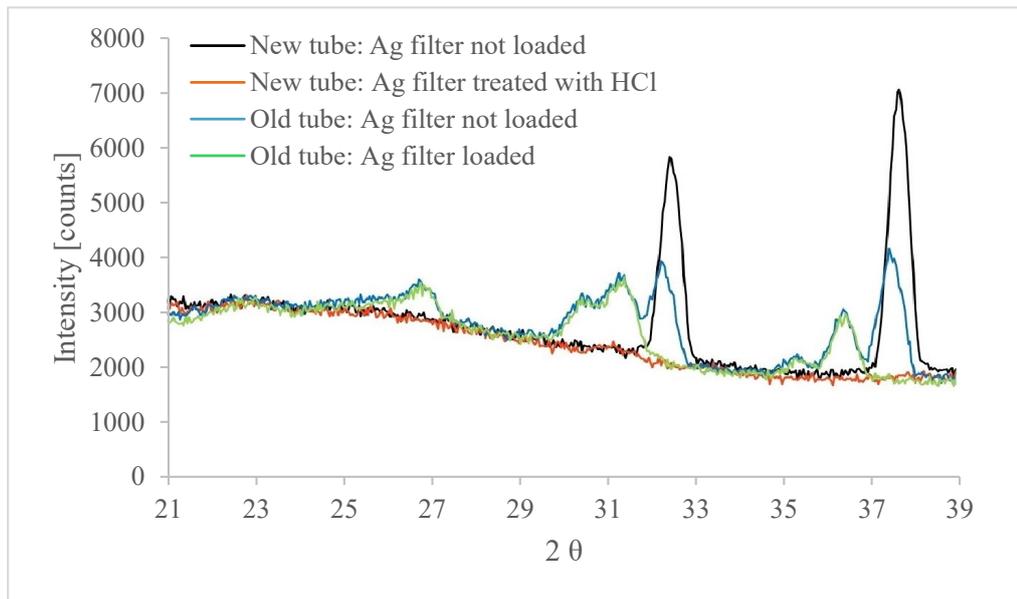


Fig. 4 X-ray diffractograms of non-loaded silver membrane filters with and without hydrochloric acid treatment and measured using an old and a new X-ray tube, respectively

5 Evaluation

With the help of a calibration factor F_C from the linear calibration function, which passes through the intercept, the absolute mass m in mg of quartz or cristobalite in the analysed sample is calculated based on the measured integral intensity I of the respective peak position (see Equation 1). The change in the intensity of the X-ray beam is taken into account by the factor F_X , if necessary.

$$m = I \times F_C \times F_X \quad (1)$$

where:

m is the absolute mass of quartz or cristobalite in mg

I is the integral intensity

F_C is the calibration factor

F_X is the correction factor for the X-ray beam

If a large or thickly loaded sample filter is divided and only a part of the dust is used for analysis, this must be taken into account in the calculation by a correction factor P . The concentration of quartz or cristobalite c in mg/m^3 is calculated on the basis of the air sample volume V in m^3 (see Equation 2).

$$c = \frac{m}{V} \times P \quad (2)$$

where:

c is the concentration of quartz or cristobalite in workplace air in mg/m^3

- V is the air sample volume in m^3
 F_X is the correction factor for the X-ray beam
 P is the fraction of dust of the sample used in %

6 Reliability of the method

6.1 Precision and recovery

Determining the recovery is problematic, as the respirable dust fraction of a commercially used quartz dust serves as a standard for quantification. The content of the quartz in the calibration material is estimated by optical microscopy and is based on the fraction of concomitant substances e.g. clay minerals. The calibration is carried out on the basis of the estimated content.

The standard deviation, determined on the basis of 10 repeat measurements of a sample with 1080 μg of quartz was 3.7%.

6.2 Limits of detection and quantification

The limits of detection and quantification for quartz and cristobalite were determined based on DIN 32645 (DIN 2008) using the calibration function in the lower measurement range (see Section 4.1) or the blank value method. Both methods yield comparable results.

According to the blank value method, the limits of detection of pure quartz or cristobalite dusts ('ideal') can be estimated as three times the standard deviation of 10 measurements of a silver membrane filter loaded with the standard in the range of 10 to 30 μg . The limit of quantification is three times the limit of detection (see Table 2).

Tab. 2 'Ideal' absolute limits of detection and quantification for quartz and cristobalite, derived from the calibrations of the individual substances

Substance	Reflection used d-spacing	Limit of detection [mg/silver membrane filter]	Limit of quantification [mg/silver membrane filter]
Quartz	0.426 nm	0.005	0.015
	0.334 nm	0.003	0.009
	0.182 nm	0.010	0.030
Cristobalite	0.404 nm	0.005	0.015

The analysis of pure quartz or cristobalite dusts results in an absolute limit of quantification of 0.030 mg for quartz (d-spacing 0.182 nm) and of 0.015 mg for cristobalite (d-spacing 0.404 nm) at a statistical certainty of 95% and $k=3$ (see Table 2). However, these low values are sometimes not achieved when filters are analysed that were loaded with dust under real conditions. Experience has shown that the absolute limits of quantification are higher by up to a factor of 3. Depending on the sampling system, the relative limits of quantification vary and are listed in Table 3 for quartz and cristobalite when evaluated at the reflection positions stated above. The continuous slight variation in the limits of quantification due to the aging of the X-ray tube or the detector must also be taken into consideration (see Section 4.2.2 and 4.2.3).

Tab. 3 'Real'^{a)} relative limits of quantification for quartz (at reflection position 0.182 nm) and cristobalite (0.404 nm)

Sampling system	Filter diameter [mm]	Flow rate [m ³ /h]	Sampling period [h]	Air sample volume [m ³]	'Real' ^{a)} relative limits of quantification [mg/m ³] at	
					0.182 nm	0.404 nm
VC 25F	150	22.5	2	45	0.0040	0.0020
				180	0.0010	0.0005
PM 4F	70	4.0	2	8	0.011	0.0056
				32	0.0028	0.0014
FSP-10	37	0.6	2	1.2	0.075	0.038
				4.8	0.019	0.0094
FSP-BIA	37	0.12	2	0.24	0.38	0.19
				0.96	0.094	0.047
MPG III / II	47	2.8	2	5.6	0.016	0.0080
				22	0.0040	0.0020

^{a)} Limits of quantification in an unfavourable sample matrix or interferences in the range of the relevant reflections

6.3 Expanded uncertainty

The requirements for the expanded uncertainty of the analytical method and its calculation are described in DIN EN 482 (DIN 2021). The expanded uncertainty is calculated as given exemplarily in Table 4 for quartz (evaluation at 0.182 nm) with an FSP-10 personal sampling system (flow rate 10 l/min). The systematic uncertainty components associated with sample storage and transport are negligible and are assumed to be zero (SiO₂ mineral samples are stable).

Tab. 4 Calculation of the expanded uncertainty of the analytical method for quartz

Sampling (with FSP-10)	
Sampling period	2 h
Flow rate	10 l/min
Uncertainty of sampling, respirable particles (Hebisch et al. 2012)	11.1%
Analysis	
Recovery:	
Systematic error <i>A</i> from the recovery (deviation of the recovery from 100%), determined on the basis of 10 repeat measurements of samples with a quartz mass $\bar{x} = 1080 \mu\text{g}$	3.7%
Calculated systematic uncertainty in relation to the analytical recovery ($= A/\sqrt{3}$)	2.1%
Analytical measurement uncertainty extrapolation (DIN 2010)	
Absolute limit of detection	30 μg
Standard deviation of the blank value; s_0	3.0 μg
Analytical precision as a coefficient of variation; $K_{v,3}$	6.67%
$K_{v,3} = \frac{s_x}{\bar{x}}$	
Relative standard deviation of the analyte; s_r	6.7%
$s_r = 100 \cdot \sqrt{(K_{v,3})^2 - \left(\frac{s_0}{\bar{x}}\right)^2}$	
($s_x = 72 \mu\text{g}$; determined on the basis of 10 repeat measurements of 1080 μg of quartz)	
Random analytical uncertainty; u_{ap}	Examples:
Calculated from the precision for other masses <i>y</i> in μg :	<i>y</i> = 18 μg : $u_{ap} = 18.0\%$
	<i>y</i> = 90 μg : $u_{ap} = 7.5\%$
	<i>y</i> = 360 μg : $u_{ap} = 6.8\%$
$u_{ap} = K_{v,y} \cdot 100 = \left(\frac{100}{y}\right) \cdot \sqrt{s_0^2 + \left(\frac{s_r \times y}{100}\right)^2}$	

Tab. 4 (continued)

Sampling (with FSP-10)	
Random uncertainty; u_{ap} from the precision for three different concentrations and a sampling volume of 1.2 m ³	
at 0.015 mg/m ³ : Analyte mass 18 µg of quartz	18.0%
at 0.075 mg/m ³ : Analyte mass 90 µg of quartz	7.5%
at 0.300 mg/m ³ : Analyte mass 360 µg of quartz	6.8%
Systematic uncertainty for the purity of the standard substance (= 1%/√3) (> 99% for a correction of the quartz content)	
	0.6%
Estimated random uncertainty of the calibration	
	2%
Maximum drift of the measurement device display	
	5%
Calculated systematic uncertainty of the measurement device drift (= 5%/√3)	
	2.9%
Calculated random uncertainty of the analysis; u_{ar}	
at 0.015 mg/m ³	18.1%
at 0.075 mg/m ³	7.7%
at 0.300 mg/m ³	7.0%
Calculated systematic uncertainty of the analysis; u_{anr}	
	3.6%
Uncertainty of the analysis; u_a	
$u_a = \sqrt{a_{ar}^2 + u_{anr}^2}$	
	18.5%
at 0.015 mg/m ³	8.5%
at 0.075 mg/m ³	7.9%
at 0.300 mg/m ³	
Combined uncertainty u_c (sampling and analysis)	
at 0.015 mg/m ³	21.6%
at 0.075 mg/m ³	14.0%
at 0.300 mg/m ³	13.6%
Expanded uncertainty U	
$U = 2 \cdot u_c$	
	43.2%
at 0.015 mg/m ³	28.0%
at 0.075 mg/m ³	27.2%
at 0.300 mg/m ³	

The exemplary calculation for sampling using FSP-10 complies with DIN EN 482 (DIN 2021) which requires that the expanded uncertainty for a long-term measurement in the range of one tenth to less than half the limit value is $\leq 50\%$ and for half to twice the limit value is $\leq 30\%$. During the validation of the method, there was no valid OELV in Germany. A plausible substance-specific concentration was assumed to be 0.15 mg/m³. The validation was performed from one tenth to twice this value. It should be noted that the expanded uncertainty of a 4-hour sampling period with the FSP-BIA (2 l/min) does not comply with the above mentioned requirements.

For cristobalite, a lower expanded uncertainty can be anticipated as only the reflection at 0.404 nm with high intensity is used for quantification in comparison to the reflection for quartz (0.182 nm) discussed above (see Table 2 in Section 6.2).

6.4 Cross-sensitivities

X-ray reflections of minerals that commonly occur together with quartz in mineral dusts can overlap with certain quartz reflections. The main reflection of quartz at 0.334 nm is often affected by interference from silicates e.g. mica which gives false positive results. Certain feldspars can cause interference with the quartz reflection at 0.182 nm. Alternatively, the reflection at 0.426 or 0.182 nm should be evaluated.

Elements with high mass attenuation coefficients e.g. lead sulphate, barium sulphate, which are not or not fully removed by treatment of the annealed sample with hydrochloric acid, can cause an underestimation of the silica content. Chromium(III) oxide can be mistaken for quartz due to a reflection at 0.182 nm.

The cristobalite analysis using the 0.404 nm reflection can for instance be affected by interference by very wide reflections of silica glass or amorphous silica (opal C or opal CT, e.g. in bentonite, see Elzea et al. 1994). Shifts in the reflections up to 0.413 nm are possible. Alternatively, the weak reflection at 0.187 nm can be evaluated, however, with limits of detection that are higher by a factor of approx. three to four than those of when the reflection at 0.404 nm is evaluated.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (www.dfg.de/mak/conflicts_interest) ensure that the content and conclusions of the publication are strictly science-based.

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Appendix

Influence of absorption during X-ray diffraction analysis of dusts

Among other factors, the intensity of a defined reflection of quartz is influenced by X-ray absorption in X-ray diffraction analysis. This depends essentially on how densely the dust is deposited on the analysis filter and the mass absorption coefficient of the concomitant dust components (Elzea et al. 1994; Heidermanns 1974; Heidermanns and Lichtenstein 1993).

Under certain conditions, the correction of the absorption effects can be omitted in the analysis of quartz in thin layers and it can be assumed that there is an approximately linear correlation between the quartz mass and the integral intensity. Therefore, on the one hand, according to Elzea et al. (1994), the deposit density on the analysis filters should be less than 1 mg/cm². On the other hand, it is desirable that the mass attenuation coefficients of the concomitant minerals in the quartz are as low as possible. Thus, cobalt tubes – instead of the commonly used copper tubes – should be used to carry out the analyses. Table 5 lists the mass attenuation coefficients of typical concomitant phases of quartz in dusts for Cu_{Kα} as well as Co_{Kα} radiation. In the case of Cu_{Kα} radiation it should be noted that in particular iron has a comparatively high mass attenuation coefficient. As the samples undergo an acid treatment as part of the preparation, only the acid-resistant phases are of interest for an estimation of the mean influence of the mass attenuation of the concomitant dusts. Calcium shows a greater coefficient for the Co_{Kα} radiation. However, the mass attenuation coefficient is not significantly higher for the silicate minerals that typically contain Ca. When using Co_{Kα} radiation, a distinctly greater mass attenuation coefficient can only be expected for dusts with large Ba proportions (e.g. baryte, BaSO₄). BaSO₄ fractions can be partially removed by treatment with acid in the course of sample preparation.

Tab. 5 Mass attenuation coefficients [cm²/g] of various minerals (from Elzea et al. 1994)

Mineral	Composition	Radiation	
		Cu _{Kα}	Co _{Kα}
Corundum	Al ₂ O ₃	31.8	48.4
Haematite	Fe ₂ O ₃	230.4	47.7
Quartz	SiO ₂	35.0	54.8
Calcite	CaCO ₃	75.6	113.7
Dolomite	MgCa[CO ₃] ₂	75.4	50.1
Forsterite	Mg ₂ [SiO ₄]	31.8	48.7
Olivine	(Mg,Fe) ₂ [SiO ₄]	125.3	50.6
Sillimanite	Al ₂ O ₃ ·SiO ₄	32.9	50.7
Mullite	3Al ₂ O ₃ ·2SiO ₂	32.8	50.2
Diopside	MgCa[Si ₂ O ₆]	57.7	87.7
Talc	Mg ₃ [(OH) ₂ Si ₄ O ₁₀]	32.1	49.6
Montmorillonite	Al ₂ [(OH) ₂ Si ₄ O ₁₀]	32.9	51.1
Kaolinite	Al ₄ [(OH) ₈ Si ₄ O ₁₀]	30.4	47.1

Tab. 5 (continued)

Mineral	Composition	Radiation	
		Cu _{Kα}	Co _{Kα}
Orthoclase	K[AlSi ₃ O ₈]	48.9	75.5
Albite	Na[AlSi ₃ O ₈]	33.3	51.7
Anorthite	Ca[AlSi ₃ O ₈]	52.3	79.6
Baryte	BaSO ₄	319.7	209.9