

Method for the determination of quartz and cristobalite

German Social Accident Insurance

**Expert Committee Raw Materials and Chemical Industry
Subcommittee Hazardous Substances**

Analytical Subcommittee of the Chemistry Board of Experts*

**Recognized analysis procedures for carcinogenic mutagenic or substances
toxic to reproduction**

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This method has been tested and recommended by the German Social Accident Insurance for the determination of quartz and cristobalite in working areas.

Both personal and stationary sampling can be performed for the assessment of working areas.

Sampling is carried out using a pump and collection on a membrane filter. In the first step analysis of the respirable dust fraction is performed gravimetrically, with subsequent measurement of the concentration of quartz and cristobalite in the respirable dust fraction by infrared spectroscopy.

The method is validated for the following substances:

Name	Quartz	Cristobalite
CAS No.	14808-60-7	14464-46-1
Empirical formula	SiO ₂	SiO ₂
Molar mass	60.08 g/mol	60.08 g/mol

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Summary

The method permits the determination of quartz and cristobalite concentrations in working areas averaged over the sampling time after personal or stationary sampling.

- Measurement Principle:** A defined volume of air is drawn through a particle filter using a pump. Gravimetric determination of the respirable dust fraction is initially carried out, and then the quartz and cristobalite concentrations in the respirable dust fraction are determined by infrared spectroscopy.
- Limit of quantification:** absolute: approx. 0.03 mg (based on experience of real dust samples of quartz and cristobalite)
relative: 0.0013 to 0.13 mg/m³ (for a sampling duration of two hours (0.24 to 8 m³ air sample) and between 0.0003 and 0.031 mg/m³ for a sampling duration of 8 hours (0.96 to 180 m³ air sample), depending on the sampling system used)
- Selectivity:** The determination is selective for quartz and cristobalite. However, other dust components can cause interference. Therefore, a conclusive identification can prove difficult, particularly in the case of low proportions of quartz and cristobalite.
In cases such as this it may be advisable to resort to an X-ray diffractometric method.
- Advantages:** Comparatively simple procedure requiring less equipment. In contrast to X-ray diffraction, the limit of quantification is lower by a factor of two approximately.
- Disadvantages:** Other dust components can cause greater interference in the analysis compared to X-ray diffraction.
- Apparatus:** Flow-regulated pump with sampling head and particle filter, vacuum pump, vibratory mill or mortar, annealing furnace, heating plate, sedimentation apparatus or fractionating dust samplers (e.g. impactors with several particle size fractions < 10 µm), Fourier transformation infrared spectrometer (FTIR).

Detailed description of the method

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1

Equipment, materials and chemicals

1.1

Equipment and materials for sampling

- Flow-regulated pump for personal or stationary sampling (in the case of VC25 and PM-4F in combination with the sampling device) with a suitable nominal flow rate, e.g. SG10 (10 L/min), from GSA Messgerätebau, 40880 Ratingen, Germany
- Dust collection device for personal or stationary sampling of the respirable fraction, e.g. FSP-10 or PM-4F, from GSA Messgerätebau
- Membrane filter (nitrocellulose), pore size 8.0 μm , e.g. type SM11301, from Sartorius Stedim Biotech, 37075 Göttingen, Germany, or AE99, from Whatman, 37586 Dassel, Germany

1.2

Equipment for sample preparation and determination

- Heating plate with thermostat (temperature adjustable up to 300 °C), e.g. PZ60ET heating plate (100 to 350 °C) with PR5SR program regulation from H. Gestigkeit, 40489 Düsseldorf, Germany
- Small metal dish (weighing dish)
- Vibratory mill (ball mill) with metal beakers and balls made of V2A stainless steel, e.g. MM300 ball mill, from Retsch, 42781 Haan, Germany
- Porcelain crucibles, volume 20 mL, e.g. No. 79C-1, from Haldenwanger, 84478 Waldkraiburg, Germany
- Porcelain dishes, Ø 5 cm (used for covering the crucibles in the furnace), e.g. No. 33D-4, from Haldenwanger
- Crucible holders made of iron used for insertion into the chamber furnace for annealing (constructed in own workshop)
- Annealing furnace, preferably programmable, e.g. chamber furnace, from Heraeus, 63450 Hanau, Germany
- Vacuum pump (final pressure < 80 hPa), e.g. from Ilmvac, 98693 Ilmenau, Germany
- Compression tooling (for the preparation of KBr disks), e.g. electro-hydraulic press, from Perkin Elmer, 63110 Rodgau, Germany
- FTIR device, wavelength range from at least 4000 cm⁻¹ to 400 cm⁻¹, e.g. Nicolet 380 FTIR, from Thermo Fischer Scientific, 63303 Dreieich, Germany or Bruker Vector 22, from Bruker, 76275 Ettlingen, Germany
- Analytical balance (weighing range: approx. 220 g, reading accuracy: ±0.01 mg), e.g. MC1 type, from Sartorius, 37075 Göttingen, Germany or from Mettler, 35353 Gießen, Germany
- Sedimentation vessels or cascade impactors for quartz or cristobalite particle size fractionation
- Mortar made from agate or boron carbide
- Brush (badger hair brush, used to prevent the build-up of static charge)
- Nitrocellulose membrane filter, 0.45 µm pore size, e.g. No. 11306-30-N, from Sartorius Stedim Biotech, 37075 Göttingen, Germany
- Microlitre pipettes, variable volumes, range of between 50 and 1000 µL, e.g. from Eppendorf, 22339 Hamburg, Germany (for the preparation of calibration standards from a suspension)
- Bath thermostat with built-in cooling coil, working temperature range must include 20 °C, e.g. ED-13, from Julabo Labortechnik, 77960 Seelbach, Germany (for the preparation of calibration standards from a suspension)
- Desiccator with silica gel orange desiccant
- Volumetric flasks, 100 mL and 250 mL
- Drying cabinet, explosion-proofed if necessary

Note:

The listed sample vessels are to be cleaned (including prior to their first use) with distilled water followed by ethanol and then dried and stored at 40 to 50 °C until their next use.

1.3

Chemicals

- Potassium bromide, Uvasol, e.g. No. 1.04907 from Merck, 64293 Darmstadt, Germany
- 1,3-Butanediol for synthesis, e.g. No. 8.01964.1000 from Merck
- Ethanol, denatured, anhydrous, e.g. No. 642, from Werner Hofmann, 40547 Düsseldorf, Germany
- Hydrochloric acid, fuming, 37%, p.a., e.g. No. 113386, from Merck
- Sodium hydroxide 2 N, e.g. No. 109136, from Merck
- Quartz dust types, e.g. Sikron SF600, from Quarzwerke, 50226 Frechen, Germany or Minusil 5, from U.S. Silica, Berkley Springs, USA
- Cristobalite dust types, e.g. Sikron SF6000, from Quarzwerke
- Silica gel orange, e.g. type. No. P077.2, from Carl Roth, 76185 Karlsruhe, Germany

2

Sampling

A pump draws a defined volume of air through a sample filter located in the sampling head of the sampling device. The respirable dust fraction is collected during sampling as stipulated in DIN EN 481 [1]. Examples of sampling systems that have proved successful are PM 4F, VC 25F, FSP-10, FSP-BIA and MPG II (see Table 2 in Section 5.2). It is necessary to ensure that the filters are sealed with dustproof caps so that dust is excluded during transport. The material of the containers should be such that a build-up of static charge is avoided as far as possible.

Specific aspects of dust sampling and possible sources of error are described in the “Preliminary Remarks” Part III, Vol. 9 chapter “Sampling and determining aerosols and their chemical components” 2005.

3

Analytical determination

As a rule the dust mass is also measured in the case of air samples in which the concentration of silicogenic components is to be determined in order to establish the concentration of the respirable dust fraction. Only a certain mass of dust (up to 2 mg) can be used for analysis by means of infrared spectroscopy, therefore it is important to know the quantity of dust that is deposited on the sampling filter.

3.1

Sample preparation

Two variations for the preparation of samples are described in the following section. Preliminary tests are to be used to establish which method is most suitable.

Variation 1, for instance, can lead to non-reproducible diminished values if the heating rate is too rapid during pre-treatment on the heating plate. This is assumed to be due to a reaction between the filter material, potassium bromide (KBr) and dust during sample preparation: When the loaded nitrocellulose filter is heated too rapidly in the presence of KBr, potassium nitrate or nitrite and potassium oxide can be formed, which can subsequently react to form silicates with the quartz present in the sample (formation of KNO_2 from KNO_3 above 330 °C, and from this K_2O and nitrous gases above 441 °C). In this manner the quartz to be determined in the sample is selectively converted. If diminished values for quartz are discovered during preliminary tests in the laboratory, then a slower heating rate should be selected or the procedure according to Variation 2 should be followed. Comparable effects must also be checked for the preparation of dust containing cristobalite.

As a general rule for the preparation methods described below, KBr disks should not contain more than 2 mg of dust and not more than 1 mg of quartz. Generally a quartz content of considerably less than 1 mg can be expected when using up to 2 mg of dust, as a quartz content of less than 20% occurs at most workplaces. However, in certain areas (e.g. processing of quartz sand or quartz powder) the quartz contents found in the dust can be even greater than 50%. The amount of KBr required for the preparation of a KBr disk varies between 250 and 450 mg, depending on the equipment used. The masses of the KBr disks for calibration as well as for sampling should not deviate by more than 10% from each other.

Preliminary tests are recommended to establish the maximum dust mass to be used in a KBr disk. When the dust mass used in a KBr disk is too high, this leads to a reduction in transmission, which in turn results in a less satisfactory limit of quantification. In individual cases even a mass of less than 1 mg of certain concomitant components in workplace dusts can lead to transmission interference.

Variation 1*Filter incineration for dust masses of less than 5 mg*

Filters with dust masses of less than 5 mg are reduced to ash with addition of 250 to 450 mg of KBr. Deviations can be made in the following cases:

- Known low ash content in the sample (e.g. measurements in coal mines): Filter samples with dust masses of greater than 5 mg can be reduced to ash with addition of the above-mentioned quantities of KBr if it is anticipated that a residue of approx. 2 mg of mineral ash will not be exceeded.
- High quartz contents of > 20% are expected: If the quartz content is found to be too high in the IR analysis, then it is possible to divide and grind the KBr disks again, dilute them further with additional KBr and perform a separate analysis.

The filter is halved with a scalpel or scissors and the halves are placed upon each other with the dust-loaded sides touching. A pinch of KBr (i.e. the amount to fit on the tip of a spatula) is dispersed in a flat, conditioned porcelain crucible (previously annealed at 550 °C, cooled in the desiccator and weighed), the filter halves are placed on the KBr layer and the remaining KBr (total mass 250 to 450 mg) is spread on top of the filter halves.

The crucible is placed into the fume cupboard on a cold heating plate and the heat is adjusted so that the heating plate temperature reaches approx. 220 °C at this setting. Heating continues until the filter appears completely blackish-brown (approx. 2 h, heating for a longer period poses no problems).

The crucible is then heated in the annealing furnace and annealed at 550 °C (1 to 1.5 h heating, 2.5 to 3 h dwell time). On opening the furnace, the cooled, but still slightly warm crucible is transferred to the desiccator with silica gel as a desiccant without applying a vacuum. When the crucible has cooled down the contents are transferred to a mortar using a spatula and brush, ground until homogeneous with the pestle while applying light pressure, and then transferred by means of a spatula and brush to the disk compression tooling for preparation of the KBr pressed disks.

Filter incineration for dust masses greater than 5 mg

The filter is folded in the middle so that the dust-loaded halves are touching, placed into a pre-conditioned and weighed porcelain crucible and covered with 1,3-butenediol until saturated. As described above, the sample in the crucible is pre-ashed on the heating plate and annealed at 550 °C in the annealing furnace (1 to 1.5 h heating, 2.5 to 3 h dwell time). The crucibles are left in the desiccator to cool and the amount of ash residue is determined. The ash residue is collected together in the crucible using a spatula and brush and an exactly weighed aliquot in the range of 0.5 to 2.5 mg is transferred to the mortar (if information is available on anticipated excessive quartz or cristobalite content, then weighing lower amounts is advisable). The ash residue is mixed with approx. 250 to 450 mg of KBr, ground until homogeneous with the pestle while applying light pressure, and then transferred by means of a spatula and brush to the disk compression tooling.

Variation 2

The membrane filter loaded with the respirable dust fraction is soaked with 1,3-butanediol (up to 3 mL) in a pre-conditioned and weighed porcelain crucible and heated incrementally on the heating plate to remove the filter material:

- over the course of one hour up to 140 °C, subsequently
- for another hour each up to 220 °C and 300 °C, until the filter has been reduced to ash and the 1,3-butanediol has evaporated.

A black residue remains. Thereafter the remaining sample is slowly heated in the annealing furnace up to 600 °C (approx. 1 to 2 hours heating-up time). Incineration takes approx. 6 hours in total and should prevent interference in the IR determination. After cooling, a defined amount of KBr is added to the ash residue (= respirable dust containing quartz). 250 to 450 mg of KBr are added to a maximum of 2 mg of dust in each case. In order to entirely remove the substance from the crucible walls the crucible with the dust and KBr is treated in an ultrasonic bath for 15 minutes. Following transfer into a metal beaker of the mill, the sample mixture is homogenised by grinding for 5 minutes. Extended milling times do not improve results.

Preparation of the KBr disks

The KBr quantity required for the preparation of the pressed disk (exact determination by weighing, typical disk diameter: 13 mm) is weighed from the mixture of sample substance and KBr (sample mixture). When filling the mixture into the disk compression tooling a homogeneous distribution must be ensured to avoid mass aggregation during compression of the disks. Thus the greatest possible uniformity of the disk thickness is achieved. After inserting the disk compression tooling into the hydraulic press, the tooling is degassed with the vacuum pump for approx. 1 minute and the KBr disk is compressed with a pressure of 80 kN/cm² for approx. 1 minute.

Visible opacity at the edge of the finished disk is a sign of non-optimal compression with a non-uniformly distributed mixture. The compression process and the compression equipment can be checked by analysing disks four times, each having been rotated by 90 degrees in the same direction in the holder. If significant deviations in the results are found, then the compression process must be optimised.

Generally, in order to avoid opacity in the pressed disks, the sample mixture, the KBr, the milling vessels and compression tooling should be dried at 40 °C in the drying cabinet and stored there between pressing procedures. If pressed disks are not immediately analysed, they can be stored in the drying cabinet for a short period. The pressed disks must be ground and pressed again after prolonged storage (losses in mass must be taken into consideration; each disk must be weighed before and after renewed compression!).

Preparation of calibration standards

The use of certified reference materials (these also contain amorphous SiO₂ in the respirable dust fraction) is not necessary for calibration. Quartz dusts that are com-

parable to those utilised or occurring in the workplace should be used as reference material. A purity of e.g. 97% quartz, i.e. crystalline content, is sufficient. The proportion of other phases in the chosen standard should be less than 5% and can be estimated in a phase-contrast microscope (e.g. by application of the analysis procedure according to DGUV Information 213-530 (former name: BGI 505-30) [8]; eugenol as a mounting liquid for differentiation between quartz and other mineral phases). Technically used cristobalite dusts are not of the above-mentioned purity; typical cristobalite contents are approx. 70% (often together with quartz and amorphous silica). The microscopically estimated cristobalite content is used in the calibration; alternatively respirable cristobalite dusts that have been treated with NaOH and whose quartz content has been determined by X-ray diffraction can be used [6].

Disks for calibration series have to undergo the same preparation steps as those performed on the samples in order to be able to realistically assess the limit of quantification of the method based on this calibration standard.

Two methods have proved successful for the addition of defined masses of quartz or cristobalite standard to a calibration sample:

- The mass of the standard is weighed directly and added to the KBr mass. In addition, a 37 mm cellulose nitrate membrane filter is added, before the sample is prepared as described above. It is advisable to prepare a dilution with KBr in advance of weighing small masses of the standard (less than 100 µg). For this purpose a mixture of KBr and the standard is prepared, e.g. with a ratio of 1990 mg of KBr to 10 mg of quartz. From this mixture e.g. 10 mg are weighed, in order to obtain a quartz mass of 50 µg for a calibration standard. In this way the necessary mass of the standard can be weighed with greater accuracy by indirect use of the mixture and then KBr can be added if the quantity for the disks is insufficient.
- A defined quantity of the standard is suspended in water or ethanol in a 100 or 250 mL volumetric flask. After transferring the suspension into an Erlenmeyer flask and while stirring (magnetic stirrer) at a controlled temperature of 20 °C (bath thermostat), the quantities of suspension necessary for the preparation of the respective calibration standard are taken using a microlitre pipette. After drying the necessary KBr quantity for preparation, as described above, is added to the loaded filter. The stirring velocity of the magnetic stirrer is set so that no bubbles are formed in the suspension. These conditions ensure that the dust in the suspension is completely stirred up. Repeated extraction of a defined amount and subsequent analysis is recommended to check the homogeneity of the suspension.

It is advisable to prepare two calibration series. One calibration should cover the entire application range of the method (maximum 1 mg) and consist of at least 6, preferably 10 equidistant concentration steps between 0.1 and 1 mg (determination in duplicate in each case). Thus the linearity of the calibration can be checked and verified for the entire evaluation range. In order to be able to estimate the limit of

detection of the method and to optimise the evaluation procedure (for evaluation problems see Section 4), a second calibration in the range between 0.01 and 0.1 mg quartz or cristobalite should be performed, also consisting of at least 6 equidistant concentration steps.

3.2

Analysis

While measuring, the room temperature should be kept stable at the location of the FTIR device and draught as well as direct sunlight should be avoided. Exposure of the instrumentation of the beam to external vibrations (e.g. from adjacent devices) also causes interference when a spectrum is recorded and increases the background in an uncontrolled manner (baseline noise).

The manufacturer's user manuals must be consulted for conditions under which the devices should be operated; e.g. it may be necessary to purge the measurement chambers with desiccated air or use desiccant cartridges to avoid haze in certain elements of the optical system.

Preliminary tests should be carried out to establish the optimal number of scans to be performed for analysis of a sample. Recommendations from the device manufacturer can be consulted for the selection of the apodisation or preliminary tests can lead to an optimal application of the method. A spectral resolution of 4 cm^{-1} is sufficient for the analyses performed according to this method (example of parameters for Bruker Vector 22: spectral resolution 4 cm^{-1} , range 4000 cm^{-1} to 350 cm^{-1} , apodisation: Blackman-Harris 3-term, zero filling factor 4, 120 scans, forward-backward operation, phase correction: Mertz method, phase resolution: 128 points).

4

Evaluation

For quantitative determination of the quartz mass the FTIR spectrum is evaluated in the range of the double bands at wavenumbers 798 cm^{-1} and 779 cm^{-1} , that cover the range from 850 to 720 cm^{-1} (see Figure 1). The cristobalite mass is determined using the band at wavenumber 621.5 cm^{-1} (see Figure 7).

Two crucial aspects should be considered during the evaluation.

- Interference due to concomitant substances in the dusts (the baseline shows troughs or humps, interference with bands of other components)
- Dependence of the integral intensity and absorbance from the particle size of the dust to be investigated

The following three methods are available for evaluation:

- Determination of the integral absorbance in the range of the analytical bands
- Subtraction of a reference spectrum
- Method that takes the influence of particle size into consideration

The evaluation must consist of at least a combined application of the evaluation methods based on the integral absorbance (Section 4.1) and subtraction of reference spectra (Section 4.2). The use of the method that takes the influence of the particle size into consideration (Section 4.3) is optional and is recommended, particularly when it is suspected that the utilised materials or the prevalent dusts show a particle size distribution that markedly deviates from that of the applied standard in the range of the respirable fraction (e.g. ore mining, coal mining, use of ultra-fine powders with a median particle diameter of 1 μm). The particle size distribution is not recognisable in the FTIR spectrum, therefore information should be taken over from e.g. safety data sheets or technical information.

The three methods are described in detail below, outlining their advantages and limitations as well as the error that can be expected due to their use.

To facilitate better estimation of the three evaluation methods and their errors it is recommended to prepare sample mixtures that contain different proportions of interference components (e.g. TiO_2 , CaCO_3 , corundum, feldspars, sillimanite) in addition to the standard quartz/cristobalite. The sample mixtures are suitable for practice purposes to ensure lessons are learned in how to deal with interfering influences during quantification. Furthermore, expected interference in the case of known dust composition can be recognised more readily and the evaluation strategy can therefore be optimised accordingly. A calibration series in the lower application range is suitable for optimising the evaluation of the samples with only low proportions of quartz or cristobalite (see Section 3.1).

The selection of a suitable standard for calibration can be problematic. On principle, the standard used must show a particle size distribution equivalent to the respirable dust fraction described in DIN EN 481 [1] due to the strong influence of particle size. This does not mean that the standard should consist of an ideal quartz in the sense of a ground single crystal. Samples from cultured, crystallographic, nearly interference-free single crystals are known to show higher integral absorbance in FTIR analyses than quartz found at workplaces. The use of such ideal quartz would result in the quartz concentrations at workplaces being underestimated. Therefore it is advisable to select quartz dusts for calibration standards that are also used in industry. Examples of these are Sikron SF600 from Quarzwerke, Frechen, Germany or Minusil 5 from U.S. Silica, USA. In any case a microscopic or laser granulometry check of the particle size distribution should be carried out. Possible proportions of coarser particles must be removed by sifting or sedimentation. Detailed information on the selection and preparation of quartz and cristobalite samples for use as standards can be found in Section 4.3.

4.1

Evaluation by means of determining the integral absorbance

Determination of the quartz or cristobalite mass in a dust sample by integral absorbance in the range of the double band or band to be evaluated is the simplest evaluation method. Figure 1 shows examples for quartz (absorption spectrum of pure quartz, not impaired by other dust components). However, this method also shows the largest errors in the case of interference from other concomitant substances in the dust to be analysed. The basic problems when determining the integral absorbance are interferences in the flanks by absorption bands of other phases and a baseline that is not level in the area of integration due to trough- or hump-shaped interferences. Interference in the flanks means that integration limits cannot be conclusively set, and the areas to be integrated cannot be systematically identified as false positive or false negative findings due to overlaps. Equally problematic is the determination of the integral absorbance with hump-shaped (false positive finding) or trough-shaped interference on the baseline (false negative finding; see Figure 2). The influence of the baseline profile is particularly marked in the case of low quartz or cristobalite concentrations (see Figures 3a and 3b). In quartz masses of less than approx. 100 µg relative errors of more than 50% can be expected.

An evaluation based solely on the determination of the integral absorbance should not be carried out. It is advisable to apply this method only in combination with the methods listed in Section 4.2 and/or Section 4.3 in order to be able to identify possible interferences. Spectra subtraction as described in Section 4.2 can give an indication of the actual baseline profile.

Generally it can be concluded that in the determination of the quartz or cristobalite mass using integral absorbance the influence of the particle size (see Section 4.3) is not taken into consideration. In extreme cases (dust fractions with median diameter of < 0.8 µm or > 4 µm) this can lead to relative errors of up to ± 20%. Errors of up to ± 10% can be anticipated in dusts containing quartz or cristobalite with particle size distributions that commonly occur at workplaces.

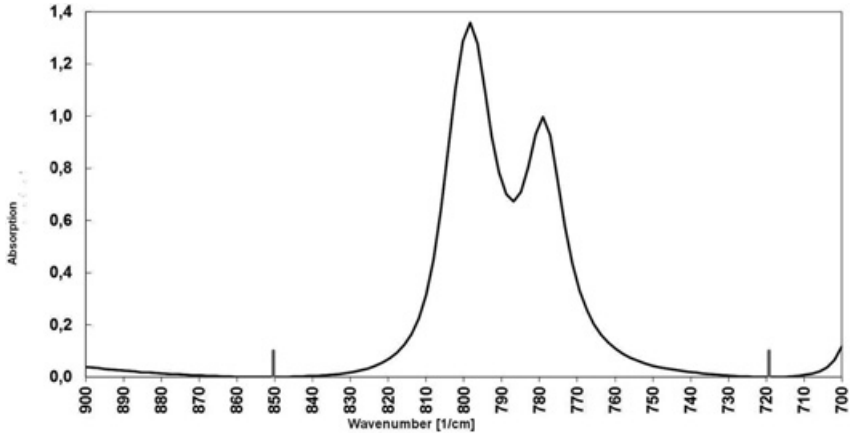


Fig. 1 Absorption spectrum of quartz in the area of the double band at wavenumbers 798 cm^{-1} and 779 cm^{-1} . The markers at wavenumbers 850 cm^{-1} and 720 cm^{-1} show the integration limits.

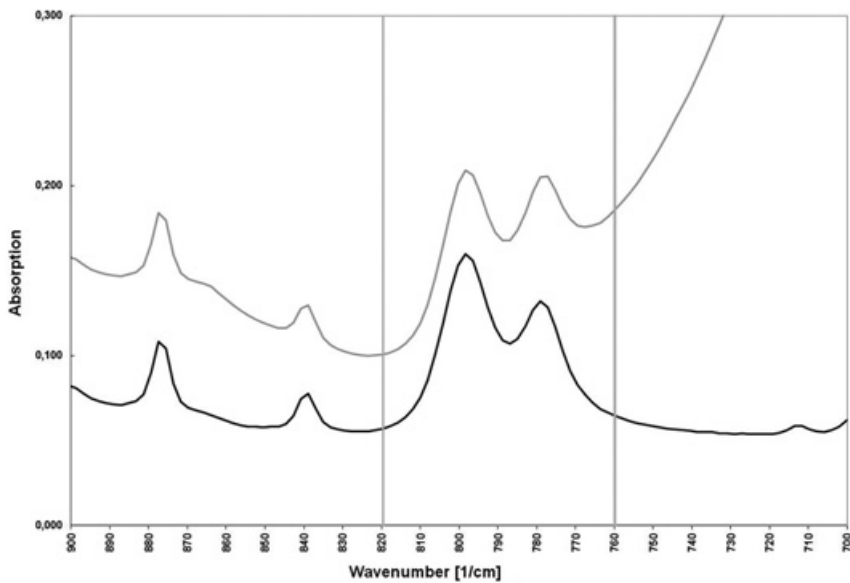


Fig. 2 Absorption spectrum of quartz ($80\text{ }\mu\text{g}$) in the area of the double band with a level baseline (black) and trough-shaped baseline (grey). The limit on the right of the area of the double band to be integrated is apparently shifted from 720 cm^{-1} to approx. 765 cm^{-1} at the location of the trough.

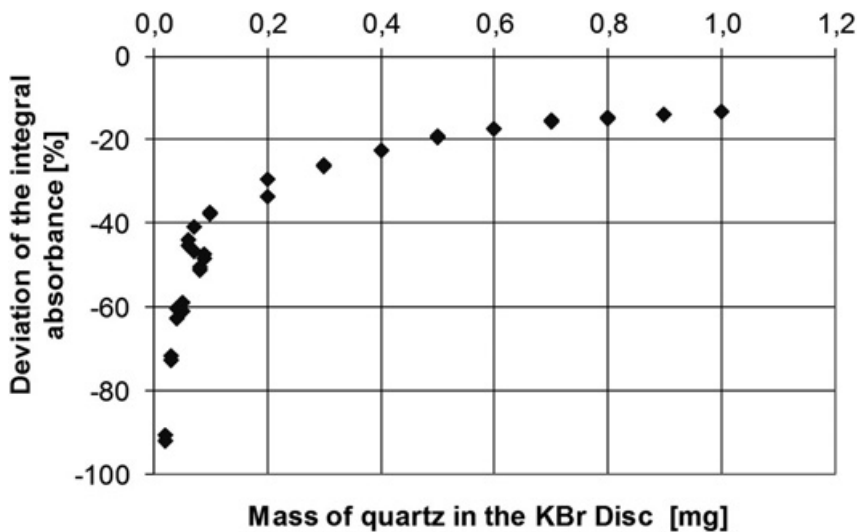


Fig. 3a Relative error when determining the quartz mass by means of determination of the integral absorbance when hump-shaped interferences are present on the baseline.

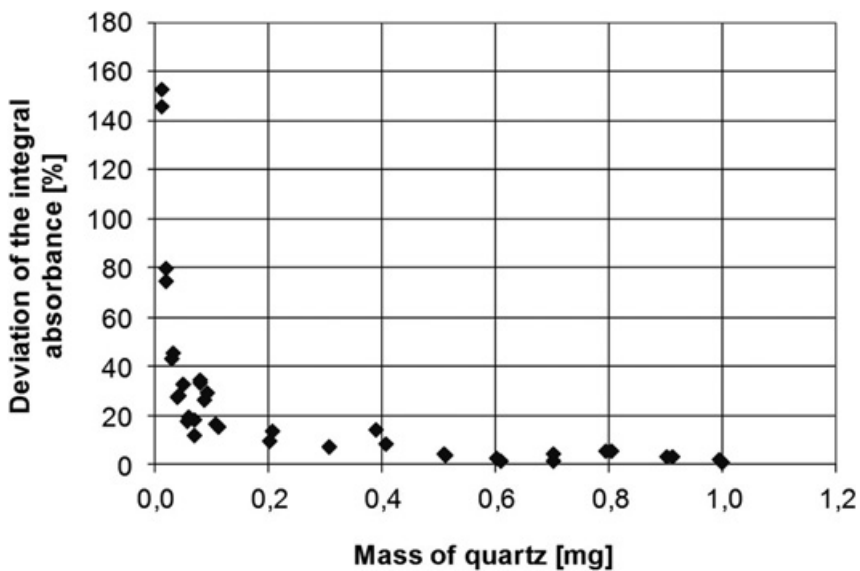


Fig. 3b Relative error when determining the quartz mass by means of determination of the integral absorbance when trough-shaped interferences are present on the baseline.

4.2

Evaluation by means of subtraction of a reference spectrum

Determination of the quartz or cristobalite mass can be carried out by subtracting the spectrum of a pure standard with a defined weight from the absorption spectrum of the sample to be analysed. The subtraction is carried out for the evaluation range of the double band or band that is also used for the determination of the integral intensity (see Section 4.1). The subtraction factor is selected so that the subsequent subtraction result leads to the most plausible baseline profile. In this case it is advisable to vary the subtraction factor around the chosen factor so that it is possible to recognise when the subtraction is not yet sufficient or is already too large. As different types of quartz or cristobalite do not always exhibit a completely identical morphology of the absorption bands, standard spectra of different available quartz or cristobalite respirable dusts with known purity should be recorded if possible and used for spectral subtraction. An example of the result of a spectral substitution for a sample containing quartz is shown in Figure 4. The resulting baseline (excessive in Figure 4) becomes a doubly curved wave as the position of both of the absorption maxima of the double band of the sample and the standard do not exactly coincide. In this case a different quartz standard should be used in order to be able to determine the subtraction factor optimally.

The advantage of applying this evaluation method compared with determination of the integral absorbance according to Section 4.1 is that even with baselines sub-

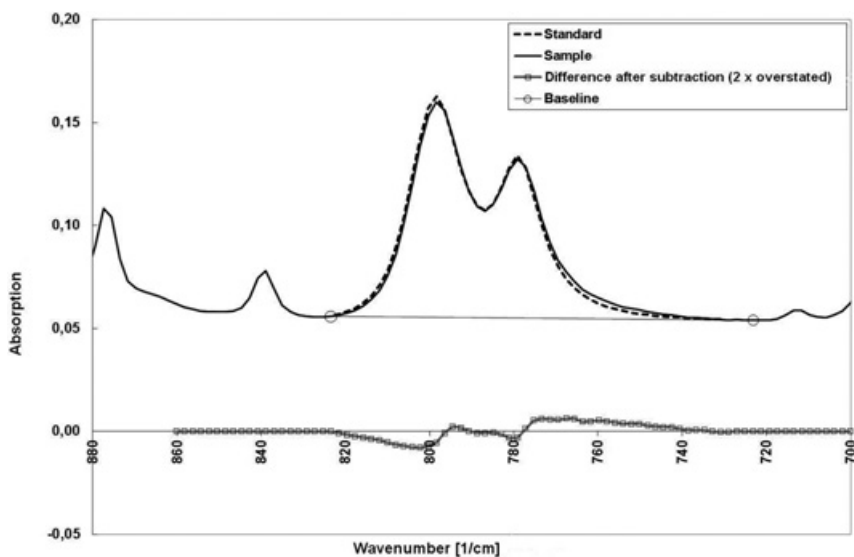


Fig. 4 Determination of the quartz mass of a dust sample by subtraction of the spectrum of a quartz standard from the absorption spectrum of the sample in the range of the double band (for detailed information see the text of Section 4.2).

ject to strong interference, including hump and trough-shaped baselines and flank positions of the absorption bands, satisfactory quantifications can usually be carried out. If the application of this method does not lead to satisfactory (plausible) baseline profiles for the subtraction result, then the X-ray diffractometric analytical method should be resorted to. In that case a reliable quantification of the quartz or cristobalite mass is not possible by means of infrared spectroscopy.

As in the method described in Section 4.1 the influence of the particle size of the samples to be analysed is also not taken into account in this case.

4.3

Evaluation taking the influence of particle size into consideration

Quartz

The analytical absorption bands at 798 and 779 cm^{-1} are subject to interfering influences from many minerals, when for the quantitative determination of the peak area (F) the baseline between 850 and 720 cm^{-1} is used, which extends over a wide range and possibly extends into the slope areas of other mineral bands (see Section 4.1). Therefore in the case of the evaluation method described below narrower baseline ranges are utilised and the double band with baselines between 814 and 784 cm^{-1} and between 788 and 764 cm^{-1} are used, as shown in Figure 5 [2, 3].

The investigations included industrially manufactured quartz powder made of sands and ground rock crystals derived from different origins.

The quartz bands are also very dependent on the particle size in terms of the particle size range of respirable dust; therefore the deviation of absorption that de-

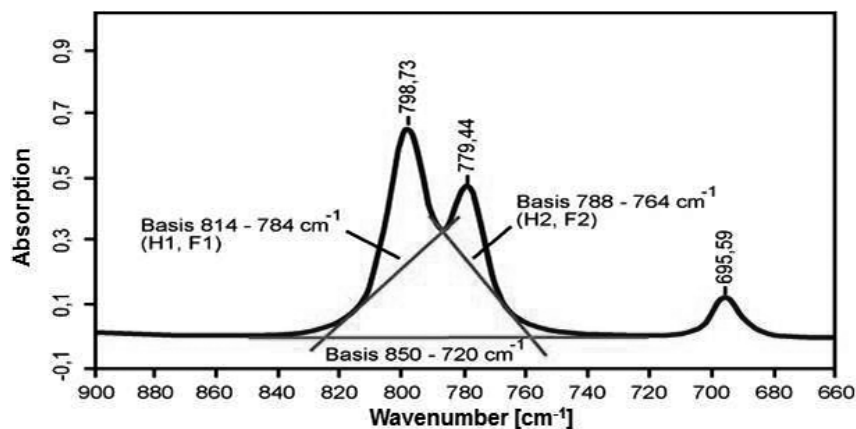


Fig. 5 IR spectrum of quartz showing the baselines for integration of the quartz double band; H : Perpendicular peak maximum to baseline, F : integral absorbance over baseline (absorption).

depends on the particle size can lead to relative errors of up to $\pm 20\%$ in the quartz determination (with respect to the determination of the integral absorbance) in extreme cases when the quartz standard is not selected to reflect the particle size in the sample. For this reason a function was derived that shows a linear relationship by plotting the absorption H (peak height above the baseline) that are standardised to the quartz mass $m = 1$ mg and F (peak area) with $(H_1 \cdot H_2)^{1/2}/m_{real}$ versus $((H_1 \cdot H_2)/(F_1 \cdot F_2))^{1/2}$ of quartzes derived from different origins and particle size distributions (within the respirable dust fraction) (see equation (1)). Thus the quartz masses m can be determined regardless of particle size (see Figure 6).

$$m_{real} = \sqrt{H_1 \cdot H_2} / (A \cdot \sqrt{H_1 \cdot H_2 / F_1 \cdot F_2} - B) \quad (1)$$

where:

m_{real} is the analysed mass of quartz in the sample [mg]

H_1, H_2 is the band height of peak 1 and 2 [absorption of the peak maximum]

F_1, F_2 is the area of peak 1 and 2 [integral absorbance of the peak area]

A is the slope of the regression line (see Figure 6)

B is the intercept of the regression line (see Figure 6)

The quartz mass m should not exceed 1 mg.

The coefficients A (24.218) and B (1.585) are calculated from the regression line of the calibration (Figure 6). They are device- and software-specific (integration

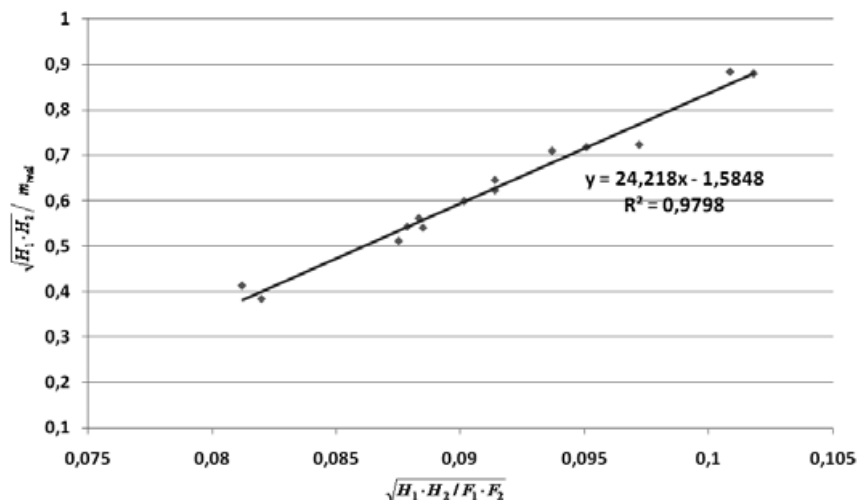


Fig. 6 Relationship between height (H) and area (F) of different quartzes of differing particle size distribution.

parameters) and are not transferable to other IR devices; in this case the Bruker Vector 22 device was used with the OPUS 6 software.

The analysis of various quartz fractions with different medians in the particle size distribution between approx. 1.5 and 4 μm is the prerequisite for determining the necessary parameters for the application of this evaluation method. Different particle fractions of a material can be separated using e.g. a cascade impactor or sedimentation processes to achieve the most narrow particle size distribution possible.

Quartz derived from different origins e.g. ground rock crystals can also be used in addition to quartz dust fractions prepared from quartz used in industry.

The production of a standard of respirable quartz dust from quartz powder e.g. Dörentruper quartz No. 12 (DQ12) or Sikron SF600 from Quarzwerke, Frechen, Germany can be prepared by creating a vortex of quartz powder using a light stream of air in a vessel connected to a fine dust sampling device MPG II (see e.g. [9]).

In particle size fractions of less than approx. 1.5 μm the quartz contains significant amounts of amorphous SiO_2 due to the milling process. Therefore, for the purpose of calibration, they must be purified by treatment with sodium hydroxide solution according to Baumann [4, 5] (dissolution of the amorphous SiO_2). However, a quartz dust fraction with a mean particle size of less than 1.5 μm is not absolutely necessary for the derivation of coefficients A and B .

A calibration function without correction for the influence of the particle size is derived by plotting various masses of a standard of defined particle size distribution versus the absorption, e.g. versus the geometric mean value of H_1 and H_2 (equation (2))

$$\sqrt{H_1 \cdot H_2} = b \cdot m_{\text{uncorr}} \quad (2)$$

where:

b is the gradient of the calibration function

In this case a standard of respirable quartz dust (e.g. DQ12 respirable dust) with a median diameter of approx. 2.2 μm is used, which is found in the middle range of the function in Figure 6. The factor F is defined as $m_{\text{uncorr}}/m_{\text{real}}$. It expresses the deviation of the mass of a sample when evaluating using a calibration without taking particle size correction into consideration. The factor F is calculated according to equation ((3)).

$$F = \left(A \cdot \sqrt{\frac{H_1 \cdot H_2}{F_1 \cdot F_2}} - B \right) / b \quad (3)$$

The factor F is 1, when the absorptions of the used standard of respirable quartz dust are applied. The F factors are calculated for the endpoints of the function in Figure 6 (coarsest and finest particle fraction); thus values of between $F = 0.6$ for the coarsest particles (median of the particle size distribution is 4 μm) and $F = 1.4$

for the finest particles (median of the particle size distribution is 0.8 μm) result for the range of the equation. Outside these limits this evaluation is not applicable. The factor F must therefore also be determined for each analysis.

It is necessary to individually calculate the equation for each FTIR device using quartz dust fractions classified by particle size.

Note:

Storage of these KBr disks can lead to opacity in the KBr disks, which results in measurement result deviations. In this case the KBr disks must be ground and re-pressed to disks prior to measurement.

When analysing quartz each sample spectrum must be checked to see whether the baseline shows intersections from above or below in the flanks of the bands. Figure 5 and the text below provide guidance on determining the baseline points. If this is the case, then a baseline correction using the entire spectrum with as many reference points as possible should be attempted. Generally, the evaluation software provided with the FTIR devices offers suitable possibilities to achieve this. Experience is necessary in order to be able to carry out a baseline correction. It must be gained in advance using example spectra with known interference components.

Cristobalite

Errors of up to $\pm 15\%$ (integral absorbance F) in the determinations of the cristobalite mass based on the band at 621.5 cm^{-1} are possible without correction of the particle size effect. As in the case of quartz an equation for the determination of the cristobalite concentration in respirable dusts was derived, which includes the correction for the Christiansen effect [6]. It represents the dependence of the absorption (height and area values) of different cristobalite samples on their mean particle sizes and at the same time on the concentration. Equation ((1)) is simplified for cristobalite to the following equation ((4)), as only one absorption band each is evaluated:

$$m_{\text{real}} = \frac{H}{A \cdot (H/F) - B} \quad (4)$$

where:

- m_{real} is the analysed mass of cristobalite in the sample [mg]
- H is the band height [absorption of the peak maximum]
- F is the area [integral absorbance of the peak area]
- A is the gradient of the regression line
- B is the intercept of the regression line

Investigations into fractionated cristobalite SF 6000, SF 3000 or Sepasil (from Quarzwerke, Frechen) have shown that this equation is applicable to the mean particle diameter range from 1 to 8 μm and to a mass of up to 1.0 mg of cristobalite to approx. 400 mg of KBr, regardless of which of the absorption bands is used

(621.5 cm^{-1} or, in the absence of quartz, 794.6 cm^{-1}) for the quantitative evaluation. Greater contamination by amorphous SiO_2 can be expected when using these very finely ground cristobalites to obtain finer fractions in comparison to quartz. Hence, all fine cristobalite dust samples (obtained by e.g. sedimentation or collection of fine dust with the MPG II) are subjected to the following multi-step purification:

- Suspension of the cristobalite in sodium hydroxide (2 N) in a glass beaker (a suspension of low viscosity, e.g. 20 mg cristobalite in 2 to 5 mL). Leave to stand for 15 – 20 minutes at 100 °C
- After cooling, filtration through a nitrocellulose filter (membrane filter) with 0.45 μm pore size and rinsing with water
- Neutralisation of the sodium hydroxide adhering to the cristobalite by rinsing the loaded filter with dilute hydrochloric acid (approx. 0.01 N)
- Repeated rinsing of the cristobalite fraction with water
- Drying in a drying cabinet at approx. 105 °C

The treatment with sodium hydroxide results in slight shifts in the medians of the particle size distribution in the particle size fractions, which are considered negligible in this case.

Target factors f (equivalent to F in quartz) were calculated to describe the range of real samples. The target factor indicates whether the mean particle diameter of a real sample lies within the range of the equation for the particle size-corrected determination of the mass m_{real} of cristobalite. Table 1 summarises the values of the axial intercept B and the slope A , the equations for calculating the target factor as well as the respective intervals for the three evaluation models that have been developed.

For the purpose of evaluation the band not subject to interferences from quartz, tridymite and amorphous SiO_2 (621.5 cm^{-1}) is usually selected.

An alternative evaluation can be carried out in the evaluation range between 630 and 610 cm^{-1} should interferences occur in the flank areas of this band, determination of the height and area is carried out after baseline correction (see Figure 7). Generally, this is facilitated by modules of the evaluation software, which are supplied with commonly used FTIR devices. Experience is necessary in order to be able

Table 1 Data for calculation of the cristobalite content and target factor f (example for the FTIR Bruker Vector 22)

Evaluation model	Determination of the mass	Equation for the target factor	Interval for the target factor
680 – 585 cm^{-1}	$A = 20.304$ $B = 0.686$	$f = (45.31 \cdot H/F) - 1.53$	0.77 – 1.21
630 – 610 cm^{-1}	$A = 23.964$ $B = 1.320$	$f = (53.48 \cdot H/F) - 2.95$	0.78 – 1.22
900 – 707 cm^{-1}	$A = 30.817$ $B = 0.271$	$f = (43.9 \cdot H/F) - 0.386$	0.65 – 1.41

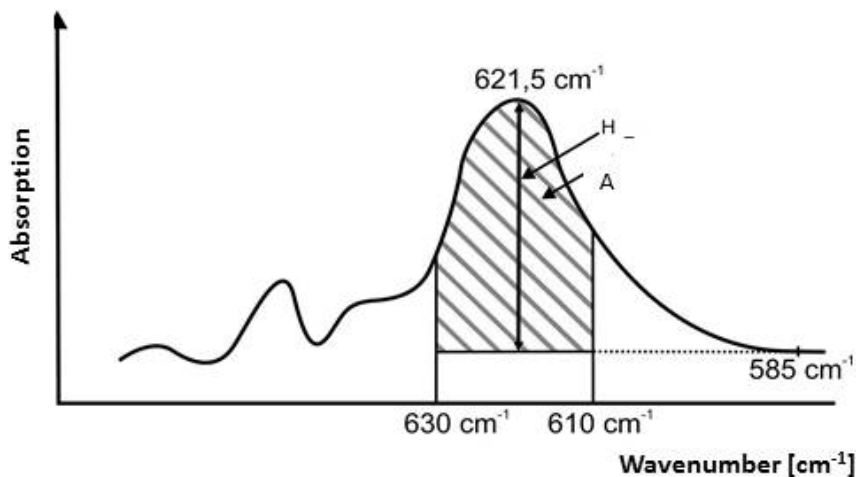


Fig. 7 Illustration of the integration of the baseline-corrected band at 621.5 cm^{-1} in the case of flank interferences.

to carry out a baseline correction. It must be gained in advance based on example spectra with known interference components.

The baseline runs horizontal to the wavenumber axis and is positioned using the available baseline point on the left or right flank of absorption band at 621.5 cm^{-1} according to empirical experience (Note: In Figure 7 the right flank is the absorption minimum with the fixed baseline point at 585 cm^{-1}). The integration limits are set to 630 and 610 cm^{-1} , which is approximately equivalent to the flank points of the half-value width of the absorption band of cristobalite. The application of this evaluation model is only possible provided one of the flanks of the absorption band of cristobalite or one of the set baseline reference points at 680 cm^{-1} or 585 cm^{-1} is free from interference.

When analysing cristobalite each sample spectrum must be checked for overlaps with bands of other phases in the baselines at the flanks of the band of the cristobalite. If this is the case, then a baseline correction using the entire spectrum with as many reference points as possible should be attempted. Should this prove unsuccessful, evaluation is not possible. In this case X-ray diffractometric analysis should be performed.

5 Reliability of the method

5.1

Precision and recovery

Recovery: The recovery for quartz and cristobalite (band at 621.5 cm^{-1}) was calculated separately for the various evaluations.

- The recovery was carried out for three concentrations six determinations each according to Sections 4.1 and 4.2. The recovery for 0.01 mg of quartz is 104.7% where $s = 2.3\%$, for 0.1 mg of quartz at 103.5% where $s = 1.9\%$ and for 1.0 mg of quartz at 101.3% where $s = 3.0\%$.
- If the evaluation is carried out according to Section 4.3, then quartz or cristobalite masses of between 0.4 and 0.7 mg result in recoveries between 95 and 104% or 97 and 103% for three determinations each of 14 standards of known particle size distribution.

5.2

Limit of quantification

The limit of quantification was determined on the basis of DIN 32645 [7] for quartz and cristobalite using the calibration function in the lower measurement range (see Section 3.1) and the blank value method. Both methods yield comparable results.

The analysis of pure quartz or cristobalite dusts leads to absolute limits of quantification of 0.01 mg for quartz and cristobalite (statistical certainty of 95%; $k = 3$). These favourable values are, however, not always achieved under real conditions when analysing dust-loaded filters. Experience has shown that the absolute limit of quantification in that case is approx. 0.03 mg. The relative limit of quantification values listed in Table 2 for quartz and cristobalite (band at 621.5 cm^{-1}) are obtained with the various sampling systems.

Table 2 Relative limits of quantification for quartz and cristobalite

Sampling system	Filter diameter [mm]	Air flow rate [m ³ /h]	Sampling time [h]	Air sample volume [m ³]	Relative limit of quantification	
					Ideal [mg/m ³]	real ^{*)} [mg/m ³]
VC 25F	150	22.5	2	45	0.0004	0.0013
			8	180	0.0001	0.0003
PM 4F	70	4.0	2	8	0.001	0.004
			8	32	0.0003	0.001
FSP-10	37	0.6	2	1.2	0.008	0.025
			8	4.8	0.002	0.006
FSP-BIA	37	0.12	2	0.24	0.042	0.13
			8	0.96	0.010	0.031
MPG II	47	2.8	2	5.6	0.0018	0.0054
			8	22.4	0.0004	0.0013

^{*)} Limit of quantification in the case of an unfavourable sample matrix or interferences in the range of the relevant absorption bands

5.3

Expanded uncertainty

The expanded uncertainty *U* according to DIN EN 482 [10] was estimated for quartz and cristobalite using the sampling systems FSP-10 (10 L/min) and PM 4F (4 m³/h) on the basis of the analytical precision (method as described in Section 4.3) of 2.0% for 0.5 mg of quartz or 1.9% for 0.43 mg of cristobalite for the ideal and real absolute limit of quantification (0.01 or 0.03 mg) [3, 6].

The expanded uncertainty for quartz or cristobalite is approximately 24% at concentrations of 0.01, 0.05, 0.10 and 0.15 mg/m³ at a sampling time of between 2 and 8 hours when the PM 4 sampling system is used.

The FSP-10 sampling system has an expanded uncertainty of 24 to 26%, with the exception of the 2-hour sampling at a concentration of 0.01 mg/m³. In this case an expanded uncertainty of 30 or 56% is calculated (based on the ideal or real limit of quantification).

An example of a detailed calculation of the expanded uncertainty according to DIN EN 482 [10] can be found in [6] and [11].

In individual cases the influence of the ubiquitous exposure should be taken into consideration, when estimating the expanded uncertainty in very low concentrations in the range of 0.01 mg/m³. It should be noted that the ubiquitous exposure to respirable quartz dust in the air lies in the magnitude of 0.001 mg/m³, however, values of up to approx. 0.01 mg/m³ can also be reached.

5.4

Cross-sensitivities

It is advisable to carry out a preliminary qualitative interpretation, before the identification of cross-sensitivities due to other minerals in the quantitative evaluation of an IR spectrum. Evidence of the existence of other components apart from quartz or cristobalite is almost always found in the range of the wavenumbers from 4000 cm^{-1} to 350 cm^{-1} when the entire IR spectrum is recorded. Spectra of some potentially interfering phases are shown in the appendix. Furthermore, additional information such as data on the origin of the sample (workplace), greatly simplifies targeted testing for components contained in the sample. On the whole the qualitative interpretation offers information on how possible cross-sensitivities can be eliminated or be taken into consideration.

Should cross-sensitivities exist from carbonates, certain oxides and other compounds that are soluble in hydrochloric acid then they can be eliminated as follows:

- Dissolution of the KBr disks in 40 mL of concentrated hydrochloric acid at boiling point over 30 minutes
- Addition of 50 mL of water and subsequent treatment in an ultrasonic bath for 10 minutes
- Filtration through a $0.45\text{ }\mu\text{m}$ nitrocellulose membrane filter
- Incineration of the membrane filter
- Preparation of a new KBr disk
- Renewed measurement

Interferences in the evaluation band of quartz

Cross-sensitivities were discovered in the mixtures shown in Table 3 consisting of synthetic sample mixtures of respirable quartz dust and other minerals in the quartz analysis with particle size correction as described in Section 4.3, which showed a deviation in the recovery of more than $\pm 10\%$ for quartz.

The greatest interferences arise from albite, orthoclase, microcline and sillimanite. Cristobalite shows a strong cross-sensitivity when its proportion in a mixture with quartz is greater than approx. 50%. The above-mentioned interferences cannot be satisfactorily eliminated by a targeted sample pre-treatment. The integration of the quartz band at 695 cm^{-1} (reduced influence of particle size) or the spectral subtraction as described in Section 4.2 can offer an alternative quantification of the quartz content in individual cases; as a rule X-ray diffractometric analysis should also be carried out.

The influence on the recovery remained less than $\pm 10\%$ for the following mixtures of quartz and other minerals e.g. oligoclase, bytownite, kaolinite, Portland cement, montmorillonite, labradorite, talc, chamotte, amorphous silica, sodium bentonite.

Table 3 Relevant cross-sensitivities due to other mineral phases in the determination of quartz in the range of the double band at 798 and 779 cm^{-1} based on the evaluation method described in Section 4.3

Mineral	Mineral proportion in the mixture [%]	Recovery of quartz [%]
Orthoclase	17	110
	38	137
	50	150
Microcline	19	106
	37	117
	53	137
Albite	17	85
	37	75
	52	59
Sillimanite	21	80
	38	59
	49	44
Cristobalite	49	90
	66	39

Interferences in the evaluation band of cristobalite

Due to the many cross-sensitivities the infrared spectrometric method for the determination of cristobalite is more suitable for workplaces where substances that interfere with the cristobalite IR analysis do not occur. In case of any doubt an additional X-ray diffractometric analysis should be carried out, if necessary after recovery of the dust through dissolution of the KBr disks.

Cross-sensitivities of the cristobalite analysis with particle size correction according to Section 4.3

An additional sample treatment using hydrochloric acid can eliminate interferences from certain minerals almost entirely or entirely (for procedure see Section 5.4). This applies to e.g. carbonates (calcite, dolomite, magnesite), oxides (haematite), silicates (wollastonite, nepheline) and sulphates (anhydrite, baryte).

A list of potentially interfering minerals is provided in Table 4.

Table 4 Minerals occurring in dusts that can lead to cross-sensitivities in the cristobalite determination

Designation	Interferences [cm^{-1}] of the cristobalite band at	
	621 cm^{-1}	794.6 cm^{-1}
Quartz	–	798; 779
Amorphous silica	–	approx. 820 to 720
Haematite	552; 596	–
Corundum	607; 642	797
Albite	646; 587; 534	787; 761; 744; 724
Orthoclase	583; 605; 649	772; 729
Microcline	585; 646	772; 729
Sanidine	545; 586; 638	780; 725
Wollastonite	681; 645; 567	965; 930; 903
Sillimanite	573; 635; 690	889; 818; 750
Talc	535; 670; 691	–
Kaolin (annealed at 550 °C)	–	wide band 950 to 700
Biotite	680	730
Phlogopite	692	816; 732
Anhydrite	595; 613; 677	–
Baryte	610; 639	–
Calcite	–	876; 712

Procedure for the evaluation of the band at 621.5 cm^{-1}

Corundum, orthoclase, microcline, sanidine and sillimanite interfere even in small amounts; as a rule such samples must be analysed using X-ray diffraction.

Amorphous silica and annealed kaolin (metakaolinite) do not interfere in the analysis. Quartz only interferes when a high quartz concentration is associated with a low cristobalite concentration. Interferences from talc, biotite and phlogopite can be minimised by application of the evaluation model between 630 and 610 cm^{-1} (see Section 4.3 for cristobalite). Anhydrite, calcite and baryte do not interfere if the hydrochloric acid treatment is applied as described in Section 5.4. When greater proportions of baryte are present, however, a larger amount of hydrochloric acid and a longer treatment duration are required for its removal.

Interferences due to wollastonite can be avoided by hydrochloric acid pre-treatment (disadvantage: possible formation of amorphous silica).

Further information for minimizing interferences in the flank areas of the evaluation bands can be found in [6].

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Appendix

Method for the determination of quartz and cristobalite- Spectra of quartz, cristobalite and typical interfering substances

The entire IR spectrum is shown for each substance. However, in the case of the relevant wavenumber range between 550 and 950 cm^{-1} the evaluation of quartz and cristobalite is additionally shown in an enlarged illustration (Figure A1 to A17), in order to have a better overview for recognizing the kind of the cross-sensitivities in the quartz or cristobalite determination.

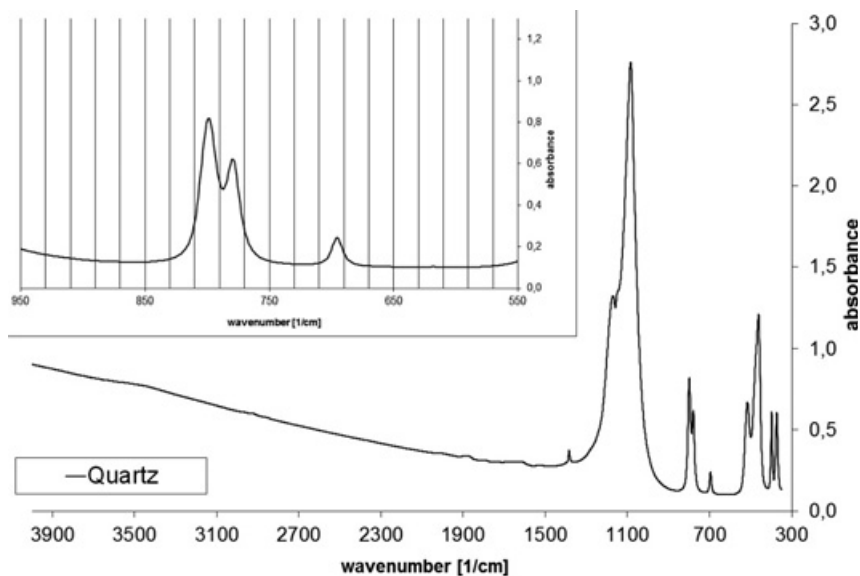


Fig. A1 FTIR spectrum of quartz.

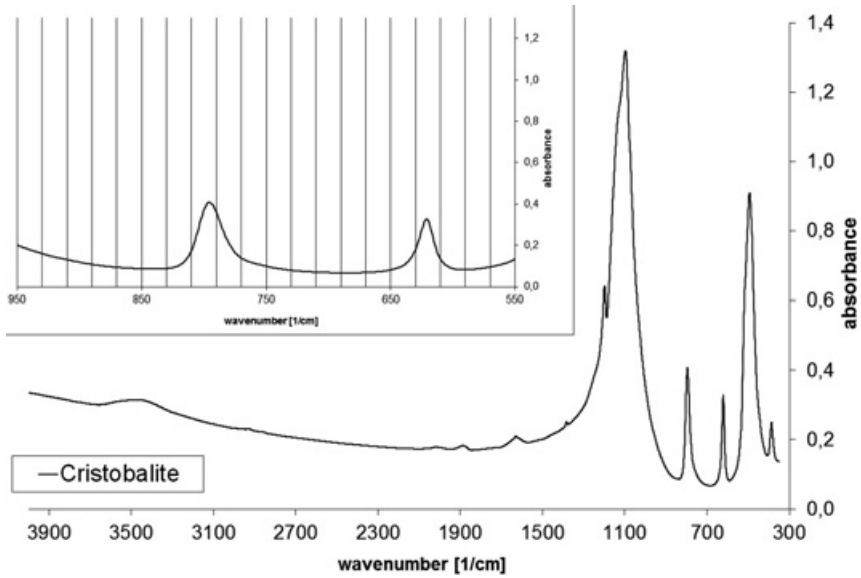


Fig. A2 FTIR spectrum of cristobalite.

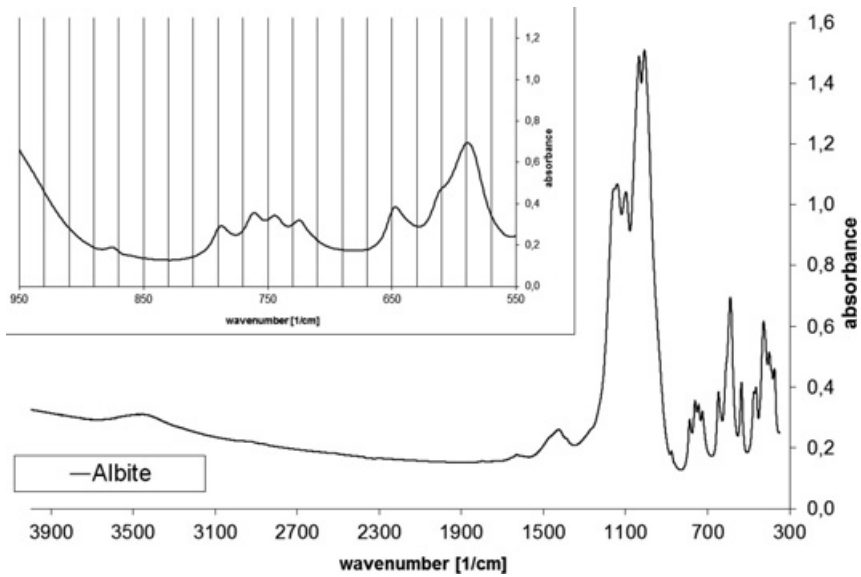


Fig. A3 FTIR spectrum of albite.

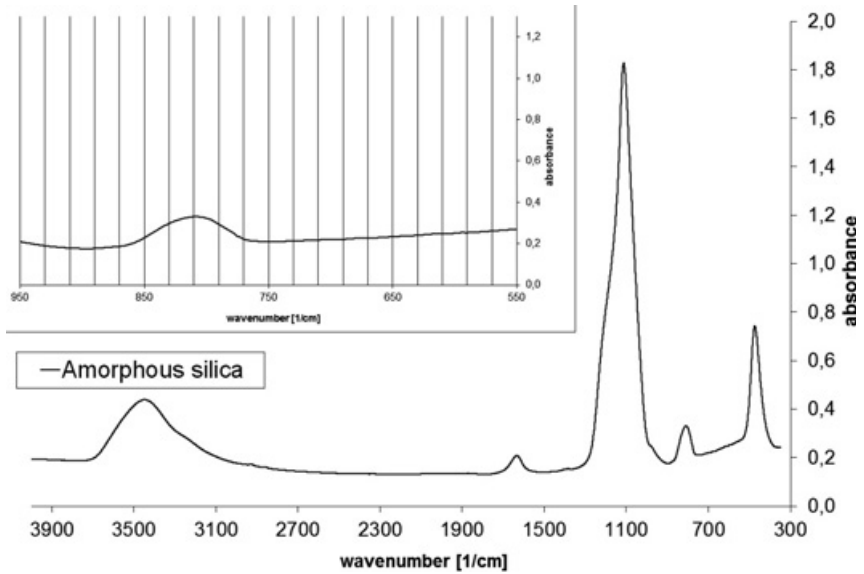


Fig. A4 FTIR spectrum of amorphous silica.

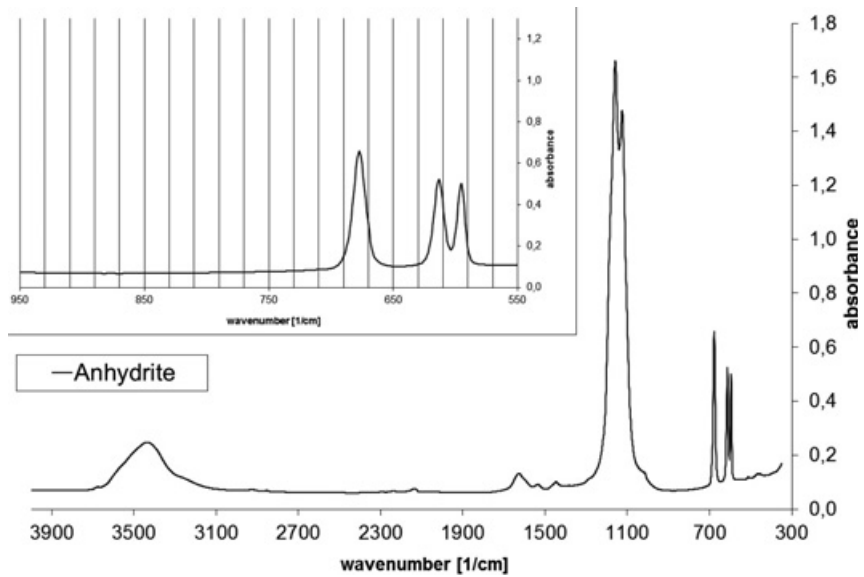


Fig. A5 FTIR spectrum of anhydrite.

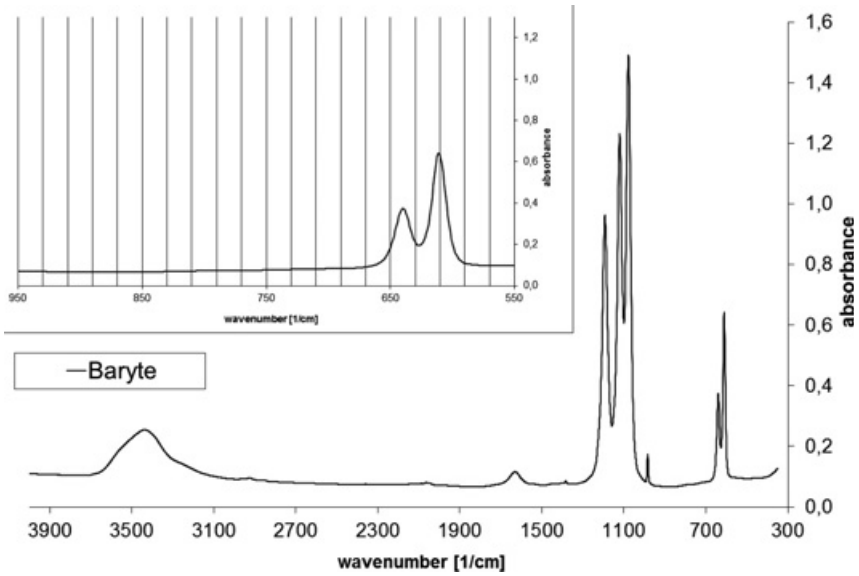


Fig. A6 FTIR spectrum of baryte.

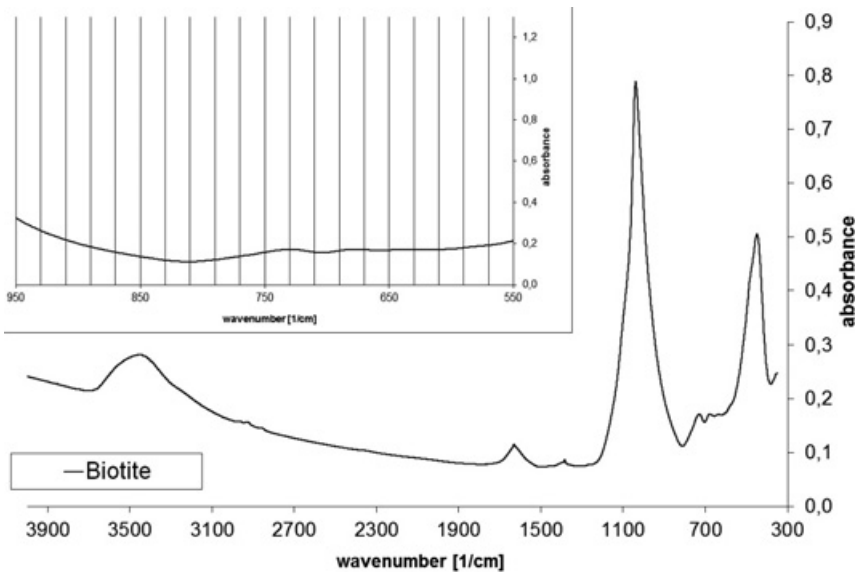


Fig. A7 FTIR spectrum of biotite.

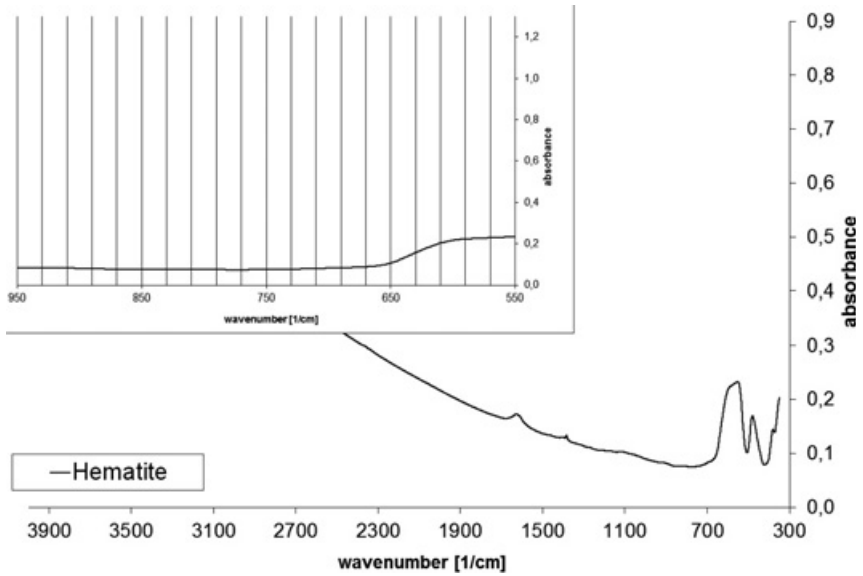


Fig. A8 FTIR spectrum of haematite.

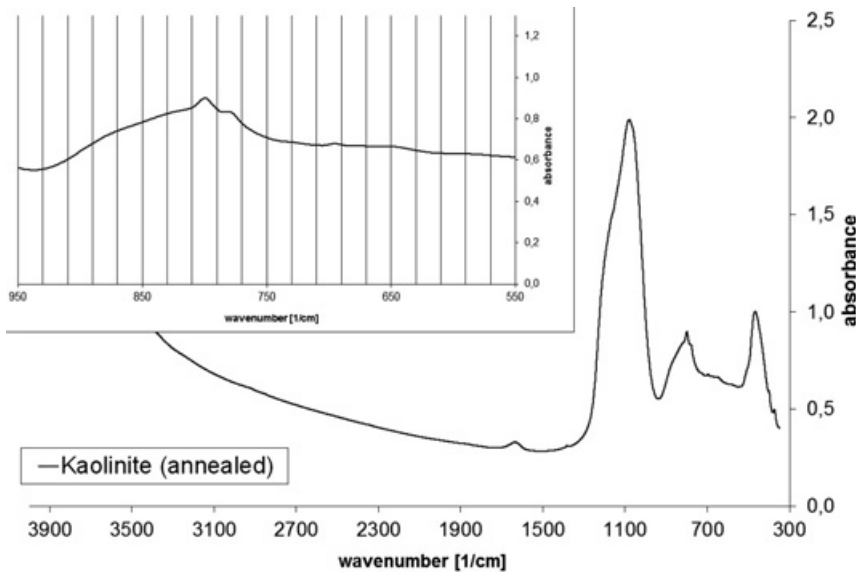


Fig. A9 FTIR spectrum of annealed kaolin.

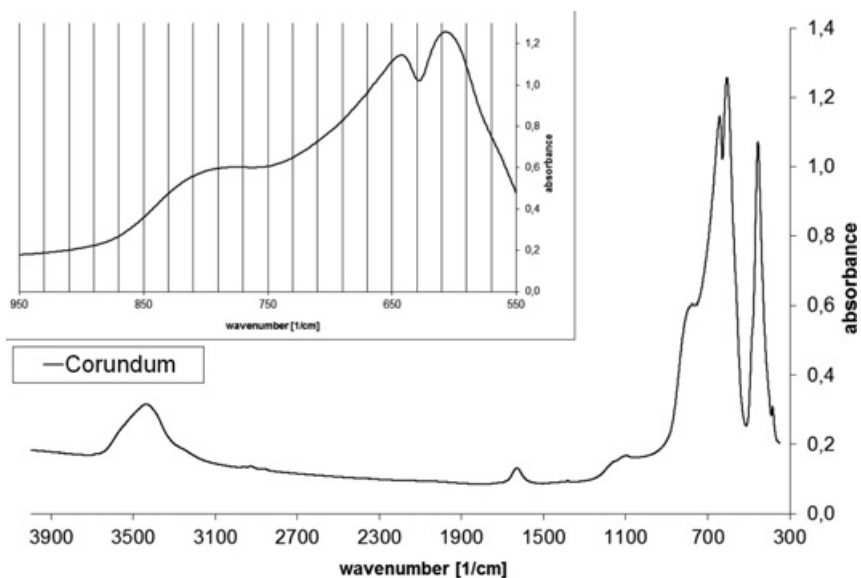


Fig. A10 FTIR spectrum of corundum.

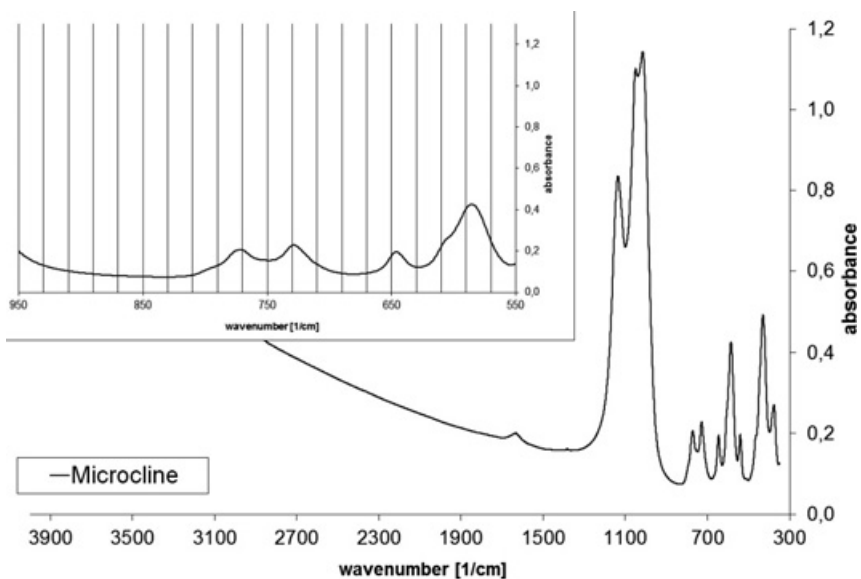


Fig. A11 FTIR spectrum of microcline.

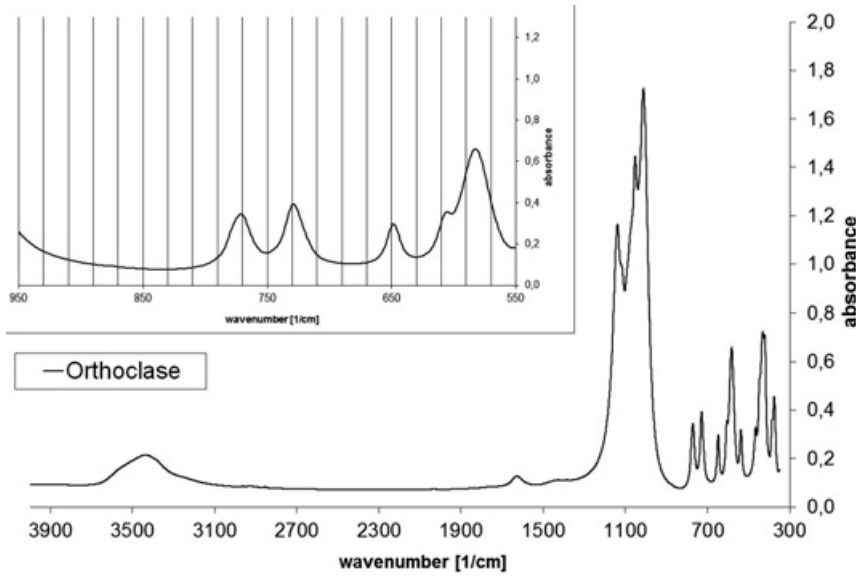


Fig. A12 FTIR spectrum of orthoclase.

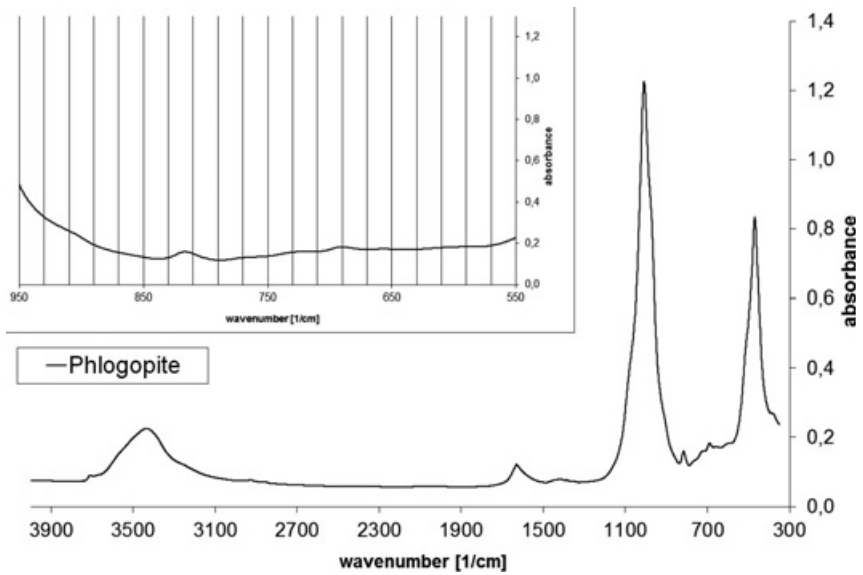


Fig. A13 FTIR spectrum of phlogopite.

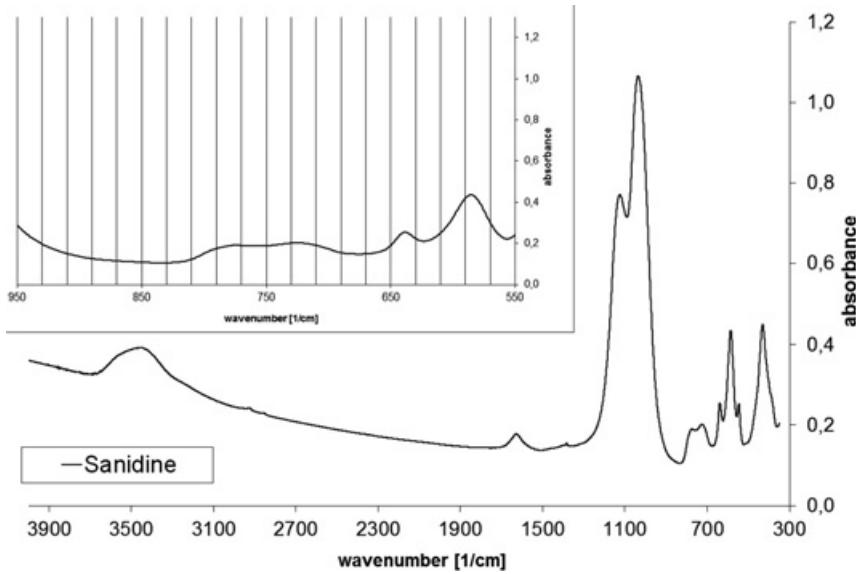


Fig. A14 FTIR spectrum of sanidine.

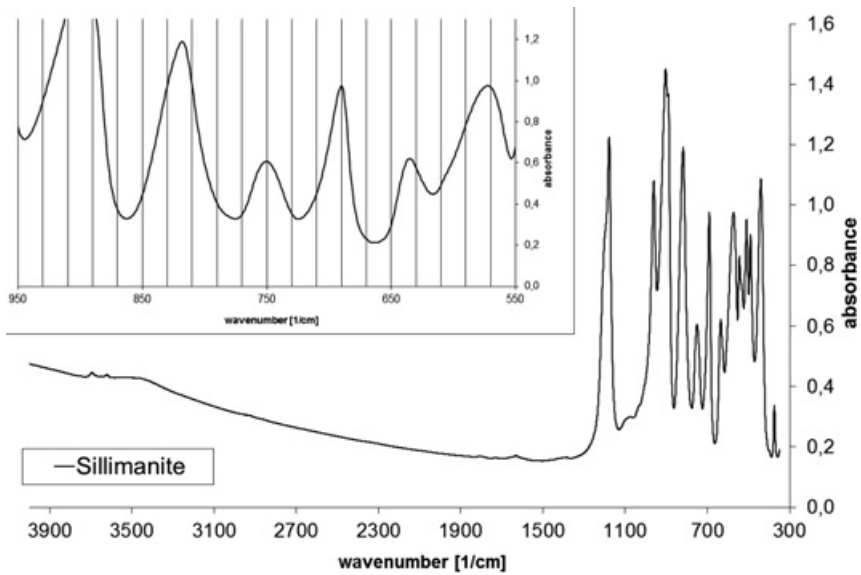


Fig. A15 FTIR spectrum of sillimanite.

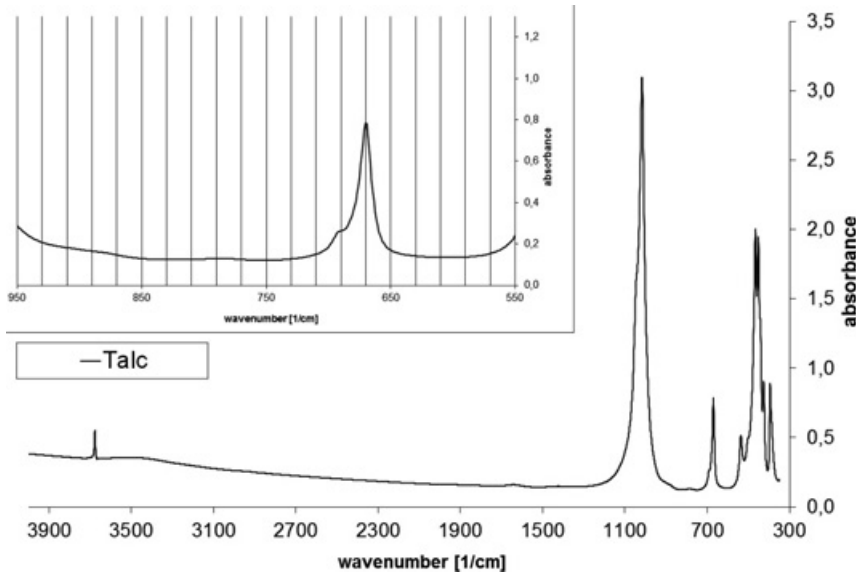


Fig. A16 FTIR spectrum of talc.

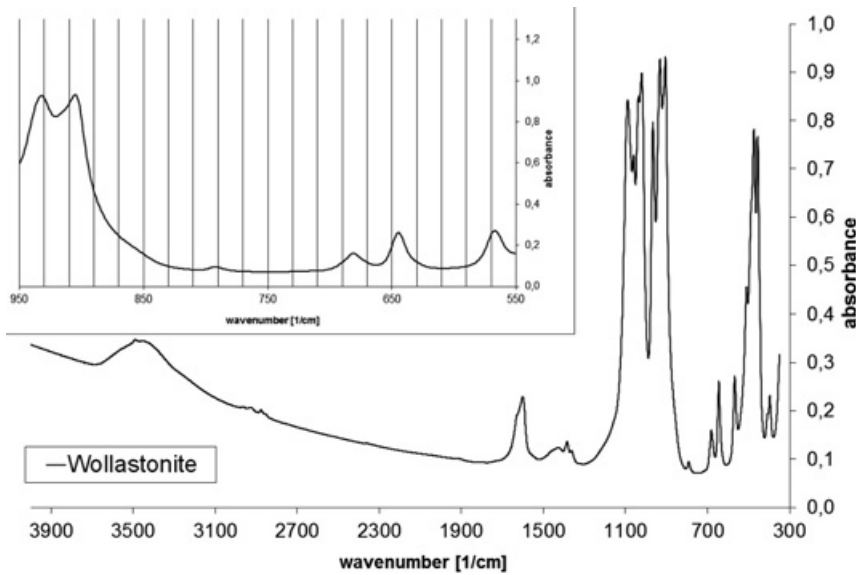


Fig. A17 FTIR spectrum of wollastonite.